Applications of Proton Magnetic Resonance to Rotational Isomerism in Halotoluene Derivatives. V. α,α,α',α',2,3,5,6-Octachloro-*p*-xylene, Semiempirical Barrier Calculations

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In toluene- d_8 solution the p.m.r. spectrum of $\alpha, \alpha, \alpha', \alpha', 2, 3, 5, 6$ -octachloro-*p*-xylene at temperatures below -25 °C consists of two sharp peaks corresponding to the two conformations in which the methine protons lie *cis* and *trans* to each other in the plane of the aromatic ring. The barrier to rotation of the dichloromethyl groups is derived from a line-shape analysis of the rate-dependent spectra using the computer program ABXFIT. The activation parameters are $E_A = 13.6 \pm 0.4 \text{ kcal/mol}, \log A = 11.3 \pm 0.3, \Delta H \ddagger = 13.1 \pm 0.4 \text{ kcal/mol}, \Delta S \ddagger -7.3 \pm 1.3 \text{ e.u.}, \Delta G \ddagger = 15.4 \text{ kcal/mol} at 286 °K.$ The quoted errors are standard errors from least squares fits. These parameters are compared to the extensive data known for $\alpha, \alpha, 2, 4, 6$ -pentachlorotoluene. A series of barrier calculations, based on modified Buckingham and on van der Waals potential energy functions, are discussed with reference to various halotoluenes.

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Introduction

In previous studies (1–3) of the barrier to rotation about the sp²-sp³ carbon-carbon bond in $\alpha,\alpha,2,4,6$ -pentachlorotoluene (PCT) and α,α dichloro-2,4,6-tribromotoluene (DCTBT), various spectral types and line-shape analyses were used to establish the probably small and negative entropies of activation for the rotation as well as the conformations of the unactivated molecules. In this study, a similar investigation is carried out for $\alpha,\alpha,\alpha',\alpha',2,3,5,6$ - octachloro - *p* - xylene (POCX) and is briefly described. In addition, a moderately successful barrier calculation is carried out for PCT and similar molecules using the modified Buckingham and van der Waals potential energy functions (4–6).

Experimental

The POCX was prepared by chlorination of 2,3,5,6tetrachloro-*p*-xylene and was also obtained from Aldrich Chemical Company. A 3 mol % solution of POCX in toluene- d_8 was degassed by the freeze-pump-thaw technique and tetramethylsilane (TMS) served as an internal reference and lock signal.

The p.m.r. measurements were made on an HA-100D spectrometer in the frequency sweep mode. Frequency calibrations were obtained by a period averaging technique. Variable temperature work involved the V4341/V6057 accessory and temperature calibrations were based on thermocouple measurements in a dummy toluene sample. All spectra were recorded at a sweep rate of 0.02 Hz/s.

Results and Discussion

(1) Determination of Rate Constants (a) General Remarks

In the low temperature region the spectrum consists of two sharp peaks, of *equal* intensity within experimental error, which are attributed to 1 and 2. The C—H bonds lie in the plane of the



ring in 1 and 2 as expected on the basis of the behavior of PCT (1, 2) and on the basis of potential barrier calculations described below. At higher temperatures the peaks broaden and eventually collapse to a single sharp peak. The equal populations of 1 and 2 are somewhat surprising because 1 is expected to have a finite dipole moment² and therefore a higher stability

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²A 3 mol % solution of POCX in the polar solvent CH₂ClBr (dielectric constant = 8.5) also displayed two peaks of equal intensity with an internal shift at -15 °C of 3.6 Hz. Solubility problems at lower temperatures did not allow a determination of the intrinsic temperature dependence of the shift. The small shift of 3.6 Hz made an accurate determination of other than ΔG_{τ}^{z} very difficult (small temperature range).

in a solvent of dielectric constant greater than unity. On the other hand, it is likely that **1** is less stable than **2** because of steric strain arising from the dichloromethyl group orientation in **1**. It may be that the two opposing causes fortuitously cancel in POCX.

