

state and gas-phase structures recently noted for $(\text{CH}_3)_3\text{N-SO}_2^{27}$ (0.21 Å) is encouraging in this respect, as it demonstrates the possibility of a substantial "dynamic range" in N-S bond lengths.

Conclusion

Microwave spectroscopy has been used to observe the gas-phase adduct formed between CH_3CN and BF_3 . The structure has been determined to be intermediate between the limits normally expected for van der Waals and covalent interactions and is significantly different from that observed in the crystalline material. The correlation between the boron-nitrogen bond length and the N-B-F angle in a series of BX_3 species with nitrogen donors provides the first gas-phase example of a structure correlation

analogous to those used frequently to map reaction paths in crystalline systems.

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Registry No. $\text{CH}_3\text{C}^{24}\text{N-}^{11}\text{BF}_3$, 136954-55-7; $\text{CH}_3\text{C}^{14}\text{N-}^{10}\text{BF}_3$, 27840-20-6; $\text{CH}_3\text{C}^{15}\text{N-}^{11}\text{BF}_3$, 136954-56-8; $\text{CH}_3\text{C}^{15}\text{N-}^{10}\text{BF}_3$, 136954-57-9; $\text{CD}_3\text{C}^{14}\text{N-}^{11}\text{BF}_3$, 136984-71-9; $\text{CD}_3\text{C}^{14}\text{N-}^{10}\text{BF}_3$, 27840-21-7.

Synthesis, Microwave Spectrum, and ab Initio Calculations for Difluorocyclopropenone

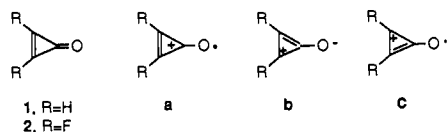
Carolyn A. Jacobs,[†] John C. Brahms,[†] William P. Dailey,^{*,†} Kyle Beran,[†] and Marlin D. Harmony^{*,†,§}

Contribution from the Departments of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19104-6323, and University of Kansas, Lawrence, Kansas 66045-0046.

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Abstract: Difluorocyclopropenone was prepared by gas-phase photolysis of difluoromaleic anhydride and was characterized spectroscopically. It is unstable at room temperature but may be stored for long periods of time at -78°C . Microwave spectra of the normal and ^{18}O isotopomer for difluorocyclopropenone were measured. The structural parameters were determined to be $r(\text{C}_1\text{O}) = 1.192 \text{ \AA}$, $r(\text{C}_1\text{C}_2) = 1.453 \text{ \AA}$, $r(\text{C}_2\text{C}_3) = 1.324 \text{ \AA}$, and $r(\text{CF}) = 1.314 \text{ \AA}$, and the electric dipole moment was found to be 2.32 D. Ab initio calculations at the CISD/6-31G* level are reported for cyclopropenone, difluorocyclopropenone, and related cyclopropenes and are in good agreement with the experimental results. The experimental geometry and ab initio computations indicate that difluorocyclopropenone enjoys a resonance energy comparable to that of the parent compound.

Cyclopropenone (**1**) has received considerable attention because of its potential aromaticity based on Huckel's $4N + 2$ rule.¹ This stability is predicted to arise because of the relative importance of resonance structures such as **1a-c**. In accord with this rea-



soning, cyclopropenones have high dipole moments and low $\text{p}K_b$ values.¹ Staley and co-workers have recently used several criteria to quantify the degree of aromaticity enjoyed by cyclopropenone and concluded that it is a moderately aromatic compound.² Although the exact value is still in question, the resonance energy of cyclopropenone is in the range of 14–24 kcal/mol.³

Substitution of hydrogen by fluorine often causes remarkable changes in the structures, relative energies, and kinetic stabilities of organic molecules.⁴ Our recent synthesis⁵ of difluorocyclopropenone (**2**) under matrix-isolation conditions prompted our interest in how fluorine substitution might affect the degree of aromaticity in this compound compared with that in **1**. On the basis of the high electronegativity of fluorine, one might expect that resonance structures such as **2a-c** might be less important for **2** than for **1**. This would then serve to decrease the aromaticity in **2**. On the other hand, if fluorine were able to efficiently donate π -electron density to the cyclopropenone using one of its lone pairs

of electrons,⁶ it may serve to enhance the stability and relative importance of resonance structures **2a-c**. To address these questions, we report the details of the isolation, structural characterization by microwave spectroscopy, and high-level ab initio calculations for difluorocyclopropenone. A comparison with the properties of the parent cyclopropenone will also be made. The sensitivity of various criteria for the determination of aromaticity in **2** will be examined.

Experimental Section

Synthesis of Difluorocyclopropenone. Difluoromaleic anhydride⁷ (85 mg) was transferred into an evacuated 2.5-L gas-tight photolysis well fitted with a water-cooled quartz immersion well containing a 450-W medium-pressure mercury vapor lamp and a Vycor filter. The whole assembly was cooled in ice water, and the lamp was operated for 45 min. The volatile products were isolated by vacuum transfer through a series of three U-traps cooled to -40 , -78 , and -196°C . The middle trap

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* To whom correspondence should be addressed.

[†] University of Pennsylvania.

[‡] University of Kansas.

[§] All correspondence about microwave spectroscopy should be addressed to this author.

contains almost pure difluorocyclopropenone (12 mg, 21%).

Synthesis of Difluoromaleic Anhydride-¹⁸O. Difluoromaleic anhydride (0.427 g) was added to a solution of 3 mL of tetrahydrofuran and 0.10 g of H₂¹⁸O (97.7% ¹⁸O). After being allowed to stand at room temperature for 1 h, the solution was evaporated to leave 0.484 g of difluoromaleic acid. The acid was converted to the anhydride in 90% yield by heating it to 130 °C with 1 g of phosphorus pentoxide under vacuum and collecting the product in a U-trap cooled in dry ice/acetone. The anhydride was again treated with excess H₂¹⁸O and then dehydrated with P₂O₅. By mass spectroscopy, the anhydride contained 42% ¹⁸O.

