The use of molecular orbital calculations and electrochemistry to predict the reduction pathways of organochlorine compounds

by Frederick Arthur Beland

A thesis submitted in partial fulfillment of the requirements for the degree of DOCTOR OF PHILOSOPHY in Chemistry
Montana State University

Abstract:
The CNDO/2 molecular orbital method was used to investigate the electrochemical reduction of organochlorine compounds of environmental interest. As the degree of chlorination increased in chlorinated benzenes and biphenyls, the LUMO-ς and LUMO-π both decreased in energy. The HOMO of the radical anions for each of these species was always a ς orbital. The location of highest electron density in the LUMO-ς for all of the chlorobenzenes, DDT, lindane and heptachlor predicted which chlorine was lost during electrochemical reduction. The electron density distribution in higher unoccupied ς orbitals of DDT and heptachlor predicted the order of carbon-chlorine bond scission in succeeding reductions.

Electrochemical reduction pathways correctly predicted the observed anaerobic degradation pathways for DDT, DTE, lindane and hexachlorobenzene. 2,3,4,5,6-Pentachlorobiphenyl and decachlorobiphenyl were resistant to anaerobic reduction. The first electrochemical reduction product of decachlorobiphenyl did undergo anaerobic reduction. During anaerobic degradation heptachlor lost the allylic chlorine first as opposed to the "anti" methylene bridge chlorine observed electrochemically. These results indicate that if a compound has an E2d more cathodic than -1.75 V (vs. SCE) in a DMSO-TEABr solvent system, it will not reduce in an anaerobic environment. Compounds with an E2d more anodic than this value may be reduced in the environment. Whether they do or not seems to depend on their actual structure which indicates that these compounds may have to fit into some type of an "active site."

THE USE OF MOLECULAR ORBITAL CALCULATIONS AND ELECTROCHEMISTRY TO PREDICT THE REDUCTION PATHWAYS OF ORGANOCHLORINE COMPOUNDS

by

Frederick Arthur Beland

A thesis submitted in partial fulfillment
of the requirements for the degree

of

DOCTOR OF PHILOSOPHY

in

Chemistry

Approved:

Richard D Geer
Chairman, Examining Committee

Ralph A Olson
Head, Major Department

K Goering
Graduate Dean

MONTANA STATE UNIVERSITY
Bozeman, Montana

August, 1974

ACKNOWLEDGMENT

This work would not have been possible without the generous time and effort given by many individuals. I thank James Enderson for introducing me to this subject area and Richard Geer for increasing my knowledge in this field while at the same time allowing me to go off on various tangents. Even a cursory reader will be aware that this work is built on the foundation established by Sherry Farwell. He has provided invaluable suggestions in this specific area as well as giving me insight into other disciplines in chemistry.

Robert Wilson and G. David Smith gave immense help with the computer aspects of this problem, and the quantum mechanical portion would have been impossible without the aid of Patrik Callis. Robert Fifield collected large amounts of data in this project and Elaine Robocker was intimately involved with the anaerobic degradation aspects of this work. Larry Jackson and Arnold Craig helped broaden my horizons in chemistry, thus allowing me to feel more comfortable with this subject matter.

This research was supported by U. S. D. A. Regional Project W-45. At various times I have been funded by the Montana State University Chemistry Department, Dean Kenneth Goering, and by the Federal Water Pollution Control Commission on a grant administered by John Wright. Samuel Rogers was invaluable in helping me obtain some of this support. The computer time used in this project was provided by the Montana State University Computing Center.

My parents, Dr. and Mrs. A. J. Beland, unselfishly gave financial assistance when it was so desperately needed. My wife Susan provided the encouragement and endless help in overcoming the hurdles that are a part of any Ph. D. project. I wish to thank all of these people and organizations and hope that this work does in some way reflect their great contribution.

TABLE OF CONTENTS

Page

LIST OF TABLES

LIST OF FIGURES

Figure Page

ABSTRACT

The CNDO/2 molecular orbital method was used to investigate the electrochemical reduction of organochlorine compounds of environmental interest. As the degree of chlorination increased in chlorinated benzenes and biphenyls, the LUMO-σ and LUMO-π both decreased in energy. The HOMO of the radical anions for each of these species was always a σ orbital. The location of highest electron density in the LUMO-σ for all of the chlorobenzenes, DDT, lindane and heptachlor predicted which chlorine was lost during electrochemical reduction. The electron density distribution in higher unoccupied σ orbitals of DDT and heptachlor predicted the order of carbon-chlorine bond scission in succeeding reductions.

Electrochemical reduction pathways correctly predicted the observed anaerobic degradation pathways for DDT, DTE, lindane and hexachlorobenzene. 2,3,4,5,6-Pentachlorobiphenyl and decachlorobiphenyl were resistant to anaerobic reduction. The first electrochemical reduction product of decachlorobiphenyl did undergo anaerobic reduction. During anaerobic degradation heptachlor lost the allylic chlorine first as opposed to the "anti" methylene bridge chlorine observed electrochemically. These results indicate that if a compound has an E_{2d} more cathodic than -1.75 V (vs. SCE) in a DMSO-TEABr solvent system, it will not reduce in an anaerobic environment. Compounds with an E_{2d} more anodic than this value may be reduced in the environment. Whether they do or not seems to depend on their actual structure which indicates that these compounds may have to fit into some type of an "active site."

INTRODUCTION

Organochlorine compounds have been used in agriculture and industry for the last thirty years. Their extensive use has been in part due to their chemical stability which has resulted in their becoming widespread pollutants. Great effort has been expended in developing the techniques to monitor the amount and presence of these residues. Considerable work has also been devoted to the chemistry of these compounds to better understand their mode of action and degradative pathways. We embarked on a project originally aimed at providing a technique for the specific identification of chlorinated hydrocarbon pollutants through the use of voltammetric identification. The results of this work have been reported by Farwell.[1] This investigation led us to the belief that perhaps reductive voltammetry could also be used to provide insight into the degradative pathways of these compounds. Furthermore since electrochemical reduction has provided a good test for quantum mechanics, we felt that molecular orbital calculations could provide insight into the breakdown pathways observed electrochemically and ultimately to those observed environmentally. The following sections in the introduction are offered to the reader so that the nature of the problem will be better understood.

Electrochemical Reduction of Carbon Halogen Bonds

The history of the reduction of carbon halogen bonds is centered around the now classical work of Von Stackelberg and Stracke.[2] They systematically investigated a large number of alkyl halides and polyhalides and made the following observations (as modified by Fry[3]).

1. The ease of reduction of carbon halogen bonds decreases in the following order: allylic ≈ benzylic > saturated ≈ aryl > vinyl. Thus allylbromide has an $E_{\frac{1}{2}}$ (half-wave potential) = -1.29 V (vs. SCE), n-butylbromide, -2.27 V, bromobenzene, -2.27 V, and vinylbromide, -2.47 V. (Solvent: 75% dioxane containing tetraethylammonium bromide (TEABr)).
2. The double bond in unsaturated halides is not electrochemically reducible.
3. Comparing different halides, the ease of reduction decreases as follows: I > Br > Cl > F.
4. Geminal and vicinal halides reduce more easily than simple halides. Thus: $CX_4 > CHX_3 > CH_2X_2 > CH_3X$ and $X\text{-}CH_2\text{-}CH_2\text{-}X > CH_3\text{-}CH\text{-}X_2 > CH_3\text{-}CH_2\text{-}X$, where X = I, Br or Cl.
5. Increasing the chain length of a saturated aliphatic hydrocarbon increases the reduction potential. For example, the

$E_{\frac{1}{2}}$ increases as follows (i.e., the reduction becomes more difficult): methylbromide < n-butylbromide < n-octylbromide.

6. The half-wave potentials are pH independent and the reductions are irreversible.

7. Except for vicinal dihalides, two electrons are gained for every halogen lost with concomitant gain of a proton. They suggested the following mechanism to account for this observation.

$$RX + e^- \rightarrow R\cdot + X^-$$

$$R\cdot + e^- \rightarrow R^-$$

$$R^- + H^+ \rightarrow RH$$

The initial addition of an electron was proposed to be the rate determining step.

8. For vicinal dihalides the proposed mechanism was:

$$R\text{-}\overset{X}{\underset{|}{C}}H\text{-}\overset{X}{\underset{|}{C}}H\text{-}CH_3 + 2e^- \rightarrow R\text{-}\overset{\cdot}{C}H\text{-}\overset{X}{\underset{|}{C}}H\text{-}CH_3 + X^-$$

$$R\text{-}\overset{\cdot}{C}H\text{-}\overset{X}{\underset{|}{C}}H\text{-}CH_3 \rightarrow R\text{-}CH{=}CH\text{-}CH_3 + X^-$$

Building on the foundation established by Von Strackelberg and Stracke, others have continued the investigation of the reduction of the carbon halogen bond. C. K. Mann[4] has suggested that the first step in the reduction involves the formation of a radical anion which rapidly decomposes to the free radical.

$$R\text{-}X + e^- \rightarrow [R\text{-}X]^{\cdot -} \rightarrow R\cdot + X^-$$

This step should be reversible (the formation of the radical anion), but when employing cyclic voltammetry there has been no evidence of reversibility at even very high scan rates.[5] Fry argues that while the radical anion may represent a transition state, it is not a true intermediate.[3] His argument is based on the fact that while the reduction of alkyl chlorides by hydrated electrons (which generates radical anions) is independent of alkyl chain length, this is not what is observed under electrochemical reduction.

Von Stackelberg and Stracke's[2] mechanism for alkyl halide reduction invokes the formation of a radical ($R\cdot$) and a carbanion (R^-). Both of these species have been demonstrated, although through indirect evidence. Thus dimeric products,[5] organomercurial compounds,[4] and rearranged products,[3] have been detected which indicates the formation of free radicals. When the reduction solvent is aprotic, the Hoffman elimination product of the quaternary ammonium salt used as the supporting electrolyte was detected, which provides evidence for carbanion formation.[4]

$$R\text{-}X \xrightarrow{+e^-} R\cdot \xrightarrow{+e^-} R^- \xrightarrow{Et_4)\text{-}N} R\text{-}H + CH_2{=}CH_2 + Et_3N$$

It is generally assumed that the radical ($R\cdot$) will be able to gain an electron more easily (at a more anodic potential) than the parent alkyl halide. Thus only one polarographic wave is observed which represents a 2-electron transfer. However, there are exceptions; for instance two waves are observed

during the reduction of t-butyliodide, whereas only one was observed for t-butylbromide.[6] This again lends support for the formation of a radical ($R\cdot$) followed by a carbanion (R^-).

As previously mentioned, vinyl and aryl halides are reduced at potentials equal to or slightly greater than saturated halides. While the two former types of halides have not been studied as extensively as the corresponding saturated compounds, some interesting observations have been made. The most thorough study on aryl halides has been made by Farwell.[1] He performed polarographic studies on chlorinated benzenes, biphenyls, naphthalenes, diphenylethanes and -ethylenes. When the chlorine was substituted on the aryl moiety, the carbon-halogen bond was reduced by a 2-electron pH independent irreversible process. He furthermore performed controlled potential electrolysis on the benzene and biphenyl series and determined the reductive pathways for these series. The results of his work will be dealt with more extensively in later sections of this dissertation. Campbell[7] has studied the electrochemical reduction of a limited number of fluorinated benzenes, biphenyls, and naphthalenes. His results are consistent with previous observations that the halogens are lost in a 2-electron per halogen process, the fluoride being replaced by a hydrogen. Renaud[8] investigated the reduction of 1-halonaphthalenes in the presence of deuterated water. He postulated that bromo- and iodo-naphthalenes are reduced via an organometallic radical

intermediate or by the simultaneous addition of two electrons to form a carbanion.

$$R\text{-}X \rightarrow \overset{\overset{\nearrow}{\downarrow}\ RHg\cdot}{R^-} \xrightarrow{D_2O} RD$$

However, since the amount of deutermium incorporated is much lower during the reduction of 1-chloronaphthalene, he proposes that it goes by either a simultaneous addition of two electrons or by a discrete radical pathway if a radical is formed. This could strip a hydrogen atom from the solvent thus giving an unlabeled product.

$$R\text{-}Cl \rightarrow \overset{\overset{\searrow}{\uparrow}\ R\cdot}{R^-} \begin{matrix} \xrightarrow{D_2O} RD \\ \xrightarrow{solvent} RH \end{matrix}$$

A number of investigators have postulated that during the reduction of aryl and vinyl halides the electron is initially transferred to the pi (π) system followed by cleavage of the sigma (σ) carbon halogen bond. This supposedly occurs with nitrophenyl,[9] nitrobenzyl,[10], polyphenylethylenic and vinyl halides,[11] and with halobenzophenones.[12] Finally, in comparison with alkyl halides the formation of dimers and alkyl mercury compounds during the reduction of aryl and vinyl halides is negligible.[3]

Polyhalogenation generally facilitates the ease of reduction and also usually increases the number of waves observed. For instance, in aqueous solvents, three 2-electron waves are observed during the reduction of carbon tetrachloride. These represent the formation (at each successive reduction)

of chloroform, methylene chloride and finally methylchloride.[13] [It should be mentioned that the situation changes drastically in aprotic solvents (in this case acetonitrile). Here carbon tetrachloride exhibits only two 2-electron waves resulting in the formation of methylene chloride. The interesting point is that a carbene intermediate is invoked.][13]

In contrast to geminal dihalides, vicinal dihalides are reduced by the transfer of one electron per halogen. This results in the formation of olefins in what is thought to be a concerted process. The main evidence for this is that olefins are always found even in protic solvents, which should trap out a carbanion if one was formed. Since vicinal dihalides are reduced more easily than simple halides, they must possess a pathway not available to simple halides, such as a concerted pathway. This mechanism is supported by the results of Zavada et al.[14] Using rigid cyclic vicinal dihalides, they found the reduction to proceed most easily when the halogen-halogen dihedral angle was near 0^{o} or 180^{o}, while the most cathodic potentials occurred when the dihedral angle between the chlorines is 90^{o}. This coplanarity would tend to facilitate a concerted reduction.

This review, while hopefully an aid to the reader, is not intended to be extensive. For a more eloquent presentation, the texts by Fry[3] and Mann and Barnes[15] are suggested.

Molecular Orbital Studies on Electrochemical Reductions

The rate determining step in the electrochemical reduction of a compound is the addition of the first electron. This appears to be the case in both reversible and irreversible systems. Thus if one can determine the level of the lowest unoccupied molecular orbital (LUMO), i.e., the orbital into which this electron will go, one should be able to develop a linear relationship between reduction potential and the energy level of the LUMO.

Maccoll[16] was the first to attempt this relationship, and applied it to a series of aromatic hydrocarbons. Since the LUMO for compounds of this type will be a π orbital he used a simple Huckel molecular orbital (HMO) approach, which only treats the π system, and was able to obtain a linear relationship.

Hoijtink and Van Schooten extended this concept.[17] The reduction pathway for aromatic hydrocarbons was considered to be:

$$R + e^- \rightarrow R^- \quad \text{(reversible)}$$

$$R^- + e^- \rightarrow R^= \quad \text{(irreversible)}$$

$$R^= + 2H_2O \rightarrow RH_2 + OH^-$$

In their treatment they assumed that the log K_1/K_2 (where K_1 and K_2 are the diffusion coefficients of R and R^- respectively) and the $\Delta G_{solvation}$ are nearly the same for related molecules. If this is the case, then the electron affinity will be approximately equal to the energy of the LUMO. This is

Maccoll's original conclusion.[16] Hoijtink's and Van Schooten's real contribution was to predict reaction products based on the results of the molecular orbital calculations. Thus the location of greatest electron density in the highest occupied molecular orbital (HOMO) in $R^{=}$ will be the site of proton attack to give RH^{-}. Furthermore, the location of highest electron density in the HOMO of RH^{-} will predict where the second proton attacks to give RH_2. They predicted that 1,4-dihydronaphthalene will be the 2-electron reduction product of naphthalene, which has since been proven experimentally.[18]

Our discussion on theoretical studies until now has only dealt with the π electron system. This has been based on the Huckel approximation that the π electrons will act independently of the σ system. While this is a rather simplistic approximation, it does lead to rather good predictions of chemical behavior.

Certain molecules, such as carbon tetrachloride, do not possess π systems and yet are electrochemically reducible. If a molecular orbital method could be developed to treat σ systems (even to the exclusion of the π electrons), insight could be gained into the reduction of compounds of this type. Theories of this type have been developed independently by Sandorfy[19] and Fukui et al.[20-24] When Fukui and coworkers applied their system to the reduction of organic halides, they made the following observations:[23]

1. Increasing the degree of halogen substitution does not seriously

affect the energy levels of the occupied σ molecular orbitals, but markedly lowers the σ LUMO.

2. There is a linear relationship between the σ LUMO and $E_{\frac{1}{2}}$ for halomethanes.
3. The potential determining step is the addition of the first electron.
4. The electron distribution of the LUMO is greatly localized in the carbon halogen bond and the bond order is negative and large in absolute magnitude. This should cause the carbon halogen bond to break quite easily when the LUMO becomes occupied by an electron.
5. The π LUMO energy levels (obtained from HMO calculations) for chloroethylenes and chlorobenzenes do not significantly change upon increasing halogen substitution.
6. Finally, it was suggested that the LUMO for conjugated halides might be a σ rather than π orbital.

The next level of approximation would be to use a method that would allow calculation of σ and π energy levels simultaneously. The inherent advantages of this type of calculation will be discussed in a later section. For the present it should be mentioned that Dewar et al. have applied a theory of this type to study the electrochemical reduction of aromatic hydrocarbons.[25]

Instead of using the energy of the LUMO to estimate the electron affinity (EA) of the hydrocarbon, they calculated the EA by taking the difference between the heats of atomization of the radical anion and the parent hydrocarbon. One distinct advantage of their method is that it allows EA to be calculated in absolute energy terms instead of in units of β. This allows direct comparison of the energies obtained from calculations and experiments. When EA is plotted against $E_{\frac{1}{2}}$, a linear correlation was observed with the slope of the line equal to 0.99. They suggested that this implies that the differences in solvation energy between the parent hydrocarbons and the corresponding radical anions are constant. (This tends to confirm Hoijtink's and Van Schooten's original approximation).[17] This is because the reductions were performed in aprotic solvents which should not solvate the radical anions very efficiently. Dewar et al. offered as further evidence the fact that the slope of the line for the reduction of quinones was 0.39 (versus 0.50 theoretical value). In this latter case the reductions were perfromed in a protic solvent which should solvate the anions quite strongly.[26] Finally, they were able to predict reduction products in a manner quite analogous to Hoijtink and Van Schooten.

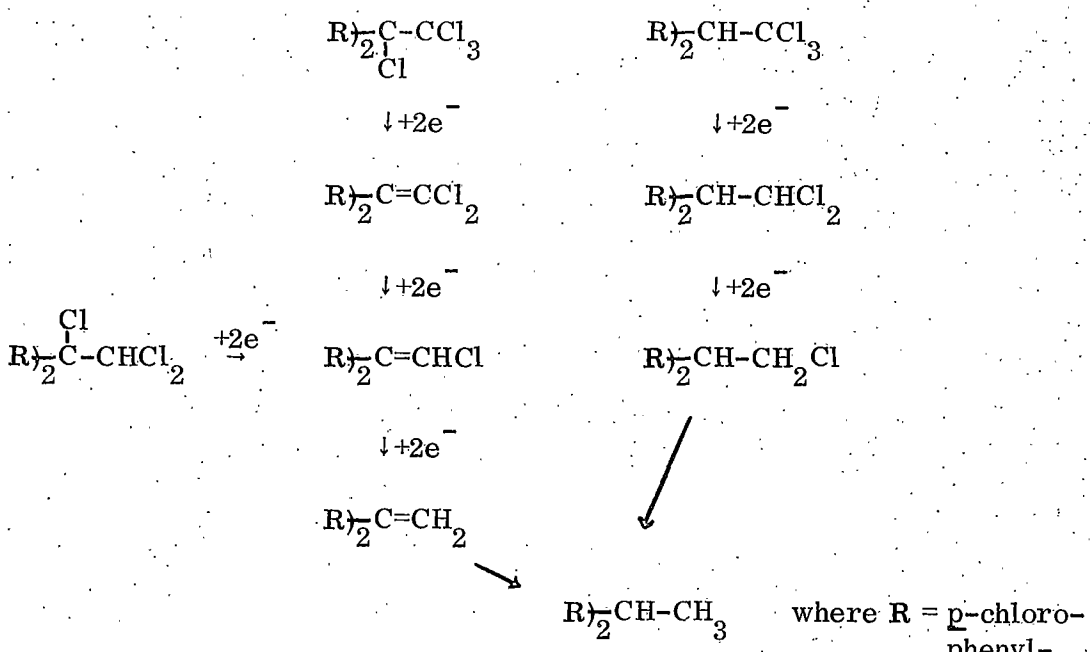
Electrochemical Reduction of Chlorinated Insecticides and Chlorinated Hydrocarbon Pollutants

There have been a number of studies on the electrochemical reduction of compounds of environmental interest. These have been primarily twofold in

nature: first to develop the analytical methodology to detect these contaminants and second to understand the nature of the carbon-chlorine reduction.

By far the most extensive study has been that of Farwell[1] and Farwell et al.[27-29] Besides establishing the reductive pathways for chlorinated benzenes and chlorinated biphenyls with chlorines on one ring he investigated the voltammetric behavior of chloronaphthalenes, DDT (1,1,1-trichloro-2,2-bis-(p-chlorophenyl)ethane) and its various chlorinated analogues and other chlorinated insecticides including lindane (γ-1,2,3,4,5,6-hexachlorocyclohexane), dieldrin (1,2,3,4,10,10-hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydro-endo-exo-1,4:5,8-dimethanonaphthalene), aldrin (1,2,3,4,10,10-hexachloro-1,4,4a,5,8,8a-hexahydro-endo-exo-1,4:5,8-dimethanonaphthalene), and heptachlor (1,4,5,6,7,8,8-heptachloro-3a,4,7,7a-octachloro-2,3,3a,4,7,7a-hexahydro-4,7-methanoindene).

Rosenthal et al.[31] conducted a systematic study on the polarographic behavior of the diphenylethanes and ethylenes found in the DDT series. Their work included controlled potential electrolysis and they were able to demonstrate the following reduction pathways.



Farwell[1] was able to reduce the last compound, 2,2-bis(p-chlorophenyl)-ethane (DDMS), presumably to 2,2-diphenylethane.

The electrochemical reduction of dieldrin and aldrin has been investigated by Swanepoel et al.[32] Using a solvent system of 75% aqueous methanol containing 0.1 M tetramethylammonium bromide (TEABr) they performed controlled potential electrolysis at potentials between -1.0 and -2.0 V (vs. silver/silver chloride electrode. Two products, representing successive reductions, were found from dieldrin, while only one from aldrin. These compounds were isolated and their identity established by nmr spectroscopy. Figure 1 shows the reduction pathways they determined.

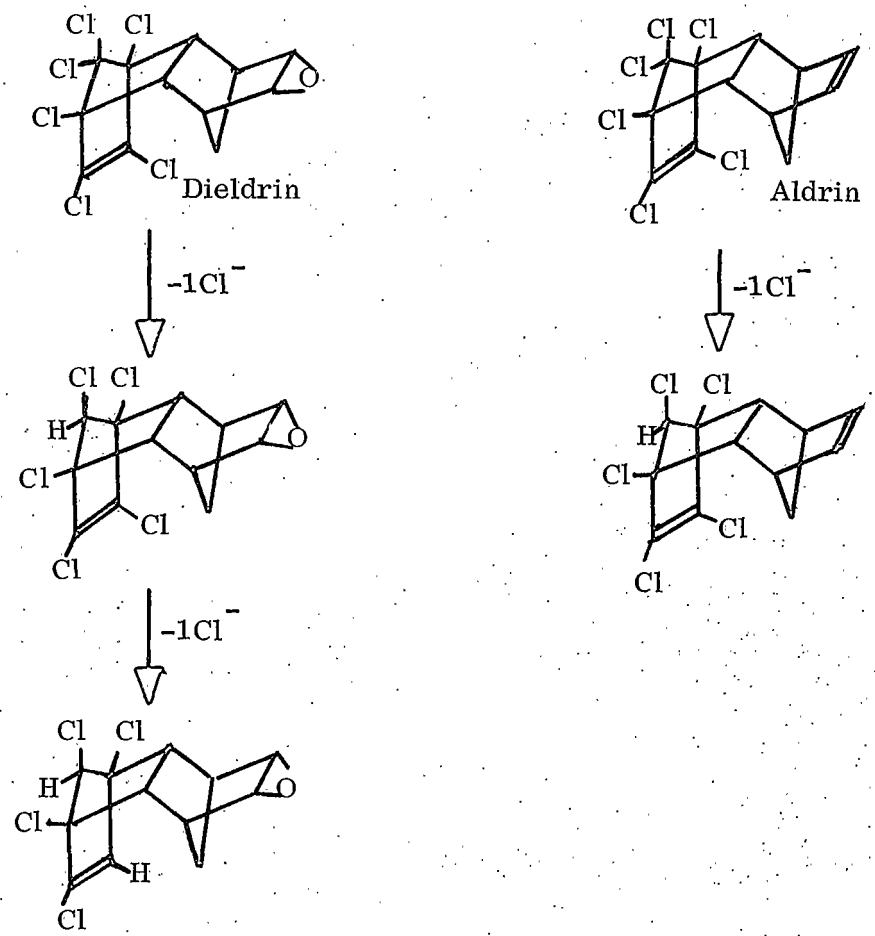


Figure 1. Reductive Electrochemical Products of Dieldrin and Aldrin as Established by Swanepoel et al [32]

Cisak also investigated the electro-reduction of dieldrin and aldrin, and, in addition, endrin (1,2,3,4,10,10-hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8-octahydro-endo-endo-1,4:5,8-dimethanonaphthalene), isodrin (1,2,3,4,10,10-hexachloro-1,4,4a,5,8,8a-hexahydro-endo-endo-1,4:5,8-dimethanonaphthalene) and α- and β-chlordane (1,2,4,5,6,7,8,8-octachloro-2,3,3a,4,7,7a-hexahydro-4,7-methanoindene).[33-37] Altogether nine reduction products were isolated and identified, four each from dieldrin and endrin and one from β-chlordane. Figure 2 shows the reduction products obtained, presumably through a stepwise process. The first reduction product from dieldrin (minus one chlorine) is identical to the first reduction compound Swanepoel et al. isolated.[32] Moreover, Cisak was able to establish the absolute configuration of the chlorine at the methylene bridge carbon as being syn as opposed to the anti configuration indicated by Swanepoel and coworkers.

A number of investigators have studied the electrochemical reduction of lindane. Schwabe and Frind[38] determined that six electrons are transferred to produce benzene. Fukame et al.[39] established that benzene is formed quantitatively. Comparing various hexachlorocyclohexane isomers Senda and coworkers[40] found that the ease of reduction decreases in the following order: $\gamma >> \alpha > \beta \approx \delta$.

Chau and his colleagues have also investigated the reduction of a number of chlorinated insecticides. While these reductions are chemical, rather than

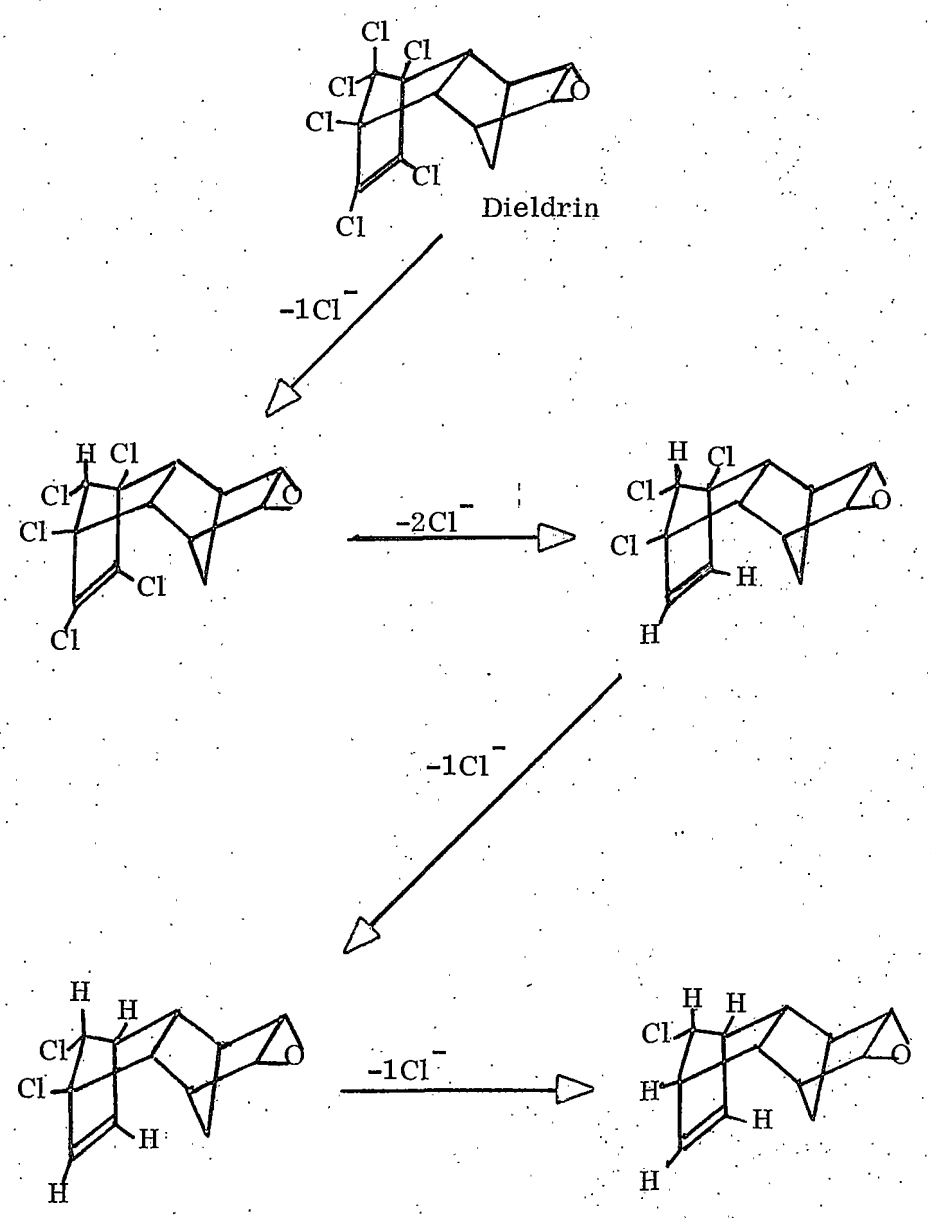


Figure 2. Reductive Electrochemical Products of Dieldrin, Aldrin and β-Chlordane as Established by Cisak [33-37]

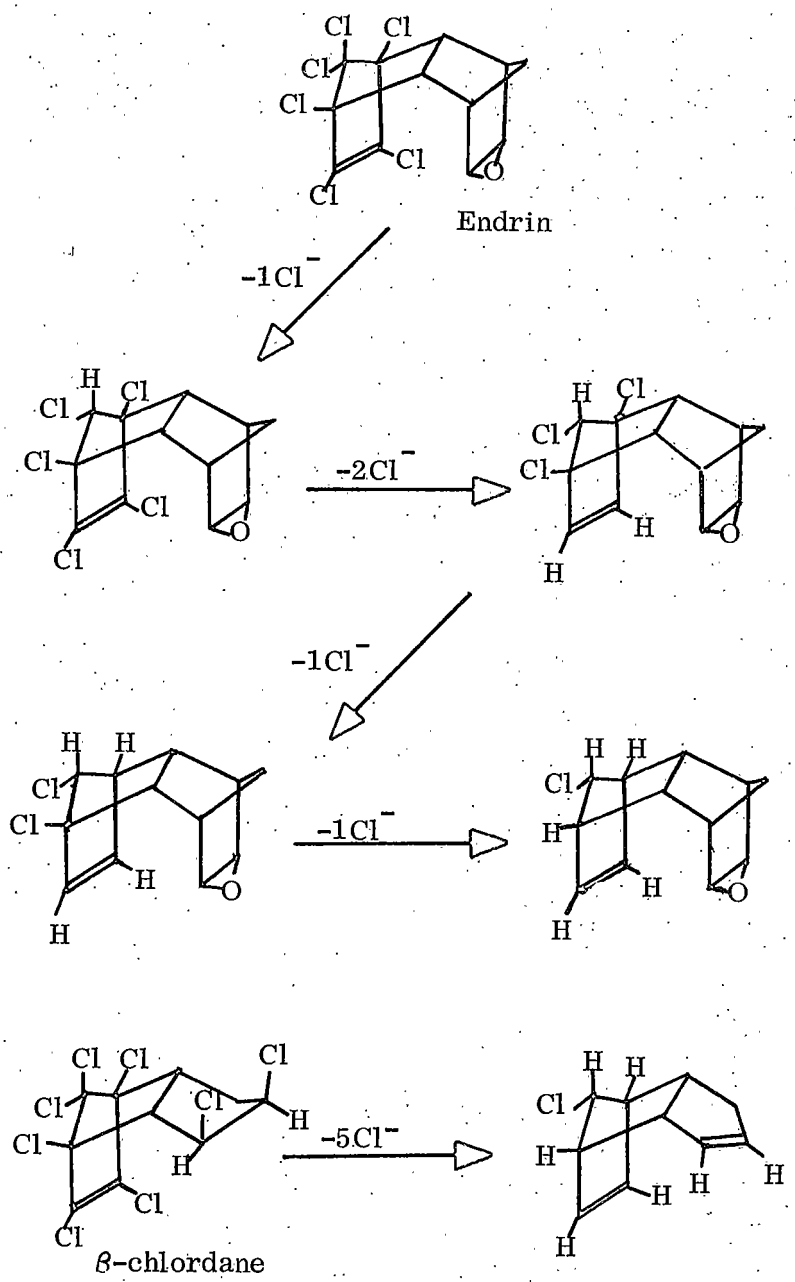


Figure 2. (Continued)

electrochemical, his results merit discussion.[41-47] Chau used chromous chloride as the reducing agent and in the case of DDT the reaction proceeded smoothly to initially form DDD (1,1-dichloro-2,2-bis(p-chlorophenyl)ethane). Upon further reaction, DCS (trans-p,p'-dichlorostilbene) was isolated in 45-55 per cent yield, with DDNU(1,1-bis(p-chlorophenyl)ethylene), DBP (p,p'-dichlorobenzophenone), and DDMU (1-chloro-2,2-bis(p-chlorophenyl)ethylene), forming the remainder.[41] Thus while the initial step in the chromous chloride reduction is quite analogous to electrochemical reduction, there are marked differences at later steps in the reaction sequence.

