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A PULSED NMR STUDY OF MOLECULAR MOTION IN SOLID 5,5-DIMETHYL-5,6,11,12-TETRAHYDRO-5*H*-DIBENZO[*b,f*]SILOCIN

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Summary

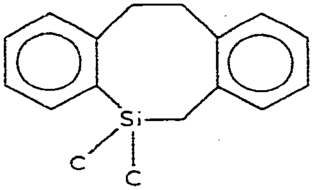
A pulsed NMR study of relaxation times, T_1 and T_{1D}, and second moments for solid 5,5-dimethyl-5,6,11,12-tetrahydro-5*H*-dibenzo[*b,f*]silocin is reported. The compound was studied over the temperature range —175 to 50°C. Evidence was obtained for three motions characerized by activation energies, 2.70, 1.2, and $\geqslant 4$ kcal/mole, respectively. The first motion is methyl reorientation. The second motion is not assigned but is probably a relatively small amplitude flexing of the central ring. The third motion is also unassigned and may be large amplitude flexing of the central ring, libration, or anisotropic molecular reorientation. The motions were assigned by comparison of X-ray crystallographic data with NMR second moment data.

Introduction

We have previously reported the results of pulsed NMR studies of molecular motion in tricyclic compounds with central eight-membered rings in the solid phase. The compounds studied were 6,12,12-trimethyl-5,6-dihydro-7*H*,12*H*-dibenzo[*c,f*][1,5]silazocine [1] and *N*-methyl-5,6-dihydro-7*H*,12*H*-dibenz[*c,f*]-azocine [2]. In the solid phase, the silazocine adopts a flexible, distorted twist boat (TB) conformation and the azocine adopts the rigid, boat-chair (BC) conformation. The motions exhibited by each compound were found to depend upon the conformation of the central 8-membered ring. Recently, a dibenzosilocin was synthesized [3] and its X-ray structure was reported [4]. This compound adopts a basket conformation in the solid phase, and examination of molecular models suggests that the central ring of this compound may exhibit some degree of flexibility. We have performed a pulsed NMR study of this compound to determine the degree of flexibility of the central ring and to compare the results from this compound with those reported previously.

Experimental

The silocin, 5,5-dimethyl-5,6,11,12-tetrahydro-5*H*-dibenzo[*b,f*]silocin (I), the subject of this study, was prepared by the ring expansion reaction of 5-chloromethyl-5-methyl-10,11-dihydrodibenzo[*b,f*]silepin in the presence of $AlCl_3$ followed by quenching with methyllithium. Distillation of the crude reaction product followed by recrystallization from ethanol gave pure silocin, m.p. 60—70.5°C *. The sample was placed in a glass container for study. The proton NMR measurements [5] ** of the Zeeman spin lattice relaxation time (T_1), the dipolar relaxation time (T_{1D}), and the second moment (M_2) were made using a Polaron (Watford, England) high power pulsed NMR spectrometer operating at 60 MHz, as described previously [1]. The second moment values were obtained from analysis of the "solid echo" following a $90—\tau—90$ pulse sequence [6,7], in which the second pulse is phase shifted by 90° from the first pulse. The Bloch decays were found to be Gaussian within experimental error for this polycrystalline sample.



Computer calculations were done on an IBM 370/168 computer.

Results

Experimental values of the Zeeman spin-lattice relaxation time (T_1) and the dipolar relaxation time (T_{1D}) are presented in Fig. 1. T_1 exhibits a relaxation minimum centered at $10^3/T = 7.3$ (~138 K) due to molecular motion (motion *I*). The solid line for T_1 in Fig. 1 represents values for T_1 calculated from eq. 1.

$$\frac{1}{T_1} = \frac{2}{3}\gamma^2 M_{2\mathrm{mod}}\left[\frac{\tau_c}{1+\omega_o^2\tau_c^2} + \frac{4\tau_c}{1+4\omega_o^2\tau_c^2}\right] \qquad (1)$$

Where γ is the gyromagnetic ratio for protons, $M_{2\mathrm{mod}}$ is the portion of the second moment M_2 which is modulated by the motion, ω_o is the Larmor frequency in the laboratory magnetic field, and τ_c is the correlation time of the motion. The line for T_1 in Fig. 1 is calculated assuming an Arrhenius expression

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* Details of the synthetic procedures will be published at a later date.

