Studies of Conjugated Ring Hydrocarbons. II.[1a,b] Structure of Spiro[2.4]hepta-4,6-diene

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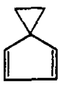
Abstract: The structure of spiro[2.4]hepta-4,6-diene has been determined by electron diffraction in the gas phase. The internuclear distances and bond angles were obtained by applying a least-squares analysis to the experimental molecular intensities. The conjugated carbon–carbon double bond in the five-membered ring was found to be 1.341 ± 0.003 Å. The sp^2–sp^2 single bond between the two double bonds is 1.460 ± 0.005 Å while the sp^2–sp^3 single bond is 1.509 ± 0.002 Å. The C–C bonds in the three-membered ring are 1.510 ± 0.002 Å. The angle $C_2C_3C_4$ = 1–9.5 ± 0.2°. The three-membered ring is perpendicular to the five-membered ring and bisects the angle $C_2C_1C_4$. From these data it follows that the three-membered ring shows little interaction with the five-membered ring, a conclusion opposite to that drawn from nmr data.

The hydrocarbon spiro[2.4]hepta-4,6-diene (**1**) has been investigated by ultraviolet[2] and nmr[3] spectroscopy for evidence of electron delocalization of the strained three-membered ring bonds into the cyclopentadiene ring. In both studies there were implicit assumptions regarding the structure of **1**. The present paper describes the results of an electron diffraction structure determination of **1** and compares it with those of dimethylfulvene (**2**) and cyclopentadiene (**3**). The degree of cyclopropyl conjugation is examined in light of these structural parameters.



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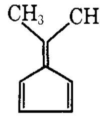

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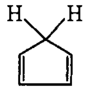

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Experimental Section

A sample of spiro[2.4]heptadiene was prepared as described earlier[2] and purified by distillation. Glpc analysis indicated greater than 99% peak purity.

Sectored electron diffraction patterns were taken with the Cornell instrument[4] on Kodak Electron Image plates. Two sets of data were obtained for this compound under the following conditions: 65 kV at 262.4 mm sample-to-plate distance covered the angular range from q = 10–54 Å^{-1}, and 65 kV, 129.4 mm, covered the range q = 43–115 Å^{-1} [$q = (40/\lambda) \sin \theta/2$].

Three plates were taken at each distance with exposures ranging from 15 to 90 sec at a beam current of 0.3 μA. The sample was kept at −20° during scattering. MgO diffraction patterns were also recorded concurrently to establish the scale factor. The patterns were microphotometered with a double beam Jarrell-Ash microdensitometer interfaced with a digital recorder[5] (each plate was measured twice and the readings averaged). The procedure for data reduction and structure analysis has been described in several previous publications.[6] The elastic and inelastic form factors of Tavard, *et al.*,[7] were used in conjunction with the Ibers and Hoerni[8] phase-shift approximation in the intensity calculations.

Analysis and Results

The total experimental intensity curves for the two sets of data along with the refined background are plotted in Figure 1. The data are given in Table I. The reduced experimental molecular intensity curve and that calculated for the best model are compared in Figure 2; the lower oscillating curve is the difference curve between the experimental and theoretical curves. The refined radial distribution curve and the difference between that and the best theoretical radial distribution curves are shown in Figure 3. C_2 and C_{2v} symmetries have been assumed for calculating the geometry of spiro[2.4]heptadiene. For C_{2v} symmetry, the following geometrical parameters were used (the numbering is given in Figure 4): C_1–C_2, C_1–C_3, C_3–C_4, C_4=C_5, C_5–C_6, C_2–H_{14}, C_7–H_8, $\angle C_5C_6C_7$ (α), $\angle C_5C_6H_9$ (δ), $\angle H_{12}C_3H_{13}$ (β), and θ, the angle between C_7–H_8 and the x-axis. For C_2 symmetry, in addition to the above-mentioned geometrical parameters, another parameter is also used, the angle between the planes of the five-membered and three-membered rings. None of the C_2 symmetry models tried fit the experimental intensity better than the C_{2v} symmetry model, and when the parameters were allowed to vary, the structure always converged on the C_{2v} structure shown in Figure 4. The Cartesian coordinates are given in Table II. The values of all geometrical parameters and some of the mean amplitudes of vibration, l_{17}, l_{12} (l_{23}), l_{56}, l_{67}, were refined by applying a least-squares analysis on the reduced molecular intensity. All the geometrical parameters and the above-mentioned mean amplitudes of vibration were allowed to vary, except the C–H distances which were determined from the radial distribution function. All other mean amplitudes of vibrations were chosen at values which had previously been determined for typical hydrocarbons. The final values of the parameters are listed in Table III. The error matrix is reproduced in Table IV. The error limits cited in Table III are three times the standard devia-

