Tetrahedron. Vol 25, pp 631 to 639. Pergamon Press 1969. Printed in Great Britain

SEMIEMPIRICAL CALCULATIONS ON 2,3-HOMOFULVENE

W. HUG and G. WAGNIÈRE

Institute of Physical Chemistry of the University of Zürich

(*Received in the UK* 26 *August* 1968; *Accepted for publication* 10 *September* 1968)

Abstract—The electronic structure of homofulvene is examined by the Extended Hückel method. The angle between the 3- and 5-membered ring is calculated to be about 60°, in fair agreement with simple predictions based on Dreiding models. The UV spectrum of homofulvene is compared with the spectra of fulvene, dihydrofulvene and butadiene. The predicted charge distribution in homofulvene shows a rather fundamental difference to the one in fulvene, leading to an almost opposite direction for the predicted dipole moment.

THE recent synthesis of homofulvenes by Rey, Huber and Dreiding[1] and the measurements of the electronic spectra of these compounds have stimulated the present theoretical study. In particular, we have attempted to correlate the electronic properties of 2,3-homofulvene with butadiene and with fulvene. The conjugative properties of a cyclopropane ring are well known[2] and have been investigated spectroscopically[3–5] and theoretically.[6–8] Homofulvene is particularly well suited to this problem, as here the cyclopropane ring may be assumed to be sterically fixed with respect to the double bonds. However, the angle between the plane of the cyclopropane ring and the 5-membered ring has not yet been established experimentally and must consequently be assessed from extended Hückel calculations of the energy of the molecule for various geometries. Having thus determined the energy minimum, a most probable conformation is deduced, and the electronic properties, such as the energy of the electronic transitions, the charge distribution and the dipole moment are calculated within the frame of a simple one-electron model.

Methods of calculation

Extended Hückel (EH) calculations have been applied to a variety of molecules in inorganic[9–11] and organic[12] chemistry. A multitude of different variants to this general scheme have appeared in the literature and a critical examination of the basis of extended Hückel calculations has recently been published.[13] It has therefore seemed important to apply various possible modifications of the general method to the problem. As the hydrocarbons investigated do not contain hetero-atoms, we have not considered it necessary to apply also iterative methods[14] or methods taking into account inter-atomic coulomb corrections.[15] Instead our attention has been concentrated in a purely pragmatic way on the calculation of the off-diagonal matrix elements. In particular we have set:

Diagonal elements:

$H_{1s,1s} = -13{\cdot}6$ eV — for a H atom

$H_{2s,2s} = -21{\cdot}4$ eV, $H_{2p,2p} = -11{\cdot}4$ eV — for a C atom

Off-diagonal elements:

Case I $H_{pq} = k \cdot S_{pq} \cdot (H_{pp} + H_{qq})/2$ [9]

Case II $H_{pq} = -k \cdot S_{pq} \cdot \sqrt{(H_{pp} \cdot H_{qq})}$ [10]

Case III $H_{pq} = k \cdot S_{pq} \cdot 2 \cdot H_{pp} \cdot H_{qq}/(H_{pp} + H_{qq})$ [16]

Case IV $H_{pq} = (k - |S_{pq}|) \cdot S_{pq} \cdot (H_{pp} + H_{qq})/2$ [17] *

Orbitals used as a basis set were of the simple Slater type with an exponent value μ_C of 1·625 for carbon 2*s* and 2*p* orbitals. Adopted values for the hydrogen 1*s* exponent μ_H range from 1·00 to 1·20.

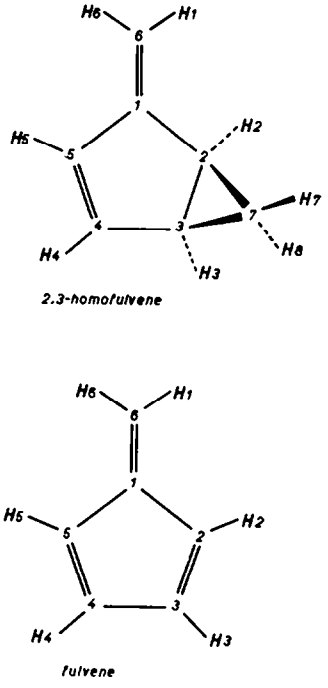


FIG. 1 Adopted numbering of atoms in fulvene and homofulvene

The conformation of homofulvene

We have considered in detail the variation of the angle α between the plane of the cyclopropane ring and the plane of the 5-membered ring (Fig. 2) and do not believe that the 5-membered ring deviates significantly from planarity. Our further assumptions are the following. All bond lengths are fixed at average experimental values for the particular types of bonds. All bond angles are fixed, of course with the exception of those depending on the positions of C7, H2, and H3 (Fig. 1). In particular, we have

* Case IV has been applied in such a way that H_{pq} remains invariant with respect to rotation of the coordinate system. See Ref. 18.

set the angles C6—C1—C2 and C6—C1—C5 equal to 126°.* Consequently the atoms C1 to C6, H1, H4—H6 all lie in the same plane and their positions are given and fixed. The positions of C7, H7 and H8 are directly and simply related to α. The positions of H2 and H3, on the other hand, require further assumptions (Fig. 2).