** Definitions of the NMR parameters and brief discussions of theory are also given in ref. 1.

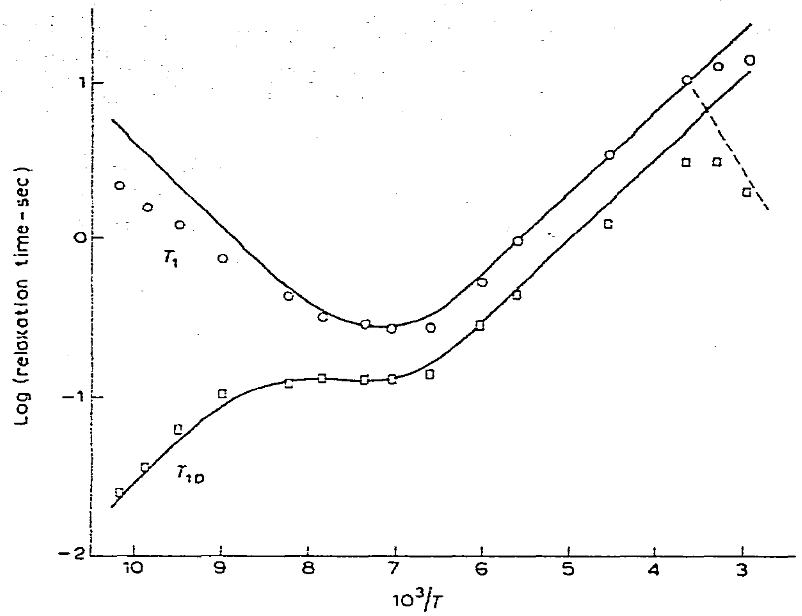

Fig. 1. Observed and calculated values of spin-lattice and dipolar relaxation times for dibenzsilocin vs. reciprocal temperature.

(eq. 2), in which $E_A = 2.5$ kcal/mole and $\tau_o = 2.1 \times 10^{-13}$ sec. It can be seen in

$$\tau_c = \tau_o \exp(E_A/RT) \qquad (2)$$

Fig. 1 that the calculated T_1 values deviate from the experimental values on the low temperature side of the minimum. The gradient of the observed T_1 values for $10^3/T > 8$ corresponds to $E_A \sim 1.7$ kcal/mole. In addition, there is some discrepancy between observed and calculated T_1 values for $10^3/T < 3.5$.

For $10^3/T > 4$, values of T_{1D} are dominated by the same process (motion I) that controls T_1. For $10^3/T < 4$, there is an indication that an additional process (motion II) contributes to T_{1D}. The solid line for T_{1D} in Fig. 1 is calculated from an expression of Goldman [8], which assumes completely uncorrelated motion (eqn. 3).

$$T_{1D} = T_1/(2 + \omega_o^2\tau_c^2/3) \qquad (3)$$

It can be seen in Fig. 1 that there is good agreement between calculated and observed values of T_{1D} for $10^3/T > 4$. The dominant process (motion I) controlling T_1 and T_{1D} in Fig. 1 is random reorientation of both methyl groups, as discussed below.

For $10^3/T < 4$, both motion I and motion II contribute to the observed value of T_{1D} according to eq. 4.

$$\left(\frac{1}{T_{1D}}\right)_{obs} = \left(\frac{1}{T_{1D}}\right)_{I} + \left(\frac{1}{T_{1D}}\right)_{II} \qquad (4)$$

Values of $(T_{1D})_{II}$ obtained from eq. 4 are presented as a dashed line in Fig. 1. The gradient of this line corresponds to $(E_A)_{II} = 4.1$ kcal/mole; however, this can be taken only as a rough lower limit of the activation energy for motion II.

