



Determination of the relative steric sizes of alkyl groups using a calculational approach
by Ann Marie Bowler

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in
Chemistry

Montana State University

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Abstract:

Allopolar isomerism in merocyanine dye models was studied using molecular mechanics, semi-empirical, and *ab initio* techniques. The relative steric sizes of alkyl groups were determined by comparing the energy differences between meropolar and holopolar conformations of a model system. The results indicate that methyl, ethyl, and propyl groups have approximately the same amount of steric bulk when they are in a 1,3 sandwiched configuration and, also, that an isopropyl group has significantly more steric bulk than the straight chain alkyl groups.

MNDO calculations also showed a significant amount of charge separation in the holopolar isomers of the model system. Because these results agree with experimental data and with predictions made on the basis of resonance theory, it is suggested that MNDO calculations may provide a useful means for predicting the charge distribution in other delocalized systems.

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MONTANA STATE UNIVERSITY
Bozeman, Montana

November 1986

N378
B681
Cap. 2

APPROVAL

of a thesis submitted by

Ann Marie Bowler

This thesis has been read by each member of the thesis committee and has been found to be satisfactory regarding content, English usage, format, citations, bibliographic style, and consistency, and is ready for submission to the College of Graduate Studies.

November 3 1986
Date

Arnold C. Craig
Chairperson, Graduate Committee

Approved for the Major Department

Nov 3, 1986
Date

Edwin H. Abbott
Head, Major Department

Approved for the College of Graduate Studies

November 20, 1986
Date

Henry L. Parsons
Graduate Dean

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ABSTRACT

Allopolar isomerism in merocyanine dye models was studied using molecular mechanics, semi-empirical, and ab initio techniques. The relative steric sizes of alkyl groups were determined by comparing the energy differences between meropolar and holopolar conformations of a model system. The results indicate that methyl, ethyl, and propyl groups have approximately the same amount of steric bulk when they are in a 1,3 sandwiched configuration and, also, that an isopropyl group has significantly more steric bulk than the straight chain alkyl groups.

MNDO calculations also showed a significant amount of charge separation in the holopolar isomers of the model system. Because these results agree with experimental data and with predictions made on the basis of resonance theory, it is suggested that MNDO calculations may provide a useful means for predicting the charge distribution in other delocalized systems.

INTRODUCTION

Since their discovery in the 1930's, members of the subclass of cyanine dyes known as merocyanines have found wide use as photographic sensitizers and as intermediates for the synthesis of larger dyes. (See Reference 1.) Merocyanines, which are derived from an acidic heterocyclic nucleus and a basic heterocyclic nucleus, contain the primary chromophore shown in Figure 1. The merocyanines are best represented as a hybrid of two resonance forms. One of these resonance species, (1a), is neutral; and the other, (1b), has permanent charge separation brought about by conjugation of the two nuclei through a methine linkage.

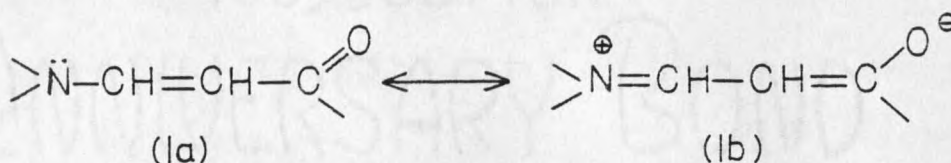


Figure 1. Chromophoric System of a Dipolar Amidic Merocyanine System.

Allopolar cyanine dyes are composed of three heterocyclic nuclei. Two of the nuclei contain heteroatoms that can act as electron donors, or bases; and the third contains a heteroatom that can act as an electron acceptor, or acid. Because each of the nuclei can exist in two distinct valence states, the cyanines are also best described as resonance hybrids.

Some of the cyanines have been the subject of considerable investigation because they have been found to exist in two distinct conformations. The trinuclear dye (2) is sterically crowded; and it is impossible for all three nuclei to be simultaneously coplanar. However, if two nuclei remain coplanar and the third resides in a plane perpendicular to the other two, resonance stabilization is partially preserved; and steric crowding is significantly reduced. This situation gives rise to two possible conformations.

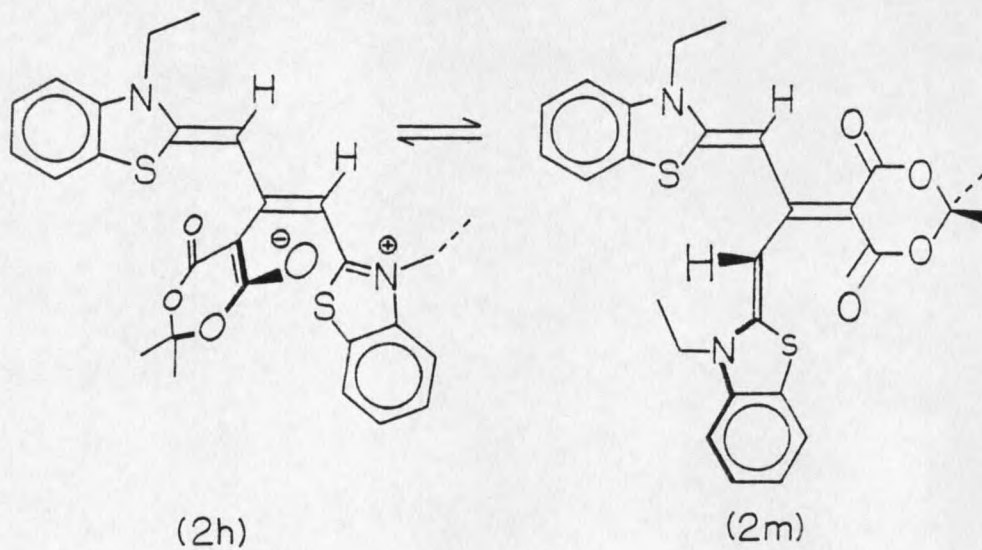
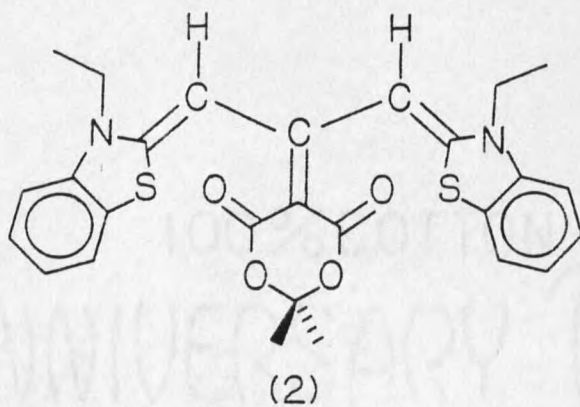


Figure 2. Conformational Equilibrium of a Trinuclear Cyanine Dye.

The so-called holopolar isomer, (2h), has permanent charge separation; and, although it is polar, the meropolar isomer, (2m), exists as an uncharged species. Since the system is resonance stabilized, interconversion between the two isomers requires rotation around three bonds having total bond orders between 1.0 and 2.0. It has been demonstrated that the equilibrium in Figure 2 is highly solvent sensitive, with the holopolar isomer predominating in polar solvents. (See Reference 2.) The term allopolarm isomerism is used to describe solvent-sensitive, ground state conformational equilibria such as this.

Interest in the present investigation stems from the discovery that the methyl substituted merocyanine, (3m), exhibits what appears to be allopolarm isomerism. As solvent polarity is increased, the typical merocyanine absorption at about 460 nm becomes less intense; and absorptions in the ultraviolet region, which are presumably due to the propenylbenzothiazolium salts and diketodioxane anion, increase. An equilibrium such as the one shown in Figure 3 would be consistent with this observation and would represent the first reported incidence of allopolarm isomerism in a simple merocyanine dye.

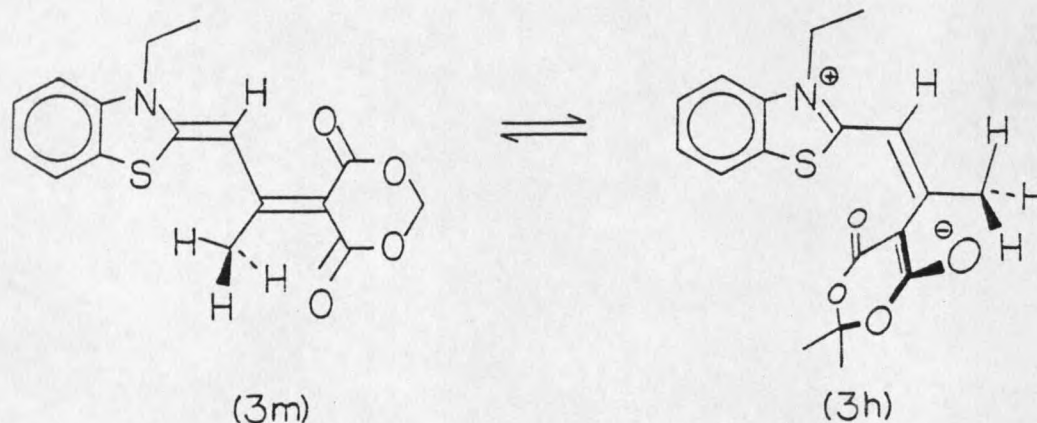


Figure 3. Conformational Equilibrium of a Merocyanine Dye.

