

The Calculated Electronic Spectra and Structures of Some Cyclic Conjugated Hydrocarbons^{1,2}

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The ground-state conformations of cyclooctatetraene and tropilidene were calculated to be nonplanar by a combination of Pariser-Parr-type treatments of the π -systems and Westheimer treatments of the σ -systems. The barriers to inversion were calculated, and were in fair agreement with experiment. Heptalene was similarly calculated to be very close to planar. The ultraviolet spectra of these molecules were also calculated, and were in reasonable agreement with experiment.

Introduction

The most successful calculations on the ultraviolet spectra of complicated conjugated hydrocarbon molecules have been carried out starting from the basic Goeppert-Mayer and Sklar approximation which considers only the π -electrons moving in the field of a "core" composed of the nuclei and remaining electrons of the system.^{1,3-5} To keep the computations from becoming unwieldy and to obtain numerical results which are in agreement with experiment, it is necessary to modify the original method by means of two types of approximations introduced by Pariser and Parr, which are to neglect large numbers of numerically small integrals (the zero-differential overlap approximation)⁶ and to use empirical values for certain integrals.⁴ The method has been generally successful and, in particular, has been shown to be capable of predicting the wave lengths of maximum absorption in the ultraviolet spectra of hydrocarbons to within 10 or 15 $m\mu$, and at least qualitative values for the oscillator strengths of the transitions.

The calculation of conformational energies of saturated molecules was developed mainly by Westheimer and utilized by him to predict activation energies for the racemization of hindered biphenyls at an early date.⁷ The basic method has subsequently been

extended, amplified, and applied to many systems by a number of other workers, and it is generally applicable to any molecule which behaves classically (*i.e.*, any which do not contain delocalized bonds, or in which the delocalized bonding is independent of conformation). Hendrickson and Wiberg have shown⁸ that by using machine computation the Westheimer method can be made to give quite good relative conformational energies in very complicated molecules.

We would like to consider in this paper the calculation of conformational energies for unsaturated molecules, in which the basic Westheimer method can be used to deal with the σ -system but to which one must add the effects of the delocalized π -system. In the present work, the latter has been taken into account by utilizing the Pariser-Parr method⁴ with the modifications introduced earlier.⁵ This type of approach has been applied before at the level of the Hückel-type calculation many times.⁹ More exact treatments have also been carried out in a few cases.¹⁰⁻¹¹ In particular, in an earlier paper in this series,¹¹ an attempt was made to calculate the ground-state geometries for benzene, cyclooctatetraene, the dianion of cyclooctatetraene, and a few other simple substances. The predictions were only moderately successful; conspicuous deviations between the calculations and the known experimental facts were found for benzene, for which the calculations predicted a ground state containing alternating long and short bonds, and for cyclooctatetraene, for which the ground state was predicted to be planar. More recently it was found that a few minor modifications of certain numerical values in the conventional Pariser-Parr approximation⁵ allowed a much more accurate prediction of ultraviolet spectra than had been possible previously for other than alternant aromatics, so the use of these numerical values was extended to the present application.

Since satisfactory programs for the computation of σ -system energies such as those described by Wiberg or by Hendrickson were not available to us, the σ -systems were treated by hand calculation. Consequently, it was not feasible to investigate all possible arrangements of the σ -system. More properly, a treatment of the π -system such as given here should be superimposed upon a treatment of the σ -system as given by Wiberg so that their total energy is minimized, and it is intended to extend the calculations in

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(2) Supported by Grant DA-ARO-D-31-124-G494 from the Army Research Office (Durham).

(3) (a) A. Julg and B. Pullman, *J. chim. phys.*, **52**, 481 (1955); (b) P. Schiess and A. Pullman, *ibid.*, **53**, 101 (1956); (c) R. Pariser, *J. Chem. Phys.*, **24**, 250 (1956); (e) K. L. McEwen and H. C. Longuet-Higgins, *ibid.*, **24**, 771 (1956); (d) N. S. Ham and K. Ruedenberg, *ibid.*, **25**, 13 (1956); (f) C. F. Wilcox, Jr., S. Winstein, and W. G. McMillan, *J. Am. Chem. Soc.*, **82**, 5450 (1960); (h) R. L. Hummel and K. Ruedenberg, *J. Phys. Chem.*, **66**, 2334 (1962); (g) R. B. Hermann, *J. Org. Chem.*, **27**, 441 (1962).

(4) R. Pariser and R. G. Parr, *J. Chem. Phys.*, **21**, 466, 767 (1953).

(5) N. L. Allinger and M. A. Miller, *J. Am. Chem. Soc.*, **86**, 2811 (1964).

(6) H. M. Gladney, *Theoret. Chim. Acta*, **1**, 245 (1963), and K. Ruedenberg, *J. Chem. Phys.*, **34**, 1861 (1961).