Chromous chloride reduction of heptachlor gave two products--chlordene (4,5,6,7,8,8-hexachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene) and a pentachloro compound (4,5,6,7,8-pentachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene). Chemical reduction of chlordene gave only this latter product.[43] (See Figure 3). The loss of the allylic chlorine in the first reduction would be what would be expected electrochemically since this a rather facile reduction.[2] The loss of the anti chlorine in the methylene bridge during the second reduction step mimics the already observed results for compounds possessing a cyclodiene type structure.[32,37]

The chemical reduction of endrin[44-46] (Figure 4) gives products that are not at all similar to the previously discussed electrochemical reactions.[32,37] There is an acid catalyzed isomerization to a pentacyclic ketone,

followed by chromous chloride reduction at the methylene bridge. This is probably an artifact of the reaction media rather than the reduction itself.

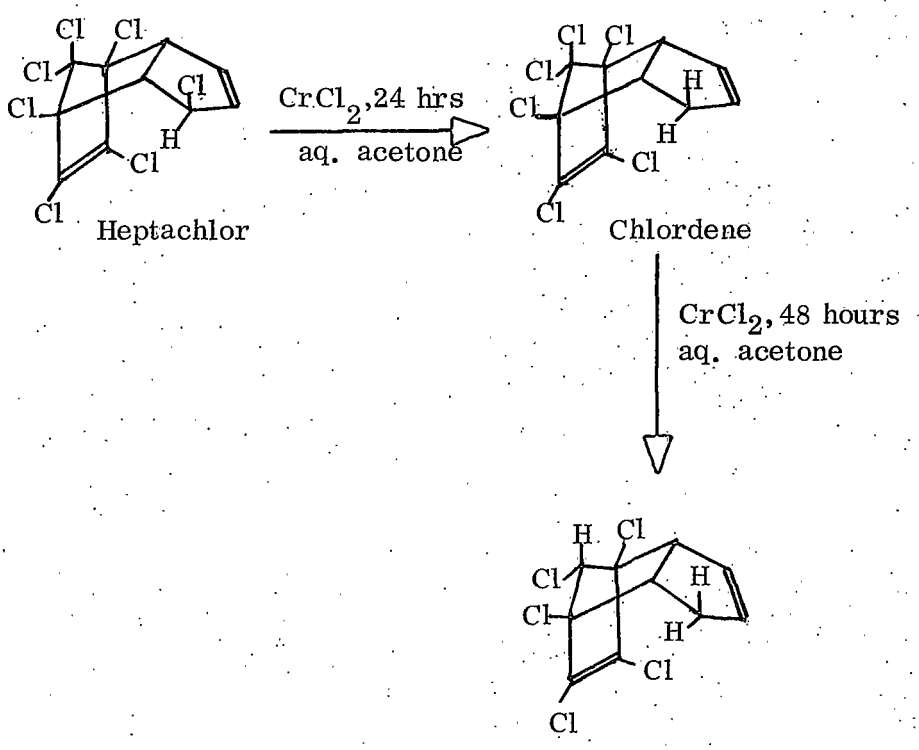


Figure 3. Chromous Chloride Reduction of Heptachlor and Chlordene [43]

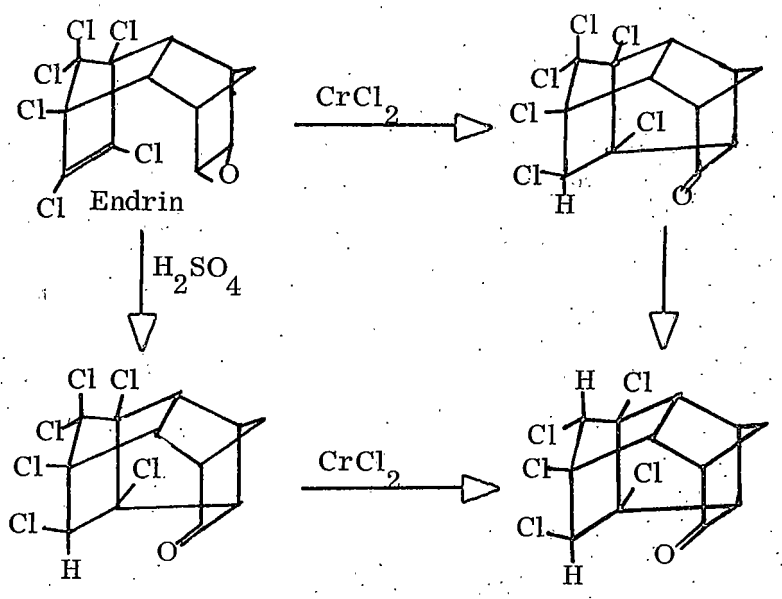


Figure 4. Chromous Chloride Reduction of Endrin [44-46]

Anaerobic Reduction of Chlorinated Hydrocarbons

There have been numerous investigations into the anaerobic degradation of chlorinated insecticides. Perhaps the most interesting finding is that while these compounds are generally quite stable under aerobic conditions, they are quickly degraded in a reductive environment. For instance, in flooded soil conditions and in moist soil under anaerobic conditions, DDT is rapidly converted into DDD.[48-53]

Other metabolites have been reported from anaerobic DDT degradation. These include DDE (1,1-dichloro-2,2-bis(p-chlorophenyl)ethylene), DDMU, DDMS (1-chloro-2,2-bis(p-chlorophenyl)ethane), DDNU, DPM (p,p'-dichlorodiphenylmethane), DBH (p,p'-dichlorobenzhydrol), DBP, Kelthane

(1,1,1-trichloro-2,2-bis(p-chlorophenyl)ethanol), and BA (p-chlorobenzoic acid).[48,54-56] There is some question as to whether any or all of these intermediates are formed under true anaerobic conditions. In most studies DDD and occasionally DDE (the latter from dehydrochlorination) are the only products detected.

Recently a rather novel product has been isolated when DDT was incubated in the presence of biologically-active anaerobic sewage sludge.[57,58] This compound, bis(p-chlorophenyl)-acetonitrile (DDCN) was detected in 11% yield following an incubation period of 88 days. A possible reaction scheme was proposed[57] via DDA (bis(p-chlorophenyl) acetic acid) → amide → nitrile, although the authors had no evidence to substantiate their claim.

The reductive dechlorination of DDT has also been reported by Hassall and coworkers in pigeon liver preparations under anaerobic conditions.[59-61] Their work indicates that the main route of DDD formation is enzymatic, but there are some heat resistant factors in the 12,000 g supernatant which can in the presence of riboflavin convert DDT to DDD.

Considerable effort has been expended on the study of the anaerobic degradation of lindane. Ragnu and MacRae[62] demonstrated that lindane disappeared in non-sterile flooded soil conditions within 60 days. The rate of degradation was not as rapid in sterile soils. MacRae in another investigation found that the α, β and δ isomers of hexachlorocyclohexane disappeared almost

as rapidly as lindane.[63] A more interesting finding was the detection of ^{14}C-labeled carbon dioxide after the incubation of ^{14}C-lindane. This would imply that the organisms are capable of utilizing lindane or more probably one of its degradation products as a carbon source.

Degradation of lindane in simulated lake impoundments was studied by Newland et al.[64] They detected the α and δ isomers of hexachlorocyclohexane and attributed this to a chemical transformation of the γ isomer to more thermodynamically stable structures. Other workers[65, 66] have detected a metabolite from the anaerobic degradation of lindane by Clostridium that did not have a retention time corresponding to the other hexachlorocyclohexane isomers. Nor did it match γ-pentachlorocyclohexene, 1,3,5- or 1,2,4-trichlorobenzene which are aerobic metabolites. Sethunathan et al.[66] proposed pentachlorocyclohexane as the intermediate using the conversion of DDT to DDD as an analogy. The unidentified degradation compound has since been identified as γ-tetrachlorocyclohexene (γ-BTC) by Tsukano and Kobayashi.[67] Its formation has been confirmed by Benezet and Matsumura who also detected α-hexachlorocyclohexane which they claimed was formed by biological isomerization of lindane.[68]

Heptachlor can be anaerobically degraded. For instance, Castro and Yoshida[69] found it to disappear completely within as little time as one month in flooded soil conditions. Hill and McCarthy could only find heptachlor

twenty minutes after addition to anaerobic sewage sludge.[70] It was replaced by a "heptachlor early elution" compound which persisted for at least 42 days. This product may be chlordene which was formed from heptachlor by soil bacteria under anaerobic conditions.[71]

In flooded soil, pentachlorophenol is rapidly (within four weeks) decomposed to lower chlorinated phenols (PCP).[72] All three possible tetrachlorophenols plus unidentified lower chlorinated analogues were found. When 2,3,4,5-PCP was incubated, 2,3,5-, 2,4,5-,3,4- and 3-PCP were formed; 2,3,4,6-PCP gave 2,4,5-PCP and 2,3,5,6-PCP produced 2,3,5-, 3,5- and 3-PCP.

Cyclodiene insecticides such as dieldrin and endrin all contain a hexachlorinated norbornene moiety. Therefore, Schuphan and Ballschmiter investigated the anaerobic degradation of 1,2,3,4,7,7-hexachloronorborn-2-en as a model for cyclodiene metabolism.[73] Figure 5 shows the various pathways they observed using the bacterium Clostridium butyricum.

The fate of other chlorinated insecticides under anaerobic conditions is somewhat more confusing. Hill and McCarthy[70] studied the degradation of a number of compounds in biologically active anaerobic sewage sludge. They ranked the pesticides in order of increasing persistence as: lindane, heptachlor, endrin, DDT, DDD, aldrin, heptachlor epoxide (1,4,5,6,7,8,8-heptachloro-2,3-epoxy-3a,4,7,7a-tetrahydro-4,7-methanoindan), and

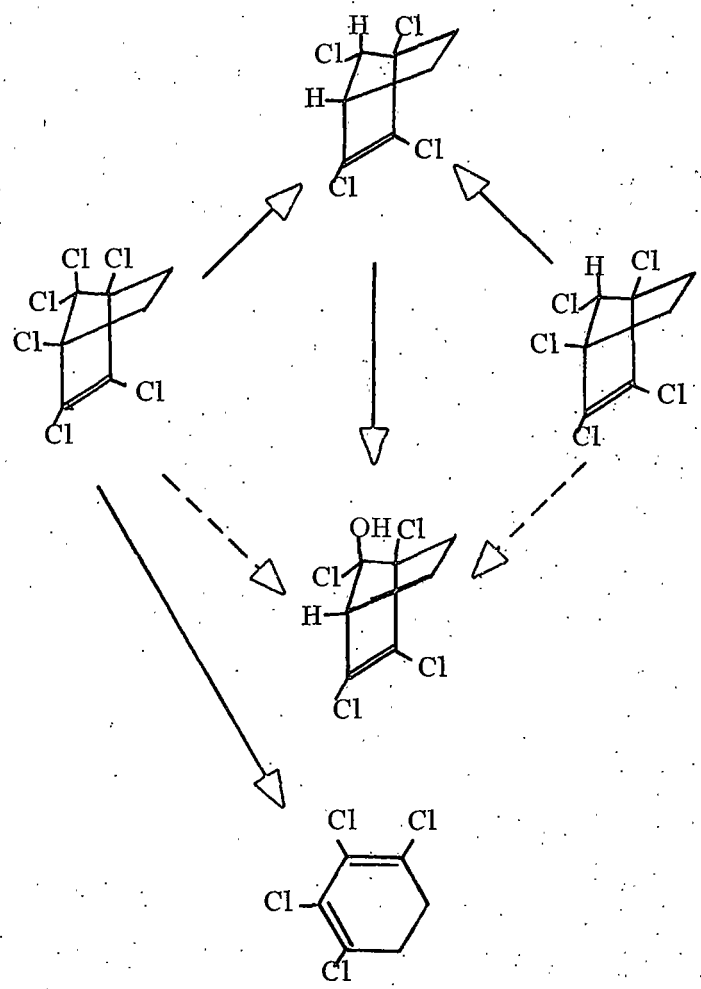


Figure 5. Metabolism of Hexa-, Penta- and Tetrachloronorbornene under Anaerobic Conditions by Clostridium butyricum[73]

dieldrin. Dieldrin and heptachlor epoxide were very persistent in this environment. Heptachlor, endrin, and DDT formed extractible degradation products which were more persistent than the parent compounds.

Castro and Yoshida also investigated the degradation of a broad spectrum of organochlorine pesticides.[69] Comparing flooded soil to upland soil they found DDT to be degraded much more rapidly under submerged conditions. DDD, the product formed from DDT in flooded soil was much more resistant. Methoxychlor (1,1,1-trichloro-2,2-bis(p-methoxyphenyl)ethane) and heptachlor were also readily degraded while dieldrin, chlordane and aldrin were quite stable.

The factors affecting the reductive dechlorination of organochlorine compounds has caused considerable discussion. Some observations made are:

1. An increase in temperature increases the rate of degradation. Thus lindane in sewage sludge was metabolized at a greater rate at 35°C than at 20°C.[70] The same effect was noted in flooded soils.[74]
2. MnO_2, by acting as an electron acceptor, depresses the lowering of Eh (redox potential) and therefore impedes the anaerobic degradation of lindane.[74] This also occurs upon addition of nitrite.[66]

3. The inclusion of easily oxidizable organic substrates such as alfalfa,[49] glucose,[50] or the volatile components of alfalfa[51] increases the rate of conversion of DDT to DDD.
4. The breakdown of organochlorine compounds occurs at a slower rate in flooded soil that has been sterilized.[49,51,53,62,63,66] The same effect is noted with the inclusion of oxygen[49,50,64,69,70] or poisoning the system with cobaltous and mercuric salts.[70]

The above evidence lends support to the concept that the reduction is biological in nature. For example, these compounds might serve as a terminal acceptor in electron transport.

Others, however, refute this idea that the reduction is essentially biological. Glass[52] suggests that these reductions are mediated by the iron-(III-II) couple which is the dominant redox system in reduced soils.[75] Thus as the ferrous to ferric iron ratio increases, the amount of DDT decreases. Castro[76] noted a rapid oxidation of reduced iron porphyrins and the conversion of DDT to DDD. Miskus[77] duplicated these findings using an aqueous system. These results have led Zoro et al.[78] to suggest that under anaerobic conditions there should be reduced iron porphyrins (perhaps released from decaying matter) and that these porphyrins catalyze the reduction of DDT to DDD. They based their proposal on the following observations. If after the

sterilization of anaerobic sewage sludge dithionite (a reducing agent) is added, the ratio of DDD/DDT dramatically increases. Furthermore, in an artifical media consisting of dithionite, ethanol, Tween 80 (a solubilizer) the DDD/DDT ratio is quite low. However, upon the addition of haematin (the iron(III) porphyrin corresponding to the iron(II) porphyrin, protohaem), the DDD/DDT ratio again increases dramatically. Here it should be pointed out that it seems that even if anaerobic microorganisms do not directly participate in the reduction, they seem to be necessary to generate the conditions in which reduced porphyrins can exist.

Finally it has been demonstrated that elemental mercury is formed by the chemical reduction of mercuric ion in the presence of humic acid.[79] Humic acid, a constituent of soil, is known to contain a free radical component and is capable of reducing ferric to ferrous iron in aqueous solutions.[80] It could also mediate chlorinated hydrocarbon reduction. For further information on anaerobic degradation, the reviews by Fries,[81] Sethunathan[82] and Watanabe[83] are suggested.

Approximate Molecular Orbital Methods

A large part of this work is involved with molecular orbital calculations to predict reaction pathways and products. Therefore a brief introduction into this area seems appropriate. We have already seen that various attempts

have been made to correlate quantum theory and electrochemical reduction. With the exception of Dewar's work[25,26] these methods have been restricted to either the σ or the π electron systems. While some of the molecules we will discuss could be treated with an exclusive σ molecular orbital treatment, the majority of the molecules have both σ and π systems of interest. For instance, chlorobenzene has a π electron system involving the aromatic ring and yet at the same time we would like to learn something about the σ carbon chlorine bond.

While ideally it would be desirable to use "ab initio" methods, these are limited to very simple molecules because of extensive computation time required. This leads us directly to semiempirical approximate molecular orbital theories, in which the molecular properties are derived through correlations with experimental data.

Probably the most widely accepted semiempirical approach to date is the complete neglect of differential overlap (CNDO) method of Pople and coworkers.[84-88] Their basic approximation is that the electron repulsion integrals involving overlap distributions are zero. This assumption allows for a drastic reduction in the number of integrals that must be evaluated, and thus markedly reduces the computation time. They feel that the approximation is valid because many of the integrals have near zero values. This method only treats valence electrons as these are the "chemically effective"

electrons. There are two empirical parameters that they introduce. The matrix elements of the one-electron Hamiltonian are obtained from ionization potential and electron affinity data and the bonding parameters are selected to give best overall fit with the results obtained from accurate LCAOSCF calculations.

Others have developed methods that are extensions of Pople's basic idea. They mainly differ in the manner in which the empirical parameters are selected. Some notable examples are the MINDO method of Dewar,[89] CNDO/SW approach of Sichel and Whitehead[90,91] which has been recently reparameterized to give the CNDO/BW method.[92] Finally the CNDO/2 variant has now been extended to include third-row atoms.[93]

EXPERIMENTAL SECTION

Synthesis of Compounds

We started this project with the goal of using reductive voltammetry to identify the constituents found in commercial biphenyl mixtures. At that time very few individual isomers existed (for a list see Hubbard)[94] and therefore to allow a complete a study as possible, we found it necessary to synthesize a number of compounds. Since then there have been numerous compounds reported in the literature, most of which are now available from Analabs Inc. in limited quantities. Although most of the following compounds are not used in my study *per se*, a large part of my work is based upon the results Farwell[1] obtained from the reductive electrochemistry of these compounds.

Unless otherwise stated, all compounds were at least 95 per cent pure by gas chromatographic (g.c.) analysis. Two different gas chromatographs were used: An F & M model 400 equipped with 6' x $\frac{1}{4}$" silanized Pyrex glass columns and a flame ionization detector, and a Varian model 1200 equipped with 12' x 1/8" silanized Pyrex glass columns and an electron capture detector. At least three different column packings were used: 10% Carbowax 20 M on 60/80 mesh Chromosorb W; 3% OV-101 on 80/100 Chromosorb G, and 5% QF-1 on 80/100 HMOS Chromosorb W. Nmr analysis was performed on a Varian model A-60. Melting points were obtained on a Fisher-Johns apparatus and are uncorrected. Mass spectra were obtained on a Varian CH-5 mass spectrometer using an ionization voltage of 70 eV. The yields reported are

representative for these types of reaction.

2-Chlorobiphenyl: synthesized by the Gomberg reaction using basically the method of Weingarten.[95] Specifically 0.2 mole of 2-chloroaniline (Aldrich Chemical Co., Inc.) was added to 60 ml concentrated hydrochloric acid (Baker, reagent grade) and cooled to 0-5°C in an ice bath. The chloroaniline was diazotized by slowly adding 20 g (0.30 mole) sodium nitrite (Mallinckrot, analytical reagent grade) in 30 ml water keeping the temperature below 5°C. Following the addition of the sodium nitrite, the solution was stirred for 1 hr and then added to 600 ml ice cold benzene (Baker, reagent grade). The heterogeneous solution was stirred vigorously and an aqueous solution of 100 g sodium acetate (Baker, reagent grade) was added. The mixture was then removed from the ice bath and stirred overnight at room temperature. The reaction solution was then transferred to a separatory funnel, and the organic layer washed three times with water. The benzene layer was then evaporated in a rotary evaporator under reduced pressure. Hexane was added to the remaining tar and the solution was passed through a silica gel column using hexane as the eluent. Following evaporation of the hexane 7.0 g (19% yield) of 2-chlorobiphenyl was isolated, m.p. 33-34°C (literature 33-34°C[96]).

3-Chlorobiphenyl: synthesized using the same procedure as 2-chlorobiphenyl starting with 3-chloroaniline (Aldrich), and isolated as an oil (7.4 g, 20% yield). Gomberg[97] reported as an oil, while Hutzinger reported a m.p.

of 16-17°C.[96] Nmr analysis showed only a multiplet in the aromatic region.

4-Chlorobiphenyl: obtained from Aldrich Chemical Company, Inc.

2,3-Dichlorobiphenyl: synthesized using the same procedure as 2-chlorobiphenyl starting with 2,3-dichloroaniline (Aldrich). It was isolated as an oil (33% yield) which had an identical gas chromatographic retention time to an authentic sample.[98] Weingarten[95] reported a m.p. of 27.7-28.2°C.

2,4-Dichlorobiphenyl: synthesized using the same procedure as 2-chlorobiphenyl starting with 2,4-dichloroaniline (Aldrich). The compound isolated was yellow so it was added to concentrated sulfuric acid, swirled for about five minutes, extracted with hexane and passed through another silica gel column. The biphenyl was isolated as an oil (literature m.p. 24-25°C[96]).

2,5-Dichlorobiphenyl: synthesized using the same procedure as 2-chlorobiphenyl starting with 2,5-dichloroaniline (Aldrich). The compound was isolated as an oil (47% yield) with a g.c. retention time identical to an authentic sample.[98] It was reported in the literature as an oil.[99] Nmr showed only a multiplet in the aromatic region.

2,6-Dichlorobiphenyl: synthesized using the same procedure as 2,4-dichlorobiphenyl starting with 2,6-dichloroaniline (Aldrich), m.p. 35-36°C (literature, 35-36°C[96]). The isotopic abundance ration (based on the number of chlorines) determined by mass spectrometry was consistent with that reported in the literature.[100]

3,4-Dichlorobiphenyl: synthesized using the same procedure as 2-chlorobiphenyl starting with 3,4-dichloroaniline (Aldrich), m.p. 48-49°C (literature, 45-46°C,[96] 48-49°C[95]). Mass spectrometry was consistent with dichlorobiphenyl.[100]

3,5-Dichlorobiphenyl: synthesized using the same procedure as 2,4-dichlorobiphenyl starting with 3,5-dichloroaniline (Aldrich), m.p. 32-33°C, (literature 36°C[101]). Mass spectrum isotopic abundance was consistent with dichlorobiphenyl.[100]

2,3,4-Trichlorobiphenyl: synthesized using the same procedure as 2,4-dichlorobiphenyl starting with 2,3,4-trichloroaniline. This latter compound was synthesized from 2,3,4-trichloronitrobenzene (Aldrich) by an iron/hydrochloric acid reduction using the method of El-Hewehi.[102] The aniline was isolated in 70% yield, m.p. 63-64°C (literature, 64.5°C[103]). The chlorobiphenyl was isolated in 53% yield, m.p. 100-101°C and had a mass spectrum consistent with a trichlorobiphenyl.[100]

2,3,5-Trichlorobiphenyl: The starting material for this synthesis was 2-nitroaniline (Aldrich). This compound was chlorinated to yield 2,4-dichloro-6-nitroaniline.[104] (Synthesis performed by R.D. Geer). This compound was converted to 2,3,6-trichloronitrobenzene by a Sandmeyer reaction.[105] Thus the nitroaniline (16.2 g) was added to 190 ml hot glacial acetic acid (DuPont), cooled to room temperature, and then added to 6.0 g sodium nitrite in 42 ml

concentrated sulfuric acid, keeping the temperature between 5-10°C. The solution was stirred one half hour at 5°C after all the aniline-glacial acetic acid had been added and was then added to a mixture of 16 g cuprous chloride (Baker) in 78 ml concentrated hydrochloric acid. This solution was stirred three hours, then filtered. The solid was washed with water, yielding bright yellow crystals in 60% yield, m.p. 43-44°C (literature 44-45°C[106]). The chloronitrobenzene was reduced and diazotized[107] as follows to yield the desired 2,3,5-trichlorobiphenyl. Stannous chloride (30 g) (Allied) was added to 40 ml concentrated hydrochloric acid and cooled to 5°C. The solution was stirred vigorously and 10 g 2,3,5-trichloronitrobenzene was added. The temperature rose to approximately 100°C whereupon the solution was cooled to about 0°C and the aniline was then diazotized and coupled to benzene in a manner similar to 2-chlorobiphenyl. The chlorobiphenyl was isolated in 37% yield and had a m.p. of 35-36°C (literature, 41°C[101]).

2,3,6-Trichlorobiphenyl: It has been reported that benzoic acids can be converted into anilines by the use of nitromethane[108] or sodium azide[109] in polyphosphoric acid. Therefore in an attempt to synthesize 2,3,6-trichloroaniline the method of Bachman and Goldmacher[108] was followed. While there was considerable gas evolution during the reaction, upon workup there was a large amount of unreacted benzoic acid, and no trichloroaniline was detected. This reaction does not proceed very well in the presence of

electron withdrawing groups (i.e., chlorines) which probably accounts for the failure to synthesize the aniline. The same reaction was attempted using sodium azide instead of nitromethane, again with no success. The desired compound was finally synthesized as follows. 2,5-dichloro-6-nitroacetanilide was synthesized by S. O. Farwell by nitration of 2,5-dichloroacetanilide[110] and isolated by the procedure of Tas and Kleipool.[111] The chloronitroacetanilide (1.82 g) was added to 5 ml concentrated sulfuric acid and hydrolyzed 1 hr at 90-100°C. The solution was cooled, poured on cracked ice, the solid filtered and resuspended in 21.2 ml concentrated hydrochloric acid. The dichloronitroaniline was diazotized and coupled to benzene in a manner similar to 2-chlorobiphenyl with one notable exception--the diazotization was performed at 25-35°C. This allows the nitro- group to be substituted by a chlorine. The product isolated (0.50 g) was analyzed by g.c. which revealed approximately 80 % 2,3,6-trichlorobiphenyl, 15% 2,4,5-trichloro-, and minor amounts of 2,5-dichloro- and 2,3,4,6-tetrachlorobiphenyls.

2,4,5-Trichlorobiphenyl: synthesized using the same procedure as 2-chlorobiphenyl starting with 2,4,5-trichloroaniline (Aldrich), m.p. 78-79°C (literature, 78-79°C[112]). Nmr (δ (vs. TMS), solvent, carbon tetrachloride): 7.25, apparent singlet, 6 protons on unsubstituted ring; 7.30, singlet, 1 proton at 6- position; 7.45, singlet, 1 proton at 3- position). The mass spectrum was consistent with a trichlorobiphenyl.[100]

2,4,6-Trichlorobiphenyl: synthesized using the same procedure as 2-chlorobiphenyl starting with 2,4,6-trichloroaniline (Aldrich). The product isolated (8% yield) had a m.p. of 60-61°C (literature, 62.5°C[96]). The nmr revealed only a multiplet in the aromatic region.

3,4,5-Trichlorobiphenyl: the starting material for this synthesis was 2,6-dichloro-4-nitroaniline (Aldrich). A Sandmeyer reaction was run on this compound in a manner analogous to 2,4-dichloro-6-nitroaniline (see 2,3,5-trichlorobiphenyl) to yield 3,4,5-trichloronitrobenzene in 70% yield, m.p. 67-68°C (literature, 71°C[113]). This latter compound was reduced to 3,4,5-trichloroaniline by an iron/hydrochloric acid reduction[102] in 53% yield, m.p. (from ethanol) 96-96°C (literature, 94-95°C[102]). 3,4,5-trichlorobiphenyl was then synthesized by the procedure analogous to 2,4-dichlorobiphenyl (23% yield), m.p. 72.5-73.5°C. The mass spectrum was consistent with a trichlorobiphenyl.[100]

2,3,4,5-Tetrachlorobiphenyl: synthesized by the procedure used for 2-chlorobiphenyl, starting with 2,3,4,5-tetrachloroaniline (Aldrich). Gas chromatographic analysis revealed considerable contamination by an early eluting compound, presumably 1,2,3,4-tetrachlorobenzene.

2,3,4,6-Tetrachlorobiphenyl: This compound proved rather difficult to synthesize and the end product isolated was never quite satisfactory. Zincko and Schaum[114] and Claus and Wallbaum[115] reportedly synthesized 2,3,4,6-

tetrachloroaniline by chlorination of 3-chloroaniline in concentrated hydrochloric acid. I attempted this using the procedure of Atkinson et al.[116] The end result was a gummy black tar that resisted cleanup. Next the 3-chloroaniline was acetylated by adding 25 g of the chloroaniline to 75 ml acetic anhydride and refluxing for 2 hours. Water was then added and the solution boiled a while longer. Upon cooling an oil separated which crystallized upon standing, 9.7 g yield, m.p. 73-75°C (literature, 77-78°C[117]). The previous acylation was repeated to yield more material and then 19.7 g 3-chloroacetanilde was added to 220 ml glacial acetic acid. The temperature of the solution was raised to about 60°C and a stream of chlorine gas was passed through the mixture. After 1 hour the solution had gained 12 g; this weight held constant another hour during which time a white precipitate formed. Chlorination continued 1 more hour and then the solution was filtered. 20.5 g of white solid was isolated, m.p. 175-176°C. Five g of the chloroacetanilde was deacetylated in 20 % sulfuric acid. The recovered amine had an identical g.c. retention time (column 3% OV-101) to 2,4,5-trichloroaniline. Furthermore, a mass spectrum was obtained on the chloroacetanilde. This revealed a trichloro- substitution pattern. Therefore the rest of the trichloroacetanilide was added back to glacial acetic acid and the chlorination was continued at 100°C for 12.5 hours more. After 9 hours there was no appreciable change, and g.c. analysis indicated approximately 85% tetrachloro- and 15% trichloro-

acetanilides. The solution was cooled to room temperature and the solid which formed was isolated by filtration, m.p. 159-161°C. Approximately 11 g of the tetrachloroacetanilide was hydrolyzed 3 hr in 20% sulfuric acid at 100°C. Only a small amount (approximately 1 g) went to the amine, m.p. 87-89°C (literature, 89°C[114,115]). Five g of the unhydrolyzed acetanilide was added to 6.5 ml concentrated sulfuric acid and refluxed 0.5 hr. Upon cooling the biphenyl was synthesized as described for 2-chlorobiphenyl (sulfuric acid used instead of hydrochloric). A minute amount of oil was isolated, which eventually solidified upon standing. Gas chromatographic analysis revealed only one peak and voltammetric results were consistent with a tetrachlorobiphenyl.

