this stabilization will be much smaller than 25 kcal/mol, but it will certainly play some role. Thus, while an identification of the 6.7 pK_a as due to His-57 would, in our opinion, definitively show the triple ion as the relevant species during catalysis, its identification as due to Asp-102 would not rule out the triple ion, since the presence of the incipient serine oxyanion could only change the proton positions in the direction of the triple-ion structure.

Conclusions

The most important conclusion of this paper is that the triple-ion structure is lower in energy than the double proton-transfer structure, even for a simple "gas-phase" model. This is in contrast to the conclusions of previous studies,[6–9] which found the double proton-transferred structure favored. In fact, our uncorrected STO-3G calculations would conclude similarly to the semiempirical studies[6–9] that the double proton-transferred structure is more stable than the triple ion by ~30 kcal/mol. When we correct the STO-3G calculations for proton affinity errors in the monomers, the triple ion is *more* stable by 26 kcal/mol; 4-31G calculations on dimers plus model corrections for nonadditivity find the triple ion *more* stable by 6 kcal/mol, and direct 4-31G trimer calculations find the triple ion *more* stable by 7 kcal/mol.

It is clear that modeling enzyme mechanisms using minimal basis ab initio or semiempirical methods is unreliable unless corrections such as employed here are applied. These corrections are not totally satisfactory (see above) but are superior to uncorrected values. Another, even better, compromise is to use 4-31G ab initio calculations on dimers and simple model systems to estimate nonadditivities in order to calculate the energetics of proton-transfer reactions.

Given that the triple ion and the double proton-transferred structure are of comparable stability in the gas phase, general or specific solvation effects considered in this paper would further stabilize the triple ion.

Furthermore, it would be an entropic advantage for an enzyme to use only a single proton transfer, rather than requiring the precise alignment of all three residues for concerted proton transfer in its mechanism. This is particularly true since the proton must be delivered back to the substrate before the acyl enzyme can be formed. Thus, our calculations support the view of the enzyme mechanism of ref 33–35 and not those of ref 31 and 32. The use of experimental model systems for "charge-relay" catalysis in aqueous solutions have led to similar conclusions.[38]

Acknowledgment. We are pleased to acknowledge the NIH (Grant CA-25644) and the NRCC for support of this work. Discussions with Tony Fink, George Kenyon, Wim Hol, Peter Desmeulles, and Lee Allen were essential to the study; Kenyon suggested the subtilisin–chymotrypsin electrostatic potential comparison, Fink suggested the papain conformational change, Hol brought the inactivity of thiosubtilisin to our attention, and we learned from Desmeulles and Allen of their recent calculations on Im···HCOOH and ImH^+···^-OOCH, which interpret the pK_a of 7 as due to His-57.

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(38) G. Rogers and T. C. Bruice, *J. Am. Chem. Soc.* **1974**, *96*, 2473.

(39) **Note Added in Proof**: A recent study by NaKagawa et al. (*Chem. Pharm. Bull.* **1980**, *28*, 1342), employing a somewhat different geometrical model than that used here and a 431-G basis set, concludes similarly to our previous study[13] and this work that the "triple ion" is more stable than the "double proton transferred" structure. T. Kosiakoff (personal communication) has shown, using neutron diffraction on DIP inhibited trypsin, that a "triple ion" (Asp^- His^+ $>PO_2^-$) rather than a "double proton transferred" (Asp His $>PO_2^-$) structure exists in the active site of this enzyme inhibitor complex. This is strong evidence for this type of structure in the transition state of enzyme substrate complexes as well.

Complete Microwave Structure and Electron Distribution for Spiro[2.4]hepta-4,6-diene

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Abstract: Microwave spectra of the normal and seven additional isotopic species of spiro[2.4]hepta-4,6-diene have been observed and analyzed. The resulting rotational constants yield a complete substitution (r_s) structure with the following bond lengths: $C_1C_2 = 1.494 \pm 0.003$, $C_1C_3 = 1.546 \pm 0.003$, $C_3C_4 = 1.462 \pm 0.003$, $C_4C_5 = 1.361 \pm 0.004$, $C_5C_6 = 1.467 \pm 0.003$, $C_1H_{12} = 1.079 \pm 0.002$, $C_4H_{10} = 1.095 \pm 0.007$, $C_5H_8 = 1.080 \pm 0.002$. Ab initio quantum mechanical calculations at the STO-3G and 6-31G levels have been utilized to describe the electron distribution and to rationalize various experimental results. Both the experimental and the theoretical results provide strong evidence for π-electron donation from the cyclopropyl ring to the cyclopentadiene ring. This π conjugation makes an important contribution to the molecular dipole moment and is the principal factor in determining the changes in C–C bond lengths relative to the parent ring systems.

Introduction

In an earlier communication[1] we presented microwave and theoretical evidence for a conjugative interaction of the cyclopropyl ring with the diene system in spiro[2.4]hepta-4,6-diene (see Figure 1). We report here the complete microwave substitution (r_s) structure for this interesting C_7H_8 hydrocarbon and provide further theoretical interpretation of the results. An earlier electron diffraction structure[2] is apparently in error, reflecting again the previously encountered difficulty of sorting out similar but inequivalent C–C bond lengths from gas diffraction data. Current work represents a continuation of our fundamental studies of structure and bonding in cyclic systems.[3,4]

[†] University of Kansas.
[‡] University of Nebraska.