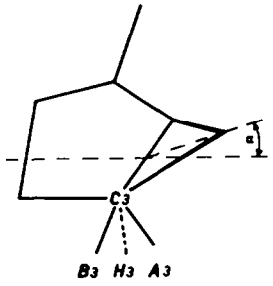


FIG. 2. The angle α. The position of the hydrogen atom H3.

These two atoms may be viewed as either (a) belonging to a (hypothetical) dihydrofulvene molecule, or (b) to a (hypothetical) cyclopropane molecule. Viewed from the point of view of (a) their positions (A_2, A_3) would remain independent of the angle α. Viewed from the point of view of (b) their positions (B_2, B_3) would change with α in a similar way as do H7 or H8. Neither view is really correct, however. We thus assume that H3 (H2) lies in a plane defined by A_3, C_3, B_3 (A_2, C_2, B_2) and on a line bisecting the angle $A_3\,C_3\,B_3$ ($A_2\,C_2\,B_2$).

The results of the calculations for the different cases I–IV are shown in Table 1.

TABLE 1. THE ENERGY AND ANGLE α FOR THE MOST STABLE CONFORMATION OF 2,3-HOMOFULVENE CALCULATED ACCORDING TO DIFFERENT APPROXIMATIONS AND DIFFERENT PARAMETERS

Case	k	μ_H	α_{min} (°)	Energy (eV)	"Energy of racemization" (eV)
I	1·75	1·00	63	−629·20	6·00
I	1·75	1·20	58	−632·82	6·16
I	2·30	1·20	59	−726·70	9·71
II	1·75	1·00	63	−624·84	5·92
III	1·75	1·00	63	−621·15	5·85
IV	2·00	1·00	58	−591·41	4·34
IV	2·55	1·00	59	−683·11	7·68
IV	2·55	1·20	58	−689·51	7·99

* We have also performed some calculations with other values for this angle. The adopted value corresponds to a relative energy minimum.

For cases I and IV the values of k and μ_H have also been varied. The greater the value of μ_H, the smaller the positive charge at the site of the H-atom in any C—H bond. α-values for which the electronic energy of the molecule is a minimum vary between 58° and 63°. This is only a minor change in comparison with the large differences in the absolute values of the total energy.* It illustrates the fact that geometric properties may be more consistently predicted by the method than absolute energies. In case IV there are practically no variations of the value of α_{min} for a different values of μ_H. This is in accord with observations by Cusachs[17] and Carroll and McGlynn[19] who reported that case IV leads to the best agreement between calculated and experimental values of bond angles in various polar hydrides. A change of the value of α from $\sim 60°$ to $\sim -60°$ leads to the opposite enantiomer. At $\alpha = 0°$ one must then also assume H2 and H3 to go through the plane of the molecule. The energy of this completely planar system, $E(\alpha = 0°)$, minus E_{min}, gives us an "energy of racemization". As may be seen in Table 1, the lowest value which we have obtained is 100 kcal/mole.

The electronic spectrum

Spectral predictions with the EH scheme are at best semiquantitative and must be viewed very cautiously. In many molecules, in particular in molecules of higher symmetry, as for instance in benzene, an interpretation of the lower electronic transitions is impossible without explicitly considering electron interaction. In the *EH* method electron interaction is explicitly neglected. Nevertheless, we have attempted to calculate the energy of the lowest electronic transitions in ethylene, butadiene, dihydrofulvene and homofulvene, as shown in Table 2. The parameter k was adjusted

