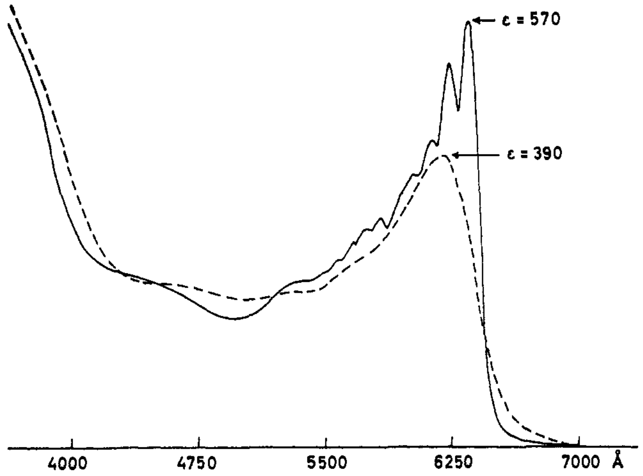

Figure 2. Electronic absorption spectra of $[Fe(cp)_2](BF_4)$ in 10 *M* LiCl aqueous solution: - - - -, 300°K; ——, 77°K.

The origin (0,0) of the system is placed at 15,733 cm^{-1} and the average spacing between peaks in the progression is 280 cm^{-1}. The 16,200-cm^{-1} band is assigned as primarily $^2E_{2g} \rightarrow {}^2E_{1u}$, which is the allowed charge-transfer transition from the e_{1u} bonding ligand level to the hole in the e_{2g} metal level. By analogy to ferricyanide,[11] low-energy ligand → metal charge-transfer transitions are expected in the ferricenium spectrum. As a final point of interest, the integrated intensity of the 16,200-cm^{-1} system increases by approximately 20% in going from 300 to to 77°K (1.9×10^{-3} to 2.3×10^{-3}); this unusual intensity enhancement is compatible with the increase at 77°K in the population of the E'' component of the $^2E_{2g}$ state.

Acknowledgment. This research was supported by the National Science Foundation. We thank Professor C. J. Ballhausen for several stimulating discussions.

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Y. S. Sohn, David N. Hendrickson, Harry B. Gray
Contribution No. 4011, Arthur Amos Noyes
Laboratory of Chemical Physics
California Institute of Technology, Pasadena, California 91109
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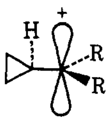
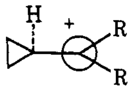
Nuclear Magnetic Double Resonance Studies of the Dimethylcyclopropylcarbinyl Cation. Measurement of the Rotation Barrier

Sir:

The elucidation of the role of the cyclopropyl ring in the chemistry of the cyclopropylcarbinyl and related systems remains a topic of considerable interest.[1] The cyclopropylcarbinyl cation prefers the bisected structure (**1a**) to the perpendicular conformation (**2a**). In the bisected form, the "vacant" p orbital is parallel to the ring and maximum overlap is attained. The magnitude of the energy difference between the two conformations has been estimated by molecular orbital calculations to be: 25 (CNDO),[2a] 9 (EHT),[2b] 19 (AS MO-SCF),[2c] and 22 kcal/mol (NNDO).[2d]



1a, R = H
1b, R = CH_3



2a, R = H
2b, R = CH_3

In 1965, Pittman and Olah reported the direct observation of the dimethylcyclopropylcarbinyl cation.[3] The pmr spectrum showed two nonequivalent methyl groups, and no temperature dependence in the range investigated. They concluded that the ion prefers the bisected form (**1b**). The absence of temperature dependence indicates that rotation around the cyclopropyl–C^+ bond is slow on the nmr time scale. The rotation barrier was estimated to be at least 8–10 kcal/mol.