Substituents that increase the steric hindrance of a dye can alter several of its properties including absorption wavelength, photographic sensitization, and crystallization and aggregation patterns. Therefore, the effects of steric crowding on dye properties have been of considerable historical importance. Deviations from planarity induced by steric crowding in pyrrole dyes were demonstrated spectrophotometrically as early as 1947. (See Reference 3.) More recently, x-ray crystallographic studies of highly overcrowded cyanines have shown angles of as much as 60 degrees between the planes defined by heterocyclic rings. (See Reference 4.) It is anticipated that the equilibrium between (3h) and (3m) will not only be solvent sensitive but also highly "bulk" sensitive.

As the R group in (4m) is changed from hydrogen to methyl to ethyl to propyl, and finally, to isopropyl, the equilibrium should systematically shift toward the holopolar isomer, (4h). Because the 1,3 sandwiched configuration of (4m) doesn't allow steric crowding to be reduced by rotation of the alkyl groups, the position of the equilibrium should provide a measure of the relative steric sizes of these groups.

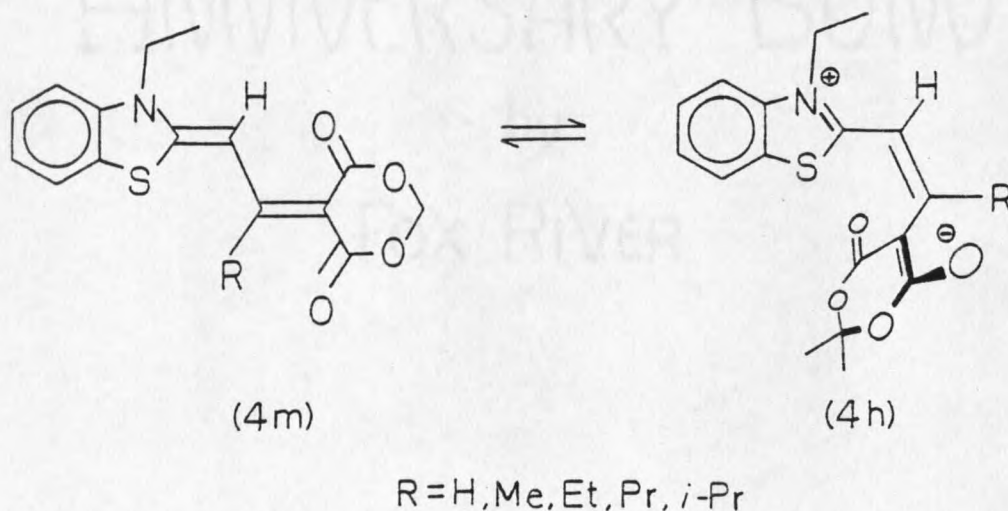


Figure 4. Conformational Equilibria of Sterically Crowded Merocyanines.

The recent "birth" of theoretical calculations as powerful tools in structural chemistry seems to lend itself to this situation. Darden, et. al., were able to successfully calculate the minimum energy conformations of highly conjugated diethylstilbestrol isomers using molecular mechanics, semi-empirical, and ab initio techniques. (See Reference 5.) Because the basic structure of the merocyanines is similar to these compounds, it was thought that the effect of steric crowding on the equilibrium between (4m) and (4h) could be studied using a calculational approach.

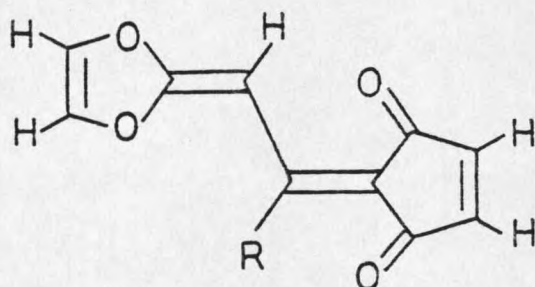
The primary purposes of this investigation were: (1) to determine the level of sophistication at which calculations could be performed on model dye systems; (2) to test the ability of computational methods to mimic experimental observations; and (3) to determine the relative steric sizes of alkyl groups by calculating the energies of the meropolar and holopolar conformations of merocyanine models.

METHODS AND RESULTS

Molecular mechanics, semi-empirical, and ab initio methods were employed in the present study. These methods are discussed in detail in Reference 6. Semi-empirical calculations were done primarily at the MNDO level; and the ab initio methods were mainly confined to single point, closed shell, restricted Hartree-Fock calculations on small model systems. All calculations were performed using a DIGITAL VAX/11 780 system with the Molecular Mechanics 2, Molecular Orbital Package, and Gaussian 80 programs made available through the Quantum Chemistry Program Exchange. Some additional information about using the Molecular Mechanics 2 and Gaussian 80 programs is provided in the Appendices.

Initial attempts to study the merocyanine dye skeleton shown in Figure 5 using the Molecular Mechanics 2 program were, for the most part, unsuccessful because the program is not parameterized to treat conjugated pi systems. The program gave "realistic" results for compound (5a); but when R was changed to methyl and then ethyl, it produced minimum energy conformations that were "bent" in the plane, rather than twisted out of the plane. This result should have been anticipated because the torsional energy terms that the

program uses for bonds between SP^2 atoms are set at arbitrarily large values; and, therefore, rotation around double bonds is forbidden.



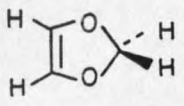
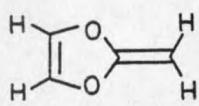
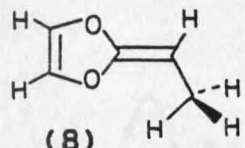
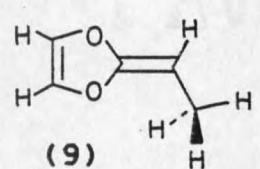
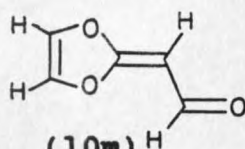
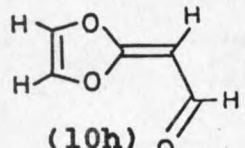
- (5a) R=H
- (5b) R=Me
- (5c) R=Et

Figure 5. Merocyanine Dye Skeleton Studied Using MM2.

Attempts were made to modify the MM2 program; however, these were also futile. Several of the torsional and bending constants in the program data base were changed; and some of the atom types in (5b) were varied to allow more free rotation in the pi system. This valiant effort came to an abrupt halt when distortions were introduced in the rings and a tendency toward tetrahedral geometries around SP^2 carbon atoms was observed.

Ab initio molecular orbital calculations were employed in the next phase of the investigation. In order to determine whether a large enough system could be studied at this advanced level, the Gaussian 80 program was used to calculate the energies of the molecules in Table I. These single point calculations were done using an STO-3G basis set with coordinates that were generated by MM2. Not surprisingly, the model compounds (10m) and (10h) had the largest skeleton that could be studied within our time and financial constraints. It did, however, seem that this model system contained the necessary functional framework to study the problem of steric crowding. More specifically, the conjugated pi system of (4) was adequately represented; and it was thought that the carbonyl oxygen would supply enough bulk to mimic the diketocyclopentene ring in (4).

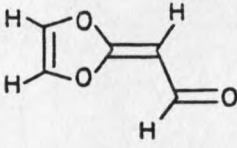
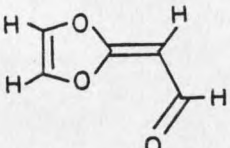
Table I. Gaussian 80 Test Results.

STRUCTURAL FORMULA	TOTAL ENERGY (HARTREES)	COMPUTATION TIME (MIN)
 (6)	-262.17492	8.5
 (7)	-299.55830	14.3
 (8)	-338.14528	28.6
 (9)	-338.14348	32.2
 (10m)	-410.77974	21.1
 (10h)	-410.77890	22.7

To say that the three methods are in disagreement might be to make an understatement. Not only are the absolute energies of the isomeric pair substantially different in each case; but the relative energies of the two isomers are also the subject of some debate. MNDO and MINDO/3 both predict that the holopolar species is more stable; however, the energy differences that these methods predict between the two isomers are not in sparkling agreement. The reputedly more sophisticated AM1 hamiltonian, on the other hand, predicts that the meropolar isomer is more stable than the holopolar one by about 1 kcal.

Meanwhile, at the ab initio level, the meropolar isomer, (10m), was predicted to be more stable by 0.5 kcal when coordinates generated by MM2 were used, as shown in Table III. (MM2 predicted a difference of 0.6 kcal between the two isomers.) When coordinates from MNDO became available, the ab initio calculation was repeated; and the meropolar isomer was predicted to be more stable by about 1 kcal. The fact that this result was in total disagreement with the result from MNDO caused some skepticism. It may be that there is such a small energy difference between the two isomers that it can't accurately be predicted within the error limits of the MNDO and MINDO/3 methods.

Table III. Gaussian 80 Results for Hydrogen Substituted Dioxole Models.

