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Dynamic NMR Study of Cyclopropylcarbonyl Fluoride. A Comparison of the Conjugating Abilities of the Cyclopropyl, Vinyl, and Phenyl Groups

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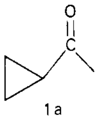
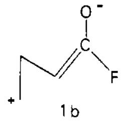
Abstract: Rotation about the bond between the COF group and C-1 of cyclopropylcarbonyl fluoride is slow on the NMR time scale at −163 °C. The fluorine NMR spectrum at this temperature shows signals for two conformations, which have nearly identical free energies. A free energy barrier of 5.5 ± 0.2 kcal/mol was calculated for interconversion of isomers at −134 °C. Comparison of this barrier with the rotational barriers for acryloyl fluoride and benzoyl fluoride indicates that the π-donating abilities of the vinyl and cyclopropyl groups are nearly equal and are lower than for phenyl, at least with the fluorocarbonyl group as the π acceptor.

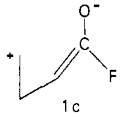
Many experimental[1,2] and theoretical[1,3] studies have shown that conjugation occurs between a three-membered ring and an adjacent π acceptor. Among the consequences of this interaction are the high reactivity of cyclopropylcarbinyl halides toward solvolysis[2a] and the bathochromic shift of the n → π^* band of simple ketones upon attachment of a cyclopropyl ring to the carbonyl group.[2b] Thus, conjugation with the three-membered ring has qualitatively the same effect as conjugation with a double bond or phenyl group. In order to obtain quantitative information about the π-donating ability of the cyclopropyl group, we have carried out a dynamic NMR study of cyclopropylcarbonyl fluoride (**1**). Comparison of the results for **1** with the previously determined barriers for acryloyl fluoride (**2**)[4] and benzoyl fluoride (**3**)[5] could then be used to determine the relative importance of conjugation for the cyclopropyl, vinyl, and phenyl groups.



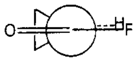
1a



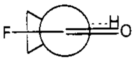
1b



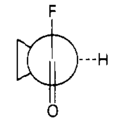
1c



1d



1e



1f

The interaction of the carbonyl group of cyclopropylcarbonyl fluoride with the three-membered ring can be represented by the hyperconjugation structures **1b** and **1c**.[7] The maximum contributions of **1b** and **1c** occur in conformations **1d** and **1e**. These conformations, which represent the ground states for **1**, are interconverted by rotation of the COF group through conformation **1f** (or its enantiomer), for which conjugation should be minimal. Thus, the rotational barriers should give an estimate of the importance of conjugation in this compound. Pittman and Olah[2c] have demonstrated the preference of the (dimethylcyclopropyl)carbinyl cation for the analogous "bisected" conformation, and the rotational barrier (E_a) for the cation was subsequently determined to be 13.7 kcal/mol.[8] Barriers to rotation have been determined for several other cyclopropylcarbinyl cations,[9] but no dynamic NMR studies of electron donation by the cyclopropyl group in neutral compounds have been described.[10] We report here the first observation of slow rotation about the bond between a cyclopropyl ring and an adjacent carbonyl group using low-temperature NMR spectroscopy.

Experimental Section

Cyclopropylcarbonyl fluoride was prepared from cyclopropanecarboxylic acid, benzoyl fluoride, and sodium fluoride, using the procedure of Olah and Comisarow,[12] and was stored over sodium fluoride.

Fluorine NMR spectra were recorded on a Bruker WH-90 spectrometer operating at 84.706 MHz. An external deuterium lock was used. Temperatures were measured by replacing the sample with an NMR tube containing solvent and a copper-constantan thermocouple. The accuracy of the thermocouple was checked by measuring the temperature of a pentane slush obtained by adding liquid nitrogen to pentane.