(b) Solvent Effects on the Internal Chemical Shift

The well-known solvent shifts induced by aromatic solvents vary with temperature (7) and, as described for PCT(1), must be accounted for before a proper line-shape fit can be made. Below -4 °C the exchange rate is slow enough to cause little shifting of the two peaks. An assumed linear decrease of the internal shift as the temperature increases between -39 and -4 °C gave the least squares eq. 1 (r = 0.9863). Rate-independent

[1] internal shift (Hz) = $0.0438 \pm 0.002T(^{\circ}C)$

+ 7.118 \pm 0.075

shifts were calculated at higher temperatures using eq. 1 in a manner similar to that described for PCT (1). The internal shift in absence of exchange varies from 8.84 Hz at -39.3 °C to 4.21 Hz at 66.5 °C.

(c) Line-shape Fitting Procedure

Line-shapes were fitted as before (1) to theoretical spectra generated by the computer program ABXFIT (1), based on a proper density-matrix treatment of the exchange process. The effective T_2 values were determined from the width at half-height of a weak impurity peak arising from $\alpha, \alpha, \alpha', \alpha', \alpha', 2, 3, 5, 6$ - nonachloro - *p* - xylene. This width could be kept constant at 0.185 \pm 0.02 Hz over the temperature range and yields $T_2 =$ 1.72 s.

The rate constants k ranged from 185 s^{-1} at 52.3 °C to 0.0535 s⁻¹ at -35 °C, a change of more than a factor of 10^3 .

(2) Derivation of Activation Parameters

Plots of log k vs. 1/T (r = 0.9964) gave the activation energy and the frequency factor. A plot of log k/T vs. 1/T (8) is shown in Fig. 1 (r = 0.9961) from which the enthalpy of activation, ΔH^{\ddagger} , and the entropy of activation, ΔS^{\ddagger} , were derived. The parameters are $E_A = 13.6 \pm 0.4$ kcal/mol, log $A = 11.3 \pm 0.3$, $\Delta H^{\ddagger} = 13.1 \pm 0.4$ kcal/mol, $\Delta S^{\ddagger}_{\ddagger} = -7.3 \pm 1.3$ e.u., $\Delta G^{\ddagger}_{\ddagger} = 15.4 \pm 0.1$ kcal/mol at 286 °K. The errors are



FIG. 1. A plot of log (k/T) vs. 1/T for the internal rotation in $\alpha, \alpha, \alpha', \alpha', 2, 3, 5, 6$ -octachloro-*p*-xylene. The error bars reflect the estimated error in the rate constant derived from the line-shape analysis at various temperatures. The least squares line is drawn.

standard errors from the least squares fits. In CH₂ClBr we found $\Delta G^{\ddagger}_{\ddagger} = 15.2 \pm 0.1$ kcal/mol at 286 °K. The values for PCT in methylcyclohexane, toluene- d_8 , and carbon disulfide solutions (2) are $E_A = 14.2 \pm 0.3$ kcal/mol, log $A = 11.9_5 \pm 0.2$, $\Delta H^{\ddagger}_{\ddagger} = 13.7 \pm 0.3$ kcal/mol, $\Delta S^{\ddagger}_{\ddagger} = -4.4 \pm 1.0$ e.u., and $\Delta G^{\ddagger}_{\ddagger} = 15.1 \pm 0.1$ kcal/mol at 286 °K.

(3) Discussion of Activation Parameters

Within experimental error the activation parameters are nearly equal for PCT and POCX. Yet the barrier calculations below indicate that if normal bond angles are maintained throughout the rotation of the dichloromethyl group in PCT, the barrier should be considerably greater than the experimental values. Consequently a certain degree of bond bending probably occurs in order to relieve the repulsive interactions and thereby lowers the barrier. In PCT the ring substituents in the ortho positions are relatively free to relieve

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the strain but in POCX a further source of steric hindrance is met in the adjacent chlorine ring substituents.

