Application of proton magnetic resonance to rotational isomerism in halotoluene derivatives. III. α, α -Dichloro-2,4,6-tribromotoluene

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At room temperature the proton magnetic resonance spectrum of α, α -dichloro-2,4,6-tribromotoluene is ABX where the methine proton in the sidechain is X and is lying in the plane of the aromatic ring. At higher temperatures the ring proton spectrum, AB, broadens and eventually collapses to yield an A₂X spectrum. From an analysis of the ring proton line shapes the barrier to rotation of the dichloromethyl group about the sp²-sp³ carbon-carbon bond is obtained; $\Delta G^* = 17.5 \pm 0.1$ kcal/mole at 304 °K, $\Delta H^* = 15.67 \pm 0.08$ kcal/mole, $\Delta S^* = -7$ e.u., $E_a = 16.38 \pm 0.08$ kcal/mole, log $A = 11.78 \pm 0.23$ where the least squares errors given should probably be multiplied by a factor of from 3 to 5 to take possible systematic errors into account. The barrier is about 2 kcal/mole higher than in $\alpha, \alpha, 2, 4, 6$ -pentachlorotoluene. The barrier to rotation arises from the conformation in which chlorine and bromine atoms are eclipsed.

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Introduction

The previous paper (1) in this series presented a detailed description of a proton magnetic resonance (p.m.r.) study of hindered rotation of the dichloromethyl group in $\alpha, \alpha, 2, 4, 6$ -pentachlorotoluene (PCT). A computer program based on a density matrix treatment of intramolecular proton exchange was developed and applied in the extraction of preexchange lifetimes from the temperature dependent ring proton spectrum of PCT. The present paper gives the results of a similar application to the ring proton spectrum of α, α -dichloro-2,4,6-tribromotoluene (DCTBT).

Experimental

(1) Preparation of DCTBT

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A mixture of 2,4,6-tribromotoluene (20 g) and phosphorous pentachloride (0.2 g) in a 50 ml flask (pyrex) was heated with a small flame into a melt. The mixture was then irradiated with ultraviolet (u.v.) light while a stream of chlorine gas was bubbling into the mixture through a gas dispersing tube. The progress of chlorination was followed by observing the disappearance of the proton resonance peaks at 7.5 τ and 5.7 τ corresponding to the methyl and the monochloromethyl groups, respectively. The product was then distilled under reduced pressure to give PCT (14.5 g), identified by analysis and by comparing the p.m.r. and infrared (i.r.) spectra with those of an authentic sample prepared by chlorination of 2,4,6trichlorotoluene. The residue (3 g) was transferred to a microdistillation flask and another portion of the PCT (1.8 g) was distilled out. The residue was then purified by extensive thin-layer chromatography (t.l.c.) on silica and DCTBT was isolated, slightly contaminated with PCT.

(2) Proton Magnetic Resonance Spectra

The available amount of DCTBT was insufficient to produce a reasonable signal to noise ratio on a DA60I spectrometer. Its solubility was also very low in methylcyclohexane, hexamethyldisiloxane, and other solvents of low dielectric constant. In perchlorobutadiene the 100 MHz proton spectrum consisted of a tightly coupled ABC spectrum at 30 °C. However, in toluene- d_8 the 100 MHz proton spectrum is ABX, very similar to the spectrum for PCT at -40 °C (1). It was previously shown that the intrinsic temperature dependence of the internal ring proton shift of PCT in toluene- d_8 can and must be found in order to obtain reliable exchange rates from fitted spectra. A similar procedure was followed with DCTBT.

The p.m.r. spectrum of an approximately 4 mole % solution of DCTBT in degassed toluene-d₈ was recorded at 2° intervals between 40 and 74 °C on an HA-100-D spectrometer under conditions of a signal to noise ratio of about 80:1. The residual proton resonance of the solvent (Merck) interfered with the low-field ring proton resonance (H_A) so that only the line shapes of the highfield ring proton peaks (H_B) could be reliably measured (a very small amount of PCT did not overlap with signals of interest between 40 and 74 °C). The spectra were repeatedly calibrated by reading oscillator frequencies in the frequency sweep mode. The homogeneity of the external magnetic field was monitored by the appearance of the methine proton peaks (H_x) , whose widths are independent of exchange times (1). Over the temperature range used here, the homogeneity could be accurately controlled to give an effective $T_2 = 1.72 \pm 0.12$ s. The internal ring proton shift was measured as a function of temperature in the region of slow exchange (10-35 °C).

