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On the Electronic Character of Methylenecyclopropene: Microwave Spectrum, Structure, and Dipole Moment

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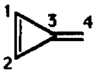
Abstract: The electric dipole moment ($\mu = 1.90 \pm 0.02$ D) and the heavy-atom molecular structure ($r(C_1C_2) = 1.323$ Å, $r(C_1C_3) = 1.441$ Å, and $r(C_3C_4) = 1.332$ Å) have been determined for methylenecyclopropene (**1**) by microwave spectroscopy. In addition, the C_{2v} or D_{3h} geometry-optimized ab initio molecular structures for cyclopropane, cyclopropene, methylenecyclopropane, **1**, and the cyclopropenium cation have been calculated at various levels up to MP2/6-31G*. The mean discrepency between the MP2/6-31G*-optimized and experimental bond lengths is <0.006 Å and in only one case is it >0.007 Å. Analysis of the experimental and calculated dipole moments, the calculated electron distribution, and the experimental and calculated molecular structures for **1** and related compounds has led to the conclusion that dipolar resonance form **1d** constitutes about one-fifth of the ground state character of **1**, but it only contributes a π-delocalization energy comparable to that of 1,3-butadiene. The heat of formation of methylenecyclopropene is calculated to be 93.4 kcal/mol. It is concluded that **1** is nonaromatic.

Recently we[2] and others[3,4] have reported the first syntheses and direct observations of methylenecyclopropene (**1**), the simplest cross-conjugated π-electron system. This molecule has elicited a long-standing theoretical interest which derives from its potentially pseudoaromatic character. The latter is represented by contributions from highly polar resonance structures **1a–c** (equivalent to **1d**) to the ground state of **1**.



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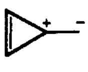
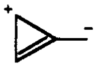


1a

1b



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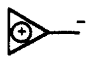

1d

There is no consensus in the literature regarding this fundamental problem, in that methylenecyclopropene has been variously regarded as being aromatic (or pseudoaromatic),[5] nonaromatic,[6] and antiaromatic.[7] With the recent availability of **1**, we sought to resolve this issue through a determination of its electric dipole moment and heavy-atom molecular structure by microwave spectroscopy. These results, coupled with high-level ab initio calculations of the molecular structure, electron distribution, and total molecular energy of **1** and related molecules, have allowed us to undertake a detailed analysis of this problem.

Experimental Section

Synthesis. Methylenecyclopropene was prepared in a continuous flow apparatus (Figure 1) by passing 2-bromomethylenecyclopropane through a horizontal column filled halfway with potassium *tert*-butoxide on Chromosorb W at a temperature of approximately 110 °C and a pressure of <200 mTorr.[2] After passage through the column and a trap at −78 °C, the effluent gases flowed through the 6-ft sample cell of an HP-8460A microwave spectrometer cooled to dry ice temperature. Pressures at the outlet of the sample cell were typically in the range of 15–30 mTorr.

The spectrum of the column effluent showed weak transitions attributed to 2-bromomethylenecyclopropane which had been previously identified by studying the neat compound. In addition to signals from this precursor, the only identifiable transitions arose from an intense spectrum easily identified as that of methylenecyclopropene. Analysis by photoelectron spectroscopy in a separate experiment showed the effluent to be >95% methylenecyclopropene.

Microwave Spectroscopy. The microwave spectrum was sufficiently intense that two of the ^{13}C isotopic species could be identified in natural abundance. Although the observation is not very quantitative, we found that a sample of methylenecyclopropene had a half-life of approximately 5 min when trapped in the waveguide at dry ice temperatures.

Dipole moment measurements were performed by measuring frequency shifts of various J_τ, M components as a function of the square wave ground-to-base modulation voltage. Cell calibration was performed by observing the OCS Stark effect and using the known dipole moment value of 0.71521 D.[8] All frequency measurements have expected uncertainties of ±0.05 MHz or less.

Quantum Mechanical Methods. Ab initio calculations were performed with Pople's GAUSSIAN 82 series of programs[9] which employed the STO-3G,[10] 6-31G,[11] and 6-31G*[12] basis sets. Electron correlation effects were included at the MP2/6-31G* level by the use of analytical second-derivative techniques.[13] Geometry optimizations were performed by employing analytically evaluated atomic forces in a Berny multiparameter search routine.[9] Full basis sets were employed and geometries were optimized completely, subject only to molecular symmetry (C_{2v} or D_{3h}) constraints. Symmetry-specific Mulliken overlap populations were calculated at the STO-3G level for several compounds with Gallup's GSCF program.[14]

Results

Observed Spectrum. The observed spectrum of the normal isotopic species of methylenecyclopropene exhibited a small number of easily identified a-type R- and Q-branch transitions as summarized in Table I. Stark effect observations provided important substantiation of assignments in the initial stages of the study. Table II presents the rotational constants of the ground vibrational state resulting from a rigid-rotor least-squares fit, and Table I shows the quality of the fit in the obsd − calcd column.

With the normal isotopic-species spectrum as a guide, and taking careful account of intensities, we were able to observe and