Conformational calculations show that 2,3,5,6tetrahalosubstitution of the benzene nucleus introduces considerable distortion of the bond angles in the plane of the ring (9). The calculated equilibrium conformation of 2,3,5,6-tetrachlorobenzene has an adjacent chlorine–chlorine internuclear distance of 3.18 Å whereas the equilibrium van der Waals distance for chlorine– chlorine is 3.60 Å (10). Steric interactions of this nature very likely raise the ground state of the tetrachloro structure relative to the 2,6-dichloro structure.

It would appear, therefore, that the ground state energy of POCX is raised by more than its transition state energy, leading to an equal or slightly lower energy barrier than in PCT. It is tempting to suggest that the transition state in POCX will be more crowded than in PCT, thus rationalizing a tendency towards a somewhat more negative ΔS^{\ddagger} in POCX. The transition state in both molecules has eclipsed Cl–Cl interactions (see below).

In summary, the rate of rotation of the dichloromethyl group is not significantly different at any given temperature in POCX and PCT. Any "buttressing" effect of the ring chlorine atoms apparently does not dramatically alter the nature of the internal rotation.

(4) Semiempirical Barrier Calculations(a) The Potential Functions

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Molecular orbital methods are not at present suitable for the calculations of barriers to internal rotation in molecules containing halogens (11). Therefore, following Jonas *et al.* (6) and, on the assumption that the largest part of the rotational barrier arises from the pair-wise, nonbonded steric and electrostatic interactions between the dichloromethyl group and the ortho ring substituents (4), two separate potential energy functions were used. In eqs. 2 (modified Bucking-

2]
$$V(\theta) = \sum_{j} A_{j} \exp(-B_{j}r_{j}) - C_{j}/r_{j}^{6} + D_{j}/r_{j}$$

[3]
$$V(\theta) = \sum_{i} A_{i} \exp(-r_{i}/P_{i})$$

ham potential) and 3 (van der Waals function)

each summation is over the *j*th pair of atoms and r_i is the internuclear distance.

Equation 2 was applied in the form developed by Scott and Scheraga (4). The parameters A, B, and C are the normal ones for the six-exponential potential (12–14). The constant D enters as the dipole moment contribution (15). Equation 3 was employed as described by Howlett (5) and the interaction constants A_j and P_j , including Br–Cl, F–Cl, and Br–F interactions as estimated by the geometric mean method (4, 15) are tabulated in ref. 16.

(b) Computational Method

The computation of the barrier involved the determination of six internuclear distances, *i.e.*, the distance of each ring substituent to each of the three methyl group substituents for each degree of the rotation, and applying these distances to the designated function. The bond lengths were taken from data available for analogous compounds (17).

Two programs were written in Fortran IV for use on an IBM 360/65 computer. One program, POTL1, was designed to handle asymmetric ring substitution and the other, POTL2, handles symmetric substitution. For example, for the compound, $\alpha, \alpha, 2, 6$ -tetrachlorotoluene, the input parameters include the C--Cl bond length of the ring, the C-Cl bond length of the methyl group substituent, and the methyl C—H bond length in Å. Depending upon the choice of potential function, one requires the appropriate interaction constants for the Cl-Cl and Cl-H interactions. The value of the potential energy in kcal/mol is output for each degree of rotation about the sp²-sp³ carbon-carbon bond and can be had as data on the line printer and/or as a Calcomp plot. Both programs in their present form require that two of the methyl substituents be the same, although three different substituents on the methyl rotor could be accommodated by a modest modification.

In realization of the probable importance of bond bending in the rotation process, a rather naive approach (necessary to retain simplicity in the computing) consisted of repetition of the calculation after changing from normal bond angles³ of all bonds to a geometry where all bonds

³Normal bond angles in this context refer to $109^{\circ} 28^{\prime}$ at the sp³ carbon, and 120° at sp² carbon, atoms.



FIG. 2. The shape of the potential energy barrier to rotation as given by both the modified Buckingham and the van der Waals functions for $\alpha, \alpha, 2, 6$ -tetrachlorotoluene. The values of the barriers A and B are collected in Table 1. The 0° angle of rotation has the C—H bond of the sidechain in the plane of the aromatic ring.

