# Proton Magnetic Resonance Studies of Rotational Isomerism in Halotoluene Derivatives. XI. Experimental and Theoretical Barriers to Rotation in $\alpha, \alpha, 2, 4, 6$ -Pentabromo-, $\alpha, \alpha$ -Dibromo-2,4,6-trichloro-, and $\alpha, \alpha$ -Dibromo-2,6-dichlorotoluene

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Using rate constants determined from an analysis of the p.m.r. lineshape of the ring protons as a function of temperature, the activation parameters for the hindered rotation about the sp<sup>2</sup>-sp<sup>3</sup> carbon-carbon single bond in  $\alpha, \alpha, 2, 4, 6$ -pentabromotoluene dissolved in perchlorobutadiene are determined. Values of  $\Delta G^{\pm}$  for the analogous hindered rotations in  $\alpha, \alpha$ -dibromo-2,6-dichlorotoluene in toluene- $d_8$ , and for  $\alpha, \alpha$ -dibromo-2,4,6-trichlorotoluene in solutions of toluene- $d_8$  and methylcyclohexane are also given. The results are compared with semiempirical potential energy barrier calculations employing partial geometry optimization. The agreement is satisfactory.

A l'aide des constantes de vitesse déterminées en fonction de la température par l'analyse du signal des protons du cycle en r.m.n., on a déterminé les paramètres d'activation pour les rotations empêchées autours de la liaison simple carbone-carbone de type  $sp^2-sp^3$ , dans le pentabromo- $\alpha, \alpha, 2, 4, 6$  toluène dissout dans le perchlorobutadiène. Les valeurs de  $\Delta G^{+}$  sont aussi rapportées pour les rotations empêchées analogues du dibromo- $\alpha, \alpha$  dichloro-2, 6 toluène en solution dans le toluène- $d_8$ , et du dibromo- $\alpha, \alpha$  trichloro-2,4,6 toluène en solution dans le toluène- $d_8$  et le méthylcyclohexane. Les résultats sont comparés avec les calculs empiriques de la barrière d'énergie potentielle en utilisant la géométrie partielle d'optimalisation. L'accord est satisfaisant. [Traduit par le journal]

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## Introduction

Proton magnetic resonance (p.m.r.) studies of the hindered rotation of the dichloromethyl group in  $\alpha, \alpha, 2, 4, 6$ -pentachlorotoluene (PCT) (1) and  $\alpha,\alpha$ -dichloro-2,4,6-tribromotoluene (DCTBT) (2) have been presented in previous papers of this series. A similiar study of the hindered rotation of the dibromomethyl group about the  $sp^2-sp^3$ carbon-carbon single bond in  $\alpha, \alpha, 2, 4, 6$ -pentabromotoluene (PBT), a,a-dibromo-2,4,6-trichlorotoluene (DBTCT), and in a,a-dibromo-2,6-dichlorotoluene (DBDCT) is presented in this paper. The results are compared with semiempirical calculations in which the sp<sup>2</sup>-sp<sup>3</sup> carboncarbon bond length and the bond angles involving the halogen substituents are optimized for each rotational arrangement (3).

## Experimental

#### Preparation of PBT

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2,4,6-Tribromotoluene (prepared by following Lock and Schreckeneder (4)) was treated in a quartz flask with a large excess of bromine at 200-250 °C under u.v. radiation for 6 days. The reaction mixture was extracted

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with ether. The solution was then filtered, washed successively with aqueous sodium hydrogen sulfite and water, dried over magnesium sulfate, and the solvent was evaporated. The residue was dissolved in petroleum ether and stored at -20 °C. A brown oil which separated was discarded and the petroleum ether was evaporated. The product was a yellow oil. The p.m.r. spectrum at room temperature displayed the expected ABX pattern and a number of impurity peaks. Repeated attempts to purify the product by distillation under reduced pressure, by t.l.c., and by dry column chromatography failed to reduce the intensities of the impurity peaks significantly.

#### Preparation of DBTCT

2,4,6-Trichlorotoluene (prepared as described previously (1)) was treated with an excess of bromine in a quartz flask at 150–220 °C under u.v. radiation for 3 days. The reaction mixture was treated as above (PBT), leaving a yellow-brown oil containing about 80% DBTCT and 20%  $\alpha$ -bromo-2,4,6-trichlorotoluene. Repeated attempts to purify the product by the methods above were unsuccessful.

#### Preparation of DBDCT

2,6-Dichlorobenzyl bromide (Aldrich) in carbon tetrachloride was treated with an excess of bromine under u.v. radiation. The bromination was monitored by observation of the proton chemical shift of the side-chain protons. The product was purified by vacuum sublimation.

