Tetrahedron, 1966, Vol. 22, pp. 1367 to 1372. Pergamon Press Ltd. Printed in Northern Ireland

THE CALCULATED ELECTRONIC SPECTRA AND STRUCTURES OF HEPTAFULVENE AND THE BENZOHEPTAFULVENES[1,2]

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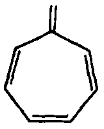
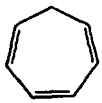
(*Received* 19 *August* 1965; *in revised form* 25 *October* 1965)

Abstract—The ground state conformation of heptafulvene was calculated (by a combination of a Pariser-Parr type treatment of the π system and a Westheimer treatment of the sigma system) to be planar, with alternating bond lengths. The calculated electronic spectrum of this conformation agrees with that observed. The 2,3- and the 4,5-benzoheptafulvenes were also studied.

INTRODUCTION

IN A recent paper[1] it was shown that the ground state conformations of a number of unsaturated hydrocarbons could be predicted rather well by treating their σ systems by the classical Westheimer method,[1,3] their π systems by a modification of the Pariser-Parr method,[4] and by then summing the energies of the system.[5] The electronic spectra of the molecules were also predictable to a fair degree of accuracy.[1,4] The present paper is concerned with applications of these methods to the heptafulvene (I) molecule and some related systems.


I


II

DISCUSSION

Heptafulvene itself is a rather reactive compound which can be kept and studied in dilute solutions or at low temperatures.[6,7] It is reported[7] to show UV absorption bands as follows: λ_{max} 427(log ϵ 2·7); λ_{max} 279(log ϵ 4·1); λ_{max} 212(log ϵ 4·6).

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[1] This paper is numbered XI in the series *Organic Quantum Chemistry* Paper X, N. L. Allinger, M. A. Miller, L. W. Chow, R. A. Ford and J. C. Graham, *J. Amer. Chem. Soc.* **87**, 3430 (1965); and XLVIII in the series *Conformational Analysis* Paper XLVII, N. L. Allinger and L. A. Freiberg, *J. Org. Chem.* **31**, *in press* (1966).

[2] Supported by grant DA-ARO-D-31-124-G494 from the Army Research Office.

[3] E. L. Eliel, N. L. Allinger, S. J. Angyal and G. A. Morrison, *Conformational Analysis* p. 435. Interscience Division of J. Wiley, New York (1965).

[4a] N. L. Allinger and M. A. Miller, *J. Amer. Chem. Soc.* **86**, 2811 (1964);

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

[5] This approach is not fundamentally different from those used earlier (for example, Y. Ooshika, *J. Phys. Soc. Japan* **12**, 1238, 1246 (1957); H. C. Longuet-Higgins and L. Salem, *Proc. Roy. Soc.* **A251**, 172 (1959)), but utilizes slightly different numerical values. The particular approach used here is convenient in that it is completely general, and it treats the π and σ systems separately until the last possible moment. This permits an easy extension to utilizing SCF orbitals (especially VESCF orbitals) and including multiply excited states in the configuration interaction treatment, which extensions are in progress.

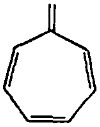
[6] R. B. Turner, W. R. Meador, W. von E. Doering, L. H. Knox, J. R. Mayer and D. W. Wiley, *J. Amer. Chem. Soc.* **79**, 4127 (1957).

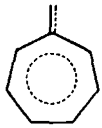
[7] W. von E. Doering and D. W. Wiley, *Tetrahedron* **11**, 183 (1960).

A number of recent theoretical studies on the molecule have been carried out, all of which have assumed the molecule to be planar.[8] It was recently predicted[1] and found[9] that a somewhat similar molecule, tropilidene (II), was preferentially non-planar with an inversion barrier of several kcal/mole, so the possibility that heptafulvene was non-planar also required consideration.

The objectives in the present work were (a) to calculate the preferred geometry of the molecule, and (b) to calculate the electronic spectrum of the molecule for various conceivable geometries, and (c) to show, hopefully, that the geometry calculated to be the most stable corresponded to the observed spectrum. There were no adjustable parameters in the calculation; all the numerical data necessary were available from earlier work[1,4] except, of course, the actual molecular geometry.