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[1] (a) Presented, in part, at the 162nd National Meeting of the American Chemical Society, Washington, D. C., Sept 12–17, 1971; (b) part I: J. F. Chiang and S. H. Bauer, *J. Amer. Chem. Soc.*, **92**, 261 (1970); (c) State University of New York; (d) Cornell University.

[2] C. F. Wilcox, Jr., and R. R. Craig, *J. Amer. Chem. Soc.*, **83**, 4258 (1961).

[3] R. A. Clark and R. A. Fiato, *ibid.*, **92**, 4736 (1970).

[4] S. H. Bauer and K. Kimura, *J. Phys. Soc. Jap.*, **17**, 300 (1962).

[5] J. F. Chiang and S. H. Bauer, *Trans. Faraday Soc.*, **64**, 2247 (1968).

[6] K. Kimura and S. H. Bauer, *J. Chem. Phys.*, **39**, 3171 (1963); J. L. Hencher and S. H. Bauer, *J. Amer. Chem. Soc.*, **89**, 5527 (1967).

[7] C. Tavard, D. Nicholas, and M. Rouault, *J. Chim. Phys. Physicochim. Biol.*, **64**, 540 (1967).

[8] J. A. Ibers and J. A. Hoerni, *Acta Crystallogr.*, **7**, 405 (1954).

Table I. Set 1

q	Intensity	q	Intensity	q	Intensity	q	Intensity	q	Intensity
10	1.4317	34	0.4932	43	0.5693	68	0.2297	93	0.3152
11	1.4511	36	0.4617	44	0.5675	69	0.2304	94	0.3238
12	1.3804	37	0.4504	45	0.5460	70	0.2327	95	0.3308
13	1.2382	38	0.4558	46	0.5053	71	0.2335	96	0.3372
14	1.1640	39	0.4593	47	0.4539	72	0.2326	97	0.3432
15	1.2764	40	0.4491	48	0.4058	73	0.2296	98	0.3470
16	1.5426	41	0.4355	49	0.3722	74	0.2253	99	0.3500
17	1.8179	42	0.4330	50	0.3504	75	0.2250	100	0.3550
18	1.9203	43	0.4421	51	0.3358	76	0.2277	101	0.3595
19	1.7567	44	0.4550	52	0.3293	77	0.2328	102	0.3662
20	1.4384	45	0.4555	53	0.3278	78	0.2388	103	0.3723
21	1.1457	46	0.4396	54	0.3276	79	0.2438	104	0.3802
22	0.9648	47	0.4130	55	0.3266	80	0.2463	105	0.3876
23	0.8659	48	0.3897	56	0.3180	81	0.2494	106	0.3980
24	0.7923	49	0.3728	57	0.3010	82	0.2538	107	0.4071
25	0.7670	50	0.3664	58	0.2836	83	0.2566	108	0.4150
26	0.7914	51	0.3702	59	0.2755	84	0.2593	109	0.4222
27	0.8465	52	0.3816	60	0.2723	85	0.2620	110	0.4285
28	0.8860	53	0.4105	61	0.2688	86	0.2650	111	0.4340
29	0.8804	54	0.4396	62	0.2607	87	0.2700	112	0.4400
30	0.8173			63	0.2477	88	0.2760	113	0.4440
31	0.7295			64	0.2378	89	0.2815	114	0.4478
32	0.6447			65	0.2321	90	0.2895	115	0.4540
33	0.5805			66	0.2304	91	0.2971		
34	0.5326			67	0.2297	92	0.3060		

