

of Brønsted's law for such systems. Fluorene exchanges its methylene hydrogens at a convenient rate for deuterium or tritium<sup>9</sup> in methanol-sodium methoxide. At 44.9°, the second-order rate constant for tritium exchange,  $10^4 k_2 = 3.68 + 2.3[\text{NaOCH}_3]$  (1. mole<sup>-1</sup> sec.<sup>-1</sup>), shows a mild positive salt effect. The relative rates of several fluorene hydrocarbons in Table II give a fair Brønsted plot with  $\alpha = 0.4$  (Figure 1). This correlation gains significance from the common use of exchange rates as measures of relative acidity.

(9) S. Andreades, *J. Am. Chem. Soc.*, **86**, 2003 (1964).

(10) (a) National Science Foundation Predoctoral Fellow, 1959-1962; (b) Fellow of the Indonesian AID Program.

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### Long-Range Shielding Effect of a Cyclopropane Ring<sup>1</sup>

Sir:

In recent years much interest has been shown in the long-range shielding effect of a three-membered ring, which has generally been ascribed to the ring current.<sup>2</sup> A recent theoretical study by Patel, Howden, and Roberts<sup>3</sup> demonstrated that the comparison between experiment and theory cannot be used to establish the existence of ring current in cyclopropanes, but the trends are reasonably consistent with a ring-current effect. Burke and Lauterbur<sup>4</sup> published further work dealing with the calculations based on a simple form of a ring-current model to account satisfactorily for the hydrogen and carbon magnetic shieldings and the magnetic susceptibility of cyclopropane itself. Since the chemistry of cyclopropane derivatives has received much attention in recent years, it seems desirable for their structure determination to estimate simply the shielding effects of a cyclopropane ring. Recently, Forsén and Norin<sup>5</sup> estimated the anisotropy of a cyclopropane ring using the point dipole approximation. However, it seems to us that this approximation is too rough to predict the magnitude of the effect. On the other hand, the Johnson and Bovey method<sup>3,6</sup> is thought to be tedious to carry out the calculation without availability of a computer or computation results in actual cases. Thus, we propose a simple method for rapid estimation of the magnitude of the long-range shielding effect of a cyclopropane

(1) N.m.r. Studies of Bridged Ring Systems Part VI. For Part V, see K. Tori, Y. Hamashima, and A. Takamizawa, *Chem. Pharm. Bull.* (Tokyo), **12**, 924 (1964).

(2) K. B. Wiberg and B. J. Nist, *J. Am. Chem. Soc.*, **83**, 1226 (1961); J. D. Graham and M. T. Rogers, *ibid.*, **84**, 2249 (1962); B. P. Dailey, A. Gawer, and W. C. Neikam, *Discussions Faraday Soc.*, **34**, 18 (1962); J. Tadanier and W. Cole, *J. Org. Chem.*, **27**, 4610 (1962); R. R. Sauers and P. E. Sonnet, *Chem. Ind.* (London), 786 (1963); R. S. Boikess and S. Winstein, *J. Am. Chem. Soc.*, **85**, 343 (1963); P. R. Jefferies, R. S. Rosich, and D. E. White, *Tetrahedron Letters*, No. 27, 1853 (1963); K. Tori, K. Kitahonoki, Y. Takano, H. Tanida, and T. Tsuji, *ibid.*, No. 11, 559 (1964); M. S. Bergqvist and T. Norin, *Arkiv Kemi*, **22**, 137 (1964).

(3) D. J. Patel, M. E. H. Howden, and J. D. Roberts, *J. Am. Chem. Soc.*, **85**, 3218 (1963).

(4) J. J. Burke and P. C. Lauterbur, *ibid.*, **86**, 1870 (1964).

(5) S. Forsén and T. Norin, *Tetrahedron Letters*, No. 39, 2845 (1964).

(6) C. E. Johnson, Jr., and F. A. Bovey, *J. Chem. Phys.*, **29**, 1012 (1958).

ring by employing McConnell's equation<sup>7</sup> with an empirically deduced constant.

In order to evaluate the long-range shielding effect of a cyclopropane ring as exactly as possible we have to observe the n.m.r. spectra of a pair of compounds, one of which has a cyclopropane ring introduced into the other without any significant alterations in the geometry of the remaining part of the molecule.<sup>8</sup> We prepared the six tricyclo[3.2.2.0<sup>2,4</sup>]nonane derivatives<sup>10</sup> I-VI to compare their n.m.r. spectra with those of the corresponding bicyclo[2.2.2]octane derivatives<sup>11</sup> which differ from the tricyclononanes only in the lack of the cyclopropane methylene. Table I shows the n.m.r. spectral data on these tricyclononanes and the values of additional signal shifts arising from the long-range shielding effects of an introduced cyclopropane ring. Thus the anisotropy of the shielding effect of a cyclopropane ring was disclosed clearly.

