dition. The cumulative double bond, C=C=C, in fluoroallene is found to be slightly bent by 1.8 ± 0.6° from the linear configuration on the other side of fluorine. Another feature of the structure is that the $C_1{=}C_2$ bond, 1.301 ± 0.004 Å, is shorter than the $C_2{=}C_3$ bond, 1.309 ± 0.003 Å, by approximately 0.008 Å. The ab initio calculation of the structure optimization was carried out with the GAUSSIAN 80 program. The structure, fully optimized with the STO-3G basis set, is in fair agreement with the observed structure. The structural parameters in allene and fluorine-substituted allenes are found to change systematically with the number of substituted fluorine atoms.

Acknowledgment. The authors thank Drs. C. Matsumura, H. Takeo, and M. Sugie at the National Chemical Laboratory for Industry for the use of microwave spectrometer and helpful discussions. They express their thanks to Prof. Kozo Kuchitsu and Dr. A. P. Cox for critical reading of the manuscript and useful comments. They also thank the Computer Center, Institute for Molecular Science, Okazaki National Research Institute for the use of the HITAC-680H and S810/10 computer.

Registry No. $FCH{=}C{=}CH_2$, 51584-22-6; $F^{13}CH{=}C{=}CH_2$, 110971-94-3; $FCH{=}^{13}C{=}CH_2$, 110971-95-4; $FCH{=}C{=}^{13}CH_2$, 110971-96-5; $FCD{=}C{=}CH_2$, 110971-97-6; $FCH{=}C{=}CHD$, 110971-98-7; carbon suboxide, 504-64-3; fluoroethene, 75-02-5.

Supplementary Material Available: Table I, transition frequencies of fluoroallene and its isotopic species (1 page). Ordering information is given on any current masthead page.

Electronic Structure of Cyclopropenone and Its Relationship to Methylenecyclopropene. Evaluation of Criteria for Aromaticity

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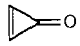
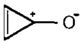
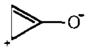
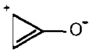
Abstract: The heavy-atom microwave (r_s) structure of cyclopropenone has been redetermined to be $r(C_1O)$ = 1.212 Å, $r(C_1C_2)$ = 1.423 Å, and $r(C_2C_3)$ = 1.349 Å. These values agree closely with ab initio geometry-optimized bond lengths calculated at the MP2/6-31G* level. Cyclopropenone has approximately twice the π-delocalization energy of methylenecyclopropene and can be considered to be moderately "aromatic". In addition, this molecule is significantly stabilized by in-plane lone-pair donation from oxygen to the unoccupied $4b_1$ orbital of the ring. It is concluded that structure, electron distribution, and thermodynamic stability respond to a similar degree to π delocalization relative to appropriate model compounds.

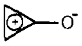
Cyclopropenone (**1**) has received considerable attention during the last three decades owing primarily to its possible description as an "aromatic" compound.[2] The latter is exemplified by dipolar resonance forms **1a–c** (equivalent to **1d**) and is expected to result in a high polarity and increased stability relative to related compounds, such as cyclopropanone (**2**). (Structures and their numbering are given in Figure 1.) This has indeed been shown to be the case,[2] but a consensus has by no means been reached concerning the electronic character of **1**.


1


1a


1b


1c


1d

Thermodynamic results (both thermochemical[3] and ab initio molecular orbital calculations[3a,4]) have led to the conclusion that there is substantial ground-state "aromatic" stabilization in this molecule. The results of an early thermochemical study[5] that pointed to the opposite conclusion for 2,3-diphenylcyclopropenone have been invalidated by subsequent studies.[3] Hase et al.[4b] employed the technique of conjugative interruption to suggest that significant stabilization arises from π-electron delocalization, in support of previous conclusions based on simple π-electron calculations.[6]

The available evidence concerning molecular structure and electron distribution is more ambiguous. The key study is the microwave study of Benson et al. in which the C=C length ($r(C_2C_3)$) was found to be 1.302 Å,[7] essentially identical with the 1.296-Å value found for cyclopropene.[8] This, along with an analysis of the magnetic susceptibility anisotropy of **1**, led these authors to conclude that resonance forms **1b** and **1c** are relatively unimportant and that the large molecular dipole (4.39 D) and quadrupole moments are largely a reflection of the importance of the C=O bond polarity alone, as exemplified by **1a**. This view appeared to be supported by a partial geometry optimization of **1** at the HF/STO-3G level[9] and by an analysis of the bond lengths in **1** and related compounds.[10]

Although Ammon concluded that the crystallographic molecular structure of 2,3-diphenylcyclopropenone monohydrate suggests

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(1) (a) Present address: Carnegie Mellon University. (b) University of Nebraska. (c) University of Kansas.

(2) Reviews: (a) Krebs, A. W. *Angew. Chem., Int. Ed. Engl.* **1965**, *4*, 10. (b) Eicher, T.; Weber, J. L. *Top. Curr. Chem.* **1975**, *57*, 1.

(3) (a) Greenberg, A.; Tomkins, R. P. T.; Dobrovolny, M.; Liebman, J. F. *J. Am. Chem. Soc.* **1983**, *105*, 6855. (b) Grabowski, J. J.; Simon, J. D.; Peters, K. S. *Ibid.* **1984**, *106*, 4615. (c) Steele, W. V.; Gammon, B. E.; Smith, N. K.; Chickos, J. S.; Greenberg, A.; Liebman, J. F. *J. Chem. Thermodyn.* **1985**, *17*, 505.

(4) (a) Clark, D. T.; Lilley, D. M. J. *J. Chem. Soc., Chem. Commun.* **1970**, *147*. (b) Hase, H.-L.; Müller, C.; Schweig, A. *Tetrahedron* **1978**, *34*, 2983. (c) Budzelaar, P. H. M.; Kraka, E.; Cremer, D.; Schleyer, P. v. R. *J. Am Chem. Soc.* **1986**, *108*, 561.

(5) Hopkins, H. P., Jr.; Bostwick, D.; Alexander, C. J. *J. Am. Chem. Soc.* **1976**, *98*, 1355.

(6) (a) Manatt, S. L.; Roberts, J. D. *J. Org. Chem.* **1959**, *24*, 1336. (b) Hess, B. A., Jr.; Schaad, L. J.; Holyoke, C. W., Jr. *Tetrahedron* **1972**, *28*, 5299. (c) Aihara, J. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 1501. (d) Herndon, W. C. *Pure Appl. Chem.* **1980**, *52*, 1459.

