Table II. Positional Parameters and esd's for Hydrogens ($\times 10^3$)[a]

Atom	x/a	y/b	z/c
C(1)H	−24 (11)	147 (11)	701 (23)
C(3)H	102 (10)	248 (14)	78 (21)
C(4)H(1)	2 (11)	53 (11)	233 (24)
C(4)H(2)	−72 (12)	138 (11)	191 (23)
C(5)H(1)	129 (11)	115 (12)	453 (24)
C(5)H(2)	221 (11)	182 (11)	654 (24)
C(7)H	−192 (11)	224 (10)	680 (22)
C(8)H	−355 (11)	379 (11)	538 (24)
C(9)H	615 (12)	456 (11)	189 (24)
C(10)H	−242 (11)	483 (11)	−143 (24)
C(11)H	−85 (12)	401 (12)	20 (25)
C(14)H	358 (11)	466 (11)	465 (25)
C(15)H	519 (12)	592 (11)	531 (26)
C(17)H	592 (11)	211 (10)	−136 (22)
C(18)H	735 (11)	94 (11)	−139 (24)
NH	180 (12)	449 (11)	862 (24)

[a] The isotropic temperature factors were arbitrarily assigned a value of 3.0 Å^2.

finement was $w^{-1} = ((|F_o| - 2.5)/20)^2 + 1$, such that $\langle w\Delta^2\rangle$ was relatively constant over the whole range of the $|F_o|$'s. The unobserved data were given zero weight. The final R value was 0.067 for the observed data, and the goodness of fit ($\Sigma w\Delta^2/(m - n)$), 1.03.[24]

In all the above calculations the atomic form factors utilized where those of Cromer and Waber,[25] except those for hydrogen.[26] The bromine atom was corrected for the real part of the anomalous scattering curve. Tables I and II show the final least-squares parameters for the various atoms. The numbering scheme is shown in the accompanying figures. The estimated standard deviations were calculated from the inverse of the full equation blocks for each atom (*i.e.*, 9 × 9 blocks for x, y, z and the β_{ij}'s). The esd's for the bond lengths and angles between the nonhydrogen atoms are on the average 0.015 Å and 0.4°, respectively. The hydrogen atoms were found to have standard deviations about ten times greater than the other atoms, which precludes any detailed discussion of them.

Acknowledgment. We are very appreciative to the University Computing Center for the generous gift of computing time, and to Mrs. Phyllis Sackman for her technical assistance. We are also indebted to Mr. David Eastman for the ^{13}C–H nmr measurements.

[24] A list of the observed and calculated structure factors will be included in the Ph.D. thesis of E. Alexander, State University of New York at Buffalo, Buffalo, N. Y.

[25] D. T. Cromer and J. T. Waber, *Acta Cryst.*, 18, 104 (1965).

[26] "International Tables for X-ray Crystallography," Vol. III, Kynock Press, Birmingham, 1962.

On the Question of 7-*syn*- and 7-*anti*-Proton Absorptions in the Nuclear Magnetic Resonance Spectra of Norbornenes

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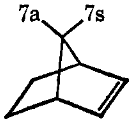
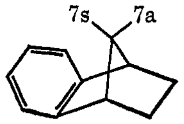
Contribution from the Central Basic Research Laboratory, Esso Research and Engineering Company, Linden, New Jersey 07036. *Received December 22, 1967*

Abstract: The analysis of the nmr spectrum of *exo,exo*-5,6-dideuterionorbornene by means of spin decoupling clearly demonstrates that the 7-*syn* proton absorbs at lower fields than the 7-*anti* proton. A geometric argument is invoked as a rationale for the observed phenomenon.

Shielding and deshielding effects have been employed as a basis for structural assignments of various tricyclic[2] and bicyclic compounds and in particular for various norbornenyl derivatives.[3] In their first paper[3] Tori, *et al.*, incorrectly assigned the 7-*syn* (7s) proton to a higher field than the 7-*anti* (7a) proton in the nmr spectra of norbornene (I) and benzonorbornene (II).