#### Proton Magnetic Resonance Spectra

A 10 mol % solution of PBT in perchlorobutadiene, containing a small amount of hexamethyldisilane as a

lock and reference signal, was prepared and carefully degassed by the freeze-pump-thaw technique. Fourteen p.m.r. spectra were recorded at different temperatures from 18.9-125.9 °C in a manner described previously (2). In the case of DBTCT, two degassed solutions, 10 mol % in methylcyclohexane and 10 mol % in toluene- $d_8$ , each containing tetramethysilane as a lock and reference material, were prepared. Spectra were recorded at five temperatures from -9.7 to 82.6 °C for the former solution and at four temperatures from 21.0-78.5 °C for the latter solution. Spectra were recorded at five temperatures from -10.0 to 80.0 °C for DBDCT as a 15 mol % solution in toluene- $d_8$  containing a small amount of tetramethylsilane. All spectra were taken on a HA100D spectrometer.

For all samples the homogeneity of the external magnetic field was monitored by the appearance of impurity peaks and of the methine proton peaks, whose widths are independent of the preexchange lifetimes (1). Temperatures were measured as described previously (2) and are believed to be accurate to  $\pm 0.5$  °C.

#### Determination of Preexchange Lifetimes

The computer program for an ABX spectrum in which A and B undergo mutual exchange (1) was used to fit the experimental spectra of PBT and DBTCT. Rate constants for the internal rotation in DBDCT were determined by matching spectra with the computer program DNMR2 (5, 6). The usual precautions (2) concerning linewidth corrections, aromatic solvent shifts (7), and impurity peaks were taken.

#### **Results and Discussion**

## Spectral Parameters in the Region of Slow Exchange

Below about 45 °C the mean lifetime of 1 before exchange to its mirror image isomer is relatively long, and the p.m.r. spectra of PBT show no sign of broadening. There is no noticeable broadening in the spectra of DBTCT or DBDCT below about 30 °C, indicating that the preexchange lifetime of 2 is relatively long below this temperature. The spectra of PBT and DBTCT



are similar to those of PCT (1) and DCTBT (2), except that in the case of PBT the  $H_x$  resonance lies to high field of  $H_a$  and  $H_b$ . Figure 1 displays the spectrum of PBT at ambient temperature.

The chemical shifts and coupling constants were determined from the spectra using the



FIG. 1. The p.m.r. spectrum of a 10 mol % solution of  $\alpha,\alpha,2,4,6$ -pentabromotoluene (PBT) in perchlorobutadiene at 100 MHz at ambient temperature. The chemical shift scale is in p.p.m. to low field of internal hexamethyldisilane. The structural formula is given as 1 in the text. The splitting of the H<sub>x</sub> resonance is 0.50 Hz. Impurity peaks are marked by crosses.

iterative computer program LAME (8). The values obtained at a representative temperature for each sample are given in Table 1. The errors are standard deviations in the computer analyses.

# Proton Magnetic Resonance Spectra Under Conditions of Exchange

Preexchange lifetimes,  $\tau$ , for PBT were determined at 10 temperatures from 54.8–125.9 °C and are listed in Table 2. The two values of  $\tau$ for each temperature are the limits of  $\tau$  which give reasonable fits to the observed line shapes. Some representative calculated and experimental spectra are given in Fig. 2. Coalescence of the signals from H<sub>a</sub> and H<sub>b</sub> occurred at about 98 °C. Above 125 °C the magnetic field homogeneity decreased to such an extent that really accurate fitting of calculated to experimental spectra was not possible.

Coalescence of the  $H_a$  and  $H_b$  signals of DBTCT and DBDCT occurred at about 75 °C. Preexchange lifetimes were determined at 72.6 and 82.6 °C for the sample of DBTCT in methylcyclohexane, at 70.0 and 78.5 °C for the toluene $d_8$  solution of DBTCT, and at 70.9 and 80.0 °C for DBDCT in toluene- $d_8$  solution, in order to calculate  $\Delta G^{\ddagger}$  at these temperatures.

## Activation Parameters for the Hindered Rotations

### (a) Experimental Values

Table 3 gives the activation parameters determined in this work with the results for PCT and DCTBT included for comparison. The values of  $E_a$ , log A,  $\Delta H^{\pm}$ , and  $\Delta S^{\pm}$  and their respective errors given in Table 3 are the results