2,3,5,6-Tetrachlorobiphenyl: purchased from Analabs, Inc.

2,3,4,5,6-Pentachlorobiphenyl: Numerous attempts were made to synthesize this compound starting with pentachloroaniline. This latter compound was synthesized from pentachloronitrobenzene (Aldrich) by an iron/hydrochloric acid reduction,[102] yield 62%, m.p. 229-231°C (literature 229°C[118]). Using a procedure similar to 2-chlorobiphenyl failed to give pentachlorobiphenyl because there was no apparent diazotization. Pentachloroaniline could be diazotized by using glacial acetic acid and sulfuric acid; however when the solid diazonium sulfate was isolated (cf. Hodgson and Mahadevan[119]) and added to benzene the major product isolated appeared to be pentachlorobenzene (by g.c. analysis). 2,3,4,5,6-pentachlorobiphenyl was finally synthesized

by using the method of Cadogan.[120] Isopentylnitrite (3.1 g) was added to 5 g pentachloroaniline in 70 ml benzene and the solution refluxed 2 hours. Upon cooling the benzene and unreacted isopentyl nitrite were removed under reduced pressure on a rotary evaporator. The chlorobiphenyl was taken up in hexane and passed through a silica gel column with hexane as the eluent. Two recrystallizations from hexane afforded pure 2,3,4,5,6-pentachlorobiphenyl, m.p. 122-123°C (literature, 123°C[96]). Gas chromatographic retention time was identical to a sample from Analabs, Inc.

3,3'-Dichlorobiphenyl: 10 g of 3,3'-dichlorobenzidine (K & K Laboratories) was added to 43 ml concentrated sulfuric acid. The solution was cooled and 92 ml of water was slowly added keeping the temperature below 50°C. The mixture was cooled to 5°C and 6.2 g sodium nitrite in 55 ml water was slowly added while the temperature was kept below 5°C, after which the solution was stirred 0.5 hours. The tetrazodized solution was then rapidly added to 53 ml ice cold hypophosphorus acid and stirred at 5°C for 16 hours and then at room temperature for 4 hours. The precipitate formed was isolated by filtration, washed with water, dried, taken up in hexane and eluted through a silica gel column with hexane. The dichlorobiphenyl was isolated in 36% yield as an oil (literature m.p., 26-27°C[96]).

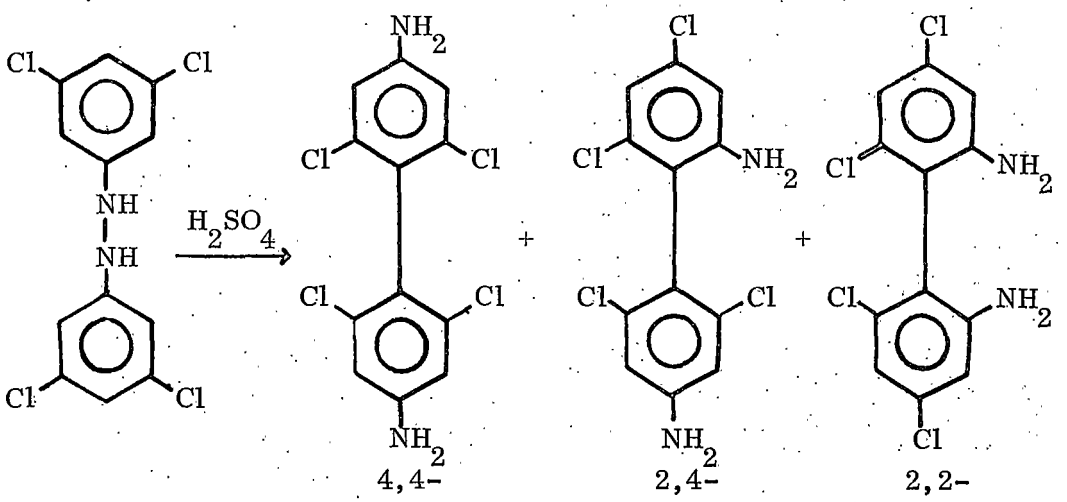
4,4'-Dichlorobiphenyl: 120 ml concentrated hydrochloric acid was added to 0.2 mole benzidine hydrochloride (Baker). The solution was cooled to 5°C

and 28 g sodium nitrite in 42 ml water was added while the temperature of the solution was kept below 5°C. The resultant solution was then stirred 0.5 hr and then added to 0.8 mole cuprous chloride with stirring. The mixture was stirred overnight, then diluted with water, the precipitate filtered, washed with water, dried and eluted through a silica gel column with hexane. The isolated biphenyl had an identical g.c. retention to an authentic sample[98] and had a m.p. of 144-146°C (literature, 148-149°C[96]).

2,5,2',5'-Tetrachlorobiphenyl: This compound was synthesized in a manner similar to 3,3'-dichlorobiphenyl starting with 2,5,2',5'-tetrachlorobenzidine (Pfaltz and Bauer). The resulting biphenyl which had a g.c. retention time identical to an authentic sample[121] had a m.p. of 87-88°C (literature, 85-86.5°C[122]) and a mass spectrum consistent with a tetrachlorobiphenyl.[100]

2,6,2',6'-Tetrachlorobiphenyl: The starting material for this compound was 2,6-dichloro-4-nitroaniline. 50 g of the nitroaniline was added to 500 ml glacial acetic acid which was slowly added to 18.2 g sodium nitrite in 130 ml concentrated sulfuric acid (cf. Hodgson and Walker[105]) while keeping the temperature below 10°C. The resultant solution was added to 160 ml of ice cold hypophosphorus acid and stirred 16 hours at 5°C and then 4 hours at room temperature. The precipitate that formed was isolated by filtration and recrystallized from ethanol. There was a small amount of non-soluble yellow material which was apparently unreacted nitroaniline. The desired

product, 3,5-dichloronitrobenzene, was isolated as red plates in 50% yield, m.p. 58-61°C (literature, 62-63.5°C[123]), and an infrared spectrum consistent to one reported in the literature.[124] The dichloronitrobenzene was coupled to form 3,5,3',5'-tetrachloroazobenzene and then reduced to form 3,5,3',5'-tetrachlorohydrazobenzene by the method of Van Roosmalen[125] in 96% yield, m.p. 120-123°C (literature, 120°C[125]). Van Roosmalen's procedure was also followed to convert the chlorohydrazobenzene into what was supposedly 2,6,2',6'-tetrachlorobenzidine in 70% yield. This chlorobenzidine was tetrazodized and then treated with hypophosphorus acid by the method used for 3,3'-dichlorobenzidine, to yield a crude tetrachloro- product in 36% yield. Chromatographic analysis revealed three products. This can be accounted for by the following. Normally on a benzidine rearrangement, a 4,4- linkage occurs, but it is also possible to get a 2,4- and a 2,2- linkage thus giving the following products,



4,4- 2,4- 2,2-

which upon tetrazotization will give three different tetrachlorobiphenyls. That this is the case can be seen from the synthesis of 2,4,6,2',4',6'-hexachlorobiphenyl. When a Sandmeyer reaction is run on the mixture of diaminotetrachlorobiphenyls above only one product should be obtained as indeed was the case. The mixture of tetrachlorobiphenyls was repeatedly recrystallized from glacial acetic acid to finally give pure 2,6,2',6'-tetrachlorobiphenyl in 7% yield, m.p. 197-198°C (literature, 198°C[96]).

3,4,3',4'-Tetrachlorobiphenyl: 3,3'-dichlorobenzidine (10 g) was slowly added to 42 ml concentrated sulfuric acid and cooled. Water (92 ml) was slowly added while the temperature was held below 50°C. The solution was cooled to 0-5°C and 6.2 g sodium nitrite in 55 ml water was added, while keeping the temperature below 5°C. The resulting solution was stirred 0.5 hours, then added to 6.2 g cuprous chloride in 31 ml concentrated hydrochloric aicd and stirred overnight at room temperature. The precipitate formed was isolated by filtration, washed with water, dried and then eluted through a silica gel column using 10% benzene in hexane, m.p. 170-171°C (literature, 171°C[125]).

3,5,3',5'-Tetrachlorobiphenyl: The first attempt to synthesize this compound was by direct chlorination of benzidine in hydrochloric acid to yield 3,5,3',5'-tetrachlorobenzidine. The end product from this reaction was a black mass that resisted cleanup. This led to an attempt to chlorinate the

diacetylated benzidine. The acetyl group is not as strong a director; however, this type of a compound should be more resistant to the oxidizing action of the chlorine. Benzidine was acetylated and chlorinated by the method of Van Roosmalen[125] to yield 3,5,3',5'-tetrachloro-N,N'-diacetylbenzidine. The chlorination proceeded in a slightly different manner than he described. After 1.5 hours of chlorination the solid disappeared; after 2 hours a solid appeared which disappeared after another 2 hours of chlorination. When solid material again appeared the chlorination was stopped and the product isolated by filtration in 70% yield. There was also approximately 19% starting material and smaller amounts of other compounds. Since 3,5,3',5'-tetrachloro-N,N'-diacetylbenzidine is only sparingly soluble in glacial acetic acid, the precipitate suspended in hot glacial acetic acid and filtered hot in an attempt to get rid of the undesired isomers. The acetylated benzidine was hydrolyzed in concentrated sulfuric acid for 0.5 hr at 110°C and following the addition of water was tetrazodized and treated with hypophosphorus acid in a manner analogous to 3,3'-dichlorobenzidine. Following cleanup g.c. analysis indicated at least six components of which two were major. For a discussion on the nature and causes of this mixture see Ayres.[126] Recrystallization from glacial acetic acid afforded one component in greater than 90% purity, m.p. 158-160°C (literature, 162°C[125]).

2,5,3',5'-Tetrachlorobiphenyl: This compound was synthesized by the

procedure used to make 2,3,4,5,6-pentachlorobiphenyl. The starting materials were 3,5-dichloroaniline and 1,4-dichlorobenzene (Aldrich). The reaction was run at a temperature of 80°C. Unreacted dichlorobenzene was removed by reduced pressure distillation and the crude product was treated with concentrated sulfuric acid, then extracted with hexane and passed through a silica gel column with hexane. The product was isolated in 29% yield with a m.p. of 103.5-104.5°C (literature, 105.5-106.5°C[122]).

2,5,2',4',5'-Pentachlorobiphenyl: In an attempt to diazotize (rather than tetrazodize) benzidine and various benzidine analogues, just one mole of sodium nitrite for each mole of benzidine was used. A reaction of this type had been reported in the literature,[127,128] but in my hands the end result contained two components: an acid soluble (6 N hydrochloric acid) fraction with a m.p. of 117°C and an infrared spectrum identical to benzidine; and an acid insoluble fraction which after being passed through a silica gel column with hexane had a m.p. of 130°C and an infrared spectrum identical to 4,4'-dichlorobiphenyl. The diazotization of just one of the amino groups of 2,5,2',5'-tetrachlorobenzidine by using just one mole of sodium nitrite per mole of benzidine was also attempted. Following addition to cuprous chloride (to perform a Sandmeyer) the reaction products were isolated an analyzed by g.c. This revealed approximately 50% 2,4,5,2',4',5'-hexachlorobiphenyl and 50% unreacted 2,5,2',5'-tetrachlorobenzidine. I next attempted to monoacetylate one

of the amino groups on benzidine. Gelmo[129] reported that it was possible to monoacetylate benzidine with oxalic acid, then run a Sandmeyer reaction, which after saponification with sulfuric acid yields 4-amino-4'-chlorobiphenyl. His procedure was followed and the desired product was isolated; however when the same reaction was attempted with 3,3'-dichlorobenzidine the monoacetylated benzidine was only recovered in about a 1% yield. I then tried to form monoacetylated 2,5,2',5'-tetrachlorobenzidine with acetic anhydride in chloroform. 2,5,2',5'-tetrachlorobenzidine (50 g) was added to 1200 ml chloroform (Baker). Acetic anhydride (15.7 ml) in 204 ml chloroform was then added and the solution was refluxed 5 hours, after which 3.5 ml more acetic anhydride was added and refluxing was continued an additional 1.5 hours. On cooling 2,5,2',5'-tetrachloro-N,N'-diacetylbenzidine precipitated and was filtered off. The chloroform was removed under reduced pressure by rotary evaporator. Repeated recrystallization from aqueous ethanol afforded 2,5,2',5'-tetrachloro-N-acetylbenzidine in 50% yield. The tetrachloro-N-acetylbenzidine (10 g) was added to 62 ml hot glacial acetic acid and rapidly cooled to 15°C. To this mixture was added 2.5 g sodium nitrite in 16 ml concentrated sulfuric aicd while keeping the temperature below 15°C. After the addition, the solution was stirred 0.5 hour and then added to 5.9 g cuprous chloride in 30 ml concentrated hydrochloric acid. The solution was stirred two hours, the precipitate isolated by filtration, washed with water and recrystallized with aqueous

ethanol to give 2,5,2',4',5'-pentachloro-N-acetyl-4-aminobiphenyl in 77% yield. A mass spectrum of this compound was consistent with a pentachloro-compound.[100] A small portion of this compound was deacetylated and following isolation was subjected to nmr analysis: δ4.1, singlet, 2 protons, amino group; δ 6.75, apparent singlet, 1 proton, 3- position (?); δ 7.08, apparent singlet, 1 proton, 6- position (?); δ7.25, multiplet, 3 protons. The acetylated amino-tetrachlorobiphenyl was added to 12.7 ml concentrated sulfuric acid and hydrolyzed at 110°C for 0.5 hour. Upon cooling 27.5 ml water was added and the compound diazotized as above, then added to 16 ml ice cold 50% hypo-phosphorus acid, stirred at 5°C for 16 hours and at room temperature for 4 hours. The precipitate formed was filtered, washed with water, dried and passed through a silica gel column with hexane. Repeated recrystallication from hexane and then ethanol gave at least 99.9% pure 2,5,2',4',5'-pentachloro-biphenyl. This compound had an identical g.c. retention time to an authentic sample,[121] m.p. 75-76°C (literature, 74-76°C[130]).

2,4,5,2',4',5'-Hexachlorobiphenyl: 2,5,2',5'-tetrachlorobenzidine was tetrazodized and treated with cuprous chloride in a manner analogous to the synthesis of 3,4,3',4'-tetrachlorobiphenyl. The product was eluted through a silica gel column with hexane and isolated in a 45% yield, m.p. 101-102°C (literature, 100-102°C[130]). An apparently erroneous value of 137-138°C has been reported.[131]

2,4,6,2',4',6'-Hexachlorobiphenyl: 2,6,2',6'-tetrachlorobenzidine (cf. section on 2,6,2',6'-tetrachlorobiphenyl) was tetrazodized and treated with cuprous chloride in a manner analogous to the synthesis of 3,4,3',4'-tetrachlorobiphenyl. The product was eluted through a silica gel column with hexane and isolated in a 24% yield, m.p. 111-112°C (literature, 112-113°C[96]).

3,5,2',3',5'-Pentachlorobiphenyl: synthesized using the same procedure as 2,5,3',5'-tetrachlorobiphenyl starting with 3,5-dichloroaniline and 1,2,4-trichlorobenzene (Aldrich). As expected, three products were detected by g.c. analysis. Using Weingarten's work[95] as an analogy we expected to obtain about 50 to 60% 3,5, ',3',6'-, 30 to 40% 3,5,2',4',5'- and about 10% 3,5,2',3',5'-pentachlorobiphenyls. Sissons and Welti's work[132] predicts the g.c. elution order to be 3,5, ',3',6'-, followed by 3,5,2',3',5'- and then 3,5,2',4',5'-pentachlorobiphenyls. If this is the correct order the relative amounts of each compound we found (assuming identical electron capture g.c. responses) is 40:30:30 respectively.

3,4,5,3',4',5'-Hexachlorobiphenyl: 3,5,3',5'-tetrachloro-N,N'-diacetylbenzidine (cf. section on 3,5,3',5'-tetrachlorobiphenyl) was deacetylated and tetrazodized by the same method used in the synthesis of 3,5,3',5'-tetrachlorobiphenyl. Following tetrazotization the benzidine (10 g) was added to 2.5 g cuprous chloride in 12.5 ml concentrated hydrochloric acid, stirred 3 hours, the precipitate isolated by filtration, washed with water and dried.

The product was recrystallized from glacial acetic acid and passed through a silica gel column eluting with 10% benzene in hexane. Gas chromatographic analysis indicated at least six components. One component was obtained in about 70% purity after repeated recrystallizations.

Decachlorobiphenyl: synthesized by the method of Hutzinger et al.[96] substituting Arochlor® 1262 for Arochlor 1268 and using more antimony pentachloride (Baker) (12 g) to make up for the lower chlorine content of the mixture, m.p. 306-307°C (literature, 305-306°C[96]).

Part of this work on the reduction of organochlorine compounds of environmental interest involved looking at chlorinated naphthalenes.[1] While the great majority of these compounds were obtained as gifts from various sources it was necessary to synthesize a few lower chlorinated analogues to complete the series of di- and trichlorinated naphthalenes. I also conducted a brief survey into synthetic routes that would give us other higher chlorinated naphthalenes.

1,2,3-Trichloronaphthalene: Fenyes[133] reported using phosphorus pentachloride to convert 1,2-dichloro-3-nitronaphthalene into 1,2,3-trichloronaphthalene. This same reaction was attempted (the dichloronitronaphthalene was obtained as a gift from Dr. Julius Hyman, Berkeley, California) following Fenyes' procedure. The reaction was quenched by the addition of water and the product extracted with hexane. Cleanup was afforded by passing the

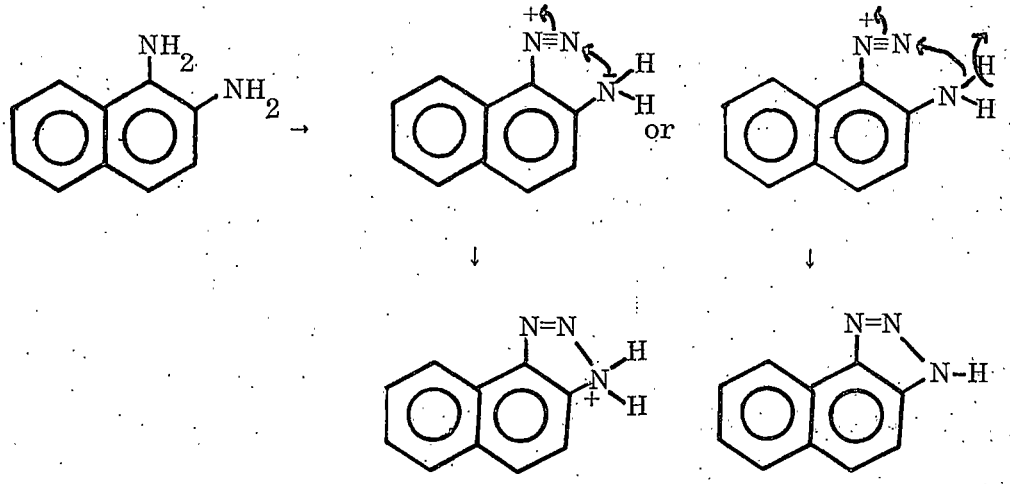
product through a silica gel column with hexane and then recrystallizing from methanol. Gas chromatographic analysis using the flame ionization detector indicated the formation of 1,2,3-trichloronaphthalene in greater than 90% purity. The contaminants appeared to be higher chlorinated analogues.

2,3-Dichloronaphthalene: Since phosphorus pentachloride did appear to convert nitronaphthalenes into their chloro- analogues I next attempted to synthesize 2,3-dichloronaphthalene by the same method. 2,3-Dinitronaphthalene (150 mg, obtained from J. Hyman) was added to 1500 mg phosphorus pentachloride and the mixture was heated for 3 hours at 160-165°C. The reaction was quenched by the addition of water, extracted with hexane and analyzed by g.c. Three peaks were observed, all of different retention times than the starting material. After passing the material through a silica gel column with hexane only two compounds remained. Recrystallization from ethanol gave pure 2,3-dichloronaphthalene, m.p. 118-119°C (literature, 119.5-120.5°C[134]).

1,2,3,4,5,6,7-Heptachloronaphthalene: The same procedure was used to synthesize 1,2,3,4,5,6,7-heptachloronaphthalene. Thus 150 mg 1,2,3,4,5,6-hexachloro-7-nitronaphthalene (obtained from J. Hyman) was added to 375 mg phosphorus pentachloride and heated at 150-160°C for 5 hours. The reaction was quenched and extracted in the usual manner, passed through a silica gel column with hexane and the product recrystallized from hexane, m.p. 164-71°C.

1,8-Dichloronaphthalene: 5 g 1,8-diaminonaphthalene (Pfaltz and Bauer) was tetrazodized and added to cuprous chloride in hydrochloric acid in a manner analogous to the synthesis of 3,4,3',4'-tetrachlorobiphenyl. The product was passed through a silica gel column with hexane and isolated in 18% yield, m.p. 87-88°C (literature, 88.5-90°C[135]).

1,2-Dichloronaphthalene: Since 1,8-diaminonaphthalene was so readily tetrazodized the same process was attempted with 1,2-diaminonaphthalene (Aldrich) to synthesize 1,2-dichloronaphthalene. Despite repeated attempts I failed to isolate the desired compound. This was somewhat disturbing since in addition to the 1,8- compound, 1,6-diaminonaphthalene readily tetrazodizes.[134] One possible explanation for the failure of 1,2-diaminonaphthalene to tetrazodize is that when the diazonium salt of one of the amino groups if formed it is immediately attacked by the other amino group.



Next I attempted to treat the diamino compound with phosphorus pentachloride in a manner similar to the nitro compounds. This also did not work. Finally the desired product was obtained by treating 1-chloro-2-naphthylamine hydrochloride (Aldrich) with sodium nitrite and hydrochloric acid and then adding the diazonium compound to cuprous chloride-hydrochloric acid. The dichloronaphthalene was purifed by passing it through a silica gel column with hexane, m.p. 34-35°C (literature, 34-35°C[135]).

γ-BTC: synthesized by a zinc reduction of lindane. Specifically, 5 g of lindane and 1.2 g of zinc dust were added to 20 ml of 95% ethanol and the mixture was refluxed 1 hr. Upon cooling 20 ml of water was added and the solution extracted three times with 50 ml portions of hexane. Three major components were revealed by g.c. analysis, an unidentified early eluting fraction followed by γ-BTC, and then by unreacted lindane. The γ-BTC was isolated by preparatory g.c. and had a melting point of 88-89°C and an infrared spectrum in agreement with the values reported by Orloff et al.[136]

4,5,6,7,8-Pentachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene: This compound was synthesized by a chromous chloride reduction of heptachlor using the method of Chau,[43] m.p. 102-103°C (literature 102-103°C[43]). The chromous chloride was generated by Rosenkranz's et al. procedure.[137]

Modifications to CNDO/2 Program

A large part of this work involved performing molecular orbital calculations on the compounds investigated by reductive electrochemistry and under anaerobic conditions. The currently available CNDO/2 program[138] requires in excess of 50,000 (50K) words of core to run. This very large core requirement is basically due to the labeled COMMON-ARRAYS which contain three 80 x 80 arrays. Since all calculations are done in double precision this requires that 38,400 words be set aside for this common. The rest of the program requires approximately 11K words.

The user of the Xerox Sigma 7 computer at Montana State University has direct access to approximately 48K of core. In order to be able to perform the desired calculations it was necessary to modify the program to meet the 48K limit.

The program obtained from QCPE[138] was written in double precision. By changing all values, with the exception of total energy, to single precision, the core requirement for the common arrays was reduced to 19,600 and the overall program requirement to 35K. Since another 13K was still available, this indicates that the program can be redimensioned from the presently allowed 80 orbitals and still stay within the 48K maximum. The program was successfully expanded to accommodate 100 orbitals; this value was selected because it would allow pentachlorobiphenyl to be run. The core

requirement for this modification (stored under the name CNDOT) is 40.9 The specific changes performed to produce this version are outlined in Table 1.

Since redimensioning the program turned out to be a relatively easy task, the original double precision program was altered to a size that could be accommodated by the Sigma 7. We were unsure as to whether performing molecular orbital calculations in single precision was producing a non-random error which could give us erroneous results. By redimensioning the original program we could then compare single and double precision results. The program chosen to be modified was the unaltered version obtained from QPCE.[138] In addition to dimensional changes, the program was modified to provide greater ease in data entering. This version will handle 74 orbitals in double precision accuracy. This is of sufficient size to allow calculations on molecules the size of pentachlorobenzene. The specific changes are similar to those outlined in Table 1, based on a 74 orbital size.

There now existed two programs one of which was capable of handling up to 100 orbitals. It now seemed desirable to expand the program even further so that molecules of the size of DDT could be handled. As previously mentioned, there are three arrays in the labeled COMMON-ARRAYS. These arrays can be considered the limiting factor on the number of orbitals that can be

Table 1. Modifications to CNDO/2 Program To Generate 100 Orbital Version

Area of Program	Old Program	New Program
MAIN PROGRAM	COMMON/ARRAYS/ABC(19200) COMMON/GAB/XYZ(2000) COMMON/INFO1/...U(80)...	COMMON/ARRAYS/ABC(30000) COMMON/GAB/XYZ(2180) COMMON/INFO1/...U(100)...
SUBROUTINE COEFFT	COMMON/ARRAYS/S(80,80)...XX(2900)	COMMON/ARRAYS/S(100,100)...XX(10100)
SUBROUTINE INTGRL	COMMON/ARRAYS/S(80,80)...XX(2900) COMMON/INFO1/...U(80)... COMMON/GAB/XXX(400)...YYY(126) DIMENSION P(80,80)	COMMON/ARRAYS/S(100,100)...XX(10100) COMMON/INFO1/...U(100)... COMMON/GAB/XXX(500)...YYY(206) DIMENSION P(100,100)
FUNCTION SS	COMMON/ARRAYS/S(80,80)...XX(2900)	COMMON/ARRAYS/S(100,100)...XX(10100)
SUBROUTINE MATOUT	COMMON/ARRAYS/A(80,80,3)	COMMON/ARRAYS/A(100,100,3)
SUBROUTINE HUCKEL	COMMON/ARRAYS/A(80,80),B(80,80),D(80,80) COMMON/INFO1/...U(80)... COMMON/GAB/XXX(400),G(35,35),Q(80)YYY(80),ZZZ,ENERGY,OLDEIG(80),DMD(80)XXY(52)	COMMON/ARRAYS/A(100,100),B(100,100),D(100,100) COMMON/INFO1/...U(100)... COMMON/GAB/XXX(500),G(35,35),Q(100),YYY(100),ZZZ,ENERGY,OLDEIG(100),DMD(100),XXY(52)
SUBROUTINE SCFCLO	SAME AS SUBROUTINE HUCKEL DIF=(ABS(OLDEIG(I)...240)) OLDEIG(I)=XXX(I+240)	SAME AS SUBROUTINE HUCKEL DIF=(ABS(OLDEIG(I)...300)) OLDEIG(I)=XXX(I+300)

Table 1. (Continued)

Area of Program	Old Program	New Program
SUBROUTINE CPRINT	SAME AS SUBROUTINE HUCKEL	SAME AS SUBROUTINE HUCKEL
SUBROUTINE HUCKOP	COMMON/ARRAYS/A(80,80),B (80,80),Q(80,80) COMMON/GAB/XXX(400),G(35, 35),FDIAG(80),PDIAG(80), ZZZ,ENERGY,OLDEIG(80), DMD(80),XXY(52) COMMON/INFO1/...U(80)...	COMMON/ARRAYS/A(100,100),B (100,100),Q(100,100) COMMON/GAB/XXX(500),G(35, 35), FDIAG(100),PDIAG(100), ZZZ,ENERGY,OLDEIG(100), DMD(100),XXY(52) COMMON/INFO1/...U(100)...
SUBROUTINE SCFOPN	SAME AS SUBROUTINE HUCKOP DIF=ABS(OLDEIG(I)...240)) OLDEIG(I)=XXX(I+240)	SAME AS SUBROUTINE HUCKOP DIF=ABS(OLDEIG(I)...300)) OLDEIG(I)=XXX(I+300)
SUBROUTINE OPRINT	SAME AS SUBROUTINE HUCKOP	SAME AS SUBROUTINE HUCKOP
SUBROUTINE EIGN	COMMON/ARRAYS/A(80,80),VEC (80,80),X(80,80) COMMON/GAB/GAMMA(80),BETA (80),BETASQ(80),EIG(80),W (80),XYZ(1600) DIMENSION P(80),Q(80) DIMENSION IPOSV(80),IVPOS (80),IORD(80)	COMMON/ARRAYS/A(100,100),VEC (100,100),X(100,100) COMMON/GAB/GAMMA(100),BETA (100),BETASQ(100),EIG(100),W (100),XYZ(1680) DIMENSION P(100),Q(100) DIMENSION IPOSV(100),IVPOS (100),IORD(100)

Table 1. (Continued)

Area of Program	Old Program	New Program
SUBROUTINE SCFOUT	COMMON/ARRAYS/A(80,80,3) COMMON/GAB/XXX(2000) COMMON/INFO1/...U(80)...	COMMON/ARRAYS/A(100,100,3) COMMON/GAB/XXX(2180) COMMON/INFO1/...U(100)...
SUBROUTINE EIGOUT	COMMON/GAB/XXX(240), EPSILN (80), YYY(1680)	COMMON/GAB/XXX(300), EPSILN (100), YYY(1780)

handled. For open shell calculations, all three arrays appear to be used while only two of the 80 x 80 arrays are used in closed shell calculations. Since the closed shell calculations appeared to be confirming the electrochemical data, it should be worthwhile to expand the program so that more orbitals could be included even though the open shell portion would have to be sacrificed.

The program contains two large tables, Y and Z that are stored in SUBROUTINE COEFFT. The first of these tables contains 9135 elements all of which are zero except for 224 locations. The second has 765 elements, all but 87 being equal to zero. These tables are stored in the last two 80 x 80 arrays of COMMON-ARRAYS. To eliminate the third 80 x 80 array it is necessary to cut down the two tables to the size of their non-zero elements (approximately 250 terms).

Two new tables were generated to replace Y and Z which contained 224 and 68 elements respectively. Each element in the new tables contains three items, the old location, followed by the coefficient stored at that location and then the sign of that coefficient. For example, in the old program, 64.EO was stored at location Y (7039). In the new program it is stored at location M (1) as 70390642. The first four digits refer to the old location (7039), the next three to the coefficient (064) and the last digit to the sign (2 if plus, 1 if minus).

The new table Y, which is now called M, was generated by using the following program. Table Y was used as the data for this program, and the output was stored in a new subroutine called COEFFY.

```
      DIMENSION M(250)
 10   DO 100 II=1,224
      READ (10,1) I,K
  1   FORMAT (8X,I4,4X,I4)
      IF(K)30,40,40
 30   L=1
      GO TO 60
 40   L=2
 60   M(II)=I*10000+IABS(K)*10+L
      WRITE(11,2) II,M(II)
  2   FORMAT (6X,'M(',I3,')=',2X,I8
100   CONTINUE
      STOP
      END
```

Table Z was treated in the same manner and is stored in SUBROUTINE COEFFZ as Table N.

We now need to obtain the correct coefficient when necessary. This is accomplished in FUNCTION SS. In FUNCTION SS the Y table is transformed from a single dimensional array to a 9 x 5 x 203; Table Z is likewise changed into a 17 x 45 array. The three-dimensional array is back-transformed into a single dimensional one as follows:

```
KZ(1)=765-(17-(I+1))-17*(45-L)
KY(1)=9135-(9-(I+1))-9*(5-(J+1))-45*(203-1)
```

Once a KZ(1) or a KY(1) has been established the program searches the appropriate subroutine, COEFFZ or COEFFY, to find the correct coefficient.