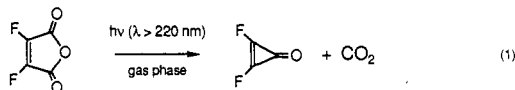
Microwave Spectroscopy. Microwave spectra of difluorocyclopropenone were obtained in the 26.5–40.0-GHz frequency region using an HP-8460A microwave spectrometer. Except for blended or overlapped lines, all frequency measurements are expected to have an accuracy of ±0.05 MHz or better. Spectra were observed for the normal isotopomer and the ¹⁸O isotopomer in the 40% enrichment. The spectra were exceedingly dense and of high intensity. It was extremely important to maintain the sample cell at temperatures approaching –78 °C, since otherwise the samples decomposed rapidly. Sample pressures were generally in the range of 10–40 mTorr.

Dipole moment measurements were performed by observing Stark shifts of selected components ($\Delta M = 0$ selection rules) of several rotational lines as a function of applied dc (ground to base) voltage. The Stark cell was calibrated using the precisely and accurately known Stark effect of OCS.⁸

Computational Methods. Ab initio calculations were performed with the GAUSSIAN 88⁹ series of programs and the 6-31G* basis set. Complete geometry optimizations were performed at the SCF, MP2, and CISD levels of theory using analytical gradient techniques. Single-point energy calculations were carried out at the MP4SDTQ(FC) level. The SCF wave functions were analyzed using the PROAIM¹⁰ series of programs of Bader and the BONDER¹¹ program of Cioslowski. NMR chemical shifts were calculated with the IGL0 program¹² of Kutzelnigg and Schindler using the SCF and CISD optimized geometries. The basis sets used were those of Huzinaga:¹³ C, O, and F, 9s5p1d contracted to [51111,2111,1], d exponent 1.0; H, 5s1p contracted to [311,1], p exponent 0.7.

Results

Synthesis and Spectroscopic Characterization of Difluorocyclopropenone. Gas-phase photolysis of difluoromaleic anhydride yields difluorocyclopropenone in 21% isolated yield (eq 1). This material is reasonably unstable at room temperature, decomposing with a half-life of about 20 min, but may be stored at –78 °C for extended periods of time.



The gas-phase infrared spectrum is similar to that reported for matrix-isolated difluorocyclopropenone with major bands at 1919, 1786, 1283, and 862 cm⁻¹. The mass spectrum (70 eV) of difluorocyclopropenone has peaks at *m/z* 90 (M⁺, 62%), 71 (M – F, 18%), and 62 (M – CO, 100%). The ¹⁹F NMR spectrum in CDCl₃ appears as a sharp singlet at –82.3 ppm vs internal CFCl₃. Analysis of the ¹³C satellite peaks allows the determination of ¹*J*(¹⁹F¹³C) = 520 Hz, ³*J*(FF) = 23 Hz, and $\delta_{19F(12C)} - \delta_{19F(13C)} = 0.158$ ppm. The ¹³C NMR spectrum is composed of two signals: The one corresponding to the two vinyl carbons occurs at 126.3 ppm (dd, ¹*J*(¹⁹F¹³C) = 520, ²*J*(¹⁹F¹³C) = 8.7 Hz), and the one for the carbonyl carbon occurs at 136.5 ppm (t, ²*J*(¹⁹F¹³C) = 7 Hz). The one-bond ¹³C–¹⁹F coupling constant of 520 Hz is one of the largest yet reported.¹⁴ As others have noted,¹⁵ there does

Table I. Observed Microwave Spectrum of Normal Isotopomers of Difluorocyclopropenone^a

transition	obs	obs – calc ^b
5(3,3)–4(3,2)	29 333.31	–0.01
7(0,7)–6(0,6)	29 363.98	0.04
6(1,5)–5(1,4)	29 373.20	0.02
6(3,4)–5(3,3)	33 295.96	–0.02
7(1,6)–6(1,5)	33 287.43	–0.04
8(1,7)–7(1,6)	37 201.92	0.02
7(3,5)–6(3,4)	37 212.23	0.04
16(7,9)–16(9,8)	33 251.02	0.01
9(1,8)–9(3,7)	29 414.68	–0.02
10(3,8)–10(3,7)	29 406.16	0.09
11(3,8)–11(5,7)	29 395.37	–0.03
12(5,8)–12(5,7)	29 381.45	–0.02
14(7,8)–14(7,7)	29 342.40	0.03
16(9,8)–16(9,7)	29 284.30	0.00
17(9,8)–17(11,7)	29 246.54	0.00
19(11,8)–19(13,7)	29 149.09	–0.06
20(13,8)–20(13,7)	29 084.85	0.01
5(3,2)–4(3,1)	33 777.29	0.00
4(3,1)–3(3,0)	28 626.32	–0.01
5(2,3)–4(2,2)	29 453.04	0.04
6(3,3)–5(3,2)	37 383.00	–0.03
6(2,4)–5(2,3)	33 304.22	–0.04
9(1,9)–8(1,8)	37 193.08	–0.02
13(5,9)–13(5,8)	33 307.40	–0.04
13(3,10)–13(5,9)	37 243.61	0.08
11(3,9)–11(3,8)	33 330.04	–0.04
14(5,9)–14(7,8)	33 292.00	–0.02
15(7,9)–15(7,8)	33 273.38	–0.01
17(9,9)–17(9,8)	33 224.45	0.02
18(9,9)–18(11,8)	33 193.18	0.01
14(5,10)–14(5,9)	37 232.02	–0.03
15(5,10)–15(7,9)	37 217.99	–0.04
17(7,10)–17(9,9)	37 181.49	–0.02
18(9,10)–18(9,9)	37 158.27	0.05
21(13,8)–21(15,7)	29 017.01	0.02

^aAll values in megahertz. ^bCalculated from Table II results.