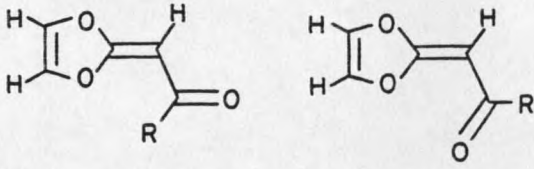
			
	(10m)	(10h)	
BASIS SET	TOTAL ENERGY (HARTREES)	TOTAL ENERGY (HARTREES)	ΔE (KCAL)
STO-3G (MM2 COORDINATES)	-410.77974	-410.77890	0.527
STO-3G (MNDO COORDINATES)	-410.79924	-410.79773	0.948
4-31G (MM2 COORDINATES)	-415.53134	-415.52542	3.715

Ab initio calculations were also performed on (10m) and (10h) using an extended, 4-31G basis set with coordinates from MM2; and the meropolar isomer was predicted to be more stable by 3.7 kcal. The absolute energies predicted at the 4-31G level are substantially different than those predicted at the STO-3G level; and the calculated energy difference between the two isomers is four times as large. This result seems to reinforce the results of the STO-3G and AM1 calculations and to further discredit the results from MNDO and MINDO/3; but the fact that MM2 coordinates were used here may make the comparison invalid. It should also be noted that the differences in the energies of the two

isomers that were predicted with both the STO-3G and the 4-31G basis set appeared near or beyond the level of significance of the coordinates. Consequently, these results may be misleading. Because the 4-31G calculations took over 3 hours each, no further comparisons were made using this extended basis set.

The meropolar, (11m), and holopolar, (11h), dioxole analogs of the methyl substituted merocyanine, (4), were also studied using ab initio and MNDO methods. Table IV compares some of these results with those for the hydrogen isomers. Initially, the MNDO calculations were performed with all of the torsional angles in the molecule fixed; so the pi system was confined to planarity. Calculations were also performed with the methyl group in both a staggered (11m and 11h) and an eclipsed (12m and 12h) conformation with respect to the carbonyl oxygen. The staggered conformations had lower energies. As was the case with the hydrogen substituted isomers, the holopolar methyl isomer, (11h), was predicted to be more stable by MNDO; but, in this case, the energy difference between the two isomers was slightly larger. This result was cautiously interpreted to mean that some steric crowding had been introduced into the system.

Table IV. MNDO and Gaussian 80 Results for Hydrogen and Methyl Substituted Dioxole Isomers.

R	METHOD			ΔE (KCAL)
		(m) ISOMER TOTAL ENERGY	(h) ISOMER TOTAL ENERGY	
H (10)	MNDO	-1660.8131 eV	-1660.8283 eV	-0.351
H (10)	G-80	-410.7992 H	-410.7977 H	0.948
ME (STAGGERED) (11)	MNDO	-1817.1465 eV	-1817.3257 eV	-4.132
ME (STAGGERED) (11)	G-80	-449.3796 H	-449.3831 H	-2.188
ME (ECLIPSED) (12)	MNDO	-1811.4457 eV	-1811.4506 eV	-0.113

In order to further test this hypothesis, attempts were made to optimize the C-C-C-O torsional angles in both isomers as shown in Figure 6 to determine whether a nonplanar conformation would be more stable. No such minimum could be detected within this constraint; so a more frightening series of optimizations was undertaken in which

rotation was allowed around various combinations of torsional angles. The results of these efforts were amusing at best. The program either did not move the molecules at all; or it distorted them into configurations in which sp^2 carbon atoms had "tetrahedral" geometries. The result of one such attempted optimization is shown in Figure 7. Similar failures to estimate the stabilizing effect of conjugation have been observed with other semi-empirical methods. (See Reference 8.) No suitable combination of constraints could be found to produce a realistic optimized geometry even though slightly nonplanar conformations had lower calculated energies than the planar ones.

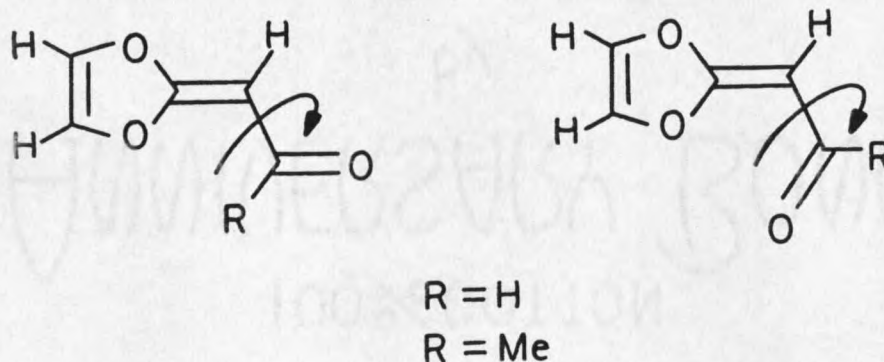


Figure 6. Torsional Angle Marked for Optimization by MNDO.

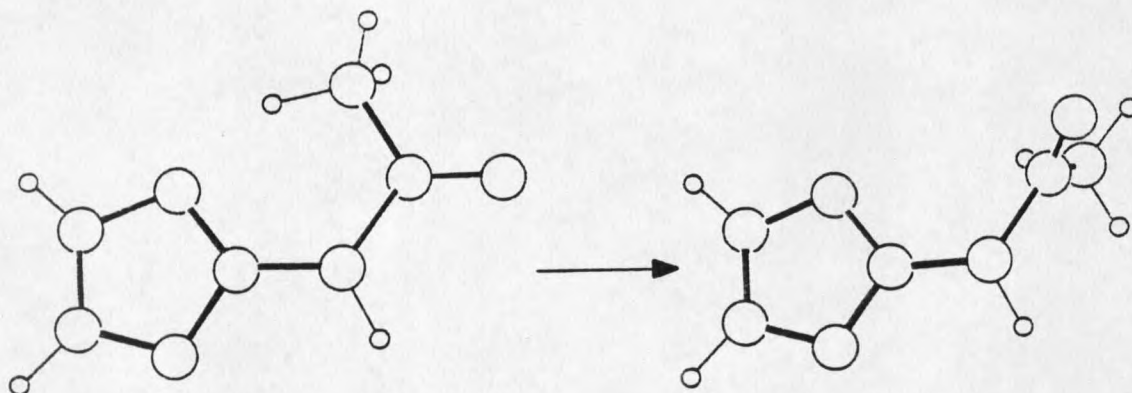


Figure 7. Conformation of (11m) Before and After MNDO Torsional Angle Optimization.

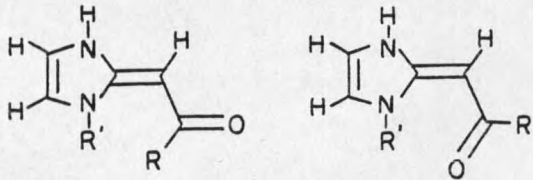
Ab initio calculations were performed on (11m) and (11h) with partially optimized (planar pi system) coordinates from MNDO. The energies were calculated with the methyl group staggered relative to the carbonyl oxygen because MNDO predicted that this was the more stable conformation. These results, which are also listed in Table IV, are in fairly good agreement with those from MNDO in the respect that both methods predict that (11h) is more stable. Although the relative energy differences that the two methods predict are still considerably different, the fact that the differences are larger than they were for the hydrogen isomers (and that the two methods agree) instills some confidence that the results are correct.

Three attempts to locate an out-of-plane minimum were made at the ab initio level. First, the C-C-C-O torsional angle of the less stable hydrogen isomer, (10h), was allowed to move in the manner illustrated in Figure 6. The planar conformation was predicted to be the minimum energy conformation in this case. The same torsional angle was optimized in the two methyl isomers; and the planar conformation of the holopolar isomer was again preferred. No minimum could be detected by the program for the meropolar isomer even though a lower energy was calculated for a conformation with the methyl and carbonyl groups 10 degrees out of the plane. It seems that the ab initio method is quite sensitive to the steric crowding introduced by the methyl group in (11m); but there is apparently such a shallow potential energy well for the nonplanar conformational minimum for this model that the program can't detect it.

Even though the results of the calculations performed on models (10)-(12) were somewhat inconclusive, it was felt that additional calculations on models that more closely resembled (4) would provide more enlightenment. One attempt to find a more suitable model focused on a series of nitrogen analogs of (10). The results of the MNDO and ab initio calculations that were performed on this series of compounds are presented in Table V. Because insurmountable problems were encountered when the torsional angles in (11)

were optimized using MNDO, all of these calculations were performed within the constraint that the molecules remained planar. Presumably, this constraint would have the same effect on both the holopolar and meropolar isomers; and, therefore, the relative energies of the two would not be substantially affected.

Table V. MNDO and Gaussian 80 Results for Diazoline Models.