The temperature settings on the dial of the 6040 proportional controller were calibrated against an ethylene glycol sample. The dial settings were then checked with a thermocouple immersed in a sample of toluene. Temperature gradients near the receiver coil were apparently very small between 30 and 70 °C. The thermocouple had been calibrated at a few set points. It is fairly certain that the temperature data are accurate to ± 1 °C and precise to ± 0.5 °C.

(3) Extraction of Rate Constants

The computer program for an ABX spectrum in which A and B exchange under conservation of spin states (1) was used to fit calculated to observed spectra as exten-

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TABLE 1

The chemical shifts and proton-proton coupling constants of DCTBT in toluene- d_8 solution between 10 and 35 °C

Temperature (°C)	Chemical shift*			Coupling constants (Hz)†		
	H _x	H _A	Н _в	J _{AB}	J _{AX}	J _{BX}
10	7.267	6.872	6.658	2.165	0.521	-0.001
15	7.271	6.883	6.672	2.16_7	0.53_{6}	-0.00_{1}
20	7.276	6.895	6.886	2.15	0.544	-0.00_{1}
25	7.281	6.909	6.702	2.19_{7}^{-}	0.553	-0.00_{2}
28	7.283	6.915	6.711	2.17	0.556	-0.00_{1}
35	7.290	6.933	6.731	2.171	0.53 ₉	-0.00_{1}

*In p.p.m. to low field from internal tetramethylsilane.

, the coupling constants are given as obtained from the computer analysis and we feel their accuracy lies near 0.03 Hz. J_{BX} , of course, is unmeasurably small and of unknown sign.

sively described previously (1). The intrinsic temperature dependence of the internal ring proton shift is fitted by the least squares equation: shift in Hz = 21.81 – 0.0456 $T(^{\circ}C)$. These shifts were used as input parameters in the computer program. A constant T_2 of 1.72 s was assumed throughout (see above).

Results and Discussion

(1) Spectral Parameters at Low Exchange Rates

The program LAOCOON 3 (2) was used to extract the chemical shifts and coupling constants from the 3-spin p.m.r. spectra between 10 and 35 °C. At these temperatures the mean lifetime before exchange in conformation 1 or its mirror image is relatively long. The spectra themselves



are very similar to those of PCT presented in ref. 1. Table 1 gives the spectral parameters in the region of slow exchange. Figure 1 displays the plot of the internal shift of H_A and H_B vs. temperature in this region. The least squares equations representing this dependence are:

shift of
$$H_A = 0.2489T$$
 (°C) + 684.61 Hz

shift of $H_B = 0.2945T(^{\circ}C) + 662.80 \text{ Hz}$

where shifts are in Hz to low field of internal tetramethylsilane. These equations were used to calculate the internal ring proton shift in the presence of exchange at each of 18 temperatures between 40 and 74 °C. As was shown in ref. 1, this procedure is necessary if large errors in activation parameters are to be avoided.



The internal chemical shift, in Hz, of protons FIG. 1. H_A and H_B of α,α -dichloro-2,4,6-tribromotoluene, as a dilute solution in toluene- d_8 , is plotted vs. temperature between 10 and 35 °C.

(2) Proton Resonance Spectra under Conditions of Exchange

Coalescence of the spectral peaks from H_A and H_B occurs at about 80 °C. The line-shape fitting procedure (1) was applied at 2° intervals between 40 and 74 °C to the H_B resonance for reasons mentioned earlier. The preexchange lifetimes, τ , are listed in Table 2. For most temperatures, two values of τ are given. These represent the limits of τ which gave a reasonable fit of calculated to experimental line shapes. Because of the experimental difficulties mentioned above, τ varies only between 0.50 and 0.036 s, a factor of 14.