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Table I. Observed Microwave Spectrum of Methylenecyclopropene[a]

normal species			$1\text{-}^{13}C$ species			$4\text{-}^{13}C$ species		
transition	obsd freq	obsd - calcd[b]	transition	obsd freq	obsd - calcd[b]	transition	obsd freq	obsd - calcd
$1_{10} \rightarrow 2_{11}$	27 207.47	0.17	$1_{10} \rightarrow 2_{11}$	26 820.73	0.23	$2_{02} \rightarrow 3_{03}$	37 229.35	-0.04
$2_{02} \rightarrow 3_{03}$	38 436.00	0.25	$2_{02} \rightarrow 3_{03}$	37 863.85	-0.04	$2_{12} \rightarrow 3_{13}$	35 437.85	0.13
$2_{12} \rightarrow 3_{13}$	36 540.88	0.18	$2_{12} \rightarrow 3_{13}$	35 984.12	0.09	$2_{11} \rightarrow 3_{12}$	39 402.98	0.13
$2_{21} \rightarrow 3_{22}$	38 695.53	-0.23	$2_{21} \rightarrow 3_{22}$	38 127.43	-0.18	$2_{21} \rightarrow 3_{22}$	37 455.56	-0.24
$2_{20} \rightarrow 3_{21}$	38 955.44	-0.33	$2_{20} \rightarrow 3_{21}$	38 391.30	-0.03	$2_{20} \rightarrow 3_{21}$	37 682.22	0.01
$6_{16} \rightarrow 6_{15}$	29 454.45	-0.79	$6_{16} \rightarrow 6_{15}$	29 281.19	0.00			
$11_{2,10} \rightarrow 11_{29}$	34 760.46	1.25						
$16_{3,14} \rightarrow 16_{3,13}$	35 015.64	-0.57						

[a] All values in MHz. [b] Computed from the results in Table II.

Table II. Rotational Constants[a] and Moment of Inertia Relations[b] of Methylenecyclopropene

	normal species	$1\text{-}^{13}C$ species	$4\text{-}^{13}C$ species
A	29294.60 ± 1.02[c]	28618.83 ± 10.19	29322.21 ± 15.99
B	7154.36 ± 0.06	7055.65 ± 0.02	6903.74 ± 0.05
C	5744.23 ± 0.06	5653.55 ± 0.02	5581.52 ± 0.05
Δ[d]	-0.0894	-0.1048	-0.1059
ΔI_b			2.5644
ΔI_c			2.5647

[a] Units of MHz. [b] Units of amu Å^2, computed with a conversion factor of 505 379.0 MHz amu Å^2. [c] Uncertainties are the standard deviations. [d] $\Delta = I_a + I_b - I_c$.

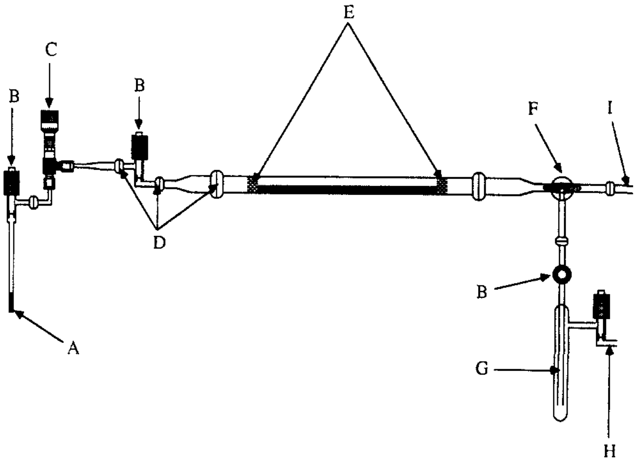

Figure 1. Apparatus employed in the generation of methylenecyclopropene in the gas phase (A, 2-bromomethylenecyclopropane sample; B, glass needle valve; C, microvalve; D, ball and socket joints; E, glass wool plugs; F, three-way stopcock; G, -78 °C trap; H, to microwave spectrometer; I, to thermocouple vacuum gauge).

Table III. Dipole Moment Results for Methylenecyclopropene

		$\Delta\nu/\epsilon^2$ [a]	
transition	M	obsd	calcd[b]
$2_{12} \rightarrow 3_{13}$	0	-0.0533 (5)[c]	-0.0534
	1	0.5628 (14)	0.5589
	2	2.430 (6)	2.396
$1_{10} \rightarrow 2_{11}$	1	-14.78 (4)	-15.02

$|\mu_a| = |\mu_T| = 1.90 \pm 0.02$ D[d]

[a] Units are 10^{-5} MHz (V/cm)$^{-2}$. [b] Computed using $|\mu_a| = 1.897$ D. [c] Uncertainties in last digits. [d] From weighted least-squares fit; uncertainty respresents 3σ.

Table IV. Experimental Structure of Methylenecyclopropene

determined parameters:
$C_1C_2 = 1.323 \pm 0.003$ Å
$C_1C_3 = 1.441 \pm 0.006$ Å
$C_3C_4 = 1.332 \pm 0.006$ Å
$\angle C_1C_3C_2 = 54.7°$ [a]

fixed parameters:[b]
$C_1H = 1.080$ Å
$C_4H = 1.085$ Å
$\angle C_2C_1H = 147.5°$
$\angle HC_4H = 118.0°$

[a] Redundent parameter. [b] See text for discussion.

assign transitions of both the $1\text{-}^{13}C$ and $4\text{-}^{13}C$ isotopomers. However, the weak Q-branch transitions were not observable except in one case. Sufficient transitions were obtained to permit determination of rotational constants, albeit with poor precision for the A constants. Tables I and II present the results for the isotopic species.

For a molecule such as methylenecyclopropene, the inertial defect, $\Delta = I_a + I_b - I_c$, provides an experimental test of planarity. The small negative values given in Table II are compatible with observed values for other analogous planar species which would be expected to yield vanishing defects for an ideal rigid molecule. The nearly identical values of ΔI_b and ΔI_c for the $4\text{-}^{13}C$ species show, moreover, that C_4 lies on the axis of symmetry.

Attempts were made to observe the natural abundance spectrum of the $3\text{-}^{13}C$ species, but these efforts failed because the weak transitions were obscured by much more intense transitions from the ground and excited vibrational states for the normal isotopic species. This problem did not occur for the other two ^{13}C isotopic species because the much larger isotope frequency shifts put these spectra in relatively clear spectral regions.