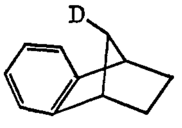


I

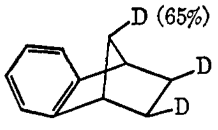


II

However, in their second paper,[4] Tori and coworkers reversed their initial assignment of the 7-*syn* and 7-*anti* proton absorptions by spin-decoupling compounds III and IV; the 7s proton was assigned to a lower field than that of the 7a proton. Tori did not spin-decouple



III



IV

an analogously deuterated norbornene (I); however, on the basis of his results with III and IV he revised his previous chemical shift assignments[3] of the 7s and 7a protons in compound I.

The well-known shielding of protons above the plane of the double bond phenomenon[5] would predict that the 7s proton *should* resonate at a higher field than the 7a proton, contrary to Tori's observed results. Indeed, this is exactly what is observed for 7-substituted norbornenes (V and VI).[6] In addition, it has been

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[1] (a) Central Basic Research Laboratory, Esso Research and Engineering Co., Linden, N. J. 07036. (b) Esso Research and Engineering Co., Baytown, Texas. (c) Department of Chemistry, University of Connecticut, Storrs, Conn.

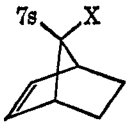
[2] J. P. Snyder and D. G. Farnum, *J. Org. Chem.*, 31, 1699 (1966), and references therein.

[3] K. Tori, Y. Hata, R. Muneyuki, Y. Takano, T. Tsuji, and H. Tanida, *Can. J. Chem.*, 42, 926 (1964).

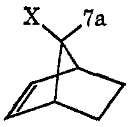
[4] K. Tori, K. Aono, Y. Hata, R. Muneyuki, T. Tsuji, and H. Tanida, *Tetrahedron Letters*, 9 (1966).

[5] L. M. Jackman, "Applications of Nuclear Magnetic Resonance in Organic Chemistry," Pergamon Press Inc., New York, N. Y., 1961, p 112.

[6] E. I. Snyder and B. Franzus, *J. Am. Chem. Soc.*, 86, 1166 (1964).



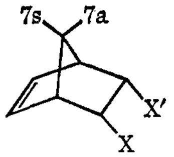
V



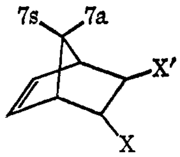
VI

X = OH, OAc

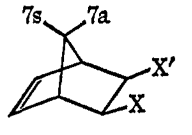
observed by LeBel[7] that the relative absorptions of 7s and 7a protons of 5,6-dihalo-2-norbornenes (VII, VIII, IX) varied dependent upon whether the halogens were di-*endo* (VII), *exo,endo* (VIII), or di-*exo* (IX). In particular, for compound VII 7a absorbed at higher fields than 7s (consistent with Tori's observations) but absorbed at lower fields than 7s for compounds VIII and IX. However, as LeBel has noted, proton 7s absorption remained fairly constant in compounds VII–IX, but the absorption of 7a varied markedly. LeBel has attributed this deshielding to anisotropic effects of the halogens and not to any steric effects. Indeed LeBel's hypothesis has been fully supported by Marchand,[8] who has noted that in the absence of anisotropic constituents in close proximity to the bridge hydrogen, that in general the *anti*-bridge hydrogen (7a) absorbs at higher fields than the *syn*-bridge hydrogen (7s).



VII

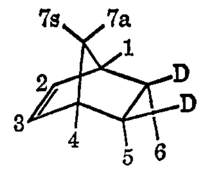


VIII



IX

This paper describes the detailed nmr analysis of *exo,exo*-5,6-dideuterionorbornene (X), which permits an accurate assignment of the chemical shifts of the 7-*syn* and 7-*anti* protons and provides a reasonable explanation for the observed variations in the chemical shifts of the bridge hydrogens among 7-substituted norbornenes and norbornene.



X

Results

The reduction of norbornadiene by PdD_2, PtD_2,[9–11] or N_2D_2[12] results in formation of X and of *exo,exo,exo,exo*-2,3,5,6-tetradeuterionorbornane. Deuterium incorporation in compound X as shown by electron-impact mass spectroscopy is ~99% d_2 and 1% d_1. Mass spectra determined by the chemical ionization method[13] indicated 95% d_2 and 5% d_1. The nmr spectrum of X is shown in Figure 1 with the *endo*-proton absorption at δ 0.9 ppm and complete absence of absorption at $\delta \cong 2$ as anticipated for *exo* protons,[14] thus confirming the structural assignment of compound X. In addition the chemical shifts and coupling constants found for X agree well with the chemical shifts and coupling constants found for the *exo*- and *endo*-substituted norbornenes studied by Davis and VanAuken.[15]

