Halogeno-1,4-dioxans and their Derivatives. Part VII.[1] Conformations and ^{1}H Nuclear Magnetic Resonance Parameters of Some Chloro-1,4-dioxans and 5-Chloro-2,3-dihydro-1,4-dioxin

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^{1}H N.m.r. parameters have been obtained for 5-chloro-2,3-dihydro-1,4-dioxin, and for 2-chloro-, 2,2-dichloro-, 2,2,3-trichloro-, and for two 2,3,5,6-tetrachloro-1,4-dioxans of m.p.s 142 and 70°; some anomalies are observed regarding long range shielding by chlorine. The fourth and sixth of these have rigid conformations, that of the last being in agreement with previous findings for the solid. New preparations of 4,4',5,5'-tetrachlorobi-1,3-dioxolan-2-yl from a di- and a tetra-chloro-1,4-dioxan are reported.

THERE has been confusion concerning the conformations, and sometimes the configurations, of certain 1,4-dioxans. Thus for *cis*-2,3-dichloro-1,4-dioxan a rigid boat was first proposed [2] with the chlorine atoms diequatorial and

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[1] Part VI, L. A. Cort, B. C. Stace, and D. P. C. Thackeray, *J.C.S. Perkin I*, 1972, 177.

[2] E. Caspi, T. A. Wittstruck, and D. M. Piatak, *J. Org. Chem.*, 1962, **27**, 3183.

eclipsed, but it was shown subsequently[3-6] that a mixture of interconverting chair forms is involved. 2,3-Diphenyl-1,4-dioxan, m.p. 130—132°, was thought[2] to exist in a rigid boat conformation with the phenyl groups in axial positions; later[3] it was thought that the isomer had the *trans*-configuration, but it has since become apparent[6] that the substituents are *cis* with the molecule undergoing rapid interconversion between chair forms. Hexahydro-1,4-dioxino[2,3-*b*][1,4]dioxin, m.p. 128—132°, was thought[2] to be of the rigid *trans*-fused chair form, but later analysis showed[6] it to be a mobile molecule with *cis*-fusion.

Contributing to this confusion was the non-rigorous analysis of complex n.m.r. spectra, and the situation improved considerably when rigorous analysis became possible, the n.m.r. results then agreeing with and complementing analyses by dipole moment measurement and by *X*-ray crystallography. Accordingly we have made computer analyses of the ^1H n.m.r. spectra of two 1,4-dioxans and a 1,4-dioxen to establish unequivocally some more n.m.r. parameters in this series.

5-Chloro-2,3-dihydro-1,4-dioxin has the half-chair conformation interconverting rapidly with its mirror image as shown by observation of an AA'BB' spectrum from the ethylene system. The appropriate constants extracted using the LAOCOON 1968 program[7] are: τ (C_6D_6) 6·51 and 6·66 (J' 5·6, J 2·3 Hz), and τ ($CDCl_3$) 5·82 and 6·00 (J' 5·6, J 2·3 Hz), with the computer spectra insensitive to the values of geminal coupling constants used ($-14{\cdot}0$ Hz $< J_A = J_B < -10{\cdot}0$ Hz).

A similar spectrum from 2,2-dichloro-1,4-dioxan yields τ ($CDCl_3$) 5·87 and 6·19 (J' 6·5 Hz, J 3·0 Hz), with the couplings agreeing well with those for similar cases.[4-6,8] It is to be noted that even with a knowledge of the computer-obtained results, these spectra cannot be analysed by the method of Abraham, although this has proved worthwhile for some similar cases.[9]

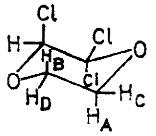
Since *trans*-2,3-dichloro-1,4-dioxan exists in solution[2,10] and in the crystal[11] in a rigid chair conformation with the chlorine axial, it is resonable to expect that substitution of the C(2) equatorial proton by chlorine would be accomplished without any significant change in conformation, and the n.m.r. spectra of the 2,2,3-trichloro-compound analyse consistently for such a conformation [(I), together with its mirror image]. An iterative procedure could be used with this analysis[7] and the results are shown in the Table; the experimental and theoretical spectra for carbon tetrachloride solution are shown in the Figure.