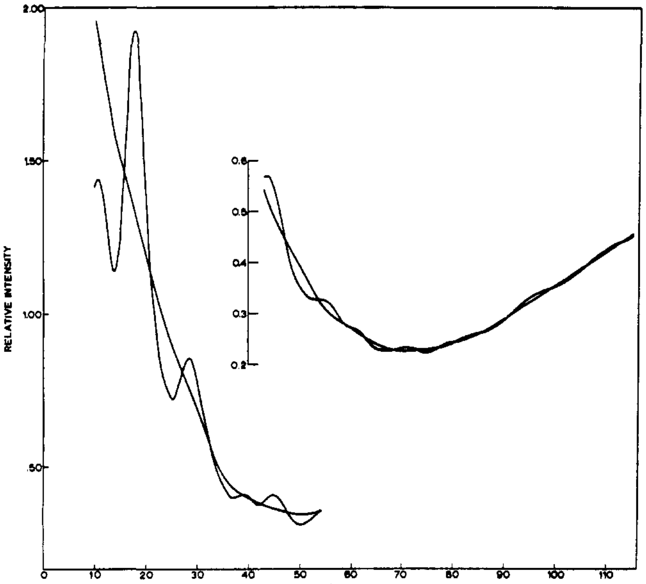

Figure 1. Relative intensities as a function of diffraction angle [$q = (40/\lambda) \sin \theta/2$] for long and short sample-plate distances and the refined background.

Table II. Coordinates of Spiro[2.4]heptadiene

	x	y	z
C_1	0.00	2.2077	0.00
C_2	0.00	3.5154	0.7550
C_3	0.00	3.5154	−0.7550
C_4	−1.1779	1.2637	0.00
C_5	−0.7301	0.00	0.00
C_6	0.7301	0.00	0.00
C_7	1.1779	1.2637	0.00
H_8	2.2608	1.4568	0.00
H_9	1.4558	−0.8266	0.00
H_{10}	−1.4558	−0.8266	0.00
H_{11}	−2.2608	1.4568	0.00
H_{12}	0.9395	3.8203	1.2830
H_{13}	−0.9395	3.8203	1.2830
H_{14}	0.9395	3.8203	−1.2830
H_{15}	−0.9395	3.8203	−1.2830

Table III. Structural Parameters and Vibrational Amplitudes of Spiro[2.4]heptadiene

	r_{ij}, Å	l_{ij}, Å
C_1–C_2	$1.510_1 \pm 0.005_4$	$0.063_3 \pm 0.005_7$
C_1–C_4	$1.509_4 \pm 0.003_3$	$0.0610_0 \pm 0.009_3$
C_2–C_3	$1.509_8 \pm 0.011_4$	$0.063_3 \pm 0.005_7$
C_4=C_5	$1.340_7 \pm 0.002_1$	$0.050_3 \pm 0.002_4$
C_5–C_6	$1.460_4 \pm 0.005_4$	$0.059_2 \pm 0.002_4$
C_3–H_{12}	1.120	
C_7–H_8	1.100	
$\angle C_5C_6C_7$	109.5 ± 0.2°	
$\angle C_5C_6H_9$	131.3 ± 0.6°	
θ	10.1 ± 0.3°	
$\angle H_{12}C_3H_{13}$	114.0 ± 0.3°	

tions which are the diagonal elements of the error matrix. The R_f value was 0.0406.

The sensitivity of the least-squares structure fit to small variations of the twist angle of the three-membered and five-membered rings about the C_2 axis was explored. In a structure refinement in which the rings were constrained to a 5° twist about the C_2 axis the bonded distances showed no appreciable changes but the R_f value increased to 0.051. Application of the F test[9] (92 degrees of freedom, 15 parameters) to the increase in R_f value indicated that the 5° twisted structure could be rejected at better than the 10^{-8} significance level; *i.e.*, if the twisted structure were correct, there is only one chance in 10^8, assuming random errors, that the observed ratio of variances would be found.

In Figure 3, the first peak is due to C_7–H_8 = 1.100 Å, C_3–H_{12} = 1.120 Å, H_{12}–H_{13} = 1.879 Å, and all bonded carbon–carbon distances: C_4–C_5 = 1.341 Å, C_5–C_6 = 1.460 Å, C_1–C_4 = 1.509 Å, and C_1–C_2 = 1.510 Å. The peaks between 1.90 and 3.0 Å are contributed by C···C nonbonded distances, C_4–C_6 = 2.289 Å,

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[9] (a) W. C. Hamilton, "Statistics in Physical Science," Ronald Press, New York, N. Y., 1964, pp 157–162; (b) "Handbook of Mathematical Functions," M. Abramowitz and I. A. Stegun, Ed., Report No. NBS-AMS 55, U. S. Government Printing Office, Washington, D. C., 1964, eq 26.6.15 and Tables 26.1 and 26.2.