(3) Activation Parameters for the Hindered Rotation

Plots of log k and of log (k/T) vs. 1/T were prepared $(k = 1/\tau)$ and were used to extract E_a , ΔH^* , and ΔS^* in the usual way (3). Further-

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Temperature (°C)	τ (s)	Temperature (°C)	τ (s)
40	0.4825-0.5225	58	0.110-0.1125
42	0.4050-0.4125	60	0.08375-0.0839
44	0.305-0.280	62	0.079-0.080
46	0.265-0.295	64	0.067
48	0.1900-0.2025	66	0.056
50	0.1725-0.1950	68	0.048-0.049
52	0.170-0.175	70	0.048-0.049
54	0.1275-0.1500	72	0.0375-0.0400
56	0.1125-0.1175	74	0.0350-0.0375





FIG. 2. A plot of log (k/T) vs. 1/T for α, α -dichloro-2,4,6-tribromotoluene in toluene- d_8 solution between 40 and 74 °C; $k = 1/\tau$ where τ is the mean lifetime before effective exchange of the ring protons. The error bars in log (k/T) indicated for the lowest and highest temperatures are typical but many are smaller. The correlation coefficient, r = 0.995 for the least squares straight line and the derived parameters are given in the text.

more, ΔG^* was calculated from log k at each temperature using the equation from transition state theory and assuming a transmission coefficient of 1/2 (1). Plots of ΔG^* vs. T were also prepared. In Fig. 2 a plot of log (k/T) vs. 1/T is displayed as an example (correlation coefficient, r = 0.995, 18 values).

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The results of the least squares analyses with statistical errors given are as follows: $E_A = 16.38 \pm 0.08 \text{ kcal/mole}, \log A = 11.78 \pm 0.23; \Delta H^* = 15.69 \pm 0.08 \text{ kcal/mole} from \log (k/T) \text{ vs. } 1/T; \Delta H^* = 15.65 \pm 0.40 \text{ kcal/mole} from \Delta F^* \text{ vs. } T; \Delta S^* = -10 \pm 1 \text{ e.u.} from \log (k/T) \text{ vs. } 1/T; \Delta S^* = -5.6 \pm 0.3 \text{ e.u.} from \Delta G^* \text{ vs. } T; \Delta S^* = -5 \pm 1 \text{ e.u.} from A = e(kT/2h) \exp(\Delta S^*/R); \Delta G^* = 17.5 \pm 0.1 \text{ kcal/mole} at 304 ^{\circ}K.$ In view of the possible systematic errors in these parameters, a more reasonable estimate of the errors

in E_A and ΔH^* is probably nearer 0.4 kcal/mole. The three different estimates of ΔS^* can be arbitrarily averaged to give $\Delta S^* = -7.2$ e.u. implying that ΔS^* is very probably negative but small in magnitude.

(4) Comparison with Activation Parameters for PCT

Perhaps the best comparison of the present results for DCTBT with those for PCT (1) involves the composite treatment of the rate data for the latter in the two solvents, methylcyclohexane and toluene- d_8 . In ref. 1 the rate data were treated separately for the two solvents, in particular because of the problem of the internal ring proton shift. However, there exists a satisfactory least squares fit of the data for PCT if log (k/T) is plotted vs. 1/T without reference to

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the solvent. One finds $\Delta H^* = 13.9 \pm 0.2$ kcal/ mole and $\Delta S^* = -3.7 \pm 0.6$ e.u. where the correlation coefficient, r = 0.991 for 19 values.

Apparently the potential energy barrier to rotation about the sp²-sp³ carbon-carbon bond is 10% or nearly 2 kcal/mole higher in DCTBT than in PCT; reasonably indicating that an eclipsed Cl...Br interaction is sterically less favorable than an eclipsed Cl...Cl interaction. As with PCT the conformation 2 is of highest energy and represents the activated state during the rotation of the dichloromethyl group. Con-

$$\begin{array}{cccc}
H & H \\
Br---Cl & Br & -Br \\
Cl & Cl & Cl \\
2 & 3
\end{array}$$

formation 1 and its mirror image are the ground state of the molecule. From the arguments in ref. 1 it follows that conformation 3 is of intermediate stability, but at least 10 kcal/mole less stable than 1. Hence 3 is not appreciably populated at any of the temperatures under consideration.

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