

ence between their  $z$  coordinates, and  $\psi_\mu$  and  $\psi_\nu$  are the singly occupied MOs. The values for the integrals, calculated using Slater AOs, were taken from the literature.<sup>13,14</sup> The values ( $\text{cm}^{-1}$ ) obtained were as follows: ( $\text{CH}_5^+$  calcd 0.153, obsd<sup>8</sup>  $0.1868 \pm 0.0005$ ; ( $\text{CCl}_5^+$  calcd 0.111, obsd<sup>9</sup> 0.1495. The agreement is gratifying, particularly since we did not include the spin-orbit contribution<sup>15</sup> which may be quite large in the case of 7.

These results, together with those for methylene,<sup>6</sup> seem to suggest that MINDO/3 may prove useful for the study of triplet states.

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Michael J. S. Dewar,\* Robert C. Haddon

Department of Chemistry, The University of Texas at Austin  
Austin, Texas 78712

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### High Resolution Deuterium Magnetic Resonance. The Stereochemical Dependence of Relaxation Times

Sir:

We have measured deuterium spin-lattice relaxation times ( $T_1$ ) for the series of compounds shown in Table I, by the inversion recovery method.<sup>1</sup> Magnetic relaxation of deuterium is induced entirely by an intramolecular quadrupole mechanism,<sup>2</sup> and the interpretation of  $^2\text{H}$  relaxation times is consequently much simpler than for  $^1\text{H}$  or  $^{13}\text{C}$ . For the compounds in Table I,  $^2\text{H}$  relaxation may be controlled by two kinds of molecular motion—anisotropic molecular tumbling and intramolecular rotation. The magnitude of  $T_1$  can change by a factor of 10, depending on the rate of internal rotation.<sup>3</sup> We should like to emphasize in this communication the general utility and simplicity of interpretation of  $^2\text{H}$  relaxation data in exploration of stereochemistry, intramolecular rotation, and anisotropic motion.

Compounds 1 and 2 (group I) are considered to allow free rotation of the deuteriomethyl group, which should result in relatively long relaxation times. This rotation can be hindered by substitution of chlorine or bromine into the methyl group, resulting in shorter values of  $T_1$  for compounds 3–6.<sup>4</sup> Group II in Table I shows the deuterium relaxation times for various aromatic compounds. For benzene and pyridine symmetry considerations dictate equal (or almost equal) relaxation times for all deuterons. From the geometry of compounds 9–14 the molecular motion in solution is expected to be anisotropic. Rotations about the axes through the substituent and in the aromatic plane are expected to be the most rapid, leading to a lengthening of relaxation times for those deuterons whose position relative to the applied magnetic field is altered. There-

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(2) A. Abragam, "The Principles of Nuclear Magnetism," Oxford, 1961, Chapter 8.

(3) M. D. Zeidler, *Ber. Bunsenges. Phys. Chem.*, **69**, 659 (1965).

(4) The molecular weight dependence of the overall rotation should be of second order and it is ignored. A lack of significant contribution to the deuterium relaxation by quadrupolar nuclei such as chlorine and bromine is implied by the absence of line broadening of the neighboring deuterium resonance.

fore the shortest relaxation time is realized for the C–D group of 14. Similarly, the relaxation times of deuterium in the para position of substituted benzenes 10, 12, and 13 are shorter than those of the meta and ortho positions. In 9 and 11 the accidentally degenerate deuterium resonances do not permit measurement of individual relaxation times. Similar conclusions regarding the influence of anisotropic motion on  $^{13}\text{C}$  relaxation times have been reached by Levy, *et al.*<sup>5</sup> Although relaxation by rapid ring inversion in 15 tends to diminish the difference in the relaxation times at different positions, the small differences may still be interpreted in terms of favored rotation about an axis through the C=O bond. The large difference in  $T_1$  for 16 and 17 is greater than expected from the increase in overall correlation time due to increased molecular size of 17. This is attributable to preferred rotation of 17 about the  $C_3$  axis which is less effective in averaging out the quadrupolar contribution than motion about the  $C_2$  axis of 16. In the substituted naphthalenes it is clear from the  $T_1$  values that steric hindrance for  $\text{CD}_3$  rotation decreases in the order 18 ( $\alpha$ ) > 19 > 18 ( $\beta$ ) > 20. Comparison of the data for 21 and 22 demonstrates the relative efficacies of rotations about the two indicated axes at averaging out the quadrupole contribution to  $^2\text{H}$  relaxation.