This is accomplished by the following statements using the Z table as an example.

```
      DO 10 J=1,87
      IF(KZ(1)-N(J)/100000) 10,20,10
10    CONTINUE
      Z(1)=0.0
      GO TO 21
20    IS=MOD (N(J),10)
      Z(1)=FLOAT(MOD(N(J),10000)/10)*(-1)**IS
21    RETURN
      END
```

The program checks to see if IZ(1) matches the first four digits in a particular location. When it does the program established the sign (IS=MOD(N(J),10) and combines this sign with the coefficient and returns the coefficient to FUNCTION SS as Z(1).

The rest of the changes are basically redimensioning to include 130 orbitals, as in the previous cases, with the marked difference the loss of the third array in the labeled COMMON-ARRAYS. This program is stored under the name CNDOMEG and requires 43K. The specific changes are shown in Table 2.

In the CNDO approximation[88] the total energy of a molecule is found from:

$$E_{total} = \tfrac{1}{2} \sum_{\mu\nu} P_{\mu\nu}(H_{\mu\nu} + F_{\mu\nu}) + \sum_{A<B} Z_A Z_B / R_{AB}$$

where μ = orbital on atom A

Table 2. Modification to CNDO/2 Program To Generate 130 Orbital Version

Area of Program	Old Program	New Program
MAIN PROGRAM	COMMON/ARRAYS/ABC(19200)	COMMON/ARRAYS/ABC(33800)
	COMMON/GAB/XYZ(2000)	COMMON/GAB/XYZ(2398)
	COMMON/INFO1/...U(80)...	COMMON/INFO1/...U(130)...
	CALL COEFFT	DELETED
	IF(OPNCLO. EQ. OPEN) GO TO 90	DELETED
	90 CALL HUCKOP	DELETED
	CALL SCFOPN	DELETED
	CALL OPRINT	DELETED
SUBROUTINE COEFFT		DELETED ENTIRE SUBROUTINE
SUBROUTINE INTGRL	COMMON/ARRAYS/S(80,80) ...XX(2900)	COMMON/ARRAYS/S(130,130) ...XX(16900)
	COMMON/INFO1/...U(80)...	COMMON/INFO1/...U(130)...
	COMMON/GAB/XXX(400)... YYY(126)	COMMON/GAB/XXX(650)... YYY(274)
	DIMENSION P(80,80)	DIMENSION P(130,130)
FUNCTION SS	COMMON/ARRAYS/S(80,80), Y (9,5,203), Z(17,45), XX(2900)	COMMON/ARRAYS/S(130,130), Y (1), Z(1), KY(1), KZ(1), XX(16896)
	AFTER NNI1=N1+N2-I+1	INSERT KZ(1)=765-(17-(I+1))-17*(45-L) CALL COEFFZ
	S=S+Z(I+1,L)*A(I+1)*B(NNI1)/ 2.E0	X=X+Z(1)*A(I+1)...
	AFTER IIII=2*J+MOD(K+I,2)+1	INSERT KY(1)=9135-(9-(I+1))-9*(5-(J+1))-45*(203-L)

Table 2. (Continued)

Area of Program	Old Program	New Program
	70 X=X+Y(I+1, J+1, L)*A(I+1)*B (IIII)	CALL COEFFY 70 X=X+Y(1)*A(I+1)*B(IIII)
SUBROUTINE COEFFZ		INSERTED
SUBROUTINE COEFFY		INSERTED
SUBROUTINE MATOUT	COMMON/ARRAYS/A(80, 80, 3)	COMMON/ARRAYS/A(130, 130, 2)
SUBROUTINE HUCKEL	COMMON/ARRAYS/A(80, 80), B (80, 80), D(80, 80) COMMON/INFO1/...U(80)... COMMON/GAB/XXX(400), G(35, 35), Q(80), YYY(80), ZZZ, ENERGY, OLDEIG(80), DMD (80), XXY(52)	COMMON/ARRAYS/A(130, 130), B (130, 130) COMMON/INFO1/...U(130)... COMMON/GAB/XXX(650), G(35, 35), Q(130), YYY(130), ZZZ, ENERGY, OLDEIG(130), DMD (130)
SUBROUTINE SCFCLO	SAME AS SUBROUTINE HUCKEL DIF=ABS(OLDEIG(I)...240)) OLDEIG(I)=XXX(I+240)	SAME AS SUBROUTINE HUCKEL DIF=ABS(OLDEIG(I)...390)) OLDEIG(I)=XXX(I+390)
SUBROUTINE CPRINT	SAME AS SUBROUTINE HUCKEL	SAME AS SUBROUTINE HUCKEL
SUBROUTINE HUCKOP		DELETED ENTIRE SUBROUTINE
SUBROUTINE SCFOPN		DELETED ENTIRE SUBROUTINE
SUBROUTINE OPRINT		DELETED ENTIRE SUBROUTINE

Table 2. (Continued)

Area of Program	Old Program	New Program
SUBROUTINE EIGN	COMMON/ARRAYS/A(80,80), VEC (80,80), X(80,80) COMMON/GAB/GAMMA(80), BETA (80), BETASQ(80), EIG(80), W (80), XYZ(1600) DIMENSION P(80), Q(80) DIMENSION IPOSV(80), IVPOS (80), IORD(80)	COMMON/ARRAYS/A(130,130), VEC (130,130) COMMON/GAB/GAMMA(130), BETA (130), BETASQ(130), EIG(130), W (130), XYZ(1748) DIMENSION P(130), Q(130) DIMENSION IPOSV(130), IVPOS (130), IORD(130)
SUBROUTINE SCFOUT	COMMON/ARRAYS/A(80,80,3) COMMON/GAB/XXX(2000) COMMON/INFO1/...U(80)...	COMMON/ARRAYS/A(130,130,2) COMMON/GAB/XXX(2398) COMMON/INFO1/...U(130)...
SUBROUTINE EIGOUT	COMMON/GAB/XXX(240), EPSILN(80), YYY(1680)	COMMON/GAB/XXX(390), EPSILN(130), YYY(1878)

ν = orbital on atom B

$P_{\mu\nu}$ = electron density matrix element

$H_{\mu\nu}$ = core Hamiltonian matrix element

$F_{\mu\nu}$ = Hartree-Fock matrix element

Z_A = core charge of atom A

Z_B = core charge of atom B

R_{AB} = distance between atoms A and B

It is possible to break up the total energy into the sum of mono- and diatomic contributions. Thus:

$$E_{total} = \sum_{A} E_{AA} + \sum_{A<B} E_{AB}$$

where E_A = monatomic contributions

E_B = diatomic contributions

In the full expanded form the monatomic term is

$$E_{AA} = \tfrac{1}{2} \sum_{\mu\nu}^{A} P_{\mu\nu}(H_{\mu\nu} + P_{\mu\nu}) - P_{AA}\left(\sum_{B(\neq A)} (Z_B - P_{BB})\right)\gamma_{AB}$$

where γ_{AB} = electron repulsion integral between electrons in orbitals on A and those in orbitals on B

The first term is the attraction of the core of A for all electrons; the second subtracts out the attraction of the electrons for all other cores. The diatomic term is:

$$E_{AB} = 2 \sum_{\mu}^{A} \sum_{\nu}^{B} P_{\mu\nu} \left(\frac{H_{\mu\nu} + F_{\mu\nu}}{2}\right) + (P_{AA}P_{BB} - P_{AA}Z_B - P_{BB}Z_A)\gamma_{AB} +$$

$$\frac{Z_A Z_B}{R_{AB}}$$

The first term is the attraction of atoms A and B for all electrons; the second is a composite repulsion term which subtracts out the repulsion between electrons of A and those on B while taking into account the attraction of core A for the electrons on B and vice versa. The last term subtracts out the repulsion between the two cores, A and B.

The program as obtained from QPCE[138] is written in such a manner that it was a distinct advantage to treat the above equations in a slightly different manner to obtain the desired result. The electronic energy of a molecule is:

$$E_{\text{electronic}} = \tfrac{1}{2} \sum_{\mu\nu} P_{\mu\nu} (F_{\mu\nu} + H_{\mu\nu})$$

Another way of expressing this is:

$$E_{\text{electronic}} = \tfrac{1}{2} \text{Tr} \left\{ \mathbb{P} (\mathbb{F} + \mathbb{H} \right\}$$

where $\mathbb{P}$ = a submatrix of the density matrix which contains the elements associated with a particular atom or with the interaction between two atoms

$\mathbb{F}$ and $\mathbb{H}$ = the analogous terms in the Fock and core Hamiltonian matrices, respectively

Using this expression we can generate two monatomic and diatomic energy terms:

$$E_{AA} = \tfrac{1}{2}\,\mathrm{Tr}\left\{\mathbb{P}^{AA}\,(\mathbb{F}^{AA}\,\mathbb{H}^{AA})\right\} + \mathrm{Tr}\;\mathbb{P}^{AA} \sum_{B\neq A} \left[(Z_B - \tfrac{1}{2}(\mathrm{Tr}\,\mathbb{P}_{BB})G_{AB}\right]$$

$$E_{AB} = 2\,\mathrm{Tr}\left\{\mathbb{P}_{AB}\left(\frac{\mathbb{F}^{AB} + \mathbb{H}^{AB}}{2}\right)\right\} + Z_A Z_B / R_{AB} - (Z_B \mathrm{Tr}\,\mathbb{P}^{AA} + Z_A \mathrm{Tr}\,\mathbb{P}^{BB})G_{AB} + (\mathrm{Tr}\,\mathbb{P}^{AA})(\mathrm{Tr}\,\mathbb{P}^{BB})G_{AB}$$

The specific program used to set up this "atom-atom energy" matrix is shown in Table 3. This program was inserted after the formation of the "radii matrix" [R(A, B) - located in B (upper)] in SUBROUTINE CPRINT.

There is one other modification that had to be made. The Hartree-Fock matrix (H-F) is stored in the lower part of matrix A. When convergence is reached, the H-F matrix is printed (see SUBROUTINE SCFCLO[88, p. 178]). Then SUBROUTINE EIGN is called to generate a new eigenvector matrix and eigenvalues, which destroys the H-F matrix. Therefore after coming out of SUBROUTINE EIGN for the last time it is again necessary to return to the beginning of SUBROUTINE SCFCLO to generate the Fock matrix again.

To establish that I had indeed calculated the atom-atom energy matrix correctly I performed two checks. First, the sum of the energy from the atom-atom energy matrix should equal the total energy. Second, I compared our calculated values for water with bond angles of 105° and 180° with the values Pople reported.[88, p. 93] Both of these checks confirmed that method does indeed work.

Table 3. Program Written To Generate "Atom-Atom" Energy Matrix

```
C       FORM ATOM-ATOM ENERGY MATRIX IN LOWER A
        DO 400 I=1,NATOMS
        TR=0.
        DO 410 K=LLIM(I),ULIM(I)
        DO 420 L=LLIM(I),ULIM(I)
        IF(L-K)430,440,450
430     TR=TR+(B(L,K)*(A(K,L)+A(L,K)))
        GO TO 420
440     TR=TR+(B(K,L)*(A(K,L)+Q(K)))
        GO TO 420
450     TR=TR+(B(K,L)*(A(L,K)+A(K,L)))
420     CONTINUE
410     CONTINUE
        SUBTOT = 0.
        DO 460 II=1,NATOMS
        IF(II-I)470,460,470
470     SUBTOT=SUBTOT+((FLOAT(CZ(II))-(XXX(II)*0.5))*G(I,II))
460     CONTINUE
400     A(I,I)=(TR*0.5)+(XXX(I)*SUBTOT)
        DO 600 I+1,NATOMS-1
        DO 600 II=I+1,NATOMS
        TR=0.
        DO 630 K=LLIM(I),ULIM(I)
        DO 630 L=LLIM(II),ULIM(II)
630     TR=TR+(B(K,L)*((A(L,K)+A(K,L))*0.5))
        REPUL=(FLOAT(CZ(I))*FLOAT(CZ(II)))/B(II,I)
        TERM=G(I,II)*((FLOAT(CZ(II))*XXX(I))+(FLOAT(CZ(I))*XXX(II)))
600     A(II,I)=(2.*TR)+REPUL-TERM+(XXX(I)*XXX(II)*G(I,II))
        WRITE(108,610)
610     FORMAT(1X,24H ATOM-ATOM ENERGY MATRIX)
        CALL SCFOUT(2,1,1)
```

Structures Used as Input for CNDO/2 Calculations

Pople provides a table of standard bond lengths and angles,[88, pp. 111-12] but because a number of crystal structures have been done on chlorobenzenes,[139-143] I decided to use experimental bond lengths. The values selected are based on the work of Milledge et al,[143] and are C-C: 1.387 A; C-Cl: 1.711 A; C-H: 1.083 A. All bond angles were 120° and all molecules were considered planar (i.e., there was no out of the plane bending with adjacent chlorines).

The structure of biphenyl presents a more complicated situation. This is because there can be rotation around the bond between two phenyl moieties. The basic structure we selected had the same bond lengths and angles as the chlorobenzenes with a central bond length of 1.480 A. I rotated the phenyl rings in an attempt to find the minimum energy and thus the preferred conformation. The final structures I selected will be discussed in the "Results and Discussion" section.

The preferred conformation carbon skeleton of lindane is essentially a chair form,[144,145] with the chlorines having an eeeaaa (e = equatorial, a = axial) configuration.[146,147] Thus the structure I used as an input for the CNDO/2 program was a classic chair form with bond lengths of C-C: 1.53 A; C-H: 1.095 A; C-Cl: 1.77A[148] with all bond angles being 109.47°.

Establishing the input structure for γ-BTC was somewhat more difficult. There are two possible chlorine configurations for γ-BTC, eeea and aaae with the former being the preffered configuration.[136] The carbon skeleton probably adopts a "half-chair" form as has been established for δ-1,3,4,5,6-pentachlorocyclohexene.[149] The basic bond lengths and angles for the input structure were taken from Pedone et al.[150] Carbons 1,2,3 and 6 were put in the same plane with the bond lengths and angles made symmetrical. This, while not exactly conforming to the crystal structure tends to give better wave functions.[151] Carbons 1 and 2 were treated as regular sp^2 carbons, carbons 3 and 6 as sp^3. Carbons 4 and 5 were required to be 1.54 A away from carbons 8 and 6, respectively; furthermore they had to be 1.54 A away from each other. Carbon 4 had to be the same distance above the C-1, C-2, C-3, C-6 plane as carbon 5 was below. Finally carbons 3 and 6 had to remain tetrahedral. When these conditions are met the angle of C-3, C-4, C-5 (and likewise C-4, C-5, C-6) is 109.89^{o} rather than the true tetrahedral angle of 109.47^{o}. Once the carbons were located, the remaining substituents were located using a program (NORM) written by P. Callis. The end product was checked by two different programs, BOSCAN (written by D. Smith) which checks bond lengths and angles and an ORTEP program (as modified by D. Smith). These confirmed that the desired conformation had been obtained. The specific bond lengths and angles are: $C(sp^2)$-$C(sp^2)$: 1.32A, $C(sp^2)$-

$C(sp^3)$: 1.50 A; $C(sp^3)$-$C(sp^3)$: 1.54 A; $C(sp^2)$-H: 1.084 A; $C(sp^3)$-H: 1.095 A; $C(sp^3)$-Cl: 1.77 A. All angles, except where previously noted, are either 109.47^o or 120.0^o.

The input structure for DDT was established in the following manner. Since it is possible for free rotation of the phenyl rings around carbon 2, I felt that the preferred conformation would be when there is a minimum interaction between 1) the ortho hydrogens on the phenyl rings and the chlorines on carbon 1, and 2) the ortho hydrogens on one phenyl ring and the ortho hydrogens on the other phenyl ring. To find this desired configuration a program was written which would rotate carbon 1 and also rotate each of the phenyl moieties. The first constraint placed on the structure was that all atoms be no closer than Van Der Waal's radii (3.0 A for H-Cl, 2.4 A for H-H). Once this condition was met the program then established which configuration gave minimum steric interaction. The final structure is shown in Figure 6. The angle between the two phenyl rings is 93.5^o which is somewhat more than the angle that has been found in the crystal structure.[152] The specific bond lengths and angles used were: $C(sp^3)$-$C(sp^3)$: 1.53 A; $C(sp^3)$-$C(sp^2)$: 1.53 A; $C(sp^3)$-H: 1.095 A; $C(sp^3)$-Cl: 1.77 A; $C(sp^2)$-$C(sp^2)$: 1.396 A; $C(sp^2)$-H: 1.084 A; $C(sp^2)$-Cl: 1.711 A. All angles are either 109.47^o or 120.0^o.

The input structure for heptachlor was based on a crystal structure.[153] The norbornene moiety was made symmetrical to give better wave functions.[151]

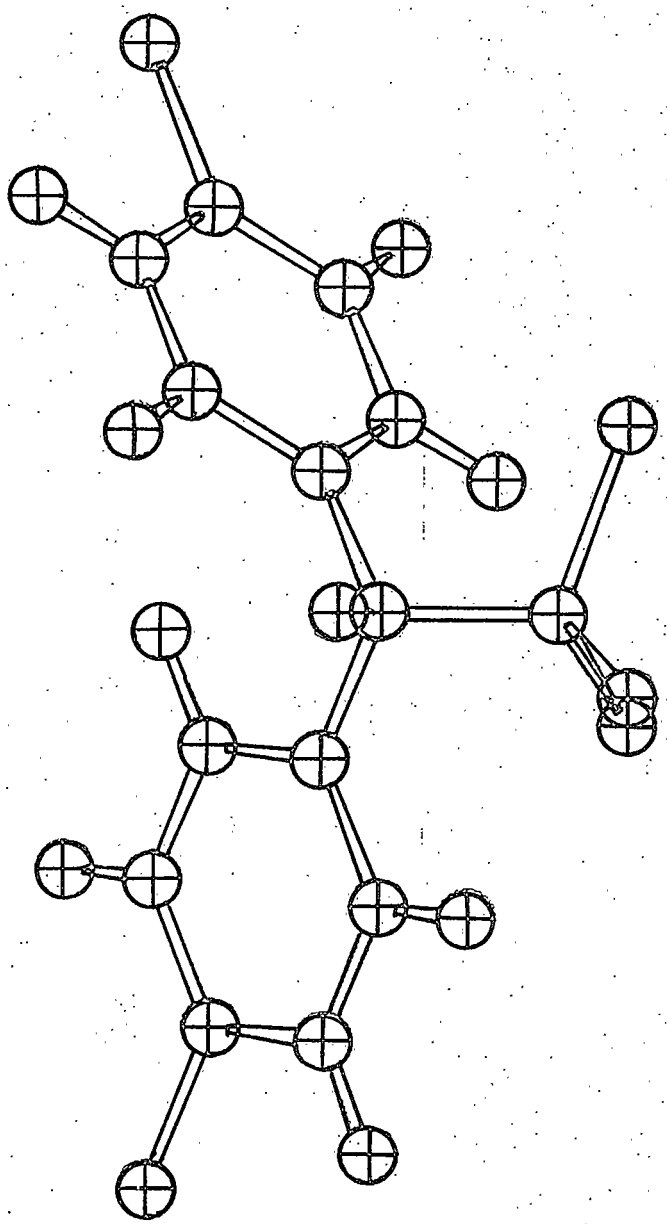


Figure 6. Structure of DDT Used for CNDO/2 Calculation

The C-C and C-Cl bond lengths and angles for pentachlorophenol were the same as those used for the chlorobenzenes. The C-O bond length was 1.329 A[154] and the O-H bond length was 0.96 A. The hydroxyl hydrogen was placed in a plane perpendicular to the ring with a C-O-H bond angle of 116.5°.[155]

Anaerobic Degradation Procedures

The organochlorine compounds were incubated under anaerobic conditions in one of two systems, soil or sewage sludge. Samples in the soil system were treated as follows. Bowdoin soil (sample 367 Mont) was taken from a depth of 0-8 inches and air dried. The physical characteristics of the soil were: pH 7.9; 1.44% organic carbon; 0.8% sand; 30.6% silt; 68.6% clay (analysis performed by G. Nielsen). The soil was then ground in a ball mill and passed through a 35 mesh screen. Five mg of the compound to be incubated was added to 10 ml acetone and the solution mixed in a 45 gram portion of soil. The soil sample was air dried to evaporate the acetone. Then 2.5 g dried and ground alfalfa was added (to serve as an energy source) plus .5 g fresh soil (to insure the presence of microbes) and the entire sample was mixed for 1 hour. Ten gram portions of soil were then transferred to 25 ml Erlenmeyer flasks, flooded with double distilled water, stoppered with gauze and incubated at room temperature.

Samples were normally analyzed at two week intervals. The initial

extraction consisted of shaking the soil sample with a hexane:isopropanol (1:1) solution. This procedure was abandoned because it gave very low recoveries. For instance, only 20% 2,3,4,5,6-pentachlorobiphenyl and 46% hexachlorobenzene could be recovered. The extraction and cleanup procedure finally adopted was as follows. The soil sample was transferred to a Soxhlet apparatus and extracted for 3 hours with acetone. The acetone-water solution was then concentrated to about 20 ml on a rotary evaporator, transferred to a separatory funnel and 100 ml of water was added. The aqueous solution was extracted three times with 50 ml portions of hexane. The hexane was concentrated to approximately 20 ml by rotary evaporator and then passed through a florisil column (Baker, 60-100 mesh) eluting with an additional 50 ml of hexane. The extract was then analyzed by electron capture gas chromatography. This procedure gave approximately 90% recovery of hexachlorobenzene.

Later anaerobic incubations were performed using sewage sludge obtained from the 35° anaerobic digestor at the Bozeman sewage treatment plant. The physical characteristics of this sludge are: pH 7.0; 1.7% total solids of which 60% are volatile solids. The sewage was collected in 2-liter Erlenmeyer flasks and treated with 20 mg of the compound to be incubated in about 10 ml acetone (except for decachlorobiphenyl for which butanol was used as the solvent). 20 g ground beef was added as an energy source and the sample

was incubated at 37°C. The solution was mixed with a magnetic stirrer and a nitrogen atmosphere was maintained over the surface to insure anaerobic conditions. The incubation apparatus is basically the same as Hill and McCarthy's.[70] Samples (100 ml) were withdrawn by applying positive pressure with the nitrogen, transferred to a soxhlet apparatus and extracted 3 hours with acetone. The acetone was removed by rotary evaporator, the resultant aqueous solution extracted three times with 50 ml portions of hexane. The remainder of the procedure was identical to that used for soil samples.

When analyzing for benzene in sewage (from the lindane incubation) only one exit tube from the incubation flask was used and it was run through a dry ice-acetone cold trap. The system was allowed to incubate in the normal fashion for 24 hours, then nitrogen was bubbled through the sewage for 12 hr to help force out any benzene that had been formed. The benzene so formed was analyzed directly by flame ionization g. c.

Benzene formation was confirmed by synthesizing the 1,3-dinitro- derivative. 15 ml concentrated sulfuric acid was added to 5 ml concentrated nitric acid and cooled in ice. The solution containing the benzene was slowly added to this, while cooling with ice. After complete addition, the mixture was warmed 10 minutes, then poured on about 100 ml ice and extracted three times with 50 ml portions of hexane. The hexane extract was concentrated by rotary evaporator and analyzed by g. c.

The degradation of all chlorinated compounds with the exception of DTE (1,1,1,2-tetrachloro-2,2-bis(p-chlorophenyl)ethane) was monitored by electron capture g.c. I was unable to separate DTE from its anaerobic metabolite, DDE, on any of the columns tried. This is probably due to a rapid thermal breakdown of DTE to DDE on the g.c. column. I was finally able to separate the two compounds by the use of high pressure liquid chromatography. A Waters model ALC 202 equipped with a U.V. detector (254 nm) was used. After trying various columns and solvents we elected to use the following operating conditions. The column was C_{18}/Corasil packed in a 2' x 1/8" stainless steel column; the elution solvent was methanol: water (67:33) with a flow of 1.2 ml/minute.

Electrolysis Procedure

All of the voltammetric reduction potentials used are based on the work of Farwell.[1] The controlled electrolysis procedure was also taken from Farwell. A three electrode system was used, a saturated calomel reference electrode (Sargent No. S-30080-25), a mercury (triple-distilled instrument mercury from Bethlehem Apparatus Co.) pool working electrode, and a 20 gauge coiled platinium auxiliary electrode. The solvent system was 0.1 M tetraethylammonium bromide (Baker) in dimethyl sulfoxide (Baker). In a typical experiment between 10 and 50 ml solvent, depending on the particular

type of investigation, was added to the sample compartment. Sufficient solvent was then added to both reference and auxiliary compartments so that the solvent level in all three compartments was equal. The auxiliary electrode solvent contained about 0.01 M hydrazine sulfate to prevent anodic attack on the electrode.

The sample solvent was stirred with a magnetic stirrer and nitrogen gas (which was passed through two wash bottles, the first containing vanadous chloride and the second dimethyl sulfoxide) was bubbled through the sample compartment to deaerate the solution throughout the duration of the electrolysis. Voltage was applied at a setting of approximately -2.30 V (vs. SCE) to electrolyze any electroactive impurities in the solvent. Following the pre-electrolysis period (about 1 hour) the applied voltage was adjusted to the potential of interest (i.e., a particular half-wave potential as established by Farwell) and sufficient compound in about 2 ml 0.1 M TEABr-DMSO was added so that the final concentration of electroactive species was 1×10^{-3} M.

Two different types of experiments were performed, first the disappearance of a compound and formation of new compounds with time. This was performed by withdrawing small samples (about 1 ml) at regular intervals, diluting the solution with an equal volume of water, partitioning the compound of interest into hexane and analyzing by g.c. In the second type of experiment, the electrolysis was continued until the electroactive species was

completely discharged (about 24 hours). The sample was then extracted as above. This latter type of experiment was performed when it was desired to obtain enough compound for identification purposes on instrumentation other than the electron capture gas chromatograph.

RESULTS AND DISCUSSION

I have elected to break the presentation of the results and discussion into two broad categories. First, we will look at the use of quantum mechanics as a means of predicting the ease of reduction and the reduction pathways of chlorinated hydrocarbons. The results here will be compared, where possible, to the electrochemical data acquired by Farwell.[1] In the instances where his data is lacking, additional electrochemical experiments were performed to help build a stronger case. In addition, we will also look at the mechanism of the breakage of the carbon chlorine bond in aromatic systems based on a quantum mechanical investigation.

The second area to be discussed is the anaerobic degradation of chlorinated hydrocarbons of environmental interest. Using data acquired by other investigators and performing experiments to provide additional data, we will see whether or not reductive electrochemistry and ultimately quantum mechanics can predict if compounds will break down in a reductive environment and if so what the products will be.

Molecular Orbital Investigation of Electrochemical Carbon-Halogen Reduction: Chlorobenzenes

Our investigation will begin with the chlorobenzenes. Since they are planar they readily lend themselves to molecular orbital calculations in that

the sigma (σ) and pi (π) systems will be quite distinctive. Farwell[1] has established the reduction potentials and the reduction pathways for the entire series, so we can compare the molecular orbital results to experimental observations.

Molecular orbital calculations were performed on all of the possible chlorobenzenes. The calculations were done in single precision (with the exception of total energy). The calculation was stopped (i.e., considered self consistent) when the difference in total energy between two cycles was equal to or less than 0.0001 a.u. (0.0629 kcal/mole).

We have previously seen that when compounds are electrochemically reduced the electron will enter the LUMO (see "Introduction"). Fukui[24] speculated that in organic halides, this may be a σ orbital instead of a π orbital as usually found in aromatic systems. Table 4 gives the first reduction potential (E_{2d}) found for each of the chlorobenzenes as established by Farwell.[1] Included with this data is the eigenvalue for the lowest σ molecular orbital (LUMO-σ) and the lowest π molecular orbital (LUMO-π). While the LUMO is a σ orbital for 1,2-di-, 1,2,3-tri-, 1,3,5-tri- and 1,2,3,4-tetrachlorobenzenes, the LUMO for the majority of the chlorobenzenes is a π orbital. Moreover, as the degree of chlorine substitution increases, which increases the ease of reduction, both the σ and π LUMO's decrease in energy. This can be seen quite readily in Figures 7 and 8 where the first reduction potential for each of the chlorobenzenes is plotted against either LUMO-σ or

Table 4. Experimental First Reduction Potential (E_{2d})[1] and Eigenvalues of the Lowest σ and π Molecular Orbitals from Closed Shell CNDO/2 Calculation on Chlorobenzenes.

Compound	E_{2d} (V)	LUMO-σ (a.u.)	LUMO-π (a.u.)
1	2.440	0.1096	0.1065
1,2	2.218	0.0815	0.0819
1,3	2.197	0.0846	0.0845
1,4	2.199	0.0972	0.0792
1,2,3	1.962	0.0521	0.0588
1,2,4	1.997	0.0679	0.0567
1,3,5	1.985	0.0625	0.0698
1,2,3,4	1.764	0.0418	0.0433
1,2,3,5	1.794	0.0433	0.0408
1,2,4,5	1.808	0.0496	0.0338
1,2,3,4,5	1.573	0.0272	0.0255
1,2,3,4,5,6	1.322	0.0169	0.0326

LUMO-π. A fairly good linear relation is observed in both cases. This result differs from Fukui's.[24] He noted a decrease in energy with increased chlorine substitution for σ orbitals, but found the LUMO-π to vary in a random manner. The LUMO-σ and LUMO-π are basically degenerate and since the slopes and intercepts of Figures 7 and 8 are not statistically different, we still cannot tell the type of orbital the electron enters.

We have been trying to decide what type of orbital the electron goes into by using a vacant orbital (virtual orbital) and assuming that there will be no significant perturbations when the orbital becomes occupied. A better method would be to put the electron in, perform the calculations, and see what type of orbital is the HOMO. Thus open shell calculations were performed on the radical anions of all the possible chlorobenzenes. The same bond lengths and angles were used as in the parent compound. The calculations were again done in single precision except for total energy and the iterations were stopped when the maximum change in electronic density for all atoms between two cycles was less than 0.01 a.u.

