Electronic States of Organic Molecules. 6. Dipole and Quadrupole Moments: The Sign of the Dipole Moment for Cyclopropene and the Microwave Spectrum of 3,3-Dimethylcyclopropene

Kenneth B. Wiberg,*[1a] G. Barney Ellison,[1a] John J. Wendoloski,[1a] William E. Pratt,[1a] and Marlin D. Harmony*[1b]

Contribution from the Departments of Chemistry, Yale University, New Haven, Connecticut 06520, and The University of Kansas, Lawrence, Kansas 66045. Received April 10, 1978

Abstract: Calculated dipole and quadrupole moments are compared with experimental values and give generally good agreement. The sign of the dipole moment of cyclopropene is discussed. A study of the microwave spectrum of 3,3-dimethylcyclopropene leads to a dipole moment in good agreement with the calculated value. The origin of the reversed sign of the dipole moment for cyclopropane is considered, and it is shown to arise largely from the π-type CH_2 and olefinic fragments.

It is now clear that geometries of molecules may satisfactorily be calculated via either ab initio or semiempirical molecular orbital methods.[2] The charge distribution is another important property of molecules. The observation that dipole moments may often be calculated with reasonable accuracy suggests that the charge distribution may be satisfactory.[3] The quadrupole moment provides another useful test of the charge distribution. The quadrupole moments for a number of compounds are now available.[4]

We have obtained restricted Hartree–Fock wave functions for a number of compounds as a result of other studies and have calculated both the dipole and quadrupole moments. The results are shown in Table I and are based on the experimental geometry. Both a minimal STO-3G[5] and a split valence 4-31G[6] basis set were used in the calculations.

The calculated magnitudes of the dipole moments are generally reasonable and with few exceptions agree with the experimental values within 0.1 D. For *cis*-2-butene and the cycloalkenes, both basis sets give essentially the same dipole moments. In the case of isobutene and the methylenecycloalkanes, the 4-31G basis set gives a significantly higher dipole moment which is in better agreement with experiment.

If one examines the calculated charge densities for the cycloalkenes, one finds that the sum of the charges at a given CH_2 or CH group is quite similar for the two basis sets. On the other hand, with the methylenecycloalkanes, the 4-31G basis set leads to a considerably larger electron density migration from the α-methylene groups to the double bond than does the 3G basis set. Thus, the use of a larger basis set appears to be more important for unsymmetrically substituted alkenes.

The STO-3G basis set gives a remarkably good dipole moment for bicyclobutane, but here, the more flexible basis set leads to a poorer calculated dipole moment.[7]

The major disagreement between experiment and theory is found with cyclopropene for which the sign of the calculated dipole moment[8] is found to be opposite to that determined experimentally. The sign of the calculated moment of cyclopropene is of interest since it is opposite to that of other alkanes. That is, the double bond is calculated to be at the positive end of the dipole. The observation that 1-methylcyclopropene[9] has a larger dipole moment than cyclopropene supports the calculated sign. It seemed important to verify that methyl substitution at the 3 position would decrease the dipole moment. For this reason, we have investigated the microwave spectrum of 3,3-dimethylcyclopropene.

The microwave spectrum consisted entirely of α-type transitions which were easily assigned by studying the Stark effect of low-*J* transitions. Although the spectrum is potentially complicated by tunnelling of the two equivalent methyl groups, we observed no splitting of any of the assigned ground state transitions. Some multiplets, which appear to involve methyl tunnelling, have been observed, but their assignment as high-*J* ground state lines or excited torisional state transitions has not been accomplished at this time. Table II presents the observed transitions and Table III the rotational constants (rigid rotor model)[10] which satisfy the observed spectrum.

Measurements of the Stark shifts of selected rotational transitions are presented in Table IV. From these data the dipole moment has been computed by the method of Golden and Wilson[11] to have the value $|\mu| = 0.287$ D (entirely in the *a* direction).