The basis for chemical shift assignments for the 7s, 7a protons depends on previous observations of a 0.6–1.0-Hz vinyl-*anti*-7-proton ($J_{2,7a}$) coupling constant[6,16] and a 2–3-Hz *syn*-7-*endo*-5 ($J_{5,7s}$) coupling constant.[16,17] Spin-decoupling experiments indicated that the vinyl protons (H_2, H_3) in addition to forming part of an A_2X_2 system with the bridgehead protons (H_1, H_4) are also coupled to the 7s and 7a protons as shown in inset A, Figure 1. The anticipated vinyl–7-*anti* ($J_{2,7a}$) long-range coupling constant, 0.6 Hz, was observed[6,16] (inset B, Figure 1); in addition a small but finite vinyl–7-*syn* coupling constant ($J_{2,7s}$) of 0.2–0.35 Hz (inset C, Figure 1) was surprisingly observed. Additional proton spin-decoupling experiments gave the other spin-coupling constants shown in Table I, including the anticipated 7-*syn*–*endo*-5 ($J_{5,7s}$) coupling constant of 2.0–2.5 Hz. This long-range coupling constant was directly observed by deuterium decoupling shown in inset D, Figure 1. The chemical shift assignment of the 7s,7a protons has been further substantiated by Marchand, who has synthesized and examined the nmr spectrum of *anti*-7-deuterionorbornene.[8]

Discussion

The above data unequivocally show that the *syn*-7 proton experiences a paramagnetic shift appearing at a lower field than the *anti*-7 proton. These results confirm Tori's second assignments,[4] are reinforced by Marchand's study,[8] and are certainly not inconsistent with LeBel's data.[7] These results do differ from those obtained with 7-substituted norbornenes where the *syn*-7 proton appears to be diamagnetically shielded by the double bond.[6] LeBel has stated that the 7 substituent was probably responsible for the chemical shift differences of the 7s,7a protons[7] and that the final answer awaited a complete analysis of this norbornene spectrum. Tori has stated, on the other hand, that there must be an unusual magnetic shielding for the 7s proton to appear at lower field than the 7a proton.[4]

The fact that the *syn*-7-proton appears to be shielded in some compounds (7-substituted norbornenes) and deshielded in almost all others[4,8] strongly suggests that the simple picture of compound I (or X) as having the 7s proton shielded by the double bond[5] must be in error. Indeed, inspection of Figure 2[18] reveals (qualitatively)

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(7) P. M. Subramanian, M. T. Emerson, and N. A. LeBel, *J. Org. Chem.*, **30**, 2624 (1965).

(8) A. P. Marchand and J. F. Rose, *J. Am. Chem. Soc.*, **90**, 3724 (1968). Dr. Marchand has kindly kept us informed of his nmr studies of the norbornene system. We are grateful to Dr. Marchand for a preprint of his manuscript.

(9) B. Franzus, W. C. Baird, Jr., E. I. Snyder, and J. H. Surridge, Regional Metropolitan American Chemical Society Meeting, New York, N. Y., Feb 1, 1965.

(10) D. R. Arnold, D. J. Trecker, and E. B. Whipple, *J. Am. Chem. Soc.*, **87**, 2596 (1965).

(11) B. Franzus, W. C. Baird, Jr., and J. H. Surridge, *J. Org. Chem.*, **33**, 1288 (1968).

(12) W. C. Baird, Jr., B. Franzus, and J. H. Surridge, *J. Am. Chem. Soc.*, **89**, 410 (1967).

(13) M. S. B. Munson and F. H. Field, *ibid.*, **88**, 2621 (1966).

(14) R. R. Fraser, *Can. J. Chem.*, 40, 78 (1962).

(15) J. C. Davis, Jr., and T. V. VanAuken, *J. Am. Chem. Soc.*, **87**, 3900 (1965).

(16) P. Laszlo and P. von R. Schleyer, *ibid.*, **86**, 1171 (1964).

(17) J. Meinwald, Y. C. Meinwald, and T. N. Baker III, *ibid.*, **86**, 4074 (1964).

(18) Figure 2 was derived using bond angles and distances from the norbornadiene skeleton; *cf.* W. G. Woods, R. A. Carboni, and J. D.