TABLE 1. Values of the energy barriers A and B to rotation for $\alpha, \alpha, 2, 6$ -tetrachlorotoluene*

	van der Waals function		Modified Buckingham function		
Bend†	Barrier A‡	Barrier B	Barrier A	Barrier B	
0	23.087§	7.575	58.748	20.246	
1	18.437	5.837	46.189	15.451	
2	5.643	1.427	15.061	3.569	
3	4.560	1.128	11.996	2,808	
4	3.689	0.896	9.542	2.220	
5	2.987	0.713	7.576	1.764	

*The compound has structure shown below with the following bond lengths: ring C-Cl, 1.71 Å; methyl C-Cl, 1.78 Å; methyl C-H, 1.11 Å.



Comment on the barrier shape: the barrier shape appears in Fig. 2 and is unchanged for 5° of bending. Both potential energy functions indicate the same barrier shape. †Note that bend = 0 refers to the normalbond angle case, bend = 1 to all five bonds involved in the rotational interactions bent back by 1°, etc. ‡All barrier values are in kcal mol⁻¹. §All barrier values are recorded to three decimal places with the realization that the accuracy of the constants does not necessarily warrant this number of significant figures in the final barrier value.

were bent back by a specified number of degrees. Thus, the methyl substituent bonds were bent towards the sp^2-sp^3 bond axis while the ring substituent bonds were bent away from the rotational site but in the plane of the ring.

This treatment of bond bending is in no way rigorous. A more realistic mechanism is more likely that of bond-wagging at points of greatest strain in the rotation and the energy of bond bending, although relatively small, should be

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TABLE 2.	Values of the energy barriers to rotation for						
α,α-dichloro-α,2-diffuorotoluene*							

Bend	van der Waals function			Modified Buckingham function	
	Barrier A†	Barrier B	Barrier C	Barrier A	Barrier B
0	1.362	2.316	2.871	2.818	3.481
1	1.113	2.012	2.357	2.600	2.818
2	0.914	1.751	1.941	2.417	2.286
3	0.754	1.527	1.602	2.262	1.861

*The compound has structure shown below with the following bond lengths: ring C-F, 1.33 Å; ring C-H, 1.04 Å, methyl C-Cl, 1.78 Å; methyl C-F, 1.39 Å.

н

ÇFCl₂



FIG. 3. The shape of the potential barrier to internal rotation as given by the modified Buckingham potential for α, α -dichloro- $\alpha, 2$ -diffuorotoluene. Barrier values at points A and B are given in Table 2. At 0° of rotation the C—F bond of the sidechain eclipses the C—F bond in the ring.

included at these points. Such a treatment would be comparable to one on a dynamic framework but would also require large amounts of computer time.

(c) An Example: PCT Barriers and Conformers

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As an example of the computations, Fig. 2 reproduces the shape of the rotational potential energy barrier for the dichloromethyl group of $\alpha, \alpha, 2, 6$ -tetrachlorotoluene. The zero angle of rotation has the C—H bond of the group in the

plane of the ring. In this case both potential functions yield the same barrier shape. The magnitude of the barrier is different for the two functions and a set of values for different degrees of bond-bending is given in Table 1. The shape of the barrier does not change as the bond angles are bent back.

The two potential functions yield the same results whether or not a chlorine is substituted in position 4 so that the computation is also valid for PCT (and roughly also for POCX). The

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FIG. 4. As in Fig. 3 but for the van der Waals function. Barriers A, B, C are tabulated in Table 2.

experimental barrier of near 14 kcal/mol is reproduced by the van der Waals function for a bond-bend of just over 1° while the Buckingham function would "demand" a bend of just over 2°.

