Carbon-13 Spin-Lattice Relaxation in Triethyl-*n*-hexylammonium Triethyl-*n*-hexylboride, a Viscous Liquid Salt[1a]

Warren T. Ford[1b]

Contribution from the Roger Adams Laboratory, Department of Chemistry, University of Illinois, Urbana, Illinois 61801.

Received August 19, 1975

Abstract: Carbon-13 spin-lattice relaxation times T_1 of almost all carbon atoms have been measured for the liquid salt triethyl-*n*-hexylammonium triethyl-*n*-hexylboride ($N_{2226}B_{2226}$) and an isoelectronic hydrocarbon analogue, 3,3-diethylnonane, over >100 °C temperature ranges, and for $N_{2226}B_{2226}$, triethyl-*n*-hexylphosphonium bromide ($P_{2226}Br$), $N_{2226}Br$, and LiB_{2226} in low-viscosity solutions. Successive increases in T_1 of each carbon atom proceeding away from the quaternary centers of each ion and molecule indicate that most of the T_1's are governed by internal rotation about carbon-carbon bonds. The slip model and microviscosity model modifications of the Stokes-Einstein equation for rotational diffusion provide reasonable estimates of the effective NMR correlation times τ_{eff} of the innermost carbon atoms of each ion and molecule in low viscosity media, but predict values of τ_{eff} much too high for the innermost carbons of the highly viscous $N_{2226}B_{2226}$ at ambient temperature. This descrepancy and the activation energies for $1/\tau_{\mathrm{eff}}$ in neat $N_{2226}B_{2226}$ indicate that at low viscosity the T_1's of these most hindered carbons are determined largely by overall tumbling, but at high viscosity internal rotation about the N-C and B-C bonds dominates their T_1's. The high viscosity of $N_{2226}B_{2226}$ not only slows overall reorientation of the ions but also raises the activation energies E_a of the internal rotations which effect relaxation in $N_{2226}B_{2226}$ compared to E_a's in 3,3-diethylnonane. Effective correlation times of benzene and toluene as 20% solutions in $N_{2226}B_{2226}$ provide approximate confirmation at high viscosity that τ_{eff}'s for reorientation about individual axes of small, rigid molecules are linearly related to shear viscosity.

Triethyl-*n*-hexylammonium triethyl-*n*-hexylboride ($N_{2226}B_{2226}$) is the least viscous of a series of tetraalkylammonium tetraalkylborides which are liquid at room temperature.[2] $N_{2226}B_{2226}$ resembles a charged alkane; each ion is isoelectronic with 3,3-diethylnonane, differing only at the quaternary center atom. Ironically it is miscible in all proportions with most organic solvents, but immiscible with hexane, which it resembles structurally, and immiscible with water, nature's ubiquitous solvent for ions. The charged centers of the N_{2226} and B_{2226} ions are shielded by alkyl groups, and they can interact with each other or with other components of a solution only by coulombic, ion-dipole, ion-induced-dipole, and London dispersion forces. The consequences of electrical charge in an alkane are dramatic: $N_{2226}B_{2226}$ is 8% more dense and >100 times more viscous than 3,3-diethylnonane at 25 °C, and it has essentially zero vapor pressure at 100 °C.

This paper reports a study of the rotational behavior of ions in liquid $N_{2226}B_{2226}$ by carbon-13 NMR spin-lattice relaxation. Comparisons of T_1's of neat $N_{2226}B_{2226}$ to those of less viscous solutions and those of structural analogues allow a qualitative analysis of how its structure affects both overall tumbling and internal rotations. Because of its highly temperature-dependent viscosity, liquid $N_{2226}B_{2226}$ is a convenient medium for study of the influence of viscosity on both kinds of motion. Viscosity effects on carbon-13 T_1's have been reported for alkylammonium trifluoroacetates in D_2O,[3] aromatic molecules in organic solvents,[4,5] dioxane in H_2O,[6] and synthetic polymers in organic solvents.[7] In most of these previous studies, viscosity effects were determined on T_1's of only one component of a solution rather than a neat liquid. Since shear viscosity is a macroscopic property, it does not necessarily provide a measure of the viscosity in the microscopic environment of a single solution component. In $N_{2226}B_{2226}$ viscosity effects have been determined on T_1 of almost every carbon atom.

Experimental Section

Lithium triethyl-*n*-hexylboride (LiB_{2226}) and triethyl-*n*-hexylammonium triethyl-*n*-hexylboride ($N_{2226}B_{2226}$) were prepared as described previously.[2] The batch of $N_{2226}B_{2226}$ used for ^{13}C NMR experiments was yellow due to slight autoxidation. Viscosities of $N_{2226}B_{2226}$ are reported elsewhere.[8]

Triethyl-*n*-hexylphosphonium Bromide ($P_{2226}Br$). A solution of 0.26 mol of redistilled 1-bromohexane and 0.21 mol of triethylphosphine (Aldrich) in 100 ml of dry acetonitrile was refluxed 12 h in a nitrogen atmosphere. The solvent was removed in vacuo, and the remaining solid was recrystallized twice from acetone to give 0.129 mol (62%) of $P_{2226}Br$, mp 110-111 °C (uncorrected). The solid was collected and transferred in a nitrogen atmosphere glove bag because it was hygroscopic. Anal. ($C_{12}H_{28}BrP$) C, H, Br. ^1H NMR and ir spectra were consistent with the assigned structure.

Triethyl-*n*-hexylphosphonium triethyl-*n*-hexylboride ($P_{2226}B_{2226}$) was prepared from LiB_{2226} and $P_{2226}Br$ by the method used for $N_{2226}B_{2226}$.[2] Anal. ($C_{24}H_{56}BP$) C, H.

3,3-Diethylnonane. A Grignard reagent was prepared by concurrent addition of 0.22 mol each of 3-chloro-3-ethylpentane[9] and 1,2-dichloroethane to excess Mg powder in dry, refluxing tetrahydrofuran and filtered through a fine glass frit. To the colorless filtrate was added with stirring 0.036 mol of 1-bromohexane and then 1.0 mmol of Li_2CuCl_4 solution in THF. In contrast to previous reports of Li_2CuCl_4-catalyzed coupling of Grignard reagents to primary alkyl bromides,[10] this reaction was slow, and a sizable amount of the alkyl halide dimer, *n*-dodecane, was formed. Progress was monitored by GLC, and after 30 h at room temperature much 1-bromohexane remained. The mixture was refluxed 56 h, during which another 0.112 mol of 1-bromohexane was added in three portions. When consumption of the 1-bromohexane stopped, the mixture was hydrolyzed with saturated aqueous NH_4Cl, dried over $MgSO_4$, and distilled. Fractions with bp's 165-220 °C were collected and analyzed by GLC to contain an 18% yield (based on 1-bromohexane) of 3,3-diethylnonane and 10% yield of *n*-dodecane. Purification of the distillate by preparative GLC on a 10 ft × 0.375 in. column of 20% Apiezon L on 60-80 Chromosorb W at 245 °C gave the 2-ml sample used for ^{13}C NMR spectra, which verified the expected structure. Its viscosity is estimated to be 1.4 cP at 30 °C by comparison to viscosities of other C_{13} alkanes.[11]