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Parameter <sup>b</sup>	PBT <sup>c</sup>	DBTCT <sup>4</sup>	DBTCT <sup>e</sup>	DBDCT
V <sub>A</sub>	772,446(5)	731.913(5)	680,900(4)	684.802(14)
VB	757.236(5)	719,190(5)	658,262(4)	665.611(14)
Vc		—		639.467(15)
$v_{x}$	737.263(5)	738,234(5)	726,714(4)	743.955(14)
$^{3}J^{\mathrm{H},\mathrm{H}} = J_{\mathrm{AC}}$	_ ``	_ ()	_ ``	8.226(21)
$^{3}J^{\mathrm{H},\mathrm{H}} \equiv J_{\mathrm{RC}}$	_		_	8,186(20)
${}^{4}J^{\mathrm{H},\mathrm{H}} = J_{\mathrm{A}\mathrm{B}}$	1.998(7)	2.140(7)	2.166(6)	1.251(19)
<sup>5</sup> J <sup>H,H</sup> =J <sub>AX</sub>	0.500(7)	0.540(7)	0.532(6)	0.551(19)
<sup>5</sup> J <sup>H,H</sup> =J <sub>BX</sub>	-0.003(7)	-0.009(7)	-0.002(6)	0.000(20)
${}^{6}J^{\mathrm{H},\mathrm{H}} \equiv J_{\mathrm{CX}}$	_		_	-0.010(21)
Root mean square error	0.007	0.007	0.006	0.032
Largest error	0.012	0.015	0.009	0.076
Lines assigned	12	12	12	32

TABLE 1. Proton chemical shifts<sup>a</sup> and coupling constants in Hz for  $\alpha, \alpha, 2, 4, 6$ -pentabromotoluene; a,a-dibromo-2,4,6-trichlorotoluene, and a,a-dibromo-2,6-dichlorotoluene

<sup>e</sup>In Hz at 100 MHz downfield from internal hexamethyldisilane for PBT and from internal tetramethylsilane for the others. <sup>b</sup>The bracketed numbers give the standard deviation in the last significant figure.

10 mol % in perchlorobutadiene at 32.4 °C. 10 mol % in methylcyclohexane at 17.1 °C. 10 mol % in toluene- $d_8$  at 21.0 °C. 15 mol % in toluene- $d_8$  at 22.3 °C.

Table 2.	Preexchange lifetimes, τ, fr	om fitted spectra at various
temp	peratures for the compounds	s studied in this work <sup>a</sup>

Compound	Temperature (°K)	τ(s)
РВТ	328.0	0.95-1.25
	329.9	0.65-0.85
	340.1	0.32-0.35
	349.4	0.14-0.16
	359.2	0.068-0.074
	367.4	0.040-0.043
	373.2	0.025-0.027
	376.9	0.0182-0.0188
	391.2	0.0069-0.0073
	399.1	0.0043-0.0046
DBTCT(in $C_7H_{14}$ )	345.8	0.055-0.062
	355.8	0.027-0.030
$DBTCT(in C_7D_8)$	343.2	0.045-0.065
	351.7	0.024-0.036
DBDCT	344.1	0.063-0.083
	353.2	0.032-0.040

<sup>a</sup>The limits given for  $\tau$  represent those values which yield computed spectra in clear disagreement with observation.

of a standard error propagation treatment (10) of the experimental rate data for each compound. Rate constants for DBDCT and for the two samples of DBTCT were measured at only two temperatures in each case, so only  $\Delta G^{\dagger}$  values are given. All values of  $\Delta G^{\pm}$  listed in Table 3 were calculated from rate constants determined by total lineshape analysis at temperatures (given in the table) very near the coalescence temperatures of the respective compounds. In this temperature region rate constants can be determined very precisely, resulting in highly accurate values of  $\Delta G^*$ . The errors in  $\Delta G^*$ given in Table 3 are the linearized statistical errors, considering the errors contributed by uncertainties in both the rate constants and the temperatures.

Solvent effects on the activation parameters for internal rotation in PCT have been shown to be small (1, 9) and that this is the rule for molecules of this type is confirmed by the values of  $\Delta G^{\dagger}$  for DBTCT in methylcyclohexane and toluene- $d_8$  solutions (Table 3). Furthermore, comparison of the  $\Delta G^*$  values for DBTCT and

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Compound	E <sub>a</sub> (kcal/mol)	$\log A (s^{-1})$	$\Delta H^{\pm}$ (kcal/mol)	$\Delta S^{\pm}(eu)$	$\Delta G^{\pm}$ (kcal/mol)	<i>T</i> (°K)	Calculated barrier(kcal/mol)
PCT (1,9) <sup>a</sup>	$14.56 \pm 0.50$	$12.19 \pm 0.88$	13.97±0.50	$-4.7 \pm 1.7$	$15.33 \pm 0.05$	300.4	13.26
DBTCT (in $C_7H_{14}$ )	_	_	_	_	$18.39 \pm 0.05$	345.8	1
					$18.44 \pm 0.05$	355.8	
DBTCT (in $C_7D_8$ )	_	_	_	_	$18.21 \pm 0.13$	343.7	16.20
					$18.26 \pm 0.15$	351.7	}
DBDCT	_	`			$18.44 \pm 0.11$	344.1	
					$18.46 \pm 0.09$	353.2	
DCTBT (2) <sup>a</sup>	$16.33 \pm 0.42$	$11.76 \pm 0.28$	$15.68 \pm 0.42$	$-7 \pm 2$	$18.14 \pm 0.05$	347.2	16.35
PBT	$19.85 \pm 0.22$	$13.23 \pm 0.13$	$19.13 \pm 0.22$	$-0.4 \pm 0.6$	$19.30 \pm 0.05$	373.2	19.68