(1) S. W. Staley, A. E. Howard, M. D. Harmony, S. N. Mathur, M. Kattija-Ari, J.-I. Choe, and G. Lind, *J. Am. Chem. Soc.*, **102**, 3639 (1980).

(2) J. F. Chiang and C. F. Wilcox, Jr., *J. Am. Chem. Soc.*, **95**, 2885 (1973).

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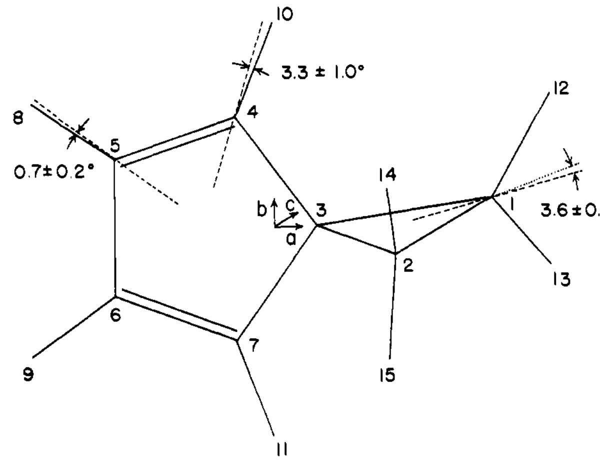
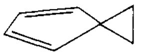


Figure 1. Spiro[2.4]hepta-4,6-diene in the principal axis system. Carbon atoms are numbered 1–7, hydrogen atoms 8–15. The angles represent methine and methylene group tilts.

Experimental Section



1

Spiro[2.4]hepta-4,6-diene (1) was prepared by the method of Wilcox and Craig[5] and purified by gas chromatography on a 1-m 10% Carbowax 20M on 80/100 mesh Chromosorb W column at 70 °C. Detailed infrared spectra (neat, 0.25-mm NaCl cells) are given in order to facilitate comparison with labeled compounds (strong intensity unless otherwise indicated, m = medium, w = weak, br = broad, sh = shoulder): 3125 (m), 3095, 3080, 3015, 1623 (br, m), 1484, 1448, 1430, 1270, 1083, 1055, 1025, 997, 959 (br, sh), 935 (m), 872 (m), 814, and 782 cm^{-1}.

Spiro[2.4]hepta-4,6-diene-*1-d* was prepared and purified by the procedure used for **1** by employing 1,2-dibromoethane-*d*, which had been prepared by the photochemical addition[6] of deuterium bromide[7] to vinyl bromide. Mass spectrometry indicated that the sample was 97% d$_1$. IR (neat): 3125 (m), 3095, 3080, 3045 (m), 3015, 2985 (br, w), 2265 (m), 1714 (br, m), 1621 (br), 1483, 1442, 1392 (w), 1373 (w), 1338 (w), 1321, 1204, 1185, 1128 (m), 1084, 1045, 998, 983 (sh), 954 (br), 941 (sh), 874 (m), 816, 781, 728, 708 (sh), and 685 (m) cm^{-1}. Weak bands have been listed only if they have no counterpart within 3 cm^{-1} in nondeuterated **1**.

Spiro[2.4]hepta-4,6-diene-*4-d* and **-*5-d*** were prepared and purified by the procedure used for **1** by employing a mixture of cyclopentadiene-*1-d*, -*2-d*, and -*5-d*.[8] Mass spectrometry indicated the sample to be 63% d$_1$ and microwave spectroscopy indicated a 1:1:1 mixture of **1** and its 4-d and 5-d analogues. IR (neat): 3090, 3016, 2478 (w), 2297 (w), 2098 (w), 2071 (w), 1619 (m), 1494 (m), 1485, 1474, 1464, 1449, 1431, 1277, 1269, 1263, 1086, 1055, 1017, 990 (sh), 961 (br), 936, 871, and 656 cm^{-1}. Weak bands have been listed only if they have no counterpart within 3 cm^{-1} in nondeuterated **1**.

Microwave Spectra. Microwave spectra were obtained with an HP-8460A spectrometer operated in R-band (26.5–40 GHz). Radio-frequency microwave double resonance (RFMDR) measurements were performed using the methods and apparatus previously described.[4b,9] Sample pressures were normally in the range 15–30 mTorr, and the waveguide sample cell was operated at room temperature (20–23 °C) and at reduced temperatures (≈−60 °C) using dry ice cooling. A few spectral measurements at intermediate temperatures were performed during controlled cell warm-up from low temperatures.

