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A THEORETICAL STUDY OF THE MOLECULAR STRUCTURE AND ELECTRONIC SPECTRUM OF OCTALENE (BICYCLO[6.6.0]TETRADECAHEPTAENE)[1,2]

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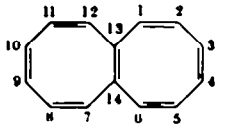
Abstract—The title compound has been studied by the Pariser-Parr method with regards to ground state geometry and electronic spectrum. It is predicted the molecule will exist in a non-planar conformation with alternating long and short bonds (similar to two tub-like cyclooctatetraenes fused together), and the expected electronic spectrum was calculated. Long wavelength absorption should cause the compound to be colored, probably yellow.

INTRODUCTION

CYCLOOCTATETRAENE has been rather thoroughly studied, both experimentally and theoretically, and its behavior and properties are now understood.[3] This molecule was of considerable interest because of its non-planarity, and the relatively low resonance energy predicted by the simple Hückel method. According to the most recent calculations,[3] cyclooctatetraene is non-planar because a planar molecule would have a highly strained sigma system, and though the pi system would have a lower energy if the molecule were planar, the total energy of the molecule is a minimum for the non-planar conformation. The energy difference between the planar and non-planar forms was calculated, and the result is in satisfactory agreement with experiment.

The molecule octalene (I) bears considerable resemblance to cyclooctatetraene,



I

and the prediction has been made[4] that this molecule should be "aromatic". No synthesis of octalene has yet been reported and the properties of this compound are not known. As the synthesis may be accomplished in the not too distant future,

[1] Part XIII, N. L. Allinger, J. C. Tai and M. A. Miller, *J. Amer. Chem. Soc.* **88**, 4495 (1966).

[2] This research was supported by grant GP 4290 from the National Science Foundation.

[3] For a recent study and leading references, see N. L. Allinger, M. A. Miller, L. W. Chow, R. A. Ford and J. C. Graham, *J. Am. Chem. Soc.* **87**, 3430 (1965).

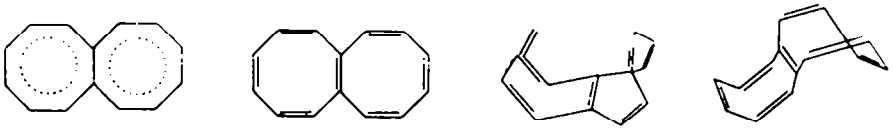
[4] D. P. Craig, *J. Chem. Soc.* 3175 (1951). Also see the discussion by D. P. Craig in *Theoretical Organic Chemistry, the Kekule Symposium* p. 20. Butterworths, London (1959); and D. Ginsburg's, *Non-benzenoid Aromatic Compounds*, chap. 1. Interscience, New York (1959).

and since we have developed methods which enable us to predict just what the molecular geometry and the spectral properties of this compound should be, the present paper reports the results of a theoretical study which we hope may be of use to experimentalists who engage in the synthesis of this substance.

DISCUSSION

If the molecule is planar, one might guess that the physical properties would be rather like those of naphthalene, and the substance would probably be crystalline. Alternatively, if the molecule is essentially a pair of fused cyclooctatetraenes with tub-like shapes, the material may crystallize with difficulty if at all. A subsidiary question then is whether the bond lengths would be more or less the same (as in naphthalene) or whether they might be instead alternating long and short (as in cyclooctatetraene or in open-chain polyenes).

Previous papers discussed methods by which one might try to calculate the degree of planarity of molecules such as cyclooctatetraene,[3] cycloheptatriene[3] and heptafulvene[5] and insofar as we have been able to compare with experimental values, the calculated numbers appear to be good. We have, therefore, applied these same methods to octalene, considering the four possible structures shown: a planar



RP *AP* *U* *S*

structure with equivalent bond lengths *RP*, a planar structure with alternating bond lengths *AP* and two structures built from tub-like forms *U* and *S*.

The pi energies were calculated by the same Pariser-Parr type approach,[3] which utilizes a configuration interaction treatment including only the singly excited configurations and the ground state, with a constant orbital exponent for the carbons. The regular planar structure has a normal closed-shell singlet ground state, with a pi energy of −183·841 ev. For the alternating planar structure, the 7th and 8th molecular orbitals (numbered in order of increasing energy) are nearly degenerate, with the result that the lowest closed-shell state has an energy of −183·252 ev, whereas if one electron is put into each of these two orbitals, with spins paired, this open-shelled singlet has an energy of −183·532 ev. Even more stable is the corresponding triplet, with an energy of −184·305 ev. Hence, as far as the pi system alone is concerned, the alternating planar molecule with a triplet ground state is of lower energy. Because of the interrupted conjugation the non-planar systems are less stable, both having the same pi energy, which is −181·487 ev.