Although no calculations or direct measurements of the energy difference between the two conformations **1b** and **2b** in tertiary cyclopropylcarbinyl cations have appeared, Schleyer and Buss[1] have estimated that "the difference. . . in tertiary systems, as solvolysis transition states, is 10 kcal/mol. In the free ions themselves this difference might be larger."[4]

Recently Olah and coworkers[5] have reported the complete ^{13}C spectrum of the dimethylcyclopropylcarbinyl cation. The ^{13}C shifts (δ, CS_2) of the carbonium ion carbon and the cyclopropyl methylene carbons were found to be −86.8 and 140.4, respectively. These shifts indicate that part of the charge is delocalized into the cyclopropane ring. Two distinct methyl resonances at 162.7 and 153.9 ppm were observed.

We wish to report the measurement of the rate of rotation in the dimethylcyclopropylcarbinyl cation[6] by the double resonance method of Forsen and Hoffman.[7] This technique enables the determination of much slower rates than can be measured by the conventional line shape method.

In the dimethylcyclopropylcarbinyl cation, the methyl groups, which are exchanged by rotation, occupy magnetically nonequivalent sites. Therefore, a perturbation of the magnetization at one site should be detectable at the other. When the low field methyl resonance was irradiated, we observed decay of the magnetization of the upfield methyl signal. Upon removal of the saturating field, the peak relaxed to its

(1) For an extensive bibliography see: P. von R. Schleyer and G. W. Van Dine, *J. Amer. Chem. Soc.*, **88**, 2321 (1966); P. von R. Schleyer and V. Buss, *ibid.*, **91**, 5882 (1969).

(2) (a) K. B. Wiberg, *Tetrahedron*, **24**, 1083 (1968). See Table II, footnote *a*. (b) R. Hoffman, *J. Chem. Phys.*, **40**, 2480 (1964). (c) T. Yonezawa, H. Nakatsuji, and H. Kato, *Bull. Chem. Soc. Jap.*, **39**, 2788 (1966). (d) V. Buss, to be published, cited in P. von R. Schleyer and V. Buss, ref 1. See also C. Trindle and O. Sinanoglu, *J. Amer. Chem. Soc.*, **91**, 4054 (1969).

(3) C. U. Pittman, Jr., and G. A. Olah, *ibid.*, **87**, 2998, 5123 (1965). See also C. D. Poulter and S. Winstein, *ibid.*, **91**, 3650 (1969).

(4) See also J. C. Martin and B. R. Ree, *ibid.*, **91**, 5882 (1969).

(5) G. A. Olah, D. P. Kelly, C. L. Jeuell, and R. D. Porter, *ibid.*, **92**, 2544 (1970). We thank Professor Olah for communicating these results to us prior to publication.

(6) Samples of the ion were prepared from dimethylcyclopropylcarbinol in SO_2–SbF_5–HSO_3F according to the method of Olah.[3] The samples were degassed and vacuum sealed. Nmr spectra were recorded on a Varian HA-100 spectrometer operating in the internal lock mode. A Hewlett-Packard wide range oscillator, Model 200CD, was used for double resonance experiments. Time-dependent spectra were recorded on a Sanborn Recorder, Series 770.

(7) S. Forsen and R. Hoffman, *Acta Chem. Scand.*, **17**, 1787 (1963); *J. Chem. Phys.*, **39**, 2893 (1963). For an application of this method see: F. A. L. Anet and A. J. R. Bourn, *J. Amer. Chem. Soc.*, **89**, 760 (1967).

initial intensity. Similar behavior was observed for the low field methyl signal.[8]

Decay of the upfield signal was followed by measuring both the actual change in intensity upon irradiation ofthe low field peak and the time rate of change of the magnetization. This rate was followed by locking in on the upfield peak, irradiating the low field signal, and recording the changing magnetization on an external recorder.

