

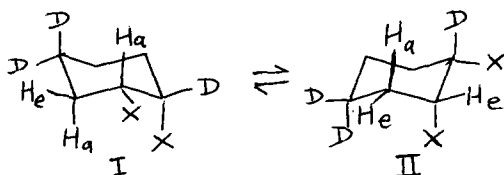
THE CONFORMATIONS OF THE CIS AND TRANS-1,2-CYCLOHEXANEDIOLS  
AND CERTAIN OF THEIR DERIVATIVES

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Nuclear magnetic resonance spectroscopy (n.m.r.) is ideally suited as a method for studying conformational equilibria in solution (1), but few cases have been reported where the magnitudes of coupling constants have been used to deduce conformational equilibria. 1,4,4-Trideuteriocyclohexene (2) was converted to the cis and trans diols, and the n.m.r. spectra of these compounds and their O-isopropylidene, di-O-acetyl and di-O-tosyl derivatives were determined. The protons at the 2 and 3 positions constituted ABX spectra, and although the AB part of the spectra were overlapped by other signals, the chemical shifts of the A and B nuclei and  $J_{AB}$  could be determined by spin decoupling at 100 M.c.p.s. (2). The spectral parameters determined at 100 M.c.p.s. are reported in Table 1. It is seen that for the trans-compounds, the chemical shift was sufficiently large for the spectra to closely approximate the first order AMX condition. However this was not the case for the cis-compounds and the coupling constants were necessarily derived by iterative calculations to obtain

values which would account for the spacings observed at both 60 and 100 M.c.p.s. in the X-signal (2-hydrogen) of the ABX system. An inspection of a conformational model allows the conclusion that the dihedral angles defined by the 2-hydrogen of O-isopropylidene-trans-1,2-cyclohexanediol with the hydrogens at the 3-position are very close to 60° and 180°. Therefore it can be concluded from the data in Table I that for this compound  $J_{AX} = J_{60^\circ} = 3.5$  c.p.s. and  $J_{BX} = J_{180^\circ} = 11.0$  c.p.s. For the cis-compounds listed in Table I, the observed coupling constants  $J_{AX}$  and  $J_{BX}$  must represent the average coupling of the cis and trans 3-hydrogens with the (2) hydrogen, respectively, in the two energetically equivalent chair conformations I and II. Therefore  $J_{ae} + J_{ea} = 2J_{AX}$  and  $J_{aa} + J_{ee} = 2J_{BX}$ . In view of the near linearity of the Karplus curve (3) in the vicinity



of 60°,  $J_{ee} + J_{ea}$  should be nearly constant and  $J_{aa}$ , being slightly dependent upon dihedral angle in the region 170° to 180°, should have very nearly the same value for all the compounds. Therefore taking  $J_{ae} = J_{60^\circ}$ , the coupling constants obtained for the trans-isopropylidene compound would lead to the expectation that  $J_{AX} + J_{BX} = \frac{J_{180^\circ} + 3J_{60^\circ}}{2} = 10.75$  c.p.s.

TABLE I

N.M.R. Spectral Parameters for the cis and trans  
1,4,4-Trideuterio-1,2-Cyclohexanediols and Derivatives

<u>cis-Compounds</u>	Solvent	X-Spacings C.P.S. 100 Mc.P.S	Chemical Shifts C.P.S. (TMS)			Calculated Coupling Constants			$J_{AX} + J_{BX}$ C.P.S.
			$\delta_A$	$\delta_B$	$\delta_X$	$J_{AX}$	$J_{BX}$	$J_{AB}$	
<u>Di-O-acetyl</u>	CCl <sub>4</sub>	3.62 6.98	180	157	492	7.1	3.6	-11	10.7
<u>Diol</u>	CHCl <sub>3</sub>	3.79 7.11	177	153	375	7.1	3.8	-11	10.9
<u>Diol</u>	D <sub>2</sub> O	4.29 6.50	218	194	421	6.7	4.1	-11	10.8
<u>Di-O-tosyl</u>	CHCl <sub>3</sub>	2.77 7.72	196	154	451	7.8	2.7	-12	10.5
<u>O-Isopropylidene</u>	CCl <sub>4</sub>	5.4 5.4	181	154	396	5.4	5.4	-12	10.8
<u>Trans-Compounds</u>									
<u>Di-O-acetyl</u>	CCl <sub>4</sub>	4.20 10.15	141	129	468	3.5	11.0	-11	
<u>Diol</u>	CHCl <sub>3</sub>	4.55 11.06	192	123	330	4.5	11.0	-11	
<u>Diol</u>	D <sub>2</sub> O	4.26 10.91	240	171	384	4.1	10.5	-12	
<u>Di-O-tosyl</u>	CHCl <sub>3</sub>	3.62 7.82	196	148	440	3.6	7.9	-12	
<u>O-Isopropylidene</u>	CCl <sub>4</sub>	3.46 10.99	205	137	310	3.5	11.0	-12	

The values found for  $J_{AX} + J_{BX}$  are in good agreement with this prediction. The cis-compounds should exist in undistorted chair forms (4) so one expects  $J_{AX} = 3.5$  c.p.s. and  $J_{BX} = 7.25$  c.p.s. Values close to these were found in the case of the cis-diacetate and the cis-diol in chloroform. The high value for  $J_{AX} = 4.1$  c.p.s. and the low value for  $J_{BX} = 6.7$  c.p.s. for the cis-diol in  $D_2O$  is attributed to distortion of the ring by hydration of the hydroxyl groups (5). The values for  $J_{AX}$  and  $J_{BX}$  for the cis-ditosylate require  $J_{ee} > J_{60^\circ}$  and  $J_{ea} < J_{60^\circ}$ , showing that the 3,4 and 5 carbons have moved toward coplanarity with the 1-carbon, thereby relieving congestion between the axial tosyloxy group and the opposing axial hydrogens. In the case of the trans-ditosylate, taking  $J_{aa} = 11.0$  c.p.s. and  $J_{ee}$  to be in the range 2.6 - 3.5 c.p.s., since  $J_{BX} = 7.9$  c.p.s., it can be shown that 59-63% of the compound resides in the diequatorial conformation, revealing greater repulsion between tosyloxy groups in gauche orientation than in the case of acetoxy groups. The values for  $J_{BX}$  observed for the trans-diacetate and the trans diol (both solvents) require the compounds to exist virtually entirely in the diequatorial conformation. This result for the latter compound is consistent with published values for the non-bonded interaction energies involved and determined in aqueous solution, namely, 0.35 kcal./mole for the interaction between gauche hydroxyl groups (6) and 1.25 kcal./mole for the A-value of the hydroxyl group (7). Recent evidence (8, 9) indicates that the parameters

of the Karplus relation are strongly dependent on the chemical nature of the -CH - CH - fragment to which it is applied. The present results are consistent with a modified relation for this series of compounds of the form:-

$$J_{\phi} = 14.7 \cos^2 \phi - 0.2 \quad (0 \leq \phi \leq 90^\circ)$$

$$J_{\phi} = 11.2 \cos^2 \phi - 0.2 \quad (90^\circ \leq \phi \leq 180^\circ)$$

On this basis, with  $\phi_{ae} = \phi_{ea} = 50^\circ$ ,  $\phi_{aa} = 170^\circ$  and  $\phi_{ee} = 70^\circ$  the values  $J_{AX} = J_{BX} = 5.9$  c.p.s. are predicted for the cis-isopropylidene, in general agreement with the observed values of 5.4 c.p.s.

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