Compared with *trans*-2,3-dichloro-1,4-dioxan[5] the only proton of the ethylene group appreciably affected by the equatorial chlorine atom at C(2) is the C(6) equatorial proton (H_C), the signal appearing downfield by 0·3 p.p.m. for carbon tetrachloride solution. The coupling constants (estimated error $\pm 0{\cdot}3$ Hz) compare very favourably with others reported[2,4,5,10,12] for rigid chair conformations of 1,4-dioxans.

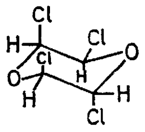
^1H N.m.r. parameters for 2,2,3-trichloro-1,4-dioxan (I)

	Chemical shift (τ)	
Proton	CCl_4	C_6H_6
H_A	5·59	6·25
H_B	5·62	6·26
H_C	5·99	6·81
H_D	6·30	7·12
Coupling constant		
J_{AB}/Hz	11·6	11·6
J_{AC}/Hz	−11·9	−12·0
J_{AD}/Hz	3·6	3·7
J_{BC}/Hz	3·5	3·3
J_{BD}/Hz	−12·4	−12·3
J_{CD}/Hz	0·87	0·98

Theory requires five stereoisomers for the 2,3,5,6-tetrachloro-1,4-dioxans, with three of them incapable of existence in optically active forms. All five are known,



(I)



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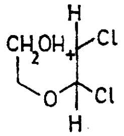

(III)

and four of these, and hence also the fifth, have been identified[2,13-15] by consideration of *X*-ray diffraction and some n.m.r. and dipole moment data. [In ref. 15 the m.p.s of the isomers are not given, but they are[16] (18) 142, (19) 101, (20) 70, and (21) 55°.]

The isomer, m.p. 101°, has the *trans-syn-trans*-configuration and in the crystal has the chair conformation with chlorine atoms exclusively axial.[14] However, the i.r. absorption is different in solution from that in the solid state.[13]

In deuteriochloroform a mixture of the two isomers of m.p. 101 and 142° shows an unresolved singlet at τ 3·93. (For the former compound a value of τ 3·89 has previously been reported.[2]) In a 1 : 1 mixture of acetone–diethyl ether, an unequal mixture of the two compounds gives a single response at τ 3·67; as the temperature is lowered from room temperature both signals move downfield, but at unequal rates. That from the isomer of m.p. 101° remains as a singlet which has shifted to τ 3·21 at −90° and which does not move further as the temperature is lowered to −100°. The signal from the isomer, m.p. 142°, begins to broaden at −70°, and at −90° has