(7) Benson, R. C.; Flygare, W. H.; Oda, M.; Breslow, R. *J. Am. Chem. Soc.* **1973**, *95*, 2772.

(8) Stigliani, W. M.; Laurie, V. W.; Li, J. C. *J. Chem. Phys.* **1975**, *62*, 1890.

(9) Fitzpatrick, N. J.; Fanning, M. O. *J. Mol. Struct.* **1975**, *25*, 197.

(10) Allen, F. H. *Tetrahedron* **1982**, *38*, 645.

0002-7863/87/1509-7641$01.50/0

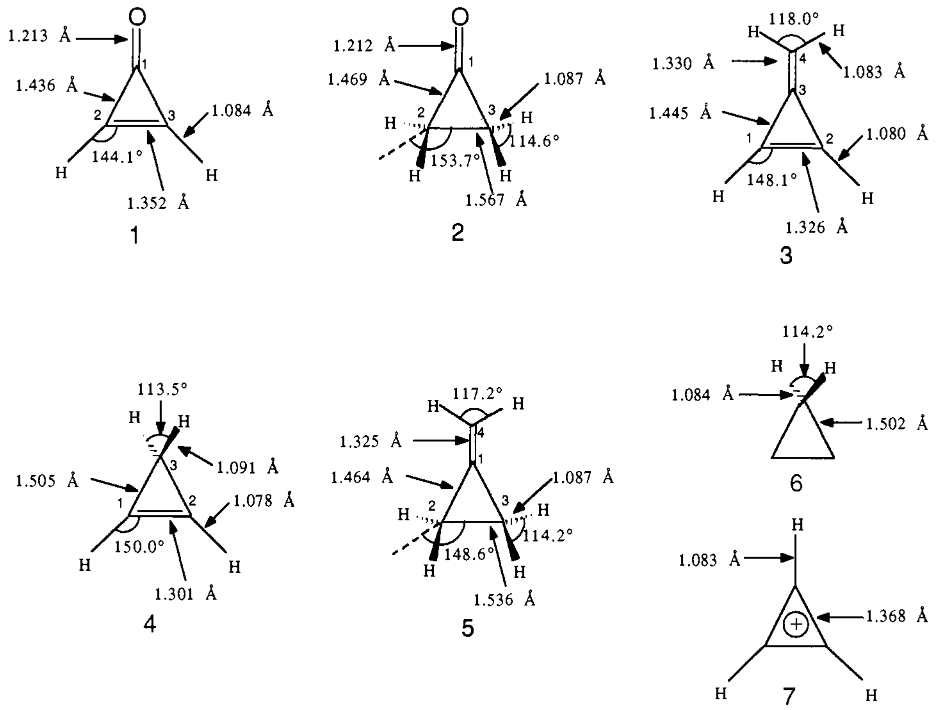

Figure 1. MP2/6-31G* geometry-optimized molecular structures for **1** and **2** (this work) and **3**–**7** (ref 16).

the contribution of some cyclopropenium character, he also acknowledged that the apparently greater (by 0.05 Å) C═C distance relative to **1** may be associated with an effect of the phenyl substituents.[11] However, hydrogen bonding undoubtedly also influences bond lengths in the monohydrate of **1**. In a similar vein, Hase et al. concluded on the basis of MINDO/3 geometry optimizations that the C═C and C═O bonds in **1** are lengthened and the C—C bond is shortened by π conjugation, but also argued that $r(C_2C_3)$ in **1** is predominantly determined by the σ system and therefore cannot be used as a guide to aromaticity.[4b]

Komornicki et al. noted without further comment that $r(C_2C_3)$ is overestimated (relative to the microwave value[7]) by ab initio geometry optimizations at the HF/4-31G and 6-31G** levels, whereas multiple bonds are normally underestimated at the Hartree–Fock limit.[12] Finally, Schleyer and co-workers have argued on the basis of ab initio geometry optimizations at the HF/3-21G level that geometric changes in **1** relative to methylenecyclopropene (**3**) indicate some effects of π delocalization.[4c]

A number of authors have regarded electron distribution as a criterion for aromaticity in **1**. The majority[4a,b,11,13] have concluded that **1** possesses some aromatic character, but a significant number[9,14] have reached the opposite conclusion. Tobey has argued for a model that is somewhat intermediate, in that there is a contribution from resonance form **1d** but no extra polarization of the C═O bond relative to that found in nonconjugated ketones.[15]

The key problem that we address in this paper, and that we believe to be of even greater importance than the question of the aromaticity of cyclopropenone, concerns the relationship between π-electron delocalization, structural effects, and resonance stabilization. Schleyer and co-workers have suggested that relatively small changes in the former two can cause considerable resonance stabilization, so that geometric arguments alone cannot be employed to exclude aromatic character.[4c] Is this argument valid or are there other ways to explain these apparent relationships?

In our recent determination of the molecular structure of methylenecyclopropene (**3**) by microwave spectroscopy, the ring C═C bond was observed to be lengthened by 0.036 Å relative to the equivalent bond in cyclopropene (**4**).[16] In addition, it was concluded that the resonance form analogous to **1d** constitutes about one-fifth of the ground-state character of **3**, although this only represents a π-delocalization energy comparable to that of 1,3-butadiene. In view of the fact that $r(C{=}C)$ in **1** was reported to be 0.02 Å *less* than $r(C{=}C)$ in **3**, it is clear that the study of Benson et al.[7] requires closer scrutiny.

Quantum Chemical Methods

Ab initio molecular orbital calculations were performed with Pople's GAUSSIAN 82 series of programs,[17] which employed the STO-3G,[18] 6-31G,[19] and 6-31G*[20] basis sets. Electron correlation effects were included at the MP2/6-31G* level by the use of analytical second-derivative techniques.[21] Geometry optimizations were performed by employing analytically evaluated atomic forces in a Berny multiparameter search routine.[17] Full basis sets were employed and geometries were optimized completely, subject only to molecular symmetry (C_{2v}) constraints. Symmetry-specific Mulliken overlap populations were calculated at the HF/STO-3G level for several compounds with Gallup's GSCF program.[22]

Revised Cyclopropenone Structure

Upon close examination of the microwave study of Benson et al.,[7] two of the reported structural parameters, viz C_2C_3 = 1.302 Å and C_2H = 1.097 Å, appeared extraordinarily suspicious to us in comparison to the results for methylenecyclopropene[16] and the earlier substitution structure for cyclopropene.[8] We have therefore

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(11) Ammon, H. L. *J. Am. Chem. Soc.* **1973**, *95*, 7093.