Thus, values of T_{1D} for $10^3/T > 4$ appear to be controlled by a single relaxation process, motion I, (methyl reorientation), whereas values of T_1 appear to be controlled principally by motion I with an indication of a contribution from at least one additional process (motion III). The discrepancy between observed and calculated T_1 values for $10^3/T < 3.5$ cannot be attributed to a contribution to T_1 from motion II, since the contribution to T_{1D} from motion II in this temperature range indicates that the correlation frequency of motion II is <10 Hz for $10^3/T > 3$, and thus the contribution to T_1 from motion II is negligible.

The behavior of T_1 over the entire range of temperature studied, as shown in Fig. 1, can be accounted for with two expressions of the form of eq. 1, corresponding to motion I and III. Values of T_1 so calculated are shown in Fig. II, and it can be seen that there is good agreement between observed and calculated T_1 values over the entire temperature range. The parameters found for motion I are: $E_A = 2.70$ kcal/mole, $\tau_o = 8.6 \times 10^{-14}$ sec, and $M_{2\text{mod}} = 2.1$ G^2; the parameters found for motion II are: $E_A = 1.15$ kcal/mole, $\tau_o = 9.2 \times 10^{-12}$ sec, and $M_{2\text{mod}} = 0.25$ G^2. Thus motion III modulates a much smaller portion of the total dipolar interaction than does motion I.

It should be noted that the qualitative shape of the methyl reorientation minimum in Fig. 1 and 2 may also be accounted for with the assumption of a temperature dependent distribution of correlation frequencies, such as is postulated for polymers [9]. However, such a circumstance is most probable for an amorphous material and is less likely in a polycrystalline sample. It should also be noted that the curves in Fig. 2 do not represent a unique fit of the experimental data. The curve for motion III is somewhat arbitrary; however, in attempting to fit the data, we conclude (a) the T_1 minimum for motion III must be near its position in Fig. 2 and (b) motion III must have an activation energy about 1 kcal/mole. The two curves in Fig. 2 represent the simplest way

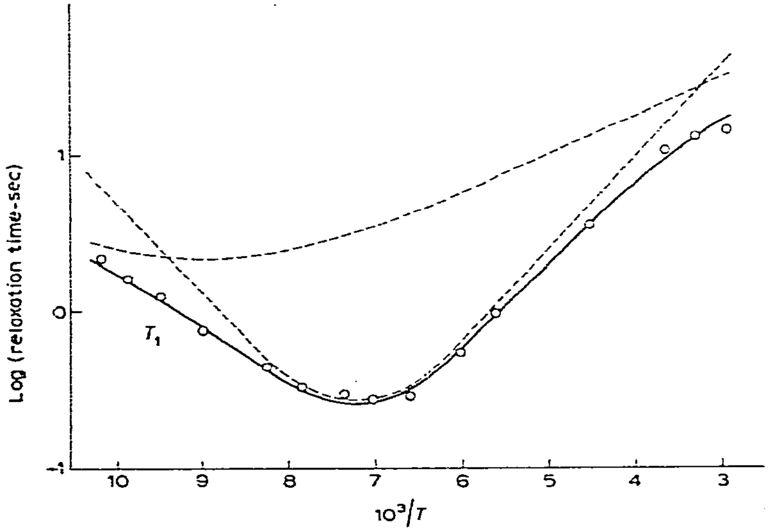

Fig. 2. Observed and calculated values of spin-lattice relaxation times for dibenzsilocin vs. reciprocal temperature.

to account for both low temperature and high temperature discrepancies between observed and calculated T_1 values in Fig. 1.

Discussion

The second moment is anticipated [1,2] to be essentially constant over the entire temperature range show in Fig. 1. Experimentally we observe $M_2 = 12.0$ G^2 at 22°C and 12.6 G^2 at −173°C. This value of M_2 corresponds to $M_{2(\mathrm{high})}$ with respect to motions I and III, and it corresponds to $M_{2(\mathrm{low})}$ with respect to motion II. $M_{2(\mathrm{high})}$ is the limiting value of M_2 when the motion is sufficiently rapid to cause the NMR line to be motionally narrowed, and $M_{2(\mathrm{low})}$ is the value of M_2 when the motion is sufficiently slow so as to have no effect on the NMR line. It is most likely that the principal motion (I) controlling T_1 in Fig. 1 and 2 is methyl group reorientation, and to confirm this assignment, we have calculated M_2 values from X-ray crystallographic data [4,10].