Table I. Rotational Constants and Moments of Inertia of the Isotopic Forms of Spiro[2.4]hepta-4,6-diene[a]

	normal	1-C^{13}
A	6102.149 ± 0.014[b]	6062.345 ± 0.114[c]
B	2454.223 ± 0.001	2410.269 ± 0.005
C	2028.890 ± 0.001	2003.061 ± 0.003
I_a	82.8198	83.3636
I_b	205.9222	209.6774
I_c	249.0914	252.3034
	3-C^{13}	4-C^{13}
A	6102.025 ± 0.205[d]	6003.000 ± 0.094[e]
B	2451.877 ± 0.008	2452.051 ± 0.005
C	2027.310 ± 0.005	2016.335 ± 0.003
I_a	82.8215	84.1877
I_b	206.1192	206.1046
I_c	249.2855	250.6424
	5-C^{13}	1-D
A	6063.945 ± 0.136[f]	5934.441 ± 0.019[g]
B	2419.796 ± 0.008	2387.133 ± 0.001
C	2001.166 ± 0.004	1988.101 ± 0.001
I_a	83.3416	85.1603
I_b	208.8519	211.7096
I_c	252.5423	254.2019
	4-D	5-D
A	5766.973 ± 0.071[h]	5977.960 ± 0.057[i]
B	2454.162 ± 0.002	2375.489 ± 0.002
C	1990.343 ± 0.003	1961.592 ± 0.002
I_a	87.6333	84.5404
I_b	205.9273	212.7474
I_c	253.9155	257.6372

[a] Rotational constants are in MHz and uncertainties represent 1 σ; moments of inertia have units of amu Å^2, computed using the factor 505 379 MHz·amu·Å^2. [b] 52-line fit. [c] 21-line fit. [d] 19-line fit. [e] 19-line fit. [f] 18-line fit. [g] 58-line fit. [h] 40-line fit. [i] 42-line fit.

Table II. Planar Second Moment Defects upon Isotopic Substitution[a]

isotopic species	ΔP_b	ΔP_c
1-C^{13}	0.0003	
3-C^{13}	−0.0006	0.0023
4-C^{13}		−0.0004
5-C^{13}		0.0003
4-D		−0.0028
5-D		0.0000

[a] Computed from moments of inertia of Table I. Units are amu Å^2.

Observed Spectra. In the previous communication we reported the spectrum of the normal isotopic species.[1] Here we report the corresponding spectra of four monosubstituted ^{13}C (natural abundance) and three monosubstituted ^{2}H (D) (isotopically labeled) species. The spectrum in each case was analogous to that of the normal isotopic species, consisting primarily of characteristic *a*-type, near-prolate asymmetric rotor, R-branch transitions. For the isotopically enriched deuterium species it was possible also to assign a few of the very weak, high-*J*, Q-branch transitions. The isotopic species spectral data are collected and reported as supplementary material (Tables S-I to S-VII), and Table I of this paper summarizes the derived rotational constants and moments of inertia. In these tables, deuterium-substituted species are identified according to Figure 1 by the carbon site upon which substitution occurs, and ^{13}C species are identified by the substitution site. Spectral fits were performed using a standard Hamiltonian model consisting of rigid rotor plus centrifugal distortion terms. Inclusion of the latter terms improved the fit of the high-*J*, Q-branch transitions (up to $J = 24$), but since they are incidental to our aims we have not tabulated the resulting distortion constants. It is important to note that the resulting rotational constants are altered only slightly by inclusion of the high-*J*, Q-branch transitions.

Deuterium isotopic species, enriched as described above, were easily assigned by Stark effect observations[10] and by comparing R-branch

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(3) (a) S. W. Staley, *J. Am Chem. Soc.*, **89**, 1532 (1967); (b) S. W. Staley and W. G. Kingsley, **95**, 5804 (1973); (c) S. W. Staley, M. A. Fox, and A. Cairncross, *J. Am. Chem. Soc.*, **99**, 4524 (1977).

(4) (a) R. D. Suenram and M. D. Harmony, *J. Am. Chem. Soc.*, **95**, 4506 (1973); (b) S. N. Mathur and M. D. Harmony, *J. Mol. Spectrosc.*, **69**, 37 (1978); (c) C. S. Wang and M. D. Harmony, *J. Am. Chem. Soc.*, **98**, 1108 (1976).

(5) C. F. Wilcox, Jr., and R. R. Craig, *J. Am. Chem. Soc.*, **83**, 3866 (1961).

(6) H. L. Goering and D. W. Larsen, *J. Am. Chem. Soc.*, **81**, 5937 (1959).

(7) R. J. Abraham and J. R. Monasterios, *J. Chem. Soc., Perkin Trans. 2*, 574 (1975).

(8) V. A. Mironov, E. V. Sobolev, and A. N. Elizarova, *Dokl. Akad. Nauk SSSR* (*Engl. Trans.*), **143**, 321 (1962).

(9) F. J. Wodarczyk and E. B. Wilson, *J. Mol. Spectrosc.*, **37**, 445 (1971).

(10) S. Golden and E. B. Wilson, Jr., *J. Chem. Phys.*, **16**, 669 (1948).