For *N,N*-dimethylformamide (23), correct resonance assignments can be made by  $^2\text{H}$  nmr by simply taking into account preferential rotational axes. Both hydrogen and  $^{13}\text{C}$  spectra show two peaks, arising from the methyl groups cis and trans to the carbonyl group. Assignment of these two peaks was made by use of the nuclear Overhauser enhancement between the methyl and formyl protons in  $^1\text{H}$  nmr,<sup>6</sup> while the  $^{13}\text{C}$  resonances were assigned on the basis of a steric upfield shift.<sup>7</sup> The different relaxation times for the  $\text{CD}_3$  groups in 23 can be best explained in terms of anisotropic rotation. It has already been shown that for 23, the rotational correlation time about an  $\text{N}\cdots\text{O}$  axis (Table I) is approximately 50 times shorter than the rotation perpendicular to this axis.<sup>8</sup> Therefore we may expect the cis  $\text{CD}_3$  group, located perpendicular to this axis, to experience a very efficient averaging of quadrupole effects (*i.e.*, long relaxation times), while the trans  $\text{CD}_3$  group, located on the axis, should have shorter  $T_1$ 's. Since deuterium and  $^{13}\text{C}$  relaxation times can be correlated very well<sup>9</sup> we feel that even the different  $^{13}\text{C}$  relaxation times for 23 and those for the syn and anti methyl groups in acetoxime<sup>7</sup> have to be explained in terms of anisotropic rotation, instead of the initially proposed steric hindrance.

It is clear from the foregoing that high resolution  $^2\text{H}$  nmr provides a powerful indicator of stereochemistry and anisotropic motion. It is thus complementary to the earlier technique developed by Lehn and coworkers<sup>10</sup> where the influence of a  $^2\text{H}$  coupled to  $^1\text{H}$  was measured

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(6) F. A. L. Anet and A. R. J. Bourn, *J. Amer. Chem. Soc.*, **87**, 5250 (1965).

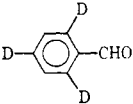
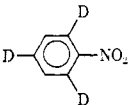
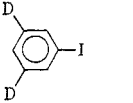
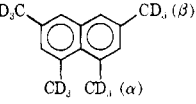
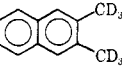
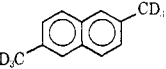
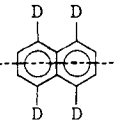
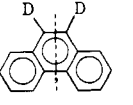
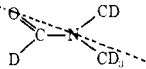
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**Table I.** Deuterium Spin-Lattice Relaxation Times ( $T_1$ ) of Deuterated Compounds, in Carbon Tetrachloride Solutions (5%) or as Neat Liquids<sup>a</sup>