Table II. Rotational and Centrifugal Distortion Constants of Difluorocyclopropenone^a

	normal species	¹⁸ O species
<i>A</i>	3995.945 ± 0.005	3995.975 ± 0.015
<i>B</i>	3845.023 ± 0.004	3589.809 ± 0.007
<i>C</i>	1957.303 ± 0.003	1888.900 ± 0.004
<i>r'</i> _{aaaa}	–7.88 ± 0.35	–8.36 ± 0.23
<i>r'</i> _{bbbb}	–6.46 ± 0.23	–5.75 ± 0.24
<i>r'</i> _{cccc}	–0.06 ± 0.10	0.00 ± 0.15
<i>r'</i> _{aabb}	–12.10 ± 0.72	–10.44 ± 0.35
<i>r'</i> _{aacc} + <i>r'</i> _{bbcc}	–0.73 ± 0.21	–0.55 ± 0.42

^aRotational constants in megahertz; distortion constants in kilohertz. Uncertainties are 1σ.

not seem to be a relationship between C–F bond hybridization and ¹*J*(¹⁹F¹³C). For instance, ¹*J*(¹⁹F¹³C) values in the series fluoromethane,¹⁶ fluorotrichloroethene,¹⁷ and difluoroacetylene¹⁸ are 158, 303, and 287 Hz, respectively. A study of the chemistry of difluorocyclopropenone is under way and will be reported in a future paper.

Analysis of Microwave Spectrum. The first spectral observations of the normal species produced a dense, intense, and unreproducible spectrum. The latter occurrence was rather promptly traced to a sample decomposition which occurred with a half-life of 15–30 min if the sample cell was not rigorously maintained at temperatures near –78 °C. Once this problem was overcome, it was relatively straightforward to observe the expected a-type Q-branch series of a near-oblate symmetric rotor ($\kappa \sim 0.85$). Assignments of the *J*(K_{-1,7}) → *J*(K_{-1,8}), *J*(K_{-1,8}), → *J*(K_{-1,9}),

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Table III. Observed Microwave Spectrum of ^{18}O Isotopomers of Difluorocyclopropenone^a

transition	obs	obs - calc ^b
8(1,7)-7(1,6)	35 903.10	-0.06
7(3,5)-6(3,4)	35 915.93	-0.03
11(3,9)-11(3,8)	32 065.23	0.06
12(5,8)-12(5,7)	28 098.58	0.07
14(7,8)-14(7,7)	27 806.02	-0.03
14(5,9)-14(7,8)	31 811.13	0.00
15(7,9)-15(7,8)	31 678.38	0.00
15(6,9)-15(8,8)	31 681.22	0.07
13(6,8)-13(6,7)	27 971.46	-0.05
12(3,9)-12(5,8)	31 999.69	0.02
18(9,9)-18(11,8)	31 110.25	0.01
17(9,9)-17(9,8)	31 310.11	-0.01
16(7,9)-16(9,8)	31 522.91	0.06
20(11,9)-20(13,8)	30 582.33	-0.02
17(8,9)-17(10,8)	31 333.05	0.05
20(11,10)-20(11,9)	34 778.76	-0.01
19(10,10)-19(10,9)	35 018.85	0.01
19(9,10)-19(11,9)	35 028.18	0.01
17(7,10)-17(9,9)	35 383.22	-0.07
15(5,10)-15(7,9)	35 631.08	-0.04
14(5,10)-14(5,9)	35 723.06	-0.06
6(3,3)-5(3,2)	36 642.89	0.05
5(3,2)-4(3,1)	32 395.61	0.03
5(3,3)-4(3,2)	28 047.08	0.09
6(1,5)-5(1,4)	28 352.33	-0.02
8(1,8)-7(1,7)	32 115.64	0.02
6(3,4)-5(3,3)	32 090.79	-0.09
7(1,6)-6(1,5)	32 126.42	-0.01
10(3,8)-10(3,7)	28 270.83	-0.06
9(1,9)-8(1,8)	35 893.42	0.04

^aAll values in megahertz. ^bCalculated from Table II results.

and $J(K_{-1},9) \rightarrow J(K_{-1},10)$ series were obtained with minor difficulty. It was somewhat more challenging to locate R-branch lines because, for this nearly equilateral triangular species ($I_a \sim I_b \sim I_c/2$), the R-branch line locations were very sensitive functions of the precise values of the principal moments. The assignments were obtained by careful Stark effect observations which initially led to identification of the $6(0,6) \rightarrow 7(0,7)$, $5(1,4) \rightarrow 6(1,5)$, and $4(3,2) \rightarrow 5(3,3)$ transitions. Some 40–50 transitions were eventually identified; Table I presents a summary of measurements for 35 lines that were used to obtain the rotational and distortion constants of Table II.

In a like manner, the ^{18}O species was assigned by first locating the Q-branch series and then the R-branch lines with the aid of Stark effect observations. It was deceptively difficult to sort out the ^{18}O spectrum initially because of frequent line overlaps and Stark interferences from the normal species. This problem arises from several sources, including the fact that there are several strong vibrational satellite series and numerous high J lines from all states. It would have taken a formidable effort to assign the excited states and high J lines whose centrifugal distortion terms becomes substantial. In any case, the ^{18}O species was successfully assigned as summarized in Table III, and the resulting constants are presented in Table II.

The spectral fits for both species are of high quality, although the precision of some of the distortion constants is poor. Indeed, r'_{ccc} is entirely undetermined statistically by the available spectral lines. (We include all the constants for numerical consistency.) It is especially pleasing that the A rotational constants of the two species are nearly identical and that the inertial defects of the normal and ^{18}O species have very similar values (0.292 and 0.298 $\text{amu } \text{Å}^2$, respectively).