Table III. Atomic Coordinates of Spiroheptadiene in the Principal Axis System of the Normal Isotopic Species[a]

atom[b]	*a*	*b*	*c*
C_1	1.7959 (4)	0	0.7471 (9)
C_2	1.7959 (4)	0	−0.7471 (9)
C_3	0.4429 (25)	0	0
C_4	−0.4267 (15)	1.1750 (5)	0
C_5	−1.7143 (5)	0.7334 (12)	0
C_6	−1.7143 (5)	−0.7334 (12)	0
C_7	−0.4267 (5)	−1.1750 (5)	0
H_8	−2.6002 (2)	1.3507 (3)	0
H_9	−2.6002 (2)	−1.3507 (3)	0
H_{10}	−0.0412 (205)	2.2001 (2)	0
H_{11}	−0.0412 (205)	−2.2001 (2)	0
H_{12}	2.0569 (1)	0.9135 (2)	1.2588 (2)
H_{13}	2.0569 (1)	−0.9135 (2)	1.2588 (2)
H_{14}	2.0569 (1)	0.9135 (2)	−1.2588 (2)
H_{15}	2.0569 (1)	−0.9135 (2)	−1.2588 (2)

[a] All values in Å; parenthetical numbers are the experimental uncertainties in the final digits. [b] See Figure 1 for atom identifications.

patterns with those of the normal species. In addition, we routinely observed the K_{-1} = 4 transitions using RFMDR methods.[4b,9]

For the ^{13}C species, observed in natural abundance, our spectral measurements were much less extensive since many of the weak transitions were obscured by zero-field lines and also by Stark components of the normal isotopic species. Nevertheless, the relatively high intensity (S/N ≈ 10/1) of the spectra of the 1-^{13}C, 4-^{13}C, and 5-^{13}C species (present in approximately 2% abundance) permitted reasonably easy assignments. In all cases, initial assignments were obtained by observations of the K_{-1} = 4 RFMDR transitions, and intensities were compared carefully with those of the normal isotopic species. Special care was taken in the assignment of the spectrum of the 3-^{13}C species (present in 1% abundance). Again, RFMDR measurements were utilized, and relative intensities were studied as a function of temperature. The temperature-dependence studies showed conclusively that the assigned spectra were those of the desired isotopic species, not vibrational satellites. The overall high quality of the isotopic species data is shown by the planar second moment isotopic defects tabulated in Table II and discussed further in the next section.

Structure. Since each of the unique atoms of the C_{2v} spiroheptadiene molecule has been isotopically substituted, a complete substitution (r_s) structure can be obtained by the method of Costain[11] with the use of Kraitchman's[12] equations. In lieu of an r_e structure, this method is generally believed to yield the best possible spectroscopic structure for complex polyatomic molecules since it tends to minimize the effects of zero-point vibrations.[13] Some measurement of the extent of the zero-point vibration problem can be obtained by evaluating the change in planar second moments upon isotopic substitution in molecular symmetry planes. Thus, for substitution of an atom lying in the *ac* plane of symmetry, $\Delta P_b = (1/2)(\Delta I_a + \Delta I_c - \Delta I_b) = 0$ should result for a rigid, vibrationless molecule. Table II contains a summary of the experimental second moment values for each of the atoms lying in a symmetry plane. The resulting isotopic defects are all pleasingly small, and suggest the absence of any unusual zero-point vibration–rotation effects. Note that the results are all in accord with expectations for the C_{2v} molecule of Figure 1. In particular, for atom 3 it is found that the rigid molecule relation for an atom on the *a* axis, $\Delta P_b = \Delta P_c = \Delta I_a = 0$, is very closely satisfied.

Table III presents the complete enumeration of the atomic coordinates of spiroheptadiene. These are all true r_s coordinates, except in the case of H_{10} and H_{11}, where the tabulated values have been obtained from the first moment relation, $\sum m_i a_i = 0$. These atoms lie very near to the *bc* plane, and consequently the *a* coordinate computed from Kraitchman's equations, $|a| = 0.070 \pm 0.005$, is expected to be subject to a large vibration–rotation uncertainty. Since all other atoms have been accurately located, the first moment value is preferred and is expected to incur no substantial vibration–rotation errors. The uncertainties listed in Table III are in all cases the experimental uncertainties. Note that the relatively large experimental uncertainty for a_{10} (and a_{11}) arises simply from the *a*-coordinate errors in the other atoms.

A complete set of molecular structural parameters has been computed and presented in Table IV based on the atomic coordinates of Table III. We have accounted approximately for vibration–rotation uncertainties by assessing a coordinate error of $\pm 0.0015/g$ for each coordinate g (excepting a_{10} and a_{11}), as recommended earlier.[13,14] These uncertainties are all considerably larger than the experimental values given in Table III and are expected to provide upper limits to the coordinate errors. The parameter uncertainties of Table IV have been computed by propagating these coordinate errors in standard fashion. In the case of those parameters involving a_{10}, however, we use the experimental uncertainty, since the first moment coordinate determination obviates the alternative procedure. Overall, it is evident from the table that the structural quality is extremely high, with no poorly determined parameters.