(7) (a) F. H. Westheimer, "Steric Effects in Organic Chemistry," N. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, p. 523; (b) E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Interscience Publishers, Inc., Division of John Wiley and Sons, Inc., New York, N. Y., 1965, p. 435.

(8) (a) J. B. Hendrickson, *J. Am. Chem. Soc.*, **83**, 4537 (1961), and subsequent papers; (b) K. Wiberg, *ibid.*, **87**, 1070 (1965).

(9) For example, G. Favini and M. Simonetta, *Theoret. Chim. Acta*, **1**, 294 (1963); T. H. Goodwin and D. A. Morton-Blake, *ibid.*, **1**, 458 (1963); C. A. Coulson, *Tetrahedron*, **12**, 193 (1961); N. L. Allinger and G. Youngdale, *J. Org. Chem.*, **25**, 1509 (1960).

(10) I. Fischer-Hjalmar, *Tetrahedron*, **19**, 1805 (1963), studied butadiene and biphenyl, and R. B. Hermann, Ph.D. Thesis, Wayne State University, 1962, studied 1,4,5-triazacyclohepta-2,4,6-triene.

(11) N. L. Allinger, *J. Org. Chem.*, **27**, 443 (1962).

this way at a future time. Both the earlier literature³ and other studies carried on concurrently with the present work¹² suggest that other modifications in the calculations on π -systems can be made which will improve the agreement between the calculated and observed ultraviolet spectra of molecules such as those discussed here. The methods used in the present paper are not regarded by the authors as the best that can be done by any means, but they are working methods which are already available, and it was thought that they ought to be able to predict moderately well both the spectral and the geometric properties of unsaturated hydrocarbons. Such applications are reported herein. The systems specifically studied in this work were benzene, cyclooctatetraene, tropilidene, and heptalene. The objectives were: to calculate for benzene the relative energies of a structure with alternating long and short bonds compared to one with equal bond lengths and to find the bond length of minimum energy in the latter case; for cyclooctatetraene, it was desired to calculate whether the planar or nonplanar form was more stable and whether the bond lengths preferred to be alternating or equal. The barriers to inversion of the nonplanar form were also calculated. The ground-state geometry¹³ and inversion barriers¹⁴ are both known experimentally for comparison. For tropilidene, the objectives were the same as for cyclooctatetraene. Experimental data on the geometry of tropilidene^{15,16} became available only after the calculations had been carried out, and the agreement was found to be satisfactory. For heptalene, it was desired to predict whether the bond lengths would be equal or alternating, and whether or not the system would be planar. The ultraviolet spectra of all of these molecules were also calculated.

Method of Calculation

The π - and σ -systems were treated separately in the calculations. In order to correctly balance one system against the other, it was necessary to introduce two parameters into the calculation, the natural bond length for a carbon-carbon sp^2 - sp^2 single bond,¹⁷ and the stretching force constant of such a bond. Only the latter was an arbitrary parameter, and it was fixed by the known bond length in ethylene.¹⁸ There are many other empirical quantities that come into the calculations, but they are all established values used earlier.⁵

The π -System. The π -electronic energies and spectra were calculated as before⁵ with the following minor changes. Coulomb penetration integrals of the type $(q:pp)$ between orbital χ_p and neutral carbon atoms q were calculated by eq. 1 and were included in calculating the one-center Coulomb attraction integrals.

$$(q:pp) = 4\{\cos^2 \theta [K_{\sigma\sigma} - (s_q s_p |\sigma_p \sigma_p|)] + \sin^2 \theta [K_{\pi\pi} - (s_q s_p |\pi_p \pi_p|)]\} \quad (1)$$

(12) J. C. Tai, unpublished results

(13) O. Bastiansen, L. Hedberg, and K. Hedberg, *J. Chem. Phys.*, **27**, 1311 (1957).

(14) (a) F. A. L. Anet, A. J. R. Bourn, and Y. S. Lin, *J. Am. Chem. Soc.*, **86**, 3576 (1964); (b) F. A. L. Anet, *ibid.*, **84**, 671 (1962).

(15) (a) F. A. L. Anet, *ibid.*, **86**, 458 (1964); (b) F. R. Jensen and L. A. Smith, *ibid.*, **86**, 956 (1964).

(16) M. Traetteberg, *ibid.*, **86**, 4265 (1964).

(17) B. Bak and L. Hansen-Nygaard, *J. Chem. Phys.*, **33**, 418 (1960).