Although a precise structure cannot be obtained from the data for the single isotopic species, a good estimate of the heavy-atom structure can be made since only four heavy-atom parameters are involved. We assume the methyl groups to be tetrahedral with $R(CH) = 1.090$ Å and assume also that the olefinic hydrogens are positioned exactly as in cyclopropene ($R(CH) = 1.070$ Å, $\angle C_1C_2H = 149.9°$).[12] Systematic investigation of the values of the heavy-atom parameters which satisfy the observed rotational constants leads to the following results: $R(C=C) = 1.294 \pm 0.01$ Å, $R(C_1C_3) = R(C_2C_3) = 1.520 \pm 0.01$ Å, $R(C_3–CH_3) = 1.521 \pm 0.01$ Å, and $\angle CH_3–C_3–CH_3 = 114.1 \pm 1°$. Diagnostic fitting procedures indicate that $R(C=C)$ is the best determined of the four parameters. The listed uncertainties are likely to encompass the true r_0 values. For cyclopropene the corresponding values are $R(C=C) = 1.300$ Å, $R(C_1C_3) = 1.515$ Å.

The calculated STO-3G dipole moments for methyl-substituted derivatives are shown below:

μ_{obsd}, D	0.454		0.287
μ_{calcd}, D	0.513	0.864	0.387

The decrease in the observed dipole moments on 3-methyl substitution agrees well with calculated decrease. It was not possible to obtain the dipole moment of 1,2-dimethylcyclopropene,[13] but the observed value for 1-methylcyclopropene indicates that the 1,2-dimethyl derivative would have a dipole moment in agreement with the calculated value.

Hehre and Pople have explained the difference between cyclopropene, with a large reversed dipole moment, and cy-

Table I. Calculated Dipole and Quadrupole Moments

molecule	dipole moments[a] calcd STO-3G	calcd 4-31G	obsd	quadrupole moments[b] calcd STO-3G	obsd[k]
ethylene				0.652	
				0.943	
				−1.595	
cis-2-butene	0.145	0.128	0.253[c]	0.890	
				0.020	
				−0.910	
cyclopropene	0.513	0.528	0.454[d]	−0.556	−0.4 ± 0.4
				1.389	2.4 ± 0.3
				−0.833	−2.0 ± 0.6
cyclobutene	0.048	0.067	0.132[e]	0.175	0.3 ± 0.6
				0.405	1.6 ± 0.7
				−0.580	−1.3 ± 1.0
cyclopentene				0.125	
	0.126	0.118	0.190[f]	0.264	
	0.003		0.05	−0.388	
isobutene	0.421	0.527	0.503[g]	0.243	
				0.672	
				−0.915	
methylenecyclopro-pane	0.186	0.311	0.402[h]	0.079	−0.7 ± 0.5
				0.076	0.9 ± 0.6
				−0.155	−0.2 ± 0.9
methylenecyclobu-tane	0.384	0.515	0.506[i]		−1.2 ± 1.1
					−1.1 ± 2.0
					2.3 ± 2.4
bicyclobutane				0.951	1.3 ± 0.2
				−2.387	−2.6 ± 0.3
	0.664		0.675[j]	1.436	1.3 ± 0.4

[a] The dipole moments are given in the order μ_a, μ_b, μ_c. [b] The quadrupole moments are given in the order Q_{aa}, Q_{bb}, Q_{cc}. Calculated quadrupole moments for ethylene and cyclopropene using a double-ζ basis set have been given by Snyder and Basch,[4b] and Ditchfield has given the values obtained using a 4-31G basis set.[2b] In the case of ethylene, there is a significant change in calculated moment on going from an STO-3G to a 4-31G basis set.[2b] [c] S. Kondo, Y. Sakurai, E. Hirota, and Y. Morino, *J. Mol. Spectrosc.*, **34**, 231 (1970). [d] P. H. Kasai, R. J. Meyers, D. F. Eggers, and K. B. Wiberg, *J. Chem. Phys.*, **30**, 512 (1959). [e] H. Kim and W. D. Gwinn, *J. Chem. Phys.*, **42**, 3728 (1965). [f] S. S. Butcher and C. C. Costain, *J. Mol. Spectrosc.*, **15**, 40 (1965). [g] L. H. Scharpen and V. W. Laurie, *J. Chem. Phys.*, **39**, 1732 (1963). [h] V. W. Laurie and W. M. Stigliani, *J. Am. Chem. Soc.*, **92**, 1485 (1970). [i] L. H. Scharpen and V. W. Laurie, *J. Chem. Phys.*, **49**, 3041 (1968). [j] M. D. Harmony and K. W. Cox, *J. Am. Chem. Soc.*, **88**, 5049 (1966). [k] W. H. Flygare and R. C. Benson, *Mol. Phys.*, **20**, 225 (1971).

clobutene, with a small normal moment, in terms of charge-transfer arguments.[8] The two molecules are viewed as being formed from the olefinic and CH_2 fragments shown in Figure 1. In cyclobutene, back-bonding to the unoccupied (virtual) orbitals is possible for both the olefinic and methylene fragments, so the net change transfer is zero and the dipole moment is small. For cyclopropene, however, charge transfer is possible only for the olefinic fragment. Mixing between the CH_2 fragment and the virtual π orbital in Figure 1 is forbidden by symmetry (i.e., the virtual orbital and the CH_2 orbital transform differently under reflection in the plane perpendicular to the C=C bond). Thus, charge is transferred from the double bond to the methylene group giving rise to the observed dipole.