(12) Komornicki, A.; Dykstra, C. E.; Vincent, M. A.; Radom, L. *J. Am. Chem. Soc.* **1981**, *103*, 1652.

(13) (a) Schäfer, W.; Schweig, A. *Tetrahedron Lett.* **1974**, 1213. (b) Yamabe, S.; Morokuma, K. *J. Am. Chem. Soc.* **1975**, *97*, 4458. (c) Grier, D. L.; Streitwieser, A., Jr. *Ibid.* **1982**, 104, 3556.

(14) (a) Pittman, C. U., Jr.; Kress, A.; Patterson, T. B.; Walton, P.; Kispert, L. D. *J. Org. Chem.* **1974**, *39*, 373. (b) Skancke, A. *J. Mol. Struct.* **1976**, *30*, 95.

(15) Tobey, S. W. *The Jerusalem Symposia on Quantum Chemistry and Biochemistry. III. Aromaticity, Pseudoaromaticity, and Antiaromaticity*; Bergman, E. D., Pullman, B.; Eds.; Academic Press: New York, 1971; p 351.

(16) Norden, T. D.; Staley, S. W.; Taylor, W. H.; Harmony, M. D. *J. Am. Chem. Soc.* **1986**, *108*, 7912.

(17) Binkley, J. S.; Frisch, M.; Raghavachari, K.; DeFrees, D.; Schlegel, H. B.; Whiteside, R.; Fluder, E.; Seeger, R.; Pople, J. A. GAUSSIAN 82, Release H, Carnegie Mellon University.

(18) Hehre, W. J.; Stewart, R. F.; Pople, J. A. *J. Chem. Phys.* **1969**, *51*, 2657.

(19) (a) Ditchfield, R.; Hehre, W. J.; Pople, J. A. *J. Chem. Phys.* **1971**, *54*, 724. (b) Hehre, W. J.; Ditchfield, R.; Pople, J. A. *Ibid.* **1972**, *56*, 2257.

(20) (a) Hariharan, P. C.; Pople, J. A. *Chem. Phys. Lett.* **1972**, *16*, 217. (b) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213.

(21) Binkley, J. S.; Pople, J. A. *Int. J. Quantum Chem.* **1975**, *9*, 229.

(22) Gallup, G. A. Program GSCF, unpublished; we thank Professor Gallup for the use of this program.

Table I. Revised Molecular Structure of Cyclopropenone[a]

	published r_s[b]	revised r_s[c]	least squares[c]
C=O	1.212	1.212 ± 0.006	1.206 ± 0.006
C=C	1.302	1.349 ± 0.003	1.354 ± 0.003
C—C	1.412	1.423 ± 0.005	1.428 ± 0.005
C—H	1.097	1.079 ± 0.002	1.078 ± 0.002
∠HC=C	144.9	144.3 ± 0.1	144.1 ± 0.1
$\angle C_2C_1C_3$[d]	54.9	56.6	56.6

[a] Distance in Å, angles in deg. [b] Reference 7. [c] Recomputation as described in text. [d] Redundant parameter.

reinvestigated the spectral data and structural computations for **1** and have found that the reported r_s *b* coordinate of atom C_2 is in substantial error (by ca. 0.02 Å), leading to concomitant errors in the C_2C_3, C_2H, and C_1C_2 bond lengths. The problem arose because C_2 was located from the planar Kraitchman equations by using the *A* and *B* rotational constants. Unfortunately, the *A* rotational constants for cyclopropenone were determined with very poor accuracy for the natural abundance 1-^{13}C and 2-^{13}C species. Benson et al. quote uncertainties of ±5 MHz, but since their a-type spectra (entirely analogous to the methylenecyclopropene a-type spectrum) contain only two or three high-*J*, Q-branch lines having significant sensitivity to the *A* constants, they are likely to be of even poorer quality. A significant hint of the error lies in the fact that the reported inertial defect for the 2-^{13}C species, $\Delta = -0.1394$ amu Å^2, is approximately 0.02 amu Å^2 larger in magnitude than the values for *all* the other isotopic species.[7]

On the other hand, the *B* and *C* rotational constants are well determined by the low-*J*, *R*-branch lines, and consequently atom C_2 can be accurately located from these data alone by making use of the relation $\Delta I_a = \Delta I_c - \Delta I_b$. We have recomputed the r_s coordinates of C_2 in this fashion, and for consistency have also recomputed all the remaining atomic coordinates by using only the *B* and *C* rotational constants. Actually, the remainder of the reported coordinates change very little upon recomputation. This is because Benson et al., in fact, used only ΔI_b values for the atoms on the C_2 axis (C_1 and O), and for the dideuterio species (evaluated from Chutjian's equations[23]) the *A* rotational constant is of higher precision. Table I summarizes the results of our r_s calculations and compares the results to those originally published by Benson et al.[7] For this pure r_s structure the reported uncertainties are computed according to $\Delta_g = 0.0015/g$. We emphasize that the dominant cause of the revised parameters is a change in the C_2 *b* coordinate of 0.023 Å. Finally, for comparison purposes, the complete structure has been evaluated by the least-squares method of Nösberger et al.[24] (by using $g = b$ and c only), the results of which can also be found in Table I.

Discussion

Molecular Structure. The experimental and HF/6-31G*- and MP2/6-31G*-optimized molecular structures of **1**, **2**, and related compounds are given in Figure 1 and Table II. The agreement between the microwave r_s structures and the MP2/6-31G* r_e structures is quite good. The theoretical bond lengths for **2** agree with the microwave values within experimental error in all cases. For **1**, where the experimental uncertainties are significantly less, the theoretical values are outside the r_s experimental range by only 0.003 and 0.008 Å for r(CH) and $r(C_1C_2)$, respectively, and outside the least-squares experimental range by only 0.004 (CH), 0.003 (C_1C_2), and 0.001 Å (C_1O). It is clear that there is good agreement between absolute (as well as relative) experimental and theoretical bond lengths at the MP2/6-31G* level of theory.