R	R'	METHOD			ΔE (KCAL)
			(m) ISOMER TOTAL ENERGY	(h) ISOMER TOTAL ENERGY	
H (13)	H	G-80	-371.7449 H	-371.7491 H	-2.628
H (13)	H	MNDO	-1459.5278 eV	-1459.6581 eV	-3.004
H (14)	D	MNDO	-1459.5125 eV	-1459.6413 eV	-2.969
ME (15)	H	MNDO	-1615.5189 eV	-1616.1284 eV	-14.053
H (16)	ME	MNDO	-1611.0997 eV	-1611.0024 eV	2.245

It should also be noted that while the results obtained using the AM1 hamiltonian were in better agreement with the ab initio and molecular mechanics results for model system (10), the computation time that the method requires and the fact that no sulfur parameters are available for AM1 at this time discouraged its use in subsequent calculations. It was, however, thought that because the MNDO results were consistent with ab initio results in the case of (11), this method would produce reliable results for a more "realistic" model system.

Contrary to predictions for (10), the holopolar isomer of compound (13) was predicted to be more stable than the meropolar isomer, (13m), by both MNDO and Gaussian 80. This somewhat surprising result might be explained on the basis of a hydrogen bonding argument. An intermolecular hydrogen bond such as the one illustrated in Figure 8 would, theoretically, be quite favorable because it involves the formation of a six membered ring.

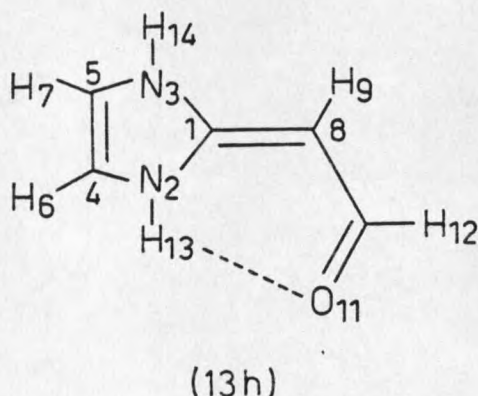
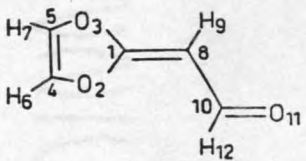
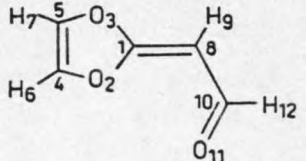
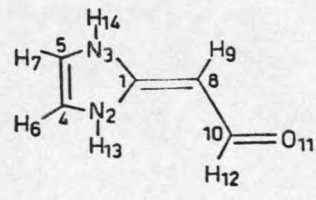
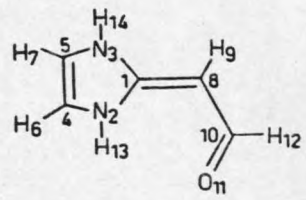


Figure 8. Proposed Hydrogen Bonding Effect in (13h).

The calculation was repeated with both of the nitrogen protons replaced by deuterium in an effort to reduce any hydrogen bonding effects; and a slightly smaller energy difference between the two isomers was predicted. A larger effect on the energy of the holopolar isomer was observed, as would be expected if hydrogen bonding was occurring. Because the calculated effect of deuterium substitution was small in both isomers, an effort was made to gather additional evidence to support this argument.

Although the differences in the calculated atomic charges for the holopolar isomer, (13h), and those for the meropolar isomer, (13m), are small, a comparison of the relative atomic charges in the two makes a "resonance" argument too enticing to overlook. For instance, (13h) might be considered as a resonance hybrid of the structures illustrated in Figure 9. The total atomic charges from Gaussian 80 for the dioxole and diazoline isomeric pairs are shown in Table VI. The fact that the holopolar nitrogen isomer is much more polar than its oxygen analog and that the largest differences occur for the atoms that would constitute the six membered hydrogen bonded ring further indicates that a hydrogen bonding effect is being observed. In addition, the ab initio calculation predicts that there is an overall bonding interaction between the oxygen and hydrogen in (13h).

Table VI. Net Atomic Charges for Dioxole and Diazoline Models.

											
ATOM	CHARGE	CHARGE	ATOM	CHARGE	CHARGE	ATOM	CHARGE	CHARGE			
1	0.275625	0.284294	1	0.262615	0.270254	1	0.262615	0.270254			
2	-0.221551	-0.210816	2	-0.341742	-0.337566	2	-0.341742	-0.337566			
3	-0.218851	-0.219531	3	-0.339519	-0.338973	3	-0.339519	-0.338973			
4	0.035805	0.038170	4	0.023194	0.024545	4	0.023194	0.024545			
5	0.036800	0.034984	5	0.024176	0.022111	5	0.024176	0.022111			
6	0.107877	0.109165	6	0.087526	0.088271	6	0.087526	0.088271			
7	0.108117	0.107452	7	0.087902	0.087002	7	0.087902	0.087002			
8	-0.152523	-0.157185	8	-0.194264	-0.199334	8	-0.194264	-0.199334			
9	0.076073	0.066398	9	0.044990	0.034326	9	0.044990	0.034326			
10	0.135842	0.135765	10	0.131093	0.127300	10	0.131093	0.127300			
11	-0.228435	-0.230184	11	-0.258383	-0.281935	11	-0.258383	-0.281935			
12	0.045221	0.041490	12	0.012687	0.029066	12	0.012687	0.029066			
			13	0.230134	0.246099	13	0.230134	0.246099			
			14	0.229592	0.228833	14	0.229592	0.228833			

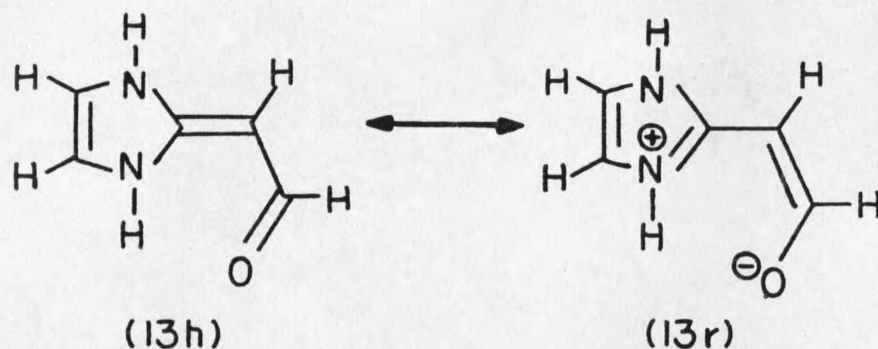


Figure 9. Proposed Resonance Structures for (13h).

The energy of a "polar" version of (13h) was obtained by averaging bond lengths in the delocalized portion of the molecule shown in Figure 9 and optimizing the bond angles involved. This structure was higher in energy than the neutral species by about 14 kcal. The fact that the energy of the polar structure is not substantially higher (considering the assumptions of the method and the magnitude of the energy differences between other neutral isomeric pairs) than that of the neutral species further indicates that a hydrogen bonding/resonance argument is not totally unreasonable. A structure such as (13r) would certainly make some contribution to the stability of the system.

An additional effort was made to study the hydrogen substituted isomers in the absence of hydrogen bonding effects by replacing the proton on N-2 with a methyl group.

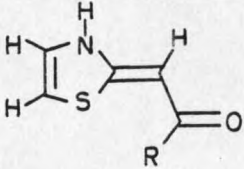
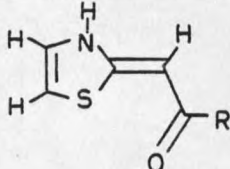
The meropolar N-methyl isomer, (16m), as one might have expected, was predicted to be slightly more stable than (16h) due to the bulk of the methyl group. As in all previous cases, the holopolar methyl substituted isomer of the diazoline system, (15h), was more stable than the meropolar isomer due to steric effects.

The thiazoline systems, (17) and (18), which even more closely resemble (4), were also studied. The results of MNDO calculations on these compounds are shown in Table VII. Unlike the MNDO result for the dioxole system (10), the hydrogen substituted meropolar isomer, (17m), has a lower calculated energy than the holopolar isomer, (17h); but the energy difference between the two isomers is quite small. One would expect that replacing oxygen by sulfur would increase the steric bulk of the ring; and any advantage gained by having the carbonyl oxygen near the ring would be reduced. The sulfur d-orbitals may also cause electronic repulsion which further contributes to the instability of the h-isomer. Therefore, while it appears that the method fails to correctly predict the more stable isomer in the dioxole model, it is able to do so when a slightly larger energy difference is involved, as it is in this case.

Once again, the holopolar methyl isomer of the thiazoline model, (18h), was predicted to be more stable than the meropolar isomer. The fact that the energy

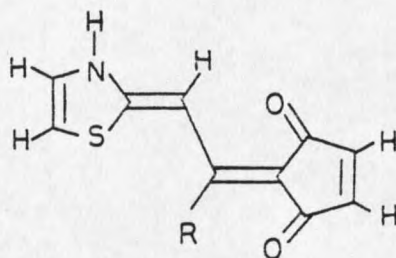
difference between the meropolar and holopolar isomers of the methyl substituted thiazoline models decreases when oxygen is replaced by sulfur further supports the conjectures presented in the previous paragraph.

Table VII. MNDO Results for Thiazoline Models.