A further analysis is assisted by an examination of the π-type (out-of-plane) molecular orbitals of cyclopropene and cyclo-
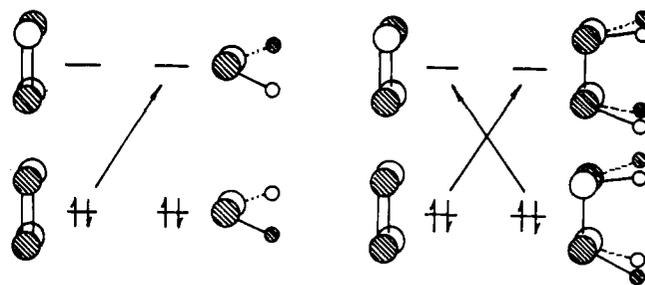
Figure 1. Cyclopropene and cyclobutene fragments.

Table II. Microwave Spectrum of 3,3-Dimethylcyclopropene (All Frequencies are in Megahertz)

transition	obsd	obsd-calcd
$2_{11} \rightarrow 3_{12}$	29 262.56	0.10
$2_{20} \rightarrow 3_{21}$	29 754.80	0.09
$2_{21} \rightarrow 3_{22}$	27 599.39	0.07
$3_{03} \rightarrow 4_{04}$	33 003.42	−0.02
$3_{13} \rightarrow 4_{14}$	32 832.34	0.06
$3_{12} \rightarrow 4_{13}$	37 727.62	−0.06
$3_{22} \rightarrow 4_{23}$	36 228.39	−0.04
$3_{31} \rightarrow 4_{32}$	37 752.38	−0.06
$3_{30} \rightarrow 4_{31}$	38 883.89	−0.06

Table III. Rotational Constants of 3,3-Dimethylcyclopropene

A	6872.96 ± 0.21 MHz[a]
B	5353.25 ± 0.03 MHz
C	3846.52 ± 0.03 MHz
κ	−0.004289

[a] Uncertainties represent three times the standard deviation of the rigid rotor fit.

Table IV. Stark Effect and Dipole Moment of 3,3-Dimethylcyclopropene

transition	M	$\Delta\nu/E^2$ obsd	calcd
$2_{21} \rightarrow 3_{22}$	1	3.028[a]	3.028
$2_{11} \rightarrow 3_{12}$	2	−0.3695	−0.3676
$3_{33} \rightarrow 4_{23}$	2	0.5618	0.5629
$|\mu_a| = |\mu| = 0.287 \pm 0.003$ D			

[a] Units are 10^{-6} MHz/(V/cm)^2. System calibration based on μ = 0.7152 for OCS.

butene (Figures 2 and 3). In both molecules, the CH_2 π fragments do not mix appreciably with the olefinic π fragments having the same symmetry. Similarly, the olefinic π MO of cyclobutene (MO 15) does not have an appreciable contribution from the CH_2 π fragment. The unique MO in this set is MO 11 for cyclopropene which contains both types of fragment orbitals, but in an antisymmetric combination. The charge-transfer argument would require a symmetric combination, and therefore it does not appear adequate to explain the sign of the cyclopropene dipole moment.

Streitwieser has shown that electron density maps, in which the total density along an axis perpendicular to a point on a reference plane is summed, are useful in analyzing electron density distributions.[14] In favorable cases, such a map will have clearly visible minimum density lines, enabling numerical integration to give the total density in each region. For example, ionic compounds such as lithium hydride work well.