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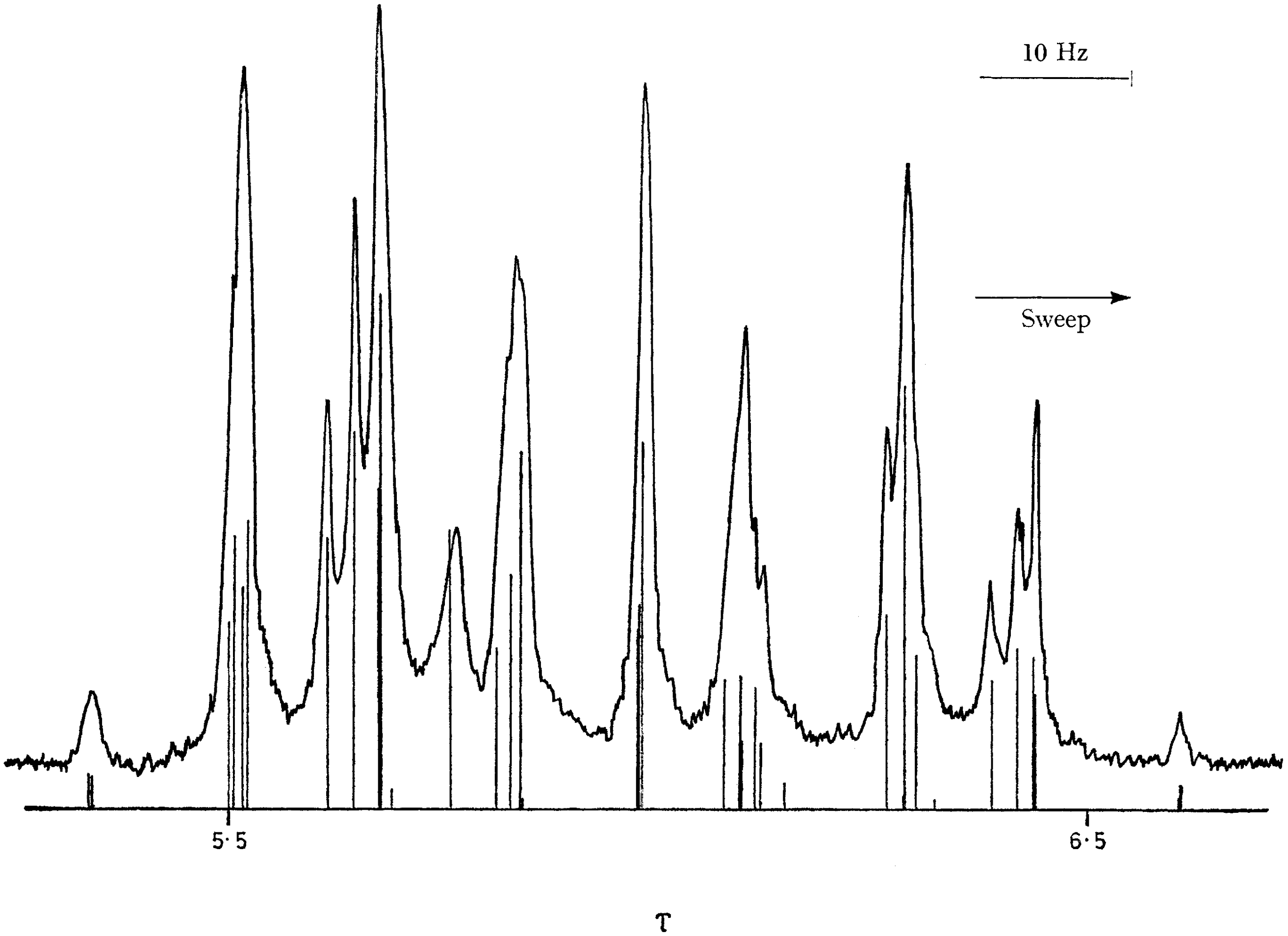
[16] C. Altona, personal communication.

separated into a pair of doublets (AB q, *J ca.* 2 Hz) at τ 3·38 and 3·47; there is no further change down to —100°.

This behaviour is as expected for the *cis-anti-cis*-isomer, m.p. 142°, and at room temperature there is interconversion between identical chair forms, and clearly the *trans-syn-trans*-isomer, m.p. 101°, also produces an equilibrium mixture at room temperature, the new form having the chair conformation with the chlorine atoms exclusively equatorial. For the latter compound the position of equilibrium is not known, thus the coincidence of n.m.r. signals, above, is fortuitous and the value of τ 3·89 (τ 3·93), previously identified[2] as that for the exclusively equatorial protons in deuteriochloroform solution obviously is not correct.



The $-CH_2-CH-$ part of the 60 MHz ^1H n.m.r. spectrum (CCl_4 solution) of 2,2,3-trichloro-1,4-dioxan, and the theoretical spectrum

In the case of the 2,3,5,6-tetrachloro-1,4-dioxan, m.p. 70°, the 60 MHz ^1H n.m.r. spectrum for deuteriochloroform solution approaches first order, and the 100 MHz spectrum yields chemical shifts and coupling constants by inspection. These are τ 3·85 (*J* 0·6, 2·25 Hz), 3·91 (*J* 0·6, 0·6, 2·35 Hz), 4·14 (*J* 0·35, 0·6, 2·25 Hz), and 4·26 (*J* 0·35, 2·35 Hz); the two vicinal coupling constants (2·25 and 2·35 Hz) were ascertained from a 220 MHz spectrum.