The HOMO and LUMO obtained from these calculations are shown in Table 5. It is immediately obvious that the HOMO in each and every case is a σ orbital. Furthermore the π orbital with which it used to be nearly degenerate is in some cases no longer the LUMO but actually a higher orbital. An objection might be raised that the structure of the radical anion might be

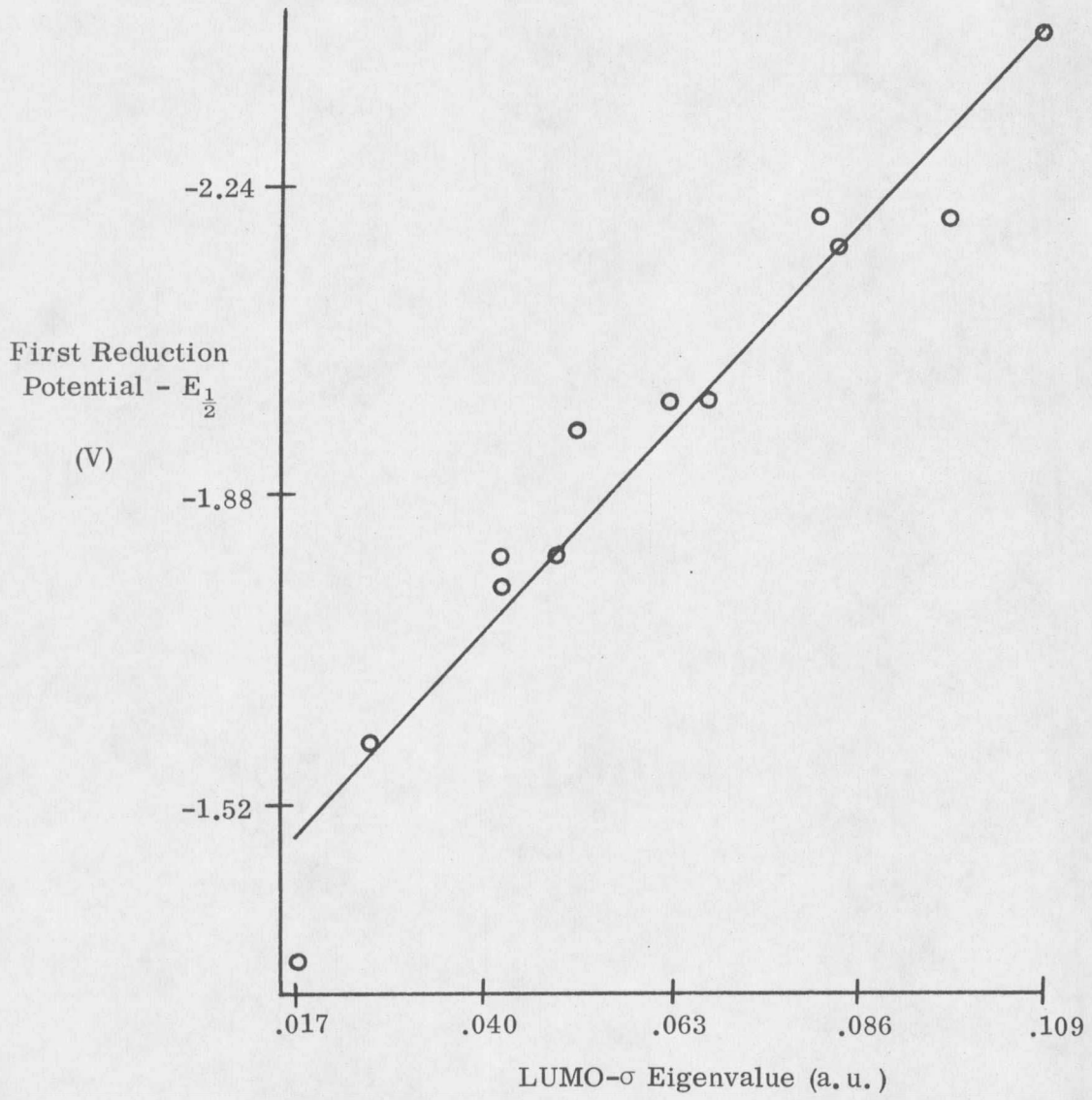


Figure 7. First Reduction Potentials for Chlorobenzenes vs. Calculated LUMO-σ. $y = 10.70 \pm 2.86x + 1.28 \pm 0.19$, $r = 0.97$

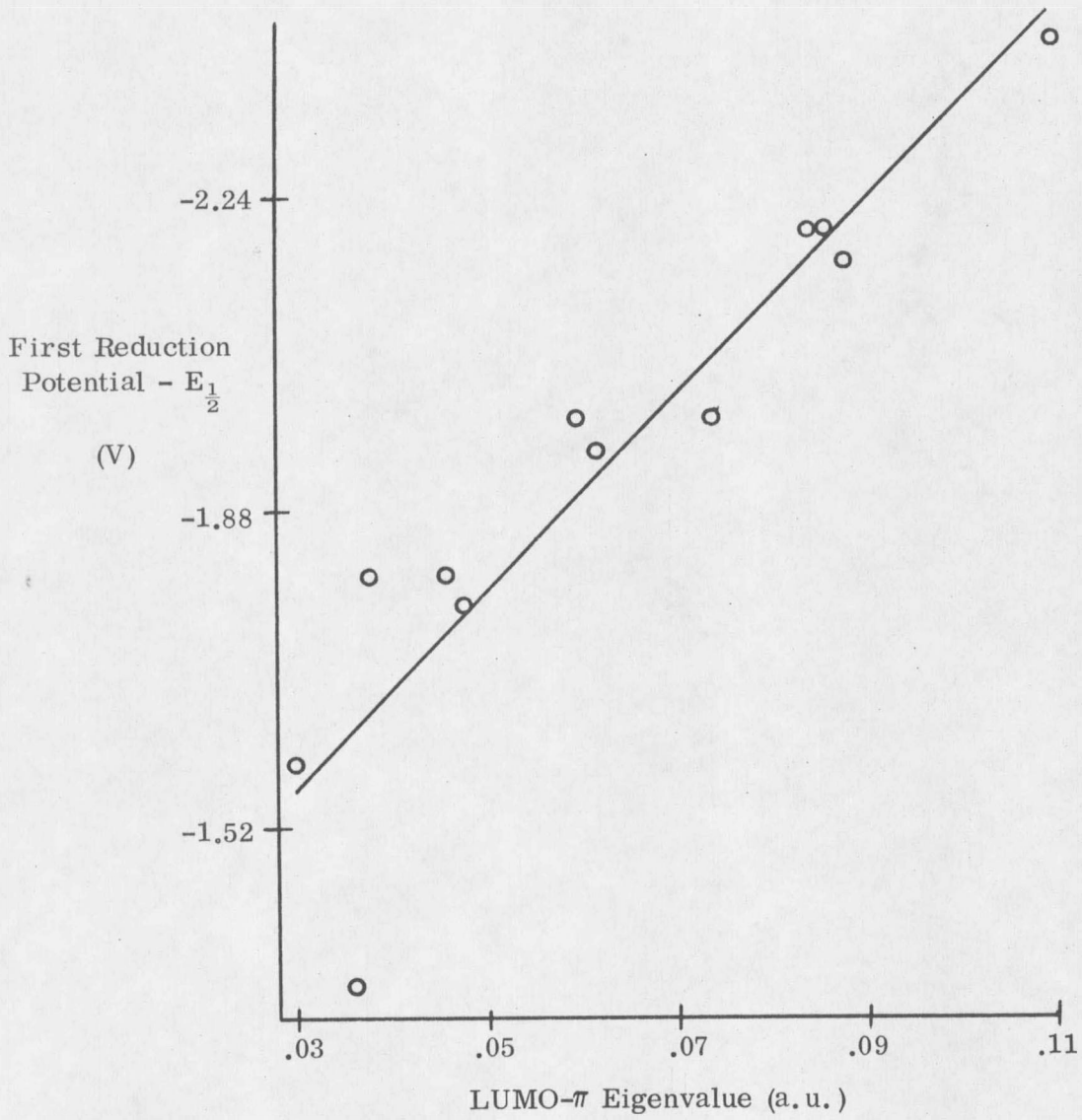


Figure 8. First Reduction Potentials for Chlorobenzenes vs. Calculated LUMO-π. $y = 11.39 \pm 5.00x + 1.26 \pm 0.32$, $r = 0.93$

Table 5. Eigenvalues of the HOMO and LUMO for the Radical Anions of the Chlorobenzene Series Obtained from Open Shell CNDO/2 Calculation

Chlorobenzene	HOMO (a.u.) (type of orbital)	LUMO (a.u.) (type of orbital)
1	0.0027 (σ)	0.3479 (π)
1,2	0.0227 (σ)	0.2724 (σ) 0.3160 (π)
1,3	0.0413 (σ)	0.2209 (σ) 0.3111 (π)
1,4	0.0622 (σ)	0.1955 (σ) 0.3114 (π)
1,2,3	0.0073 (σ)	0.2608 (σ) 0.2767 (π)
1,2,4	-0.0005 (σ)	0.2488 (σ) 0.2619 (π)
1,3,5	0.0386 (σ)	0.2221 (σ) 0.2225 (σ) 0.2815 (π)
1,2,3,4	-0.0053 (σ)	0.2204 (σ) 0.2363 (π)
1,2,3,5	0.0018 (σ)	0.2295 (σ) 0.2297 (σ) 0.2487 (π)
1,2,4,5	0.0321 (σ)	0.1840 (σ) 0.2277 (σ) 0.2405 (π)
1,2,3,4,5	-0.0234 (σ)	0.2119 (σ) 0.2122 (π)
1,2,3,4,5,6	-0.0054 (σ)	0.1768 (σ) 0.1776 (σ) 0.2015 (π)

appreciably different than the parent compound. This indeed may be the case, but there is other evidence which indicates that the electron added during reduction is placed in a sigma orbital.

This sigma orbital is a rather interesting orbital. It is a very localized anti-bonding orbital with almost all the electron density situated in carbon chlorine bonds. This presents a very nice situation since this high electron density would promote loss of a chloride ion. Thus from looking at the location and degree of electron density in LUMO-σ we should be able to predict the product formed.

Let us return to the closed shell calculations on the chlorobenzenes. Figure 9 shows the electron distribution on each of the atoms in the LUMO-σ, and, for the sake of comparison, Figure 10 gives the same for LUMO-π. These values are obtained by summing up the squares of the eigenvector coefficients for a particular atom (i.e., for chlorine there are 9 orbitals, thus 9 coefficients). In the σ case it can be seen that the electron density resides primarily on the chlorines and to some extent on carbons adjacent to the chlorines. For the LUMO-π to a rough approximation the reverse is true; the electron density is greatest on the carbons adjacent to chlorines, with the chlorines themselves making a minor contribution.

Now if one considers the electron distribution of the LUMO to be similar to what the electron distribution would be like with the electron added, then it

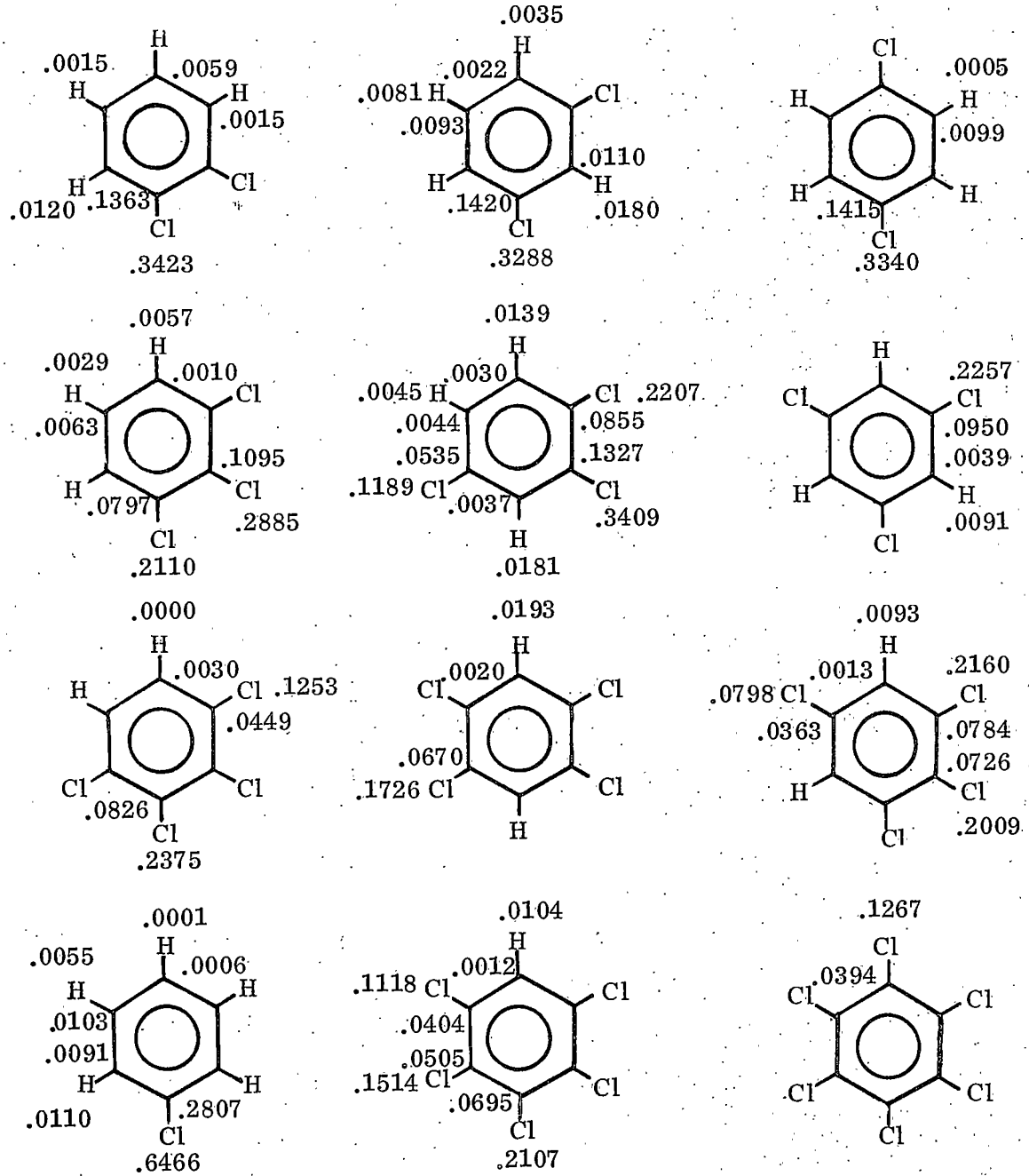


Figure 9. Electron Density Distribution in the LUMO-σ of Chlorobenzenes

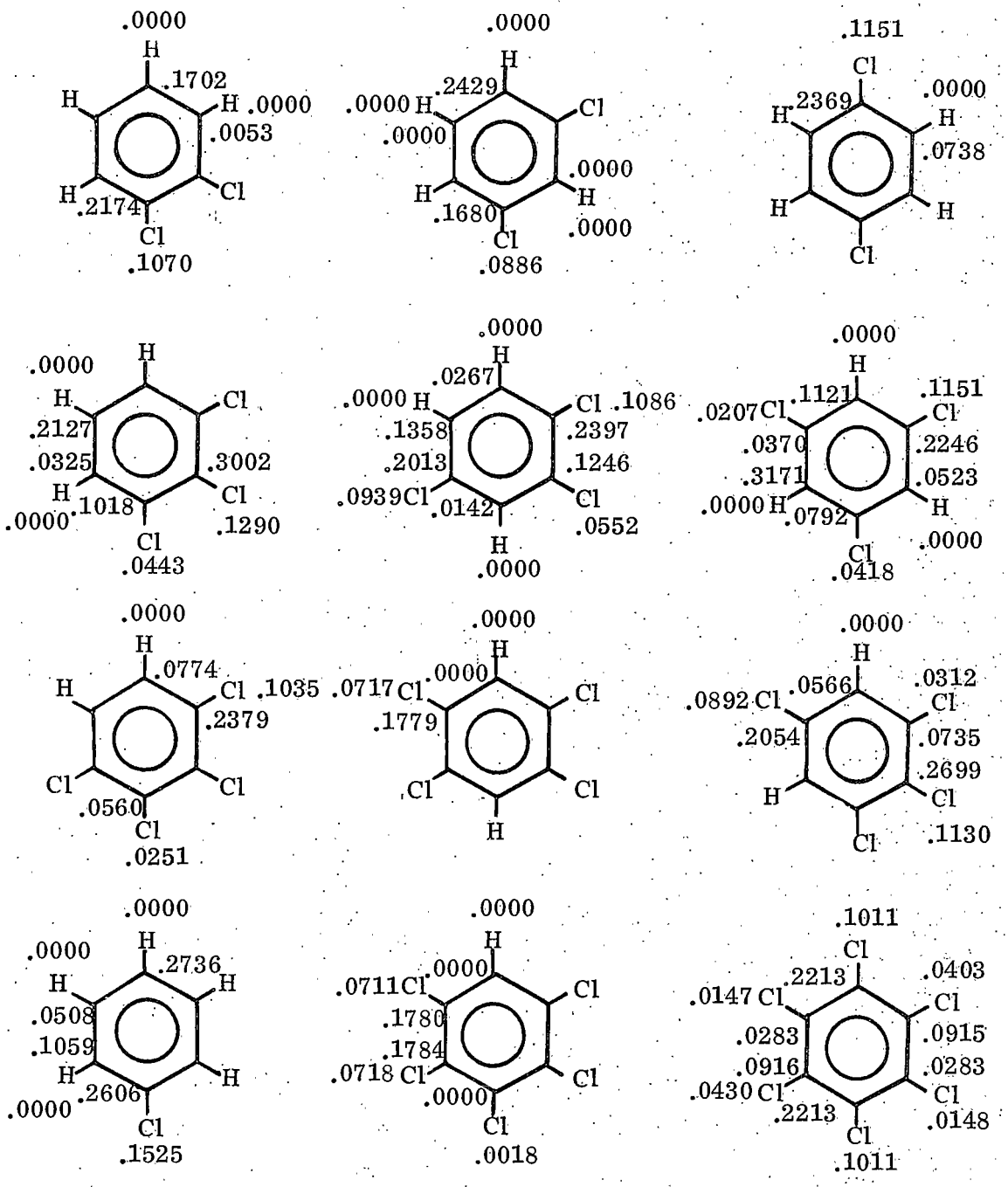


Figure 10. Electron Density Distribution in the LUMO-π of Chlorobenzenes

should be possible to predict which chlorine will be preferentially lost. This is not an altogether unreasonable approximation since the addition of one electron to a system that contains at least 36 valence electrons should not create that great a perturbation. Since in electrochemical reduction a carbon chlorine bond is going to be cleaved, the relative ease of a particular chlorine loss can be estimated as:

$$P_i = \Sigma c^2_{C\text{-}Cl_i} / \sum_i^N (\Sigma c^2_{C\text{-}Cl})$$

That is, the probability of a particular chlorine being lost should be equal to the electron density on that chlorine (and its adjacent carbon) in the LUMO divided by total electron density on all of the chlorines (with their associated carbons) in the LUMO. The results of this treatment are shown in Figure 11 for the LUMO-σ and Figure 12 for the LUMO-π along with the results established by Farwell[1] from controlled potential electrolysis of the chlorobenzenes. The electron density distribution in the LUMO-σ correctly predicts the major reduction product in every instance where more than one reduction product is possible. Moreover, this type of treatment gives a reasonable estimate of the amount of each isomer that will be formed, though it does tend to underestimate the contribution of the major component and overestimate the amount of minor isomers formed. For example, 1,2,3,5-tetrachlorobenzene is electrochemically reduced to form 1,2,4- and 1,3,5-trichlorobenzenes in relative

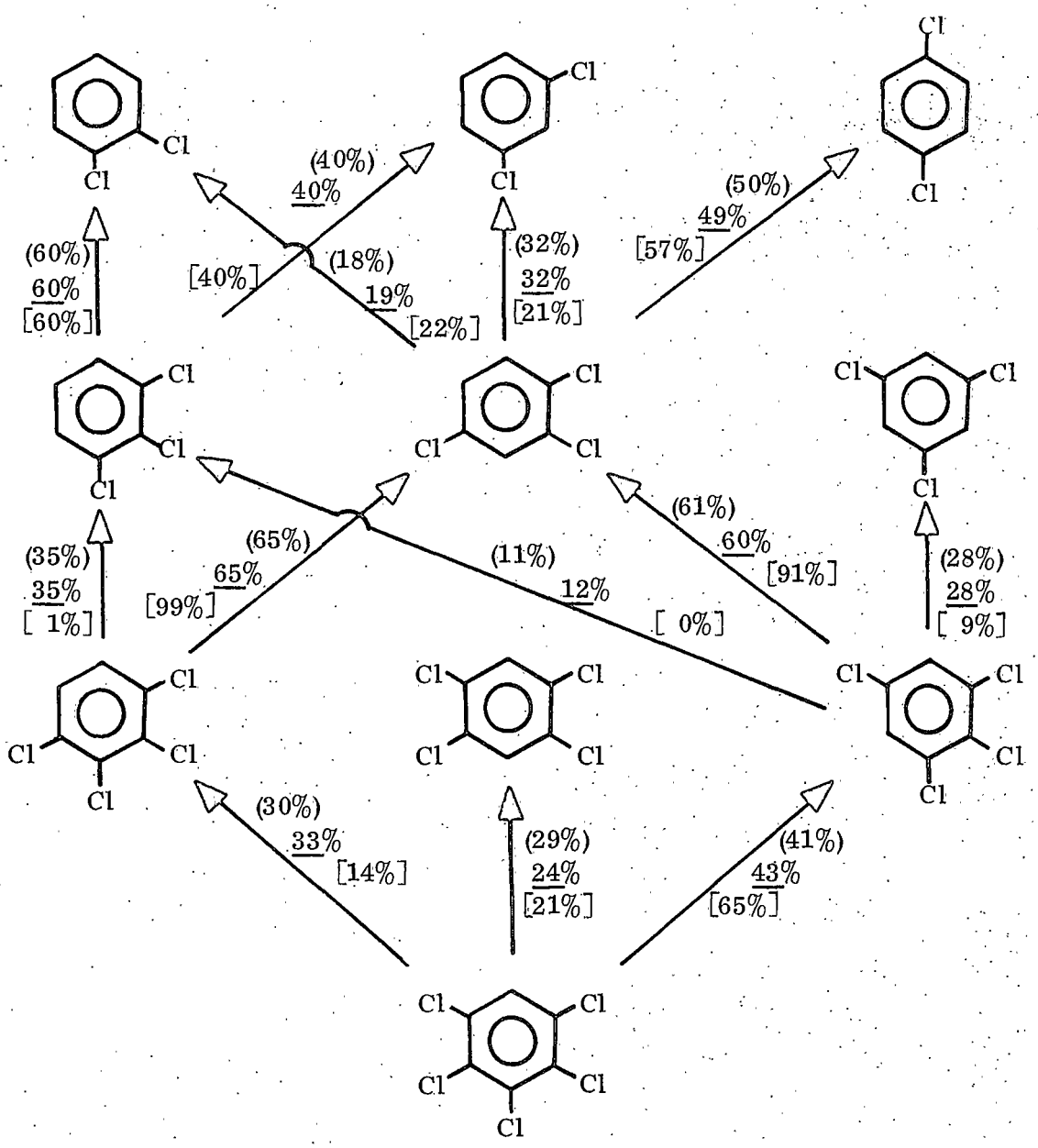


Figure 11. Reduction Pathways of Chlorobenzenes Based on Electron Density Distribution in the LUMO-σ. [ ] - electrolysis data,[1] ( ) - distribution on chlorine, ___ - distribution on chlorine and adjacent carbon.

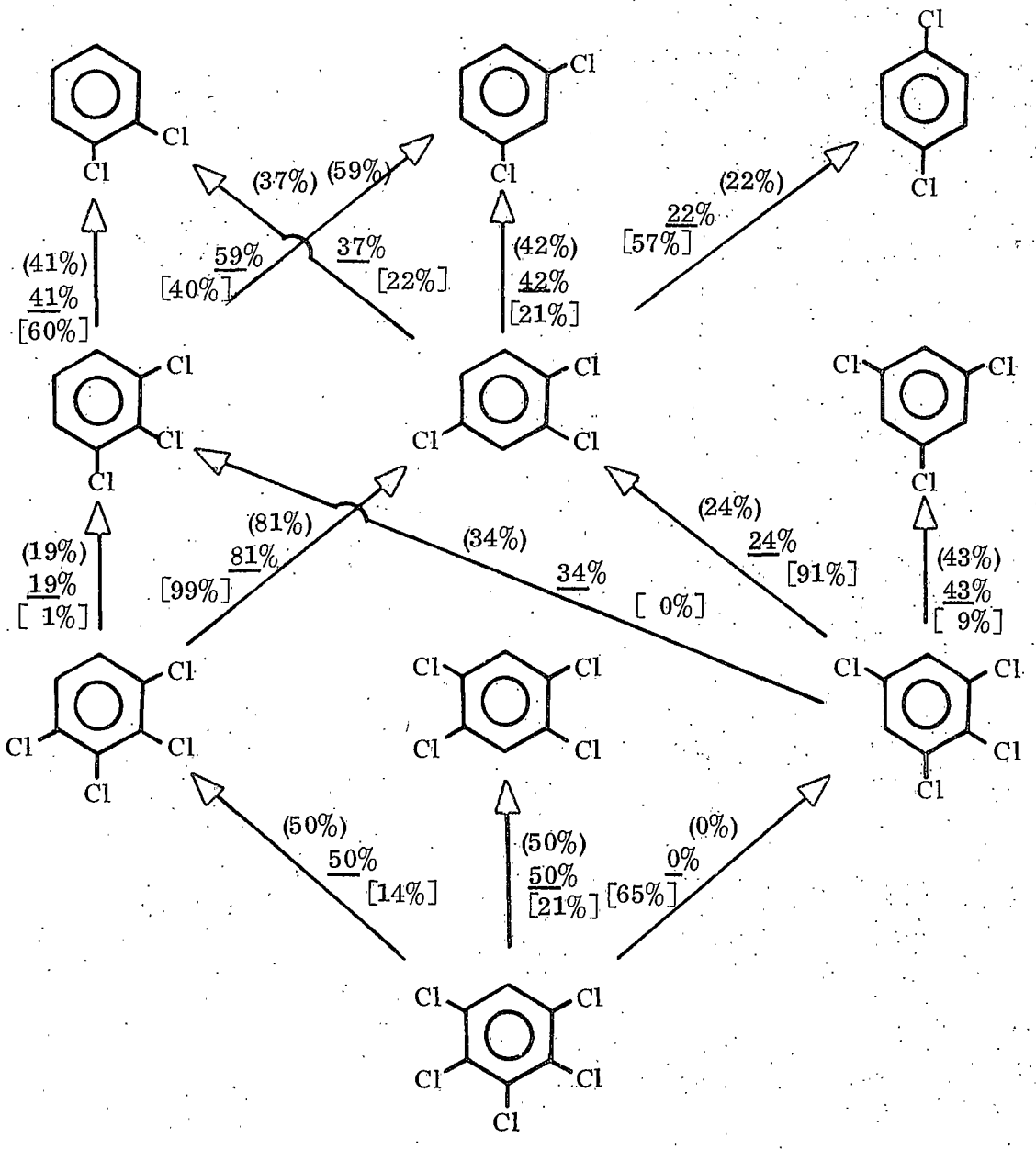


Figure 12. Reduction Pathways of Chlorobenzenes Based on Electron Density Distribution in the LUMO-π. (See Figure 11 for key).

proportions of 91:9. The electron density predicts a ratio of 60:28 with the remaining 12% being 1,2,3-trichlorobenzene. Thus while the ratios are not exact, the relative ordering of the amount of each isomer formed is correct. Basically the same results are obtained whether just the electron density on the chlorine or on both the chlorine and its adjacent carbon are considered.

When the same type of treatment is attempted with the LUMO-π the calculation fails to predict the products formed (Figure 12). In the case of pentachlorobenzene the electron density predicts an equal formation of 1,2,3,4- and 1,2,4,5-tetrachlorobenzenes with no 1,2,3,5-tetrachlorobenzene being formed. However, experimentally the latter compound is the major pathway (65%) with the other two isomers being formed in minor, and within experimental limits, equal amounts. This then is further evidence that upon electrochemical reduction the electron is added to a σ anti-bonding orbital instead of to the closely lying π orbital.

The assumption made in the above treatments is that the electron density distribution in the "virtual" orbital will be the same as when the electron actually occupies the orbital. Since the predicted pathways from the electron density distribution method correlate so well with experimental this assumption appears to be valid. An electron density treatment of the HOMO-σ obtained from open shell calculations on the radical anion should hopefully also predict the pathways, possibly to a better extent than the virtual orbital method.

Figure 13 shows the electron density distribution in the HOMO-σ. A trend becomes immediately apparent; when there are adjacent chlorines (i.e., 1,2,3-trichlorobenzene) the central chlorine contains an overwhelming electron density. In 1,2,3-trichlorobenzene 63% of the electron density is associated with the central chlorine and the carbon to which it is bonded. The 2- position chlorine in 1,2,3,5-tetrachlorobenzene has 47% and the 3- position chlorine in pentachlorobenzene has 64%. This greatly favors the loss of these chlorines as can be seen in Figure 14 where the predicted and experimental reduction pathways are outlined. The open shell calculation incorrectly predicts the major reduction products from 1,2,4,5-tetra- and 1,2,3-trichlorobenzenes and greatly underestimates the dominant pathway of 1,2,3,5-tetrachlorobenzene. All of these erroneous results can be attributed to an overemphasis of the electron density on the central chlorine.

There are other methods by which it should be possible to estimate which chlorine will be preferentially lost upon reduction. One method is to look at the virtual bond order. This is the product of eigenvector coefficients for chlorine times the eigenvector coefficient for the carbon atom to which a particular chlorine is bonded, times the overlap matrix element for this interaction. The bond order for each carbon chlorine bond in the LUMO-σ is negative which indicates the antibonding nature of this orbital. These results are shown in Figure 15. The carbon chlorine bond with the greatest anti-

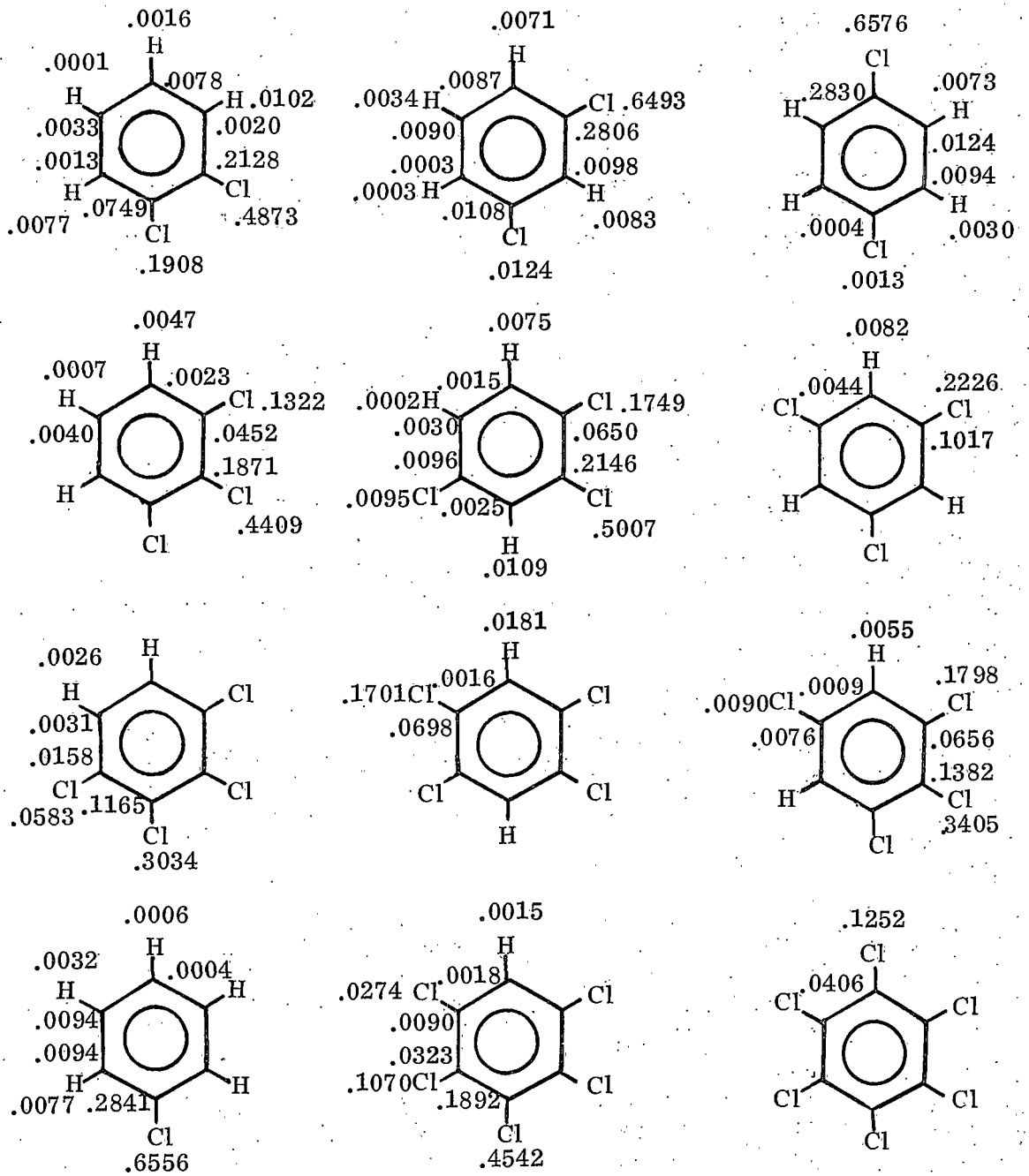


Figure 13. Electron Density Distribution in the HOMO-σ of Chlorobenzene Radical Anions Obtained from Open Shell CNDO/2 Calculations

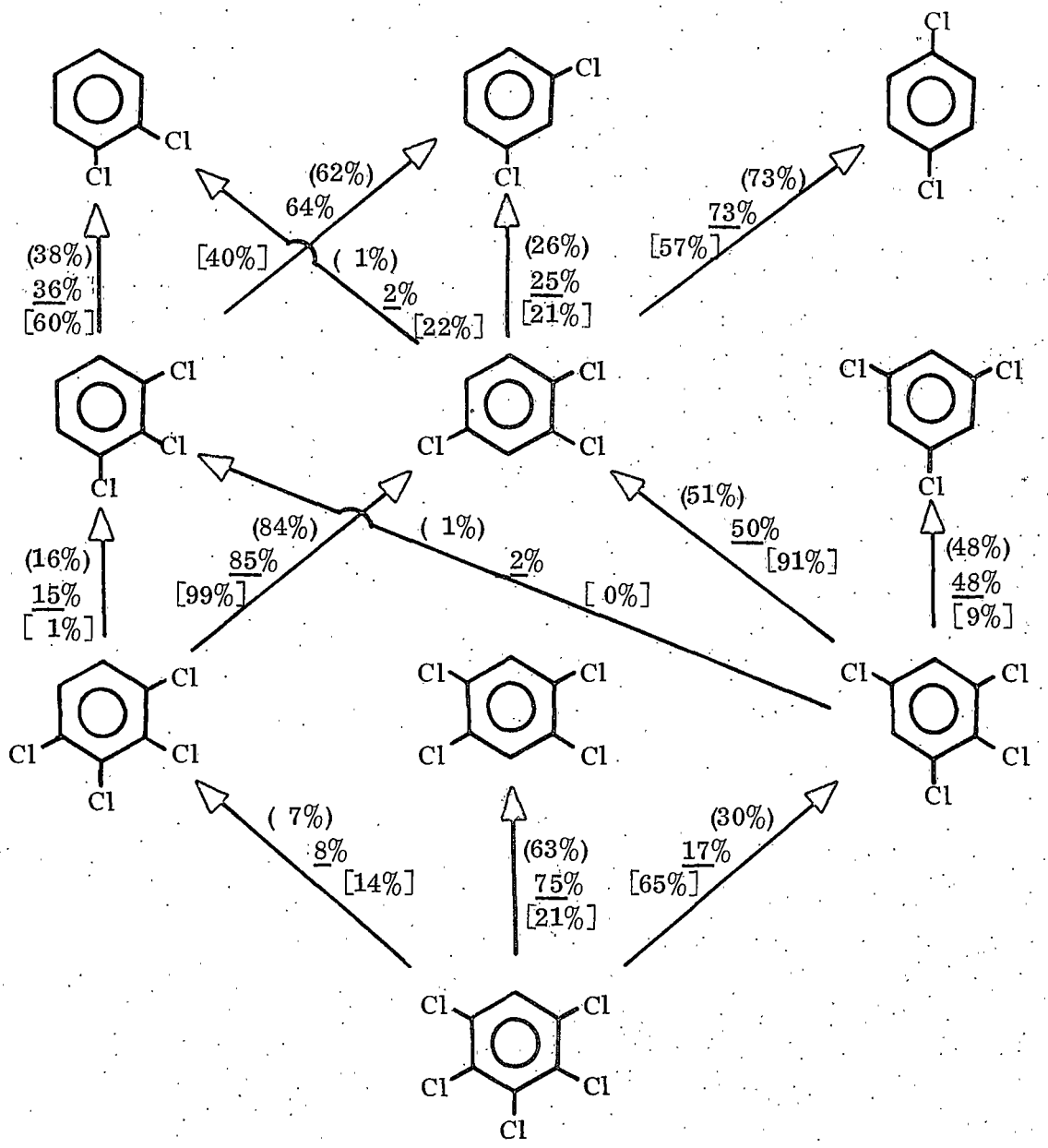


Figure 14. Reductive Pathways of Chlorobenzenes Based on Electron Density Distribution in the HOMO-σ of Chlorobenzene Radical Anions. (See Figure 11 for key).