	 (m) ISOMER	 (h) ISOMER	
R	TOTAL ENERGY (eV)	TOTAL ENERGY (eV)	ΔE (KCAL)
H (17)	-1476.4003	-1476.3854	0.344
ME (18)	-1632.7200	-1632.8768	-3.614

The cumulative results of the MNDO calculations on the three heterocyclic model systems seem to be realistic and in fairly good agreement with ab initio results. In addition, the calculational results for the thiazoline system generally agree with experimental data. The hydrogen substituted isomer, (2h), is approximately 2 kcals higher in energy than (2m); and, the difference predicted by MNDO for (17) is in the same ballpark. For this reason, it was felt that MNDO calculations on extended model systems were feasible.

The merocyanine dye skeleton shown in Figure 10 was extensively studied using MNDO methods. As mentioned previously, inherent faults in the method prevented torsional angle optimizations; so the calculations were performed with the rings and "pi" system constrained to reside in appropriate planes. Again, it was felt that this constraint was a reasonable one because our interest was focused on relative, rather than absolute, energies. The quest for nonplanar minima was abandoned and attention was directed at calculating energy differences between the meropolar and holopolar forms of the extended models.



- (19) R=H
- (20) R=Me
- (21) R=Et
- (22) R=Pr
- (23) R=i-Pr

Figure 10. Dye Skeleton Studied Using MNDO.

In each case, all bond lengths and angles were optimized; but in several instances, the criteria for minimization were not rigidly satisfied. The computation time required for these molecules was not unreasonable

considering their size. The energies of the five isomeric pairs that were studied are summarized in Table VIII; and some computational statistics are presented in Table IX.

Table VIII. MNDO Results for Alkyl Substituted Dye Skeleton.

R	(m) ISOMER TOTAL ENERGY (eV)	(h) ISOMER TOTAL ENERGY (eV)	ΔE (KCAL)
H (19)	-2464.54609	-2462.99835	35.692
ME (20)	-2620.50887	-2619.48671	23.571
ET (21)	-2776.85527	-2775.83883	23.440
PR (22)	-2933.27805	-2932.25681	23.550
i-PR (23)	-2932.60852	-2932.11202	11.450

Table IX. Computational Statistics for Alkyl Substituted Dye Skeleton.

R	MEROPOLAR ISOMER			HOLOPOLAR ISOMER		
	COMPUTATION TIME (HR)	SCF CALCULATIONS	GRADIENT TEST PASSED ?	COMPUTATION TIME (HR)	SCF CALCULATIONS	GRADIENT TEST PASSED ?
H	0.722	83	YES	0.799	87	YES
ME	1.611	67	NO	0.994	38	YES
ET	2.231	45	YES	1.470	38	NO
PR	3.523	28	NO	2.164	25	NO
i-PR	0.948	7	YES	2.924	7	YES

The geometry of the meropolar hydrogen substituted isomer, (19m), was optimized; and the minimum energy conformation that is shown in Figure 11 was produced. The bond lengths in the final conformation are characteristic of a relatively nonconjugated pi system. This result is in agreement with crystal data for similar dye structures. (See Reference 4.)

The energy of the holopolar form of (19) was calculated by restricting torsional angles; so the diketocyclopentene ring was in a plane perpendicular to that of the thiazoline ring. The bond lengths and angles were then optimized and the geometry illustrated in Figure 12 was produced. The holopolar conformation was predicted to be about 36 kcals higher in energy than the meropolar conformation, (19m).

Although the relative energy difference between these two isomers is apparently too large, the calculated geometries of the two isomers seem to parallel what has been observed experimentally for (3). More specifically, the bond lengths in (19h) are far more characteristic of a conjugated pi system, or polar resonance species, than they are predicted to be in (19m). The net atomic charges for the two isomers, which are compared in Figure 13, also demonstrate that (19h) is a much more polar species than (19m).

In order to satisfy a personal curiosity, the energy of a conformation that would certainly represent an energy maximum for (19) was calculated using the final coordinates from (19m). As Figure 14 illustrates, the diketocyclopentene ring and the thiazoline ring are severely crowded when they are forced into coplanarity, as they are in (19h'); and, not at all surprisingly, this conformation is substantially higher (200 kcals) in energy than (19m).

The procedures outlined above were also undertaken with the methyl substituted isomers, (20m) and (20h); and, as Figures 15 thru 17 illustrate, the data for the two isomers is again consistent with what would be expected on the basis of resonance theory. The calculated energy difference between the two isomers is only 23 kcals in this instance. Therefore, one might conclude that steric crowding introduced by the methyl group significantly increases the energy of the meropolar isomer. The distortion of the bond angles in the meropolar isomer, which is probably magnified by the planarity restriction, also illustrates the crowding effect of the methyl group. The fact that a significant amount of time was required to find a minimum energy conformation for (20m) and that the minimization criteria were not completely satisfied also indicates that steric crowding is significant.

The energy of the ethyl substituted compound, (21m), was calculated with the ethyl group in a staggered conformation that projected above the plane of the heterocyclic rings. Placement of the ethyl group was based on a molecular model which indicated that this conformation would afford the least overlap of van der Waals radii in the molecule and, thus, would represent the least sterically hindered conformation. The final geometry calculated for this conformation is shown in Figure 18.

When the energy of the holopolar ethyl isomer, (21h), was calculated, the ethyl group was oriented in a staggered conformation with both carbon atoms in the plane of the thiazoline ring. The final geometry of (21h) is shown in Figure 19; and the net atomic charges for the isomeric pair are shown in Figure 20. The calculation for the h-isomer was repeated with the ethyl group in two other conformations. In the first of these, the terminal carbon was fixed at 90 degrees above the plane of the thiazoline ring. In the second, the terminal carbon was in the plane of the thiazoline ring; but it was nearer to the diketocyclopentene ring. Both of these conformations had higher energies than the one shown in Figure 19.

As in the previous two instances, the holopolar ethyl isomer is completely conjugated and quite polar. The energy difference between the ethyl isomers is also 23 kcals. This

result implies that addition of another carbon atom does not significantly increase steric hindrance in the meropolar isomer. In fact, this result can easily be rationalized using molecular models. The terminal carbon of the ethyl group is well above the plane of the pi system; and it projects away from the dye skeleton. Therefore, it should produce only slightly more steric bulk than a hydrogen atom. In addition, the rotational freedom that the ethyl group has in the holopolar isomer contributes to its stability and further closes the energy gap between the two isomers.

The energy of the propyl substituted meropolar isomer, (22m), shown in Figure 21, was also calculated with the propyl group in a staggered conformation that projected above the plane of the pi system. The energy of the holopolar isomer was calculated with the propyl group in two different conformations. In one of these, all three carbon atoms of the propyl group were in the plane of the thiazoline ring. This conformation was 0.3 kcals higher in energy than the conformation illustrated in Figure 22 in which the propyl group is 90 degrees out of the plane of the thiazoline ring. The net atomic charges of the holopolar and meropolar propyl isomers are presented in Figure 23. The energy difference between (22m) and (22h) is 23 kcals; and it appears that, as in the previous case, the propyl group does not significantly increase steric crowding in the meropolar isomer. However, the fact that an out-of-plane

conformation is preferred in the holopolar isomer indicates, once again, that some crowding is being relieved through rotation of the alkyl group.

The energy of the highly crowded isopropyl substituted isomer, (23m), was calculated with the isopropyl group in the conformation illustrated in Figure 24. The placement of this group was, again, based on a molecular model which indicated that this conformation would afford the least amount of steric repulsion. Because of the computation time involved, no attempt was made to rotate the isopropyl group to determine whether this prediction was correct. However, calculations were performed with the isopropyl group in an all-staggered conformation and an all-eclipsed conformation. The all-eclipsed conformation was predicted to have a lower energy. The optimized conformation of this isomer has bond angles which are even more distorted than they were in the previous cases.

When the energy of the holopolar isomer, (23h), was calculated, the isopropyl group was positioned in an all-staggered conformation, as shown in Figure 25. Once again, no attempt was made to optimize the position of the isopropyl group. The energy difference of 11 kcals between the two isomers is significantly smaller than it was in each of the previous cases. This implies that the steric bulk of the isopropyl group is much greater than that of the

straight chain alkyl groups, as one might have predicted. The net atomic charges for the two isomers, shown in Figure 26, parallel those for the other isomeric pairs.

The relative stabilities of the alkyl substituted dye skeletons are shown in Figure 27. In accordance with initial predictions, there is essentially no incentive for the system to exist in the holopolar form when R=H. When R=Me, Et, or Pr, the energy of the holopolar form is not substantially higher than that of the meropolar form; and, when the bulky isopropyl group is introduced, the energies of the two isomers approach an even closer value.