What do these values tell us about the contribution of resonance form **1d** to the ground state of **1**? Consider the structural comparisons in Table III. As previously discussed,[4b,27] an exocyclic methylene or carbonyl group causes the opposite bond (bond a) in cyclopropane to lengthen (entries 1 and 3), with the carbonyl group having a significantly larger effect. Interestingly, entries 2 and 4 indicate that these groups cause double-bond lengthenings almost equal to those of the single bonds in entries 1 and 3, respectively, even though the double bonds have a much higher force constant for stretching. This is consistent with a significant π component to the lengthenings of the double bonds, as exemplified by resonance form **1d**.

Table II. Microwave and ab Initio Dipole Moments and Molecular Structures for Cyclopropenone and Cyclopropanone[a]

		theoretical structure	
	MW	HF/6-31G*	MP2/6-31G*
	Cyclopropenone (**1**)[b]		
dipole moment[c]	4.39[d]	4.69	4.85
$r(C_1C_2)$	1.423	1.412	1.436
$r(C_2C_3)$	1.349	1.327	1.352
$r(C_1O)$	1.212	1.190	1.213
	Cyclopropanone (**2**)[e]		
dipole moment[c]	2.67[f]	3.15	3.38
$r(C_1C_2)$	1.475[f]	1.462	1.469
$r(C_2C_3)$	1.575[f]	1.557	1.567
$r(C_1O)$	1.191[f]	1.179	1.212

[a] Dipole moments in D; bond lengths (microwave (r_s) or theoretical (r_e)) in Å. [b] Previous ab initio geometry optimizations: STO-3G, ref 9; 3-21G, ref 4c; 4-31G and 6-31G**, ref 12. [c] The theoretical dipole moments are all Hartree-Fock values. [d] Reference 7. [e] Previous ab initio geometry optimizations: STO-3G, ref 25a,b; 3-21G, ref 25a, 4c; 4-31G, ref 25c. [f] Reference 26.

The above conclusion is supported by an analogous shortening of bond b, as illustrated by (a) the increased shortening of bond b on going from entry 5 to 6 and 7, and (b) by the shortening of bond b in entry 9 in comparison to its lengthening in entry 8. In contrast, no compelling evidence exists for a lengthening of the carbonyl bond in **1** as expected from resonance form **1d**. The apparent lengthening of C=O (bond c) in entry 7 is questionable because of a large uncertainty (±0.02 Å) in the experimental bond length of cyclopropanone and because the MP2/6-31G*-optimized C=O bond lengths indicate essentially no change. The theoretical bond length changes support the experimental ones in all other cases.

Further insight can be gained by considering the relative Mulliken overlap populations presented in Table IV. Although there might be problems with such an analysis, particularly in three-membered ring compounds,[27a,30] we nevertheless believe that relative values can indicate trends. This is illustrated by the examples of the C_1C_2 and C_2C_3 bonds in Table IV, where a decrease or increase in total relative overlap population corresponds to an increase or decrease, respectively, in the relative bond length. In contrast, the same correspondence is not observed for the C_1O bond, possibly owing to its high polarity.

The first conclusion that we can draw from the data in Table IV is that the shortening of the C_1C_2 bond in **1** relative to the equivalent bond in either **2** or **4** results primarily from increased π bonding. Thus changes in $r(C_1C_2)$ can be expected to give a reasonable *structural* indication of the contribution of **1d** to the ground state of **1**.

In contrast, π bonding appears to play a secondary role in the changes in $r(C_2C_3)$. The largest effect arises from the in-plane π (π') orbitals, which are of b_1 symmetry. The origin of this effect

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(23) Chutjian, A. *J. Mol. Spectrosc.* **1964**, *14*, 361.

(24) Nösberger, P.; Bauder, A.; Günthard, Hs. H. *Chem. Phys.* **1973**, *1*, 418.

(25) (a) *The Carnegie Mellon Quantum Chemistry Archive*, 3rd ed.; Whiteside, R. A., Frisch, M. J., Pople, J. A., Eds.; Carnegie Mellon University: Pittsburgh, PA, 1983. (b) Kikuchi, O.; Nagata, H.; Morihashi, K. *J. Mol. Struct.* **1985**, *124*, 261. (c) Schaad, L. J.; Hess, B. A., Jr.; Zahradnik, *J. Org. Chem.* **1981**, *46*, 1909.

(26) Pochan, J. M.; Baldwin, J. E.; Flygare, W. H. *J. Am. Chem. Soc.* **1969**, *91*, 1896.

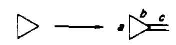
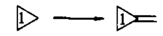
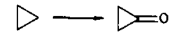
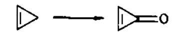
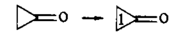
(27) (a) Deakyne, C. A.; Allen, L. C.; Laurie, V. W. *J. Am. Chem. Soc.* **1977**, *99*, 1343. (b) Jorgensen, W. L.; Salem, L. *The Organic Chemist's Book of Orbitals*; Academic Press: New York, 1973; pp 37, 38.

(28) Yamamoto, S.; Nakata, M.; Fukuyama, T.; Kuchitsu, K. *J. Phys. Chem.* **1985**, *89*, 3298.

(29) Laurie, V. W.; Stigliani, W. M. *J. Am. Chem. Soc.* **1970**, *92*, 1485.

(30) (a) Bader, R. F. W.; Henneker, W. H.; Cade, P. E. *J. Chem. Phys.* **1967**, *46*, 3341. (b) Bader, R. F. W.; Keaveny, I.; Cade, P. E. *Ibid.* **1967**, *47*, 3381. (c) Skancke, A. *Acta Chem. Scand.* **1973**, *27*, 3243.

Table III. Relative Bond Lengths of Related Three-Membered Ring Compounds

		change in bond length^a					
		Δa		Δb		Δc	
entry		exptl	MP2/6-31G*	exptl	MP2/6-31G*	exptl	MP2/6-31G*
1		+0.029	+0.034	-0.056	-0.038		
2		+0.027	+0.025	-0.068	-0.060		
3		+0.062	+0.065	-0.038	-0.033		
4		+0.053	+0.051	-0.086	-0.069		
5		-0.217	-0.201	-0.004	-0.003		
6		-0.219	-0.210	-0.016	-0.019	0	+0.005
7		-0.226	-0.215	-0.052	-0.033	+0.021	+0.001
8		+0.033	+0.031	+0.018	+0.005	+0.141	+0.113
9		+0.026	+0.026	-0.018	-0.009	-0.120	-0.117

^{a}Bond length (in Å) in the second compound minus that in the first compound. Electron diffraction or microwave values: cyclopropane, ref 28; cyclopropene, ref 8; methylenecyclopropane, ref 29; methylenecyclopropene, ref 16; cyclopropanone, ref 26; cyclopropenone, this work. Theoretical values: cyclopropanone and cyclopropenone, this work; all others, ref 16.