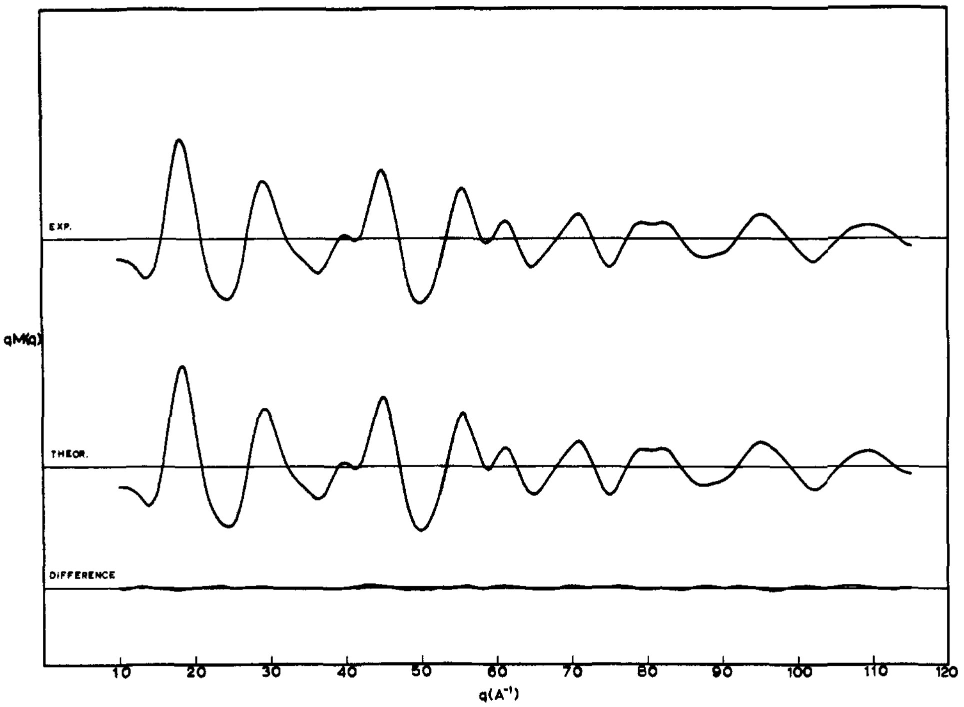

Figure 2. The experimental and theoretical $qM(q)$ curves; the lower oscillating curve is the difference between the theoretical and experimental curves.

Table IV. Error Matrix of Spiro[2.4]heptadiene

	C_1–C_4	C_4=C_5	C_5–C_6	C_1–C_2	α	δ	θ	β	C_2–C_3	l_{14}	l_{14} (l_{23})	l_{45}	l_{56}
C_1–C_4	0.0011												
C_4=C_5	−0.0006	0.0007											
C_5–C_6	−0.0012	−0.0006	0.0018										
C_1–C_2	−0.0014	0.0008	0.0015	0.0018									
α	−0.0020	0.0047	−0.0057	0.0045	0.0392								
δ	−0.0036	0.0073	−0.0114	0.0043	0.0496	0.2024							
θ	0.0040	0.0022	−0.0052	−0.0044	0.0198	0.0942	0.0966						
β	0.0042	−0.0035	−0.0012	−0.0065	−0.0363	0.0621	0.0505	0.0838					
C_2–C_3	0.0020	−0.0012	−0.0021	−0.0025	−0.0073	0.0061	0.0069	0.0110	0.0038				
l_{14}	0.0008	−0.0014	0.0015	−0.0011	−0.0092	−0.0148	−0.0055	0.0043	0.0017	0.0031			
l_{12} (l_{23})	−0.0007	0.0011	−0.0010	0.0009	0.0069	0.0108	0.0042	−0.0021	−0.0014	−0.0024	0.0019		
l_{45}	−0.0006	0.0007	−0.0006	0.0008	0.0047	0.0068	0.0009	−0.0045	−0.0013	−0.0013	0.0010	0.0008	
l_{36}	−0.0017	0.0016	0.0007	0.0021	0.0100	0.0136	−0.0036	−0.0104	−0.0034	−0.0029	0.0022	0.0017	0.0008