 $^{\alpha}$ References 1, 2, and 9 used  $\kappa = \frac{1}{2}$ : the values given here use  $\kappa = 1$ . The values for the activation parameters of PCT are obtained from the program ACTPAR (10) using the data from the three solutions combined.

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FIG. 2. Experimental and observed p.m.r. spectra of  $\alpha, \alpha, 2, 4, 6$ -pentabromotoluene in perchlorobutadiene solution at a few representative temperatures and preexchange lifetimes  $\tau$ .

DBDCT shows that a substituent *para* to the dihalomethyl group has a negligible effect on the barrier height. These conclusions are perhaps expected for barriers originating primarily in steric interactions between substituents *ortho* to the dihalomethyl group and the substituents on this group.

The entropies of activation for the hindered rotations are small and negative, indicating perhaps a loss of vibrational contribution to the entropy in the more sterically crowded, and hence rigid, transition state conformations.

The free energy of activation,  $\Delta G^{\pm}$ , increases by about 3 kcal/mol when the chlorine atoms in the  $\alpha$  positions or in the *ortho* positions of PCT are replaced by bromine atoms. On replacing the other chlorine atoms by bromine atoms to give PBT,  $\Delta G^{\pm}$  increases by 1 kcal/mol. The smaller increase on going to PBT possibly means that this molecule has a more crowded, and hence less stable, ground state conformation.

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# (b) Semiempirical Calculations of Conformational Energies

To obtain a deeper insight into the nature of the conformations involved in the rotation about the sp<sup>2</sup>-sp<sup>3</sup> bond, Westheimer's classical model (11-13) was used for calculating conformational energies of DBTCT, DCTBT, and PBT. The energy minimization procedure has been described previously (3). The only parameters that are not included in reference 3 are the three force constants for bond angle deformations<sup>3</sup> at the dibromomethyl group (see 3):  $k(C_1-C_{\alpha}-Br) 0.032$ ,  $k(Br-C_{\alpha}-Br) 0.030$ , and  $k(Br-C_{\alpha}-H) 0.026$  kcal/mol/deg<sup>2</sup>; and the  $f_{ij}$ and  $g_{ij}$  values for nonbonded interactions given in Table 4.



For all four compounds it was evident from the calculations that the most stable conformation is **a** with  $\omega = 0^{\circ}$ , *i.e.* the C<sup> $\alpha$ </sup>—H bond is coplanar with the aromatic ring. This is in accord with the experimental findings, *viz.* the large long-range spin-spin coupling between the methine and one of the *meta* protons, the zero coupling between the methine and *para* protons in compounds where there is no substituent in the 4-position, and the downfield shift of the methine proton.

The calculations show that the sum of the two repulsive X...Y interactions in **d** over dihedral angles of  $30^{\circ}$  is more severe than the

<sup>3</sup>These force constants were estimated by comparison with related compounds (3, 14).

i	j	$10^{-4} f_{ij}$ (kcal mol <sup>-1</sup> Å <sup>12</sup> )	(kcal mol <sup>-1</sup> Å <sup>6</sup> )
Cl	Bralinh	401.03	3563
Cl	Brarom	449.75	3563
$Br_{arom}$	$\mathbf{Br}_{aliph}$	716.85	5109

TABLE 4. Constants  $f_{ij}$  and  $g_{ij}$  describing the nonbonded interaction between atoms i and j for a 6-12 potential

single interaction in  $\mathbf{c}$  over a dihedral angle of 0°. A very large portion of the strain that would occur in  $\mathbf{c}$  for rigid rotation is actually avoided by opening of bond angles.

The calculated barriers should be compared to  $\Delta H^{\dagger}$  because the Westheimer method does not take into account entropy effects. As can be seen from Table 3 the right order of magnitude is reproduced by the calculations: PCT has the lowest barrier; DBTCT and DCTBT have almost identical activation parameters and lie in the middle; PBT is the highest one. In all of the compounds the shape of the barrier to internal rotation from 0 to 180° is of a very simple type with a single maximum at 90° and minima at 0 and 180°. The type of energy curve having maxima at 60 and 120°, low minima at 0 and 180°, and a high energy minimum at 90° can be ruled out (see a-d). This finding demands the use of a transmission coefficient of unity in the determination of experimental activation parameters.

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