Carbon-13 NMR spectra were obtained at 25.16 MHz on a Varian XL-100-15 instrument equipped with Digilab FTS-NMR-3 Fourier transform accessory and at 15.00 MHz on a JEOL FX-60 instrument. All spectra were proton noise decoupled. Spin-lattice relaxation times were measured by the inversion-recovery method. In the pulse sequence $(180°-\tau-90°-t)_n$ seven or eight values of τ were selected to give four to six useful data points for each carbon atom, t was ≥ 5 times the longest T_1 of any proton-bearing carbon atom, and n = 100-500. At 25 MHz 16K data points and at 15

Table I. Carbon-13 Chemical Shifts and $^{13}C-^{31}P$ Coupling Constants

	δ, ppm from TMS ($J_{^{13}C-^{31}P}$, Hz)								
Compd	$(CH_3$—	—$CH_2)_3$—	—X—	—CH_2—	—CH_2—	—CH_2—	—CH_2—	—CH_2—	—CH_3
$P_{2226}Br$[a]	6.2 (5.0)	12.6 (48.8)	P	18.5 (46.7)	21.8 (4.3)	30.5 (15.1)	31.1	22.4	13.9
$P_{2226}B_{2226}$[b]	7.1 (5.5)	13.6 (48.5)	P	19.4 (~51)	23.0 (3.4)	31.9 (~16)	32.3	23.9	15.4
	13.2	20.2	B	29.2	29.8	37.7	34.5	24.7	15.9
3,3-Diethylnonane[c]	8.5	28.8	C, 38.2	36.4	24.2	31.8	33.4	24.1	15.1

[a] 0.375 *m* in $CDCl_3$, 30 °C, internal TMS. [b] Neat liquid, 34 °C, external TMS in acetone-d_6. [c] Neat liquid, 28 °C, external TMS in acetone-d_6.

Table II. Carbon-13 Spin-Lattice Relaxation Times (T_1, s) of $N_{2226}B_{2226}$ and Its Analogues

Expt	Compd	Solution	ν_0, MHz	T, °C	$(CH_3$—	—$CH_2)_3$—	—X—	—CH_2—	—CH_2—	—CH_2—	—CH_2—	—CH_2—	—CH_3
1	$N_{2226}B_{2226}$	Neat	25.2	11	0.33	0.04	N	0.03	0.05	0.08	0.14	0.24	0.84
2				28	0.40	0.09	N	0.06	0.06	0.15	0.23	0.38	1.33
3				28	0.41	0.06	N	0.05	0.07	0.10	0.20	0.33	1.03
4			15.0	32	0.36	0.05	N	0.05	0.09	0.10	0.18	0.26	1.07
5			25.2	46	0.67	0.11	N	0.12	0.14	0.23	0.37	0.62	1.87
6				70	1.03	0.19	N	0.23	0.26	0.35	0.61	1.2	3.0
7				94	1.70	0.35	N	0.39	0.43	0.68	1.19	1.93	4.4
8				120	3.2	0.71	N	0.98	1.09	1.55	2.5	4.0	8.7
9		2.7 *m* C_6H_6	25.2	28	0.56	0.11	N	0.10	0.19	0.23	0.38	0.64	1.64
10			15.0	32	0.51	0.11	N	0.08	0.13	0.18	0.32	0.48	1.90
11		2.4 *m* $C_6H_5CH_3$	25.2	28	0.45	0.11	N	0.10	0.10	0.17	0.24	0.46	1.53
12		0.44 *m* in $CDCl_3$		30	1.59	0.44	N	0.39	0.81	0.86	1.40	2.2	3.9
13	$N_{2226}Br$	0.40 *m* in $CDCl_3$		30	1.40	0.47	N	0.52	0.66	0.95	1.52	2.1	3.0
14	$P_{2226}Br$	0.5 *m* in $CDCl_3$	15.0	32	2.7	0.81	P	0.54	0.80	0.88	1.5[a]	2.0	2.3[a]
15	$P_{2226}B_{2226}$	Neat		34	1.20	0.25	P	0.09	0.14	0.19	0.25	0.38	1.32
1	$N_{2226}B_{2226}$	Neat	25.2	11	0.44	0.04	B	*b*	0.07	0.12	0.17	0.30	0.92
2				28	0.79	0.12	B	*b*	0.17	0.14	0.28	0.43	1.52
3				28	0.75	0.11	B	*b*	0.10	0.13	0.28	0.40	1.23
4			15.0	32	0.73	0.13	B	*b*	0.10	0.13	0.22	0.31	1.14
5			25.2	46	1.25	0.28	B	*b*	0.20	0.26	0.46	0.71	2.1
6				70	2.1	0.48	B	0.28	0.34	0.38	0.81	1.2	3.6
7				94	3.0	0.49	B	0.66	0.55	0.86	1.42	2.2	4.9
8				120	5.7	1.64	B	1.43	1.41	1.9	2.7	4.6	8.5
9		2.7 *m* C_6H_6	25.2	28	1.00	0.27	B	0.25	0.21	0.26	0.42	0.66	1.75
10			15.0	32	1.03	0.20	B	*b*	0.22	0.20	0.41	0.61	1.70
11		2.4 *m* $C_6H_5CH_3$	25.2	28	1.01	0.20	B	0.13	0.16	0.20	0.43	0.57	1.70
12		0.44 *m* in $CDCl_3$		30	2.2	0.75	B	0.54	0.71	0.90	1.61	2.1	5.1
15	$P_{2226}B_{2226}$	Neat	15.0	34	0.76	0.13	B	*b*	0.10	0.14	0.27	0.39	1.43
16	LiB_{2226}	1 *m* in D_2O		32	2.2	0.59	B	0.51	0.52	0.65	0.96	1.6	4.2
17	Hydrocarbon[c]	Neat	25.2	−35	0.51	0.15	C	0.17	0.20	0.21	0.27	0.37	0.55
18				−18	0.68	0.18	C	0.22	0.27	0.33	0.44	0.57	1.03
19				10	2.0	0.69	C	1.0	1.0[a]	1.06	1.33	1.6[a]	2.6
20				30	2.7	1.12	C	1.3	1.49	1.60	2.1	2.6	3.8
21				51	3.9	1.7	C	2.3	2.4	2.9	3.7	4.7	5.7
22				71	5.3	2.6	C	3.0	3.2	3.7	5.1	*b*	*b*
23				71	6.1	2.9	C	3.9	3.7	3.9	6.0	7.0	9.9

[a] These values are less reliable because of overlapping resonances. [b] Could not be determined from spectra available. [c] 3,3-Diethylnonane.