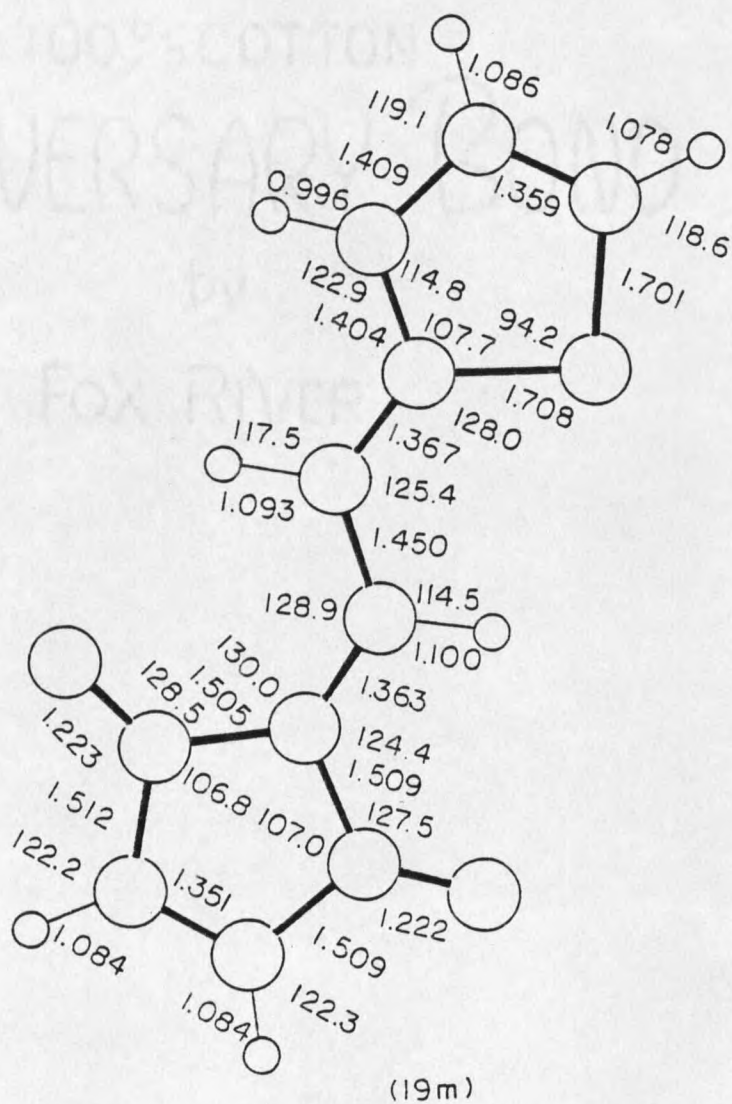


Figure 11. Final Geometry of Meropolar Hydrogen Isomer.

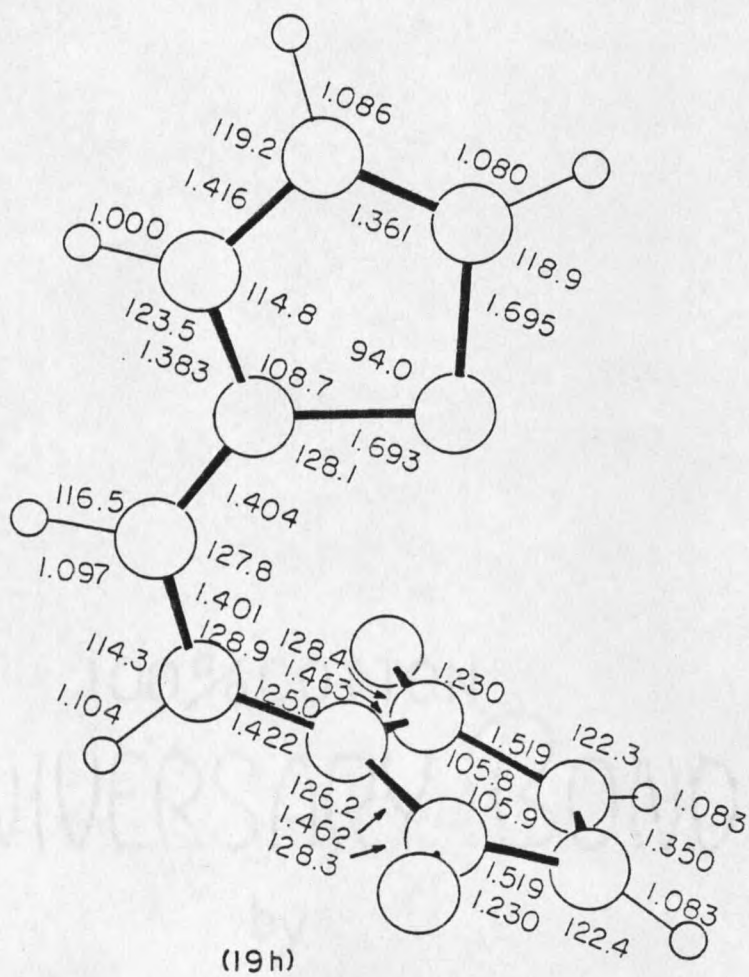


Figure 12. Final Geometry of Holopolar Hydrogen Isomer.

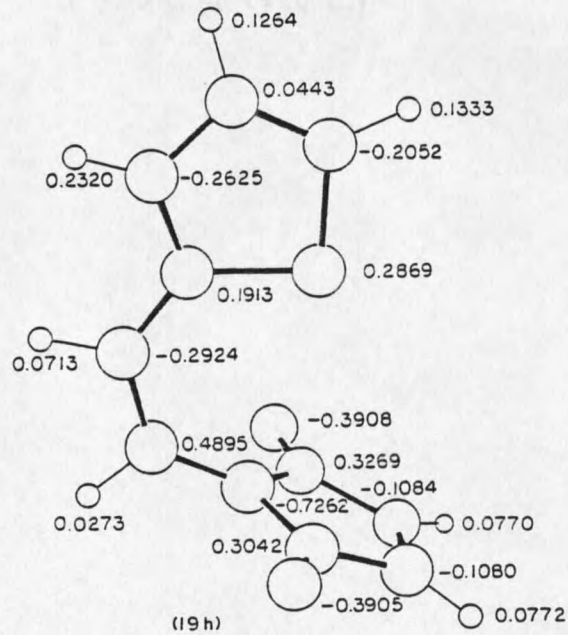
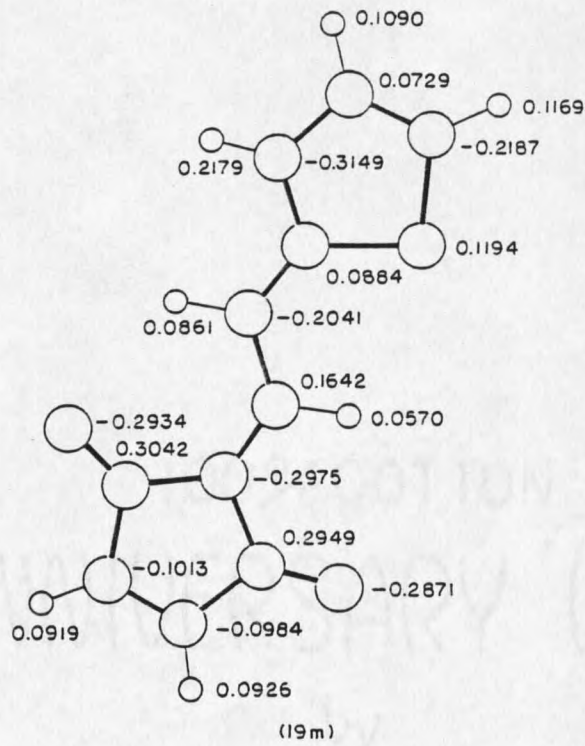
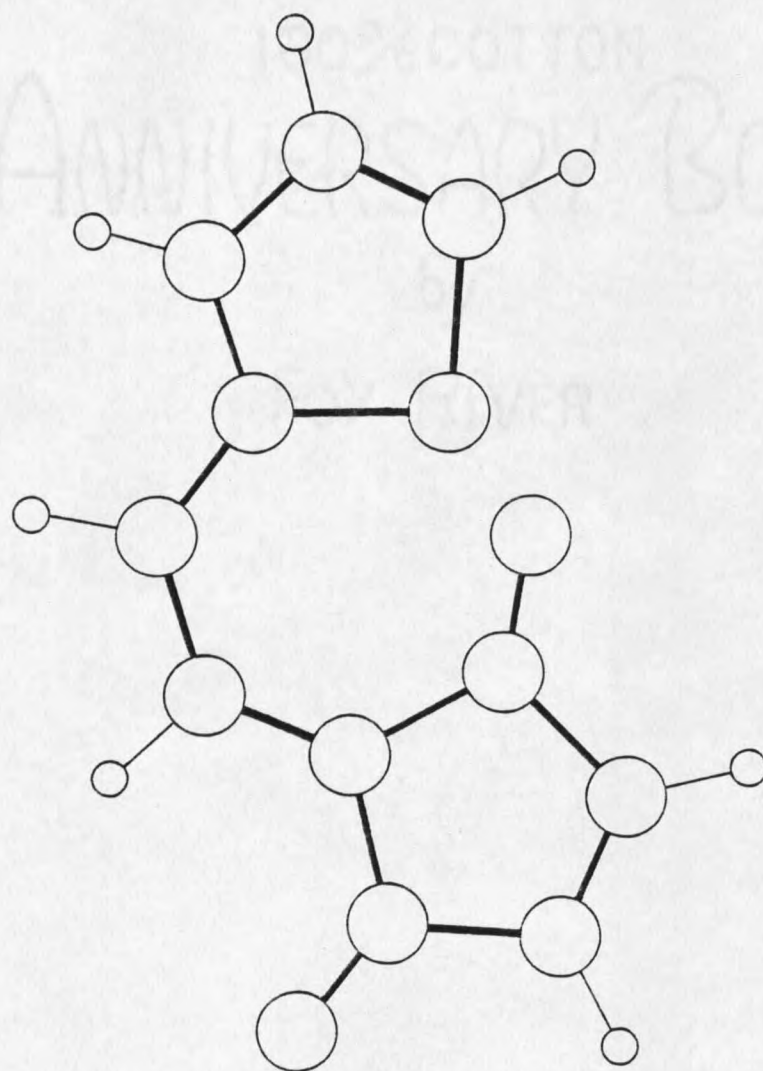
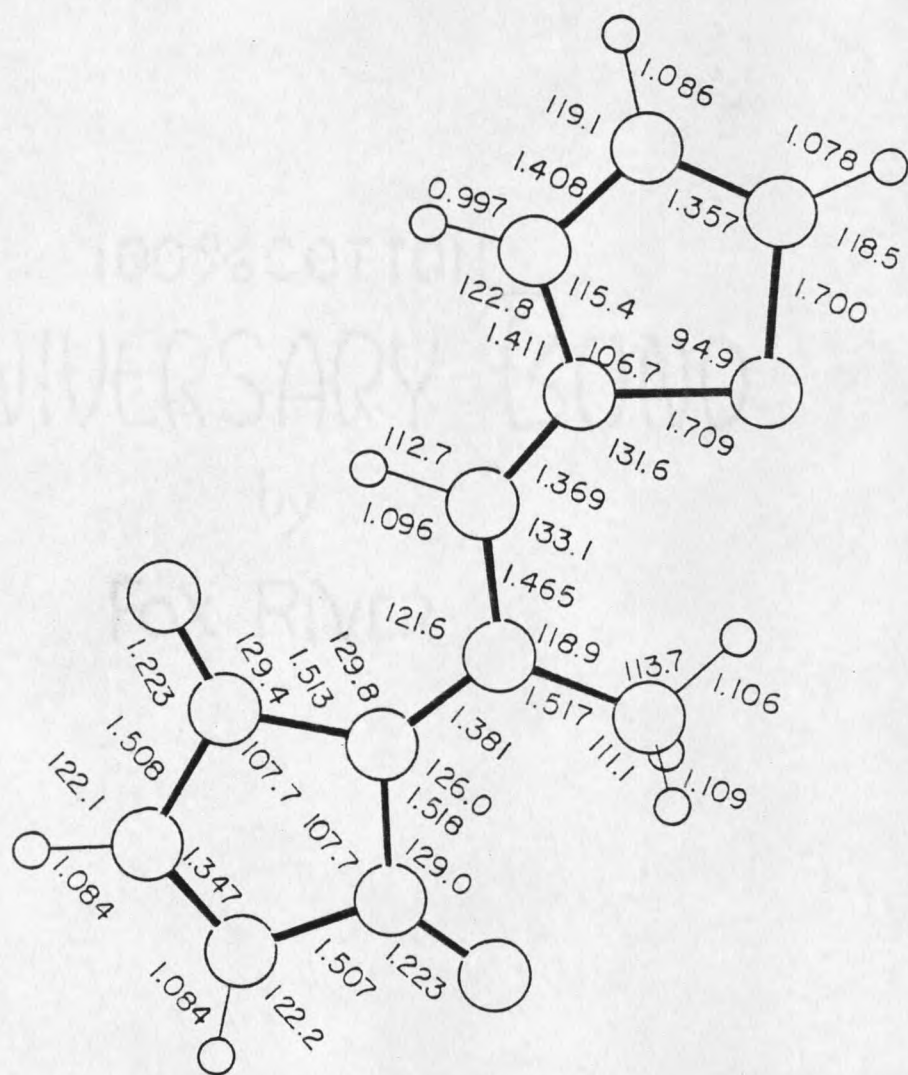