Dipole Moment. Table III presents the experimental values of the second-order Stark coefficients for four low-J components. The coefficient for the 1 → 2 transition was obtained from the slope of $\Delta\nu$ vs. ϵ^2 in the low-field limit to avoid higher-order effects. The data were analyzed by a least-squares fit with the standard theory of Golden and Wilson[15] to obtain the electric dipole moment of the molecule in its ground vibrational state. The analysis was entirely compatible with molecular C_{2v} symmetry and yielded a value of $\mu_a = \mu_T = 1.90 \pm 0.02$ D, where the uncertainty accounts for expected errors in frequency and voltage measurements. The standard deviation of the fit (precision) was actually several times smaller than the quoted uncertainty. The "calculated" values of $\Delta\nu/\epsilon^2$ in Table III were obtained by using the value $\mu_a = 1.897$ D.

Microwave Structure. With the available data it is not possible to derive a complete substitution (r_s) structure by the method of Costain[16] with Kraitchman's equations.[17] However, a reliable heavy-atom structure can be obtained with the method of Nösberger et al.[18] In this procedure the three independent heavy-atom parameters, $r(C_1C_2)$, $r(C_1C_3)$, and $r(C_3C_4)$, are adjusted in a least-squares fit to satisfy isotopic differences in moments of inertia, e.g., $\Delta I_b = I_b(\text{isotope}) - I_b(\text{normal})$. In order to avoid errors due to the poorly determined A rotational constants of the two observed ^{13}C isotopomers, only the six B and C rotational constants are used in this fitting procedure. The computations require that all the hydrogen parameters (four in number for the C_{2v} molecule) be fixed at reasonable values. Table IV summarizes the structural results which can be identified by reference to Figure 1. The Table IV structural results are only slightly dependent upon the values of the assumed parameters since

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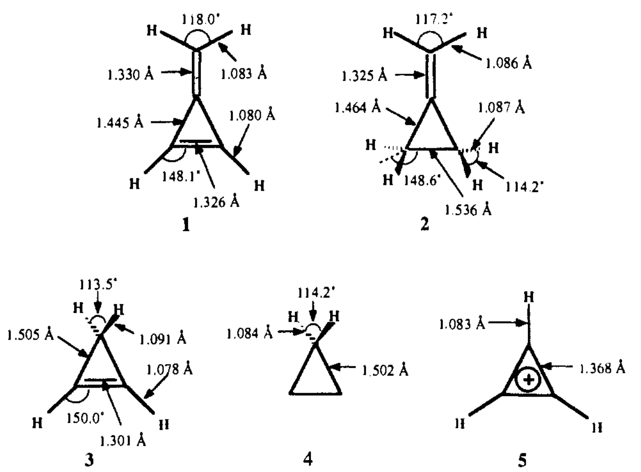


Figure 2. MP2/6-31G* geometry-optimized molecular structures for **1**–**5**.

the use of isotopic ΔIs leads to a high degree of cancellation of the hydrogen atom contributions. The selected values are in accord with expectations based on other firmly established substitution structures.[19] In particular, the CH_2 parameters $r(CH) = 1.085$ Å and $\angle HCH = 118.0°$ are unlikely to be in error by more than ±0.005 Å and ±0.5°, respectively, in this symmetrical molecular environment. There is a somewhat greater uncertainty with respect to the ring hydrogen parameters. Still, the ring CH distance must fall well within ±0.010 Å of 1.080 Å. Also, available experimental data on cyclopropene,[20] 3-cyanocyclopropene,[21] and cyclopropenone,[22] as well as ab initio computations of 6-31G* or MP2/6-31G* quality on these same species, show that $\angle HC_1C_2$ decreases smoothly as the C_1C_2 double-bond length increases. From the available data we have selected $\angle HC_1C_2 = 147.5°$ with an uncertainty of less than ±1°. The effects of these uncertainties upon the computed parameters have been assessed and are easily encompassed by the quoted uncertainties in Table IV.

An important test of the resulting structure can be performed by calculating the r_s coordinates[16] of atoms C_1 and C_4 and comparing these values to those from the least-squares structure obtained by the method of Nösberger et al.[18] These r_s coordinates (computed by using the planar Kraitchman equations with B and C rotational constants only) are as follows: for C_1, $a = -0.99797$ Å, $b = 0.66150$ Å; for C_4, $a = 1.61406$ Å, $b = 0$. The values agree to $\pm 1 \times 10^{-5}$ Å with those obtained from the least-squares fit. This unusually high degree of agreement must be considered fortuitous, of course, but the important point is that the two independent structural methods lead to essentially identical results for the C_1 and C_4 carbon atoms.

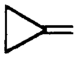
Finally, the listed parameter uncertainties in Table IV have been chosen to account for vibration–rotation uncertainties by assigning uncertainties to the nonvanishing coordinates according to $\Delta g = 0.0015/g$, $g = a, b, c$.[19,23] However, in order to account for the previously discussed uncertainties arising from the assumed parameters, the quoted uncertainties have been enlarged somewhat for the most affected heavy-atom parameters. The resulting structure should be comparable in quality to a pure r_s structure, and the quoted uncertainties should encompass errors due to vibration–rotation interactions as well as errors in the assumed hydrogen parameters.