Dipole Moment. The electric dipole moment (its magnitude only) was determined by measurements of the quadratic Stark effects and analysis with the theory of Golden and Wilson.¹⁹ Table IV summarizes the experimental $\Delta\nu/E^2$ values which were used in a weighted least-squares fit to obtain the molecular moment $\mu_{\text{T}} = \mu_a = 2.32 \pm 0.04$ D. This value is some 10% smaller than

Table IV. Dipole Moment Measurements and Results

transition	M	$(\Delta\nu/E^2) \times 10^5$	
		obs ^a	calc ^a
7(0,7)-6(0,6)	5	0.217	0.211
6(1,5)-5(1,4)	4	0.319	0.317
5(3,3)-4(3,2)	2	0.726	0.743

$$\mu_{\text{T}} = \mu_a = 2.32 \pm 0.04 \text{ D}^b$$

^aUnits are MHz/(V/cm)². ^bUncertainty is 3σ .

Table V. Experimental and Theoretical Structural Parameters in Difluorocyclopropenone and Related Molecules (Distances in Angstroms, Angles in Degrees, Dipole Moments in Debye, Total Energies in Hartrees)

	theoretical			
	exptl	6-31G*	MP2/ 6-31G*	CISD/ 6-31G*
Cyclopropenone (1)				
dipole moment	4.39	4.69	4.02	4.34
$r(\text{C}=\text{O})$	1.212	1.190	1.213	1.202
$r(\text{C}=\text{C})$	1.349	1.327	1.352	1.337
$r(\text{C}-\text{C})$	1.423	1.412	1.436	1.422
$r(\text{C}-\text{H})$	1.079	1.071	1.084	1.078
$\theta(\text{HC}=\text{C})$	144.3	145.2	144.1	144.8
total energy		-189.53398	-190.09516	-190.03721
Difluorocyclopropenone (2)				
dipole moment	2.32	2.95	2.29	2.68
$r(\text{C}=\text{O})$	1.192	1.181	1.203	1.190
$r(\text{C}=\text{C})$	1.324	1.313	1.345	1.324
$r(\text{C}-\text{C})$	1.453	1.428	1.466	1.439
$r(\text{C}-\text{F})$	1.314	1.288	1.319	1.301
$\theta(\text{FC}=\text{C})$	145.7	146.6	145.7	146.3
total energy		-387.21284	-388.12290	-387.97715
Cyclopropene (3)				
dipole moment	0.45	0.56	0.50	0.52
$r(\text{C}=\text{C})$	1.296	1.276	1.301	1.289
$r(\text{C}-\text{C})$	1.509	1.495	1.505	1.500
$r(\text{C}-\text{H})$	1.088	1.083	1.091	1.088
$\theta(\text{H}-\text{C}-\text{H})$	114.6	112.9	113.5	113.2
$r(\text{H}-\text{C}=\text{C})$	1.072	1.068	1.078	1.075
$\theta(\text{HC}=\text{C})$	149.9	150.2	150.0	150.0
total energy		-115.82305	-116.21957	-116.20177
1,2-Difluorocyclopropene (4)				
dipole moment		0.97	0.92	0.96
$r(\text{C}=\text{C})$		1.261	1.290	1.272
$r(\text{C}-\text{C})$		1.495	1.511	1.500
$r(\text{C}-\text{F})$		1.299	1.326	1.312
$r(\text{C}-\text{H})$		1.085	1.093	1.088
$\theta(\text{H}-\text{C}-\text{H})$		112.9	113.5	113.5
$\theta(\text{FC}=\text{C})$		151.7	152.3	151.9
total energy		-313.49864	-314.23937	-314.14687

the CISD/6-31G* ab initio value of 2.68 D.

Molecular Structure. The molecular structure of difluorocyclopropenone is completely described by five independent structural parameters under the reasonable restriction of C_{2v} symmetry. Thus, the experimental ground-state moments of inertia for the normal and ^{18}O isotopomers are insufficient to permit a complete structure determination since molecular planarity leads for a rigid rotor to $I_a + I_b = I_c$. We have determined a structure consistent with all the available microwave data by utilizing restrictions based on our CISD/6-31G* fully optimized ab initio structure presented in Table V. The constraints we invoke involve differences in analogous ab initio bond lengths, which are expected to approximate closely the corresponding experimental differences. Specifically, the bond length experimental differences $r(\text{C}=\text{C}) - r(\text{C}=\text{O})$ and $r(\text{C}-\text{C}) - r(\text{C}-\text{F})$ are constrained to have the ab initio values of 0.1327 and 0.1382 Å, respectively. While it is unwise to be dogmatic in the absence of overwhelming proof, there is a substantial body of evidence that suggests that even though the absolute magnitudes of the ab initio parameters may still be in error, the relative values for analogous bonds are correct to a higher order of approximation.^{20,21}

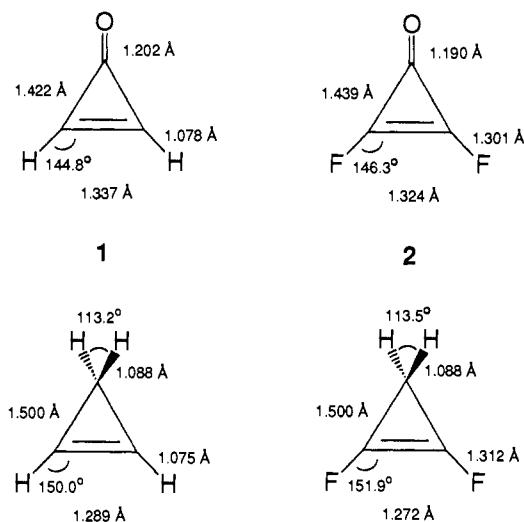


Figure 1. CISD/6-31G* geometry-optimized structures for 1-4.