TABLE 2. EXPERIMENTAL AND CALCULATED ELECTRONIC TRANSITION ENERGIES

	Experimental maxima of absorption (mμ)	Calculated transitions	
		Case I, II, III $k = 2{\cdot}3$ $\mu_H = 1{\cdot}20$	Case IV $k = 2{\cdot}55$ $\mu_H = 1{\cdot}20$
Ethylene	160	143	147
Butadiene	217	214	218
2,3-Dihydrofulvene	234	211	226
Fulvene	242 360	$a_2 \rightarrow a_2$, 243 $b_2 \rightarrow a_2$, 304	$a_2 \rightarrow a_2$, 246 $b_2 \rightarrow a_2$, 320
2,3-Homofulvene	246	214 226	231 242

on the lowest transition of butadiene. This leads to a value for k of about 2·30 for cases I–III and a value of 2·55 for case IV. Results for α_{min} are not significantly altered by the variations of k shown in Table 1. For simplicity we fixed the value of α uniformly

* See Appendix of Ref. 12.

at 60°. Case IV appears to reflect most accurately the spectral shifts encountered on going from one molecule to another. All results mentioned in the figures were obtained using case IV, with $k = 2{\cdot}55$ and $\mu_H = 1{\cdot}20$, unless indicated otherwise. The transition moments were calculated in the dipole vector form, including all crossterms, but approximating two-center integrals of the form

$$\int \chi_p \mathbf{r} \chi_q \, d\tau \quad \text{by} \quad \frac{\mathbf{r}_p + \mathbf{r}_q}{2} \cdot \int \chi_p \chi_q \, d\tau$$

where χ_p χ_q are atomic orbitals on centers p and q and $\mathbf{r}_p$ and $\mathbf{r}_q$ the corresponding position vectors.

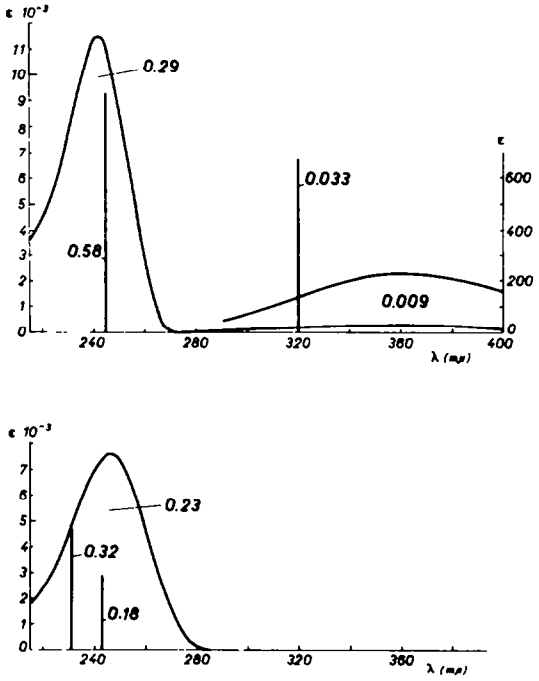


FIG. 3 Observed and calculated spectrum of fulvene (above) and homofulvene (below). The oscillator strengths are indicated; the bars representing the calculated transitions have only relative meaning and are drawn on an arbitrary absolute scale.

The observed and predicted absorptions and oscillator-strengths of fulvene[20] and homofulvene are shown in Fig. 3. The observed spectrum of fulvene is fairly well reproduced by the calculations. For homofulvene the theory predicts two allowed electronic transitions at 231 mμ and 243 mμ. This is, however, not in contradiction with the observed relatively broad single absorption band at 246 mμ. The suspicion that both calculated transitions may lie below one band is confirmed by comparison of oscillator strengths. As may be seen from the spectrum of fulvene, calculated values turn out to be 2 to 3 times the observed ones. For homofulvene this is also the case if the theoretical values for both transitions are taken together. The presence of two

transitions in the near UV as well as the comparatively large bathochromic shift must be attributed to the conjugative ability of the cyclopropane ring system. According to our calculations a second transition in butadiene and dihydrofulvene appears only around 150 mμ.

Charge distribution

Fig. 4 shows charge distributions in butadiene, fulvene and homofulvene, calculated for case IV ($k = 2{\cdot}55$, $\mu = 1{\cdot}2$). Under (a) the total net charges, as obtained by a Mulliken population analysis, are indicated. Under (b) we list the net charge of the $2p_z$ orbitals of the C atoms. In planar molecules this corresponds to the charge distribution of the π system. Under (c) we give the total net charge in the $2s$, $2p_x$, $2p_y$