Results and Discussion

The ^{19}F NMR spectrum of **1** at +21 °C in 2:1 $CHClF_2$/$CHCl_2F$ shows a single chemical shift located 8791.5 Hz (103.79 ppm) downfield from $CHClF_2$. The signal broadens at lower temperatures and splits (T_c = −134 °C) into two signals. The chemical shifts at −163 °C are 121.49 and 81.00 ppm (Figure 1), with areas in a ratio of 1.04:1 (upfield:downfield). The upfield signal, which shows an observable splitting (16 ± 4 Hz) due to coupling with the adjacent hydrogen, can be assigned to conformation **1e**, in which the hydrogen and fluorine are trans.[4,13] A rate constant of 7617 s^{-1} at −134 °C was calculated from the relationship $k_c = (\pi/2^{1/2})\Delta\nu$. The corresponding free energy barrier for interconversion of isomers is 5.5 ± 0.2 kcal/mol at this temperature.[14]

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[1] For reviews, see: (a) de Meijere, A. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 809. (b) Haywood-Farmer, J. *Chem. Rev.* **1974**, *74*, 315.

[2] Examples include: (a) Roberts, J. D.; Mazur, R. H. *J. Am. Chem. Soc.* **1951**, *73*, 2509. (b) Eastman, R. H.; Freeman, S. K. *Ibid.* **1955**, *77*, 6642. (c) Pittman, C. U.; Olah, G. A. *Ibid.* **1965**, *87*, 5123.

[3] For example, see: (a) Walsh, A. D. *Trans. Faraday Soc.* **1949**, *49*, 179. (b) Hoffman, R. *J. Chem. Phys.* **1964**, *40*, 2480. (c) Hoffmann, R. *Tetrahedron Lett.* **1965**, *43*, 3819. (d) Bernett, W. A. *J. Chem. Educ.* **1967**, *44*, 17.

[4] Lin, F. F. S.; Servis, K. *J. Am. Chem. Soc.* **1972**, *94*, 5794.

[5] Anet, F. A. L.; Ghiaci M. *J. Chem. Soc., Chem. Commun.* **1979**, *588*. This work was described also in ref 6.

[6] Drakenberg, T.; Sommer, J.; Jost, R. *J. Chem. Soc., Perkin Trans. 2* **1980**, 363.

[7] For an alternative description in terms of Walsh orbitals, see: ref 3.

[8] Kabakoff, D. S.; Namanworth, E. *J. Am. Chem. Soc.* **1970**, *92*, 3234.

[9] Okazawa, N.; Sorensen, T. *Can. J. Chem.* **1978**, *56*, 2355.

[10] Compounds that have been studied by other methods include phenylcyclopropane,[11a] cyclopropyldifluoroborane,[11b] and the cyclopropylcarbonyl radical.[11c]

[11] (a) Parr, W. J. E.; Schaefer, T. *J. Am. Chem. Soc.* **1977**, *99*, 1033. (b) Odom, J. D.; Szafran, Z.; Johnston, S. A.; Li, Y. S.; Durig, J. R. *Ibid.* **1980**, *102*, 7173. (c) Blum, P. M.; Davies, A. G.; Sutcliffe, R. *J. Chem. Soc., Chem. Commun.* **1979**, 217.

[12] Olah, G. A.; Comisarow, M. B. *J. Am. Chem. Soc.* **1966**, *88*, 4442.

[13] Williamson, K. L.; Li, Y.-F.; Hall, F. H.; Swager, S. *J. Am. Chem. Soc.* **1966**, *88*, 5678.

[14] Kost, D.; Carlson, E. H.; Raban, M. *Chem. Commun.* **1971**, 656.

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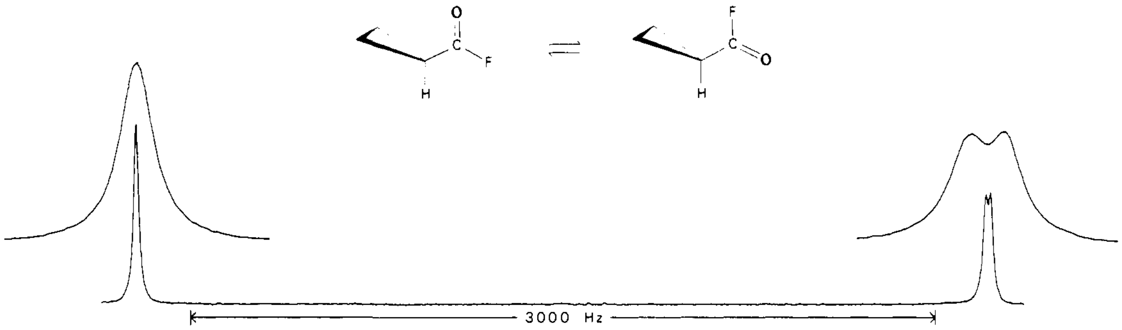
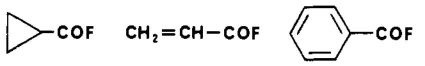