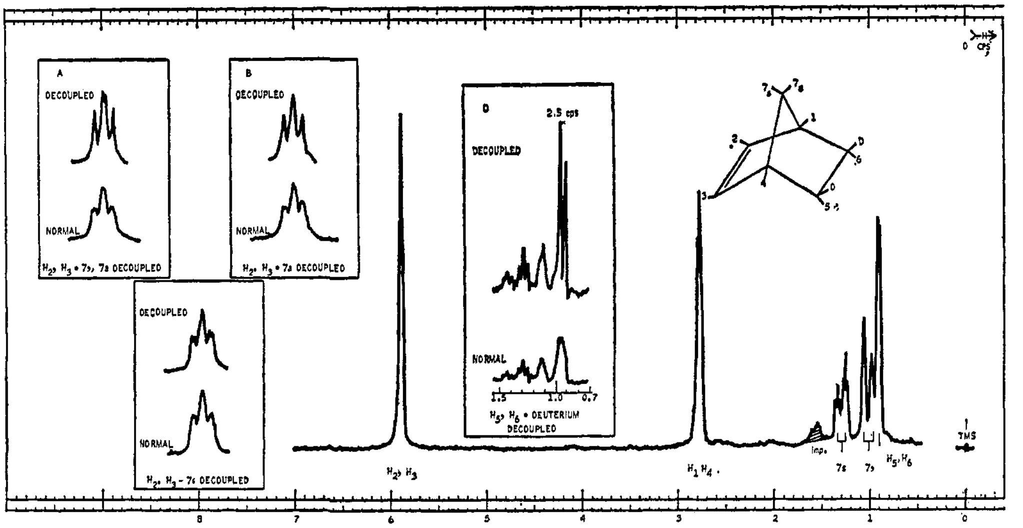

Figure 1. Nmr spectrum of *exo,exo*-5,6 dideuterionorbornene at 100 Mc (1000-cps sweep width): inset A, vinyl hydrogens (100-cps sweep width) decoupled from the 7-*syn* and 7-*anti* protons; inset B, vinyl hydrogens (100-cps sweep width) decoupled from the 7-*anti* proton; inset C, vinyl hydrogens (100-cps sweep width) decoupled from the 7-*syn* proton; inset D, *endo* hydrogens (500-cps sweep width at 60 Mc) decoupled from the *exo* deuteriums.

that the axis of the π orbitals and the C_7–H_{7s} internuclear bond are almost parallel so that the *syn*-7 proton is located at the diamagnetic–paramagnetic "border" of the π bond. Small variations in the molecular geometry could cause the 7-*syn* proton to fall in one or the other of these regions. The magnitude of the anisotropic effect of the double bond can be obtained by applying McConnell's equation[19] as modified by Nakagawa.[20,21]

$$\delta = \frac{\Delta\chi}{3}\left(\frac{1 - (3\cos^2\theta_1)}{R_1{}^3} + \frac{1 - (3\cos^2\theta_2)}{R_2{}^3}\right)$$

where $\Delta\chi \cong -10 \times 10^{-30}\,\mathrm{cm}^3$ (*cf.* ref 2), δ is in parts per million, and R_1, R_2, θ_1, θ_2 are as shown in Figure 2. At the diamagnetic–paramagnetic "border" of the π bond, $\delta = 0$. Therefore $\theta_1 = \theta_2 = 54°\,44'$. Thus the geometry of the norbornenyl system is such that $\theta_1 = \theta_2 \cong 55°$ so that no clear-cut distinction can be made as to the shielding or deshielding effect of the double bond on the bridge protons. Thus for $\delta = +0.06$ ppm ($+3.6$ Hz) $\theta_1 = \theta_2 \cong 50°$ and for $\delta = -0.06$ ppm (-3.6 Hz) $\theta_1 = \theta_2 \cong 60°$. It is quite apparent that an angle change of 10° can vary the chemical shift of the 7-*syn* proton (7s) from a shielding or paramagnetic region ($\theta \cong 50°$) to a deshielding or diamagnetic region ($\theta \cong 60°$). One must conclude therefore that the 7-*syn* proton does not experience any unusual shielding effects; in addition, one must also conclude that in 7-substituted norbornenes, the 7 substitutent in all probability alters the molecular geometry so that the 7-*syn* proton lies in a paramagnetic region above the double bond for the *anti*-7-substituted norbornene (XI) and in a diamagnetic region for the 7-*anti* proton (7a) for the *syn*-7-substituted norbornene (XII).

