Table II. Results of INDO Calculations for Proton Donor. . .Nitroxide Systems

Proton donor	$R_{\mathrm{O}\cdots\mathrm{H}}$,[a] (Å)		Calcd spin densities[b] and stabilization energies[c] π model	σ model[d]
Methanol	1.50	ρ_{OH}	−0.016	0.002
		ρ_{C}	0.000	0.000
		ΔE, kcal/mol[c]	8.87	10.10
Acetylene	1.75	$\rho_{\mathrm{H_1}}$	−0.010	0.002
		$\rho_{\mathrm{C_2}}$	0.008	−0.002
		$\rho_{\mathrm{C_3}}$	0.000	0.000
		$\rho_{\mathrm{H_4}}$	0.001	0.000
		ΔE, kcal/mol[c]	1.29	1.20

[a] Obtained by energy optimization. [b] Spin densities on the hydrogen 1s and carbon 2s atomic orbitals. [c] Energy differences between two conformations for finite and infinite separations of proton donor and dimethyl nitroxide. [d] Calculated for the model where ∠NOH = 120°. [e] Numbering of the atoms: $(CH_3)_2N—O\cdots H_1—C_2{\equiv}C_3—H_4$.

two systems; the downfield ^{13}C contact shifts in two acetylenic carbons (C_1 and C_2) require the π model.

The appearance of negative and positive spin densities in the C–H group can be explained by a spin polarization mechanism. Because positive spin density is residing on the oxygen p_π orbital, the transfer process will preferentially involve an electron in the O···H bond with a spin antiparallel to that of the oxygen electron. This results in a slight excess of positive electron spin density on another site (carbon) of the C–H bond, leading to a slight amount of unpairing of the electrons in the C–H bond. This may also be the case for other XH···DTBN systems. As is inferred from the above discussion, polarization of electron spins may propagate through the bonds and induce positive or negative spin density on the various parts of the XH molecule. Therefore, the way in which electron spin distributes itself in XH molecules is expected to follow the trend of nuclear spin coupling constants. The relative ^{13}C contact shift, *i.e.*, the relative spin densities, for acetylenic carbons (C_1 and C_2) in phenylacetylene (ρ_{C_2}/ρ_{C_1} = = 0.18) is well correlated with the relative values of the $^{13}C_1$—H and $^{13}C_2{\equiv}C_1$—H nuclear spin coupling constants ($J_{C_2\equiv C\text{-}H}/J_{C_1\text{-}H} = +251/+49 = 0.20$). This correlation appears to hold for the trend in the directly bonded ^{13}C—H coupling constants in $CHCl_3$, CH_2Cl_2, and $C_6H_5C{\equiv}CH$.[15]

This nonlocal distribution of electron spin density is also seen in the stereospecific proton contact shifts for various protons in the XH molecules. We have examined the proton nmr spectrum of 4-methylpiperidine, for example, in the presence of DTBN. Quite different values of the downfield contact shifts for α-axial and α-equatorial protons were observed, while the NH proton exhibited a pronounced upfield shift. The observation of a greater downfield contact shift for an α-axial proton than for an equatorial one ($\Delta\delta_{ax}/\Delta\delta_{eq} = 5$) is in accord with the conformation of the N–H group located preferentially at the axial position,[16] in which these protons are separated by the "zig-zag" route, the favorable arrangement for electron spin distribution and nuclear spin coupling.[17]

From the present work we can conclude that the contact shifts induced by H bonding between protic substances and the nitroxide radical serve as a sensitive probe for elucidation of the covalent character of the H bond and of the mode of electron spin distribution on the proton donor molecules. Further theoretical studies on this H-bonding system will appear elsewhere.[18]

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Isao Morishima,* Kazunaka Endo, and Teijiro Yonezawa
Department of Hydrocarbon Chemistry,
Faculty of Engineering, Kyoto University, Kyoto, Japan

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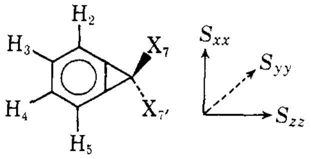
Nuclear Magnetic Resonance Spectra of Oriented Benzocyclopropene and 7,7-Difluorobenzocyclopropene

Sir:

It is well established that nmr spectra of small molecules oriented in a nematic phase yield valuable structural information on proton–proton distances.[1] We wish to report such information for the benzocyclopropene system, the smallest benzo-annelated cycloalkene.

^{1}H and ^{19}F nmr spectra of benzocyclopropene (**1**)[2] and its 7,7-difluoro derivative **2**[3] were observed in *N*-(*p*-ethoxybenzylidene)-*p*-*n*-butylaniline[4] as nematic solvent at normal magnet temperature (30°). Measurements were made on a Varian HA-100 spectrometer, operated in the HR mode. Calibration was achieved by the usual side-band technique,[5] using tetramethylsilane as internal reference compound.



1, X = H

2, X = F

The spectra of **1** and **2** are of the AA′BB′C_2 and AA′BB′X_2 type, respectively. For the analysis the following steps were taken. (1) trial spectra were calculated using direct coupling constants D_{ij} based on assumed geometries and orientation parameters S_{kl}. Input data for the indirect H,H- and H,F-coupling constants were obtained from the results in isotropic media.[6,7] (2) Iterative computer analysis was performed with the program LAOCOONOR[8] using the data of the best trial spectrum as starting parameters. In addition, the ^{1}H aa′bb′ subspectra of **2**, belonging to fluorine spin states $F_z(X_2)$ = +1, 0, and −1, have

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(1) For a recent review see: P. Diehl and C. L. Khetrapal, "NMR—Basic Principles and Progress," Vol. 1, Springer-Verlag, West Berlin, 1969.