Figure 13. Net Atomic Charges for Hydrogen Isomers.



(19h')

Figure 14. Highly Crowded Conformation of Hydrogen Isomer.



(20m)

Figure 15. Final Geometry of Meropolar Methyl Isomer.

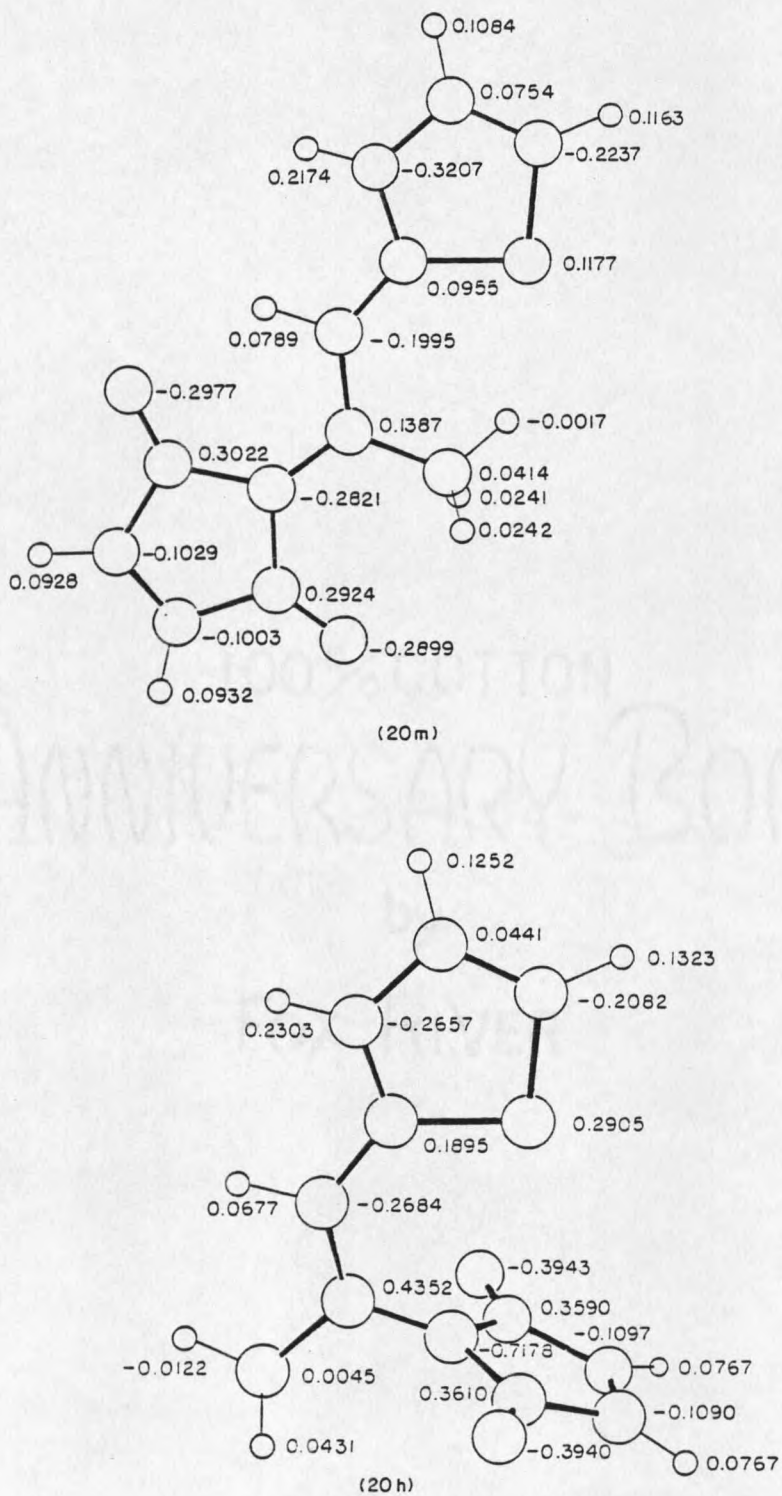
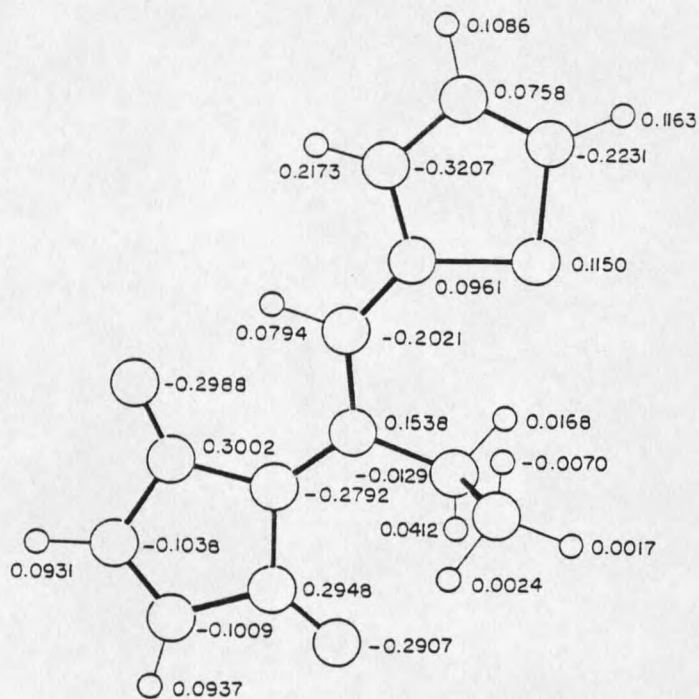
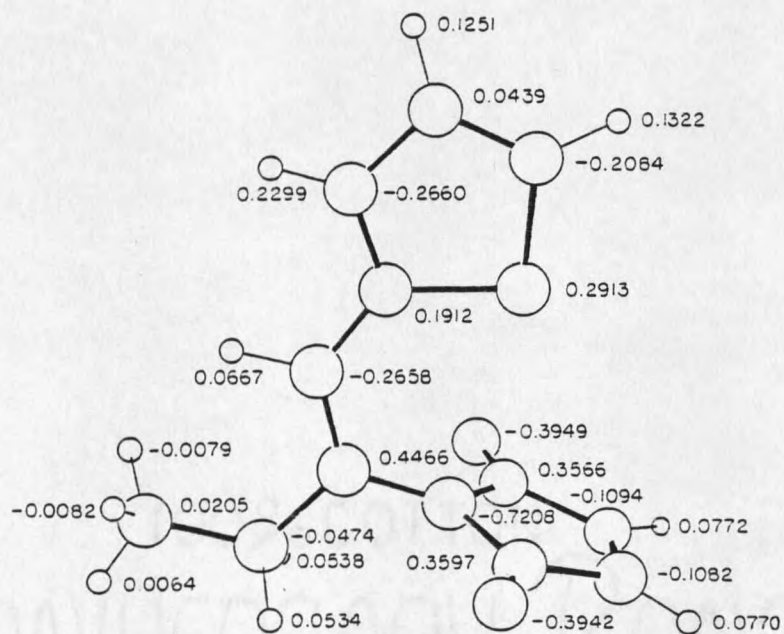