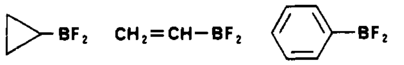
Figure 1. Slow-exchange ^{19}F NMR spectrum (84.706 MHz) of cyclopropylcarbonyl fluoride taken at −163 °C.

Chart I



	1	2	3
$\Delta G^{\ddagger}$, kcal/mol	5.5	5.37 5.62	7.0

Chart II



	4	5	6
Barriers, kcal/mol	4.23	4.17	3.18

The populations of 0.51 and 0.49 at −163 °C correspond to a free energy difference of only 0.009 kcal/mol.[15] If the chemical shifts of the individual isomers can be assumed to be invariant with temperature,[16] then populations at 21 °C of 0.56 and 0.44 for **1d** and **1e**, respectively, can be estimated from the chemical shift at room temperature. Dipole moments of 3.28 and 3.46 D have been reported[17] for **1d** and **1e** in the gas phase, and it is reasonable that the population of the less polar isomer (**1d**) should increase at higher temperatures as the dielectric constant of the solvent decreases, although a precise determination of the populations cannot be made by this indirect method.

Conformation **1d** of cyclopropylcarbonyl fluoride has been reported in a microwave study[17] to be favored in the vapor phase by 0.57 kcal/mol, and rotational barriers of 5.17 ± 0.71 and 5.70 ± 0.71 kcal/mol were estimated for this compound. Howerver, even this large uncertainty in the barriers does not take into account the neglect of V_4 and higher terms in the Fourier series. Similarly, the uncertainty of 0.41 kcal/mol reported for the barriers in cyclopropane carboxaldehyde (4.43 and 4.38 kcal/mol)[18] also does not take into account the neglect of V_n for $n \geq 4$. In this connection, it is noteworthy that these authors report lower barriers for the aldehyde than for the acid fluoride, while dynamic NMR studies show that replacement of the formyl proton of *N,N*-dimethylformamide by fluorine lowers $\Delta G^{\ddagger}$ for rotation from about 21 to 18.1 kcal/mol.[19] The barrier for benzaldehyde (7.9 kcal/mol)[20] is also higher than for benzoyl fluoride (7.0 kcal/mol).[5]

Rotational barriers obtained by dynamic NMR spectroscopy for **1**, **2**,[4] and **3**[5] are summarized in Chart I. The values for **1** and **2** are nearly equal and are lower than for **3**, suggesting that conjugating ability increases in the order cyclopropyl ~ vinyl < phenyl, at least with the fluorocarbonyl group as π acceptor.

Rotational barriers for a series of cross-conjugated *N,N*-dimethylamides, $RCON(CH_3)_2$, were reported[21] to be 16.7, 16.7, and 15.5 kcal/mol for R = cyclopropyl, vinyl, and phenyl, respectively. These values are consistent with the trend observed for the acyl fluorides, although steric effects could be important in the amides due to the bulkiness of the dimethylamino group. The steric requirements of the COF group are expected to be small and should not significantly affect the relative barriers for compounds **1**–**3**.

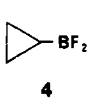
Torsional barriers obtained for cyclopropyldifluoroborane (**4**),[11b] vinyldifluoroborane (**5**),[22] and phenyldifluoroborane (**6**)[23] by infrared, Raman, and microwave spectroscopy, respectively, give a different order (Chart II). This apparent difference could be due to a reversal in the order, caused by the change in π acceptor, or to inaccuracy of one or more of the barriers for compounds **4**–**6**.