Projected density maps have been calculated for the all occupied MO's as well as selected groups of MO's of cyclopro-
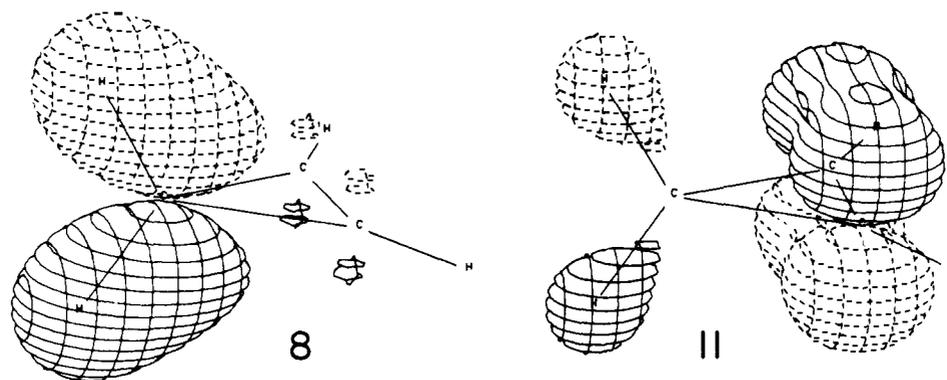
Figure 2. Molecular orbitals 8 and 11 of cyclopropene.
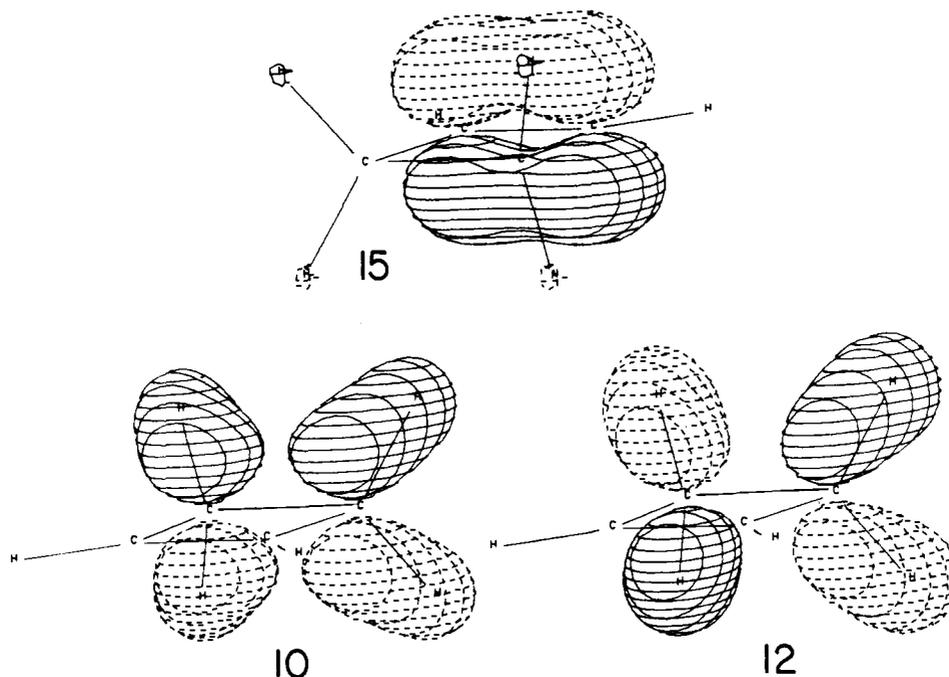

Figure 3. Molecular orbitals 10, 12, and 15 of cyclobutene.

pene and cyclobutene. These maps were integrated numerically along the minimum density path separating the olefinic and methylene fragments. The results are summarized in Table V. It is clear from these data that the anomalous cyclopropene dipole can be attributed to the π orbitals. All of the cyclobutene data and the σ part of cyclopropene agree with the normal values for the corresponding fragments, whereas the cyclopropene π component shows a large electron shift toward the methylene group.

The large π shifts in cyclopropene are due to MO 11. The reason for this shift can be understood in qualitative terms from the plots in Figures 4 and 5 which contain the projected density contours for the π MO's in cyclopropene and cyclobutene. These density maps show that the cyclopropene methylene group overlaps much more with the π orbitals than do the corresponding groups in cyclobutene. MO orthogonality then requires more mixing to occur in cyclopropene than in cyclobutene.