(18) L. S. Bartell and R. A. Bonham, *ibid.*, **31**, 400 (1959).

where θ is the acute angle between the π -orbital χ_p and a line through nuclei p and q . Theoretical values¹⁹ for the nuclear attraction and electronic repulsion integrals in eq. 1 were used. Theoretical values (γ_{pq}) were used for the repulsion integrals $(pp|qq)$ where $r_{pq} \geq 2.41$ Å. For r_{pq} less than 2.41 Å, empirical (γ'_{pq}) repulsion integrals calculated for parallel π -orbitals from eq. 2 were used.⁵ If the orbitals were

$$\gamma_{\pi\pi}' = 11.080 - 3.92327r + 0.69786r^2 \quad (r \leq 2.41 \text{ Å}) \quad (2)$$

not parallel, the empirical value $(\gamma_{\pi\pi}')$ for parallel orbitals was reduced by the ratio of the theoretical values for orbitals of the actual (γ_{pq}) and parallel $(\gamma_{\pi\pi})$ geometries (eq. 3).

$$\gamma_{pq}' = \gamma_{\pi\pi}' \gamma_{pq} / \gamma_{\pi\pi} \quad (3)$$

The σ -System. In this part of the calculation it was necessary to consider the compression and bending deformation energies of the bonds, and the van der Waals energies between the various atoms of the system. The compression energy of the σ -component of the double bond of an olefin was arrived at as follows.

Compression. Let ethylene with $r_{12} = 1.333$ Å be the reference system,¹⁸ with total energy E_T , which is the sum of the π - and σ -energies (eq. 4). From the

$$E_T = E_\pi + E_\sigma \quad (4)$$

Pariser-Parr scheme the ground configuration energy is given by

$$V_0 = E_\pi = 2 \sum_{i=1}^f I_i + \sum_{i,j}^f (2J_{ij} - K_{ij}) + \sum_{p>q}^n \gamma_{pq} \quad (5)$$

where n , the number of π -orbitals, equals 2, and f , the number of molecular orbitals doubly occupied in the ground state, equals 1, and the γ_{pq} are Coulomb repulsion integrals $(pp|qq)$. Thus, $E_\pi = 2I_1 + 2J_{11} - K_{11} + \gamma_{12}$. The molecular integrals J , K , and I can be expressed in terms of atomic integrals as in eq. 6 and 7

$$I_1 = \alpha_1 + \beta_{12} \quad (6)$$

$$J_{11} = K_{11} = 0.5\gamma_{11} + 0.5\gamma_{12} \quad (7)$$

where

$$\alpha_p = W - \sum_{p \neq q}^n [\gamma_{pq} + P_{pq}]$$

$P_{pq} \equiv (q:pp) = (C_q: \pi_p \pi_p)$ and W is the ionization potential of carbon. For ethylene $\alpha = W - P - \gamma_{12}$ (where $P = P_{12} = P_{21}$) and

$$E_\pi = 2\beta + 2W - 2P + 0.5\gamma_{11} - 0.5\gamma_{12} \quad (8)$$

The π -energy therefore decreases steadily with decreasing distance, and only the increasing σ -energy keeps the system from collapsing. Let the compression energy E_c (which for ethylene is equal to the σ -energy) be expressed by a Hook's law relation

$$E_c = k/2(r - s)^2 \quad (9)$$

where k will be the C_{sp^2} - C_{sp^2} stretching constant, $s = 1.517$ Å. (the sp^2 - sp^2 single bond length),¹⁵ and $r =$

(19) R. C. Sahni and J. W. Cooley, National Aeronautics and Space Administration, Technical Notes D-146-I, D-146-II, Washington, D. C., 1960.

the C-C bond length in question. Combining eq. 4, 8, and 9

$$E_T = 2\beta + 2W - 2P + 0.5\gamma_{11} - 0.5\gamma_{12} + \frac{k}{2}(r - s)^2 \quad (10)$$

Assuming E to be minimum at the known bond length, k can be evaluated by setting the first derivative of E with respect to r equal to zero. In order to do this, β , P , and γ must be expressed as differentiable functions of r . The integrals γ_{11} and γ_{12} are evaluated from eq. 2. In the π -energy calculations, β is evaluated from Mulliken's equation, using $W_c = -11.22$ e.v., and P from theoretical integrals calculated according Roothaan's equations.²⁰ Since both of these equations contain complicated functions of r , exponential functions were derived which reproduced the actual functions to within 0.01 e.v. over the short range (1.3-1.5 Å.) involved.