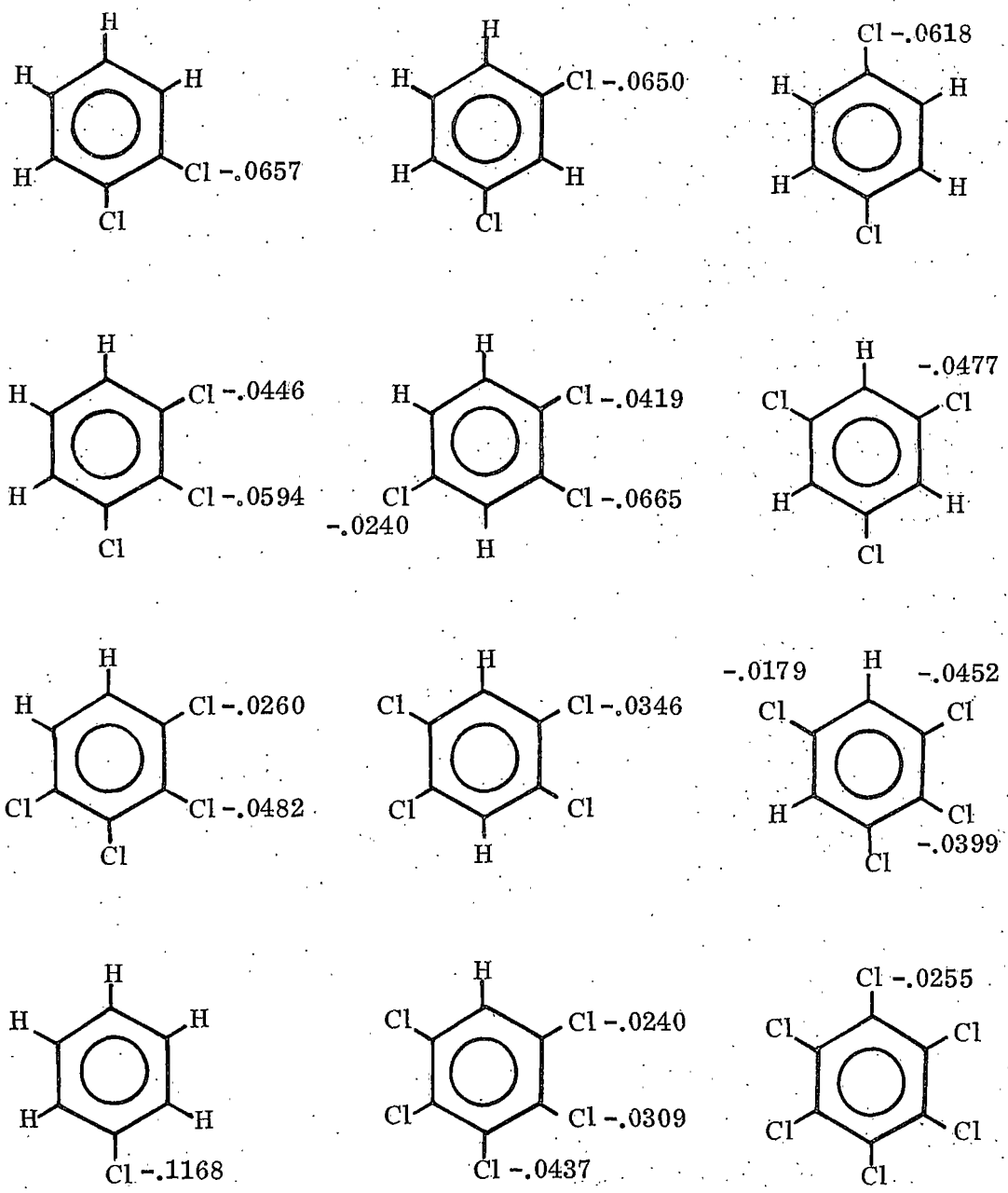


Figure 15. Bond Order of the LUMO-σ of Chlorobenzenes

bonding character should be the one which breaks most readily. Thus as before a reduction pathway can be predicted, as is shown in Figure 16. The predicted pathway from the bond orders is practically identical to the pathway obtained from using the electron density distribution found in the LUMO-σ.

If all of the occupied molecular orbitals are included, it is possible to get a total bond strength for a particular carbon chlorine bond. The total bond strength is obtained by multiplying the particular elements in the density matrix by the overlap matrix, term for term, summing the product and adding this to the virtual orbital bond strength. The results of this calculation are shown in Figure 17. Qualitatively the same trend as we have observed before is obtained. The "central" chlorines have the weakest bonds and to a first approximation should be the chlorines that are preferentially lost. As in previous methods it should be possible to develop a reduction pathway scheme based on relative bond strength. I made a crude attempt at this but was unable to develop satisfactory results. (See Figure 18). Looking at the carbon chlorine bond strengths in pentachlorobenzene, one can see that the "central" (position 3) chlorine has the weakest bond strenth. Positions 2 and 4 have the next lowest bond strength and if a statistical weight of 2 is entered (since there are two equivalent chlorines) it should be possible to develop a scheme using bond strengths to favor formation of 1,2,3,5-tetrachlorobenzene. Yet a scheme biased in such a manner would incorrectly predict that 1,3,5-trichloro-

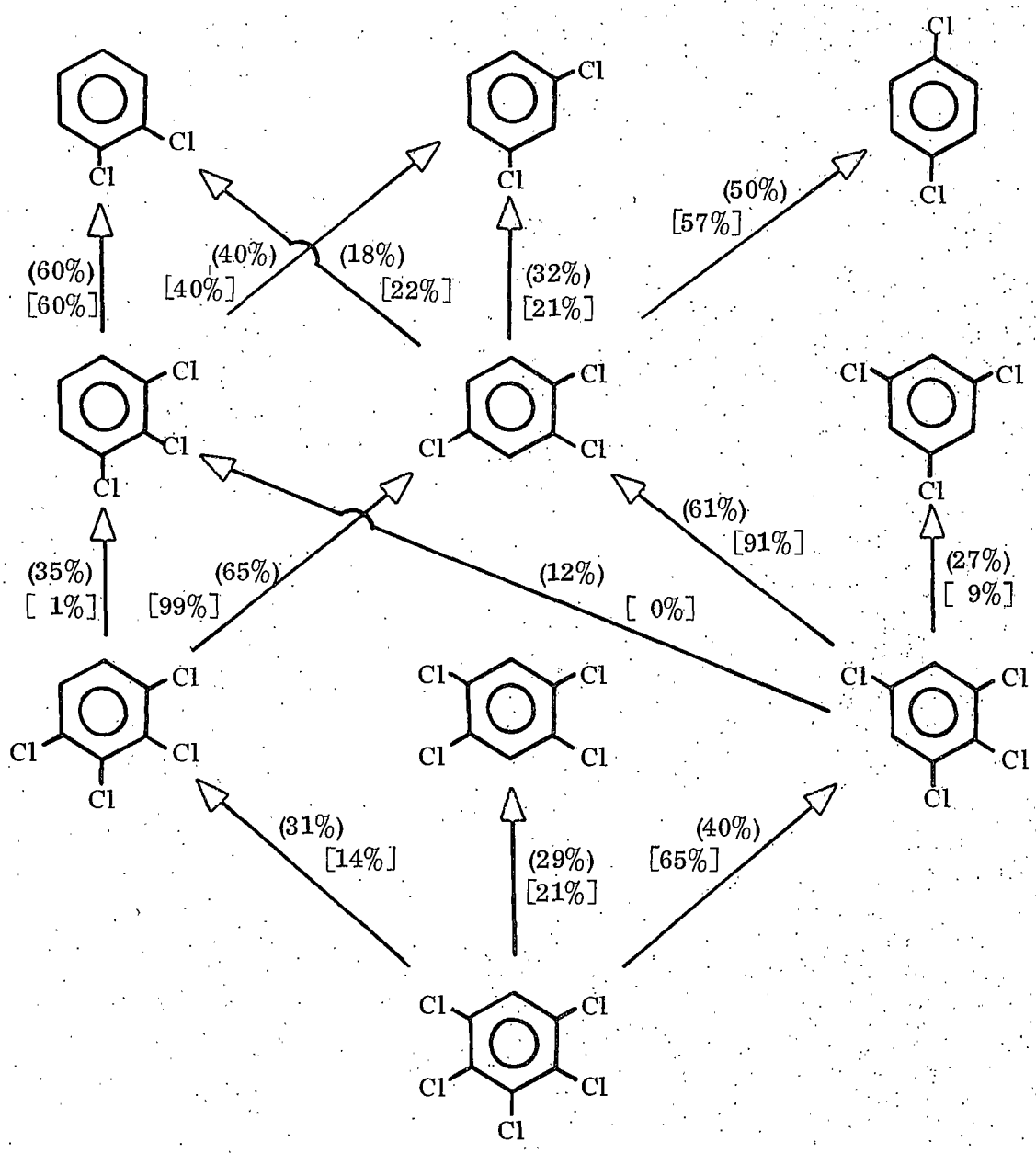


Figure 16. Reduction Pathways of Chlorobenzenes Based on Bond Order of LUMO-σ. ( ) - bond order, [ ] - electrolysis data[1]

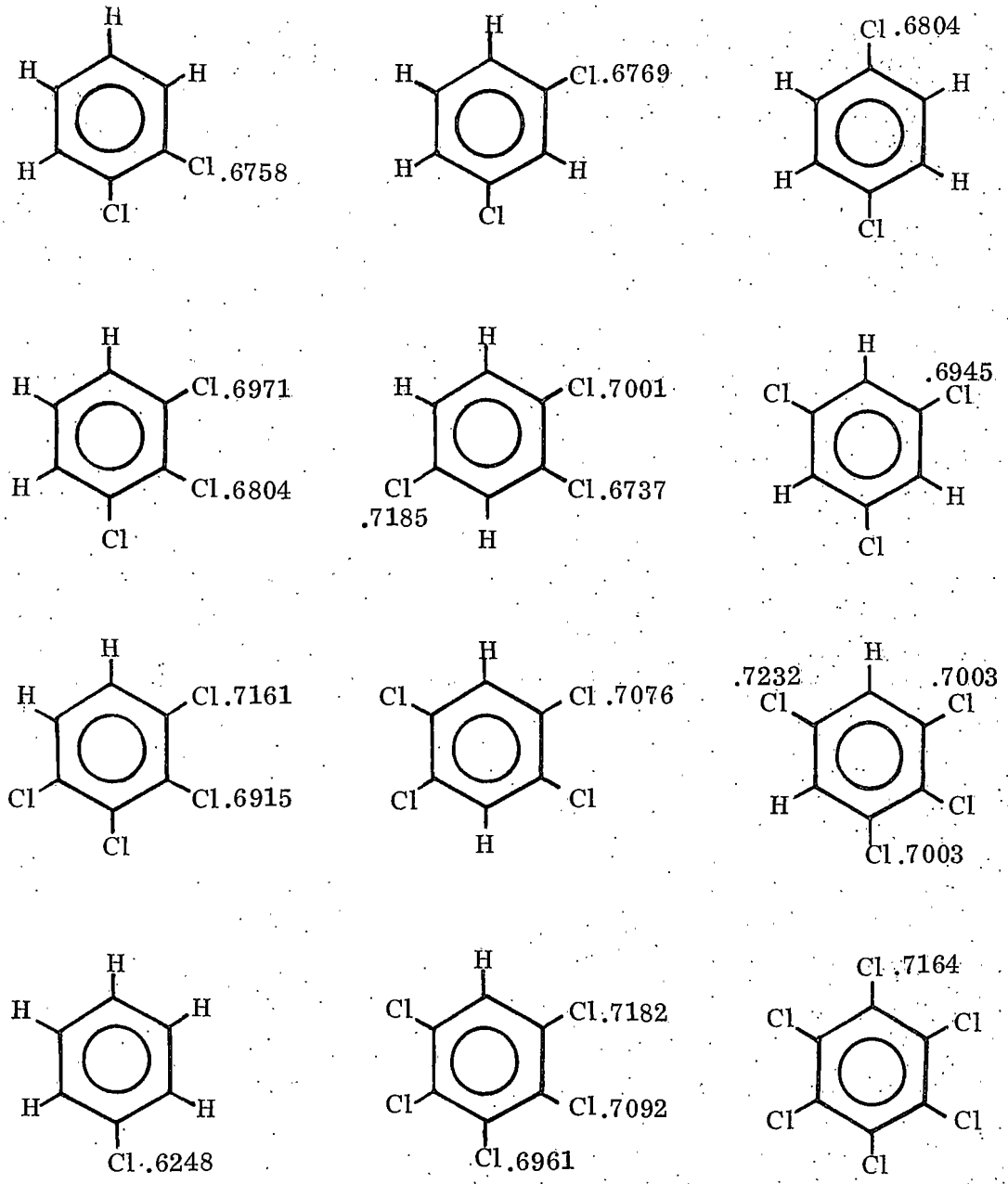


Figure 17. Total Bond Strength Including LUMO-σ for Chlorobenzenes

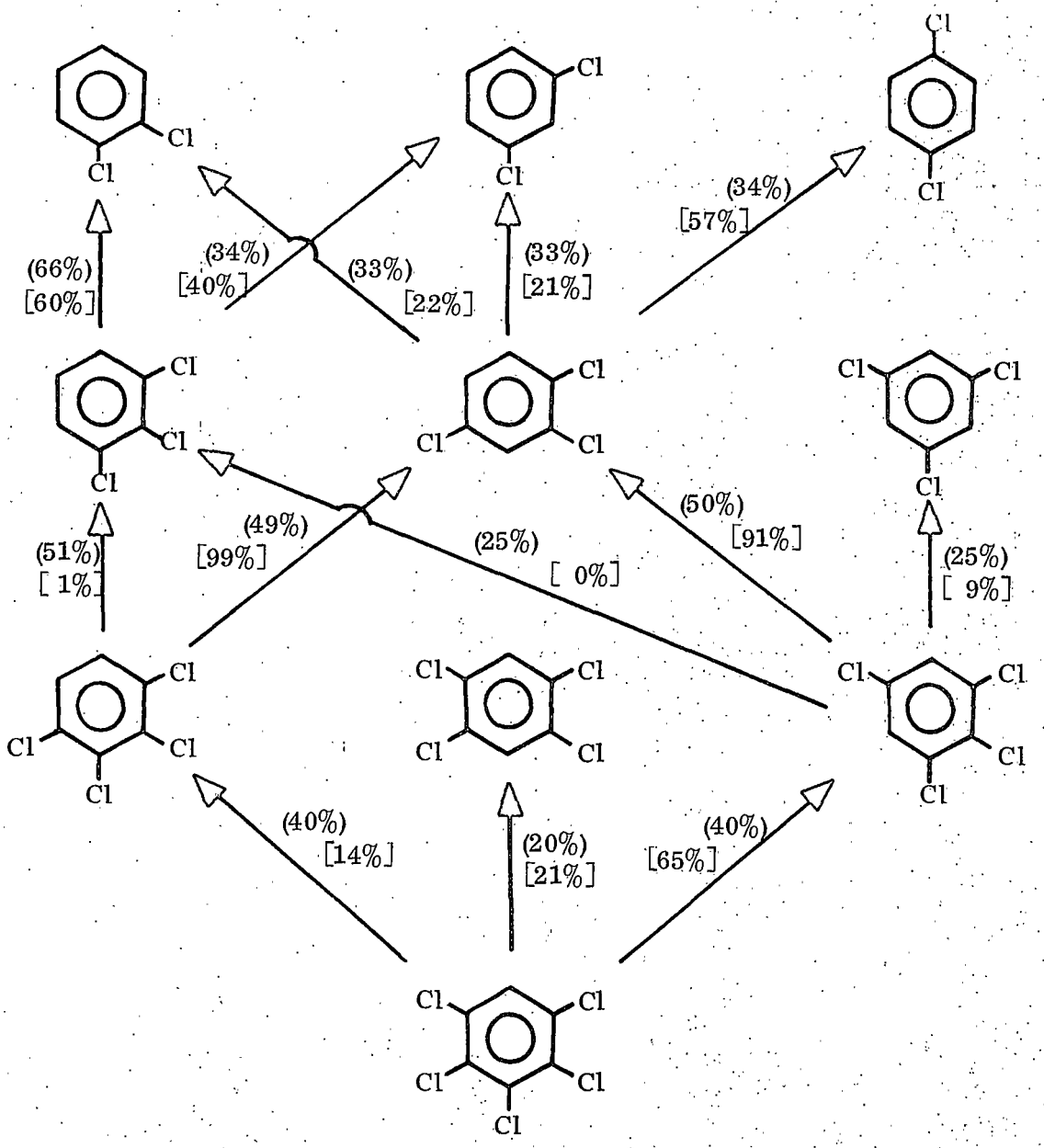


Figure 18. Reduction Pathways for Chlorobenzenes Based on Total Bond Strength Including LUMO-σ. ( ) - total bond strength, [ ] - electrolysis data[1]

benzene would be the major reduction product of 1,2,3,5-tetrachlorobenzene.

The same reasoning holds for 1,2,3,4-tetrachlorobenzene. If the scheme is formed in such a fashion as to predict the formation of 1,2,4-trichlorobenzene, then the scheme gives the incorrect reduction product of 1,2,3-trichlorobenzene. Thus this method, based on total bond strength, holds little hope.

The latter two treatments (virtual orbital and total bond strengths) can also be applied to open shell calculations on the radical anion. The "virtual orbital" in this case is the HOMO-σ which now contains one electron. The HOMO bond order is shown in Figure 19, and the reduction pathway prediction based on the virtual orbital method is shown in Figure 20. As was the case for the closed shell calculations, the results obtained from the virtual orbital method are almost identical to the electron density distribution method. Since the electron density distribution gave erroneous predictions (remember this was due to an overemphasis on the "central" chlorine), so also does the virtual orbital treatment based on open shell calculations.

Finally the total bond strength for the radical anion and the predicted pathways were calculated and are shown in Figure 21 (total bond strength) and Figure 22 (reduction pathway). Although the pathway prediction is not correct, it is identical to the pathway distribution obtained from total bond strength of the closed shell calculation. This is the sole occasion in which the open and

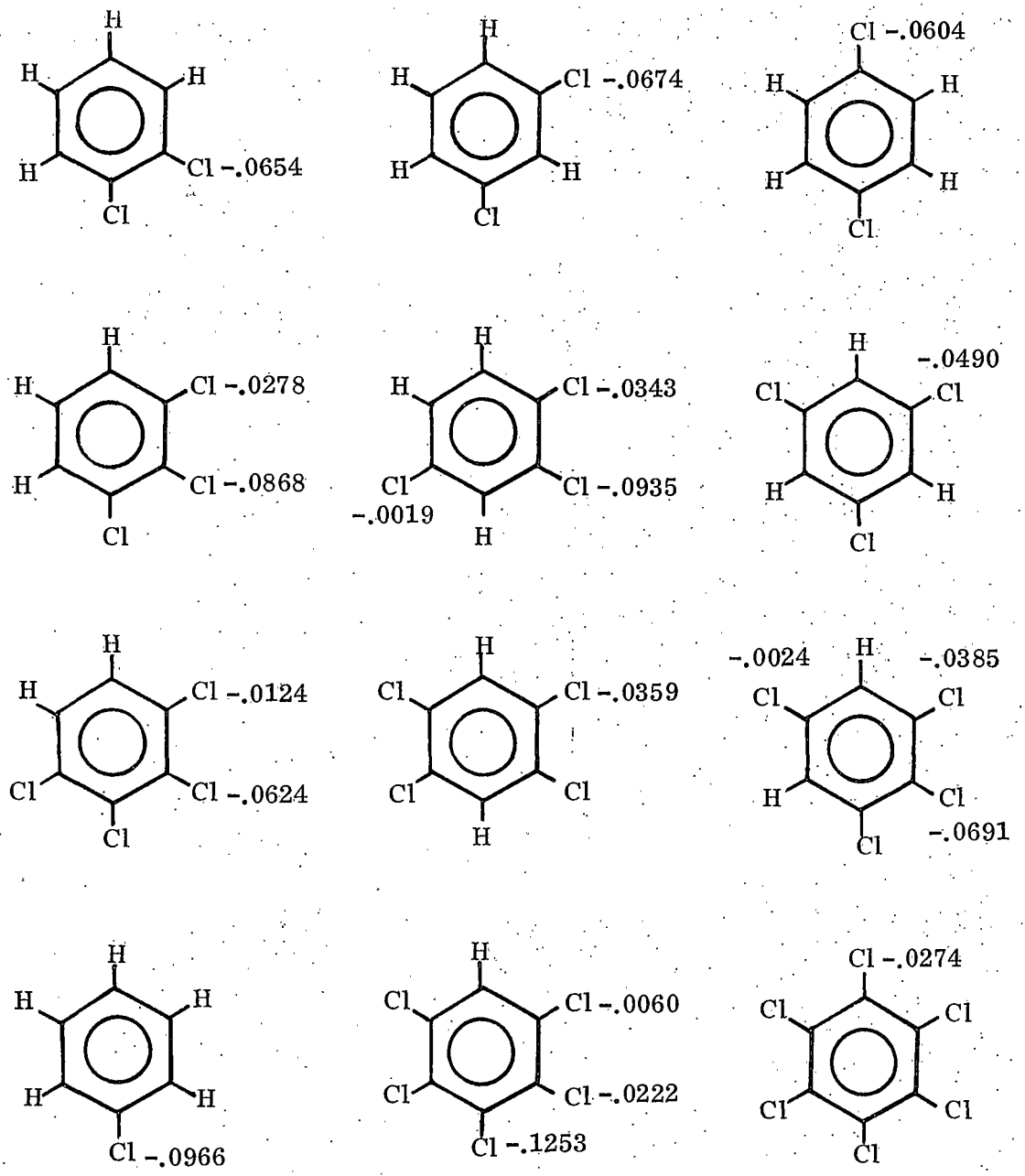


Figure 19. Bond Order in HOMO for the Radical Anion of Chlorobenzenes

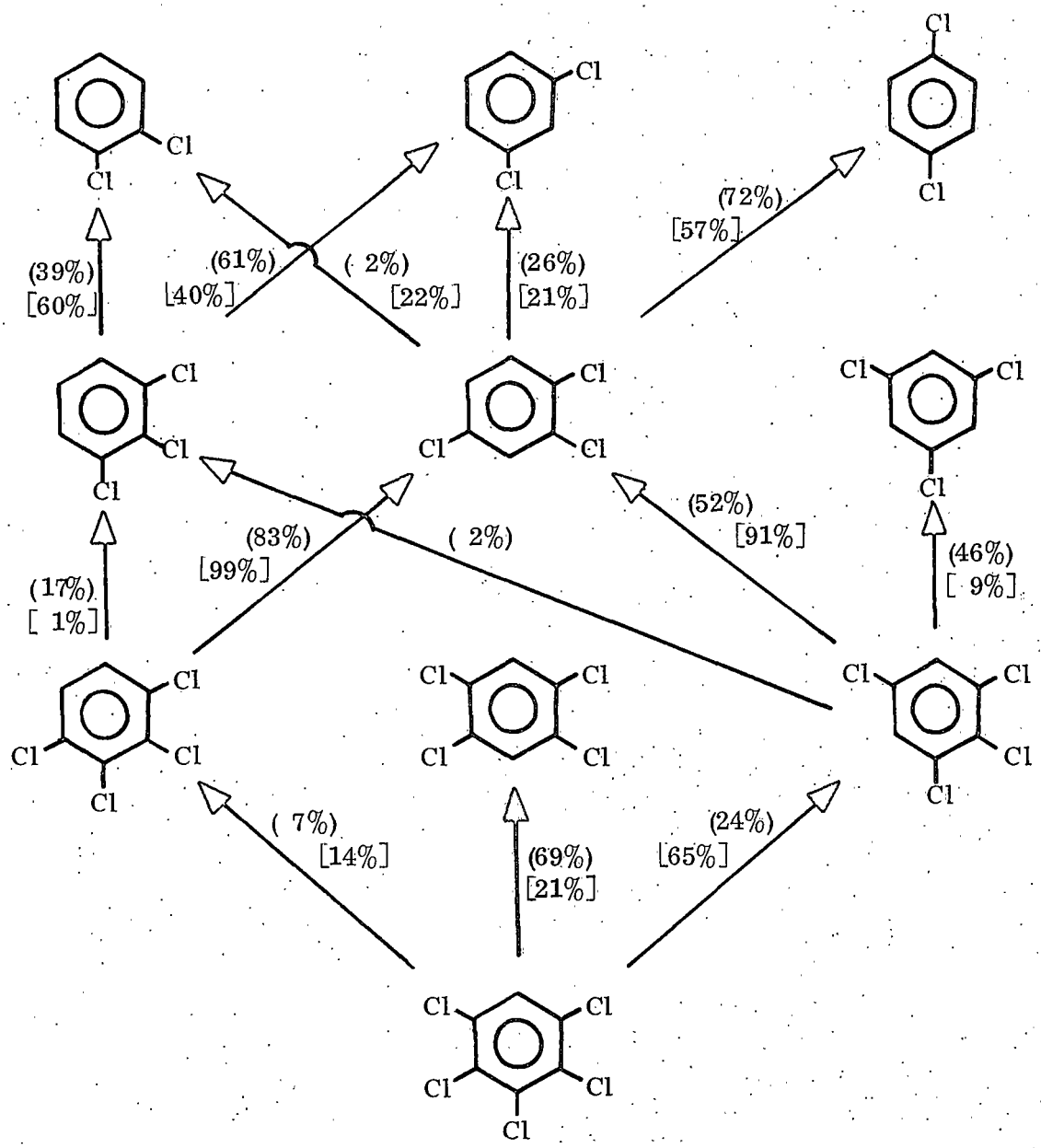


Figure 20. Reduction Pathways for Chlorobenzenes Based on Bond Order in HOMO of Radical Anion. ( ) - bond order, [ ] - electrolysis data[1]