Table V lists, then, the best values of the difluorocyclopropenone structural parameters obtained from least-squares fitting of the six experimental rotational constants subject to the two constraints just described. The resulting parameters are all entirely reasonable based upon known structures of analogous molecules and are indeed in very good agreement with the *ab initio* values. It should be noted in this regard that the *ab initio* parameters refer to the equilibrium (r_e) molecule, while the experimental results are *effective* (r_0) ground-state ($v = 0$) parameters. *Effective* distance parameters are expected *generally* to be somewhat longer than r_e parameters,^{22,23} and one can observe that this is consistent with the Table V results. The exceptionally close agreement for the C=C and C=O double bonds is probably fortuitous, although it is expected that zero-point vibrations will have less effect on double bonds.

Ab Initio Geometry-Optimized Structures. The *ab initio* optimized structures and dipole moments of difluorocyclopropenone, cyclopropenone, difluorocyclopropene, and cyclopropene at various levels of theory using the 6-31G* basis set are given in Table V. The CISD/6-31G* optimized structures are shown in Figure 1. Comparison with the experimental values, save 1,2-difluorocyclopropene which is an unknown compound, reveals that at the SCF level bond lengths are generally calculated to be too short while at the MP2 level they are slightly too long and at the CISD level they are slightly shorter than the experimental ones. Overall, however, the MP2 and CISD values are in good agreement with the experimental ones. At the SCF level calculated dipole moments are generally too large, while at the MP2 and CISD levels the values are closer to the experimental ones. These are general trends which have been noted previously.²⁴

Discussion

NMR Spectra. Several criteria have been used as a measure of aromaticity in cyclopropenone. These include relative carbon-carbon bond lengths,² charge distribution,² and thermodynamic stability.^{3,25} While NMR data have been used as a measure of aromaticity,²⁶ interpretation of the NMR spectra of cyclo-

Table VI. Relative NMR Chemical Shifts for Cyclopropenone and Difluorocyclopropenone Calculated Using IGLO Calculations^a

		calcd		
		SCF ^d	CISD ^d	exptl
cyclopropenone	¹ H	8.4	8.7	9.08
	¹³ C=C	153.6	157.1	158.3
	¹³ C=O	142.9	146.0	155.1
difluorocyclopropenone	¹⁷ O	257.4	266.8	(233 ^b , 248 ^c)
	¹⁹ F	-103.7	-94.2	-82.3
	¹³ C=C	122.4	126.0	126.3
	¹³ C=O	129.7	132.6	136.5
	¹⁷ O	223.0	233.3	

^a In ppm. For ¹H and ¹³C, the theoretical chemical shifts are referred to Si(CH₃)₄. For ¹⁹F, the theoretical chemical shifts are referred to CFCl₃ in its experimental equilibrium geometry. For ¹⁷O, the theoretical chemical shifts are referred to H₂O. ^b Value for dimethylcyclopropenone.²⁷ ^c Value for diphenylcyclopropenone.²⁷ ^d Geometry employed.

propenone with regard to aromaticity has been controversial. ¹⁷O NMR spectra suggest that the carbonyl oxygen of cyclopropenone bears about 75% of a full negative charge, a result that is more consistent with the oxygen in the form of an enolate rather than a ketone.²⁷ This result is consistent with a significant contribution of the polarized resonance structures 1a-c to the resonance hybrid. The ¹H NMR (δ_H 9.08 ppm)²⁸ and ¹³C NMR data (δ_{CO} 155.1, δ_{CC} 158.3 ppm)²⁹ suggest that cyclopropenone enjoys an aromaticity intermediate in value between that of the nonaromatic cyclopropene (δ_H 7.01 ppm, δ_{CC} 108.7 ppm)³⁰ and the aromatic cyclopropenylm ion (δ_H 11.0 ppm, δ_{CC} 177 ppm).³¹ On the other hand, a measurement of the magnetic susceptibility anisotropy suggests that the ring current in cyclopropenone is not any larger than that in cyclopropene.²⁹

The ¹⁹F NMR chemical shift (δ_F -82.3 ppm) for difluorocyclopropenone is also intermediate in value between those of perfluorocyclopropene (δ_F -145.1 ppm)¹⁴ and trifluorocyclopropenylm ion (δ_F -63.1 ppm).³² The ¹³C NMR spectrum for difluorocyclopropenone, with the carbonyl resonance shifted quite upfield of a normal ketone, is similar to that of the parent. While the spectroscopic data cannot give a quantitative measure of the degree of aromaticity of difluorocyclopropenone relative to cyclopropenone, it is clear that both compounds exhibit similar changes in their NMR spectra relative to a set of reference compounds.

As a further guide, we have determined the NMR chemical shifts for cyclopropenone and difluorocyclopropenone using the IGLO method.¹² The effects of geometry on the predicted values of the chemical shifts were examined by using both the SCF and CISD optimized geometries. The results are shown in Table VI. The agreement between the calculated and experimental chemical shifts is good using either geometry. The use of CISD geometries, which are closer to the true equilibrium geometries, gives a slightly better agreement with the experimental chemical shifts than does the use of the SCF optimized geometries.³³ It has been noted that accurate predictions of ¹⁹F NMR chemical shifts require a reasonably large basis set with polarization functions.³⁴ Even so, the calculated values can still differ from the experimental solution values by more than 10 ppm. On the other hand, calculated ¹³C NMR chemical shifts are in much better agreement

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with the experimental values. Our results are similar. The predicted ^{19}F NMR chemical shift for difluorocyclopropenone is off by 12 ppm while the calculated ^{13}C NMR chemical shifts are extremely close to the experimental values.