From Mulliken's relationship using $\beta = -2.402$ e.v. at 1.397 Å., we find that at $r = 1.337$ Å., $\beta = -2.598$ e.v.; at $r = 1.483$ Å., $\beta = -2.143$ e.v. Let $\beta = A \exp(-br)$, and solving, $A = -15.14856$ and $b = 1.31876$, so that

$$\beta = -15.14856e^{-1.31876r} \quad (11)$$

For penetration integrals, the theoretical expressions give $P = 0.886$ e.v. at $r = 1.337$ Å., and 0.552 e.v. at $r = 1.462$ Å. The exponential relation, $P = G \exp(-hr)$, is solved for G and h

$$P = 139.7e^{-3.785r} \quad (12)$$

Substituting eq. 2, 11, and 12 into 10, $E_T = 2Ae^{-br} + 2W - 2Ge^{-hr} + 0.5(11.080) - 0.5[11.080 - 3.92327r + 0.69786r^2] + k/2(r - s)^2$. Differentiating $dE/dr = 0 = -2bAe^{-br} + 2hG^{-hr} + 0.5(3.92327) - 2(0.5)(0.69786r) + k(r - s)$. Solving for $r = 1.333$ Å., $k = 80.052$ e.v. = 1845 kcal./mole = 12.825×10^5 dynes/cm. and $E_c = 922.5(r - 1.517)^2$ kcal./mole. This derived stretching constant for the sp^2-sp^2 single bond, 12.825×10^5 dynes/cm., is somewhat larger than the observed stretching constant for ethylene,²¹ 9.57×10^5 dynes/cm., as would be expected. (This is most easily seen by comparison of the energy vs. distance curve for the σ -bond and for the ethylene molecule. Addition of the π -component flattens out the latter curve, reducing the stretching constant.)

Bending. The bending constants used are the usual ones,^{7,8} as given in Table I. Force constants are not as exactly constant from one molecule to another as one would desire, but the values used here appear to be the best available. There is also some uncertainty as to the

Table I. The Bending Force Constants Pertaining to the Systems

θ	k_θ , erg/rad. ²	$\frac{1}{2}k_\theta$, cal./mole deg. ²
C-C-C	0.8×10^{-11}	17.54
C=C-H	0.68×10^{-11}	14.91
C-C-H	0.55×10^{-11}	12.06
C-C-H arom.	0.86×10^{-11}	18.85
H-C-H	0.32×10^{-11}	7.02

(20) C. C. J. Roothaan, *J. Chem. Phys.*, **19**, 1445 (1951).

(21) G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Co., Inc., New York, N. Y., 1945, p. 184.

best values to use for the "natural" angles of the systems without bending strain. These problems have been discussed elsewhere.⁷ The simplest approach has been used here by taking 109.467 and 120°, respectively, as the natural tetrahedral and trigonal values.

The angular geometries of the systems studied were determined as follows. For compounds of experimentally known geometry, the best literature values were used. For hypothetical systems, the neighboring C-C bond lengths were arbitrarily chosen (by analogy to compounds of known geometry). The angles were calculated from Dreiding models of the nonplanar systems; for planar systems, C-C-C angles were chosen so that C-C-C bending energy was a minimum. With the carbon angles θ_c fixed, the remaining angles were chosen so that their contribution to E^b was again minimum. The numerical data used are tabulated in the Appendix.

van der Waals' Energy. Properly, the van der Waals interaction between all the pairs of atoms of the molecule which are not bound to one another or to a common atom should be added to the stretching, bending, and torsional energies to obtain the total conformational energy. The van der Waals calculations are, however, subject to considerable uncertainty. They are therefore not generally included in the present work with the hope that the van der Waals energies do not vary very much from one conformation to another.

There are, however, significant van der Waals repulsions in the planar heptalene systems between the *peri* hydrogens, and these repulsions were specifically accounted for. These interactions, calculated from eq. 13²² were considered together with the bending energy in determining the C-C-C angles used

$$E_v = -2.25\epsilon_{pq}(r^*/r_{pq})^6 + 8.28 \times 10^5 \epsilon_{pq} e^{-r_{pq}/0.0736r^*} \quad (13)$$

where for H-H interactions, $\epsilon_{pq} = 0.042$ kcal./mole, and $r^* = 1.2$ Å. The hydrogens were allowed to move apart until the sum of their van der Waals repulsions and the resulting angular deformation energy was a minimum. In the regular planar heptalene this energy minimum occurs when the hydrogens are 1.86 Å. apart, and the van der Waals repulsion between each pair is 0.5 kcal./mole. For the alternating planar heptalene the corresponding numbers are 1.88 Å. and 0.4 kcal./mole.

Torsional Energy. This is considered only in the nonplanar tropilidene system (III NP) where a methylene group is adjacent to a double bond. In propene, the stable form has a methylene hydrogen eclipsing the double bond, and the measured rotational barrier is 1.98 kcal.²³ In the nonplanar tropilidenes the methylene group has an unfavorable torsional orientation with respect to both the 1,2 and the 5,6 double bonds, and E_w was taken as twice the propene barrier or 4 kcal./mole. Whether there should be a consideration of torsional barriers from the σ -systems in molecules such as ethylene cannot be decided until it is certain

(22) T. L. Hill, *J. Chem. Phys.*, **16**, 399 (1948).