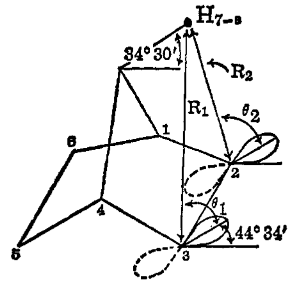

Figure 2.

Table I. Chemical Shifts (δ) and Coupling Constants (Hertz)

Hydrogen	δ	J, Hz	
$H_1 = H_4$	2.80 (2.82[b])	$J_{2,3} = 5.6$–5.9[a]	$J_{2,5} = 0$
$H_2 = H_3$	5.92 (5.93[b])	$J_{1,2} = J_{34} = 2.0$–2.2	$J_{1,7s} = 2.0$–2.2
H_{7s}	1.32 (1.33[b])	$J_{1,3} = 1.6$–1.7	$J_{1,7a} = 1.5$–1.6
H_{7a}	1.03 (1.06[b])	$J_{1,4} = 0$[a]	$J_{7a,7s} = 7.9$–8.0
$H_5 = H_6$	0.93 (0.96[b])	$J_{2,7a} = 0.5$–0.6	$J_{5,7s} = 2.0$–2.5

[a] *Cf.* ref 15. [b] *Cf.* ref 8.

In fact, using the geometric parameters from the X-ray analysis of *anti*-7-norbornenyl *p*-bromobenzoate (XI, X = *p*-bromobenzoate)[22] it is quite easy to show from

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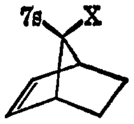
Roberts, *J. Am. Chem. Soc.*, **78**, 5653 (1956), combined with the coordinate-unit vector scheme of C. F. Wilcox, Jr., *ibid.*, **82**, 414 (1960). Note that this picture is approximate since exact geometric parameters for the norbornene system are not available.

(19) H. M. McConnell, *J. Chem. Phys.*, **27**, 226 (1957).

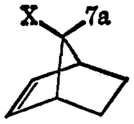
(20) S. Yamaguchi, S. Okuda, and N. Nakagawa, *Chem. Pharm. Bull. Japan*, **11**, 1465 (1963).

(21) Note that this equation is concerned solely with the chemical shielding (or deshielding) effect of the double bond on a particular proton and *not* with the over-all chemical shift of that same proton. Note also that although Nakagawa's equation has not been altered, the equation must be multiplied by 10^6 to obtain δ in parts per million, or by the field strength to obtain the shift in hertz.

(22) A. C. MacDonald and J. Trotter, *Acta Cryst.*, **19**, 456 (1965).



XI
anti



XII
syn

the above equation that the 7-*syn* proton experiences a paramagnetic shift of +5 Hz. Since the X-ray analysis of the corresponding *syn* compound (XII, X = *p*-bromobenzoate) has not yet been accomplished, it is impossible to calculate the effect of the double bond on the *anti*-7 proton (7a). Nevertheless the results do qualitatively show that only small perturbations are necessary to alter the geometry of the norbornenyl system to effect either paramagnetic or diamagnetic shifts on the bridge protons. Finally, support of the geometric interpretation over an electronic interpretation resides in Tanida's work on ring-substituted benzonorbornenes in which the relative chemical shift differences between the 7s and 7a protons remained invariant over a wide range of electron-donating to electron-attracting substituents.[23]

Experimental Section

Nmr spectra and proton decoupling experiments were performed on a Varian Associates HA-100 spectrometer. Deuterium decoupling experiments were performed on a Varian Associates A-60 spectrometer. Spectra were determined in carbon tetrachloride solution using tetramethylsilane as an internal standard.

exo,exo-5,6-Dideuterionorbornene (X) was prepared by published synthetic procedures.[11,12] The mass spectrum determined by the chemical ionization method[13] indicated a deuterium content of 95% d_2 and 5% d_1. The electron-impact spectrum gave an analysis of 99% d_2 and 1% d_1.