Geometries. Staley et al. interpreted the bond lengths in cyclopropenone and methylenecyclopropene by comparison to carefully selected model compounds.² By means of extensive consideration of orbital-interaction mechanisms and charge distributions based on ab initio calculations, they concluded that the C–C single-bond length provided the best single structural measure of the effects of π delocalization in these systems. Thus, the significant 0.052-Å decrease observed experimentally for the C–C bond in cyclopropenone relative to that in cyclopropanone, or the 0.086-Å decrease relative to cyclopropene (both values with uncertainties in the range ± 0.01 to ± 0.015 Å) suggested that cyclopropenone was moderately aromatic. Substantially smaller changes for the same single bond in methylenecyclopropene relative to analogous reference compounds led to the conclusion that the methylene species was 2 or 3 times less aromatic than the ketone.^{2,35} The somewhat smaller but still substantial changes in the C=C double bond in cyclopropenone relative to suitable reference molecules could not, on the other hand, be related unambiguously to π delocalization because of appreciable contributions from σ bonding and in-plane π bonding. Nevertheless, the lengthening of this bond relative to cyclopropene appeared to contain a significant contribution from π delocalization. Finally, Staley et al.² concluded that the carbonyl bond length was also not a clear indicator of π delocalization, presumably because of strong polarization effects of the oxygen.

Similar considerations for **2** from experimental data are not possible because of the lack of the necessary results for reference molecules. However, the ab initio structures of difluorocyclopropene and **2** in Table V predict a substantial decrease of 0.061 Å in the C–C distance of the latter compared to the former molecule. The result is entirely analogous to that for the non-fluorinated species **1** and thus suggests a more or less comparable π delocalization in difluorocyclopropenone and its parent analogue. Interestingly, the ab initio C=C double bond changes for **1** and **2** relative to cyclopropene and difluorocyclopropene are very similar also, suggesting again (but less definitively according to Staley²) that the parent and substituted cyclic enones have comparable π delocalization or resonance energy.

The remaining question one might ask is whether the small structural differences between cyclopropenone and its difluoro analogue might be interpreted in terms of π delocalization. In particular, the C–C and C=C distances in **2** are, respectively, longer by 0.031 Å and shorter by 0.014 Å than the corresponding bonds in **1**. We note first from Table V that these experimental shifts are somewhat larger than predicted by the CISD/6-31G* results. Since the experimental differences may be in error as much as ± 0.015 Å, there is, however, no substantial disagreement between theory and experiment. Thus, the Table V experimental and theoretical data show that for **2** the C–C distance has lengthened and the C=C distance has shortened relative to the parent molecule **1**. One is tempted then to conclude that the delocalized structures **2a–c** play a somewhat smaller role in **2** than do the analogous structures **1a–c** for **1**; in other words, the difluoro species appears somewhat less delocalized or aromatic than the parent species based on geometry. This conclusion requires, however, that one believe that π -delocalization effects dominate those of the σ electrons upon fluorine substitution. Based upon arguments of Deakyne et al.,³⁶ such an assumption appears questionable, since fluorine substitution on three-membered rings clearly produces substantial ring distortion even in the absence of π delocalization. This can, in fact, be observed from the Table V theoretical results for cyclopropene and difluorocyclopropene, wherein the C=C distance is shortened substantially by the

Table VII. Total and π Atomic Electron Populations Obtained Using Mulliken Population Analysis and Bader Analysis of HF/6-31G* Wave Functions

		Mulliken		Bader	
		total	π	total	π
cyclopropenone	O	8.569	1.534	9.388	1.743
	C1	5.526	0.743	4.560	0.530
	C2	6.193	0.861	6.154	0.849
	H	0.760	0.000	0.872	0.014
difluorocyclopropenone	O	8.545	1.530	9.385	1.748
	C1	5.526	0.757	4.478	0.538
	C2	5.688	0.917	5.328	0.857
	F	9.277	1.943	9.740	2.000

fluorine substitution. Such a C=C shortening has been experimentally observed for *cis*-1,2-difluoroethylene relative to the parent species.³⁷ Consequently, it is difficult to distinguish any substantial differences in π delocalization and aromaticity between difluorocyclopropenone and its parent on the basis of geometry changes.

Charge Distributions. The charge distribution of a molecule is another measure of electron delocalization and aromaticity. Molecule dipole moments are experimental quantities which contain information about the electron distribution in a molecule and do not depend on the assignment of charges to individual atoms. Molecule dipole moments can also be calculated with reasonable accuracy.³⁸ According to our calculations, the double bond in cyclopropene is the positive end of the dipole while it is the negative end of the dipole in 1,2-difluorocyclopropene. In both cyclopropenones, the oxygen is the negative end of the dipole. If one compares the change in dipole moment going from the cyclopropene to the corresponding cyclopropenone, this will provide a measure of the differences in charge redistribution in the two sets of compounds. Using the CISD values, the change in dipole moment between cyclopropenone and cyclopropene is 4.34 – 0.52 = 3.82 D while the change in dipole moment between difluorocyclopropene and difluorocyclopropenone is 2.68 + 0.96 = 3.64 D. In other words, there is slightly less charge reorganization in the fluorinated system than in the hydrocarbon. If one uses the experimental values for the dipole moments of the cyclopropenones and the parent cyclopropene and uses 0.9 D as the value for 1,2-difluorocyclopropene, then the differences between the two sets of compounds are larger, 3.94 D vs 3.22 D. While this analysis implies that there is more charge delocalization and hence more aromaticity associated with cyclopropenone than with difluorocyclopropenone, it must be remembered that the dipole moment measures the total electron distribution in a molecule while aromaticity depends on the π -electron distribution. To obtain this distribution, one must resort to calculations.