MHz 8K data points were used. Pulse widths were checked periodically and were generally 30 μs on the XL-100-15 and 24 μs on the FX-60 for a 90° pulse. Sample temperature was determined and maintained to ±2 °C. Scatter in the ln $(A_\infty - A_\tau)$ vs. τ plots suggested that temperatures probably fluctuated within that range during the course of a run. T_1's are considered reliable to ±10% or ±0.03 s, whichever is greater.

All samples were prepared in a nitrogen atmosphere. Coaxial cells which contained acetone-d_6-TMS, DMSO-d_6-TMS, or D_2O-dioxane in the central 5-mm tube and the sample in the annular region of the 10-mm or 12-mm tube were used for liquid salts. The 3,3-diethylnonane was degassed and sealed in a 10-mm Pyrex tube, which in turn was placed in a 12-mm nmr tube with acetone-d_6-TMS in the annular region.

Results

Carbon-13 chemical shifts of triethyl-*n*-hexylphosphonium salts and 3,3-diethylnonane are in Table I. The assignments are based on chemical shift correlations of branched aliphatic hydrocarbons[12,13] and analogy to $^{13}C-^{31}P$ coupling constants reported previously for phosphonium salts.[14] Chemical shifts of $N_{2226}B_{2226}$ appear in an earlier paper.[13]

Carbon-13 spin-lattice relaxation times of $N_{2226}B_{2226}$ and its analogues LiB_{2226}, $N_{2226}Br$, $P_{2226}Br$, $P_{2226}B_{2226}$, and 3,3-diethylnonane appear in Table II. Several qualitative features of the data are noteworthy. (1) Relaxation

Table III. ^{13}C NMR Correlation Times, τ_{eff}, in ps

Expt[a]	$(\mathrm{CH_3}$—	$\mathrm{CH_2})_3$—	X—	$\mathrm{CH_2}$—	$\mathrm{CH_2}$—	$\mathrm{CH_2}$—	$\mathrm{CH_2}$—	$\mathrm{CH_2}$—	$\mathrm{CH_3}$
3	38	390	N	470	330	230	117	71	15.1
7	9.1	67	N	60	54	34	19.6	12.1	3.6
9	28	210	N	230	123	101	61	36	9.5
12	9.8	53	N	60	29	27	16.6	10.6	4.0
15	12.9	93	P	270	170	120	93	61	11.8
3	21	210	B	*b*	230	180	83	58	12.6
7	5.1	48	B	35	42	27	16.4	10.5	3.2
9	15.5	86	B	93	111	90	55	35	8.9
12	6.9	31	B	43	33	26	14.5	11.1	3.0
15	20.4	180	B	*b*	230	170	86	60	10.9
20	5.8	21	C	18	15.6	14.6	11.1	9.0	4.1

[a] For conditions see Table II. [b] Could not be determined from spectra available.

times T_1 are always shortest at the innermost carbon atoms and progress to higher values at each successive carbon away from the center. (2) At all carbon atoms in $\mathrm{N_{2226}B_{2226}}$ and in 3,3-diethylnonane T_1 increases as the temperature increases. (3) At ambient temperature T_1 at every carbon atom is shorter in the highly viscous neat molten salt than in less viscous mixtures with benzene, toluene, or $\mathrm{CDCl_3}$. (4) At ambient temperature in media of equal viscosity (experiments 12 and 20) T_1's of the inner carbons of 3,3-diethylnonane are longer than T_1's of the corresponding carbon atoms of $\mathrm{N_{2226}B_{2226}}$. (5) In every experiment the T_1's of all carbon atoms in the $\mathrm{B_{2226}}$ anion are longer than those of corresponding carbon atoms in the $\mathrm{N_{2226}}$ cation. This difference is most pronounced at the inner carbon atoms, but it persists even at the terminal $\mathrm{CH_3}$ groups of the *n*-hexyl chains. Although the T_1 values of many pairs of corresponding carbon atoms in $\mathrm{N_{2226}}$ and $\mathrm{B_{2226}}$ are the same within experimental error, the fact that in 84 out of 90 such comparisons T_1 is greater in the anion than in the cation is convincing statistically. In contrast, the T_1's of the three pairs of corresponding carbon atoms farthest from the charged centers in $\mathrm{P_{2226}B_{2226}}$ are identical within experimental error (experiment 15). (6) The T_1's of carbons in the ethyl groups of phosphonium ion $\mathrm{P_{2226}}$ are longer than those of ammonium ion $\mathrm{N_{2226}}$, but the carbons in their hexyl groups have more nearly equal T_1's. (Compare experiments 13 and 14, and 4 and 15.)

Effective NMR correlation times τ_{eff} in representative experiments appear in Table III. The τ_{eff} values were calculated with eq 1 and 2 for relaxation effected only by dipolar interaction with the protons directly bound to each carbon atom.[15] In eq 1 and 2, N is the number of directly bound carbon atoms, γ_{H} and γ_{C} are the magnetogyric ratios, ω_{H} and ω_{C} are the Larmor frequencies in rad/s of ^{1}H and ^{13}C, and r is the C-H distance taken as 1.09 Å. Other mechanisms for spin-lattice relaxation[16] can be ruled out as follows. (1) Interaction with paramagnetic oxygen seldom is important for T_1 values of <10 s, and the samples were prepared under nitrogen. (2) The spin-rotation mechanism is most effective for very small, spherical molecules which can rotate rapidly in a liquid. Moreover, spin-rotation relaxation leads to a decrease in T_1 with increasing temperature, opposite to what was observed. (3) Scalar coupling of ^{13}C to quadrupolar ^{11}B or ^{14}N would give a contribution to relaxation governed by eq 3, in which I is ^{11}B or ^{14}N, A is the C-I coupling constant in rad/s, S is the spin number of I, τ_{I} is the relaxation time of I, and ω_{C} and ω_{I} are the Larmor frequencies. The frequency differences between ^{13}C and ^{11}B or ^{14}N are too large and the likely quadrupolar relaxation times for almost symmetrically substituted ^{11}B and ^{14}N nuclei are too long for scalar relaxation to contribute to the observed T_1 values of even the carbons bound directly to boron and nitrogen.