Four different chemical shifts, together with existence of long-range coupling, leads to the conclusion that the molecule in solution is the *cis-trans*-isomer with a rigid conformation. Of the two possibilities only one will have approximately equal dihedral angles for the C–H bonds in each ethylene system. This is structure (II) (together with its mirror image).

This represents an independent assignment of configuration and conformation which is an agreement with *X*-ray diffraction analysis;[15] however it is not possible to identify the individual protons giving rise to the separate n.m.r. signals because a factor must here be considered which is usually ignored.

This factor can be appreciated by considering 2,2,3-tri- and 2,3,5,6-tetra-chloro-1,4-dioxan, m.p. 70°, and comparing the chemical shift values for equatorial protons with that for H(2) in *trans*-2,3-dichloro-1,4-dioxan, when it emerges that an upfield shift of 0·1 p.p.m. (carbon tetrachloride solutions) occurs on introduction of adjacent equatorial chlorine, and a similar shift of at least 0·1 p.p.m. (deuteriochloroform solutions) occurs when two chlorine atoms are introduced on C(5) and C(6).

For rigid saturated systems, the long-range effect of chlorine can be accounted for by consideration of the anisotropy of the magnetic suceptibility and the action of the electric dipole moment of the C–Cl bond(s). In practice only the latter effect need be invoked to explain the relative chemical shifts; quantitative correlation improves only slightly when both effects are considered.[17] Although it is possible in theory for the electric dipole moment effect to be positive or negative, the observed effect is negative. However, the magnetic suceptibility, when measured, has been found to be positive, so that it is possible that the overall effect can be one of shielding. This may be the cause of the results above and also the recent similar findings[18] for the 1,2,3,4,5,6-hexachlorocyclohexanes. Fuller investigation is needed before the long-range effect of chlorine can be predicted with certainty.

When *trans*-2,3-dichloro-1,4-dioxan reacts with concentrated sulphuric acid at least two products are formed[19,20] which are stereoisomers of 4,4′,5,5′-tetrachlorobi-1,3-dioxolan-2-yl. One of these products,[1,20] m.p. 137—139°, has been shown to be a stereoisomer where the chlorine atoms are *trans* in each ring, and possible mechanisms of formation have been considered.[1] Further work shows that both *cis,trans*-2,3,5,6-tetrachloro-, m.p. 70°, and *cis*-2,3-dichloro-1,4-dioxan (m.p. 52°) separately react with concentrated sulphuric acid at room temperature to give the bidioxolanyl, m.p. 137—139°.

The new factor which conflicts with the suggested mechanism is that the *cis*-dichloro-compound is a satisfactory precursor. The simplest suggestion to account for this is that isomerisation occurs, of chlorine *cis* to *trans*, either in the starting material or in the product, and protonation of the dioxan followed by ring opening to give ion (III) could lead to isomerisation since re-establishment of the ring would presumably be governed by the configuration of the adjacent carbon atom. The *trans*-isomer is the more stable, and isomerisation induced by aluminium trichloride is known.[21]

The tetrachlorodioxan, m.p. 142°, failed to yield any of the bidioxolanyl; this isomer was insoluble in the sulphuric acid.