In a more quantitative sense, let the two π MO's in cyclopropene be written as:

$$\Phi_I = (\phi^\pi + A\phi^{CH_2})/(1 + A^2 + 2AS)^{1/2}$$

$$\Phi_{II} = (B\phi^\pi + \phi^{CH_2})/(1 + B^2 + 2BS)^{1/2}$$

where ϕ^π is the olefinic π fragment, ϕ^{CH_2} is the methylene

Table V. Electron Distribution from Projected Density Maps

compd	position	orbitals	calcd	"exact"
cyclopropene	methylene	σ	4.0	4
		π	2.4	2
		all	6.4	6
	olefinic	σ	8.0	8
		π	1.6	2
		all	9.6	10
cyclobutene	methylene	σ	8.0	8
		π	4.0	4
		all	12.0	12
	olefinic	σ	8.0	8
		π	2.0	2
		all	10.0	10

fragment, and S is the overlap of the two. Orbital orthogonality then gives:

$$A + B + S(1 + AB) = 0 \qquad (1)$$

For $S > 0$, one of the coefficients (A or B) must be positive and the other negative if eq 1 is to hold. In MO 8 (Φ_{II}), B is small and has a positive sign. This requires that in MO 11 (Φ_I) A should have a negative sign. In addition, if B is very small, A
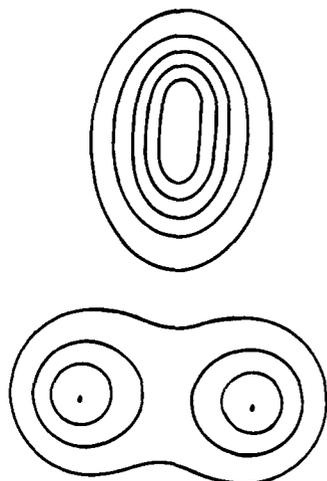
Figure 4. Electron density map for π MO's in cyclopropene.

Table VI. MO Contributions to Dipole Moment

component	cyclopropene	cyclobutene
μ^π	−0.42	−0.05
μ^σ	−0.09	0.10
μ^{tot}	−0.51	0.05

$\approx -S$. Since S is relatively large, A must have a relatively large negative value. In the case of cyclobutene, S is considerably smaller and a corresponding treatment will give a much smaller value for the mixing coefficient.

As an additional test, the contribution of each MO to the dipole moment was calculated and was grouped as σ or π. The nuclear contribution was eliminated by partitioning it equally to each MO, which should be adequate when viewed in terms of σ and π contributions. The calculated values (Table VI) indicate that the π orbitals give the dominant term. The sign difference between the σ components of cyclopropene and cyclobutene may be rationalized in terms of bond stabilization. Since MO 11 in cyclopropene introduces a node in the C–C bond region, the σ-orbital electrons must shift from hydrogen into the ring to compensate for the energy rise. Since there are two olefinic carbons and only one methylene, the net shift gives a moment parallel to the total moment.

The difference in calculated energy between 1,2-dimethyl- (A) and 3,3-dimethylcyclopropene (B) may also be noted. The hypothetical isomerization of A to B is an isodesmic process for which Pople[15] has shown good agreement between calculated and observed heats of reaction. In the present case the calculated difference in energy is 13 kcal/mol with A the more stable. This is in good agreement with the observation that the hydrogenation of cyclopropene is 16 kcal/mol[16] more exothermic than the hydrogenation of 1,2-dimethylcyclopropene.[17]

Although the dipole moments are a useful indicator of how well the calculated wave functions represent the electron density distribution, they are limited in that symmetrically related charge distributions cancel out. In this way, the quadrupole moments are of more potential value. It can be seen from Table I that there is qualitative agreement between calculated and observed values, especially when the rather large errors associated with most of the experimental values are considered. More precise experimental values, although difficult to obtain, would be very valuable.

In the case in which the quadrupole moments are best determined, bicyclobutane, there is remarkable agreement between the observed and calculated moments. The agreement
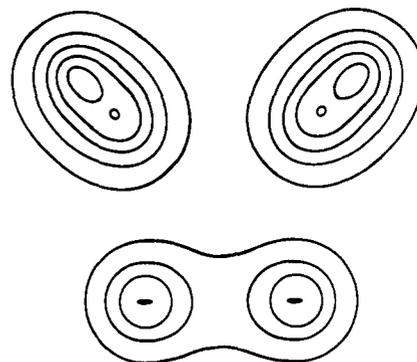

Figure 5. Electron density map for π MO's in cyclobutene.

with both the dipole and quadrupole moments suggests that the STO-3G wave functions give a good description of the electron density distribution for this compound. This is probably fortuitous since the more flexible 4-31G basis set gave a significantly smaller dipole moment.[7]

Calculations. The STO-3G calculations were carried out using POLYATOM[18] and the 4-31G calculations were carried out using GAUSSIAN-70.[19] The wave-function plots were made using the program of Jorgensen.[20]

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