Table IV. T_1's of Aromatic Carbon Atoms of Benzene and Toluene in $\mathrm{N_{2226}B_{2226}}$

Expt[a]	T_1, s
9	Benzene: 1.35
10	Benzene: 1.40
11	Toluene: ortho 1.00, meta 0.95, para 0.91

[a] For conditions see Table II.

$$1/T_1 = N\hbar^2\gamma_{\mathrm{H}}^2\gamma_{\mathrm{C}}^2 r^{-6}\tau_{\mathrm{eff}} \tag{1}$$

$$\frac{1}{T_1} = \frac{N\hbar^2\gamma_{\mathrm{H}}^2\gamma_{\mathrm{C}}^2 r^{-6}}{10}\left[\frac{\tau_{\mathrm{eff}}}{1+(\omega_{\mathrm{H}}-\omega_{\mathrm{C}})^2\tau_{\mathrm{eff}}^2} + \frac{3\tau_{\mathrm{eff}}}{1+\omega_{\mathrm{C}}^2\tau_{\mathrm{eff}}^2} + \frac{6\tau_{\mathrm{eff}}}{1+(\omega_{\mathrm{H}}+\omega_{\mathrm{C}})^2\tau_{\mathrm{eff}}^2}\right] \tag{2}$$

$$\frac{1}{T_1} = \frac{2A^2}{3}S(S+1)\frac{\tau_{\mathrm{I}}}{1+(\omega_{\mathrm{C}}-\omega_{\mathrm{I}})^2\tau_{\mathrm{I}}^2} \tag{3}$$

τ_{eff} was calculated from eq 2 when $T_1 \leq 0.17$ s in 25-MHz experiments and from eq 1 when $T_1 > 0.17$ s, the motional narrowing region in which $(\omega_{\mathrm{C}}+\omega_{\mathrm{H}})^2\tau_{\mathrm{eff}}^2 \ll 1$ and eq 2 reduces to eq 1. At 25 MHz T_1 reaches a minimum of 0.020 s when $\tau_{\mathrm{eff}} \approx 5 \times 10^{-9}$ s and increases once more as τ_{eff} becomes still longer.[15] All of the τ_{eff} values in Table III were taken from the fast rotation side of the T_1 minimum in eq 2 because an increase in temperature from 10 to 28 °C for $\mathrm{N_{2226}B_{2226}}$ caused increases in T_1 for even the innermost carbons in the $\mathrm{N_{2226}}$ ion. If τ_{eff}'s were on the slow rotation side of the T_1 minimum, increased temperature would lead to smaller T_1's.

In experiments 9-11, the T_1's of the aromatic carbon atoms in solutions of about 20% benzene or toluene by weight in $\mathrm{N_{2226}B_{2226}}$ were determined also, as shown in Table IV.

Arrhenius activation energies E_{a} for the effective correlation times in $\mathrm{N_{2226}B_{2226}}$ and 3,3-diethylnonane are in Table V. Experimental errors in T_1's of a few of the inner carbons of $\mathrm{N_{2226}B_{2226}}$ lead to considerable uncertainty in their E_{a} values (shown in footnotes of Table V), but most of the E_{a} values may be considered reliable to ±0.3 kcal/mol for $\mathrm{N_{2226}B_{2226}}$ and to ±0.2 for 3,3-diethylnonane.

Discussion

Segmental Motion. Two kinds of molecular motion can effect spin-lattice relaxation of carbon atoms having directly bound protons by the dipolar mechanism. (1) Overall tumbling by the small step diffusion model contributes equally to $1/NT_1$ at every carbon atom of a spherical mole-

Table V. Arrhenius Activation Energies (kcal/mol) for ^{13}C NMR Effective Correlation Times

Compd[a]	(CH$_3$—	—CH$_2$)$_3$—	X	CH$_2$	CH$_2$	CH$_2$	CH$_2$	CH$_2$	CH$_3$
$N_{2226}B_{2226}$	4.7	6.4	N	6.5[b]	6.2[c]	5.9[c]	5.4	5.6	4.7
$N_{2226}B_{2226}$	5.0	7.0[e]	B	[d]	6.0[c]	5.9[f]	5.6	5.6	4.7
3,3-Diethylnonane	3.8	4.7	C	4.8	4.6	4.6	4.7	4.6	4.3

[a] ±0.3 for $N_{2226}B_{2226}$ and ±0.2 for 3,3-diethylnonane unless otherwise noted. [b] ±0.8. [c] ±0.4. [d] Could not be determined from spectra available. [e] ±1.0. [f] ±0.6.

cule or ion. (2) The contribution to relaxation from internal rotation about single bonds in principle is different at every carbon atom. Consequently in large molecules all carbon atoms which cannot undergo internal rotation and have directly bound protons usually have the same effective correlation times, while values of T_1 increase (and values of τ_{eff} decrease) progressively along an alkyl chain of a large molecule from short T_1 nearest the rigid part of the molecule to long T_1 at the terminal methyl group. This general behavior[16] has been observed previously in 1-decanol,[17] proteins,[18] phospholipids,[19] synthetic polymers,[7,20] liquid crystals,[21] micelles,[3,22,23] and C_{10}–C_{20} alkanes.[24,25]

The data in Table II for salts in CDCl$_3$ solution resemble those of previous reports of T_1's for alkylammonium salts aggregated as micelles[3,22] in which the innermost carbon atoms have $T_1 \approx 0.5$ s and terminal methyl carbon atoms have $T_1 \approx 3$ s. The data for neat $N_{2226}B_{2226}$ at ambient temperature, however, resemble T_1's for alkyl chains bound to high polymers[20] in which no overall tumbling but only segmental motion contributes to T_1.

Several attempts have been made to describe the effects of internal motion on nuclear magnetic relaxation.[15,26] Levine and co-workers[24,27] have considered alkyl chains both attached to a spherical macromolecule which undergoes isotropic reorientation and as part of a molecule with prolate ellipsoid shape which reorients anisotropically. They conclude that overall tumbling in either case affects the rotational diffusion constants of atoms up to five carbon–carbon bonds removed from the center of mass. For more distant atoms "the autocorrelation function is a single exponential and the relaxation times are independent of the motion of the molecule, provided that $D_i > D_0$ (where D_i is the diffusion coefficient for rotation about the ith carbon–carbon bond)".[27] When the alkyl chain is bound to a large body undergoing slow isotropic reorientation, the diffusion coefficients increase successively for the first few bonds away from the large body. When the alkyl chain is part of an anisotropically reorienting prolate ellipsoid, the diffusion coefficients for internal rotation at all but the terminal carbon atoms are about the same (for example in *n*-alkanes and *n*-alkyl bromides).[24] In both isotropic and anisotropic systems, rotational diffusion about the terminal carbon–carbon bond is substantially faster than about the internal bonds.

Although $N_{2226}B_{2226}$ and 3,3-diethylnonane might be crudely approximated as overall anisotropic prolate ellipsoid rotors, their shape does not resemble *n*-alkanes. Instead of the roughly equal diffusion coefficients about all internal carbon–carbon bonds, molecular models suggest that rotations about at least the first two bonds away from the quaternary centers of N_{2226} are sterically hindered. As a result, the rotational diffusion coefficients are expected to increase successively along the bonds away from the center of mass, making their overall and internal rotational behavior a complex hybrid of the two systems treated by Levine. This trend of decreased steric hindrance to internal rotation is supported experimentally by the small decreases in Arrhenius E_a's for effective correlation times of carbon atoms proceeding away from the charged centers of $N_{2226}B_{2226}$ (Table V).

Table VI. Comparison of $\tau(i,i-1)$ for *n*-Hexyl Groups to Solution Viscosity

Expt[a]	Central Atom	$\tau(i,i-1)$, ps	η, cP
3	N	19.1	209
	B	16.1	
9	N	12.9	35
	B	11.9	
12	N	6.4	1.35
	B	4.1	
20	C	7.5	1.4

[a] See Table II for conditions.