Table V. Experimental and ab Initio Dipole Moments and Molecular Structures for Methylenecyclopropene, Methylenecyclopropane, Cyclopropene, Cyclopropane, and the Cyclopropenium Cation[a]

		theoretical			
	exptl	STO-3G	6-31G	6-31G*	MP2/ 6-31G*
	Methylenecyclopropene (**1**)				
dipole moment	1.90	1.88[b]	2.14	2.34[b,d]	2.33
$r(C_1C_2)$	1.323	1.303[b,c]	1.314	1.302[b,d]	1.326
$r(C_1C_3)$	1.441	1.446[b,c]	1.446	1.428[b,d]	1.445
$r(C_3C_4)$	1.332	1.303[b,c]	1.320	1.320[b,d]	1.330
	Methylenecyclopropane (**2**)				
dipole moment	0.40[f]	0.23[b]	0.36	0.40[b]	0.40
$r(C_1C_2)$[e]	1.542[f]	1.521[b,c]	1.536	1.527[b]	1.536
$r(C_1C_3)$[e]	1.457[f]	1.474[b,c]	1.469	1.462[b]	1.464
$r(C_3C_4)$[e]	1.332[f]	1.298[b,c]	1.309	1.308[b]	1.325
	Cyclopropene (**3**)				
dipole moment	0.45[g]	0.55[b]	0.50	0.56[b]	0.53
$r(C_1C_2)$	1.296[h]	1.277[b]	1.294	1.276[b,i]	1.301
$r(C_1C_3)$	1.509[h]	1.493[b]	1.508	1.495[b,i]	1.505
	Cyclopropane (**4**)				
$r(CC)$	1.513[j]	1.502[b]	1.505	1.497[b,i]	1.502
	Cyclopropenium Cation (**5**)				
$r(CC)$	1.373[k]	1.377[b]	1.365	1.341[b]	1.368

[a] Dipole moments in D; bond lengths in Å. All theoretical dipole moments and r_e values are from this work; previous studies are cited where appropriate. Experimental bond lengths are r_s values for **1**–**3** and r_z and X-ray diffraction values for **4** and **5**, respectively. [b] Reference 28. [c] Reference 24. [d] Reference 25. [e] The numbering in **2** conforms with that in **1**. [f] Reference 26. [g] Reference 27. [h] Reference 20. [i] Reference 29. [j] Reference 30. [k] Reference 31.

Ab Initio Geometry-Optimized Structures. Heavy-atom molecular structures for **1**–**5** optimized at various levels of basis set are given in Table V along with experimental structures and dipole moments. Complete MP2/6-31G*-optimized structures are given in Figure 2. The mean discrepency between the MP2/6-31G* optimized and experimental bond lengths is <0.006 Å, and in only one case (cyclopropane) is it greater than 0.007 Å.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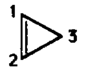

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Thus theory at the MP2/6-31G* level appears to agree with experiment in almost all cases within the uncertainty of the experimental measurements, although the exact relationship between the experimental r_s and r_z values and the theoretical r_e values is uncertain in all cases except for cyclopropane,[30] where agreement of theory with the experimental r_e value is excellent. We also note that the theoretical values of the dipole moments are, in general, somewhat larger than the experimental values, as is commonly observed.

Discussion

The fundamental question which we consider in this study is the extent to which resonance forms **1a**–**c** contribute to the ground state of **1**. As a first approximation, the electron distribution and structure of **1** might be expected to reflect the contributions of **1a**–**c** (**1d**), that is, to possess a positively-charged ring, a nega-

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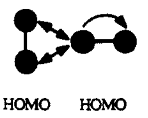
tively-charged C_4, a shortening of C_2C_3, and a lengthening of C_1C_2 and C_3C_4 relative to appropriate models. As will be seen, all of these predictions based on a π-only models have been confirmed except the last.

Of the many criteria for aromaticity, we believe the most meaningful to be those properties which are dependent on all of the electrons of a molecule, that is, the molecular structure and thermodynamic stability. However, before discussing these points, it is instructive to first consider the σ and π electron distributions in **1** and their respective origins.

Electron Distribution. The experimental electric dipole moment for **1** (1.90 D), although not unexpected from theoretical calculations, is nevertheless remarkably large for a small molecule. This value is, to our knowledge, the largest by a *factor of 2* ever determined for a hydrocarbon in the gas phase.[32]

Theoretical values for the dipole moment computed at various levels of basis set are given in Table V for geometry-optimized structures of **1** and the related hydrocarbons, methylenecyclopropane (**2**) and cyclopropene (**3**). The electron distribution can be conveniently discussed in terms of separate distributions for the π and σ electrons.

It has long been recognized that the origin of the expected polarity of methylenecyclopropene derives from its π electrons. The π polarity can best be understood on the basis of two perpendicular double bonds interacting in a "T" arrangement. Resonance form **1a** reflects the four-electron repulsion of the π electrons resulting in polarization of the C_3C_4 π bond toward C_4 (**6**), whereas resonance forms **1b** and **1c** reflect two-electron donations from the C_1C_2 bond to the C_3C_4 bond (**7**). However, as shown below, the contributions of valence bond structures **1a** and **1b,c** to the ground state of **1** are actually less than and greater than the contributions of molecular orbital interactions **6** and **7**, respectively.



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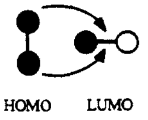

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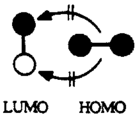

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This leads to a straightforward explanation for the high π polarity of **1**. First, four-electron π polarization is unidirectional owing to the perpendicular arrangement of the double bonds. Second, back donation cannot occur from the C_3C_4 HOMO to the C_1C_2 LUMO (**8**) because of the node in the latter orbital. Therefore, these effects reinforce each other and there is an exceptionally strong transfer of π-electron density out of the ring.

A somewhat more quantitative analysis of the π- and σ-electron distributions can be obtained from a consideration of the component dipoles calculated by treating atomic charges from the MP2/6-31G* geometry-optimized structure of **1** as point charges. This is certainly an approximation, but it is probably not unreasonable for the level of analysis employed here.

The σ and π atomic charges and the component dipole moments are given in Figure 3. The component σ dipole moments ($\mu(\sigma)$) that are listed are the resultant moments for symmetry-equivalent bonds, but the component π dipole moments ($\mu(\pi)$) are based on resonance forms **1a–c** and were calculated as follows. The π-electron-transfer dipole, $\mu(\mathbf{7})$, arises from interaction **7** and represents a net transfer of charge from the midpoint of the C_1C_2 bond to the midpoint of the C_3C_4 bond. The π-polarization dipole, $\mu(\mathbf{6})$, arises from interaction **6** and represents a net transfer of charge from C_3 to C_4.