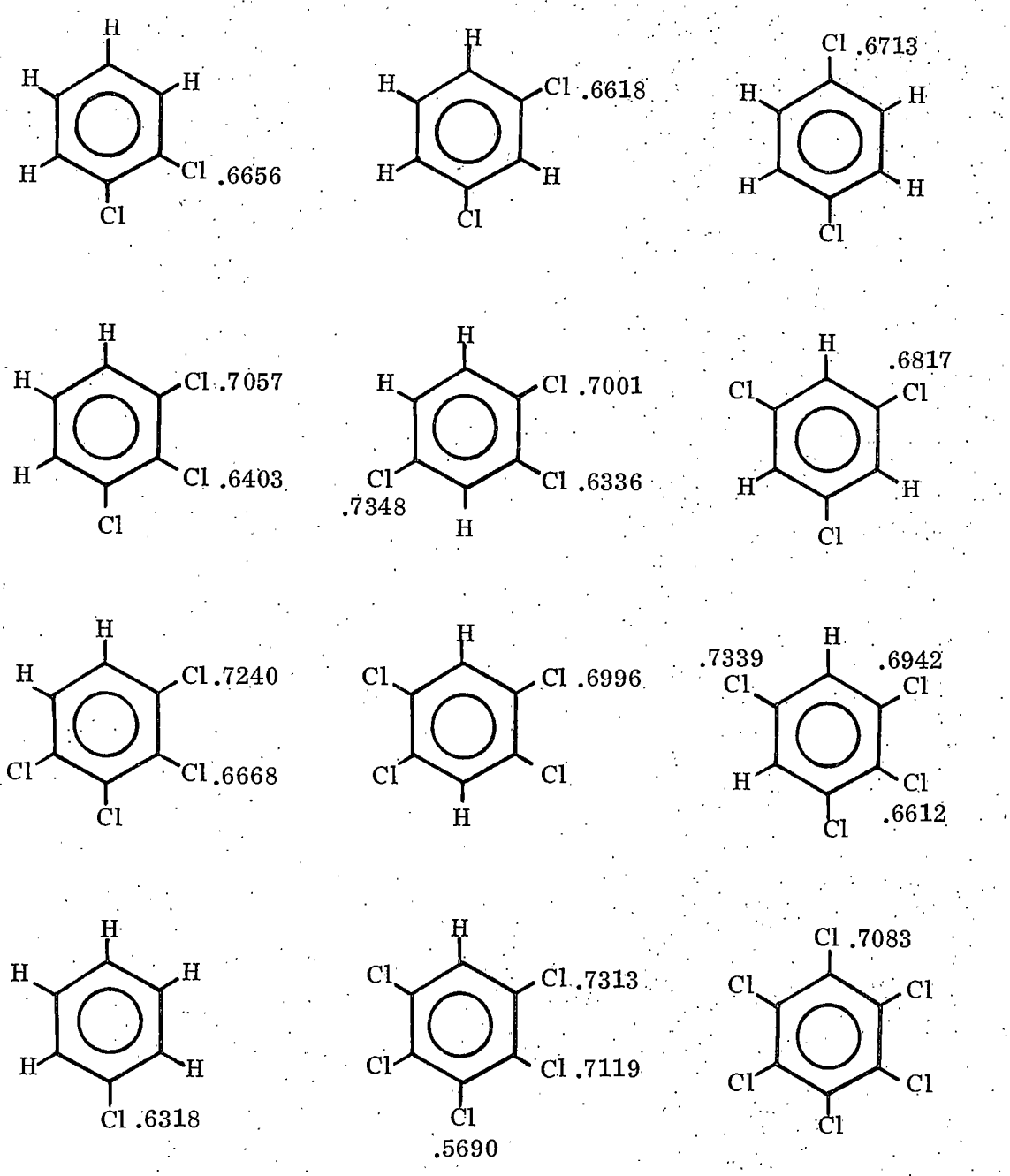


Figure 21. Total Bond Strength of the Radical Anions of Chlorobenzenes

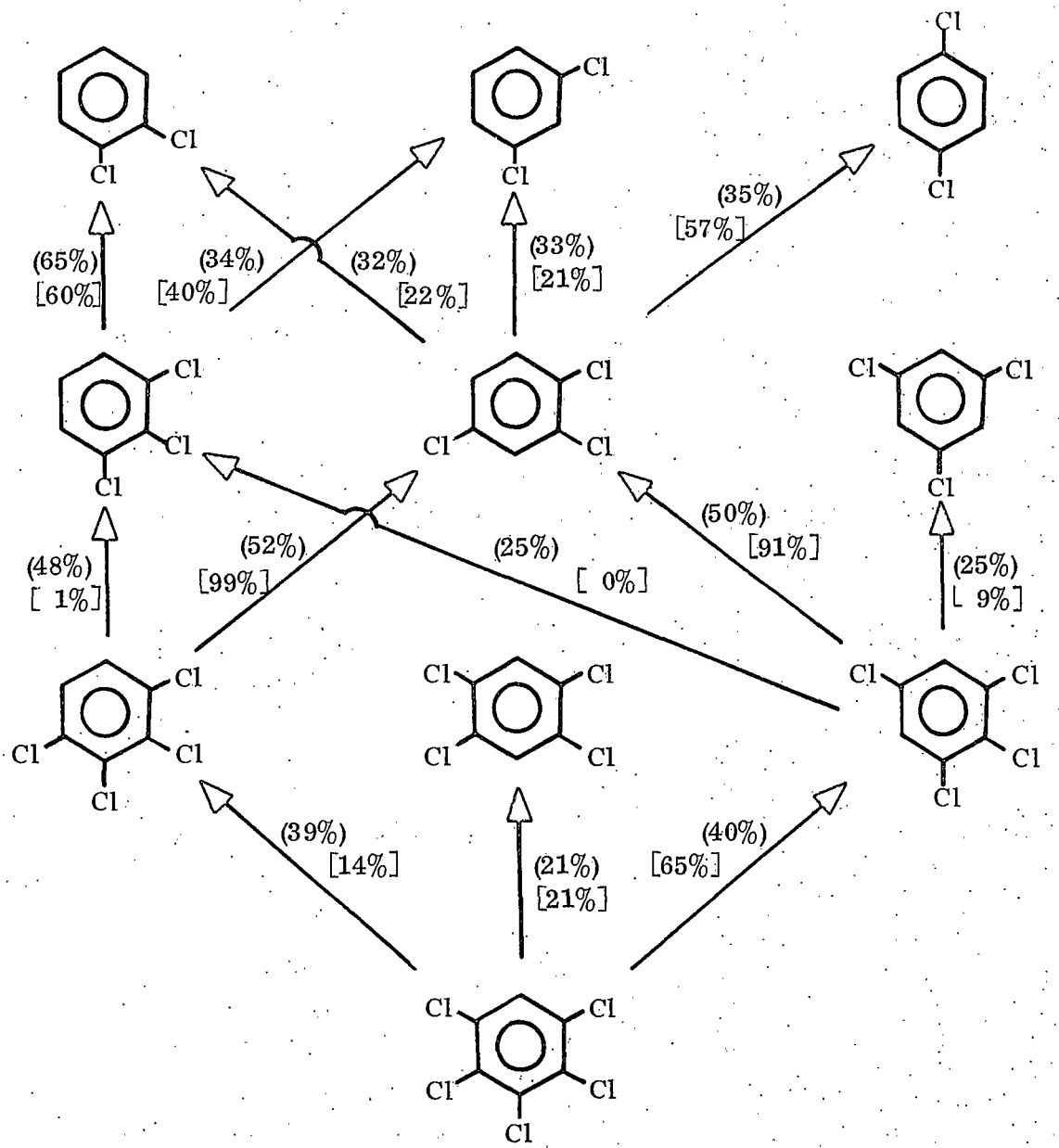


Figure 22. Reduction Pathways for Chlorobenzenes Based on Total Bond Strength in Radical Anion. ( ) - total bond strength, [ ] - electrolysis data

closed shell calculations do coincide and perhaps if the bond strength data were treated in a different manner, correct pathway predictions would result. However, since the predictions based on the electron density distribution in the LUMO-σ (which are obtained from the closed shell calculation) correspond the best with experimental results, this method will be used on all of the further compounds considered in this discussion. A further reason for adopting this method is that the computer time required for a closed shell calculation is approximately one half of the amount required for an open shell calculation.

Molecular Orbital Investigation of Electrochemical Carbon-Halogen Reduction: Chlorobiphenyls

Now that we have obtained a satisfactory method that allows us to predict with a fair degree of certainty the electrochemical reduction pathways, let us turn our attention to the chlorobiphenyls. Before one can embark on a CNDO/2 molecular orbital study on the biphenyl system, a decision must be made concerning whether to treat the molecule as planar of to have the rings rotated to some extent.

Biphenyl is planar in the solid state,[156] whereas in the vapor phase the two rings are twisted to 42°.[157] This latter value is quite close to the value obtained by allowing the ortho hydrogens (to the bridge) to get no closer to one another than Van Der Waal's radii (1.2 A for hydrogen).[158] Decafluorobiphenyl exists with an angle of 62° in the solid[159] and 70° in the gas phase.[160] Again

these are very close to the sum of the Van Der Waal's radii (for fluorine, 1.35 A).[158] p,p'-Bitolyl has twist angles of 36° and 40° in the crystalline state,[161] p-nitrobiphenyl 33°,[162] and p,p'-dinitrobiphenyl 33°.[163] Using a liquid crystal solvent, 3,5,3',5'-tetrachlorobiphenyl was found by proton nmr to have a rotation angle of 34°.[164]

The central bond length for biphenyl in the crystal state is 1.507 A,[156] for 4,4'-bitolyl, 1.486 A and 1.459 A,[161] and for 4,4'-dinitrobiphenyl 1.499 A.[163] These data lead to the conclusion that the angle of rotation should be governed to a first approximation by the sum of Van Der Waal's radii (1.2 A for hydrogen and 1.80 A for chlorine) and the central bond length should be between 1.50 A and 1.48 A. With a central bond length of 1.50 A, the minimum angle allowed (based on Van Der Waal's radii) for biphenyl is 43°; with a bond length of 1.48 A this angle increases to about 44°. When there are chlorines in the 2- and/or 6- position on one ring for a central bond length of 1.50 A, the angle is 64°, and for 1.48 A the angle approaches 65°.

In an attempt to locate the minimum energy for representative substitutions, the following trial calculations were performed. CNDO calculations were run on biphenyl at various angles with bond lengths of 1.50 A and 1.48 A. The other representative substitution patterns tried (all at central bond lengths of 1.48 A) were 2- and 4-, 2,4- and 2,6-dichlorobiphenyls. This allowed determination of what I felt was the best configuration for a particular substitution

pattern. Once this was established, closed shell calculations were performed on the rest of the chlorobiphenyls with chlorines on one ring. All of these results are presented in Table 6.

The calculations on biphenyl indicated that a minimum in energy existed at 40^{o} with a central bond length of 1.480 A. Since this bond length was apparently better than 1.500 A, the 1.480 A length was used for the rest of the calculations. For compounds without any ortho chlorines (2- or 6- position) 40^{o} was the rotation angle minimum; 50^{o} was the minimum energy for compounds with one ortho chlorine, and 52^{o} for compounds with two ortho chlorines.

These results contrast with previously attempted CNDO calculations on biphenyl. Tinland[165] used a central bond length of 1.50 A and found the energy minimum to be when the two rings were perpendicular to one another. This result was confirmed by Gropen and Seip.[166] The failure to find an energy minimum around 40^{o} is probably due to an overestimation of the core repulsions between non-bonded atoms, in this case between ortho hydrogens on each side of the bridge. Thus if the central bond length is lengthened, a minimum might be found at an angle less than 90^{o}. This was done by Tajiri et al.[167] Using a central bond length of 1.54 A they found an energy minimum around 42^{o} with a barrier of rotation of 1.8 kcal/mol (experimental 1.20 kcal/mol).

Why then is a minimum found using shorter bond length (1.48 A)? Remem-

Table 6. Total Energy for Chlorobiphenyls Obtained from CNDO/2 Calculations

Chlorobiphenyl	Central Bond Length (A)	Rotation Angle (Degrees)	Total Energy (a.u.)
Biphenyl	1.500	0	-92.7840
		45	-92.7891
		90	-92.7836
	1.480	36	-92.7873
		38	-92.7832
		40	-92.7937
		42	-92.7919
		45	-92.7859
2	1.480	45	-108.2206
		50	-108.2219
		55	-108.2217
		60	-108.2154
		70	-108.2176
4	1.480	38	-108.2128
		40	-108.2244
2,4	1.480	48	-123.4138
		50	-123.4261
2,6	1.480	50	-123.5262
		52	-123.5273
		54	-123.5219
		56	-123.5193
3	1.480	40	-108.2131
2,3	1.480	50	-123.6265
2,5	1.480	50	-123.9612
3,4	1.480	40	-123.6287
3,5	1.480	40	-123.5205
2,3,4	1.480	50	-138.8161
2,3,5	1.480	50	-139.2823

Table 6. (Continued)

Chlorobiphenyl	Central Bond Length (A)	Rotation Angle (Degrees)	Total Energy (a.u.)
2,3,6	1.480	52	-139.2911
2,4,5	1.480	50	-139.1531
2,4,6	1.480	52	-138.5164
3,4,5	1.480	40	-138.7922
2,3,4,5	1.480	50	-154.4590
2,3,4,6	1.480	52	-154.2652
2,3,5,6	1.480	52	-154.9428
2,3,4,5,6	1.480	52	-169.9035

ber that these calculations were done in single precision. It was assumed that any errors in the total energy would be random, but apparently this is not the case. Indeed, when the calculations were repeated using the double precision program I was unable to find a minimum in energy where I had previously located one. Instead 90^{o} was the low energy point.

If this is the case are the calculations done in single precision meaningful? I believe that the answer is yes. The results from the chlorobenzenes were in accord with experimental observation. This is because the electron distribution in the LUMO is not susceptible to wild fluctuations when there are small changes in the total energy. There is also a rather practical reason for using single precision calculations; the computer space

allotment is not large enough to allow calculations on a number of these molecules in double precision.

As in the case of the chlorobenzenes, one can ask what type of orbital, σ^* or π^*, receives the electron upon reduction. The low lying unoccupied orbitals for each of the most favored conformations are shown in Table 7. In every case the LUMO is a π orbital. In some cases there are actually two unoccupied π orbitals before the first σ orbital. However, because these low lying orbitals are nearly degenerate, it is not unreasonable to expect that the sigma anti-bonding would receive the electron as in the chlorobenzene case.

To see which orbital actually receives the electron, open shell calculations were performed on the radical anion of some of the lower chlorinated biphenyls. These results are presented in Table 8. The calculation gives the same result as was found with the chlorinated benzenes; the σ anti-bonding orbital receives the electron. The structure input into the calculation was identical to the parent chlorobiphenyl. The use of these parameters seems as valid as any in light of the considerable uncertainty concerning the most stable angle of rotation of the radical anion of biphenyl. Mobius,[168] using epr estimated the value to be 38 ± 2^{o}. R. Biehl et al.[169] using ENDOR spectroscopy predicted a near planar structure. There have been at least two theoretical studies; one estimated that the isolated anion would have an angle of 25^{o} while in solution the radical anion would exist at $15\text{-}19^{o}$.[170] The other

Table 7. Eigenvalues of the Lowest σ and π Molecular Orbitals from Closed Shell CNDO/2 Calculations on Chlorobiphenyls

Chlorobiphenyl	Rotation Angle in Degrees	LUMO's (type of orbital) (a.u.)
2	50	0.0927 (π) 0.1122 (σ)
3	40	0.0900 (π) 0.1098 (π?) 0.1135 (σ)
4	40	0.0835 (π) 0.1129 (σ)
2,3	50	0.0814 (π) 0.0861 (σ)
2,4	50	0.0700 (π) 0.0887 (σ)
2,5	50	0.0696 (π) 0.0974 (π?) 0.1013 (σ)
2,6	52	0.0820 (π) 0.0830 (π) 0.0889 (σ)
3,4	40	0.0653 (π) 0.0841 (σ)
3,5	40	0.0772 (π) 0.0813 (π) 0.0884 (σ)
2,3,4	50	0.0629 (π) 0.0633 (σ)
2,3,5	50	0.0554 (π) 0.0728 (σ)
2,3,6	52	0.0566 (π) 0.0739 (σ)

Table 7. (Continued)

Chlorobiphenyl	Rotation Angle in Degrees	LUMO's (type of orbital) (a.u.)
2,4,5	50	0.0490 (π) 0.0718 (σ)
2,4,6	52	0.0618 (π) 0.0688 (σ)
3,4,5	40	0.0563 (π) 0.0630 (σ)
2,3,4,5	50	0.0439 (π) 0.0486 (σ)
2,3,4,6	52	0.0396 (π) 0.0499 (σ)
2,3,5,6	52	0.0372 (π) 0.0585 (σ)
2,3,4,5,6	52	0.0288 (π) 0.0346 (σ)

Table 8. Eigenvalues of the LUMO and HOMO for the Radical Anions of the Chlorobiphenyls Obtained from Open Shell CNDO/2 Calculations

Compound	(Degrees)	Energy HOMO (a.u.) (type of orbital)	Energy LUMO (a.u.) (type of orbital)
2	50	-0.0099 (σ)	0.2702 (π)
3	40	-0.0056 (σ)	0.2423 (π)
4	40	-0.0121 (σ)	0.2460 (π)

investigation based on π-electron delocalization and non-bonded repulsions between the rings predicted the value to be 25 ± 5^{o} while the angle of rotation for the radical anion of 2, 6, 2', 6'-tetramethylbiphenyl was 80^{o}.[171]

When the first reduction potential is plotted against the LUMO-σ (Figure 23) or the LUMO-π (Figure 24), linear relationships are obtained for both as was the case with the chlorobenzenes. Thus this type of analysis does not establish which orbital the electron enters. However, using the electron density distribution in the LUMO's σ and π to predict reduction pathways might provide further evidence that the reduction process involves occupying the LUMO-σ.

The electron density in the LUMO-σ and the LUMO-π for all the chlorobiphenyls with chlorine on one ring are shown in Figures 25 and 26 respectively. Using this data it is possible to develop a reduction scheme, based on the electron distribution in a manner analogous to the treatment for the chlorobenzenes. The calculated reduction pathways along with the experimentally determined results established by Farwell[1] are given in Table 9.

The most obvious difference between the experimental reduction pathways for the chlorobenzenes and the chlorobiphenyls is that the latter pathway is considerably more complicated. For instance the reduction of tetrachlorobiphenyls gave dichloro- isomers in addition to the expected trichloro- compounds. This tends to hinder a comparison between experimental and

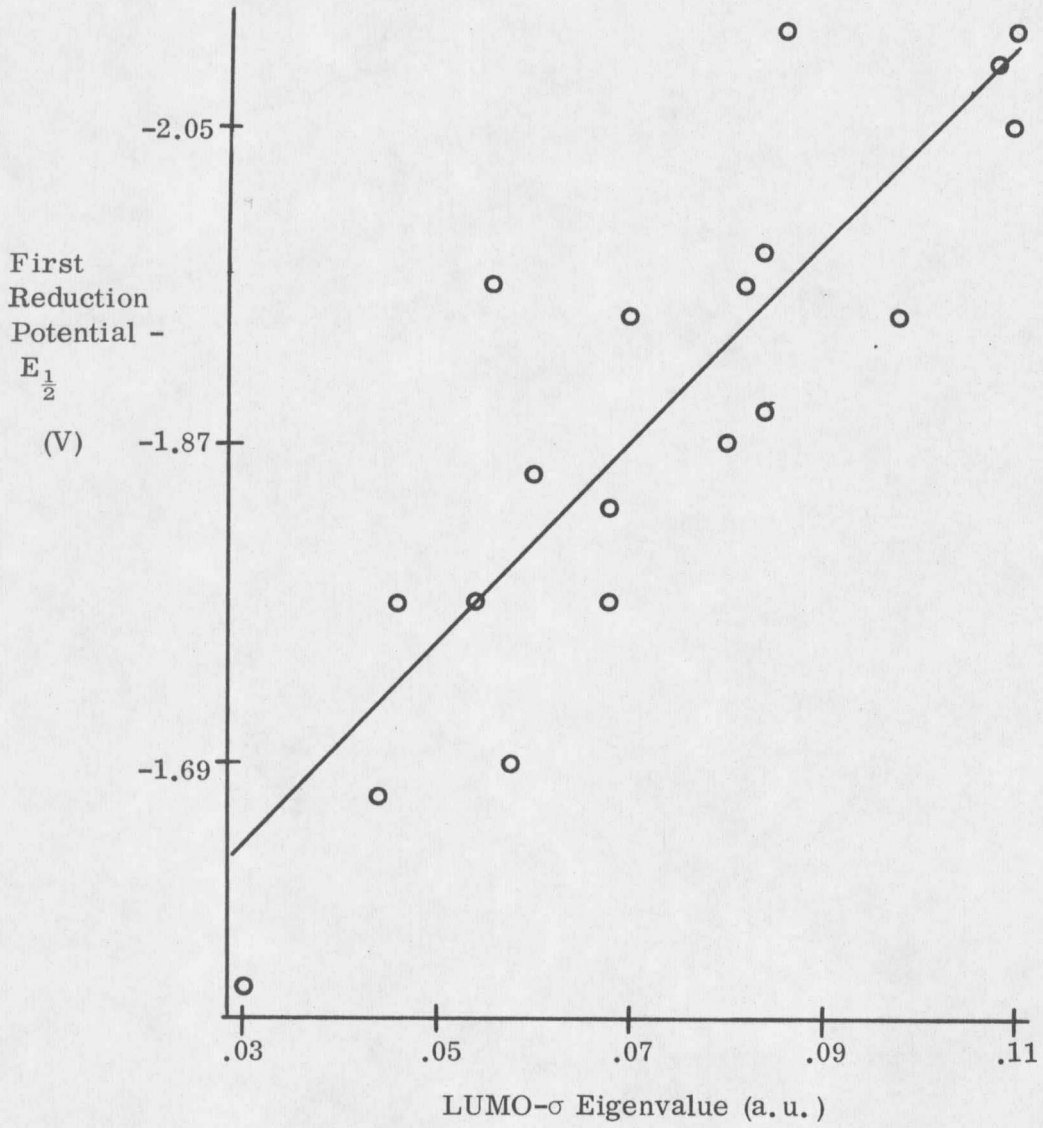


Figure 23. First Reduction Potentials for Chlorobiphenyls vs. Calculated LUMO-σ. $y = 5.75 \pm 3.54x + 1.44 \pm 0.29$, $r = 0.86$

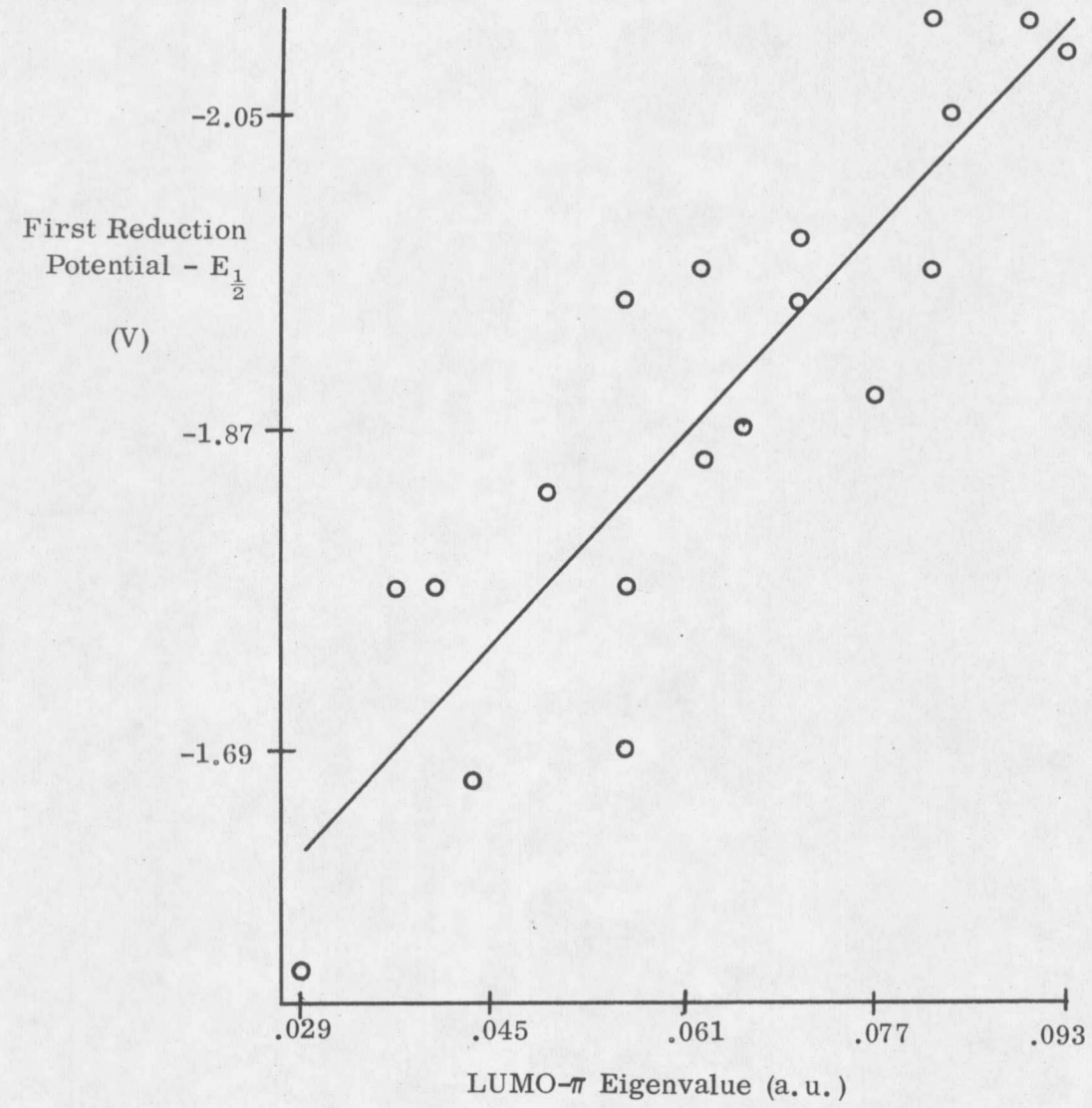


Figure 24. First Reduction Potentials for Chlorobiphenyls vs. Calculated LUMO-π. $y = 7.28 \pm 4.04x + 1.43 \pm 0.27$, $r = 0.89$

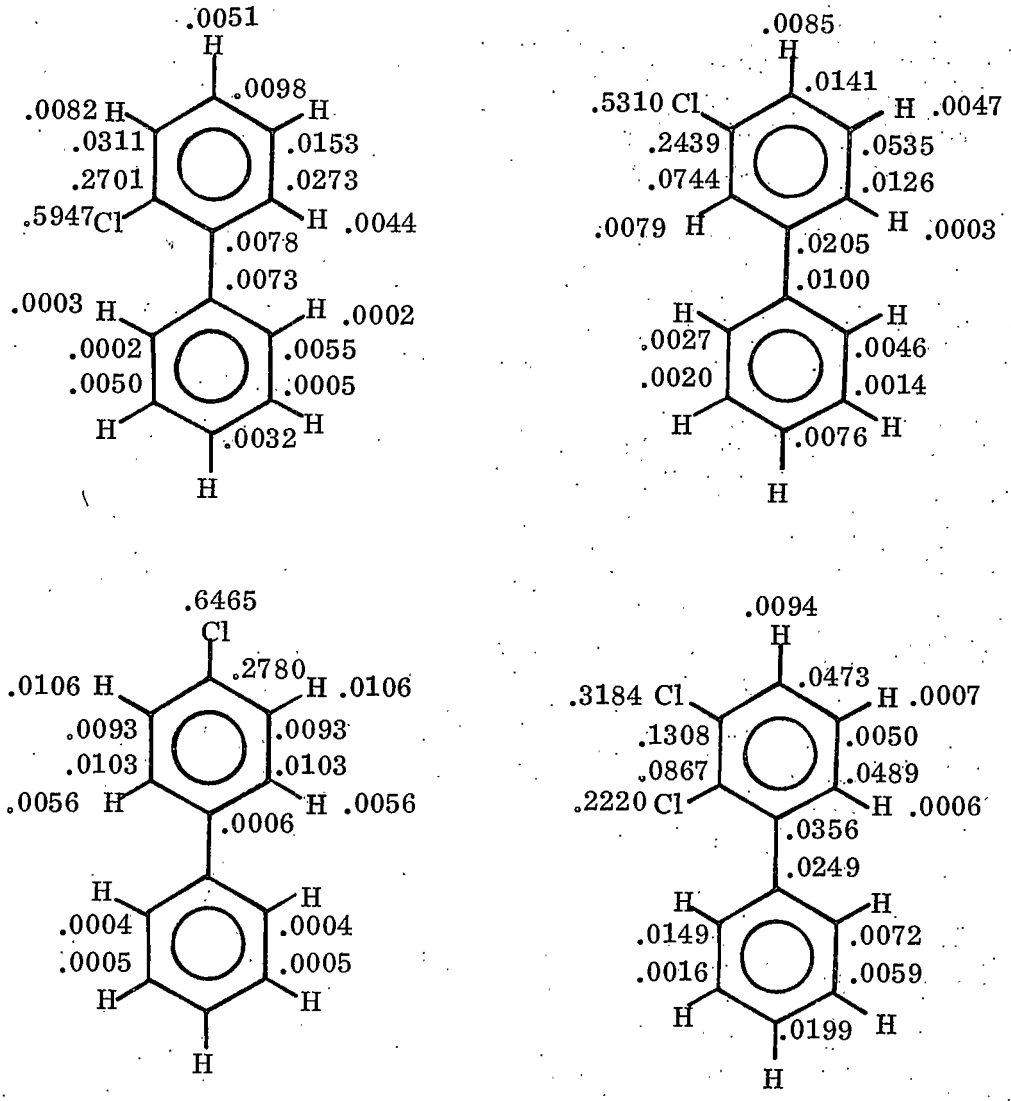
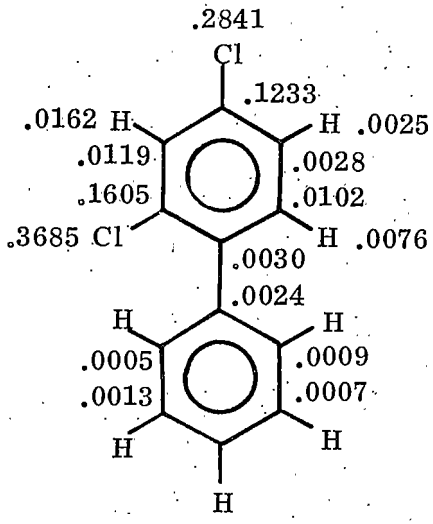
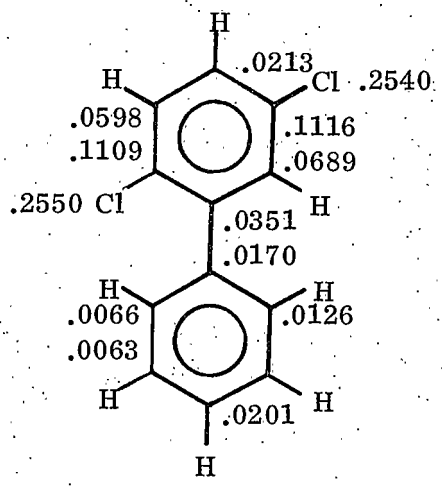
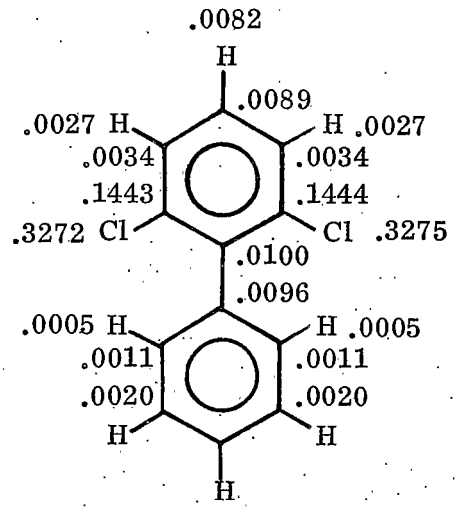


Figure 25. Electron Density Distribution in the LUMO-σ for the Chlorobiphenyls







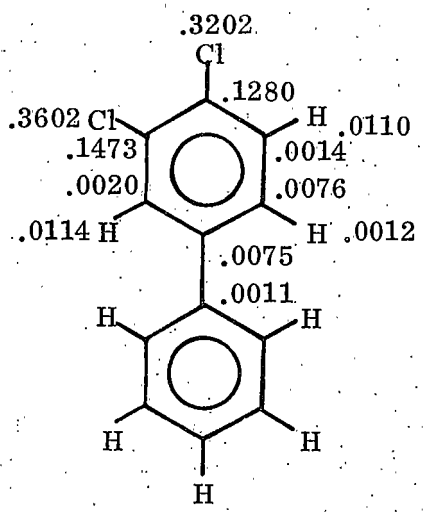
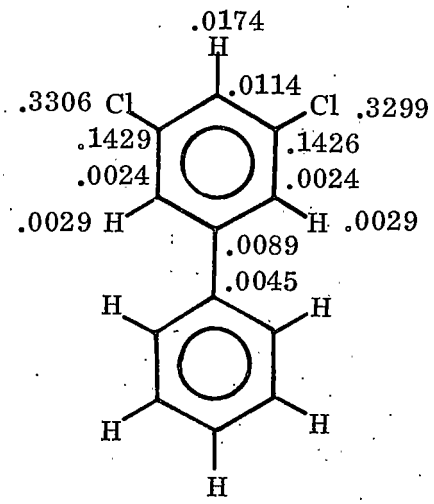
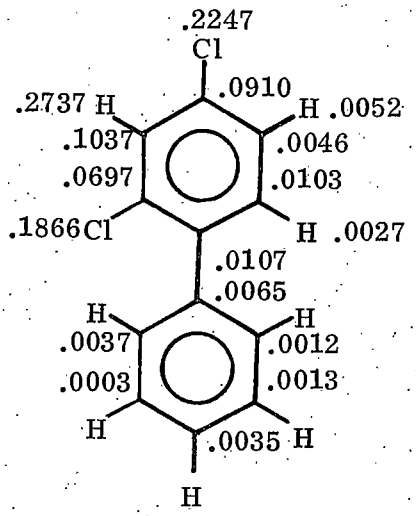
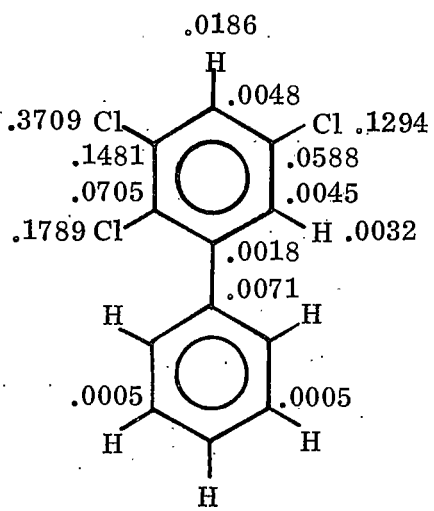