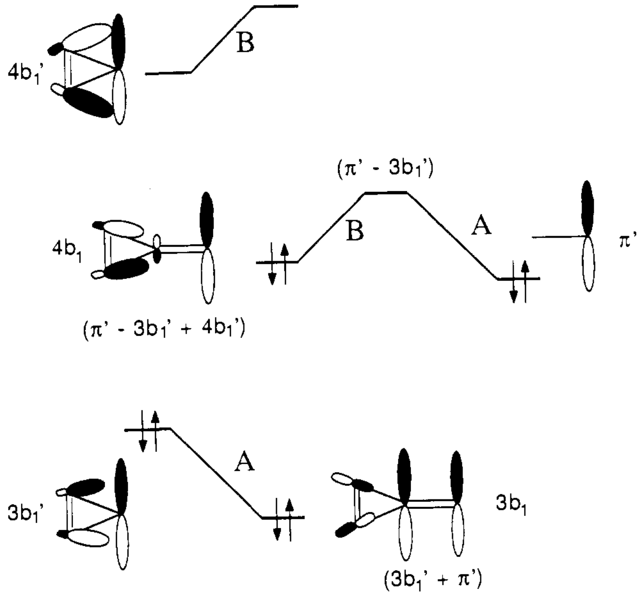


Figure 2. Interaction diagram for **1** showing the mixing of the O(2p$_x$) (π') orbital with the cyclopropene 3b$_1$ and 4b$_1$ orbitals, with interaction energies of A and B, respectively.

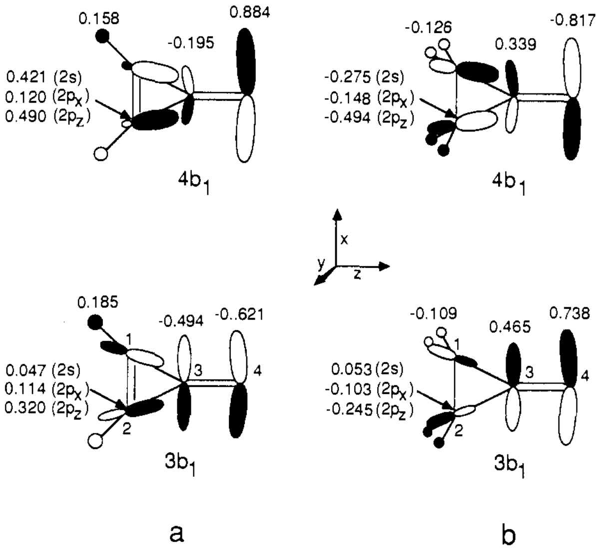


Figure 3. 3b$_1$ and 4b$_1$ orbitals (illustrated with MP2/6-31G*//MP2/6-31G* coefficients) for (a) cyclopropenone and (b) cyclopropanone. The effect of the polarization functions at C$_1$ and O is indicated by the tilting of the orbitals.

can be understood on the basis of the interactions between the π' lone-pair orbital on oxygen (O(2p$_x$)) and the highest occupied and lowest unoccupied b$_1$ ring orbitals (3b$_1$ and 4b$_1$, respectively) (Figure 2).

Two effects are undoubtedly present. First, four-electron repulsion between O(2p$_x$) and the ring 3b$_1$ orbital will polarize the ring orbital toward C$_2$ and C$_3$ and increase the antibonding interaction between these atoms. Second, two-electron donation from O(2p$_x$) into the ring 4b$_1$ orbital will also lengthen C$_2$C$_3$. This π' interaction is expected to be particularly important in **1** because π delocalization (**1d**) will increase the energy of the O(2p$_x$) basis orbital and decrease the energy of the ring 4b$_1$ basis orbital.

Related π' polarization[27a,31] and π' donation[27b] effects have already been discussed for the case of **2**. One or both of these effects is implicated by the fact that the total (MP2/6-31G*) electron density on C$_2$ of **2** is calculated to be 0.045 electron *greater* than that on C$_2$ of **5**, even though the former compound is much more polar.

Experimental evidence for π' two-electron donation in **1** from O(2p$_x$) to the ring 4b$_1$ orbital can be found in the observation that the ionization potential for the "O(2p$_x$)" orbital in **1** (9.57 eV)[32] is essentially identical with that for the equivalent orbital in **2** (9.63 eV),[33] even though the oxygen atom in **1** is much more negatively charged. We suggest that a greater O(2p$_x$) basis orbital energy in **1** compared to **2** is almost exactly balanced by a combination of a smaller O(2p$_x$)–ring 3b$_1$ interaction and a greater O(2p$_x$)–ring 4b$_1$ interaction in **1**.

Support for this interpretation is provided by the MP2/6-31G*//MP2/6-31G* wave functions in Figure 3. Note that not only are the coefficients on O in the 4b$_1$ orbital of **1** slightly larger than those for the corresponding orbital in **2**, but the coefficients on C$_1$ in 4b$_1$ (π' - 3b$_1$' + 4b$_1$') are much smaller in the former compound owing to the fact that the increased C$_1$O π'-bonding effect of interaction B at C$_1$ in Figure 2 partially cancels the corresponding antibonding effect of interaction A. Harshbarger

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(31) A similar effect has been discussed in ref 16 and in: Taylor, W. H.; Harmony, M. D.; Cassada, D. A.; Staley, S. W. *J. Chem. Phys.* **1984**, *81*, 5379.

(32) Harshbarger, W. R.; Kuebler, N. A.; Robin, M. B. *J. Chem. Phys.* **1974**, *60*, 345.

(33) Martino, P. C.; Shevlin, P. B.; Worley, S. D. *J. Am. Chem. Soc.* **1977**, *99*, 8003.