(23) D. R. Lide, Jr., and D. E. Mann, *ibid.*, **27**, 868 (1957); *Advan. Chem. Phys.*, **2**, 367 (1959); P. S. Nangia and S. W. Benson, *J. Am. Chem. Soc.*, **86**, 2773 (1964).

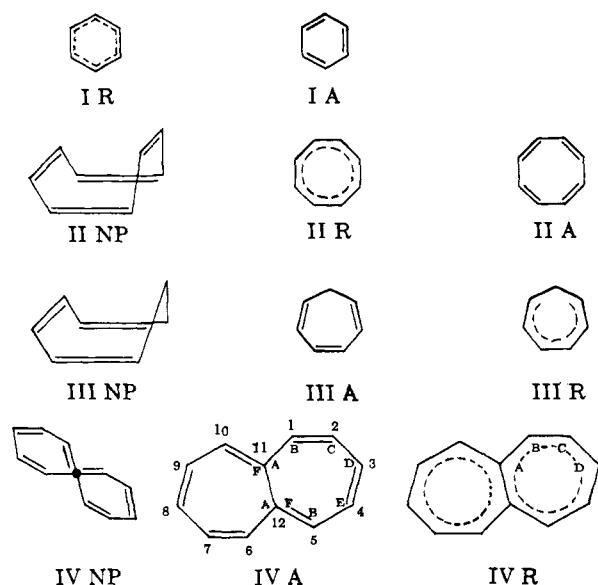
Table II. Relative Molecular Energies

Energy, kcal./mole	I, benzene		II, cyclooctatetraene			III, tropilidene			IV, heptalene		
	R	A	NP	A	R	NP	A	R	NP	A	R
E_π (relative)	5.9	0.0	33.1	0.0	25.3	11.4	0.0	23.8	51.2	0.0	32.8
E_c (compression)	79.7	101.1	134.7	134.7	106.3	81.0	91.8	66.4	198.8	197.1	160.5
E_b (bending)	0.0	0.0	8.2	43.6	48.5	3.5	17.4	18.8	2.7	30.9	33.3
E_v (van der Waals)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.8	1.0
E_ω (torsion)	0.0	0.0	0.0	0.0	0.0	4.0	0.0	0.0	0.0	0.0	0.0
E_T ($E_\pi + E_\sigma$)	85.6	101.1	176.0	178.3	180.1	99.9	109.2	109.0	252.7	228.8	227.6
E_s (relative stability)	0.0	15.5	0.0	2.3	4.1	0.0	9.3	9.1	25.1	1.2	0.0

what these barriers are due to. For now it will have to be assumed that no such barriers exist.

Results and Discussion

The first molecule examined was benzene (I). The previously calculated and observed spectra are in



good agreement,⁵ but an earlier attempt to calculate the ground-state geometry indicated that the molecule should have alternating long and short carbon-carbon bonds (I A),¹¹ while it is known experimentally that these bonds are all of equal length (I R).²⁴ The error appeared to be in the variation of β with distance. The function used here is just the Mulliken relationship, which was earlier found to correctly predict the spectra of olefins.⁵ In the present work the symmetrical structure was found to be more stable than the one with alternating bond lengths by 15.5 kcal./mole (Table II). As indicated previously,¹¹ the π -system actually prefers the alternating long- and short-bond arrangement, but the σ -system wins out.

Given that benzene was symmetrical, it was desired to establish the bond length of minimum energy. From equations 4, 5, and 9 using the symmetry orbitals $E_T = 6W - 12P_{12} - 12P_{13} - 6P_{14} + 8\beta + 1.5\gamma_{11} - 1^{1/3}\gamma_{12} - 1^{1/6}\gamma_{14} + 6k(r - 1.517)^2$. Using k , as found for ethylene, the minimum of energy occurs between $r = 1.38$ and 1.39 \AA ., in satisfactory agreement with the known bond length 1.397 \AA . Thus both the spectrum and the ground-state geometry of benzene are adequately

(24) A. Almenningen, O. Bastiansen, and L. Fernholt, *Kgl. Norske Videnskab. Selskabs Skrifter*, No. 3, 1 (1958).

accounted for, and our attention was next turned to cyclooctatetraene.

Cyclooctatetraene (II). The earlier calculations¹¹ predicted that alternating bond lengths (II A) would be favored over the symmetrical structure (II R), which is correct,¹³ but it was also predicted the planar form (II A) would be slightly preferred over the tub (II NP) which is wrong. In the present work the tub was calculated to be more stable than the planar form with alternating bond lengths by 2.3 kcal./mole, and more stable than the planar symmetrical form by 4.1 kcal./mole. Hence we can envision two kinds of inversion barriers in this molecule. The molecule can invert either with or without the long and short carbon-carbon bonds simultaneously interchanging their positions. In the latter case, the calculated barrier height (ΔH^*) would be just 2.3 kcal./mole. In the former, the symmetry of the molecule leads to some electronic peculiarities. The symmetrical intermediate has three filled and three empty orbitals, and a degenerate pair of orbitals which are half-filled, as indicated in Table III.