C_1–C_5 = 2.325 Å, C_4–C_7 = 2.356 Å, C_3–C_4 = 2.651 Å; nonbonded C–H distances, C_4–H_{10} = C_6–H_8 = 2.110 Å, C_1–H_8 = 2.382 Å and C_7–H_{12} = 2.870 Å; and some nonbonded H–H distances. The last peak centered at r = 3.66 Å is mainly due to C_3–C_6 = 3.699 Å, and some further nonbonded C–H distances and H–H distances. Most of the internuclear distances are represented by vertical lines along the abscissa, with their heights proportional to the quantity, $n_{ij}Z_iZ_j/r_{ij}$, where n_{ij} is the number of atom pairs at the distances r_{ij}, with atomic numbers Z_i and Z_j.

Discussion

According to the Walsh model for cyclopropane,[10] the C–H bonds are formed from the overlap of H 1s orbitals with the sp^2 hybridized orbitals centered on carbon. The remaining sp^2 orbitals, one for each carbon, and the set of three in-plane p orbitals combine to produce a strongly bonding a_1' level and a slightly bonding e' combination. The e' levels have π-like character in the plane of the three-membered ring and it is these orbitals that are responsible for cyclopropane

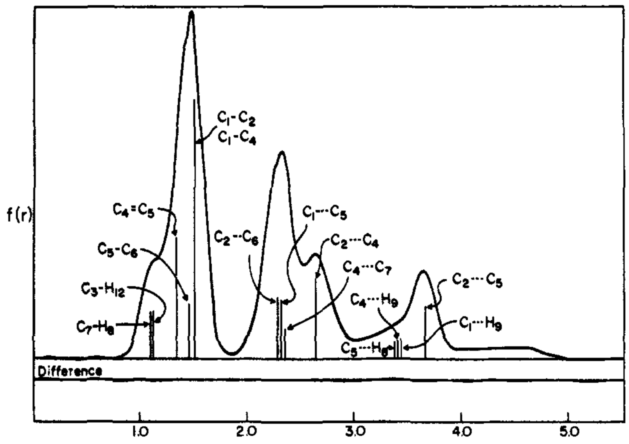

Figure 3. Experimental radial distribution curve and the difference between the experimental and theoretical curves for the best model.

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(10) A. D. Walsh, *Nature (London)*, **159**, 712 (1947); *Trans. Faraday Soc.*, **45**, 179 (1949).

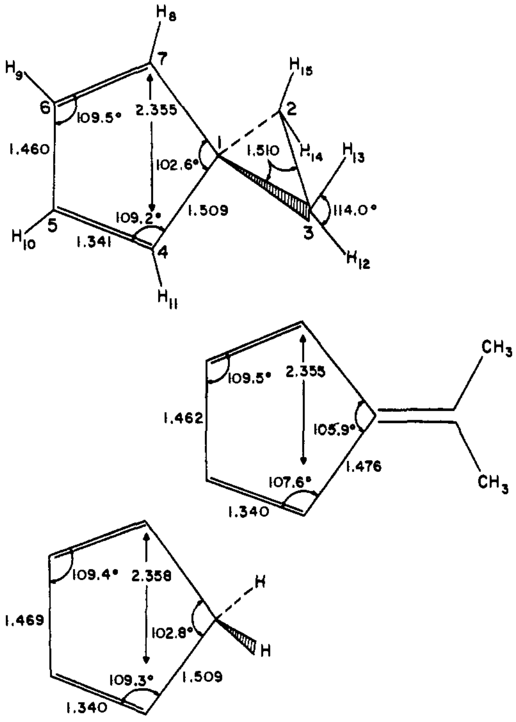
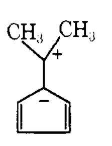


Figure 4. The structure of spiro[2.4]heptadiene and comparison of skeletal dimensions with dimethylfulvene and cyclopentadiene.

having properties intermediate between ethylene and unstrained saturated hydrocarbons.[11]