As can be seen in Figure 3b, over $^1/_3$ of the total π dipole moment results from π polarization. This corresponds to almost $^2/_3$ of the π-electron shift out of the ring. Stated another way, the π charges at C_1, C_2, and C_3 (Figure 3a) are similar so that resonance form **1d** is a reasonable approximate representation of **1a–c**, *yet almost $^2/_3$ of the negative charge on C_4 results not from a stabilizing π donation but from a destabilizing π polarization*!

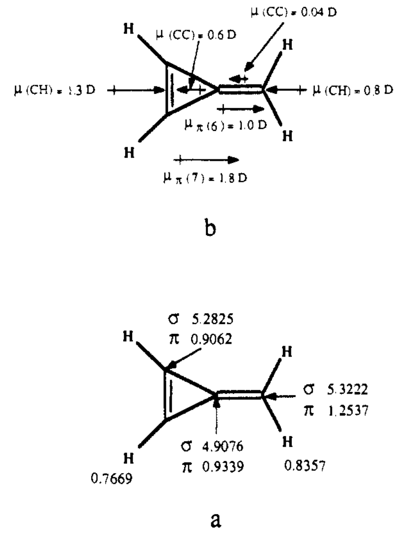

Figure 3. (a) Charge distribution calculated at the MP2/6-31G*//MP2/6-31G* level for the σ and π systems of methylenecyclopropene as obtained from a Mulliken population analysis. (b) Component σ and π dipole moments for methylenecyclopropene calculated from the charges in part a. The $\mu(\sigma)$ values are the net contributions from the CC and CH σ bonds whereas the $\mu(\pi)$ values correspond to $\mu(\mathbf{6})$ and $\mu(\mathbf{7})$ (see text).

The π charges in Figure 3a suggest that resonance form **1d** contributes about $^1/_4$ of the ground-state character of **1**. However, since the dipole moment of **1** is overestimated by 24% at the MP2/6-31G* level (Table V), it is probably more appropriate to attribute about $^1/_5$ dipolar character (**1d**) to the ground state of **1**. The structural and energetic consequences of this are discussed below.

Kollmar had previously calculated μ for nonoptimized **1** with a minimal or double-ζ basis (2.1 D) and for a reference state in which localized π MOs from a SCF calculation of ethylene were superimposed on the above σ system.[33] It was noted that μ from the latter calculation (−0.2 D), which corresponds to $\mu(\sigma)$, was remarkably small in view of the large charge transfer in the π system. Further, when the σ orbitals in this reference state were allowed to relax, the dipole moment (0.4 D) unexpectedly reversed sign and increased in absolute value.

Both of these reference-state dipole moments can be understood by consideration of the component σ dipole moments in Figure 3b. The net μ for the CH bonds of +0.5 D opposes the moment arising from the polarization of the CC σ bonds owing to the contribution of the highly polar $C_{sp}H$ bonds at C_1 and C_2. The net $\mu(\sigma)$ of −0.1 D corresponds closely to the value calculated by Kollmar, even though somewhat different geometries were employed. Furthermore, the net μ(CH) would be expected to correspond closely to the dipole moment of Kollmar's σ-relaxed reference state, as is indeed the case.

Molecular Structure. The structure of a molecule is a property of all of the electrons and, as such, is one of the most fundamental properties. However, since aromaticity is normally considered to be a property of the π-electron system, an evaluation of the "π-only" structural effect is of interest in dealing with this problem. This sort of analysis is never totally satisfactory, but a careful consideration of the σ and π systems can reveal effects attributable to the π system alone.

C_3C_4 Bond. We first consider the exocyclic double bond. As seen in Table V, this bond in **1** is calculated at the MP2/6-31G* level to be only marginally (0.005 Å) longer than the corresponding bond in **2** and was determined to be identical in length by microwave spectroscopy. One might ask why, if dipolar form **1d** contributes significantly to the ground state of **1**, C_3C_4 in **1** is not experimentally lengthened relative to C_3C_4 in **2**. Several possi-

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[32] The dipole moment of spiro[2.4]hepta-4,6-diene is 0.95 D: Harmony, M. D.; Mathur, S. N.; Choe, J.-I.; Kattija-Ari, M.; Howard, A. E.; Staley, S. W. *J. Am. Chem. Soc.* **1981**, *103*, 2961.

[33] Kollmar, H. *J. Am. Chem. Soc.* **1979**, *101*, 4832.

Table VI. Relative ab Initio STO-3G and MP2/6-31G* Mulliken Overlap Populations and Relative Experimental and Theoretical Bond Lengths for Methylenecyclopropene and Related Compounds

			bond		
	symmetry	basis set	C_1C_2[a]	C_1C_3[b]	C_3C_4[c]
rel Mulliken overlap population for all orbitals[d]	a_1	STO-3G	−0.0381	+0.0105	−0.0033
	a_1	MP2/6-31G*			+0.0143
	b_1	STO-3G	−0.0481	+0.0296	+0.0005
	b_1	MP2/6-31G*			+0.0059
	b_2	STO-3G	−0.0532	+0.0400	−0.0225
	b_2	MP2/6-31G*	−0.0756	+0.0471	−0.0192
	total	STO-3G	−0.1394	+0.0801	−0.0253
		MP2/6-31G*	−0.1777	+0.0742	+0.0010
rel bond length		microwave	+0.027	−0.068	0.000
		MP2/6-31G*	+0.025	−0.060	+0.005

[a] Relative to C_1C_2 of cyclopropene. [b] Relative to C_1C_3 of cyclopropene. [c] Relative to C_3C_4 of methylenecyclopropane. [d] STO-3G and MP2/6-31G* calculations were performed at the experimental and MP2/6-31G*-optimized geometries, respectively, in Table V.

bilities must be considered. One, of course, is that the structural changes caused by **1d** are obscured by the experimental errors inherent in the measurements of $r(C_3C_4)$ in **1** and **2** (ca. ±0.005 Å each).