EXPERIMENTAL

M.p.s are uncorrected. The n.m.r. spectra were obtained at 34° using a Perkin-Elmer R10 60 MHz spectrometer.

trans-2,3-Dichloro-1,4-dioxan[21] had m.p. 30—31°, $\nu_{\max.}$ 875 cm^{-1} with no absorption at 948 cm^{-1}. The *cis*-isomer had m.p. 52—53° (from n-pentane), $\nu_{\max.}$ 948 cm^{-1} and no absorption at 875 cm^{-1}, τ (CDCl$_3$) 4·04. 5-Chloro-2,3-dihydro-1,4-dioxin[21] had b.p. 52° at 14 mmHg, $\nu_{\max.}$ 840, 884, 923s, 997, 1 073, 1 115s, 1 148s, 1 243, 1 275, 1 308m, 1 380, 1 463, 1 670m, 2 900, 2 950, and 3 000 cm^{-1}, τ (CDCl$_3$) 3·96, τ (C$_6$H$_6$) 4·04 (=CH–). 2,2-Dichloro-1,4-dioxan[22] had b.p. 45—50° at 4 mmHg. On distillation no fraction could be obtained which did not contain an appreciable amount of 5-chloro-2,3-dihydro-1,4-dioxin. Spectral determinations were carried out on the material obtained before distillation, the n.m.r. spectrum showing the absence of any significant amounts of impurity. It had $\nu_{\max.}$ 822s, 893s, 957s, 1 050s, 1 077s, 1 160, 1 232, 1 265m, 2 900m, and 3 000 cm^{-1}, τ (CDCl$_3$) 6·06, τ (C$_6$H$_6$) 6·39 (3-H$_2$). 2,2,3-Trichloro-1,4-dioxan[22] had b.p. 59—61° at 0·7 mmHg, $\nu_{\max.}$ 690s, 780, 817, 883s, 936, 970s, 1 038m, 1 053s, 1 109s, 1 138, 1 250, 1 275m, 1 460m, 2 890, 2 950, and 3 000 cm^{-1}, τ (CCl$_4$) 4·13, τ (C$_6$H$_6$) 4·40 (3-H).

2,3,5,6-*Tetrachloro*-1,4-*dioxans*.—The *cis-trans*-isomer,[23] m.p. 70°, had $\nu_{\max.}$ (CCl$_4$) 894, 910m, 960s, 984, 1 028m, 1 058, 1 081m, 1 119s, 1 145s, 1 229, 1 280m, 1 325m, 1 344m, 1 362, 1 460, 2 850, 2 910, and 3 000 cm^{-1} (only the absorption at 1 058 cm^{-1} is absent[24] for KBr disc). The 100 MHz n.m.r. spectrum was obtained on a Varian HA 100 spectrometer, and the 220 MHz spectrum on the spectrometer operated by I.C.I. Limited (Runcorn).

The *trans-syn-trans*-isomer,[25] m.p. 101°, had $\nu_{\max.}$ (CCl$_4$) 880m, 918s, 972m, 1 008m, 1 050m, 1 088m, 1 103, 1 152s, 1 230, 1 272, 1 323s, 1 391m, 1 458, 2 850, 2 910, and 3 000 cm^{-1} (*cf.* ref. 13). The *cis-anti-cis*-isomer,[23] m.p. 142°, had $\nu_{\max.}$ (CCl$_4$) 898s, 978s, 1 023, 1 120s, 1 140, 1 280s, 1 339s, 1 396, 1 460, 2 910, and 3 000 cm^{-1} (*cf.* ref. 13).

Interactions with Sulphuric Acid.—The tetrachlorodioxan of m.p. 70° (1·0 g) was added to concentrated acid (5 ml). After stirring for 18 h the mixture was poured on to ice and the solid recrystallised from pentane to give 4,4′,5,5′-tetrachlorobi-1,3-dioxolan-2-yl[1] (0·22 g), identified by m.p., mixed m.p. (137—139°), and i.r. absorption.

The tetrachlorodioxan of m.p. 142° (2·0 g) was added to concentrated acid (7 ml) and stirred and gently heated (<50°) for 8 h. After pouring onto ice only starting material (0·2 g) was isolated, m.p. and mixed m.p. 142°.

cis-2,3-Dichloro-1,4-dioxan (3·0 g), m.p. 52°, was treated as for the tetrachlorodioxan of m.p. 70°. After 2 h the clear solution had darkened considerably and was poured onto ice, to yield the bidioxolanyl (0·40 g), identified as above.

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