The HF/6-31G* wave functions for cyclopropenone and difluorocyclopropenone were analyzed using the standard Mulliken population analysis³⁹ in addition to the virial partitioning method of Bader.¹⁰ While both methods have been criticized as to how they partition the electron density,⁴⁰ both are useful when comparing similar compounds. The total atomic electron populations as well as the π atomic electron populations are shown in Table VII. Although electron populations calculated using the two methods can differ greatly, within each partitioning method, C1 and O have almost exactly the same total and π atomic populations in **1** and **2**. Because of the high electronegativity of fluorine compared with hydrogen, the total charge of C2 is much more positive in **2** than in **1**. For **2**, the Mulliken population analysis suggests that the fluorine atom donates some π -electron density (0.057 e) to C2. However, with the Bader analysis, this π -electron donation is completely absent and the π -electron distributions in

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Table VIII. Covalent Bond Orders Calculated Using HF/6-31G* Wave Functions

Cyclopropanone			
C=O	1.218	C=C	1.747
C—C	1.177	C—H	0.994
Difluorocyclopropanone			
C=O	1.216	C=C	1.668
C—C	1.118	C—F	0.754
Cyclopropene			
C—C	1.054	H—C=	1.010
C=C	1.967	H—C	1.001
1,2-Difluorocyclopropene			
C—C	1.016	F—C	0.756
C=C	1.869	H—C	0.995

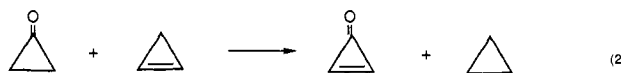
1 and **2** are almost the same. Likewise, if one subtracts the π -electron density donated by F to C2 in the Mulliken analysis, then the π -electron distributions of **1** and **2** are again almost the same.

Another quantity that can be derived from an analysis of the electron density using the theory of atoms in molecules is bond order. Bader has shown that there is a relationship between the amount of electron density at the bond critical point and bond order.⁴¹ Unfortunately, this relationship is empirical and must be fitted to each type of bond. Very recently Cioslowski has developed a method for the determination of covalent bond order which is based on the number of electrons within the topological theory of atoms in molecules.¹¹ This method has no empirical parameters and can be used to obtain the covalent bond order of any bond. It provides bond orders that are in good agreement with those based on chemical intuition. For instance, with HF/6-31G* geometry-optimized wave functions, the calculated covalent carbon-carbon bond orders for ethane, ethene, ethyne, and benzene are 1.047, 1.958, 2.920, and 1.435, respectively.¹¹ An analysis of the HF/6-31G* wave functions of cyclopropanone, difluorocyclopropanone, cyclopropene, and 1,2-difluorocyclopropene using Cioslowski's BONDER program is given in Table VIII.

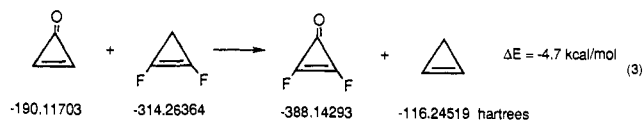
The carbon-carbon single bonds in cyclopropene and 1,2-difluorocyclopropene have covalent bond orders close to 1, with values of 1.054 and 1.016, respectively, while the carbon-carbon double bonds have values of 1.967 and 1.869, respectively. The slightly lower bond order for the carbon-carbon bonds in the fluorinated cyclopropene is a consequence of the ionic character of the carbon-fluorine bonds. The calculated bond orders for both types of carbon-carbon bonds in the two cyclopropenes are close to what one would expect. For cyclopropanone and difluorocyclopropanone, the covalent bond orders of the formally single carbon-carbon bonds in both compounds are larger than 1, with values of 1.177 and 1.118, respectively, while the bond orders for the double bonds are less than 2, having values of 1.747 and 1.668, respectively. For both cyclopropenes, the carbon-carbon double bonds have a lower and the carbon-carbon single bonds a higher bond order than similar bonds in the respective cyclopropene. These values are consistent with about a 15% contribution from resonance structures **1b** and **1c** or **2b** and **2c**, respectively. The covalent bond orders of the carbonyl bonds, 1.218 and 1.216, respectively, appear quite low. For comparison, the carbon-oxygen bonds in methanol, acetone, and carbon monoxide have covalent bond orders of 0.847, 1.273, and 1.509 respectively. Thus, the carbonyl bond orders for both cyclopropenes are slightly less than those of a typical carbon-oxygen double bond but substantially greater than that of a single bond. What is more important for this discussion is the fact that the differences between the calculated covalent bond orders for a particular type of bond in cyclopropanone and difluorocyclopropanone are relatively small. In fact, the ratio of the covalent carbon-carbon bond orders within each cyclopropene is almost exactly the same, 1.484 and 1.492, respectively. The electronic distribution in both cyclopropenes

is consistent with a moderate degree of electron delocalization and aromaticity.

Thermodynamic Stability. Another measure of aromaticity is the extra thermodynamic stability associated with the conjugation of the double bond and the carbonyl group relative to the appropriate reference compounds.^{3,25} This quantity has been determined for the parent cyclopropanone based on ab initio calculations^{2,3,25} and for the diphenyl derivative based on careful rotating bomb calorimetry.^{25b} As has been noted several times, a realistic value for the resonance energy of cyclopropanone depends on the proper choice of reference compounds.³ Using the following isodesmic reaction (eq 2) and taking into account the inherent delocalization energy associated with the conjugating groups, Bachrach has recently determined that cyclopropanone has a resonance energy of 14 kcal/mol.³ A similar analysis predicts that methylenecyclopropene has no resonance energy.

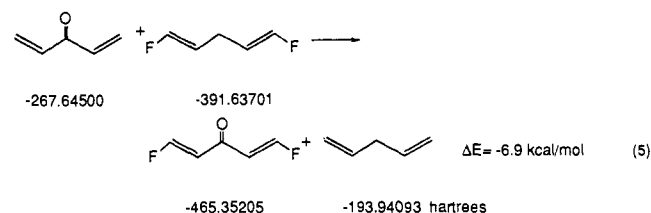
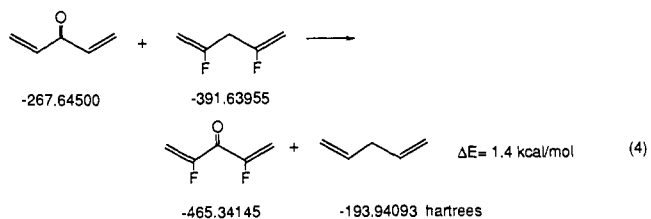


In principle, one could use the same type of isodesmic reaction for the fluorinated system and make the appropriate corrections. However, it is known that fluorine can have a substantial effect on the structures and energies of strained-ring systems, especially in systems with three-membered rings.^{4,36} Changes in carbon-fluorine bond hybridization also can dramatically effect the relative energies. Rather than try to analyze the fluorinated system alone, we desired to compare it with the parent system. To a first approximation, the following isodesmic reaction (eq 3) is a measure



of the difference in aromaticity between the parent cyclopropanone and difluorocyclopropanone. This isodesmic reaction will serve to minimize the problems associated with the changes in rehybridization of the carbon-fluorine bonds on the three-membered rings. Using MP4SDTQ(FC)/6-31G**/HF/6-31G* values, one concludes that difluorocyclopropanone is about 5 kcal/mol more aromatic than cyclopropanone.