Table IV. Structural Parameters of Spiroheptadiene[a]

	Independent Structural Parameters		
C_1C_2	1.494 ± 0.003[b]	$H_8C_5C_4$	126.2 ± 0.2
C_1C_3	1.546 ± 0.003	$H_{10}C_4C_5$	129.5 ± 1.0
C_3C_4	1.462 ± 0.003	$C_2C_1H_{12}$	118.3 ± 0.1
C_4C_5	1.361 ± 0.004	$C_3C_1H_{12}$	116.2 ± 0.1
C_5C_6	1.467 ± 0.003		
C_1H_{12}	1.079 ± 0.002		
C_4H_{10}	1.095 ± 0.007		
C_5H_8	1.080 ± 0.002		
	Redundant Structural Parameters		
$C_1C_3C_2$	57.8 ± 0.1	$C_5C_4C_3$	107.6 ± 0.2
$C_3C_1C_2$	61.1 ± 0.1	$C_6C_5C_4$	108.9 ± 0.1
$C_4C_3C_1$	121.4 ± 0.1	$C_4C_3C_7$	107.0 ± 0.2
$H_{12}C_1H_{13}$	115.7 ± 0.2		

[a] See Figure 1 for parameter identification. [b] Distances in Å, angles in degrees. See Structure section for discussion of quoted uncertainties.

Table V. Structural Parameters of Spiro[2.4]hepta-4,6-diene and Related Molecules

parameter[a]	cyclopropane ED[b]	cyclopentadiene mw[c]	fulvene mw[d]	spiro[2.4]hepta-4,6-diene	
				mw[e]	ED[f]
C_1C_2	1.510			1.474	1.510
C_2C_3	1.510			1.546	1.510
C_3C_4		1.506	1.468	1.462	1.509
C_4C_5		1.344	1.357	1.361	1.341
C_5C_6		1.468	1.476	1.467	1.460

[a] Distances in Å. All rings have been numbered to correspond to 1. [b] Electron diffraction, ref 18; spectroscopic studies, ref 35, give a C–C distance of 1.512 Å. [c] Microwave, ref 19. [d] Microwave, ref 28. [e] This work. [f] Electron diffraction, ref 2.

Discussion

Carbon Skeleton. Table V provides a comparison of the structural results of this study with those for related molecules and with the previously reported electron diffraction values.[2] The differences between the microwave (mw) and electron diffraction (ED) values are substantial, and are well outside the quoted error limits in most cases. Similar discrepancies have occurred for other moderately complex cyclic hydrocarbon systems in the past.[15] It is clear that the use of electron diffraction alone for structural determinations of such systems is risky, since there seems to be little guarantee that similar but inequivalent C–C bond lengths will be adequately distinguished. Kuchitsu has shown, however, that such problems can be avoided by the proper combination of diffraction data with a small amount of microwave data (i.e., moments of inertia).[16]

The microwave structural results, as previously noted,[1] are in agreement with expectations based on a conjugative interaction of the cyclopropyl ring with the diene system in **1**. Application of a simple frontier orbital model[17] leads to the prediction that

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(11) C. C. Costain, *J. Chem. Phys.*, **29**, 864 (1958).

(12) J. Kraitchman, *Am. J. Phys.*, **21**, 17 (1953).

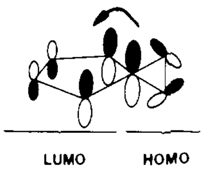
(13) M. D. Harmony, V. W. Laurie, R. L. Kuczkowski, R. H. Schwendeman, D. A. Ramsay, F. J. Lovas, W. J. Lafferty, and A. G. Maki, *J. Phys. Chem. Ref. Data*, **8**, 619 (1979).

(14) C. C. Costain, *Trans. Am. Crystallogr. Assoc.*, **2**, 157 (1966).

(15) See ref 4c and R. D. Suenram and M. D. Harmony, *J. Chem. Phys.*, **56**, 3837 (1972), for the microwave results, and references therein for the corresponding electron diffraction studies.

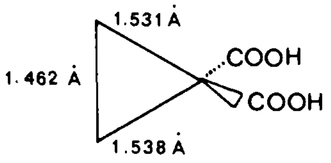
(16) K. Kuchitsu, *MTP Int. Rev. Sci., Phys. Chem., Ser. One*, **2**, 203 (1972).

the major interaction (HOMO of cyclopropyl with LUMO of diene) (**2**) causes a shortening of C_1–C_2, C_3–C_4, C_3–C_7, and C_5–C_6 and a lengthening of C_1–C_3, C_2–C_3, C_4–C_5, and C_6–C_7. The carbon–carbon bond lengths for **1** in Table V support all these predictions when compared with the corresponding data for cyclopropane[18] and cyclopentadiene.[19] It is particularly satisfying that the structural results are now in agreement with NMR[20] and PES[21] studies which suggested the presence of significant π conjugation.



2

A recent extensive analysis of the X-ray crystallographic geometries of 91 cyclopropyl derivatives has established that electron-acceptor substituents cause a shortening of the distal cyclopropyl bond and a lengthening of the vicinal bond.[22] Mean distal-bond shortenings for bisected conformations were determined to be −0.026, −0.022, and −0.017 Å for C=O, C=C, and C≡N, respectively. Evidence for the lengthening of the vicinal bonds is not as clear-cut. However, the X-ray structures of two simple 1,1-disubstituted cyclopropanes (**3**[23] and **4**[24]) show clear evidence for lengthening of the vicinal bonds as well as for shortening of the distal bonds.