Figure 25. (Continued)







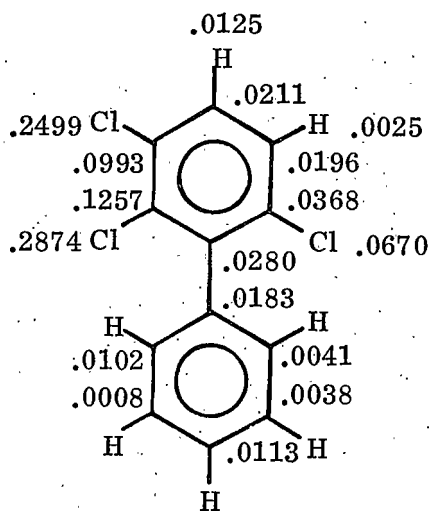
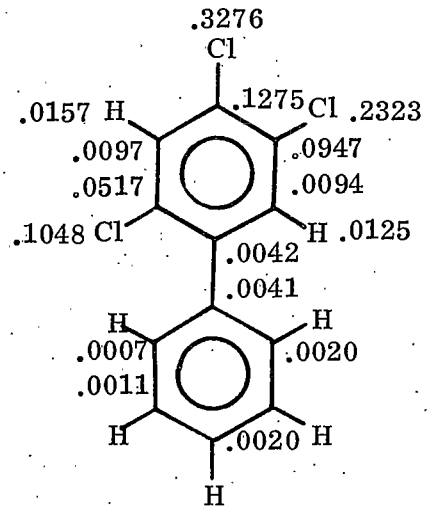
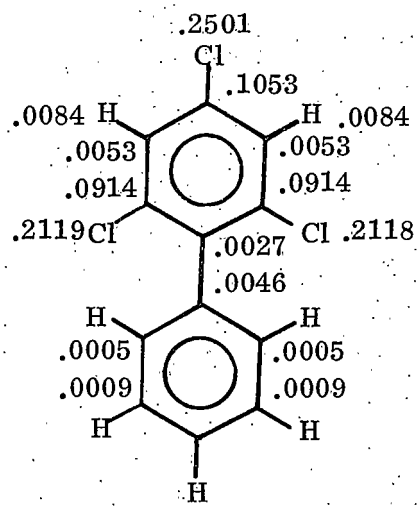
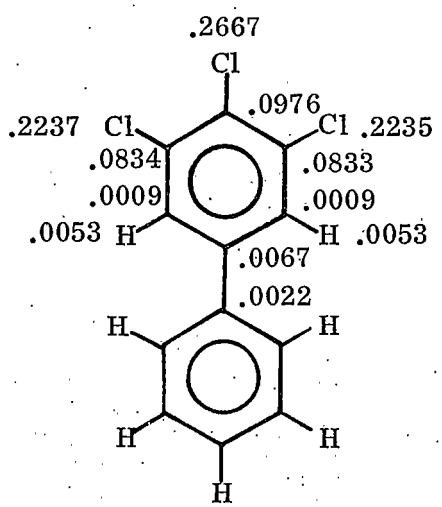


Figure 25. (Continued)







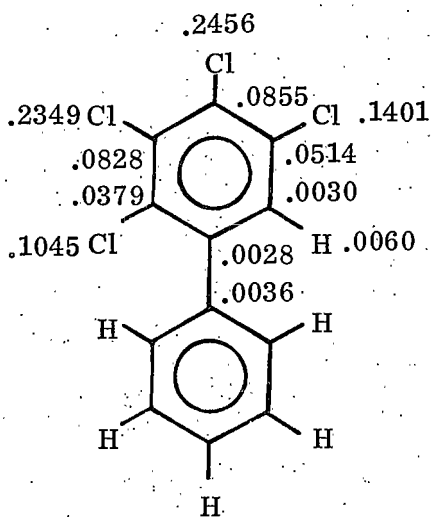
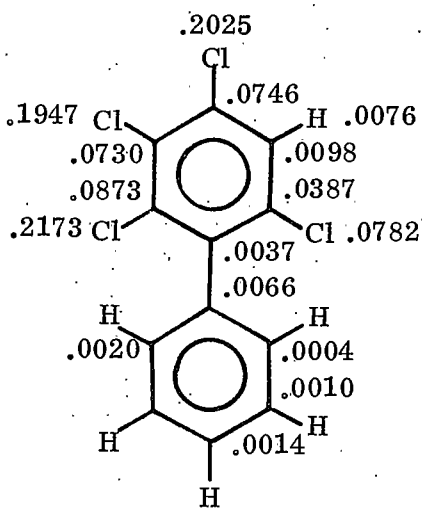
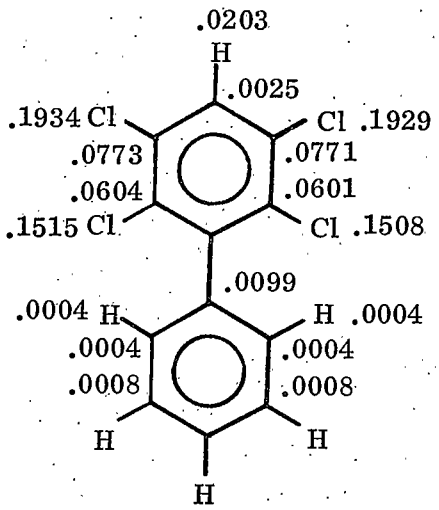


Figure 25. (Continued)





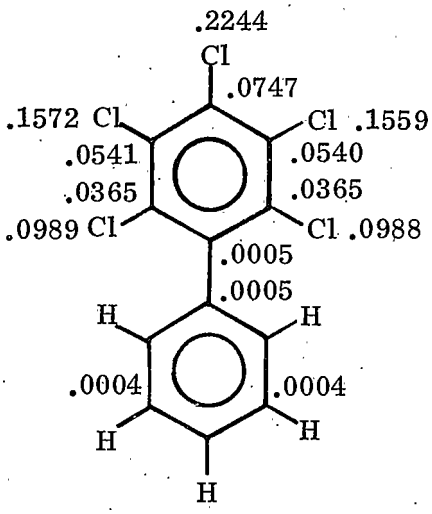


Figure 25. (Continued)

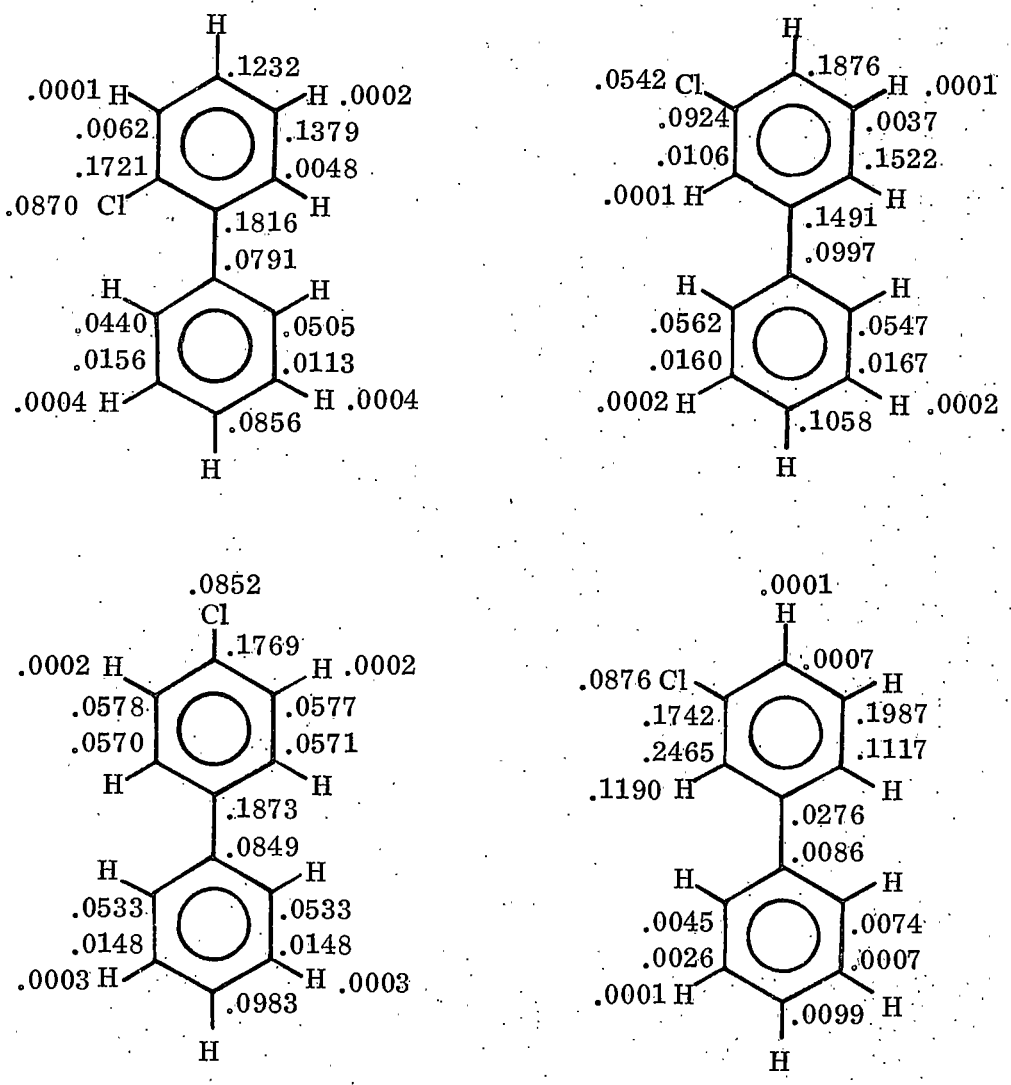
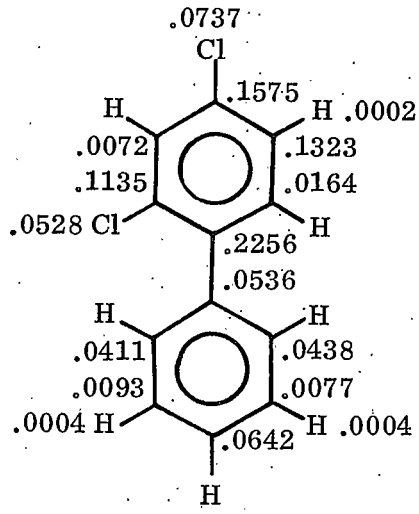
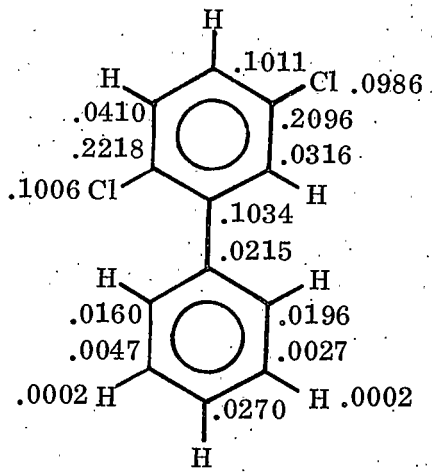
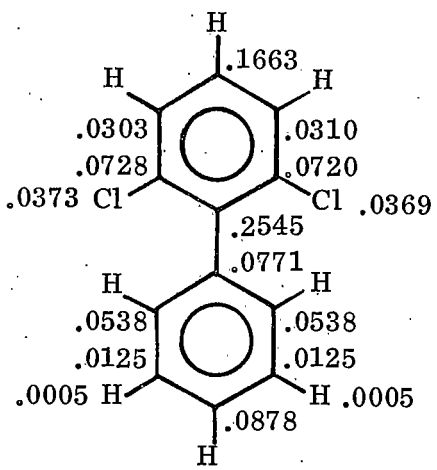


Figure 26. Electron Density Distribution in the LUMO-π for the Chlorobiphenyls







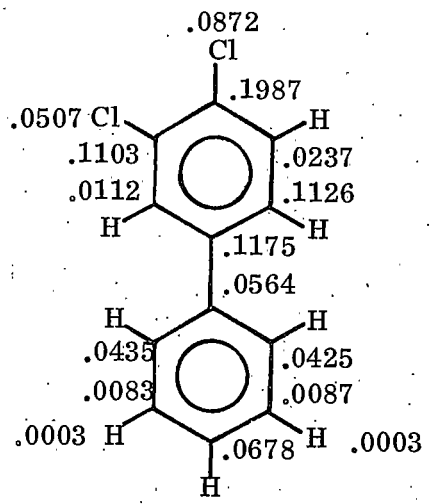


Figure 26. (Continued)

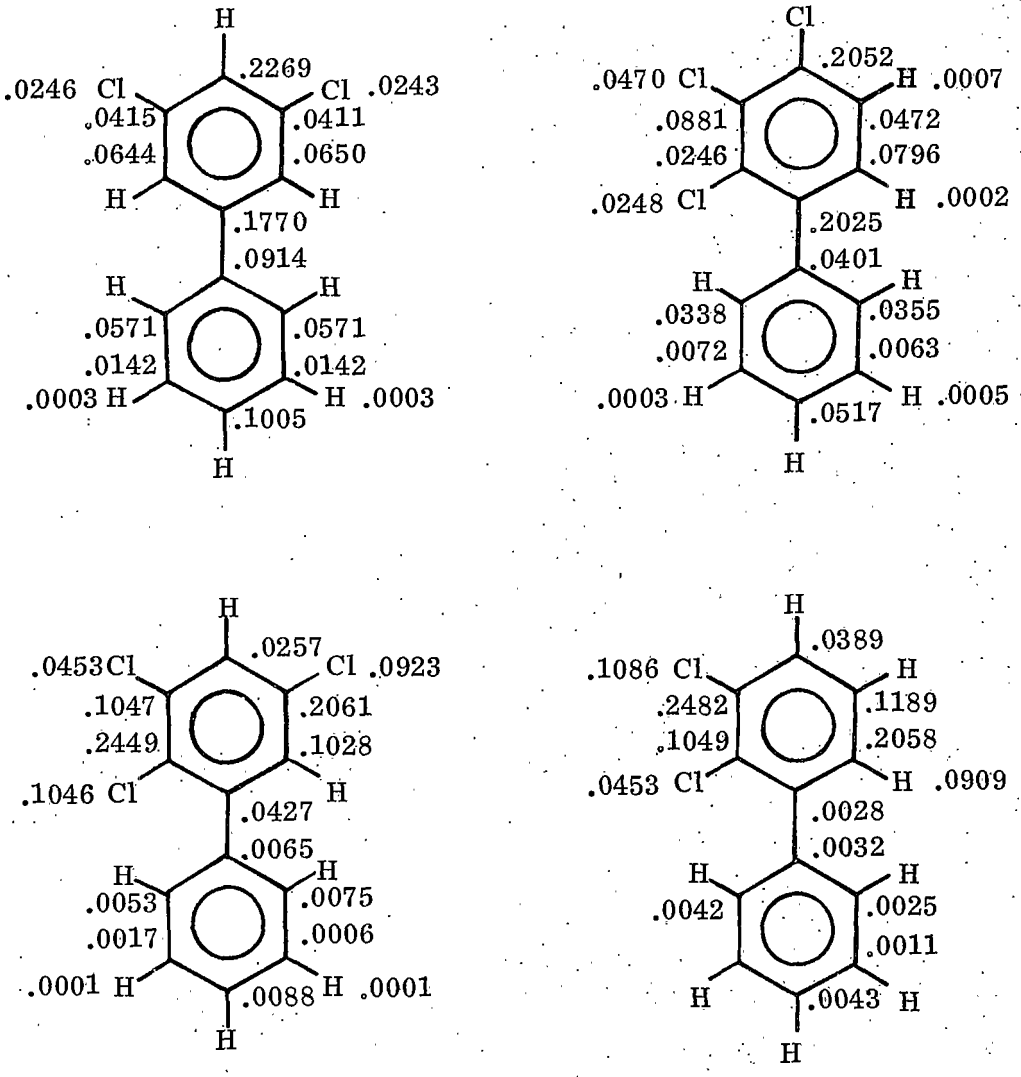
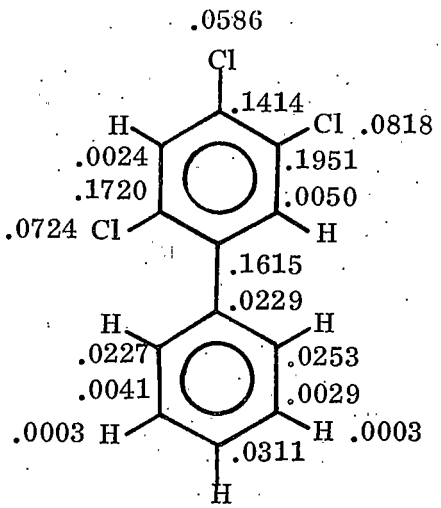
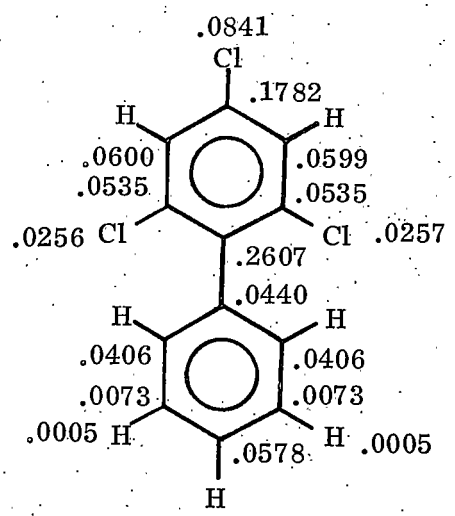
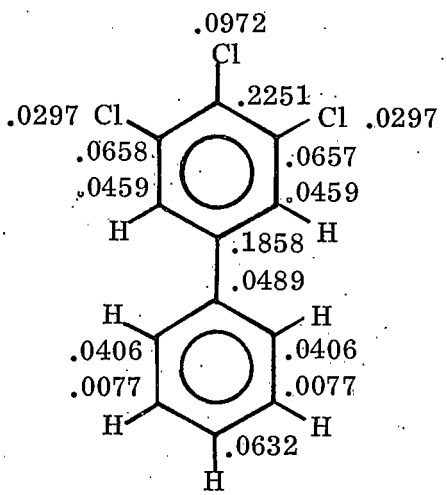


Figure 26. (Continued)







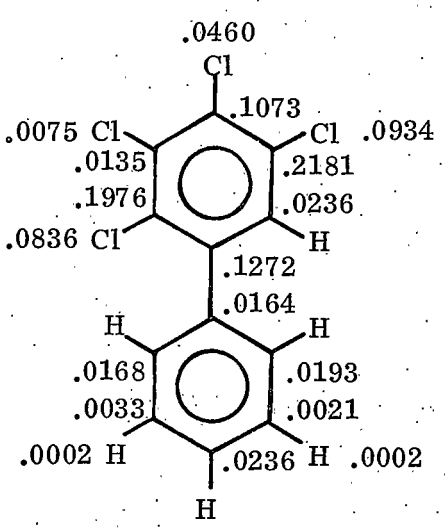
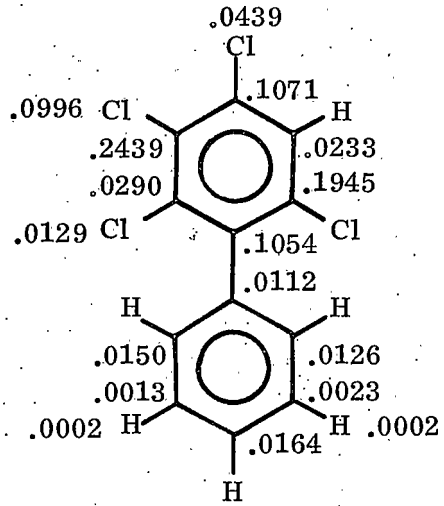
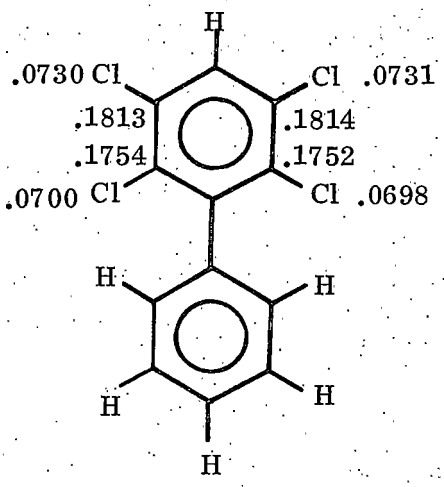


Figure 26. (Continued)





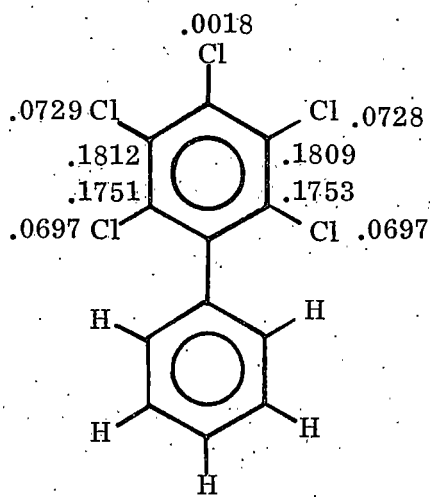


Figure 26. (Continued)

Table 9. Experimental and Predicted Reduction Pathways, Based on Electron Density Distribution in LUMO-σ or -π for Biphenyls

Chlorobiphenyl	Reduction Product	Product Distribution (%) Experimental (Farwell)[1]	LUMO-σ	LUMO-π
2,3	2	11	59	42
	3	89	41	58
2,4	2	47	44	58
	4	53	56	42
2,5	2	50	50	49
	3	50	50	51
3,4	3	81	47	63
	4	19	53	37
2,3,4	2	17		
	3	21		
	4	7		
	2,3	10	33	59
	2,4	45	40	27
	3,4	0	27	14
2,3,5	2,3	0	19	38
	2,5	11	55	19
	3,5	89	26	43
2,3,6	2	10		
	3	88		
	2,3	0	11	37
	2,5	1	48	19
	2,6	1	41	44
2,4,5	2,4	3	35	38
	2,5	97	49	28
	3,4	0	16	34
2,4,6	2	16		
	4	8		
	2,4	0	63	38
	2,6	4	37	62

Table 9. (Continued)

Chlorobiphenyl	Reduction Product	Product Distribution (%) Experimental (Farwell)[1]	LUMO-σ	LUMO-π
3,4,5	3,4	0	63	38
	3,5	100	37	62
2,3,4,5	2,5	15		
	3,5	49		
	2,3,4	0	19	41
	2,3,5	36	34	20
	2,4,5		32	3
	3,4,5	0	15	36
2,3,4,6	2,5	64		
	2,3,4	0	11	34
	2,3,6	23	29	19
	2,4,5	0	32	5
	2,4,6	13	28	42
2,3,5,6	2,5	27		
	3,5	58		
	2,3,5	1	44	49
	2,3,6	14	56	51
2,3,4,5,6	2,3,4,5	5	27	49
	2,3,4,6	37	43	51
	2,3,5,6	58	30	0

theoretical results.

There are a number of cases when the results coincide. Using the LUMO-σ electron density the relative ordering of the product distribution for 2,4- and 2,5-dichloro- and 2,4,5-trichlorobiphenyls is correct. The relative ordering of the products predicted by the LUMO-σ is also correct for 2,3,4-trichlorobiphenyl. However, there is quite a large proportion of monochlorobiphenyls formed experimentally. The question that must be asked is whether a small amount of 3,4-dichlorobiphenyl was formed which was immediately reduced to 3-chlorobiphenyl. This could explain this disparity between the experimental and theoretical values for the amount of the 2,3- and 3,4-isomers formed. By the same token the amount of 2-chlorobiphenyl formed would have to cause an increase in the amounts of 2,3- and/or 2,4-dichlorobiphenyls formed.

The LUMO-σ product distribution for the reduction of 2,3,6-trichlorobiphenyl is also correct, but this may be fortuitous since very little of either of the two dichlorobiphenyls was found. The large amount of 3-chlorobiphenyl found would have to increase the relative proportion of the 2,3- and/or 2,5-dichloro- isomers, which could significantly change the experimental results. The calculated value for 2,3,4,5-tetrachlorobiphenyl is also satisfactory considering that Farwell[1] could not establish the relative amounts of 2,3,5- and 2,4,5-trichlorobiphenyl. The large amount of 3,5-dichlorobiphenyl found

would cause an increase of either 2,3,5- and/or 3,4,5-trichlorobiphenyls, since this is almost the exclusive pathway for both of these isomers. The calculation also tends to coincide with the experimental pathway for 2,3,4,6-tetrachlorobiphenyl, if the amount of 2,5-dichlorobiphenyl formed is taken into consideration. This dichloro- isomer is almost the exclusive product of 2,4,5-trichlorobiphenyl so it is conceivable that any of the latter compound formed is immediately reduced. This would then give the correct pathway prediction, even if a minor portion of the 2,5- isomer came from 2,3,6-trichlorobiphenyl. The same type of argument can be invoked for the reduction pathway for 2,3,5,6-tetrachlorobiphenyl. Thus 3,5-dichlorobiphenyl is almost the exclusive route for 2,3,5-trichlorobiphenyl. This would give a total of 59% 2,3,5-trichlorobiphenyl, the remainder being the 2,3,6-trichloro- isomer which compares quite favorably with the calculated results.

There are six chlorobiphenyls with which the calculation does not predict the correct reduction scheme. These are 2,3- and 3,4-dichloro-, 2,3,5-, 2,4,6- and 3,4,5-trichloro- and 2,3,4,5,6-pentachlorobiphenyls. We can group these into two classes. All except 3,4-dichloro- and 3,4,5-trichlorobiphenyl have ortho chlorines. The method fails for these because the electron density in the ortho chlorine in the LUMO-σ is not sufficiently great. 3,4-dichloro- and 3,4,5-trichloro- do not have a high enough electron density distribution in the para chlorines or conversely have too high a value in the

meta chlorines. Both of these effects might be due to a non-bonding interaction between the ortho substituents on one ring with the ortho substituents on another. This interaction could cause a depopulation of electron density in this region, the net result being a net increase in the meta positions.

Let us turn our attention to the pathways predicted by the electron density distribution in the LUMO-π (Table 9). This scheme correctly predicts the product ordering from the reduction of 2,3-, 2,5- and 3,4-di-, 2,4,6- and 3,4,5-trichlorobiphenyls within Farwell's[1] experimental accuracy. The products from 2,4-di- and 2,3,5,6-tetrachlorobiphenyls are also correctly predicted. The wrong pathways are indicated for 2,3,5- and 2,4,5-tri-, 2,3,4,6- and 2,3,4,5-tetra- and 2,3,4,5,6-pentachlorobiphenyls. This is because the electron density is too high on the meta chlorines. In 2,3,4-trichlorobiphenyl the distribution is too great on the para chlorine which again causes the wrong products to be predicted. Thus using the LUMO-π does not seem to be any better and in fact may be worse than the LUMO-σ for predicting the reduction pathways for the chlorobiphenyl series. Since this is the case, we must rely solely on the results of the open shell calculations on the radical anions to state that the electron enters the LUMO-σ as opposed to the LUMO-π.

Molecular Orbital Investigation of Electrochemical Carbon-Halogen Reduction: DDT

DDT is the first system that we have looked at that contains aliphatic chlorines. Moreover, since the molecule also contains aryl chlorines, this should provide a nice test for quantum theory concerning the reductive pathways.

The electrochemical reductive pathways for the DDT series have been worked out by Rosenthal and Lacoste[30,31] (based on electrolysis) and by Farwell[1] (based on voltammetry). The reduction scheme has been previously shown (see page 13). Rosenthal and Lacoste did not observe the formation of 1,1-diphenylethane. This, however, is not surprising, for they were using an aqueous solvent system. Only in aprotic solvents has it been possible to reduce electrochemically monochlorophenyl compounds. It is reasonable that 1,1-diphenylethane is the final reduction product since the reduction potential for 1,1-bis(p-chlorophenyl)ethane is -2.375 V which is quite similar to the -2.440 V observed for the reduction of chlorobenzene.[1]

The LUMO obtained from the CNDO/2 calculations on DDT is a σ antibonding with the greatest extent (98%) of the electron density localized in the region of the trichloromethyl moiety. (See Figure 27). Using the electron distribution method this implies that a methyl chlorine, as opposed to one of the phenyl chlorines, would be preferentially cleaved to form DDD, the same

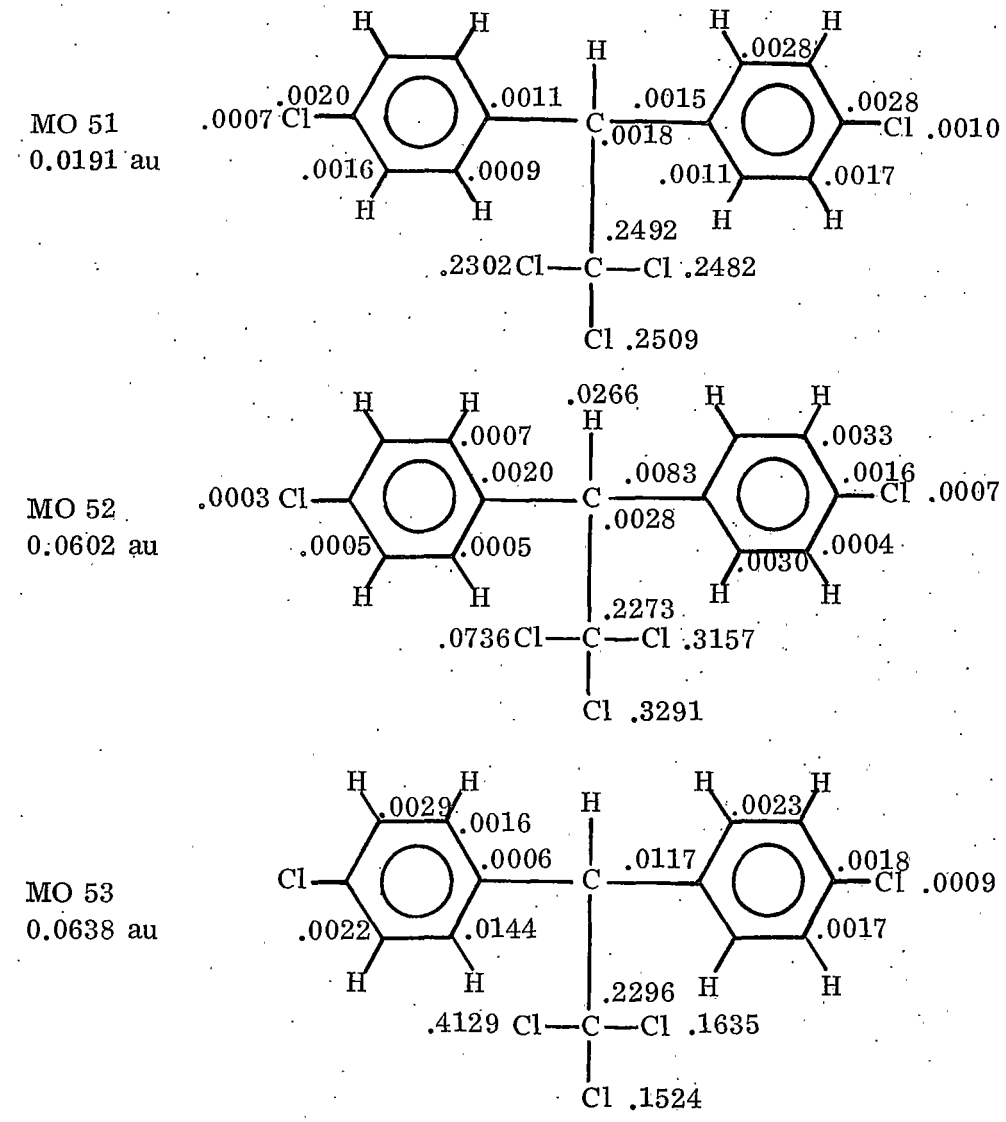


Figure 27. Electron Density Distribution in Low Lying Unoccupied σ Anti-Bonding Orbitals for DDT Obtained from CNDO/2 Calculations