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Table I. Relative Chemical Shifts and Dipolar Coupling Constants of **1** and **2** (All Values in Hertz)

Compd	$\nu_2 - \nu_3$[a]	$\nu_2 - \nu_7$	$\nu_3 - \nu_7$	D_{23}[a]	D_{24}	D_{25}	D_{34}	D_{27}	D_{37}	$D_{77'}$	Δf[b]	c, mol %[c]
1	0.7	346.5	347.2	−450.4	−51.6	−20.4	−183.6	−50.1	−79.5	1795.0	0.65	16
2	−17.2[d]			−393.5	14.1	36.6	330.1	−48.6	−48.2	455.1	0.63	13
	−21.7[e]			−393.8	14.2	37.2	329.7					
	−17.3[e]			−393.4	14.1	36.5	330.5					
	−11.9[e]			−393.5	14.1	36.5	330.0					

[a] Probable error of parameters <0.8 Hz. [b] Root-mean-square error for calculated and observed line positions. [c] Concentration. [d] Complete analysis. [e] Subspectral analysis.

Table II. r_{ij} Ratios and Orientation Parameters for **1** and **2**

Compd	r_{23}/r_{34}	r_{24}/r_{34}	r_{25}/r_{34}	r_{27}/r_{34}	r_{37}/r_{34}	$r_{77'}/r_{34}$	S_{xx}[a]	S_{yy}[a]	S_{zz}[a]
1	1.028 ±0.020	1.771 ±0.018	2.081 ±0.028	1.669 ±0.038	2.214 ±0.051	0.760 ±0.013	0.0233 ±0.0001	−0.1003 ±0.0061	0.0770 ±0.0061
2	1.024 ±0.006	1.769 ±0.006	2.081 ±0.015	1.741 ±0.028	2.293 ±0.030	0.879 ±0.055	−0.0419 ±0.0001	−0.0487 ±0.0021	0.0906 ±0.0021
Benzene	1.000	1.732	2.000						

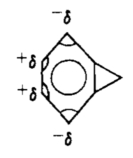
[a] Based on an assumed H_3–H_4 distance of 2.48 A.

been analyzed separately. The results for both compounds are collected in Table I.

Orientation parameters S_{kl} and the ratios of the various H,H, H,F, and F,F distances r_{ij} were then calculated from the experimental data of Table I using an iterative procedure.[9] Since both compounds possess C_{2v} symmetry,[10] two independent parameters are sufficient to characterize their orientation. For these calculations, the distance H_3–H_4 was held constant. The r_{ij} ratios are insensitive to this limitation.[1] To check the results obtained in this way, the ratios of the H,H distances in the six-membered ring of **1** and **2** have also been derived from explicit expressions given for the oriented AA'BB' system.[11] They were identical with those found by the iterative method. The results, together with the orientation parameters and the relevant r_{ij} ratios of benzene, are presented in Table II. From these values those based on H,F- and F,F-coupling constants in **2**, *i.e.*, r_{27}/r_{34}, r_{37}/r_{34}, and $r_{77'}/r_{34}$, are less reliable, since the experimental D_{HF} and D_{FF} values contain unknown contributions from the anisotropy of the indirect spin–spin coupling.[12]

From the negative signs of the dipolar coupling constants it follows that **1**, as other aromatics,[1] orients with its x,z plane preferentially parallel to the external magnetic field. For **2**, however, a different orientation is indicated by the positive sign found for D_{24}, D_{34}, and D_{25} and, more directly, by the different S_{xx} value. In contrast to **1**, the y as well as the x axis of the molecular coordinate system orient preferentially perpendicular to the magnetic field direction.

Within the limits of error, our measurements yield identical proton geometry for the six-membered ring of **1** and **2**. Compared to benzene, all r_{ij}/r_{34} ratios have increased. This seems to indicate that the benzocyclopropene system suffers a distortion of type **3** with positive changes δ for the CCC bond angles at C_3 and C_4 and negative changes for these parameters at C_2 and C_5. Similar angle distortions have been measured for 7,8-dichlorobenzocyclobutene[13] and benzocyclobutene-7,8-dione,[14] where the strain effects should be comparable to those operating in **1** and **2**. Attempts to obtain the "best" carbon skeleton which fits into the geometry determined by the proton positions in both compounds using "molecular mechanics"[15] are at present under way.



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(9) Details of the method will be given in the full paper.

(10) The magnetic equivalence of X_7 and $X_{7'}$ in **1** and **2** demonstrates C_{2v} symmetry only on the nmr time scale, but it seems reasonable to assume that both compounds are planar.

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Josef Bernd Pawliczek, Harald Günther*
Institut für Organische Chemie, Universität Köln
Cologne, Germany

Pyrolysis of Cyclopropyl Azides. A Route to 1-Azetines[1]

Sir:

Photolytic or pyrolytic decomposition of cyclopropyl azides with ring enlargement or substituent migration presents a potential route to 1-azetines or N-substituted cyclopropylimines. Neither the latter nor 2-alkyl- (or aryl-) 1-azetines have heretofore been reported.[2] In

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(1) Stereochemistry. LXIII. For the previous paper in this series, see G. L'abbé and A. Hassner, *Angew. Chem.*, **83**, 103 (1971).

(2) The only 1-azetines in the literature have ether or thioether linkages at the 2 position and are obtained from β-lactams. See, for