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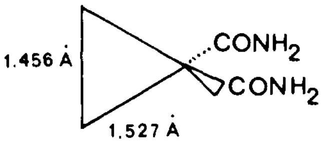

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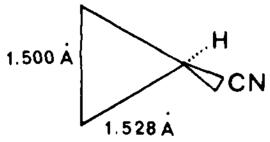

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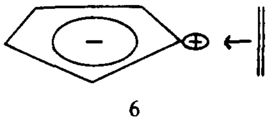
The only previous gas-phase example where both vicinal and distal cyclopropyl bond lengths in acceptor-substituted cyclopropanes have been shown to change in accordance with the model in **2** is in the case of cyclopropanecarbonitrile (**5**), for which a partial structure was obtained.[25] In this compound the distal bond is ca. 0.03 Å shorter than the other bonds, somewhat less than the ca. 0.05 Å difference observed for **1**. This result has been supported by extended basis set ab initio calculations.[26] Additional microwave evidence for π conjugation has been obtained by Penn and Boggs from the analysis of the planar second moments of various π acceptor-substituted cyclopropanes.[27] These workers observed a consistent shortening of the distal C–C bond.

An interesting qualitative measure of the conjugative effect of the cyclopropyl ring in **1** is suggested by the observation (see Table V) that the C_3–C_4 bond is slightly shorter than the corresponding bond in fulvene.[28] Although the difference is on the edge of experimental reliability, the result suggests that the cyclopropyl group is at least as good a conjugating group as the double bond when interacting with the ends of an *s-cis*-1,3-butadiene moiety.

Finally, it is interesting to consider the structural results in terms of simple valence bond concepts. In this view, spiro[2.4]hepta-4,6-diene is perhaps best represented as a resonance hybrid of valence bond structures **1** and **6**. If one assumes that the length of the C_1–C_2 bond in spiroheptadiene is proportional to the contribution of **6**, then one estimates that the resonance hybrid can be represented as 91% **1** and 9% **6** based on the C–C bond lengths in ethylene (1.339 Å),[29] cyclopropane (1.510 Å),[18] and C_1–C_2 in **1** (1.494 Å). The overall resonance hybrid is well represented in a single structure by **7**. Our estimate of the contribution of **6** is somewhat less than was estimated on the basis of NMR chemical shifts.[20] However, as was previously noted,[2] the basis for the chemical shifts of cyclopropyl protons is not well understood, so it is not surprising that a conclusion based on NMR data differs somewhat from one based on structural data.



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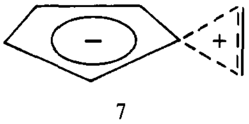

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Electron Distribution and Dipole Moment. The dipole moment of 0.947 D which we have reported previously[1] for **1** is, to our knowledge, the largest dipole moment determined to date for a hydrocarbon in the gas phase. It exceeds, for example, the value of 0.80 D determined for azulene.[30] There are, of course, solution dipole moments reported for hydrocarbons which are substantially higher.

The dipole moments obtained for **1** on the basis of ab initio minimal basis set (STO-3G) and extended basis set (6-31G) calculations[31] in our reported geometry are 0.90 and 1.09 D, respectively, in reasonable agreement with the experimental value. The calculated value at the STO-3G level of the dipole moment of **1** in the electron diffraction geometry[2] is 0.63 D, whereas that for the STO-3G optimized geometry is only 0.58 D.[32] This illustrates the importance of a correct geometry in ab initio dipole moment calculations.

In the following analysis we consider the nature of the polarity of **1**. We treat cyclopropane according to a Walsh-type model.[33] In this model, the C–C bonds are constructed of two cyclic arrays of orbitals, an outer Möbius array of p orbitals (3e′ and 1a′$_2$) and an inner Hückel array of sp^2 orbitals (2a′$_1$ and 4e′). The remaining carbon orbitals are used to construct the six sp^2 C–H bonds. Since the Möbius array has a degenerate pair of bonding orbitals whereas the Hückel array has only a single bonding orbital, the C–C bonds are constructed of what can be considered to be two "aromatic" systems, a four-electron Möbius system and a two-electron Hückel system. Views of these orbitals are presented as shown.[34]

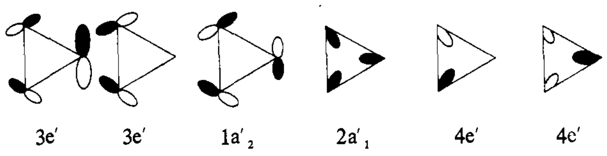

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Table VI. Charge Densities in Various Cyclopropyl Rings from STO-3G Calculations[a]

orbital or structural unit	charge density 8 C_1, C_2, C_3	9 C_1, C_2	 C_3	1 C_1, C_2	 C_3
p(π)	−0.081	−0.070	−0.104	−0.054	−0.074
p(σ)	+0.112	+0.107	+0.129	+0.113	+0.147
$\sigma(CH_2)$[b]	+0.081	+0.075	+0.095	+0.085	
σ(H)	+0.067	+0.068	+0.065	+0.077	
σ(C)[c]	−0.053	−0.062	−0.034	−0.069	+0.058
total[d]	0.0	+0.004	−0.008	+0.031	−0.016