Table III. Energy Levels and Configuration Energies for Cyclooctatetraene (II R)

-2β	—	—	—	—	—	—
-2β	—	—	—	—	—	—
0	—	↓↑	↑	↓	↑	↑
2β	↓↑	↓↑	↓↑	↓↑	↓↑	↓↑
2β	—	↓↑	—	↓↑	—	↓↑
	$V_0 - 114.921 \text{ e.v. } V_{45} - 115.800 \text{ e.v. } T_{45} - 115.805 \text{ e.v.}$					

The triplet is of lowest energy, neglecting the consequences of the Jahn-Teller theorem, the singlet only 0.005 e.v. higher, and the closed shell singlet much higher. The experimental barrier to the interchange of the long and short bonds should then be from the ground state through the open-shell planar singlet (II A), and ΔH^* has the calculated value 4.1 kcal./mole. There have been experimental measurements of both of these barriers,^{14,25} but only ΔF^* is available for cyclooctatetraene itself, and substituted derivatives have certain complications. The value of ΔF^* for the higher barrier for cyclooctatetraene (through II R) is 13.5 kcal./mole, which is reasonably close to the calculated ΔH^* . The experimental data indicate that the other barrier is lower,¹⁴ and so until the desired experi-

(25) (a) K. Mislow and H. D. Perlmutter, *J. Am. Chem. Soc.*, **84**, 3591 (1962); (b) N. L. Allinger, W. Szkrybalo, and M. A. DaRooge, *J. Org. Chem.*, **28**, 3007 (1963).

Table IV. The Ultraviolet Spectrum of Heptalene

$V_0 \rightarrow$	NP		Calcd. A		R		Exptl. λ_{\max}^a (ϵ)
	λ_{\max} , $m\mu$	f	λ_{\max} , $m\mu$	f	λ_{\max} , $m\mu$	f	
V_{67}	351	0.002	788	0.000	18,700	0.000	Long tail into visible
V_{68}	299	0.114	376	0.181	468	0.272	λ_{352} (4140)
V_{69}	244	0.111	292	0.140	343	0.274	λ_{256} (21400)
V_{58}	227	0.010	226	0.000	251	0.000	Strong absorption below 200
V_{57}	220	0.207	220	0.701			
V_{612}	205	0.001	190	0.000			
V_{48}	200	0.003	176	0.000			
V_{47}	197	0.686	204	1.756			
V_{610}	188	0.006	197	0.000			
V_{38}	184	0.476	170	1.177			
V_{37}	183	0.472	208	0.000			

^a In $m\mu$.

mental data become available, all that can be said is the agreement between theory and experiment appears to be satisfactory.

The ultraviolet spectrum calculated for cyclooctatetraene in the present work indicates three transitions in the accessible region, with wave lengths and oscillator strengths as follows: 187 (1.8), and 219 (0.0) and 329 $m\mu$ (0.0). The experimental spectrum²⁶ (gas phase) shows a broad weak band from 260–310 which tails into the visible, and an intense band at 193 (just at the cut-off of our instrument) which contains a pronounced inflection at 205 $m\mu$. The agreement is not very good.

Tropilidene (III). With this molecule we were hard pressed to keep ahead of the experimentalists. The geometries we originally considered were planar with either alternating long and short carbon-carbon bonds, or with equal bond lengths, and nonplanar with natural bond lengths and angles. The initial calculations predicted the nonplanar molecule with alternating bond lengths would be the most stable and gave a calculated barrier to inversion of only 1.7 kcal./mole, and at the time the available evidence indicated convincingly that 2-*t*-butyl-3,7,7-trimethyltropilidene was nonplanar while other tropilidenes with smaller 2-alkyl groups were more nearly, perhaps completely, planar.²⁷ However, it seemed likely that the nonplanar form we assumed was perhaps too extreme, and instead of an unstrained σ -system and a relatively unfavorable π -system, a compromise might be expected in which the molecule flattened slightly. Such flattening should improve the π -energy substantially, and the distortion energy of the σ -system should be small. At this point, two independent experimental measurements of the inversion barrier were published (5.7 and 6.3 kcal./mole.).¹⁵ The direction of the difference between theory and experiment was consistent with our suppositions. As this paper was being written, an electron diffraction study on the molecule appeared,¹⁶ and the observed geometry differed from that we had assumed slightly in the way we had qualitatively suspected. We therefore repeated the calculation using the known geometry (III NP), and in this case found the barrier height to be 9.2 or 9.4 kcal. depending on whether the planar form is regular or alternating. Minimization

(26) We are indebted to Mr. B. Gordon for the determination of this spectrum.