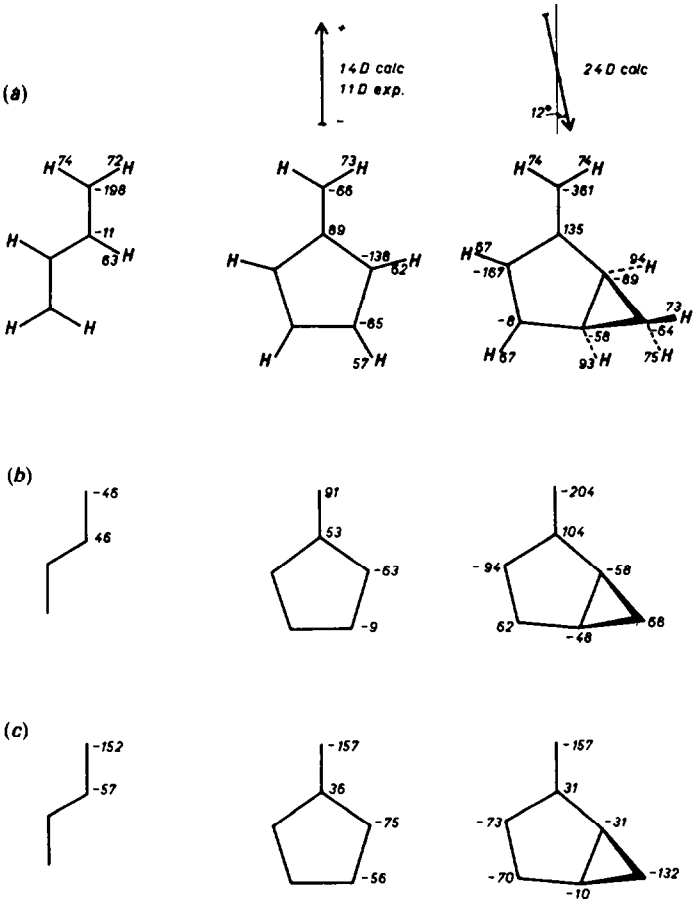
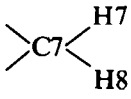


FIG. 4 (a) Total net charges in 1/1000 of the protonic charge. The projection of the calculated dipole moment onto the plane of the five-membered ring is drawn; actually it points at an angle of 13° *below* the plane. (Calculated using the same approximation as for the transition moments.)

(b) Net charges in the $2p_z$ orbitals.
(c) Net charges in the $2s$, $2p_x$ and $2p_y$ orbitals.

orbitals of the C atoms (in units of 1/1000 of the protonic charge). In a planar molecule we would call this the σ charge distribution. In homofulvene the distinction between σ and π orbitals is of course no longer strictly valid because of the absence of a plane of symmetry. However, an examination as carried out under (b) and (c), i.e. a subdivision into a "π" and "σ" charge distribution allows for an illustrative comparison with fulvene. Looking at (a) we notice a much higher negative charge on C atom 6 in homofulvene than in fulvene. This is entirely due to the different populations of the $2p_z$ orbitals, as shown by (b) and (c). While there are of course 6π electrons in fulvene, our analysis gives 6·24 "π" electrons on the C atoms 1–6 in homofulvene, the difference appearing mainly on the head atom. As the Group  as a whole exhibits only a charge of +0·084 protonic units, this increase of 0·24 in "π" electron density must come mainly from a decrease in "σ" electron density on the atoms common to both molecules. In fact we notice from (a) an unusually high positive charge on the two H atoms 2 and 3, contrary to what we would expect from their tertiary position.[12] Furthermore, the excess of electrons in the "σ" system of C atoms 1–6 (resulting from an electron transfer between H and C atoms) is reduced from 0·38 electrons in fulvene to 0·31 electrons in homofulvene. The lowering of the negative "σ" density on C atoms 2 and 3 accounts mainly for this difference.

The directions of the dipole moments of fulvene and homofulvene consequently turn out to be quite different, as shown in Fig. 4a. The calculated values for the dipole moment depend quite markedly on μ_H however. Furthermore, we find for $\mu_H = 1{\cdot}2$ a smallest value of 1·7 D in case I and a largest one of 2·4 D in case IV, while we measured a value of 0·7 D.* Though the difference between experimental and calculated results suggests that a somewhat higher value of μ_H be used, we limited it to 1·2, because otherwise calculated spectral results are impaired. In spite of these variations, the qualitative conclusions concerning the direction of the moment and the charge distribution remain unchanged.

CONCLUSIONS

Our investigation of homofulvene was preceded by a critical examination of the extended Hückel method, applied to different hydrocarbons. We notice that the four methods used (cases I–IV) to evaluate off-diagonal elements of the Hückel energy matrix may sometimes lead to rather different quantitative results. However, our main qualitative and a number of quantitative conclusions are supported in every case and for every reasonable chosen set of parameters.