The measured rates of rotation ranged from $k = 0.05$ sec^{-1} at $-49°$ to $k = 2.14$ sec^{-1} at $-21.0°$. An Arrhenius plot of the data yielded $E_a = 13.7 \pm 0.4$ kcal/mol and log $A = 12.2 \pm 0.4$, where the errors reported are standard deviations.[9] The large activation energy indicates strong interaction between the cyclopropyl ring and the adjacent positive center. This value is consistent with the theoretical[2] and estimated experimental values[1,3] cited above. It provides the first direct measurement of the energy difference between the two extreme conformations of a cyclopropylcarbinyl cation.[10]

Experiments were also performed at $-65°$ to determine the structure of the "frozen" ion. Under high resolution, the methyl signals appeared not as singlets, but as poorly resolved multiplets (Figure 1a). Upon saturation of the α-H resonance, the upfield multiplet became a quartet (Figure 1c); the low field signal remained unchanged. This line narrowing demonstrates the presence of long-range coupling between the α-H and the upfield methyl group. $J_{CH_3CH_3}$ was found to be 1.2 ± 0.1 Hz. This small coupling can be interpreted as another indication that the positive charge is delocalized into the ring.[11] When the upfield peak was saturated, the low field quartet collapsed into a singlet (Figure 1b). When the low field methyl was saturated, the upfield multiplet narrowed to a doublet, $J_{HCH_3} = 0.9 \pm 0.1$ Hz. Decoupling the spectrum of the ion formed from 2-cyclopropyl-2-propanol-1,1,1-d_3[14] confirmed our assignment of the coupling constant.

The bisected structure (**1b**), which places the α-H *cis* to the low field methyl and *trans* to the upfield methyl, is consistent with these results. Long-range coupling constants, ^4J, depend on the conformation between the interacting nuclei. Models show that the α-H and the hydrogens of the *trans*-methyl group can be connected by a W-like path. This "W coupling" is predicted to be large relative to any α-H to *cis*-methyl coupling.[15]

Figure 1. Methyl region of the 100-MHz spectrum of the dimethylcyclopropylcarbinyl cation: (a) single resonance spectrum; (b) the low field signal upon irradiation of the upfield methyl resonance; (c) the upfield signal upon irradiation of the α-H resonance.

There are several other structures which might also show such long-range couplings, for example, rapidly equilibrating bicyclobutonium ions.[5,16] We feel this structure can be eliminated in the case of the dimethylcyclopropylcarbinyl cation on the basis of the ^{13}C chemical shifts cited above.[5] Thus we offer additional evidence that the most stable structure for the cyclopropylcarbinyl system is the bisected form.

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(8) The data used in our calculations are based on experiments in which the upfield signal was observed. Data recorded by watching the behavior of the low field signal were more difficult to obtain due to the proximity of the wide, complex cyclopropyl resonance.

(9) The uncertainty in our results exceeds the statistical error because we probably have not eliminated all the systematic errors. Our subjective estimate of the error involved is ±10%.

(10) According to our interpretation, interconversion of the two methyl groups occurs by rotation in the cyclopropylcarbinyl species. Professor Martin Saunders has recently suggested that interconversion of the cyclopropylcarbinyl species with a secondary cyclobutyl cation could also explain our result. At present, we have no way of distinguishing between the two mechanisms either on the basis of spectroscopic evidence or energetics arguments.

(11) $J_{CH_3CH_3}$ values for other cations have been determined by Olah and White: phenyldimethyl, <0.5 Hz;[12] isopropyl, 6.0 Hz;[13] and *t*-butyl, 3.5 Hz.[13]

(12) Private communication from G. A. Olah and A. M. White, Case Western Reserve University, Cleveland, Ohio.

(13) G. A. Olah and A. M. White, *J. Amer. Chem. Soc.*, **91**, 5801 (1969).

(14) We thank Professor G. A. Olah for a sample of this compound.

(15) R. A. Y. Jones in "Annual Reviews of NMR Spectroscopy," New York, N. Y., Academic Press, 1968, pp 27–30; D. Gagnaire, *et al.*, in "Nuclear Magnetic Resonance in Chemistry," New York, N. Y., Academic Press, 1965, pp 165–173.

(16) We thank one of the referees for suggesting this possibility.

(17) To whom correspondence should be addressed: Department of Chemistry, Yale University, New Haven, Conn. 06520.

David S. Kabakoff,[17] Eli Namanworth
Department of Chemistry, Case Western Reserve University
Cleveland, Ohio 44106

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