There has been much interest in the relative importance of the interaction of phenyl and cyclopropyl groups with an adjacent cationic center. The calculated rotational barrier for **7a** is much higher than for **8a** (49 vs. 26 kcal/mol),[24] indicating that conjugation is more important for phenyl than for cyclopropyl in these ions. A smaller difference (roughly half) was calculated[24] for ions **7b** and **8b**. An activation energy of 13.7 kcal/mol has been reported[8] for **8c**, but the corresponding barrier for **7c** is not known; conjugation in these systems has been studied by other methods.[24-26] In the series of ions **9a**–**d**, higher torsional barriers for

7a R=R'=H

7b $R=CH_3$; R'=H

7c $R=R'=CH_3$

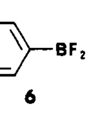


7

8a R=R'=H

8b $R=CH_3$; R'=H

8c $R=R'=CH_3$



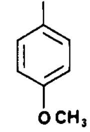
8

9a R=H; $R'=C_6H_5$

9b R=H; $R'=c\text{-}C_3H_5$

9c $R=CH_3$; $R'=C_6H_5$

9d $R=CH_3$; $R'=c\text{-}C_3H_5$

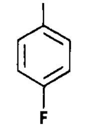


9

10a $R=CH_3$

10b $R=C_6H_5$

10c $R=c\text{-}C_3H_5$



10

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(15) One of the referees has noted that an uncertainty of ±2% in the ratio of conformations would lead to an error of ±0.004 kcal/mol in ΔG. We do not claim a greater accuracy than this and wish mainly to emphasize that ΔG is close to zero at −163 °C.

(16) Large changes in ^{19}F chemical shifts with temperature are sometimes observed. For example, the fluorine chemical shift of *sym*-difluorotetrachloroethane at 27 °C falls outside those of the gauche and anti conformers at −122 °C: Newmark, R. A.; Sederholm; C. H. *J. Chem. Phys.* **1965**, *43*, 602.

(17) Volltrauer, H. N.; Schwendeman, R. H. *J. Chem. Phys.* **1971**, *54*, 268.

(18) Volltrauer, H. N.; Schwendeman, R. H. *J. Chem. Phys.* **1971**, *54*, 260.

(19) (a) Stewart, W. E.; Siddall, T. H. III. *Chem. Rev.* **1970**, *70*, 517. (b) Reeves, L. W.; Shaw, K. N. *Can. J. Chem.* **1971**, *49*, 3671.

(20) Anet, F. A. L.; Ahmad, M. *J. Am. Chem. Soc.* **1964**, *86*, 119. A summary of rotational barriers reported for benzaldehyde is given in ref 6.

(21) Martin, G. J.; Gouesnard, J.-P. *Tetrahedron Lett.* **1975**, 4251.

(22) Durig, J. R.; Carter, R. O.; Odom, J. D. *Inorg. Chem.* **1974**, *13*, 701. A slightly higher barrier (4.42 kcal/mol) was reported by: Durig, J. R.; Hall, L. W.; Carter, R. O., Wurrey, C. J.; Kalasinsky, V. F.; Odom, J. D. *J. Phys. Chem.* **1976**, *80*, 1188.

(23) Christen, D.; Lister, D.; Sheridan, J. *J. Chem. Soc., Faraday Trans. 2.* **1975**, *70*, 1953.

(24) Wolf, J. F.; Harch, P. G.; Taft, R. W.; Hehre, W. J. *J. Am. Chem. Soc.* **1975**, *97*, 2902.

rotation about phenyl–methoxy C–O bonds were found[27] for **9a** and **9c** than for the corresponding cyclopropyl substituted ions **9b** and **9d**, and these results were interpreted in terms of greater charge delocalization for cyclopropyl than for phenyl. However, steric repulsion between ortho hydrogens of the two phenyl groups of **9a** and **9c** should prevent these ions from becoming planar, and steric inhibition of resonance could then result in lower charge delocalization for phenyl than for cyclopropyl in these systems. Similarly, Volz and co-workers[28] have concluded from a ^{19}F NMR study of the chemical shifts in ions **10a–c** that electron release is greater for the cyclopropyl group than for phenyl. Again, this result may be a consequence of a nonplanar conformation for ion **10b**. Olah and co-workers[29] have noted that the phenyl group is generally more susceptible to steric effects than is cyclopropyl.