The structures of the three hydrocarbons, **1**, **2**, and **3**, are compared in Figure 4. In forming the cyclopentadienyl anion from cyclopentadiene, it is supposed that the bond lengths become equal as a result of the complete delocalization of the charge generated at the methylene carbon. If the lengths of isolated double (1.339 Å) and single (1.483 Å for sp^2–sp^2 hybridization) bonds[12] are compared with the analogous bonds of **2** and **3**, it can be seen that there is no significant indication of such delocalization in either **1** or **2**. It can be concluded that the set of resonance structures such as **4** containing a formal cyclopentadienyl anion does not make a significant contribution to the ground state of **2**. This conclusion has been reached independently from the ultraviolet spectra of **2** and related compounds.[13] In the same way, the set of structures related to **5** is of little significance for the ground state of **1**. The stabilization gained in forming a 6-π-electron network is clearly insufficient to overcome the gain in energy required to form either a tertiary cation in **2** or what would seem to be worse a highly distorted primary cation in **1**. The lack of delocalization is in contrast to the result with a neighboring cation center for which such electron delocalization is extremely important.[11] The difference in stabilization by both an isobutenyl group reflects the much greater electron affinity of an alkyl cation (*ca.* 11 eV) *vs.* a cyclopentadienyl radical (*ca.* 1 eV).[14]



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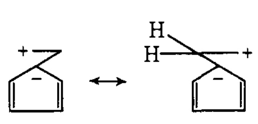

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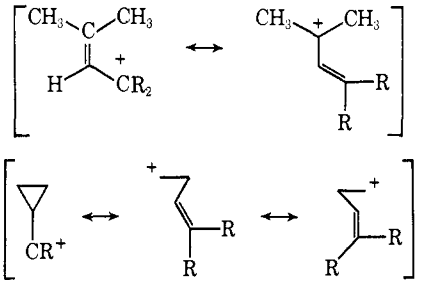
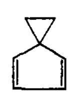
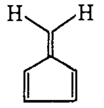
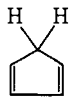
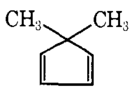


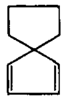
The conclusion that little cyclopropyl bond delocalization occurs in the ground state is supported indirectly by the ultraviolet spectrum of **1** compared to the spectra of related hydrocarbons. Whereas **1** shows uv maxima at 223 and 257 nm, fulvene (**6**) shows maxima at 242 and 362 nm. These maxima are to be compared to the maxima of cyclopentadiene (**3**) at 197 and 240 nm, of 5,5-dimethylcyclopentadiene (**7**) at 250 nm, and of spiro[4.4]nona-2,4-diene (**8**) at 254 nm. In a qualitative sense the double bond clearly shows much more interaction than the cyclopropane ring. Since the spectrum of fulvene has been interpreted[13,15] as not involving delocalization in the ground state but only in the excited states, it seems reasonable to conclude that the ground state of **1** shows little delocalization. A more quantitative statement is unwarrented because of the uncertainties in specific band identification in **1** and in the comparison of absorption maxima rather than 0–0 transitions.











1	**6**	**3**	**7**	**8**
223 nm	242 nm	197 nm	<210 nm	<210 nm
257 nm	362 nm	240 nm	250 nm	254 nm

Further support for the conclusion of little charge delocalization in **1** comes from an extended Hückel calculation. For the geometry shown in Figure 4 the charge transfer from carbon atoms 6 and 7 is calculated to be less than 0.01 electron (e). Even when a geometry is assumed that makes all of the five-membered ring bonds equal to 1.40 Å, the calculated charge transfer is less than 0.02 e. In both geometries there is calculated to be considerable charge transfer from carbon 1 to atoms 2, 3, 4, and 5 (*0.17* and *0.21* e, respectively) as would be expected for a tetrasubstituted carbon. In a CNDO/2 calculation the amount of charge transfer was found to be even less.

Clark and Fiato[3] have discussed the ^1H nmr spectrum of **1** which shows cyclopropane hydrogen absorp-

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(11) For a review of the interaction of cyclopropyl groups with unsaturated centers, see M. Hanack and H. J. Schneider, *Agnew. Chem.*, 79, 709 (1967).

(12) For a survey of carbon–carbon lengths and individual references, see D. R. Lide, Jr., *Tetrahedron*, 17, 125 (1962).

(13) R. Weiss and J. N. Murrell, *ibid.*, 26, 1131 (1970).