(27) A. K. Conrow, M. E. H. Howden, and D. Davis, *J. Am. Chem. Soc.*, **85**, 1929 (1963).

of the energy of the planar form would presumably lower the barrier, but it was judged that the agreement with experiment was already as good as could be expected, so this was not done.²⁸

The ultraviolet spectrum of tropilidene was quite suggestive as to the ground-state geometry of the molecule. The observed spectrum²⁹ showed λ_{\max} 261 $m\mu$ (ϵ 3470) (solution) and strong absorption below 210 $m\mu$. The wave lengths and oscillator strengths (in parentheses) calculated from the known structure are (gas phase) 184 (0.71), 185 (0.16), 228 (0.00), and 254 $m\mu$ (0.18). The latter transition would be expected to give a band at about 255 $m\mu$ in heptane, with an extinction coefficient of a few thousand.³⁰ For the planar forms, the $N \rightarrow V_1$ transition was calculated to be at 280–320 $m\mu$ (in heptane) with oscillator strengths of 0.2–0.3. The latter structural possibilities could be ruled out on the basis of the spectrum alone.

Heptalene (IV). This molecule is not well known, either experimentally or theoretically. The compound has been prepared, but is stable only in dilute solution in the cold.³¹ Its ultraviolet spectrum has been reported.³¹ The previous theoretical treatments of this molecule have assumed it to be planar.³² Ground-state energies have been calculated for a planar form with both alternating (IV A) and constant (IV R) bond lengths, and for a nonplanar form with alternating bonds in which the σ -energy was minimized (IV NP). Structure IV R had the lowest calculated ground-state energy, but IV A was higher by only an insignificant 1.2 kcal./mole. The energy of the nonplanar form, on the other hand, was 25.1 kcal./mole above that

(28) It might appear that 6.3 and 9.2 kcal./mole do not represent especially good agreement, but when it is noted that the actual calculated ground-state energies of tropilidene are on the order of -2000 kcal./mole, the errors are only of the order of 2 parts per 1000. This is really better than one has any right to expect, and such accuracy appears to be possible only because so much of the error cancels when two geometries of the same molecule are considered; see for example R. M. Pitzer and W. N. Lipscomb, *J. Chem. Phys.*, **39**, 1995 (1963).

(29) W. von E. Doering and L. H. Knox, *J. Am. Chem. Soc.*, **79**, 352 (1957).

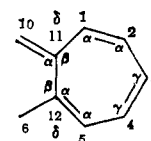
(30) The polarizability of the solvent was allowed for using the relationship given by N. S. Bayliss, *J. Chem. Phys.*, **18**, 292 (1950), using 1.46 as the refractive index of heptane, 31 cc. as the polarizability of the solute, 10.71×10^9 as the proportionality constant, and assuming the oscillator strength would be one-half the theoretical value.^{30c}

(31) H. J. Dauben, Jr., and D. J. Bertelli, *J. Am. Chem. Soc.*, **83**, 4657 (1961).

(32) (a) G. Berthier, B. Pullman, and J. Baudent, *J. chim. phys.*, **49**, 641 (1952); (b) P. C. Den Boer, D. H. W. Den Boer, C. A. Coulson, and T. H. Goodwin, *Tetrahedron*, **19**, 2163 (1963); (c) A. J. Silvestri, L. Goodman, and J. A. Dixon, *J. Chem. Phys.*, **36**, 148 (1962).