[a] The orbitals and structural units are as referred to in Figure 2. [b] All σ charge associated with CH_2 groups, i.e., $\sigma(CH_2) = \sigma(C) + \sigma(H)$. [c] All σ charge associated with carbon orbitals, i.e., $\sigma(C) = p(\sigma) + s(\sigma)$. [d] Sum over all carbon and hydrogen orbitals at each labeled carbon atom, i.e., total $= p(\pi) + \sigma(CH_2)$. Note that sums may not add because of rounding errors.

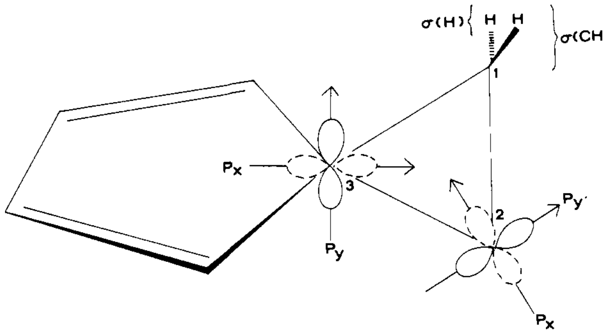
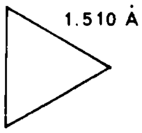


Figure 2. Orbital identifications. The (x, y) and (x', y') axes refer to orbitals at C_3 and $C_2(C_1)$, respectively.

The outer array of p orbitals is termed the π system. It consists of each p orbital whose nodal plane is coincident with the plane of the CH_2 group at that position. Note that, by this definition, the π system contains a net negative charge whereas the σ system is electron deficient.

Information on the electron distribution in **1** was obtained from ab initio STO-3G calculations on cyclopropane with the experimental geometry (**8**)[35] and on cyclopropane with the geometry of the three-membered ring in **1** (**9**).[36] The σ and π charge densities for **8** and **9** and for the cyclopropyl ring of **1** (see Figure 2) are listed in Table VI. As expected, the π system of the cyclopropyl ring is electron rich in all cases. Note, however, that the π charge at C_1–C_3 in **8** (−0.081) is reduced to −0.070 at C_1 and C_2 in **9** but is increased to −0.104 at C_3. Thus when donation occurs from the HOMO of the cyclopropyl ring to the LUMO of the diene unit in **1**, more charge transfer occurs from C_3 than from C_1 or C_2 but the negative charge density at C_3 in **1** (−0.074) is still higher than that at C_1 or C_2 (−0.054). The latter point would be difficult to comprehend without a knowledge of the π-electron distribution in **9**. In Figure 3, which summarizes the charge distributions in **1**, it is seen that the cyclopropyl π system remains electron rich relative to that of the cyclopentadiene system, even though substantial π-electron transfer has occurred.



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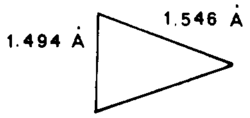

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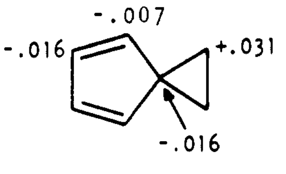

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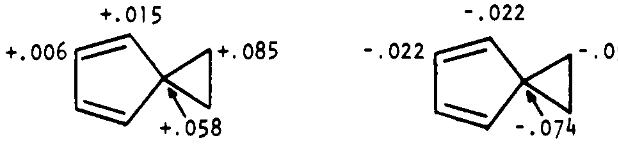

σ π

Figure 3. Spiroheptadiene charges from STO-3G computations. The σ charges include the hydrogen contributions, and the total charge is the sum of σ and π.

Table VI shows also that the σ cyclopropyl system responds in a complementary fashion to the π system upon the molecular distortion **8** → **9**; i.e., the $\sigma(CH_2)$ or σ(C) and π electron densities change in opposite directions. However, the shift in π electron density from the cyclopropyl ring to the diene unit of the five-membered ring is the overriding factor in determining the large net dipole moment. We find no *structural* evidence for a donation of cyclopropyl C–H σ electron density to the C_3C_4 and C_3C_7 σ^* orbitals (see next section).