The single exponential autocorrelation function for rotation about a bond more than five bonds removed from the center of mass corresponds to a correlation time which may be approximated from the effective correlation times obtained from the T_1 values of the ith and $(i-1)$th carbons (eq 4).[24,25] When i is the terminal CH$_3$ group, application of eq 4 to T_1 data for *n*-alkanes,[24,25] alkyl bromides,[24] alkyl amines,[3] and alkylammonium salts[3] has led to $\tau(i,i-1)$ values in the 4–8 ps range (with a few anomalous exceptions) in solutions of low to moderate viscosity. However, the data in Table VI for $N_{2226}B_{2226}$, neat and diluted with benzene, indicate that diffusion about the terminal carbon–carbon bond of each C$_6$ chain slows as the viscosity increases. That increased viscosity slows internal rotation about the terminal bonds is also suggested by the higher Arrhenius E_a for the terminal CH$_3$ correlation times in neat $N_{2226}B_{2226}$ than in 3,3-diethylnonane. No theory is available at this time for viscosity effects on internal rotation.

$$[\tau(i,i-1)]^{-1} = [\tau_{\text{eff}}(i)]^{-1} - [\tau_{\text{eff}}(i-1)]^{-1} \qquad (4)$$

Overall Reorientation. Though the terminal methyl groups of the C$_6$ chains of $N_{2226}B_{2226}$ clearly have T_1's governed by internal rotation, overall tumbling may also affect carbon T_1's nearer the centers, particularly at the innermost methylene groups bound directly to the quaternary atoms. If only overall tumbling affects the T_1's of the innermost carbons of $N_{2226}B_{2226}$, it should be possible to calculate their correlation times from an appropriately modified Stokes-Einstein equation for rotational diffusion. The unmodified eq 5, in which a is the radius of a spherical molecule and η is the coefficient of shear viscosity, works well for large molecules in small molecule solvents but not for small molecules. For nonspherical molecules $4\pi a^3/3$ is replaced by molecular volume.

$$\tau = 4\pi a^3 \eta / 3kT \qquad (5)$$

In a recent modification, the slip model, Hu and Zwanzig[28] assume that nonspherical molecules can be approximated as prolate or oblate ellipsoids which have zero frictional coefficients for rotation about the unique axis. The frictional coefficients for rotation about the axes of a prolate ellipsoid perpendicular to the unique axis have frictional coefficients ranging from zero, in the limit of a spherical

Table VII. Comparison of Experimental Correlation Times (τ_{eff}, ps) for Inner Carbon Atoms to Those Calculated by Modified Stokes-Einstein Equations

Conditions[a]	η, cP	$\tau_\perp \gg \tau_\parallel$	$\tau_\perp = \tau_\parallel$	Microviscosity model	Exptl
$N_{2226}B_{2226}$, neat, 28 °C	209	1400	5600	8000	470 (N_{2226}) 230 (B_{2226})
$N_{2226}B_{2226}$, benzene, 28 °C	35	230	930	*b*	230 (N_{2226}) 110 (B_{2226})
$N_{2226}B_{2226}$, $CDCl_3$, 30 °C	1.35	9	36	74	60 (N_{2226}) 43 (B_{2226})
3,3-Diethylnonane, 30 °C	1.4	9	37	53	21

[a] These are experiments 3, 9, 12, and 20 of Table II. [b] Not calculated because of ambiguity as to whether benzene or $N_{2226}B_{2226}$ is the solvent.

molecule, to η/kT. in the limit of a needle-shaped molecule, and depend only on the ratio of the lengths of the axes.

Application of the slip model to $N_{2226}B_{2226}$ and 3,3-diethylnonane requires several approximations. (1) The isoelectronic species have a volume of 232 Å^3, determined by summation of atomic contributions to van der Waal's volumes.[29] (2) Each species is an ellipsoid with the ratio of short axis to long axis of 0.64, determined from a model based on standard bond lengths, 109.5° bond angles, a van der Waal's radius of 1.2 Å for each methyl hydrogen atom, and fully extended conformations of the C_9 and C_5 chains of 3,3-diethylnonane. (3) Each ion in the liquid undergoes rotational diffusion independently rather than as an aggregate. With experimentally determined viscosities eq 5 divided by the correction factor[28] of 0.114 for a prolate ellipsoid with axial ratio 0.64 leads to calculated values of $\tau_\perp$, the rotational correlation time about the short axis.

The NMR correlation time for dipolar relaxation of an ellipsoid rotor in which the C-H bonds are perpendicular to the unique axis is given by eq 6[30] in which $D_\parallel$ and $D_\perp$ are the diffusion coefficients for rotation about the unique axis and the axes perpendicular to the unique axis, respectively. The relations $\tau_\perp = 1/6D_\perp$ and $\tau_\parallel = 1/6D_\parallel$ lead to eq 7. In the slip model the frictional coefficient for rotation about the long axis of a prolate ellipsoid is zero, which means that $\tau_\perp \gg \tau_\parallel$ at moderate to high viscosity. However, molecular models indicate that the shape of N_{2226} and analogues is not a smooth ellipsoid, and there should be frictional resistance to rotation about the long axis. In the extreme, this friction might make $\tau_\parallel = \tau_\perp$. The consequences of application of these two assumptions about the relative values of $\tau_\parallel$ and $\tau_\perp$ to calculated values of τ_{eff} are shown in Table VII.

$$\tau_{\mathrm{eff}} = 1/24D_\perp + 3/4(2D_\perp + 4D_\parallel) \tag{6}$$

$$\tau_{\mathrm{eff}} = \tau_\perp/4 + 9\tau_\perp\tau_\parallel/(8\tau_\perp + 4\tau_\parallel) \tag{7}$$

A simpler, common modification of the Stokes-Einstein equation for calculation of rotational correlation times is multiplication of eq 5 by the microviscosity factor f_{R}, defined by eq 8 in which r and r_{s} are the effective radii of the solute and solvent, respectively.[31] The effective radii are usually taken as radii of spheres having the same molecular volumes as the solute and solvent. Results of application of the microviscosity factor to calculated correlation times of $N_{2226}B_{2226}$ and 3,3-diethylnonane are also in Table VII.

$$f_{\mathrm{R}} = \left[6\frac{r_{\mathrm{s}}}{r} + \frac{1}{(1 + r_{\mathrm{s}}/r)^3}\right]^{-1} \tag{8}$$

Comparisons in Table VII of the calculated correlation times to experimental τ_{eff} values for the innermost carbon atoms of $N_{2226}B_{2226}$ and 3,3-diethylnonane with the shortest relaxation times show that the crude theory and approximations agree roughly with experiment for solutions of low viscosity. This indicates that the model assumed for the size and shape of N_{2226} and its analogues is reasonable, and that overall tumbling is primarily responsible for spin-lattice relaxation of their inner carbon atoms at low viscosity. On the other hand, agreement between theory and experiment is poor for the highly viscous neat $N_{2226}B_{2226}$. Two possible reasons for this discrepancy are: (1) the original assumption that τ_{eff} is governed only by overall tumbling and not by internal rotation may be wrong; (2) the sizes and shapes of the ions may differ in the neat liquid salt and in solution due to either ionic aggregation or conformational changes. Although there is no good way to test the latter possibility, additional experimental evidence is consistent with the former.