The "rigid lattice" value of M_2 is that value observed only if all motion is sufficiently slow so that the NMR line is not motionally narrowed, and this value can be calculated from the equation of Van Vleck [11] (eq. 5), where

$$M_2 = \frac{715.9}{n} \sum_{j>k} r_{jk}^{-6} \qquad (5)$$

M_2 is in Gauss^2, n is the number of protons in the sample, and r_{jk} is the distance between protons j and k in Å, as obtained from crystallographic data. The sum is taken over all proton pairs in the sample, but for convenience, M_2 is separated into intramolecular and intermolecular parts. The result for $M_{2\mathrm{intra}}$ is 24.2 G^2. The value of the intermolecular contribution was calculated using a computer. The compound crystallizes in the space group *Pbca*, with 8 molecules/unit cell. The calculation included the unit cell and all 26 adjacent unit cells. The resulting value of $M_{2\mathrm{inter}}$ is 1.9 G^2, and this yields a total value for the rigid lattice $M_{2(\mathrm{r.l.})} = 26.1$ G^2.

The observed M_2 is less than the rigid lattice M_2 due to molecular motion, and its value can be calculated for an assumed motion using the expressions of Andrew and Eades [12] as described previously [1,2]. The results were: $M_{2\mathrm{intra}} = 13.4$ G^2, $M_{2\mathrm{inter}} = 1.4$ G^2, and a total $M_{2(\mathrm{Me\ Rot})} = 14.8 \pm 0.6$ G^2. We assume that the uncertainty in this value is due primarily to random error in the crystal lographic data. This may be compared with the observed M_2 value 12.0—12.6 G^2, with an experimental uncertainty of 0.5 G^2. It can be seen that the observed M_2 appears to be beyond experimental uncertainty, about 1 G^2 smaller than that calculated assuming only methyl reorientation. Thus, the largest reduction in the second moment (~11.3 G^2) and the principal relaxation minimum in Fig. 2 may be attributed to methyl group reorientation (motion I). An additional smaller reduction in the second moment (~1 G^2) and the weaker relaxation minimum in Fig. 2 may be attributed to motion III.

It is difficult to assign motion III since it modulates only a very small portion of the dipolar interaction; however, it is likely that this motion involves the central ring. Molecular models indicate that any flexing of the central ring would probably be relatively low in amplitude due to steric interaction between methyl and ring protons. The X-ray study [4] indicates that the thermal parameters for

TABLE 1

OBSERVED MOTIONS FOR DIBENZSILOCIN

Motion	Tentative assignment	E_A (kcal/mole)	τ_0 (sec)
I	CH_3 reorient.	2.70 [a]	8.6×10^{-14}
II	—	$\geqslant 4$	—
III	(Ring flex.)	1.2 [b]	9×10^{-12}

[a] Estimated experimental error ±0.2 kcal/mole. [b] Estimated experimental error ±0.4 kcal/mole.

the methyl groups are relatively large. Thus, motion III could involve a low amplitude flexing of the central ring or a more localized flexing in the vicinity of the silicon atom. A large amplitude flexing, as was observed for the silazocine central ring [1], may definitely be ruled out in this case.

It is not possible to assign motion II since we have only a rough estimate of the activation energy and no second moment data. Motion II may be a molecular libration [13], flexing of the central ring (larger amplitude than motion III), or molecular reorientation (as discussed in ref. 1 and 2).

The activation parameters for the dibenzosilocin are summarized in Table 1. The E_A value for methyl orientation is essentially the same as previously reported barriers for rotation about Si—CH_3 bonds [1,14], 2.2—2.4 kcal/mole.

Acknowledgements

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