Hindered Rotation in *ortho*-Bis(dichloromethyl)benzenes

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Summary A study of internal rotation in *ortho*-bis(dichloromethyl)benzenes by ^{1}H n.m.r. spectroscopy shows the presence of locked conformers on the n.m.r. time scale when these substituents are flanked on one or both sides by chlorine or additional dichloromethyl groups, and that in cases where a chlorine is substituted on both sides of two *ortho*-bis(dichloromethyl)groups $\Delta G^\ddagger$ at T_c is 17·4—17·7 kcal mol^{-1}.

3,4,5,6-TETRACHLORO-1,2-BIS(DICHLOROMETHYL)BENZENE (**1**) displayed in its n.m.r. spectrum at ambient temperature two sharp singlets of equal intensity at δ 7·63 and 8·00 p.p.m. in deuteriochloroform solution, thus indicating hindered rotation about the sp^2–sp^3 carbon–carbon bonds. A similar spectrum was also obtained with 3,6-dichloro-1,2-bis(dichloromethyl)benzene (**2**). Their temperature dependent behaviour gave rotational barriers[1] for the dichloromethyl substituents (Table).

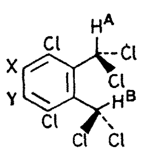
TABLE

N.m.r. and thermodynamic parameters for internal rotation of adjacent dichloromethyl groups in chlorocarbons (**1**)—(**4**)

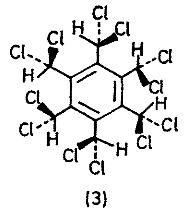
Compound	Chemical shifts[a] at ambient temp.[b] H^A	H^B	at 140° $H^A = H^B$	T_c°	$\Delta G^\ddagger$ (T_c)[d] kcal mol^{-1}
(**1**)	7·54	7·98	7·70	83	17·7
(**2**)[c]	7·47	7·96	7·66	77	17·4
(**3**)		8·32[e]	8·34[f]	>180	
(**4**)		7·90	7·97	>225	

[a] In p.p.m. to low field from internal tetramethylsilane; n-tetradecane solution. [b] Temperature of the sample 29 ± 2°. [c] At ambient temperature $\delta_X = 7{\cdot}14$, $\delta_Y = 7{\cdot}23$ p.p.m. and $J_{XY} = 9{\cdot}5$ Hz; at 140° $\delta_X = \delta_Y = 7{\cdot}11$ p.p.m. [d] A transmission coefficient of unity was assumed. [e] Deuteriochloroform solution. [f] Hexachlorobutadiene solution.

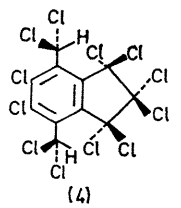
These data show that the free energy barrier to rotation of two adjacent dichloromethyl groups flanked on both sides by chlorine substituents is significantly higher than that of a single group situated between two chlorines (14·8—15·0 kcal mol^{-1}).[2] In hexakis(dichloromethyl)benzene, (**3**), in which the very low field singlet n.m.r. peak suggests a locked conformation corresponding to H^B in (**1**), we found essentially no change in the n.m.r. spectrum up to 180°, nor did we in the polychloroindan derivative (**4**).



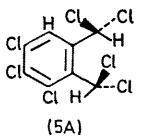
(1) X=Y=Cl
(2) X=Y=H
(6) X=H Y=Cl



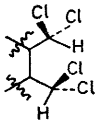
(3)



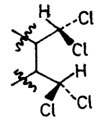
(4)



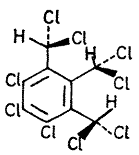
(5A)



(6A)



(6B)



(7)

The n.m.r. pattern at ambient temperature of two dichloromethyl groups as in (**1**)—(**3**), indicating locked conformation on the n.m.r. time scale, seems characteristic. When the dichloromethyl groups are replaced by monochloromethyl or monobromomethyl groups, the multiplicity of the lines vanishes at ambient temperature [3,4,5,6-tetrachloro-1,2-bis(monochloromethyl)benzene, δ 4·89; 3,4,5,6-tetrachloro-1,2-bis(monobromomethyl)benzene, δ 4·72; 3,4,5,6-tetrabromo-1,2-bis(monobromomethyl)benzene, δ 4·84 p.p.m.] as it does when even only one of the dichloromethyl groups in (**1**) is replaced by a monochloromethyl group. Thus 3,4,5,6-tetrachloro-1-dichloromethyl-2-monochloromethylbenzene yields a spectrum at 28° with only single peaks for each of the substituents, at δ 7·62 and 5·23 p.p.m., the broadness of which, however, indicates a not too distant coalescence temperature. Under the same conditions polyhalogeno-*ortho*-bis(monohalogenomethyl)benzenes yield single, narrow, sharp resonance lines, indicating free internal rotation.

Without at least one adjacent bulky (chlorine) substituent, two *ortho*-dichloromethyl or dibromomethyl, groups on the benzene nucleus display a single n.m.r. peak in their ambient temperature spectra. The presence of one flanking chlorine, however, produces the characteristic patterns described above. Thus, although 3,4,5-trichloro-1,2-bis(dichloromethyl)benzene (**5**) displays at 28° in its n.m.r. spectrum the three equal area absorptions expected from its unsymmetrical structure in a freely internally rotating state, the presence of one highly deshielded peak at 8·08 p.p.m. suggests the presence of a "locked" structure (on the n.m.r. time scale). The nearness of the coalescence temperature, however, is indicated by the broadness of both methine proton signals (δ 8·08 and 7·71 p.p.m., width at half height, $\Delta\nu_{1/2}$ 35 m.m. on the 50 Hz sweep width enlargements; the aromatic signal at δ 7·48 p.p.m. is relatively narrow, $\Delta\nu_{1/2}$ 12 m.m.). The presence of only one locked conformer, presumably (**5A**), thus distinguishes (**5**) from (**6**), but seems reasonable due to the uneven steric factors adjacent to the *ortho*-bis(dichloromethyl) functions.

Especially interesting are examples in which the aromatic nucleus is unsymmetrically substituted. The n.m.r. spectrum at ambient temperature of 3,4,6-trichloro-1,2-bis(dichloromethyl)benzene (**6**) shows *two* aromatic and *four* substituent protons, (at δ 7·388 and 7·398, and at 7·505, 7.525, 7·906, and 7·953 p.p.m. in n-tetradecane), which are present in equal intensities. The n.m.r. spectrum thus indicates that at ambient temperature (**6**) contains the two distinct stereoisomers, (**6A**) and (**6B**).

A similar n.m.r. pattern was also observed with the unsymmetrical 3,5,6-trichloro-1,2,4-tris(dichloromethyl)-benzene whereas the superficially 'symmetrical' 4,5,6-trichloro-1,2,3-tris(dichloromethyl)benzene exhibited two highly deshielded (δ 8·16 and 8·08) and one 'normal' (δ 7·68 p.p.m.) dichloromethyl resonances, thus indicating the locked conformation (**7**) for this compound at ambient temperature.

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[1] G. Binsch, in 'Topics in Stereochemistry', vol 3, p. 97; ed. E. L. Eliel and N. L. Allinger, Interscience, New York, **1968.**

[2] H. G. Gyulai, B. J. Fuhr, H. M. Hutton, and T. Schaefer, *Canad. J. Chem.*, **1970**, **48**, 3877 and references therein.