If the calculated τ_{eff} values for neat $N_{2226}B_{2226}$ are reasonable, internal rotation about the N-C and B-C bonds must be the principal motion affecting T_1's of the innermost carbon atoms at ambient temperature. The Arrhenius E_{a}'s for $1/\tau_{\mathrm{eff}}$ of the innermost carbons support this possibility because they are substantially smaller (6.4-7.0 kcal/mol) than the corresponding E_{a} values obtained from a plot of ln (η/T) vs. $1/T$ (9.0-12.7 kcal/mol). The assumption that overall tumbling controls τ_{eff} predicts that $1/\tau_{\mathrm{eff}}$ and η/T should have the same temperature dependence, as they do to within 0.1 kcal/mol for liquid benzene[32] and within 1.0 kcal/mol for 3,3-diethylnonane. (E_{a} for η/T of several C_{13} alkanes averages 3.8 kcal/mol[11] compared to E_{a} = 4.7-4.8 kcal/mol for τ_{eff} of the innermost carbons of 3,3-diethylnonane).

Another observation that supports contribution of internal rotation to relaxation of the inner carbons of $N_{2226}B_{2226}$ is that T_1's of the anion are consistently longer than those of the cation. The greater length of the B-C bond (about 1.65 Å)[33] than of the N-C bond (about 1.52 Å)[34] should provide more rotational freedom in the anion. The T_1's of the inner carbons of the P_{2226} cation (see Table II) are longer than those of B_{2226}, presumably because of the still greater P-C bond length (about 1.80 Å).[35] The differences in T_1's of corresponding carbons of N_{2226}, B_{2226}, and P_{2226} persist even in low viscosity $CDCl_3$ solutions. This suggests that even though τ_{eff} values calculated for inner carbons at low viscosity agree decently with experimental values, there are significant internal as well as overall rotation contributions to their relaxation. Persistence of longer T_1 in B_{2226} than in N_{2226} all the way out to the terminal carbon of the C_6 chain indicates that even motion of the methyl group is slightly coupled to the motion of inner carbons, and that coupled motion extends over more than the four or five bonds previously implicated by Levine et al.[24,27]

Relaxation of the inner carbons of 3,3-diethylnonane must differ substantially from that of the N_{2226} and B_{2226} ions. At the same macroscopic viscosity and temperature (experiments 12 and 20) T_1's of the carbons of N_{2226}, B_{2226}, and 3,3-diethylnonane four to six bonds removed from the quaternary center atoms are roughly the same, but the T_1's of carbons one to three bonds removed from the center are much longer in the hydrocarbon than in either ion. This difference at the inner carbons must be due to the charge of the ions and can be explained by a greater microviscosity near the centers of the ions than near the center of the isoelectronic neutral hydrocarbon. It cannot be explained by bond length effects on rotational freedom because the C-C bond is only slightly longer than the N-C bond.

The nature of the motions responsible for spin-lattice relaxation in neat $N_{2226}B_{2226}$ may be summarized as follows. At ambient temperature even the innermost carbon T_1's appear to depend on internal rotation. As the viscosity of the medium is decreased, either by raising the temperature or by dilution with solvent, overall tumbling becomes an increasingly important contributor. Segmental motion dominates relaxation of the carbon atoms more than one bond removed from the quaternary center.

The Arrhenius activation energies for $1/\tau_{\text{eff}}$ of $N_{2226}B_{2226}$ and 3,3-diethylnonane in Table V are compatible with these conclusions. E_a for each carbon of 3,3-diethylnonane is (a) smaller than for the corresponding carbons in the isoelectronic N_{2226} and B_{2226} ions and (b) in the range previously found for barriers to rotation about alkane carbon-carbon bonds in liquids and gases.[36] The higher values of E_a in $N_{2226}B_{2226}$ indicate that barriers to bond rotation depend on the viscosity of the surrounding medium. However, bond rotation is not as sensitive to the medium as the translational motion measured by shear viscosity. (E_a for ln η vs. $1/T$ of $N_{2226}B_{2226}$ is 8.4-12.0 kcal/mol at 0-80 °C.)[8] The larger differences between E_a values of the inner carbons and the methyl carbons in $N_{2226}B_{2226}$ than in 3,3-diethylnonane also suggest that bond rotation is more hindered at the centers of the ions than at the center of the hydrocarbon. This hindrance must be due to the same ionic forces which make $N_{2226}B_{2226}$ 8% denser and >100 times more viscous than 3,3-diethylnonane.

Reorientation of Benzene and Toluene in $N_{2226}B_{2226}$. Anisotropic reorientation of molecules in liquids has been studied extensively by NMR relaxation methods.[26,37] Recently Bauer, Alms, Brauman, and Pecora (BABP)[5] found by a combination of light scattering and ^{13}C NMR spin-lattice relaxation methods that rotational correlation times of small rigid molecules about each axis were linearly related to the viscosity of the medium by eq 9 in which C is a constant in ps cP^{-1}. For benzene in solutions where $\eta < 3$ cP, $C = 0.0$ for $\tau_{\parallel}$ and $C = 3.5$ for $\tau_{\perp}$.[5] Similarly for toluene $C = 3.2$ for τ_x, the reorientation time about the axis in the plane of the ring passing through the methyl group, $C = 12.5$ for τ_y, the axis in the plane of the ring orthogonal to x, and $C = 0.0$ for τ_z, the axis orthogonal to the plane of the ring.

$$\tau = C\eta + \tau_0 \qquad (9)$$

The data in Table IV provide a test of the BABP correlations for benzene and toluene at much higher viscosity. For benzene at 35 cP $\tau_{\perp} \gg \tau_{\parallel}$, and eq 7 can be approximated by $\tau_{\text{eff}} = \tau_{\perp}/4$. For toluene at high viscosity $\tau_y > \tau_x \gg \tau_z$ and eq 8 of BABP can be approximated by eq 10, where τ_o, τ_m, and τ_p are the effective correlation times for the ortho, meta, and para carbon atoms. Figure 1 incorporates ^{13}C NMR T_1 data of benzene and toluene obtained in $N_{2226}B_{2226}$ into the BABP plots of τ as a function of η. The fit of the high-viscosity points is respectable. Also, the approximation of eq 10, that all ring carbon atoms of toluene should have the same T_1, is borne out by experiment.

$$\tau_o \approx \tau_m \approx \tau_p \approx \tau_x\tau_y/2(\tau_x + \tau_y) \qquad (10)$$

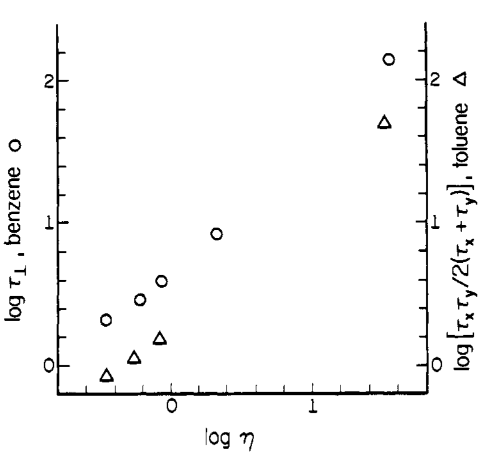

Figure 1. Reorientation times of benzene and toluene as a function of solution viscosity. Low-viscosity points are from ref 5. High-viscosity points are in $N_{2226}B_{2226}$.