For actual computations of the molecular properties of homofulvene it was necessary to establish the experimentally unknown geometry of the molecule. Starting from certain plausible assumptions concerning the dimensions of individual bonds, we used the extended Hückel method to deduce the angle between the plane of the 3- and 5-membered ring. The result of about 60° is in reasonable agreement with a simple

* This value may represent a lower limit. There is evidence from ε values of near-UV spectra that the relatively large sample of homofulvene we needed contained a significant amount of non-absorbing polymers due to rapid polymerization.

evaluation based on Dreiding models. The calculated near-UV spectrum of homofulvene shows more qualitative resemblance with the spectrum of fulvene than with the spectra of butadiene or dihydrofulvene. The long-wave-length absorption of fulvene appears however in homofulvene to be shifted to much shorter wavelength. It may therefore be hidden experimentally by the more intense absorption at 231 mμ. This situation may indicate some spectroscopic similarity between the conjugative properties of a carbon–carbon double bond and a cyclopropane ring system. On the other hand, the calculation of the charge distribution also makes obvious some marked differences, arising mainly from the fact that homofulvene is non-planar. This non-planarity allows the mixing of orbitals which we associate with the σ and π systems respectively in planar molecules. There is only a slight drift of charge from the CH_2-group of the cyclopropane ring—contrary to what one might expect from chemical intuition—, but rather a reorganization of charge within the rest of the molecule. It thus appears that deviation from planarity in itself leads to a more profound change in the charge distribution than the mere presence of additional atoms. Because of this fundamental difference in the charge distribution of fulvene and homofulvene the directions of the two dipole moments are practically opposed to one another. We suspect that analogous situations may be encountered in other compounds and that some effects of the presence of alkyl groups in otherwise planar systems (e.g. toluene) can be discussed in similar terms. Although a direct correlation of these results with chemical reactivity is difficult, we hope that they may stimulate further chemical research.

Acknowledgement—We thank Professor A. Dreiding and Mr. M. Rey for a sample of homofulvene, which enabled us to measure the dipole moment.

The extended Hückel calculations were performed on the IBM 360-40 computer of the Institute for Operations Research and Electronic Data Processing of the University of Zurich. An EH computer program was obtained by the Quantum Chemistry Program Exchange. It was then modified and expanded to include additional subroutines by one of us (W.H.).

REFERENCES

[1] M. Rey, U. A. Huber and A. S. Dreiding, *Tetrahedron Letters* 3583 (1968).
[2] N. C. Deno, *Progr. Phys. Org. Chem.* **2**, 148 (1964) and Refs cited therein.
[3] C. U. Pittmann, Jr., and G. A. Olah, *J. Am. Chem. Soc.* **87**, 5123 (1965).
[4] A. L. Goodman and R. H. Eastman, *Ibid.* **86**, 908 (1964).
[5] G. L. Closs and H. B. Klinger, *Ibid.* **87**, 3265 (1965).
[6] R. Hoffmann, *J. Chem. Phys.* **40**, 2480 (1964).
[7] R. Hoffmann, *Tetrahedron Letters* 3819 (1965).
[8] T. Yonezawa, H. Nakatsuji and H. Kato, *Bull. Chem. Soc. Japan* **39**, 2788 (1966).
[9] M. Wolfsberg and L. Helmholz, *J. Chem. Phys.* **20**, 837 (1952).
[10] C. J. Ballhausen and H. B. Gray, *Inorg. Chem.* **1**, 111 (1962).
[11] R. Hoffmann and W. N. Lipscomb, *J. Chem. Phys.* **36**, 2179, 3489 (1962); **37**, 2872 (1962).
[12] R. Hoffmann, *Ibid.* **39**, 1397 (1963).
[13] G. Blyholder and C. A. Coulson, *Theoret. Chim. Acta* **10**, 316 (1968).
[14] B. J. Duke, *Ibid.* **9**, 260 (1968) and Refs cited therein.
[15] P. Ros and G. C. A. Schuit, *Ibid.* **4**, 1 (1966).
[16] W. A. Yeranos, *J. Chem. Phys.* **44**, 2207 (1966);
W. A. Yeranos and D. A. Hasman, *Z. Naturf.* **22a**, 170 (1967).
[17] L. C. Cusachs, *J. Chem. Phys.* **43**, S157 (1965);
Ibid. **71**, 1060 (1967).

[18] N. D. Newton, *Ibid.* **45**, 2716 (1966).
[19] D. G. Carroll and S. P. McGlynn, *Ibid.* **45**, 3830 (1966).
[20] D. Meuche, M. Neuenschwander, H. Schaltegger and H. U. Schlunegger, *Helv. Chim. Acta* **47**, 1211 (1964).