The X-ray data for *anti*-7-norbornenyl *p*-bromobenzoate[22] was utilized to calculate θ_1 and θ_2 for this compound; the value of θ computed from these data was 50° 40′. The chemical shift observed for the 7-*syn* proton in the *p*-bromobenzoate[24] was δ = 4.58 ppm.

Acknowledgment. The authors are indebted to Dr. F. H. Field of these laboratories for determining the mass spectral data.

[23] N. Inamota, S. Masuda, K. Tori, K. Aono, and H. Tanida, *Can. J. Chem.*, **45**, 1185 (1967).

[24] We wish to thank Dr. R. E. Pincock of the University of British Columbia for a sample of *anti*-7-norbornenyl *p*-bromobenzoate.

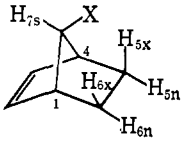
On the Question of Bridge-Proton Absorptions in the Nuclear Magnetic Resonance Spectra of Norbornene and Related Systems

Alan P. Marchand and Joseph E. Rose

Contribution from the Department of Chemistry, The University of Oklahoma, Norman, Oklahoma 73069. *Received January 8, 1968*

Abstract: *anti*-7-Deuterionorbornene has been synthesized stereospecifically. Comparison of its 100-MHz nmr spectrum with that of norbornene reveals that the *anti*-bridge proton (7a) absorbs at higher field (lower δ) than does the *syn*-bridge proton (7s). This result serves to substantiate unequivocally conclusions concerning this point which have been arrived at more recently upon reexamination of the nmr spectrum of norbornene.[6,8] The usefulness of the vinyl proton–*anti*-bridge proton long-range coupling in assigning the relative positions of bridge proton absorptions (AB pattern) is demonstrated through examination of the nmr spectra of several systems which are structurally related to the familiar insecticides aldrin (VIII) and isodrin (IX). The usefulness of coupling constant and chemical shift information as criteria for assigning stereochemical configuration in substituted norbornenes is assessed.

Analysis of the nmr spectrum of norbornene (Ia) has been a subjct of interest in recent years.[1-9] The 7-*syn* (7s), 7-*anti* (7a), 5,6-*endo* (5n,6n), and 5,6-*exo* (5x, 6x) protons absorb over a relatively narrow spectral range; assignment of the various absorption peaks arising from these protons has been facilitated by the advent of the 100-MHz nmr spectrometer. Assignments of the 5n,6n and 5x,6x absorption patterns, respectively, have been made on the basis of empirical observations[10] and on theoretical grounds.[11] The 7s and 7a



Ia, X = H_{7a}
b, X = D

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[1] K. Tori, R. Muneyuki, and H. Tanida, *Can. J. Chem.*, **41**, 3142 (1963).

[2] K. Tori, Y. Hata, R. Muneyuki, Y. Takano, T. Tsuji, and H. Tanida, *ibid.*, **42**, 926 (1964).

[3] E. I. Snyder and B. Franzus, *J. Am. Chem. Soc.*, **86**, 1166 (1964).

[4] P. Laszlo and P. von R. Schleyer, *ibid.*, **86**, 1171 (1964), and references cited therein.

[5] J. C. Davis, Jr., and T. V. Van Auken, *ibid.*, **87**, 3900 (1965).

[6] K. Tori, K. Aono, Y. Hata, R. Muneyuki, T. Tsuji, and H. Tanida, *Tetrahedron Letters*, 9 (1966).

[7] P. M. Subramanian, M. T. Emerson, and N. A. LeBel, *J. Org. Chem.*, 30, 2624 (1965).

[8] B. Franzus, W. C. Baird, Jr., N. F., Chamberlain, T. Hines, and E. I. Snyder, *J. Am. Chem. Soc.*, **90**, 3721 (1968).

[9] R. V. Moen and H. S. Makowski, Abstracts, 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 1967, No. Q9.

[10] *E.g.*, the nmr spectrum of 5,6-*exo,exo*-dideuterionorbornene has been studied: (a) D. R. Arnold, D. J. Trecker, and E. B. Whipple, *J. Am. Chem. Soc.*, **87**, 2596 (1965); (b) W. C. Baird, Jr., B. Franzus, and J. H. Surridge, *ibid.*, **89**, 410 (1967); (c) ref 8.

[11] (a) R. R. Fraser, *Can. J. Chem.*, 40, 78 (1962); (b) J. I. Musher, *Mol. Phys.*, **6**, 93 (1963).