(14) G. Diercksen and H. Pruess, *Z. Naturforsch. A*, **21**, 863 (1966), and references cited therein.

(15) E. Heilbronner, *Theor. Chim. Acta*, **4**, 64 (1966); P. A. Straub, D. E. Meuche, and E. Heilbronner, *Helv. Chim. Acta*, **49**, 517 (1966). These conclusions receive further support from a variety of calculations on the ground state of fulvene and a comparison with its thermochemical properties: T. Nakajima and S. Katagiri, *Bull. Chem. Soc. Jap.*, **35**, 910 (1962); A. L. H. Chung and M. J. S. Dewar, *J. Chem. Phys.*, **42**, 756 (1962); M. J. S. Dewar and G. J. Gleicher, *J. Amer. Chem. Soc.*, **87**, 685, 692 (1965).

tion at δ 1.62, a value that is about 1.0 ppm larger than would be expected from model compounds. These workers have demonstrated for a series of neutral and charged species an excellent linear correlation of C_{sp} 2-H chemical shift with charge density on carbon calculated from the Hückel molecular orbital model. From this correlation and the assumption that the cyclopropane hydrogens behave like C_{sp} 2-H protons in the nmr, they calculate that as much as 15% of an electron has been transferred to the five-membered ring of **1** in the ground state. If the five-membered ring had 15% cyclopentadienyl character and this were reflected proportionately[16] in the bond lengths then the bond lengths of C_1–C_4, C_1–C_7, and C_5–C_6 would have decreased by about 0.02 Å and C_4–C_5 and C_6–C_7 would have increased by about 0.008 Å. At least-squares refinement of the diffraction data with the C_1–C_4 = C_1–C_7 bond lengths constrained to 1.4945 Å ($\Delta = -0.015$ Å) and the remaining parameters allowed to vary freely gave an R_f value of 0.055 which means that this alternate model can be rejected at the 10^{-10} significance level. It follows that one of the two measures of delocalization is unreliable.

We see no simple resolution of this direct conflict[17,18] but there are several more involved explanations that need to be considered. It might be argued that all of the structure data are wrong and that both the extended Hückel and the CNDO/2 calculations are inappropriate models for the real molecule. We feel the structural parameters are correct on this point since a deliberate effort to make the bonds more nearly equal in the parameter refinement converged to the present results. Further, the extended Hückel model and the CNDO/2 model represent different balances between symmetry effects and electrostatic effects. Since both agree in predicting a small charge delocalization we feel the result is probably correct. To this can be added the weight of the uv spectral interpretations which are qualitatively in accord with the localized structure.

Alternatively, it might be argued that the chemical shifts of cyclopropyl hydrogens (which are shifted upfield in most cyclopropyl compounds by about 3.0 ppm) relative to the values calculated from the empirical correlations[19] against n in the estimated sp^n hybridization are peculiarly sensitive to withdrawal of charge from the cyclopropane ring. That is to say that the concept of delocalization propounded by Clark and Fiato is correct in principle but that the empirical linear correlation employed grossly overestimates the delocalization. Since the basis for the upfield shift of cyclopropyl hydrogens is so poorly understood, this possibility can not be evaluated critically at present. Given the combined weight of structural data, ultraviolet spectra, and numerical calculations we favor this alternative. Clearly, a more fundamental examination of the relation of charge transfer of the type discussed here on aromaticity and nmr shifts is in order.

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[16] A series of simple Hückel calculations using iteratively determined distance dependent resonance integrals was carried out and the results used to calculate both the bond distances and the McWeeny ring current [*Mol. Phys.*, 1, 311 (1938)]. A linear relationship between calculated ring current and C_1–C_4 bond length was found. The details of this calculation will be described elsewhere.

[17] A possible contributing factor to the downfield shift of the cyclopropane ring hydrogens is the unusually small C_4–C_1–C_7 angle (compared to normal external cyclopropane bond angles) which might introduce additional π character into the cyclopropane ring bonds and thereby induce electron displacements from the C_2 and C_3 atoms. Such an argument presumes that the corresponding angles of the many reference compounds cited by Clark and Fiato are nearer the normal angle.

[18] Professor Clark has indicated (private communication) that the nmr analysis may overestimate the degree of electron polarization.

[19] M. Randic and Z. Majerski, *J. Chem. Soc. B*, 1289 (1968).