First we attempted to account for these anisotropic shielding effects by the ring-current model in the point dipole (at the center of a cyclopropane ring) approximation.<sup>7,12</sup>

On the basis of the data in Table I and molecular geometries estimated with Dreiding models, the anisotropy value of a cyclopropane  $\Delta\chi$  in the McConnell equation<sup>7</sup> was evaluated to be about  $35 \times 10^{-30}$  cm.<sup>3</sup>/molecule, which is of the same order of magnitude as the values so far estimated by other workers.<sup>4,5</sup> However, the calculated additional shift values by using this  $\Delta\chi$  value do not agree well with those observed (Table I).

Increased p-character of a C-C bent bond of a cyclopropane ring<sup>13</sup> might make a change in the magnitude of molecular anisotropy of an ordinary C-C bond ( $-5.5 \times 10^{-30}$  cm.<sup>3</sup>/molecule).<sup>12</sup> Thus on the basis of the concept of bond anisotropy<sup>12</sup> instead of a ring current, we attempt to estimate additional shift values  $\Delta\delta$  of an affected proton signal due to the shielding effect of a cyclopropane ring by eq. A, provided that  $R_i$  is fairly large<sup>7</sup> (the contribution of C-H bonds was neglected), where  $R_i$  is the distance

$$\Delta\delta \text{ (p.p.m.)} = \frac{\Delta\chi}{3} \sum_{i=1}^3 \frac{3 \cos^2 \theta_i - 1}{R_i^3} \quad (\text{A})$$

in Å. between the midpoint of a C-C bond of a cyclopropane ring and an affected proton,  $\theta_i$  is the acute angle which the line  $R_i$  makes with the C-C bond, and  $\Delta\chi$  is an empirically deduced constant, to which in the present paper we tentatively gave a value of  $-20 \times 10^{-30}$  cm.<sup>3</sup>/molecule, derived from the data in Table I.

(7) H. M. McConnell, *ibid.*, **27**, 226 (1957).

(8) Most of the earlier reported compounds in which the shielding effect of a cyclopropane ring was observed<sup>2,3,5</sup> indicate appreciable changes in their molecular geometries owing to introduction of their cyclopropane ring, and, in addition, some of their geometries were not made clear because of lack of physical data or because of ignoring their molecular conformations (for example, tricyclo[3.2.1.0<sup>2,4</sup>]octane derivatives,<sup>9</sup> nortricyclenes, quadricyclenes, thujane derivatives, etc.).

(9) Also refer to W. R. Moore, W. R. Moser, and J. E. LaPrade, *J. Org. Chem.*, **28**, 2200 (1963); R. E. Pincock and J. I. Well, *ibid.*, **29**, 965 (1964).

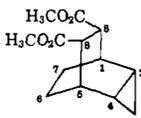
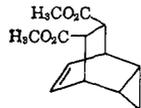
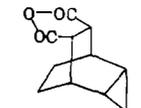
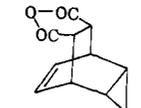
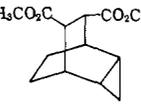
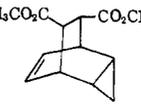
(10) K. Alder and G. Jacobs, *Chem. Ber.*, **86**, 1528 (1953).

(11) K. Tori, Y. Takano, and K. Kitahonoki, *ibid.*, **97**, 2798 (1964).

(12) For example, see L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Chapter 7, Pergamon Press, New York, N. Y., 1959.

(13) G. S. Handler and J. H. Anderson, *Tetrahedron*, **2**, 345 (1958); N. Muller and D. E. Pritchard, *J. Chem. Phys.*, **31**, 768 (1959)

Table I. N.m.r. Spectral Data on Tricyclo[3.2.2.0<sup>2,4</sup>]nonane Derivatives<sup>a</sup>