In the present work three types of structure were considered: compound I*a*, a planar form with alternating long and short bonds, I*r*, a regular planar form with bonds of equal length (benzenoid), and I*np*, a non-planar form with alternating bond lengths of such a geometry as to minimize the angular deformation energy.


I*a*


I*r*


I*np*

The bond lengths used were: all 1·397 Å for I*r*; and 1·483 Å and 1·337 Å for the bonds written as single and double respectively in the Kekule form of I*a* and I*np*, these being the bond lengths of the corresponding bonds in butadiene. The ground state energy of the π system of each form was calculated as described earlier, and the relative values are given in Table 1. For each structure the σ energy was then calculated from the appropriate bending and stretching force constants,[1] and these energies were added to the π energies to give total relative energies (Table 1). It was noted that

TABLE 1. ENERGIES OF THE STRUCTURES OF HEPTAFULVENE (KCAL/MOLE).

Structure	I*a*	I*r*	I*np*	I*a*′
π energy	0·0[a]	14·6	22·7	3·1
σ-bending	7·6	8·3	0[b]	7·6
σ-compression	123·8	106·2	123·8	114·9
Total	131·4	129·1	150·7	125·6

[a] The actual calculated π energy is $-105·255$ ev.

[b] This structure is actually not completely free of bending strain, this value is lower limit.

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[8] [a] T. Nakajima and S. Katagiri, *Bull. Chem. Soc. Japan* **35**, 910 (1962); *Mol. Phys.* **7**, 149 (1963–1964); [b] J. Koutecky, P. Hochman and J. Michl, *J. Chem. Phys.* **40**, 2439 (1964); [c] M. J. S. Dewar and G. J. Gleicher, *J. Amer. Chem. Soc.* **87**, 685, 692 (1965); [d] A. Julg, *J. Chim. Phys.* **59**, 759 (1962) and earlier papers cited therein. An early suggestion that the system might in fact be non-planar—E. D. Bergmann, E. Fischer, D. Ginsburg, Y. Hirshberg, D. Lavie, M. Mayot, A. Pullman and B. Pullman, *Bull. Soc. Chim. Fr.* **18**, 684 (1951)—seems not to have been reconsidered by the ASMO method.

[9] [a] F. A. L. Anet, *J. Amer. Chem. Soc.* **86**, 458 (1964); [b] F. R. Jensen and L. A. Smith, *Ibid.* **86**, 956 (1964); [c] M. Traetteberg, *Ibid.* **86**, 4265 (1964).

the non-planar structure (I*np*) was of quite high energy, and this structure for the molecule could thereby be excluded. The other two forms were sufficiently close in energy that further considerations were required. As is seen in Table 1, the compression energy favors the equal bond lengths, while the π energy favors alternating bond lengths. This is the same situation as was found to exist for both benzene and butadiene, which are two extreme cases in which the balance of the σ and π systems leads to quite different bond length arrangements. The high "resonance energy" of benzene tends to bring the π energy of the symmetrical system down close enough to that of the alternating system that the compression energy can dominate the situation, while this does not happen for butadiene. Heptafulvene is an intermediate case, and it is not clear *a priori* what is to be expected. One could, with a great amount of effort, systematically vary the different bond lengths in the molecule, and try to locate the absolute minimum of energy. This is not actually a very practical approach at present, but we have considered the following. Allowing the 1·337 Å distances to expand slightly would lower the compression energy greatly, and may not increase the π energy as much; on the other hand, shortening the 1·483 Å distances would have little effect on the compression energy, but should improve the π energy. As mentioned earlier,[10] the latter appears to be the reason for the 1·462 Å length in cyclooctatetraene, as compared to 1·483 Å in butadiene. Dewar[8] suggested bond lengths close to 1·35 and 1·46 Å for heptafulvene from bond order considerations, and while the latter approach is known to give erroneous predictions in a number of cases, it is as good a predictive method as is now available. The calculation of the ground state energy for I*a*′, with bond lengths of 1·350 and 1·460 Å was therefore carried out, and in this case the ground state energy was lowered somewhat, so that I*a*′ is now better than the regular form. We have not pursued the question further, but are inclined to feel that I*a*′ is probably very close to the correct structure.