Before drawing any conclusions about the molecular geometry, the sigma portion of the molecule must be included in the energy calculation. We have divided the sigma energy into three parts, the bending, compression, and van der Waals parts. The compression energy tends to cause the system to have bonds of similar length rather than alternating long and short bonds, and it was found earlier that this is in fact why benzene is symmetrical, not because the pi system energy is lower.[3,6]

[3] N. L. Allinger, *Tetrahedron* **22**, 1367 (1966).
[6] N. L. Allinger, *J. Org. Chem.* **27**, 443 (1962).

For the present structures, *RP* has a relatively low compression energy of 199·8 kcal/mole, while each of the other molecules has a compression energy of 238·6 kcal/mole.

The bending energies can be calculated using the constants described earlier,[3] as can the van der Waals repulsions between hydrogens which are too close to one another. The latter situation is found only in the planar systems, and the van der Waals energy can be substantially lowered by bending those hydrogens away from one another. Such bending was allowed to occur until the total energy reached a minimum. The results are summarized in Table 1. While there is some question about the van der Waals constants used in this calculation,[7] the final conclusions do not really depend on the exact values used.

TABLE 1. ENERGIES[a] FOR THE CONFORMERS OF I (kcal/mole).

	RP	*AP*[c]	*U*	*S*	*H*
σ-bending + van der Waals[b]	175·9	163·0	33·4	35·0	82·9
σ-compression	199·8	238·6	238·6	238·6	238·6
E_σ	375·7	410·6	272·0	273·6	321·5
E_π	4231·0	··4248·8	--4183·8	−4183·8	−4221·4
E_{total}	−3855·3	··3847·2[c]	--3911·8	−3910·2	−3899·9
$F_{relative}$	57 ± 15	64 ± 15	0	2 ± 4	12 ± 6

[a] A referee has suggested that the limits of error in the numbers in this Table be estimated, hence the probable errors are included. Insufficient data are available to allow the normal treatment of errors to be carried out, and the errors listed are "educated guesses".

[b] torsional energy of the σ system is taken as zero throughout.

[c] triplet ground state.

It was found that the non-planar forms are more stable than the planar forms by over 50 kcal/mole. Better van der Waals constants would increase this number, and hence the prediction that the system will be non-planar is unambiguous. The calculated difference in energy between the two non-planar forms is not regarded as significant. It seems likely that both forms will be present in equilibrium with one another, although we do not feel that a prediction can be made as to the value of the equilibrium constant or even as to which form is preferable.

Another point of interest is the barrier to inversion which separates *U* and *S*. If high enough, these conformers might be separately isolable. The interconversion of *U* and *S* requires that one ring becomes planar, the other may become planar or not. The calculation of the energy of *H*, in which only one ring is planar, shows that this conformation lies only 10–12 kcal/mole above those of *U* and *S*. Hence it seems clear that *U* and *S* will easily interconvert at room temperature, and the prospects for isolating them as separate compounds do not appear very bright. These conformations should lend themselves to study by the low temperature NMR method.

We have also calculated the electronic spectra which should result from the various

[7] The values were taken from E. L. Eliel, N. L. Allinger, S. J. Angyal and G. A. Morrison, *Conformational Analysis* p. 452. Interscience Division of Wiley, New York (1965). Recent extensive studies (M. A. Miller and F. A. Van Vatledge, unpublished) have clearly shown that the van der Waals radius of a hydrogen covalently bound to carbon must in fact be considerably larger than the quoted value.