Table V

(IR)	Benzene (I A)	
$r_{C-C} = 1.397 \text{ \AA}$.	$r_{12} = 1.334 \text{ \AA}$.	
$C-C-C = 120^\circ$	$r_{23} = 1.462 \text{ \AA}$.	
$C-C-H = 120^\circ$	$C=C-C = 120^\circ$	
	$C=C-H = 120^\circ$	
(II NP)	Cyclooctatetraene (II R)	
$r_{12} = 1.334 \text{ \AA}$.	$r_{C-C} = 1.397 \text{ \AA}$.	$r_{12} = 1.334 \text{ \AA}$.
$r_{23} = 1.462 \text{ \AA}$.	$C=C-C = 135^\circ$	$r_{23} = 1.462 \text{ \AA}$.
$C=C-C = 126.4^\circ$	$C=C-H = 112.5^\circ$	$C=C-C = 135^\circ$
$C=C-H = 118.3^\circ$		$C=C-H = 113.5^\circ$
(III NP)	Tropilidene	
$r_{12} = 1.356 \text{ \AA}$.	$C_1-C_2-C_3 = 127.2^\circ$	$C=C-H = 120^\circ$
$r_{23} = 1.446 \text{ \AA}$.	$C_2-C_3-C_4 = 119.8^\circ$	$H_a-C_7-H_b = 109^\circ$
$r_{17} = 1.505 \text{ \AA}$.	$C_5-C_6-C_7 = 121.8^\circ$	$H_a-C_7-C_1 = 108.68^\circ$
	$C_1-C_7-C_8 = 113.07^\circ$	
(III A)		
$r_{12} = 1.337 \text{ \AA}$.	$C_7-C_1-C_2 = 132.92^\circ$	$H_2-C_2-C_1 = 116.5^\circ$
$r_{23} = 1.483 \text{ \AA}$.	$C_1-C_2-C_3 = 128^\circ$	$H_3-C_3-C_4 = 116^\circ$
$r_{17} = 1.501 \text{ \AA}$.	$C_2-C_3-C_4 = 129^\circ$	$H_a-C_7-H_b = 107^\circ$
$C_1-C_7-C_8 = 120.17^\circ$	$H_1-C_1-C_2 = 114.08^\circ$	$H_a-C_7-C_1 = 107.47^\circ$
(III R)		
$r_{12} = 1.397 \text{ \AA}$.	$C_7-C_1-C_2 = 132^\circ$	$H_2-C_2-C_1 = 116^\circ$
$r_{23} = 1.397 \text{ \AA}$.	$C_1-C_2-C_3 = 128^\circ$	$H_3-C_3-C_4 = 115^\circ$
$r_{17} = 1.501 \text{ \AA}$.	$C_2-C_3-C_4 = 130^\circ$	$H_a-C_7-H_b = 107^\circ$
$C_1-C_7-C_8 = 120^\circ$	$H_1-C_1-C_2 = 114^\circ$	$H_a-C_7-C_1 = 107.3^\circ$
(IV NP)	Heptalene	
$r_{C-C} = 1.462 \text{ \AA}$.	$\alpha = 120^\circ$	
$r_{C-C} = 1.337 \text{ \AA}$.	$\beta = 118^\circ$	
$H_\alpha-C_\alpha=C = 120^\circ$	$\gamma = 125^\circ$	
$H_\gamma-C_\gamma=C = 118^\circ$	$\delta = 122^\circ$	
(IV A)		
$r_{12} = 1.337 \text{ \AA}$.	$C = 129.20^\circ$	$C_{11}-C_1-H = 115^\circ$
$r_{23} = 1.462 \text{ \AA}$.	$D = 126.75^\circ$	$C_{11}-C_{10}-H = 115^\circ$
$r_{11,12} = 1.483 \text{ \AA}$.	$E = 129.06^\circ$	$H_C-C_C=C = 116^\circ$
$A = 124^\circ$	$F = 127^\circ$	$H_D-C_D=C = 117^\circ$
$B = 132^\circ$		$H_E-C_E=C = 116^\circ$
(IV R)		
$r_{C-C} = 1.397 \text{ \AA}$, except $r_{11,12} = 1.483 \text{ \AA}$.	$H_1-C_1-C_{11} = 115.5^\circ$	
$A = 126^\circ$	$H_{10}-C_{10}-C_{11} = 115.5^\circ$	
$B = 131^\circ$	$H_2-C_2-C_1 = 115.17^\circ$	
$C = 129.67^\circ$	$H_8-C_3-C_4 = 116.67^\circ$	
$D = 126.67^\circ$		



of IV R. It seems likely that at the true energy minimum the molecule is slightly deformed from planarity, but clearly it does not approximate the geometry with the unstrained σ -system. Alternatively, if the planar form has the minimum of energy, it is likely that the twisting frequency corresponding to the deviation from planarity considered is very low, so the spectrum observed might be expected to differ from that calculated for the planar form in the direction of the nonplanar form. The spectra calculated for the different forms and the experimental spectrum are compared in Table IV. The observed spectrum of IV can be interpreted very well in terms of a structure which is intermediate between the planar (alternating) and the nonplanar forms in Table IV. If it is assumed that all the wave lengths and oscillator strengths show parallel changes with the degree of planarity of the system, then

an intermediate form would be predicted to show the following: $\lambda_{500} m\mu$ (f 0.001), λ_{325} (f 0.13), λ_{280} (f 0.12), λ_{220} (f 0.35), and λ_{199} (f 1.0). This spectrum may be compared with the experimental spectrum (corrected to gas phase): $\lambda_{400-600}$ weak tail, λ_{350} ($\log \epsilon$ 3.6), λ_{254} ($\log \epsilon$ 4.3), and λ_{220} —strong end absorption, ($\log \epsilon$ 4.5 below 200 $m\mu$). It would appear from the spectrum that the molecule is near to being planar.

Appendix

The coordinates of the pertinent carbon atoms in the molecules studied were deduced from the bond lengths and angles which were known or assumed, as shown in Table V.³³

(33) Other numerical data obtained in this work are available from the authors upon request.