The Flexibility of the Tribenzylamine Molecule in Both Solution and the Solid State as Revealed by NMR Measurements

Ariyuki Aihara and Masatoki Yokoi*
Department of Materials Science, Denki-Tsushin University, Chofu, Tokyo
** Department of Chemistry, Faculty of Science, Shinshu University, Matsumoto*

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The molecule of tribenzylamine has a possibility of taking a number of conformations due to the intramolecular rotation of the moieties of the molecule about various axes of rotation; there is also the possibility of the molecular inversion of the pyramidal structure of N–$(CH_2)_3$ bonds.[1,2] We have performed NMR measurements of tribenzylamine in the crystalline state as well as in solution in order to get some knowledge about the flexibility of this molecule.

A JNM-4H-100 spectrometer (100 MHz)[3] has been used to measure the high-resolution NMR absorption in the CCl_4 solution, while the measurement of the broad-line NMR was done with a conventional autodyne spectrometer constructed in our laboratory,[4] operating at a frequency of 19.8 MHz (proton) and with a modulating field of 35 Hz superimposed on the main magnetic field.

Despite a presumed complication of the molecular conformation, the NMR spectrum of tribenzylamine dissolved in CCl_4 exhibits only a single sharp absorption signal of methylene protons ($\delta=3.52$ ppm, ref. TMS). This fact suggests that the molecule must be undergoing some flexing motions in such a way that all the protons of methylene groups become magnetically equivalent on the average. In Table 1, the δ values of methylene protons as well as those of phenyl protons are compared with the chemical shift data of mono- and dibenzylamine, and also of dibenzylmethylamine, observed in CCl_4 solutions. The values are all corrected for possible intermolecular interactions by extrapolating the measured δ's at several concentrations to an infinite dilution.

It is interesting to see that the signal of the C_6H_5 protons in tribenzylamine shows somewhat complicated features, with three main peaks at $\delta=7.16$, 7.22, and 7.28 ppm, while those of mono- and dibenzylamine are rather simple. Dibenzylmethylamine seems to behave much like tribenzylamine so far as the chemical shift is concerned.

TABLE 1. THE CHEMICAL SHIFT DATA OF MONO-, DI-, AND TRIBENZYLAMINE, AND ALSO OF DIBENZYLMETHYLAMINE
(in CCl_4 solutions at 25°C;
δ in ppm, and the reference is TMS)

Compounds	δ (NH, NH_2, CH_3)	$\delta(CH_2)$	$\delta(C_6H_5)$
$NH_2(CH_2C_6H_5)$	1.21(NH_2)	3.76	7.18
$NH(CH_2C_6H_5)_2$	1.37(NH)	3.74	7.22
$N(CH_2C_6H_5)_3$	—	3.52	7.16, 7.22, 7.28
$N(CH_2C_6H_5)_2CH_3$	2.13(CH_3)	3.47	7.16, 7.22, 7.27

The results of the broad-line NMR measurements add further evidence that this molecule is flexible even in the crystalline state: the magnitude of the second moment at 29°C, 6.23±0.10 Gauss^2 (corrected for modulation broadening after Andrew[5]), is smaller than the theoretical value of the intramolecular contribution to the second moment, 7.38 Gauss^2, which is calculated with the molecular structure data obtained by Drs. Fujiko and Hitoshi Iwasaki from the three-dimensional X-ray crystal structure analysis,[6] assuming the molecule to be rigid in the crystal. It is almost certain, without calculating further the intermolecular contribution to the second moment, that the molecule has some degrees of freedom of motion in the crystal even at room temperature. The width of the absorption spectrum shows a tendency to decrease gradually with the rise in the temperature up to ~70°C.

In view of the bulky molecular structure in a rather loose-packed crystal lattice of tribenzylamine,[6] a tentative calculation has been made of the reduction in the intramolecular contribution to the second moment due to the rotational movement of the phenyl groups about axes joining them to methylene carbons to each other; this rotational motion does not cause any translational shift of the molecule as a whole.

Following the equation introduced by Gutowsky and Pake[7] to correlate the reduction of the second moment due to the rotation of a pair of protons with the angle, γ_{jk}, between the line joining the j and k protons and the axis of rotation;

$$F(\gamma_{jk}) = (3\cos^2\gamma_{jk}-1)^2/4,$$

we get 5.97 Gauss[2] as the reduced intramolecular contribution to the second moment due to the phenyl-group rotation. This value is slightly less than the observed value of the second moment, 6.23 Gauss^2, the difference being due to the intermolecular contribution to the second moment in a non-rigid lattice. Any intramolecular movements other than that postulated above are improbable, for they would cause a shift of the center of mass of the molecule in the crystal lattice. The details will be published later in this Bulletin.

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