A second possibility is suggested by the observation that the double bond in **2** is apparently shorter than the double bond in isobutene by as much as 0.01 Å.[34] This shortening, if real, could be caused by an increased contribution of s character to the double bond by the ring sp^2 carbon on going from isobutene to **2**. The hybridization of this orbital has, in fact, been calculated to be $sp^{1.64}$ and $sp^{1.17}$ in isobutene[35] and **2**,[36] respectively, corresponding to an experimentally measured decrease in $\angle C_1C_3C_2$ from 115.6° in isobutene to 63.9° in **2**. A further decrease to 54.7°, as determined in **1**, might be expected to cause a further shortening of the double bond, which would tend to counteract any lengthening resulting from polarization of the π system.

A third possibility arises through interaction of the occupied $3b_1$ Walsh orbital of the three-membered ring with the occupied b_1 CH_2 orbital which results in the polarization illustrated in Figure 4.[37] A key result of this mixing is that the resultant orbitals are polarized such that C_3C_4 overlap is maximized in the $3b_1$ orbital whereas C_3C_4 antibonding overlap is minimized in the $4b_1$ orbital. This is a general result for the interaction of two filled orbitals and occurs in order to minimize four-electron repulsion.[38]

This effect will be more important in **1** than in **2** because the occupied b_1 CH_2 orbital of the former will be higher in energy owing to the greater negative charge on C_4 in **1** relative to **2**. This is clearly seen from the MP2/6-31G*//MP2/6-31G* orbital coefficients given in Figure 4.

Although the validity of Mulliken overlap populations has frequently been questioned, particularly with regard to three-membered rings,[39] comparisons of the populations for C_3C_4 in **1** and **2** should be meaningful because of the similar nature and identical lengths (as measured by microwave spectroscopy) of these bonds. Thus, it is seen in Table VI that there is a reasonably large decrease in the total b_2 π-electron population of C_3C_4 on going from **2** to **1**, as expected for a significant contribution from resonance form **1d**. The comparable increases in the MP2/6-31G* C_3C_4 a_1 and b_1 populations suggest that the hybridization and polarization arguments given above may be valid, although our confidence in Mulliken populations is such that we consider this to still be an open question.

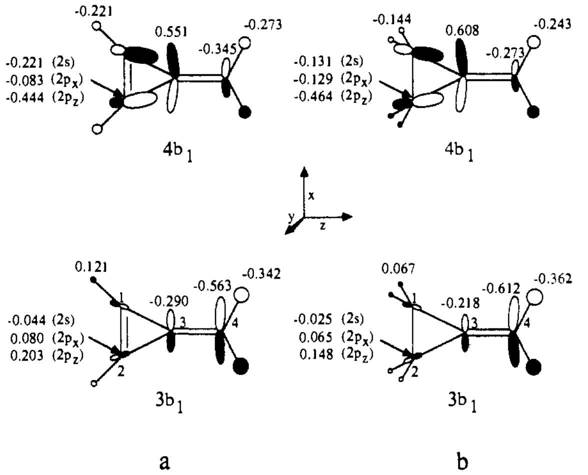

Figure 4. Resultant $3b_1$ and $4b_1$ oribtals (illustrated with MP2/6-31G*//MP2/6-31G* coefficients) from the interaction of the $3b_1$ orbital of cyclopropane or cyclopropene with the highest occupied b_1 CH_2 orbital: (a) for methylenecyclopropene; (b) for methylenecyclopropane. The effect of the polarization functions at C_3 and C_4 is indicated by the tilting of the orbitals.

In summary, we conclude that C_3C_4 π-bond weakening in **1** resulting from the contribution of **1d** is counterbalanced by increased bonding in the σ system such that any differences in the C_3C_4 bond lengths for **1** and **2** are probably within the combined experimental uncertainties in the experimental bond lengths for these compounds.

C_1C_2 Bond. The contribution of dipolar form **1d** to **1** can be assessed by comparing the experimental $r(C_1C_2)$ in **1** (1.323 Å) with the corresponding bond lengths in cyclopropene (1.296 Å) and cyclopropenium cation (**5**) (1.373 Å). On the basis of these figures, $r(C_1C_2)$ is lengthened about 35% of the way from **3** to **5**. Although the experimental $r(C_1C_2)$ value listed in Table V for **5** is only a mean value from X-ray diffraction studies of substituted cyclopropenium cations, an uncertainty of ±0.01 Å in this length introduces an uncertainty of only ±5%. If one instead employs either the 6-31G*- or the MP2/6-31G*-optimized bond lengths in Table V, one calculates changes of 40% and 37%, respectively. Thus experiment and theory agree remarkably well here.

How do these figures relate to the question of the contribution of **1d** to **1**? To answer this we first note that, as a consequence of the b_1 orbital mixing diagrammed in Figure 4, there is a net polarization of the three-membered ring Walsh orbital (which has essentially the same basis orbital energy in **3** and **4**)[40] toward C_1

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(34) (a) Scharpen, L. H.; Laurie, V. W. *J. Chem. Phys.* **1963**, *39*, 1732. (b) Tokue, I.; Fukuyama, T.; Kuchitsu, K. *J. Mol. Struct.* **1974**, *23*, 33.

(35) Maksić, Z. B.; Rubčić, A. *J. Am. Chem. Soc.* **1977**, *99*, 4233.

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(37) This effect was previously noted in methylenecyclopropane: Deakyne, C. A.; Allen, L. C.; Laurie, V. W. *J. Am. Chem. Soc.* **1977**, *99*, 1343.