No.	Compd.	Assignable proton	Chemical shift, <sup>b</sup> $\tau$ -value	Obsd. <sup>c</sup>	Additional shift value due to the cyclopropane ring, p.p.m.	
					Calcd. by point dipole approxn.	Calcd. by eq. A
I <sup>d</sup>		H <sub>7</sub> (H <sub>6</sub> )	7.68(m) <sup>e</sup>	-0.30	-0.19	-0.36
		H <sub>8</sub> (H <sub>9</sub> )	6.97(q) <sup>e</sup>	-0.11	-0.24	-0.14
		CO <sub>2</sub> CH <sub>3</sub>	6.36(s)	0.00		
II		H <sub>1</sub> (H <sub>5</sub> )	6.85(m) <sup>e</sup>	-0.23	-0.13	-0.28
		H <sub>2</sub> (H <sub>4</sub> )	9.05(m) <sup>e</sup>			
		H <sub>6</sub> (H <sub>7</sub> )	4.13(q) <sup>f</sup>	+0.46	+0.43	+0.35
		H <sub>8</sub> (H <sub>9</sub> )	6.91(s) <sup>e</sup>	-0.09	-0.25	-0.14
		CO <sub>2</sub> CH <sub>3</sub>	6.42(s)	0.00		
III		H <sub>1</sub> (H <sub>5</sub> )	7.40(m) <sup>e</sup>	-0.37	-0.19	-0.36
		H <sub>8</sub> (H <sub>9</sub> )	6.70(q) <sup>e</sup>	-0.17	-0.24	-0.14
IV		H <sub>1</sub> (H <sub>5</sub> )	6.55(m) <sup>e</sup>	-0.23	-0.13	-0.28
		H <sub>2</sub> (H <sub>4</sub> )	8.87(m) <sup>e</sup>			
		H <sub>6</sub> (H <sub>7</sub> )	4.10(q) <sup>f</sup>	+0.43	+0.43	+0.35
		H <sub>8</sub> (H <sub>9</sub> )	6.70(q)	-0.14	-0.25	-0.14
V		H <sub>1</sub> (H <sub>5</sub> )	7.56(m) <sup>e</sup>	-0.37	-0.19	-0.36
		H <sub>8</sub>	6.82(q) <sup>g</sup>	-0.06	+0.09	+0.06
		H <sub>9</sub>	6.73(q) <sup>g</sup>	-0.15	-0.24	-0.14
		CO <sub>2</sub> CH <sub>3</sub>	6.27(s) <sup>e</sup>	-0.03		
VI		H <sub>6</sub>	4.11(o) <sup>g</sup>	+0.51	+0.43	+0.35
		H <sub>7</sub>	4.29(o) <sup>g</sup>	+0.50	+0.43	+0.35
		H <sub>8</sub>	7.06(q) <sup>g</sup>	-0.03	+0.08	+0.08
		H <sub>9</sub>	6.67(q) <sup>g</sup>	-0.14	-0.25	-0.14
		CO <sub>2</sub> CH <sub>3</sub> (8)	6.27(s)	-0.01		
		CO <sub>2</sub> CH <sub>3</sub> (9)	6.35(s)	0.00		

<sup>a</sup> The spectra were taken with a Varian A-60 spectrometer on about 10% (w./v.) solutions in deuteriochloroform containing tetramethylsilane as an internal reference at room temperature. Calibration of the spectrometer was checked by the usual side-band technique. Accuracies of chemical shifts are within about  $\tau \pm 0.02$ . <sup>b</sup> For the procedure of the signal assignment, refer to ref. 11. Peak multiplicities are represented by s (singlet), q (quartet), o (octet), and m (multiplet). <sup>c</sup> Observed shift values were evaluated by comparing chemical shifts with those of the corresponding bicyclo[2.2.2]octanes reported in ref. 11. <sup>d</sup> Prepared from II by catalytic reduction over Adams' platinum catalyst in methanol, m.p. 65-67°. <sup>e</sup> Not well-resolved peaks. <sup>f</sup> An A<sub>2</sub>X<sub>2</sub>-type pattern. <sup>g</sup> The A-part of an ABXY system.

The calculated shift values by using eq. A with this constant and the geometries obtained from Dreiding models are given in the last column of Table I, and agree well with the observed values.<sup>14</sup>

Testing the applicability of eq. A, we calculated the shift values of the methyl signal in 1,1-dimethylcyclopropane<sup>15</sup> and of the bridgehead proton signal of nortricyclene<sup>16</sup> due to the cyclopropane ring to be -0.08 and -0.44 p.p.m., respectively, from eq. A with the geometries obtained from Dreiding models. These values are consistent with the respective values of -0.15 and -0.30 p.p.m. observed by Patel, *et al.*<sup>3</sup>

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(14) The contribution of an ordinary C-C bond was subtracted from that of the C-C bond in the compounds I-VI because this bond was present before a cyclopropane ring was introduced.

(15) The average position of the methyl protons was taken at the center of a circle drawn by the protons according to A. D. Cross and I. T. Harrison, *J. Am. Chem. Soc.*, **85**, 3223 (1963).

(16) This example is not quite pertinent, since an appreciable change in the molecular geometries is caused by proceeding from bicyclo[2.2.1]-heptane to nortricyclene.<sup>6</sup>

are also due to Mr. H. Takahashi for his technical assistance.

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### *trans* Opening of Monomer Double Bonds in Anionic Polymerization of Methyl Acrylate Initiated by Lithium Aluminum Hydride

Sir:

In a previous paper<sup>1</sup> we have reported that the double bond of methyl acrylate opens in a definite mode (*cis* or *trans*) in the anionic polymerization (initiated by lithium aluminum hydride in toluene) giving an isotactic polymer, while both *cis* and *trans* openings occur in equal probabilities in free-radical polymerization. The present communication is concerned with determining which of the *cis* and *trans* openings occurs in anionic polymerization.

(1) T. Yoshino, J. Komiyama, and M. Shinomiya, *J. Am. Chem. Soc.*, **86**, 4482 (1964).