Bauer, Brauman, and Pecora[38] have compared experimental viscosity dependences for rotational reorientation times of benzene and toluene with those calculated by the slip model modification of the Stokes-Einstein equation. With appropriate approximations of the molecular geometries, the model led to calculated coefficients C in eq 9 which agreed with experiment to within a factor of 1.5. The ability of the slip model to provide good estimates of the correlation times of benzene and toluene in $N_{2226}B_{2226}$ at high viscosity but not of the correlation times of the innermost carbon atoms of $N_{2226}B_{2226}$ itself also supports the conclusion that there is a sizable internal motion contribution to T_1's of all carbon atoms in neat $N_{2226}B_{2226}$.

Acknowledgment. I thank P. G. Schmidt, G. Alms, and J. Jonas for helpful discussions and S. Ulrich, S. Silber, and M. Miller for obtaining the ^{13}C NMR spectra.

References and Notes

(1) (a) This research was supported by National Science Foundation Grant GP 38493. The Varian XL-100-15 and JEOL FX-60 ^{13}C NMR systems were funded in part by National Science Foundation grants. (b) Rohm and Haas Co., Research Laboratories, Spring House, Pa., 19477.
(2) W. T. Ford, R. J. Hauri, and D. J. Hart, *J. Org. Chem.*, **38**, 3916 (1973).
(3) G. C. Levy, R. A. Komoroski, and J. A. Halstead, *J. Am. Chem. Soc.*, **96**, 5456 (1974).
(4) G. R. Alms, D. R. Bauer, J. I. Brauman, and R. Pecora, *J. Chem. Phys.*, **58**, 5570 (1973).
(5) D. R. Bauer, G. R. Alms, J. E. Brauman, and R. Pecora, *J. Chem. Phys.*, **61**, 2255 (1974).
(6) I. M. Armitage, H. Huber, D. H. Live, H. Pearson, and J. D. Roberts, *J. Magn. Reson.*, **15**, 142 (1974).
(7) G. C. Levy, *J. Am. Chem. Soc.*, **95**, 6117 (1973).
(8) W. T. Ford, *J. Phys. Chem.*, in press.
(9) H. C. Brown and M.-H. Rei, *J. Org. Chem.*, **31**, 1090 (1966).
(10) M. Tamura and J. Kochi, *Synthesis*, 303 (1971); M. Tamura and J. K. Kochi, *J. Organomet. Chem.*, **42**, 205 (1972).
(11) "Landolt-Börnstein Zahlenwerte und Funktionen", II. Band, part 5, Springer-Verlag, Heidelberg, 1969, p 172.
(12) D. M. Grant and E. G. Paul, *J. Am. Chem. Soc.*, **86**, 2984 (1964); L. P. Lindeman and J. Q. Adams, *Anal. Chem.*, **43**, 1245 (1971).
(13) D. J. Hart and W. T. Ford, *J. Org. Chem.*, **39**, 363 (1974).
(14) F. J. Weigert and J. D. Roberts, *Inorg. Chem.*, **12**, 313 (1973).
(15) D. Doddrell, V. Glushko, and A. Allerhand, *J. Chem. Phys.*, **56**, 3683 (1972).
(16) For reviews, see T. C. Farrar and E. D. Becker, "Pulse and Fourier Transform NMR", Academic Press, New York, N.Y. 1971, pp 46-65; J. R. Lyerla, Jr., and D. M. Grant, "MTP International Review of Science, Physical Chemistry", Ser. 1, Vol. 4, Butterworths University Park Press, London, 1972, pp 155-200; J. R. Lyerla, Jr., and G. C. Levy "Topics in Carbon-13 NMR Spectroscopy", Vol. 1, G. C. Levy, Ed., Wiley, New York, N.Y., 1974, pp 79-148.
(17) D. Doddrell and A. Allerhand, *J. Am. Chem. Soc.*, **93**, 1558 (1971).
(18) A. Allerhand, D. Doddrell, V. Glushko, D. W. Cochran, E. Wenkert, P. J. Lawson, and F. R. N. Gurd, *J. Am. Chem. Soc.*, **93**, 544 (1971); V. Glushko, P. J. Lawson, and F. R. N. Gurd, *J. Biol. Chem.*, **247**, 3176 (1972).
(19) Y. K. Levine, N. J. M. Birdsall, A. G. Lee, and J. C. Metcalfe, *Biochemis-*