Group	No.	Structural formula	Solvent	Obsd group	Measd $T_1$ , sec
I	1	$\text{CD}_3\text{CCl}=\text{CCl}_2$	Neat	$\text{CD}_3$	2.7
	2	$\text{CD}_3\text{CCl}_3$	$\text{CCl}_4$	$\text{CD}_3$	2.0
	3	$\text{CD}_2\text{ClCD}_2\text{Cl}$	Neat	$\text{CD}_2$	1.3
	4	$\text{CD}_2\text{BrCD}_2\text{Br}$	Neat	$\text{CD}_2$	0.64
	5	$\text{CH}_2\text{BrCDCl}_2$	Neat	$\text{CD}$	0.46
	6	$\text{CD}_3\text{CDBrCD}_2\text{Br}$	$\text{CCl}_4$	$\text{CD}_3$ $\text{CD}_2$ $\text{CD}$	0.62 0.59 0.48
II	7	$\text{C}_6\text{D}_6$	Neat	$=\text{CD}$	1.5
	8	Pyridine- $d_5$	$\text{CCl}_4$	$=\text{CD}$ ortho $=\text{CD}$ meta $=\text{CD}$ para	1.2 1.1 1.3
	9	$\text{C}_6\text{D}_5\text{CD}_3$	$\text{CCl}_4$	$\text{CD}_3$ $=\text{CD}$ av	4.3 0.86
	10		$\text{CCl}_4$	$=\text{CD}$ ortho $=\text{CD}$ para	0.57 0.40
	11	$\text{C}_6\text{D}_5\text{Cl}$	$\text{CCl}_4$	$=\text{CD}$ av	0.89
	12		$\text{CCl}_4$	$=\text{CD}$ ortho $=\text{CD}$ para	0.58 0.39
	13		$\text{CCl}_4$	$=\text{CD}$ meta	0.59
	14	$\text{C}_6\text{H}_5\text{C}\equiv\text{CD}$	$\text{CCl}_4$	$\equiv\text{CD}$	0.25
	15	Cyclohexanone- $d_{10}$	$\text{CCl}_4$	$\text{CD}_2(\alpha)$ $\text{CD}_2(\beta)$ $\text{CD}_2(\gamma)$	0.84 0.81 0.78
	16	$(\text{C}_6\text{H}_5)_2\text{CD}_2$	Neat	$\text{CD}_2$	0.19
	17	$(\text{C}_6\text{H}_5)_3\text{CD}$	$\text{CCl}_4$	$\text{CD}$	0.11
	18		$\text{CCl}_4$	$\text{CD}_3(\beta)$ $\text{CD}_3(\alpha)$	0.91 0.24
	19		$\text{CCl}_4$	$\text{CD}_3$	0.68
	20		$\text{CCl}_4$	$\text{CD}_3$	1.1
	21		$\text{CCl}_4$	$\text{CD}$	0.52
22		$\text{CCl}_4$	$\text{CD}$	0.21	
III	23		Neat	$\text{CD}_3$ cis $\text{CD}_3$ trans $\text{CD}$	3.0 1.6 0.95

<sup>a</sup> The estimated maximum error in these measurements is <5%. The differences between measurements in  $\text{CCl}_4$  and neat liquids are negligible in most cases.

by line shape analysis of the  $^1\text{H}$  spectrum. High resolution  $^2\text{H}$  nmr has only recently become possible due to the development of pulsed multinuclear instruments. A detailed review of its applications to chemistry and biology will appear shortly.<sup>11</sup> Because

experiments are usually done on selectively deuterated compounds the smaller chemical shift range of  $^2\text{H}$  nmr does not present a major problem. We believe that

(11) H. Saitô, H. H. Mantsch, and I. C. P. Smith, *Progr. Nucl. Magn. Resonance Spectrosc.*, in press.

with the increasing availability of pulsed multinuclear spectrometers chemists should turn their attention to high resolution  $^2\text{H}$  nmr for conformational and mechanistic problems. In studies of very complex biological systems such as cell membranes this technique provides a powerful and inexpensive alternative<sup>12</sup> to  $^{13}\text{C}$  enrichment.

(12) H. Saitô, S. Schreier-Muccillo, and I. C. P. Smith, *FEBS (Fed. Eur. Biochem. Soc.) Lett.*, **33**, 281 (1973).

(13) Visiting professor from the University of Cluj, str. Donath 65, Cluj, Romania.

(14) Visiting scientist from Basic Research Laboratories, Toray Industries, Inc., Kamakura, Japan 248.