Carbon–Hydrogen Bonds. In principle, comparison of the cyclopropyl CH bond lengths and HCH angles of **1** with the corresponding values in cyclopropane should provide evidence for the modified electron distribution. Cyclopropane has been studied by both electron diffraction[18] and Raman spectroscopy.[35] The structural parameters obtained by the two methods are respectively: C–H = 1.089 (3) Å, ∠HCH = 115.1 (10)°; and C–H = 1.083 (3) Å, ∠HCH = 114.0 (7)°. For **1**, we have reported in Table IV the values C–H = 1.079 (2) Å and ∠HCH = 115.7 (2)°. Although the methods are not exactly comparable, and the error limits overlap, the results strongly suggest that the C–H distance has decreased and the HCH angle has increased in going from **8** to **1**. According to simple notions of chemical bonding this suggests that the cyclopropyl C–H bonds have more s character (less p character) in **1** than in **8**. This result is in accord with NMR measurements of ^{13}C–H coupling constants (164.9 Hz[37] in **1** and 161 Hz[38] in **8**), since the magnitude of this parameter is directly proportional to the s character in the C–H bonding hybrid.[39]

Of particular interest is the observation that the opposite angles ($\angle C_3C_1C_2$ and $\angle HC_1H$) *both* increase on going from cyclopropane (**8**) to **1**. This unusual behavior can be rationalized on the basis of the following simple model. Since σ(C) at C_3 has much less electron density in **1** than in **8**, C_1 and C_2 rehybridize so as to direct more p character toward C_3 and therefore more s character toward the C_1 and C_2 hydrogens. These changes fall within the predictions of Bent's empirical rule which states that "atomic p character concentrates in orbitals directed toward electronegative substituents".[40] The σ system at C_3 is more electronegative in **1** than in **8**. The purpose of this rehybridization is, of course, to maximize the bonding in **1**.

Evidence for the foregoing model is provided by the Mulliken overlap populations obtained from STO-3G calculations. The relevant values for CH 2s–1s, $2p_x$–1s, and $2p_z$–1s (coordinates as in Figure 2) are 0.1323, 0.0741, and 0.1907, respectively, for **8**, and 0.1346, 0.0718, and 0.1918, respectively, for **1**. These values

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(36) The values of r_{C-H} and $\angle HC_3H$ are the same as those in cyclopropyl ring of **1** and the plane of the HC_3H contains the bisector of $\angle C_1C_3C_2$.

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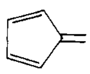
clearly reflect an increase in s character and a decrease in p character (due to a decrease in the contribution of the inplane $2p_x$ orbital) of the C–H bond. Note that maximum overlap calculations predict a slight change in the opposite direction on going from **8**[41] to **1**.[42]

We next consider the suggestion that the first ionization potential (IP) of **1** is 0.4 eV less than that of fulvene (**10**) because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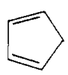
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of charge transfer due to the interaction of the symmetric 1e″ orbital of the cyclopropane ring (the fully antibonding linear combination of CH bonding orbitals) with the appropriate σ^* orbital of the C_3–C_4 and C_3–C_7 bonds.[43] In our view, this difference in IP's is in part accounted for by the longer C═C bonds in **10** compared to **1** (see Table V). However, it is of interest to determine whether any *structural* evidence for such an interaction exists. Optimized structures of the ethyl cation in the bisected geometry computed at the 4-31G[44] and 6-31G[45] levels suggest that hyperconjugation and related hybridization effects should cause the HCH angle of the out-of-plane hydrogens to decrease. Therefore, the *opening* of $\angle HC_1H$ in **1** relative to **8** is in the opposite direction to the change expected for a hyperconjugative interaction of the CH_2 groups with σ^* of the five-membered ring.

Also of interest are the "tilts" of the various C–H bonds in **1**. We define "tilt" as the angle between the projection of the C_a–H bond in the plane of the ring to which it is connected and the bisector of $\angle CC_aC$ (see Figure 1). In each case it is seen that the C–H bond is tilted away from the shorter C–C bond and toward the longer C–C bond; e.g., C_1H is tilted toward C_3 (C_1–C_3 = 1.546 Å) and away from C_2 (C_1–C_2 = 1.494 Å). Each of the observed tilts is consistent with a simple "bent spring" model in which the tilt results from unbalanced 1⋯3 steric repulsions.[46]

The C–H bonds in the cyclopentadiene moiety of **1** provide interesting contrasts. The C_5–H distance of 1.080 Å is identical with the reported values for the same bond in cyclopentadiene (**11**)[19] and fulvene (**10**).[20] On the other hand, the C_4–H value in **1** is 1.095 Å, while the values in **10** and **11** are 1.077[28] and 1.078 Å,[19] respectively. (All of these values are from microwave spectroscopic studies.) This latter disparity is well outside apparent experimental uncertainties and is difficult to understand. According to NMR ^{13}CH coupling constants in **1**, **10**, and **11** (168.9,[37] 170,[47] and 169.1 Hz,[48] respectively), the bonds appear virtually identical. A further puzzling factor is that the tilt (Figure 1) of this CH group is larger than that for fulvene (1.3 ± 0.4°) or for cyclopentadiene (1.7 ± 0.5°).[19] Although the H_{10} and H_{11} coordinates are the most poorly determined in this work (Table III), there is no apparent reason to believe they are any worse than reported. An intriguing possibility is that the parameter variations are related to the highly electron-deficient σ orbital at C_3 in **1**.

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Supplementary Material Available: Tables S-I to S-VII, complete listings of the observed spectra for seven isotopic species (6 pages). Ordering information is given on any current masthead page.

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