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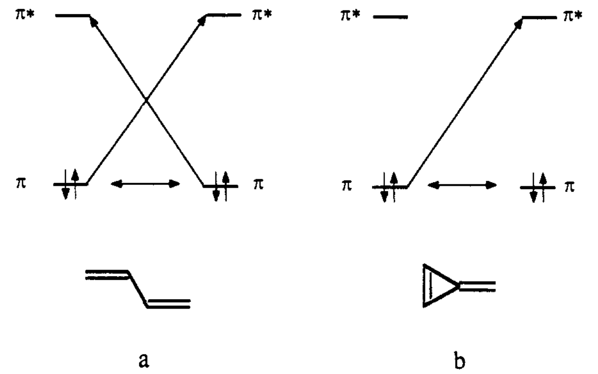


Figure 5. π-Electron interactions in (a) 1,3-butadiene and (b) methylenecyclopropene. Double-headed arrows represent destabilizing four-electron interactions between filled orbitals whereas single-headed arrows represent stabilizing two-electron interactions between a filled and an empty orbital.

and C_2. The upper ($4b_1$) orbital displays the dominant effect and, as discussed above, is more polarized in **1** than in **2**. Since this orbital is antibonding at C_1C_2, polarization causes an increase in the length of this bond. This trend is supported by the changes in STO-3G Mulliken overlap populations (Table VI) which show that the effect of the b_1 orbitals is almost as great as the effect of the b_2 (π) orbitals. Although MP2/6-31G* a_1 and b_1 populations are not available for the C_1C_2 and C_2C_3 bonds, it can be seen that the relative MP2/6-31G* b_2 and total populations closely parallel the STO-3G populations for these bonds. We cannot exactly define the influence of π-electron delocalization on $r(C_1C_2)$ in **1**, but we estimate that this factor is probably not responsible for more than about half of the total C_1C_2 bond lengthening in **1** relative to **3**.

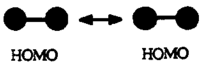
C_1C_3 Bond. There is no good model compound with which to compare $r(C_1C_3)$ in **1**, but we can make a reasonable estimate of differences in the following way. Since $r(C_1C_3)$ in **1** (1.441 Å) is most similar to $r(C_1C_3)$ in **3** (1.457 Å), we use this comparison but first correct the latter value by the difference between $r(C_1C_3)$ in cyclopropane (1.513 Å) and cyclopropene (1.509 Å). By this procedure we find that $r(C_1C_3)$ in **1** has decreased about 15% of the way from our model bond length to the value for cyclopropenium cation (1.373 Å). If we employ optimized bond lengths at the 6-31G* and MP2/6-31G* levels, we calculate decreases of 26% and 22%, respectively. Thus theory and experiment are again in reasonably good agreement.

Reference to the Mulliken overlap populations in Table VI suggests that only about $^1/_2$ to $^2/_3$ of this decrease results from π-electron delocalization. However, Mulliken populations can be unreliable in three-membered rings when bonds which are more than slightly different are compared. We therefore do not attach a great deal of significance to a comparison of the populations for C_1C_3 in **1** and **3**.

In summary, it is inherently difficult to estimate the bond length changes in **1** which result solely from π delocalization, both because of the unavailability of suitable model compounds (particularly for the C_1C_3 and C_3C_4 bonds), and because a significant proportion, perhaps on the order of half or more for C_1C_2, of the changes result from polarization of the σ system. As a rough approximation, we suggest that the estimate of a $^1/_5$ contribution of **1d** to the ground state of **1** which was obtained by an analysis of the charge distribution is also a reasonable figure based on our structural analysis.

Thermodynamic Stability. What are the energetic consequences of the dipolar character of **1**? Does it really represent "pseudoaromaticity" as is sometimes considered? We shall discuss this problem at two levels, first on the basis of a simple orbital interaction model and then in terms of the total molecular energy at the MP2/6-31G* level of theory.

A reasonable point of comparison for the π system of methylenecyclopropene is the corresponding system of 1,3-butadiene. As can be seen in Figure 5, the π bonds in 1,3-butadiene mix through one four-electron interaction (**9**) and two two-electron interactions (**10**) whereas methylenecyclopropene has only one



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interaction of each type (**6** and **7**). However, since the orbital energy change caused by each interaction is, according to second-order perturbation theory, approximately given by eq 1, where c_i and c_j are the sum of the coefficients at the interacting carbons on double bonds i and j, respectively, and ϵ_i and ϵ_j are the basis

$$\Delta\epsilon \approx \frac{c_i^2 c_j^2 \beta^2}{\epsilon_i - \epsilon_j} \qquad (1)$$

energies of the interacting orbitals, it can be seen that the effect of interaction **7** in methylenecyclopropene is twice as large ($((2/\sqrt{2})^2(1/\sqrt{2})^2\beta^2/2\beta = 0.50\beta)$) as both of the two type-**10** interactions ($(2(1/\sqrt{2})^2(1/\sqrt{2})^2\beta^2/2\beta = 0.125\beta)$) in butadiene combined. This explains why the simple Hückel molecular orbital (HMO) delocalization energy is twice as large for **1** (0.96β) as for butadiene (0.48β).

However, this result obtains because the neglect of overlap in simple HMO theory means that no destabilization is incorporated for four-electron interactions, which are clearly larger in **1** than in butadiene. If an overlap integral of 0.25 is employed, HMO π stabilization energies of 0.18γ and 0.19γ are calculated for butadiene and methylenecyclopropene, respectively.[41] At this level of calculation, the extra π repulsion in **1** almost exactly cancels the extra π delocalization (two-electron stabilization) relative to butadiene.