(15) Issued as NRCC Publication No. 13667.

Henry H. Mantsch,<sup>13</sup> Hazime Saitô<sup>14</sup>  
L. C. Leitch, Ian C. P. Smith\*  
Division of Biological Sciences,  
National Research Council of Canada<sup>15</sup>  
Ottawa, Ontario, Canada K1A 0R6

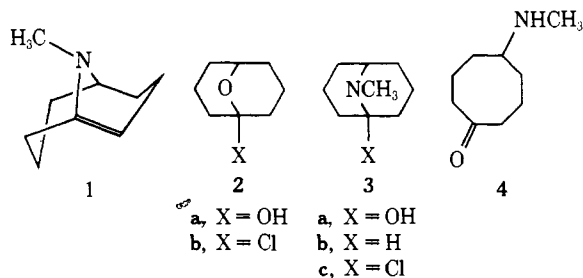
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### 9-Methyl-9-azabicyclo[3.3.1]non-1-ene<sup>1</sup>

Sir:

We have previously reported on the synthesis and chemistry of bridgehead alkenes of the bicyclo[3.3.1]nonyl system in which the 9 position is occupied by a heteroatom.<sup>2,3</sup> Such substrates are attractive for the investigation of inductive and resonance effects of heteroatoms on the properties of double bonds because the  $n-\pi, \pi^*$  resonance effects are severely inhibited by the geometry of the system.

In this report we describe the synthesis and interesting chemistry of 9-methyl-9-azabicyclo[3.3.1]non-1-ene (**1**).<sup>4-6</sup> Hemiketal **2a**<sup>2</sup> was converted in 97% yield to amino alcohol **3a** upon treatment with 20% aqueous methylamine containing some *p*-toluenesulfonic acid.<sup>7,8</sup> Amino alcohol **3a** totally predominates over the tauto-



(1) Bredt's Rule. IX. For previous paper see ref 3b.

(2) C. B. Quinn and J. R. Wiseman, *J. Amer. Chem. Soc.*, **95**, 1432 (1973).

(3) (a) C. B. Quinn and J. R. Wiseman, *J. Amer. Chem. Soc.*, **95**, 6120 (1973); (b) C. B. Quinn, J. R. Wiseman, and J. C. Calabrese, *ibid.*, **95**, 6121 (1973).

(4) For the synthesis of 11-azabicyclo[4.4.1]undec-1-ene see (a) A. C. Cope, R. J. Cotter, and G. C. Roller, *J. Amer. Chem. Soc.*, **77**, 3590 (1955); (b) K. Biemann, G. Büchi, and B. H. Walker, *ibid.*, **79**, 5558 (1957).

(5) For examples of isolable compounds containing bridgehead double bonds involving nitrogen see (a) for an imine, M. Toda, and Y. Hirata, *Chem. Commun.*, 1597 (1970); (b) for iminium salts and enamines, H. Newman and T. L. Fields, *Tetrahedron*, **28**, 4051 (1972); (c) for trans azo linkages in medium-sized rings, C. G. Overberger, M. S. Chi, D. G. Pucci, and J. A. Barry, *Tetrahedron Lett.*, 4564 (1972).

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(7) C. B. Quinn, Ph.D. Thesis, University of Michigan, 1973.

(8) Reported yields refer to isolated yields of pure materials.

meric amino ketone **4** since the infrared spectrum shows no carbonyl absorption.

A substrate suitable for elimination was prepared by converting amino alcohol **3a** into the bridgehead chloride **3c** (bp 59°, 0.45 Torr) in 62% yield using thionyl chloride. Bridgehead olefin **1** was produced in 90% yield (bp 48°, 0.9 Torr) by heating **3c** with sodium *tert*-amylate in benzene at reflux.