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

			bond		
	symmetry	basis set	C_2C_3[a]	C_1C_2[b]	C_1O[c]
ref Mulliken overlap population for all orbitals[d]	a_1 (σ)	STO-3G	−0.0633	+0.0062	−0.0217
		MP2/6-31G*			+0.0894
	b_1 (π′)	STO-3G	−0.1164	+0.0026	+0.0286
		MP2/6-31G*			+0.0764
	b_2 (π)	STO-3G	−0.0820	+0.0662	−0.0505
		MP2/6-31G*	−0.1539	+0.1364 +0.1033[e]	−0.0715
	total	STO-3G	−0.2617	+0.0750	−0.0436
		MP2/6-31G*	−0.9307	+0.0996 +0.0922[e]	+0.0943
rel bond length[f]		microwave	+0.053	−0.086 −0.052[e]	+0.021
		MP2/6-31G*	+0.051	−0.069 −0.033[e]	+0.001

[a] Relative to C_1C_2 of cyclopropene. [b] Relative to C_1C_3 of cyclopropene. [c] Relative to C_1O of cyclopropanone. [d] STO-3G and MP2/6-31G* calculations were performed at the experimental and MP2/6-31G*-optimized geometries, respectively, in Table II. [e] Relative to C_1C_2 of cyclopropanone. [f] In Å.

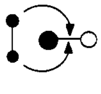
et al. have previously noted that only slightly more than half of the $4b_1$ orbital density in **1** is on oxygen.[32]

We briefly comment on two other structural studies that concluded that **1** has little π delocalization. Fitzpatrick and Fanning noted that the HF/STO-3G-optimized C=C bond length in **1** is only 0.018 Å greater than the corresponding value in ethylene, although comparison with HF/STO-3G-optimized cyclopropene (relative to which the lengthening is ca. 0.05 Å) would have been more appropriate and would have indicated π delocalization.[9] Allen suggested that $r(C_1C_2)$ in **1** should be compared with $r(C_1C_3)$ in cyclopropene (1.509 Å) adjusted by (in-plane) π′-repulsion effects (entry 1 in Table III) and "rehybridization" effects.[10] Thus a bond length of 1.424 Å was considered to be a more appropriate comparison, which leaves essentially no shortening to be attributed to π delocalization in **1**. However, entry 3 provides a better model for π′ repulsion, and we have found that the effect that Allen ascribed to rehybridization in 3,3-difluorocyclopropene relative to 1,1-difluorocyclopropane actually results primarily from increased C_1C_3 π bonding in the former compound. These modifications in the model allow one to attribute a 0.05-Å shortening of C_1C_3 in **1** to π bonding (cf. entries 3 and 4).

Comparisons such as those given above are never entirely satisfactory. Nevertheless, the choice of proper model structures is critical in order to reach an even approximately acceptable conclusion.

Electron Distribution. The experimental and calculated electric dipole moments for **1** and related compounds are given in Table II. We find it convenient to analyze the electron distribution in **1** and to compare it to that of **3** in terms of the component σ and π dipole moments. The latter are calculated by treating the atomic charges from the MP2/6-31G* calculations as point charges (Figure 4). This is only a rough approximation but is undoubtedly adequate for the level of analysis employed here.

As seen in Figure 4, the great majority of the total dipole moment in **1** originates in the π-electron system. We attribute the latter to three factors: (a) polarization of the carbonyl π bond owing to the electronegativity of the oxygen atom, (b) $\pi(C_2C_3) \rightarrow \pi^*(C_1O)$ (two-electron) donation (**8**), and (c) four-electron repulsion between the C_2C_3 and C_1O π orbitals (**9**). Note that the corresponding back donation (**10**) is symmetry forbidden. (The sizes of the π and π* coefficients in **8**–**10** are approximately proportional to those obtained from HF/3-21G-optimized calculations for ethylene and formaldehyde.)



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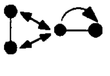

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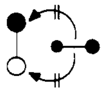

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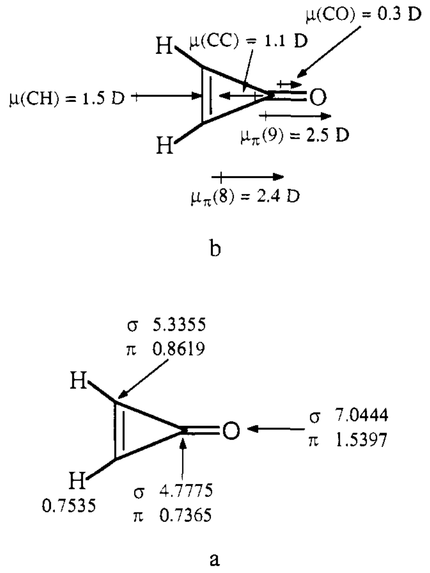


Figure 4. (a) Charge distribution calculated at the MP2/6-31G*//MP2/6-31G* level for the σ and π systems of cyclopropenone as obtained from a Mulliken population analysis. (b) Component σ and π dipole moments for cyclopropenone calculated from the charges in part a. The μ(σ) values are the net contributions from the CC and CH σ bonds whereas the μ(π) values correspond to μ(**8**) and μ(**9**) (see text).

Because of the large negative charge on the oxygen atom of **1**, the contribution of effect a will be somewhat less than the 2.3 D that we calculate for the π dipole moment of MP2/6-31G*-optimized formaldehyde. By using the π* coefficients calculated for formaldehyde with the MP2/6-31G* bond length of **1**, we can calculate a π electron-transfer dipole moment, μ(**8**), which arises from effect b and represents a net transfer of charge from the midpoint of the C_2C_3 bond to a point almost to the midpoint of the C_1O bond. The remainder of the π dipole moment is then attributed to a π-polarization dipole, μ(**9**), which represents the transfer of electron density from C_1 to O arising from effects a and c.

These component dipoles must be considered to be highly approximate since electron shifts calculated for interactions **8** and **9** are only quantitatively valid for *small* perturbations from the noninteracting C_2C_3 and C_1O π bonds, a condition clearly not met in **1** and **3**. Nevertheless, we estimate that π-electron transfer

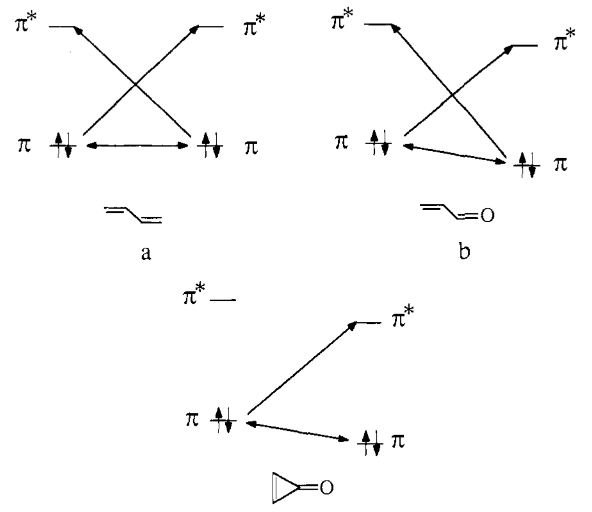


Figure 5. π-Electron interactions in (a) butadiene, (b) propenal, and (c) cyclopropenone. Double-headed arrows represent destabilizing four-electron interactions between filled orbitals whereas single-headed arrows represent stabilizing two-electron interactions between a filled and an empty orbital.

contributes about one-half (Figure 4) and two-thirds[16] of the π dipole moment in **1** and **3**, respectively.