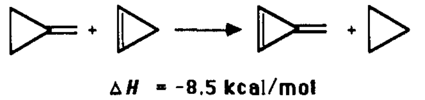
This problem can be dealt with further at the ab initio level. Consider the isodesmic reaction in eq 2 for which all structures have been optimized at the 6-31G* level.[25,28,42] Since a $C_{sp^2}H$ and a $C_{sp^2}C_{sp^2}$ bond on the left change to a $C_{sp^3}H$ and a $C_{sp^2}C_{sp^2}$ bond on the right, and since there is undoubtedly an increase in


(2)

ΔH = 0.9 kcal/mol

σ-strain energy on going from cyclopropene to methylenecyclopropene, we cannot attribute the calculated ΔH value solely to a change in π-delocalization energy. Nevertheless, it is clear that any extra π-delocalization energy in **1** relative to butadiene is not sufficient to compensate for increased strain and/or reduced σ bonding on the right side of eq 2.

ΔH for eq 3 is calculated to be −8.5 kcal/mol at the MP2/6-31G* level.[43] If one combines this value with the experimental heats of formation (ΔH_f) for all of the compounds in eq 3 except


(3)

ΔH = −8.5 kcal/mol

1,[44] then one calculates a ΔH_f of 93.4 kcal/mol for **1**. This value was previously calculated to be 62.0 kcal/mol by MINDO/2[45]

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and 81.0 kcal/mol by MINDO/3.[46]

Summary. Methylenecyclopropene is a remarkably polar compound; we estimate that dipolar form **1d** constitutes (in valence bond terms) about $^1/_5$ of the ground state of **1**. However, over $^1/_2$ of the π polarization in **1** results from four-electron repulsion and therefore corresponds to a destabilizing effect. Consequently the π delocalization energy of **1** is probably not greatly different from that for butadiene, and we conclude that it is nonaromatic.

Interestingly, although the polarity of the π system is primarily responsible for the dipole moment of **1**, there is some polarization of the σ system in the opposite direction. In particular, four-electron polarization of σ orbitals on going from **2** or **3** to **1** may contribute to a reduced lengthening of C_3C_4 and undoubtedly causes an enhanced lengthening of C_1C_2 compared to what is expected on the basis of π delocalization alone.

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Registry No. Methylenecyclopropene, 4095-06-1.

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A Correlation between β-Hydrogen Isotope Effects on Carbon-13 NMR Chemical Shifts in Unsaturated Systems and the Strength of Hyperconjugative Interactions

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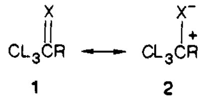
Abstract: β-Hydrogen isotope effects on the carbon-13 NMR chemical shifts of the trigonal carbon in $CL_3C(R){=}X$ (L = H or D) are reported for 15 substances in which the positive charge density at the trigonal carbon is regulated through systematic variation of R and X. A linear relationship is found between these isotope effects and the chemical shifts of the trigonal carbons, and this is taken as evidence for dependence of the magnitude of these isotope effects upon the strength of the hyperconjugative interaction between CL_3 and $C(R){=}X$. An explanation of hyperconjugative NMR isotope effects in terms of anharmonic carbon-hydrogen bond-bending vibrations is advanced.

Hydrogen isotope effects on carbon-13 NMR chemical shifts of unsaturated carbon atoms produced by isotopic substitution at a β-position have been attributed to isotopic perturbation of hyperconjugation.[1] The evidence for this interpretation includes a conformational dependence of isotope effect appropriate to hyperconjugation,[2-4] transmission of the isotope effect through π-systems,[4-7] and a general parallelism between the magnitude of these isotope effects and the need for hyperconjugative stabilization.[1,3,8] We now present additional evidence which strengthens this last line of reasoning: we have found a correlation between such isotope effects and the chemical shifts of the carbon atoms to which they refer, which implies that the magnitude of the isotope effect depends upon the strength of the hyperconjugative interaction.

We examined a series of compounds with the general formula **1** (L = H or D) in which the demand for hyperconjugative stabilization by the methyl group can be regulated by varying the groups X and R. As the dipolar resonance form **2** becomes more important and the positive charge density at the trigonal carbon atom increases, hyperconjugative stabilization of this positive charge will increase as well. Increases in positive charge density induced by increasing contribution from dipolar resonance forms have also been taken to be the cause of downfield changes in the position of NMR chemical shifts of trigonal carbon atoms in olefins and carbonyl compounds.[9] It follows then, that, if hy-



1 **2**

Table I. Carbon-13 Chemical Shifts and NMR Isotope Effects for $CL_3CR{=}X$

X	R	$\delta^{CH_3}_{C=X}$	$(\delta^{CH_3}_{C=X} - \delta^{CD_3}_{C=X})^a$
$OH^{+\,b}$	CL_3	248	−0.242 ± 0.009[c]
O[d]	CL_3	212	−0.173 ± 0.004[c]
O	2,4,6-$(CH_3)_3C_6H_2$	206	−0.147 ± 0.004
O	CL_3	204	−0.154 ± 0.004[c]
O	$C(CH_3)_3$	211	−0.117 ± 0.007
O	H	199	−0.223 ± 0.007
O	C_6H_5	197	−0.128 ± 0.007
$OH^{+\,e}$	OH	191	−0.106 ± 0.007
O	OH	178	−0.040 ± 0.005
O	OC_6H_5	170	−0.021 ± 0.007
O	Cl	170	0.000 ± 0.009
$NNHC_6H_3(NO_2)_2$	CL_3	154	0.000 ± 0.003[c]
$CHCH_3$	CL_3	132	0.086 ± 0.002[c]
CHC_6H_5	H	125	0.113 ± 0.004
$C(CH_3)_2$	CL_3	123	0.095 ± 0.002[c]

[a] Error limits are based upon uncertainties in chemical shifts, which were taken to be equal to the digital resolution. [b] The solvent was SbF_5/FSO_3H and CD_2Cl_2 was used as external reference; sample temperature −30 °C. [c] Isotope effect per CD_3 group, i.e., one-half of the observed value. [d] The solvent was H_2O, and C_6D_6 was used as external reference. [e] The solvent was 96% aqueous H_2SO_4, and C_6D_6 was used as external reference.

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