The spectral data for **1** are collected in Table I along

**Table I.** Spectral Data of Bridgehead Alkenes in the Bicyclo[3.3.1]nonyl System

Compound	$\nu_{\text{max}}$ (C=C), $\text{cm}^{-1}$	$\delta$ (vinyl H)	$J$	$\lambda_{\text{max}}$ ( $\epsilon$ ) <sup>d</sup>	Ref
<b>1</b>	1620 m <sup>a</sup>	5.86, t	(6 Hz) <sup>c</sup>	240 (1667) End absorption 184	
	1640 w <sup>b</sup>	5.74, t	(6 Hz) <sup>b</sup>	190 (6200)	2
	1600 w <sup>b</sup>	6.25, t	(7 Hz) <sup>b</sup>	196 (4560) 210 (1780)	3a
	1620 w <sup>a</sup>	5.62, t	(7 Hz) <sup>b</sup>	206 (7500)	e

<sup>a</sup> Neat. <sup>b</sup>  $\text{CCl}_4$  solution. <sup>c</sup>  $\text{CDCl}_3$  solution. <sup>d</sup> Pentane solution. <sup>e</sup> J. R. Wiseman, *J. Amer. Chem. Soc.*, **89**, 5966 (1967); J. R. Wiseman and W. A. Pletcher, *ibid.*, **92**, 956 (1970).

with the other known isolable heterobicyclic and carbocyclic bridgehead olefins of the [3.3.1] series. The infrared spectra of 1,2-dialkyl substituted enamines usually display a *strong* band between 1646 and 1652  $\text{cm}^{-1}$ .<sup>9,10</sup> Enamines in which the double bond is endocyclic in a six-membered ring normally show a chemical shift between  $\delta$  4.1 and 4.6 for the vinyl proton on the  $\beta$ -carbon atom.<sup>11</sup> Enamines wherein resonance interaction between the lone pair of electrons on nitrogen and the double bond is possible show absorption at  $230 \pm 10 \text{ nm}$  ( $\epsilon$  5000–9000).<sup>11</sup>

The ir and nmr spectra indicate a lack of interaction of the nitrogen lone pair with the bridgehead double bond in **1**. The interpretation of the uv spectrum is less certain since the absorption band at 240 nm could be taken as evidence for some residual conjugation. However, this band probably corresponds to the  $n \rightarrow \sigma^*$  band of amines, bathochromically shifted due to flattening of the bridging nitrogen atom.<sup>12,13</sup>

The chemistry of **1** also indicates a lack of conjugation. Thus treatment of **1** with methyl iodide in acetonitrile afforded quaternary ammonium bridgehead alkene **5a** in a quantitative yield while reaction of **1** with cyanogen bromide in dioxane gave cyanamide **6** along with some quaternary ammonium bromide **5b**.

(9) N. J. Leonard and V. W. Gash, *J. Amer. Chem. Soc.*, **76**, 2781 (1954).

(10) N. J. Leonard and F. P. Hauck, *J. Amer. Chem. Soc.*, **79**, 5279 (1957).

(11) (a) S. K. Malhotra in "Enamines: Synthesis, Structure, and Reactions," A. G. Cook, Ed., Marcel Dekker, New York, N. Y., 1969, Chapter 1; (b) K. Nagarajan and S. Rajappa, *Tetrahedron Lett.*, 2293 (1969).

(12) 9-Azabicyclo[3.3.3]undecane, with a flattened bridgehead nitrogen atom, shows  $\lambda_{\text{max}}$  240 nm,  $\epsilon$  2935; J. C. Coll, D. R. Crist, M. del C. G. Barrio, and N. J. Leonard, *J. Amer. Chem. Soc.*, **94**, 7092 (1972). *N*-Methylgranatinine (**3b**) shows  $\lambda_{\text{max}}$  208 nm ( $\epsilon$  1220) in pentane.

(13) For examples in which molecular geometry precludes mesomerism involving polarized and nonpolarized forms of enamines see O. Cervinka, ref 11a, p 269.