Conclusion

The rotational barriers determined for compounds **1**, **2**,[4] and **3**[5] by dynamic NMR spectroscopy indicate that conjugation increases in the order cyclopropyl $\sim$ vinyl < phenyl, at least with COF at π acceptor. The opposite order may apply with BF_2 as π acceptor (compounds **4**,[11b] **5**,[22] and **6**[23]), or the apparent change may be due to inaccuracy in one or more of the barriers for these compounds. For simple cyclopropyl- or phenyl-substituted carbenium ions, conjugation with the phenyl group appears to be more important than for cyclopropyl, although steric inhibition of resonance may cause a reversal of this order.

Acknowledgment. The preliminary work on cyclopropylcarbonyl fluoride was carried out at Wayne State University with support from the National Science Foundation (Grant No. CHE7710061 to Professor Morton Raban). Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the National Science Foundation (Undergraduate Research Participation) for support of the work done at Jackson State University.

Registry No. 1a, 694-02-0.

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(25) (a) Olah, G. A.; White, A. M. *J. Am. Chem. Soc.* **1969**, *91*, 5801. (b) Olah, G. A.; Westerman, P. W. *Ibid.* **1973**, *95*, 7530. (c) Olah, G. A.; Westerman, P. W.; Nishimura, J. *Ibid.* **1974**, *96*, 3548.

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Radiative Lifetime of Vibrationally Excited Iodo- and Bromobenzene Ions by Two-Laser Photodissociation Spectroscopy

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Abstract: The photodissociation of iodobenzene and bromobenzene ions trapped in an ICR mass spectrometer has been enhanced by prior irradiation with a low-power infrared laser. It is concluded that the thermal or near-thermal halobenzene ions absorb 10.23-μm infrared radiation to produce vibrationally excited ions that undergo a faster visible photodissociation process than the unexcited ions. Radiative relaxation lifetimes of the excited iodo- and bromobenzene ions are defined with reference to a simple two-state relaxation kinetics model and are determined to be 500 and 200 ms, respectively. The physical significance of these values is discussed to allow comparison with other experimental results.

A new approach to exploring detailed photoprocesses and energy-transfer processes in individual molecules has been opened by the discovery of multiphoton dissociation in trapped gas-phase ions.[1] Both visible-wavelength[2,3] and infrared[4] processes can be investigated, and the conditions may be varied from collision free to collision quenched: The unique aspect of these experiments is the ability to observe events occurring on a very long time scale, ranging up to several seconds.

A recent report[5] by our laboratory of experiments combining infrared and visible irradiation of ions offers possibilities for a more detailed understanding of multiphoton photochemical kinetics. We described an effect by which infrared radiation dramatically increases the visible photodissociation of iodobenzene ions. Since then bromobenzene has been found to show similar behavior. This enhancement of photodissociation was interesting in that the infrared laser was unable to cause any dissociation on its own. It became apparent that this increased dissociation was the result of the iodobenzene ions absorbing infrared photons, with a resulting effect on the visible photon dissociation process. As the visible dissociation to yield phenyl cation plus halogen atom proceeds by a two-photon sequential process, there are several possible mechanisms for participation of IR photons in the photodissociation kinetics. These first experiments involved simultaneous irradiation by both visible and IR lasers. We report here the discovery that the visible and infrared excitation processes need not be simultaneous and discuss the new insight that these sequential-excitation results add to the understanding of ion multiphoton chemistry. Of particular interest is the question of whether a molecule needs to have sufficient internal energy to put it in the "quasi-continuum", so as to absorb IR radiation efficiently, or whether near-ground-state ions can be IR excited. The experiments used gated lasers that allowed separation of the visible and infrared irradiation period. The results clearly showed that the IR laser is optically exciting near-ground-state ions which then undergo a faster visible dissociation process; the ability to separate the IR and visible laser pulses provided information about the lifetimes of these vibrationally excited iodo- and bromobenzene ions.

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