To determine the effect of fluorine substitution on appropriate model systems, the following two isodesmic reactions (eqs 4 and 5) were calculated using optimized HF/6-31G* energies.



As shown in reaction 4, the substitution of a vinylic hydrogen by fluorine in the position α to the carbonyl group is less favored than α to a methylene group. On the other hand, reaction 5 reveals that substitution of a vinylic hydrogen by fluorine in the β position is more favored with the carbonyl derivative than with a methylene group. The fluorine atoms in difluorocyclopropanone can be considered to be in both an α and β relationship to the carbonyl. Thus, one might choose to take the sum of the above values, or -5.5 kcal/mol, as a "correction" to isodesmic reaction 3. This will lead to a more thermoneutral value for the difference in

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resonance energy between **1** and **2**. Thus, thermochemically, substitution of hydrogen by fluorine has caused a very small change in the resonance energy of the cyclopropenone.

Conclusions. To obtain a measure of the aromaticity in **2** relative to that in **1**, the properties of the two compounds were compared using several different criteria. These included NMR spectra, geometry, electron distribution, and thermodynamic stability. Compared with appropriate model compounds, the NMR spectra of **2** were very similar to those of **1**. Analysis of the HF/6-31G* wave functions of **1** and **2** revealed that the π -electron distributions, covalent bond orders, and resonance energies were extremely similar for the two compounds. These three criteria suggest that there is a similar degree of aromaticity associated with **1** and **2**. Although the experimental ring geom-

etries of **1** and **2** differed somewhat, the data were not sufficiently compelling to distinguish any aromaticity difference. In this regard, it is important to note that the fluorine atoms influence strongly the σ -electron system of the ring, masking to a large extent any small changes in π delocalization that might occur. Thus, it is clear that small bond length changes may not be useful guides for distinguishing minor changes in aromaticity.

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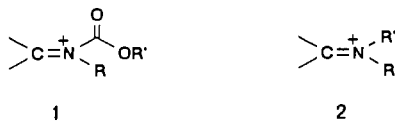
NMR Detection of *N*-Acylium Ion Intermediates Generated from α -Alkoxy carbamates

Yoshinori Yamamoto,* Tomohisa Nakada, and Hisao Nemoto

Contribution from the Department of Chemistry, Faculty of Science, Tohoku University, Sendai 980, Japan. Received March 11, 1991

Abstract: The *N*-acylium ion intermediates generated from α -alkoxy carbamates in the presence of Lewis acids were for the first time detected by ^1H and ^{13}C NMR. It was confirmed that there is an equilibrium between the starting carbamate and the intermediate and that the equilibrium is highly dependent upon a Lewis acid. By using the saturation transfer method, the rate constant for the formation of the intermediate was obtained. NOE experiments revealed that ((4-methylphenyl)methylene)methyl(methoxycarbonyl)ammonium methyltrifluoroborate **6** has *E*-geometry.

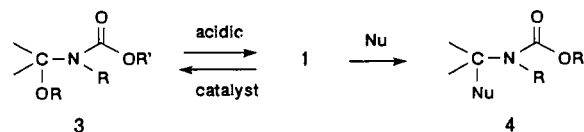
N-Acylium ions **1** are becoming important intermediates in synthetic organic chemistry.¹ The imino carbon atom in **1** is more electron-deficient than the carbon in the Mannich reagent **2**, and thus the amidoalkylating reagent **1** has been frequently used in modern organic synthesis.² There are several major



synthetic ways to **1**: (i) acylation of imines, (ii) *N*-protonation of *N*-acylimines, (iii) electrophilic addition to enamides or to *N*-acylimines, (iv) oxidation of amides (removal of a hydride from the α -carbon of amides), and (v) heterolysis of amides bearing a leaving group *X* on the α -carbon with respect to nitrogen.¹ Perhaps the most frequently used method for generating **1** is the heterolysis of the α -substituted amides (v). For example, α -alkoxy carbamates **3** have been thought to generate *N*-acylium ions **1** upon treatment with Lewis acids, which are in situ trapped with nucleophiles giving the product **4** substituted at the α -position via the $\text{S}_{\text{N}}1$ process. It has been proposed without any experimental evidence that there is an equilibrium between **3** and **1**.

However, unambiguous evidence on the formation of **1** from **3** has not been obtained. All previous mechanistic discussions have

been based on the analysis of products **4**. Iminium salts **2** (*R*,



R' = H, alkyl, aryl), which are relatively stable, have been detected in solution by NMR,³ and in some cases the solid structure has been elucidated by X-ray analysis.^{3f} The NMR analysis of the adduct between acetyl chloride and benzalaniline revealed that the corresponding α -chloroamide was formed instead of the *N*-acylium ion salt.^{4a} Generation of **1** from the *N*-protonation of *N*-acylimines,^{4b,c} from the removal of a hydride from the α -carbon of an amide,^{4d} and from the electrophilic addition to *N*-acylimines^{4e,f} has been confirmed by NMR. However, the formation of **1** from α -alkoxy carbamates which are synthetically most important has not been verified. We provide for the first time unambiguous evidence that (i) treatment of **3** with certain Lewis acids produces **1**, (ii) there is an equilibrium between **3** and **1**, and (iii) the equilibrium depends upon the Lewis acid used. We

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