The qualitative result (1) that **3** is the ground state of the molecule and that 4 is not appreciably populated at any of the temperatures up to 400 °K, is well reproduced by the computation.

$$CI-H-CI$$
 $CI-CI$ $CI-CI$ $CI-CI$

Experimentally (3) the barrier in α, α -dibromo-2,6-dichlorotoluene is about 1.5 kcal/mol higher than in PCT. For the bond-bend which reproduces the barrier in PCT, the van der Waals function predicts a barrier about 5 kcal/mol higher in the bromo compound while the Buckingham potential overestimates it by 10 kcal/mol. Of course, the amount of bond bending during the rotation could well be larger in the bromo compound than in PCT.

(d) The Usefulness of the Functions

Computations for a variety of halosubstitution patterns indicate that fluorine or hydrogen substituents lead to barriers which are too small to allow the detection of individual conformers by n.m.r. For example, in Table 2 results for some of the calculations on α, α -dichloro- $\alpha, 2$ -diffuorotoluene are given. The barriers correspond to those drawn in Figs. 3 and 4. Both potential energy functions predict the most stable conformation as one in which the C-F bond of the sidechain eclipses the ortho C-H bond of the ring for normal bond angles (0° bend) and that this conformation is the only one appreciably populated near room temperature. Again, both functions agree in predicting the highest energy for an eclipse of the ring C-F bond by the C--Cl bond in the sidechain. On the other hand, the functions predict different potential shapes in the region of a 20-100° twist of the sidechain C-F bond from its eclipsed position over the C-F bond in the ring.

By using the stereospecificity of the H-H and H-F coupling constants from the sidechain to the ring, it is probable that at least some of these predictions can be verified experimentally. Such experiments are in progress.

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- T. SCHAEFER. Can. J. Chem. 48, 1558 (1970).
 H. G. GYULAI, B. J. FUHR, H. M. HUTTON, and T. SCHAEFER. Can. J. Chem. 48, 3877 (1970).

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^{1.} B. J. FUHR, B. W. GOODWIN, H. M. HUTTON, and

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- W. J. PEELING, T. SCHAEFER, and C. M. WONG. Can. J. Chem. 48, 2839 (1970).
 R. A. SCOTT and H. A. SCHERAGA. J. Chem. Phys. 42, 2209 (1965).
- 42, 2209 (1965).
 5. K. E. HOWLETT, J. Chem. Soc. 1055 (1960).
 6. J. JONAS, L. BOROWSKI, and H. S. GUTOWSKY. J. Chem. Phys. 47, 2441 (1967).
 7. P. LASZLO. *In* Progress in nuclear magnetic resonance spectroscopy. Vol. 3. *Edited by* J. Emsley, J. Feeney, and L. H. Sutcliffe. Pergamon Press, Oxford, 1067 1967.
- 1967.
 G. BINSCH. In Topics in stereochemistry. Vol. 3. Edited by E. Eliel and N. Allinger. Interscience Pub-lishers, New York, N.Y., 1968.
 A. KITAIGORODSKII and V. G. DASHEVSKII. Theor. and Exp. Chem. 3, 22 (1967) (English translation).
 L. PAULING. The nature of the chemical bond. Cornell University Press. Ithaca, New York, N.Y., 1960
- 10. 1960.

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11. M. S. GORDON. J. Amer. Chem. Soc. 91, 3122

795

- H. M. S. GORDON, J. AMEL. CHEM. Soc. 91, 3122 (1969).
 J. O. HIRSCHFELDER, C. F. CURTISS, and R. B. BIRD. Molecular theory of gases and liquids. John Wiley and Sons, Inc., New York, N.Y., 1954.
 I. AMDUR and A. L. HARKNESS. J. Chem. Phys. 22, (1987).
- 664 (1954).
- 14. I. AMDUR and E. A. MASON. J. Chem. Phys. 23, 415 (1955).
- 15.
- 16.
- 415 (1955).
 E. A. MASON and M. M. KREEVOY. J. Amer. Chem. Soc. 77, 5808 (1955).
 B. H. BARBER. M.Sc. Thesis. University of Mani-toba, Winnipeg, Manitoba, 1970.
 L. E. SUTTON, *editor*. Tables of interatomic dis-tances and configurations in molecules and ions. The Chemical Society. London, 1958. 17.