The electronic spectra of all the structures so far considered were calculated by the methods described previously.[1,4] The results are summarized in Table 2. The agreement with experiment is satisfactory for I*a* or I*a*′ and poorer for the others, and would appear to establish the actual structure as planar with alternating long and short bonds, but the exact bond lengths cannot be specified. It should be noted that while the calculated and experimental values for the long wave-length absorption for I*a*′ are not as close as one would like, the error corresponds to only 0·3 ev at this wave length, and the value calculated is quite sensitive to the exact geometry assumed.

TABLE 2. THE UV SPECTRA OF HEPTAFULVENE

Structure	I*a*	I*r*	I*np*	I*a*′	I[a] Experiment
$\lambda_{\max}$ (log ϵ)	429(2·9)	729(2·8)	334(2·9)	475(2·9)	426 (2·7)
$\lambda_{\max}$ (log ϵ)	271(3·9)	321(3·9)	257(3·8)	282(3·9)	278 (4·1)
$\lambda_{\max}$ (log ϵ)	193(4·4)	206(4·4)	193(4·3)	196(4·5)	207[b](4·6)

[a] These values are corrected to the gas phase according to Ref. 1.

[b] The spectrum was not determined to a sufficiently low wave length to be certain this value represents the maximum absorption. Hence 207 mμ is an upper limit for the true value.

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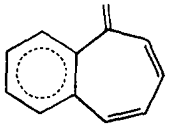
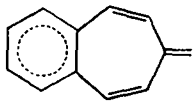
[10] N. L. Allinger, *J. Org. Chem.* **27**, 443 (1962).

Dewar[8] has emphasized that resonance energy is an artificial concept, and that it can be defined in any of various ways. He has also put forth the view that the structure I*a*′ has no resonance energy (according to his definition). The present author does not feel this is a useful viewpoint for present purposes, because one must surely conclude that if there is no resonance energy, there is no reason for the molecule to remain planar.

Our attention was next turned to the 2,3- and 4,5-benzoheptafulvenes (III and IV), which are both known.[11] The 4,5-benzoheptafulvene (III) is reported to have a rather complicated spectrum, with no less than ten absorption maxima reported over the range of 237 to 345 mμ. Clearly many of these must represent vibrational fine structure. The calculations appear to reproduce the general pattern of the spectrum at least roughly, and a closer comparison is not possible without the actual experimental spectra in hand. The calculated spectrum is given in Table 3.



IV



III

TABLE 3. THE CALCULATED SPECTRA OF THE BENZOHEPTAFULVENES

2,3-(planar)		2,3-(non-planar)		4,5-(planar)	
$\lambda_{m\mu}$	(*f*)	$\lambda_{m\mu}$	(*f*)	$\lambda_{m\mu}$	(*f*)
367	0·07	326	0·07	363	0·02
291	0·06	276	0·05	297	0·18
252	0·26	252	0·23	240	0·86
231	0·01	228	0·05	227	0·03
226	0·47	220	0·23	211	0·93
206	0·13	212	0·32	207	0·01
194	0·26	201	0·46	192	0·69
190	1·68	197	0·46	190	0·09
186	0·24	190	0·90	189	0·76
179	0·06	184	0·05	180	0·09
178	0·75	179	0·58	175	0·19

The reported[11] spectrum for the 2,3 isomer (IV) is startling; "no absorption maxima but only tailing from below 210 mμ, ε at 220 mμ (46,000) and at 340 mμ (100)." Such a spectrum for a highly unsaturated compound is certainly unusual if not unique. With this molecule there is a difficult problem regarding the geometry to be used in the calculations, because the methylene group is much too close to the *peri* position of the benzene ring if an ordinary planar geometry is maintained. The methylene must bend away from the interference, either in the plane, or perpendicular to the plane, or a combination of both. Two geometries have been considered, the planar one with a minimum of internal angular strain and bond lengths of 1·337, 1·397 or 1·483 (as directed by the Kekule forms), and the non-planar one (with the

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[11] D. J. Bertelli and C. C. Ong, presented at the meeting of the *American Chemical Society Meeting* Abstracts, p. 6P. Detroit, April (1965).