TABLE 2. CALCULATED ELECTRONIC SPECTRA FOR THE DIFFERENT CONFORMATIONS OF I[a]

RP		AP	
λ(mμ)	f	λ	f
1314	0·013	4438	0·005
1095	0·000	1028	0·000
445	0·192	349	0·000
271	0·000	287	0·903
260	3·734	253	0·534
252	0·000	246	0·000
241	0·000	244	0·000
226	0·000	242	0·000
224	0·000	218	0·000
215	0·000	207	0·000
209	0·000	196	0·116
199	0·000	191	0·000
198	0·000		
193	1·155		
189	2·390		
U		S	
λ	f	λ	f
357	0·003	356	0·003
311	0·000	310	0·000
250	0·000	246	0·000
225	0·000	225	0·000
217	0·000	217	0·000
217	0·000	217	0·000
205	0·970	199	1·640
196	0·412	194	0·674
194	0·000	193	0·000
186	0·113	186	0·000
186	0·000	183	0·000
182	0·760	182	0·000
		180	0·603

[a] Calculated for the gas phase.

conformers, because the spectrum predicted for the non-planar structures will be of potential use to an experimentalist looking for the compound in a reaction mixture, while the spectra for the other forms may be useful ultimately for decisions regarding the structure which the molecule actually does have. In Table 2 are presented the wavelengths and the corresponding oscillator strengths for the spectra calculated for each form. We will call attention only to the features which show that the planar forms would have absorption bands in the IR, from electronic transitions and in addition they have very intense absorption in the 250 to 290 mμ region. (In this calculation singlet ground states were assumed.)

The predicted spectra for the non-planar forms are essentially the same as one another. The actual spectrum will therefore be of no use for differentiating these two structures from one another, but will of course be useful in differentiating the planar and non-planar forms. A non-planar form has a feeble but allowed transition at

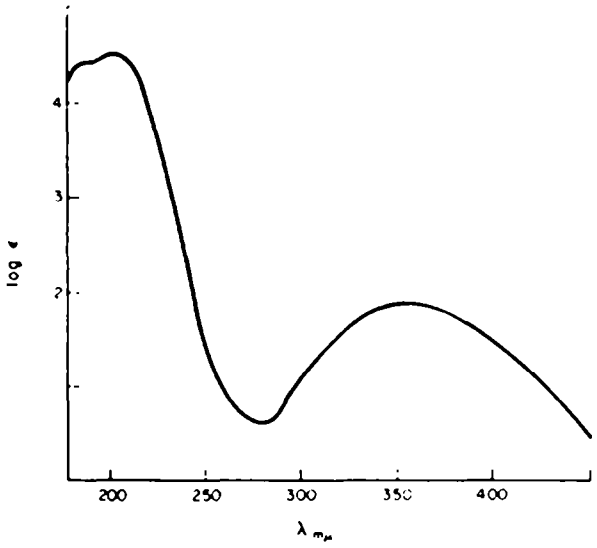


FIG. 1. The calculated electronic spectrum of I (heptane solution).

356 mμ, which should tail into the visible, and hence the compound should be colored, probably yellow. Then there are a number of forbidden transitions which may be weakly detectable, and finally there are some strong transitions at or below 205 mμ. When the spectra for the two non-planar forms are plotted, they are practically superimposable, so only one of them is reproduced here. While the spectra calculated and recorded in Table 2 refer to the gas phase, for convenience the plotted spectrum is corrected to solution in heptane by the usual methods.[3]

The free valence is a measure of the reactivity of a hydrocarbon, and these indices have been calculated for the various positions in *U* (or *S*, which are identical). The value found was 0·56 at each center subject to substitutions, which is identical with the value found for cyclooctatetraene. Our conclusion is that the molecule should show no special peculiarities which would make it hard to isolate (such as have been found for pentalene and for cyclobutadiene), but since it is a highly unsaturated polyene, its isolation may nonetheless present some experimental problems.

APPENDIX

The bond lengths and angles for the different conformations were assumed to be as follows:

RP: all C—C bond lengths 1·397 Å; all C—C—C angles 135°; C_{18}—C_1—H angle for minimum energy 124°. The calculated bond orders were similar but not identical, and ranged from 0·59 to 0·67, except for $p_{18,14} = 0·26$.

AP: C_1—C_2 bond length 1·334 Å; C_2—C_3 1·462 Å; C_1—C_2—C_3 angle 135°; C_{18}—C_1—H angle for minimum energy 122°.

U and *S:* C_1—C_2 bond length 1·334 Å; C_2—C_3 1·462 Å; C_1—C_2—C_3 angle 126·4°. The calculated bond orders were 0·95 and 0·23 for the long and short bonds respectively (as in cyclooctatetraene) except for the bridgehead double bond (0·90).

The plot of the spectrum was made utilizing a program written by Mr. John Graham and Dr. M. A. Miller which was previously described,[4] which was, however, modified by replacing the Lorentzian band shapes by Gaussian shapes, as we found these gave a more realistic appearance to the spectra. Further numerical data are available from the authors.