The component σ-dipole moments ($\mu(\sigma)$) for **1** and **3**, calculated as the resultant moments for symmetry-equivalent bonds, are also given in Figure 4. Of particular interest is the observation that, although the total $\mu(\sigma)$ for **1** is directed toward the oxygen whereas that for **3** is directed toward the ring, the *ring* $\mu(CC)$ *in* ***1*** *opposes the total* $\mu(\sigma)$ *and is actually larger than the ring* $\mu(CC)$ *in* ***3***. This can be traced in part to the fact that the total C_2H σ-electron density in **1** is *greater* than that for C_1H in the less polar **3** (Figure 4). We attribute this interesting effect to the much greater contribution of π′ interaction B in **1** (Figure 2) compared to the corresponding interaction in **3**.

The large value of $\mu(8)$ in Figure 4b clearly suggests a significant degree of π delocalization in **1**. How can this be reconciled with the conclusion of previous workers that **1** is not resonance stabilized? Skancke concluded on the basis of C_1C_2 π overlap that there is no delocalization of the π electrons. However, the bond lengths in that study ($r(C_1C_2) = 1.509$ Å, $r(C_2C_3) = 1.30$ Å) were fixed at values that would tend to minimize π delocalization.[14b] Fitzpatrick and Fanning reached a similar conclusion on the basis of a small C_1C_2 π-overlap population in partially optimized **1**.[9] However, their C_1C_2 value is actually 19% of their C_2C_3 value and 35% of the value in **7**. These are not insubstantial values.

Pittman et al. concluded that **1** has little aromatic nature because there is little positive charge on C_2H.[14a] Our calculations confirm their value and also show that there is scarcely any increase for **1** (+0.0491) compared to **3** (+0.0444). However, as indicated in Figure 4, a much more positive π charge at C_2 and C_3 in **1** compared to **2** is compensated by π′ back donation (Figure 2). Interestingly, Pittman et al. recognized the latter effect in **1** without recognizing its consequences at C_2 and C_3.

Tobey argued that the dipole moment in **1** could be explained on the basis of a carbonyl group of normal polarity coupled with a modest π delocalization in the three-membered ring.[15] However, we find that the dipole moment of **1** is consistent with a *large* π dipole moment coupled with π′ back donation.

Thermodynamic Stability. Consider the following simple π orbital-interaction model. As illustrated in Figure 5a,b, replacement of a terminal carbon in butadiene (**11**) with an oxygen to afford propenal (**12**) causes (a) a decrease in the π ↔ π four-electron repulsion, (b) an increase in one of the π → π* two-electron interactions (π(C=C) → π*(C=O)), and (c) a decrease in the second π → π* two-electron interaction (π(C=O) → π*(C=C)). Comparison of r(C=C) in **11** with that in **12**

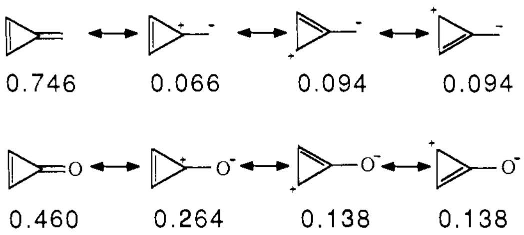
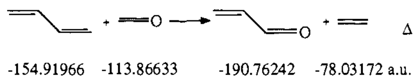


Figure 6. Valence bond representations of **1** and **3** as calculated from MP2/6-31G*//MP2/6-31G* π-electron densities.

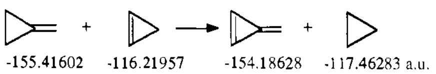
(experimental: $r_g(\mathbf{11}) = 1.345$ Å,[34] $r_s(\mathbf{12}) = 1.345$ Å;[35] theoretical (HF/3-21G-optimization): $r_e(\mathbf{11}) = 1.320$ Å, $r_e(\mathbf{12}) = 1.318$ Å) might be taken to suggest that effects a and b approximately cancel effect c from a structural standpoint, whereas isodesmic reaction 1, calculated at the HF/6-31G* level, might be taken to suggest



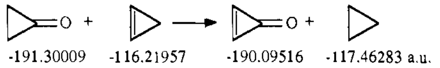
ΔH = -5.1 kcal/mol (1)

that **12** has a greater π-delocalization energy than **11**. However, σ effects associated with the π′ lone-pair orbital on oxygen in **12** probably also influence these values (vide infra).

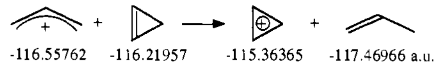
Change of the π systems of **11** or **12** into those of **3** or **1**, respectively, eliminates effect c due to symmetry (**10**). Accordingly, we expect a significant increase in π-delocalization energy on going from **3** to **1** (Figure 5c). This is supported by isodesmic reactions 2–4,[36] at the MP2/6-31G*//MP2/6-31G* level. The



ΔH = -8.5 kcal/mol (2)



ΔH = -24.1 kcal/mol (3)



ΔH = -35.2 kcal/mol (4)

value of ΔH calculated in eq 4 agrees with the value of ΔH calculated from experimental data (−31.5 kcal/mol)[37] within the limits of experimental error. Although the ΔH values are undoubtedly influenced by factors other than π delocalization, it is nevertheless clear that **1** has a greater π-delocalization energy than **3**.

Comparison of Criteria for π Delocalization. As stated in the Introduction, the key problem that we wanted to consider was whether various criteria for π delocalization ("aromaticity") respond to the same degree in **1** or **3** relative to appropriate models. The criteria that will be compared will be relative π-electron distributions, bond lengths, and thermodynamic stabilities (Table V). All calculated values were obtained at the MP2/6-31G* level of theory.

Two-electron donation from C_2C_3 to C_1O (**8**) represents essentially the sole mechanism for changing the π-electron density at C_2 and C_3. Therefore, the π charge at these positions compared to the values calculated for a fully delocalized system (**7**) and for

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[34] Kuchitsu, K.; Fukuyama, T.; Morino, Y. *J. Mol. Struct.* **1969**, *4*, 41.