same bond lengths) in which the angular strain was minimized. The energy of the latter is 1·308 ev above that of the planar form. A van der Waals calculation[3] shows a repulsion energy between the methylene group and the offending aromatic carbon and hydrogen to be on the order of 10 kcal/mole. Rough calculations by the Hill method[3] show that bending the methylene away by about 5°, and bending the hydrogens a degree or two (keeping the molecule planar) can reduce the repulsion plus the bending strain introduced to about 4 kcal/mole. Since the π energy of the non-planar form is 30 kcal/mole above that of the planar form, one might conclude that the molecule will be very close to planar, but that there will be some appreciable in-plane deformations. Actually, the van der Waals potentials for the interactions of covalently bond carbon and hydrogen atoms are not well known, and the choice of different potential curves could lead to a very different calculated geometry.[12] Hence it is not really clear whether or not one should in fact expect the molecule to be planar. The spectra for both the planar and non-planar systems were therefore considered, and the calculated results are given in Table 3. To obviate the difficulty of attempting an objective comparison of the calculated spectra with experiment, plots of the spectra were made by a standard plotting program (described in the appendix). It was found that neither geometry gave a featureless spectrum from 210 to above 340 mμ, but the puckered form came pretty close. The calculated spectrum for the puckered form is shown in Fig. 1.

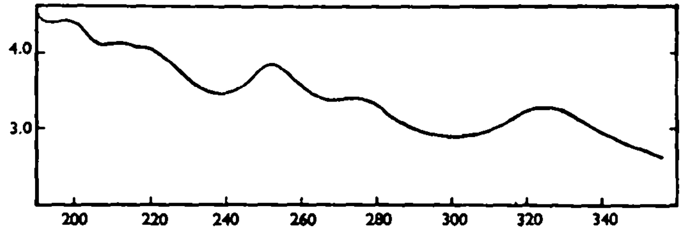

FIG. 1. The calculated UV spectrum of 2,3-benzoheptafulvene.

The agreement between calculation and experiment for the benzoheptafulvenes is not as good as desired, but would be hard to improve on without considerable effort, as there are simply too many degrees of freedom in these molecules.

Quite a lot of study has been given recently to the validity of the various approximations used in a Pariser-Parr type treatment,[13] and while most of the approximations are quite good, some are hard to really justify (neglect of σ–π interaction for example), and it is not completely clear just why the method works as well as it does.[13] This study emphasizes still another problem to be faced in the accurate prediction of electronic spectra, which is illustrated by I. The calculated band positions here may vary by 0·3 ev (not much to a theoretical chemist) or 46 mμ (quite a bit to an organic chemist) with bond length changes of 0·01–0·02 Å. Unfortunately, only for a few very simple or highly symmetrical compounds are bond lengths now known with an accuracy greater than this.

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[12] See, for example, K. B. Wiberg, *J. Amer. Chem. Soc.* **87**, 1070 (1965), and J. B. Hendrickson, *Ibid.* **83**, 4537 (1961).

[13] M. K. Orloff and O. Sinanoğlu, *J. Chem. Phys.* **43**, 49 (1965); I. Fischer-Hjalmers, *Ibid.* **42**, 1962 (1965); K. Ohno, *Theoret. Chem. Acta* **2**, 219 (1964).

Appendix

The calculations followed without change the formulations given in previous papers,[1,4] which includes all of the singly excited states (but no multiply excited states) in the configuration interaction treatment. Resonance integrals were given non-zero values only between atoms bound together. The programs have been made somewhat more efficient since the earlier papers, and the complete treatment of a molecule like benzoheptafulvene now requires about ten minutes (on the IBM 7074).

A plotting program has been obtained since the earlier paper and will be described here briefly.[14] A similar program was described earlier by Ruedenberg and Hummel.[15] A few changes were made in their approach, the most important of which was the replacement of their assumed triangular band shapes by Lorentzian shapes. In addition, since the experimental values for the oscillator strengths are ordinarily about $\frac{1}{2}$ of those obtained in this type of calculation, the theoretical values were reduced by this factor before calculating the extinction coefficients.[16] (Presumably the difference results from a partially compensating transition moment in the sigma system[17].) All theoretical spectra are calculated for the gas phase, and experimental spectra are in solution, except where otherwise stated.

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[14] The author is indebted to Dr. M. A. Miller and Mr. J. C. Graham for this program.

[15] R. L. Hummel and K. Ruedenberg, *J. Phys. Chem.* **66**, 2334 (1962).

[16] In this paper values for f are theoretical values, values of ε are calculated from $\varepsilon = 24{,}500\,f$, which allows for the empirical reduction.

[17] R. Pariser, *J. Chem. Phys.* **25**, 1112 (1956).