Figure 17. Net Atomic Charges for Methyl Isomers.

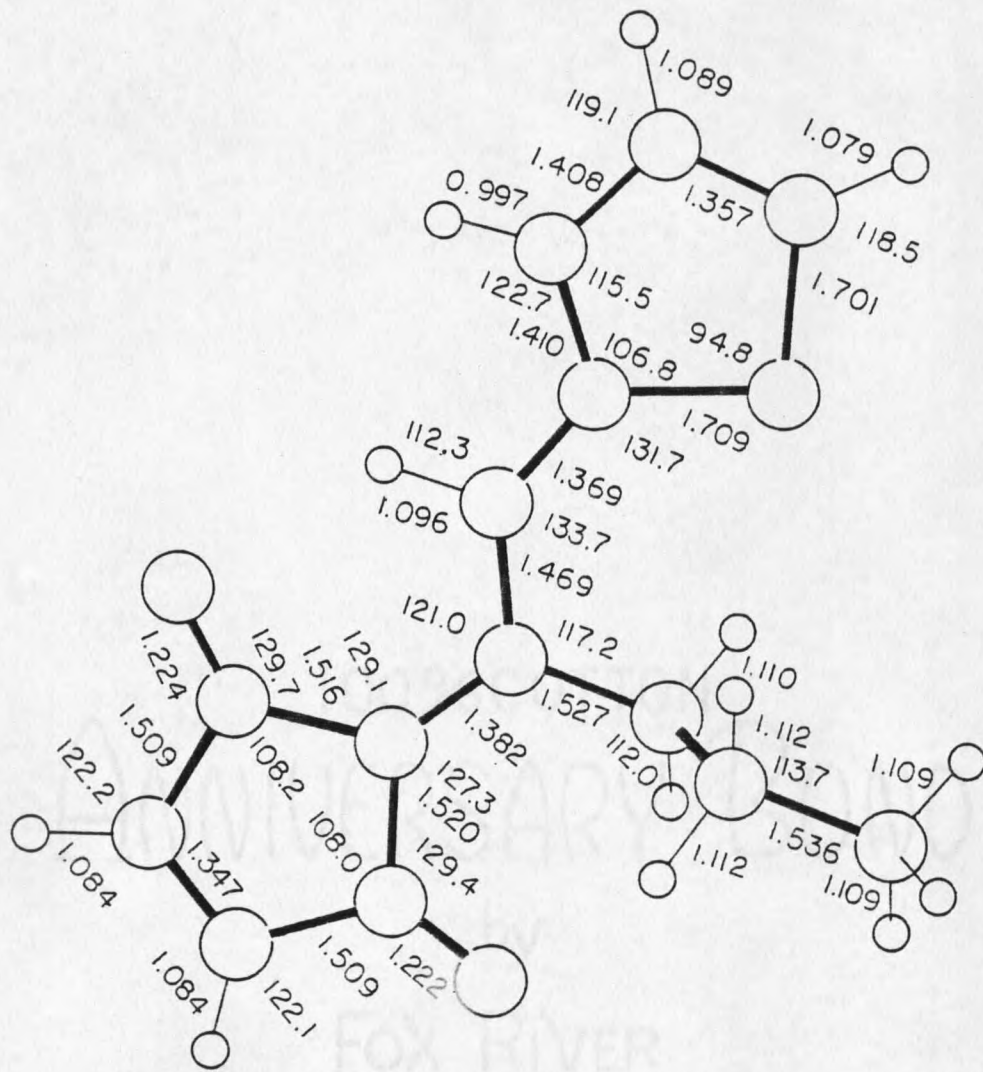


(21m)



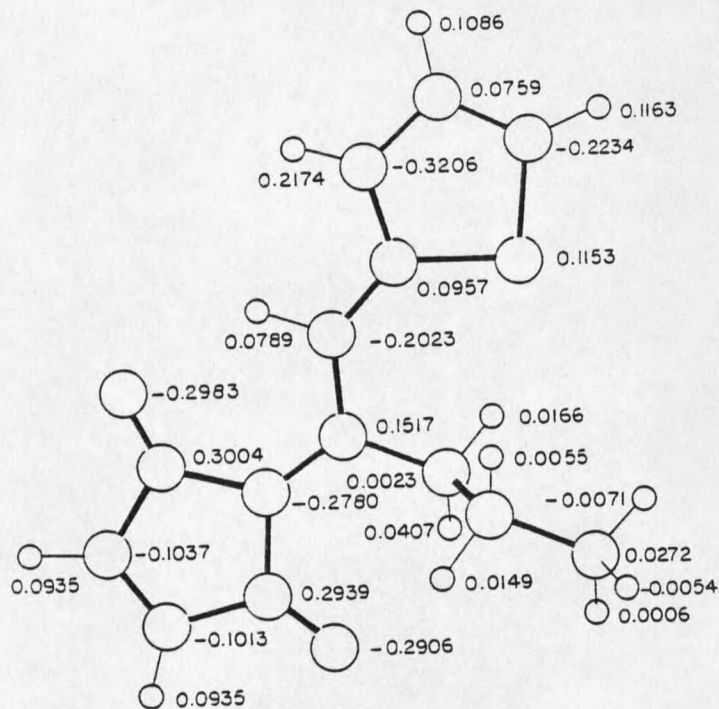
(21h)

Figure 20. Net Atomic Charges for Ethyl Isomers.

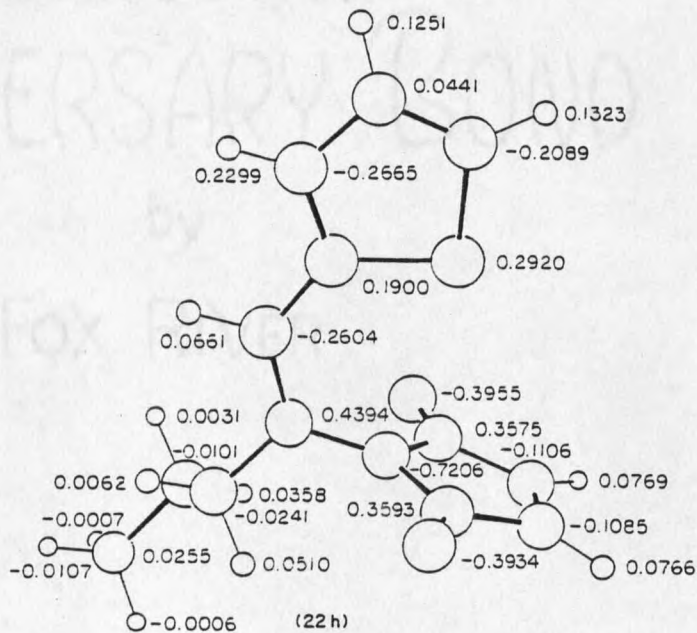


(22 m)

Figure 21. Final Geometry of Meropolar Propyl Isomer.



(22 m)



(22 h)

Figure 23. Net Atomic Charges for Propyl Isomers.