try, **11**, 1416 (1972); P. E. Goldici and F. R. Landsberger, *Ibid.*, **13**, 362 (1974); M. P. N. Gent and J. H. Prestegard, *Biochem. Biophys. Res. Commun.*, **58**, 549 (1974).
(20) J. Schaefer in "Topics in Carbon-13 NMR Spectroscopy", Vol. 1, G. C. Levy, Ed., Wiley, New York, N.Y., 1974, pp 149–208; J. Schaefer and D. F. S. Natusch, *Macromolecules*, **5**, 416 (1972); J. Schaefer, *ibid.*, **5**, 427 (1972); A. Allerhand and R. K. Hailstone, *J. Chem. Phys.*, **56**, 3718 (1972).
(21) M. Schwartz, P. E. Fagerness, C. H. Wang, and D. M. Grant, *J. Chem. Phys.*, **60**, 5066 (1974).
(22) E. Williams, B. Sears, A. Allerhand, and E. H. Cordes, *J. Am. Chem. Soc.*, **95**, 4871 (1973).
(23) M. Alexandre, C. Fouchet, and P. Rigny, *J. Chim. Phys. Phys.-Chim. Biol.*, **70**, 1073 (1973); R. T. Roberts and C. Chachaty, *Chem. Phys. Lett.*, **22**, 348 (1973); J. M. Brown and J. D. Schofield, *Chem. Commun.*, 434 (1975).
(24) Y. K. Levine, J. J. M. Birdsall, A. G. Lee, J. C. Metcalfe, P. Partington, and G. C. K. Roberts, *J. Chem. Phys.*, **60**, 2890 (1974).
(25) J. R. Lyerla, Jr., H. M. McIntyre, and D. A. Torchia, *Macromolecules*, 7, 11 (1974).
(26) D. E. Woessner, *J. Chem. Phys.*, **37**, 647 (1962); H. Shimizu, *ibid.*, **37**, 765 (1962); D. Wallach, *ibid.*, **47**, 5258 (1967); D. E. Woessner, B. S. Snowden, Jr., and G. H. Meyer, *ibid.*, **50**, 719 (1969).
(27) Y. K. Levine, P. Partington, and G. C. K. Roberts, *Mol. Phys.*, **25**, 497 (1973).
(28) C.-M. Hu and R. Zwanzig, *J. Chem. Phys.*, **60**, 4354 (1974).
(29) A. Bondi, *J. Phys. Chem.*, **68**, 441 (1964); J. T. Edward, *J. Chem. Ed.*, **47**, 261 (1970).
(30) W. T. Huntress, Jr., *J. Chem. Phys.*, **48**, 3524 (1968).
(31) A. Gierer and K. Wirtz, *Z. Naturforsch.*, *A*, **8**, 532 (1953).
(32) K. T. Gillen and J. E. Griffiths, *Chem. Phys. Lett.*, 17, 359 (1972).
(33) Typical B–C bond lengths in tetraphenylboride ion are 1.64 Å; K. Hoffmann and E. Weiss, *J. Organomet. Chem.*, **67**, 221 (1974); B–C bond lengths in B_{2226} should be slightly longer.
(34) J. D. Forrester, A. Zalkin, and D. H. Templeton, *Inorg. Chem.*, **3**, 1500 (1964); D. St. Clair, A. Zalkin, and D. H. Templeton, *ibid.*, **11**, 377 (1972).
(35) A. F. Peerdeman, J. P. C. Holst, L. Horner, and H. Winkler, *Tetrahedron Lett.*, 811 (1965); A. T. McPhail, G. M. Semeniuk, and D. B. Chestnut, *J. Chem. Soc. A*, 2174 (1971).
(36) J. P. Lowe, *Prog. Phys. Org. Chem.*, 6, 1 (1968).
(37) W. T. Huntress, Jr. *Adv. Magn. Reson.*, **4**, 1 (1970).
(38) D. R. Bauer, J. I. Brauman, and R. Pecora, *J. Am. Chem. Soc.*, **96**, 6840 (1974).

Reassignment of the Chirality to a Series of 2,6-Disubstituted Spiro[3.3]heptanes by X-Ray Methods and Implications Thereof on Empirical Rules and Theoretical Models

L. A. Hulshof,[1a] Hans Wynberg,*[1a] B. van Dijk,[1b] and J. L. de Boer[1b]

Contribution from the Departments of Organic Chemistry and Structural Chemistry, The University, Zernikelaan, Paddepoel, Groningen, The Netherlands.

Received August 11, 1975

Abstract: The absolute configuration of a series of optically active 2,6-disubstituted spiro[3.3]heptane compounds has been elucidated. Application of Klyne's sector rule to spiro[3.3]heptane-2,6-dicarboxylic acid or Fecht acid (**1**) and of Lowe's rule to the spiro[3.3]heptane system suggested the *R* configuration for *d*-**1**. Use of the major theoretical models of optical activity also resulted in an assignment of the *R* configuration to *d*-**1**. This assignment supported the result obtained previously from an x-ray study of *d*-**1**, which on the basis of the (small) anomalous scattering of oxygen and carbon tended to the *R* configuration for *d*-**1**. Definite proof of the chirality could be obtained when a well-crystallized barium salt of *d*-**1** had been prepared. X-ray work on this compound showed beyond any doubt that *d*-Fecht acid (**1**) has the *S* configuration. Renewed x-ray work on the acid itself confirmed the *S* configuration of *d*-**1**. A discussion is given on the striking invalidity of empirical rules and theoretical models for establishing the chirality of these particular spiro systems.

Optically active spiro[3.3]heptane-2,6-dicarboxylic acid or Fecht acid (**1**) has been used by Wynberg and Houbiers[2] as starting material in the synthesis of a number of enantiomeric 2,6-disubstituted spiro[3.3]heptane derivatives. Our current interest[3] in this series of compounds encouraged us to solve the intriguing problem of configurational assignment to **1** and its derivatives. Knowledge of its chirality would establish the absolute configuration of this whole series of compounds.

Very recently we proposed the *R* configuration for dextrorotatory Fecht acid (see Figure 1) on the basis of three different types of experiments: (a) ORD and CD measurements including the application of Lowe's rule[5] to *d*-**1** and other configurationally related 2,6-disubstituted spiro[3.3]heptane derivatives,[2] (b) special solvent effects of *d*-Fecht acid (**1**),[6] and (c) x-ray diffraction of *d*-**1** using anomalous scattering.[7] In the present study we wish to report unambiguous evidence for establishing the absolute configuration of **1** and related compounds. The larger part of this study describes the assignment, along different lines, of the chirality to *d*-Fecht acid (**1**). After the Experimental Section, sections II–V deal with the conventional application of some empirical rules and theoretical models of optical activity. Section VI describes the determination of the absolute configuration by x-ray work. Section VII brings forward clear consequences for the applicability of the rules and models mentioned above.

I. Experimental Section

Boiling points are uncorrected. Melting points were determined on a Mettler FP_1 apparatus at a warm-up rate of 0.2 °C/min. Ultraviolet spectra were recorded on a Zeiss PMQ II apparatus. NMR spectra were obtained on a Varian A60 instrument using tetramethylsilane as an internal standard. Microanalyses were performed in the analytical section of our department under the supervision of Mr. W. M. Hazenberg. Optical activity was measured on a Zeiss Lichtelektrisches Präzisionspolarimeter 005 using 10-cm cells for compounds **2**, **4**, and **7**, and 5-cm cells for compounds **5** and **13**. Concentrations are given in grams/100 ml. The ORD spectrum was taken on a Bendix Ericsson Polarmetric 62, provided with a 150-W xenon lamp and a 1-cm cell. The measurements were taken at room temperature. Ellipticity was measured with a Roussel-Jouan Dichrograph II, provided with a deuterium lamp.

***l*-Spiro[3.3]heptane-2,6-diamine** (**2**) was prepared from *l*-spiro[3.3]heptane-2,6-diammonium chloride (**12**) with $[\Phi]_{578}$ −6.0°, $[\Phi]_{405}$ −15.5° (*c* 2.8, water), in 50% yield according to the method of Lowry and Baldwin.[8] The obtained optical rotation of **2** was: $[\Phi]_{578}$ −4.2°, $[\Phi]_{405}$ −10.4° (*c* 3.1, chloroform).

l-Spirane **12** was obtained from *d*-spiro[3.3]heptane-2,6-dicar-

Wynberg et al. / Configuration of 2,6-Disubstituted Spiro[3.3]heptanes