[35] Cherniak, E. A.; Costain, C. C. *J. Chem. Phys.* **1966**, *45*, 104.

[36] The total energies for cyclopropene and methylenecyclopropene in eq 2–4 are lower than the MP2/6-31G*-optimized values recently published by Michalska et al. (Michalska, D.; Hess, B. A.; Jr.; Schaad, L. J. *Int. J. Quantum Chem.* **1986**, *29*, 1127) owing to the fact that these authors employed the frozen-core approximation. However, their bond lengths and ours (ref 16) agree to within 0.002 Å.

[37] (a) Allyl cation: Traeger, J. C. *Int. J. Mass Spectrom. Ion Processes* **1984**, *58*, 259; Boyd, R. K. *Ibid.* **1983**, *55*, 55. (b) Cyclopropene: Dorofeeva, O. V.; Gurvich, L. V.; Jorish, V. S. *J. Phys. Chem. Ref. Data* **1986**, *15*, 437. (c) Cyclopropenyl cation: Rosenstock, H. M.; Draxl, K.; Steiner, B. W.; Herron, J. T. *Ibid.* **1977**, *6*, *Suppl. 1.* (d) Propene: Pedley, J. B.; Naylor, R. D.; Kirby, S. P. *Thermochemical Data of Organic Compounds*, 2nd ed.; Chapman and Hall, New York, 1986; p 89.

Table V. Estimation of the Extent of π Delocalization in Methylenecyclopropene and Cyclopropenone by Various Criteria[a]

criterion	compd	localized model	**1** or **3**	**7**	"% aromaticity"	$\frac{\%(\mathbf{1})}{\%(\mathbf{3})}$
C_1 π-electron density	**3**	0.9798[b]	0.9062	0.6667	22	1.6
C_2 π-electron density	**1**	0.9798[b]	0.8619	0.6667	35	
$r(C_1C_3)$ (MW)[c]	**3**	1.453[a]	1.441[d]	1.373[e]	15	2.9
$r(C_1C_2)$ (MW)[c]	**1**	1.471[a]	1.428	1.373[e]	44	
$r(C_1C_3)$ (MP2/6-31G*)[c]	**3**	1.467[a]	1.445	1.368	22	1.6
$r(C_1C_2)$ (MP2/6-31G*)[c]	**1**	1.472[a]	1.436	1.368	35	
ΔH (eq 2 or 4)	**3**		−8.5[f]	−35.2[f]	24	2.8
ΔH (eq 3 or 4)	**1**		−24.1[f]	−35.2[f]	68	

[a] See text. [b] Cyclopropene. [c] In Å. [d] Reference 16. [e] Reference 10. [f] In kcal/mol.

cyclopropene (**5**) represents one measure of aromaticity. This is represented in valence bond terms in Figure 6.

We have not corrected the double-bond π-electron densities for the fact that the calculated total dipole moments (μ) are greater than the experimental values (Table II). This is justified because, although μ is a Hartree–Fock value calculated for an MP2/6-31G* geometry, inclusion of correlation (at the MP2 or CISD levels) in the calculation of μ does not significantly change the π-electron densities for the ring olefinic carbons in **1** and **3**.[38] In contrast, the excessive polarization calculated at the Hartree–Fock level for the C_3C_4 π bond in **3** may make comparison of the ring single-bond π-overlap populations less reliable.

There is no good model compound with which to compare $r(C_1C_2)$ in **1**, but one possible approach is as follows. Since $r(C_1C_2)$ in **1** is most similar to $r(C_1C_2)$ in **2**,[26] we use this comparison but first correct the latter value by the difference between $r(C_1C_3)$ in **4**[8] and **6**.[28] By this procedure we find that $r(C_1C_2)$ in **1** has decreased about 44% (microwave bond lengths) or 35% (MP2/6-31G* bond lengths) of the way from our model nonconjugated bond length to the value for cyclopropenium cation (Table V). A similar comparison has been made for **3** and is also given in Table V.[16]

The C_1C_3 π and total overlap populations given in Table IV suggest that the change in π bonding contributes a greater proportion of the total bonding change in **1** than it does in **3**. Although, as mentioned above, Mulliken overlap populations for small-ring and polar compounds must be regarded with caution, the change in the length of the single bond in cyclopropene derivatives is undoubtedly a better measure of π delocalization than is the change in the double-bond length.

If one now considers the last column of Table V, our models suggest that π delocalization is 1.6–2.9 times greater in **1** than in **3**. However, because the microwave structure ratio (2.9) is based on four different experimental investigations with their attendant uncertainties, this is undoubtedly the least reliable value.

Is it possible to reconcile the high thermodynamic ratio (2.8) with the smaller electron density and bond length ratios (1.6)? We believe it is, owing to the fact that eq 2 and 3 give the total stabilization, i.e., that provided by *both* the σ and π systems. As previously discussed, **1** shows evidence for an exceptionally strong donation of the π' ($O(2p_x)$) lone pair into the unoccupied $4b_1$ ring orbital. The extra stabilization provided by this interaction must account for at least part of the larger thermodynamic ratio in Table V. An analogous interaction in propenal might also contribute to the exothermicity calculated for eq 1. We therefore conclude that the π-delocalization energy in **1** is about twice as great as in **3** (as suggested also by the numbers in Figure 6) and that the following *approximate* order of π-delocalization energies can be constructed: cyclopropenium cation > cyclopropenone > methylenecyclopropene ≈ propenal ≈ butadiene.

Summary

Cyclopropenone has approximately twice the π-delocalization energy of methylenecyclopropene and can be considered to be moderately "aromatic". However, it is also significantly stabilized by donation of the π' lone pair on oxygen into the unoccupied $4b_1$ ring orbital. Thus the carbonyl bond in **1** can be considered to consist of a moderately strong π (b_2) bond and a somewhat weaker $\pi'(b_1)$ bond superimposed on a $\sigma(a_1)$ bond. Finally, and most importantly, it appears that structure, electron distribution, and thermodynamic stability respond to a similar degree to π delocalization and can all be employed as criteria for "aromaticity" if proper model compounds are chosen.

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Registry No. **1**, 2961-80-0; **2**, 5009-27-8; methylenecyclopropene, 4095-06-1.

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(38) Unpublished research with M. Head-Gordon and J. A. Pople.