

**Spectroscopic investigations on derivatives
of tetrahydrofuran. IV.
The proton magnetic resonance study of the conformation
of *trans*-2,3-dichlorotetrahydrofuran***

M. HOLÍK and I. BORKOVCOVÁ

*Research Institute of Pure Chemicals, Lachema,
621 33 Brno-Řečkovice*

Received 27 February 1973

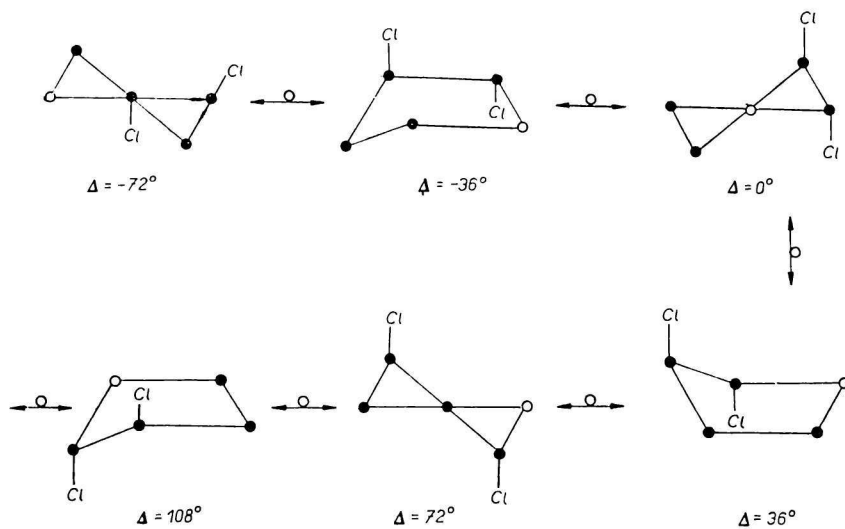
From the magnitudes of vicinal coupling constants and the paramagnetic shifts induced by addition of europium shift reagent it was deduced that *trans*-2,3-dichlorotetrahydrofuran occurs mainly in diaxial conformation with C-3 and C-4 carbons puckered above and below the C-5—O—C-2 plane respectively. Population of the energetically favoured conformers was calculated from the data obtained from the value of energy barrier to pseudorotation.

Recently, an enhanced attention has been paid to the geometry of five-membered rings: not only derivatives of cyclopentane [1], but especially substituted tetrahydrofurans were examined in more detail [2–4]. Nevertheless, the conformation of asymmetrically disubstituted tetrahydrofurans has not been studied yet. In continuation of our p.m.r. spectroscopic investigation of *trans*-2,3-disubstituted tetrahydrofurans [5], we turned our attention to conformation of *trans*-2,3-dichlorotetrahydrofuran. To describe all possible half-chair and envelope conformations of this substance, we used — in accord with other authors [2] — the so-called “phase angle of pseudorotation” designated as Δ . The half-chair conformer with C-3 and C-4 atoms puckered respectively above and below the plane formed by C-5—O—C-2 atoms is defined by the parameter of pseudorotation $\Delta = 0^\circ$. The other half-chair conformations in the cycle of pseudorotation are unambiguously characterized by the phase angles, given as even multiples of 36° . Envelope conformations are described in terms of odd multiples of 36° (Scheme 1).

In the p.m.r. spectrum of *trans*-2,3-dichlorotetrahydrofuran, similarly as in the spectra of other *trans*-2,3-disubstituted tetrahydrofurans under study [5], there is no observable spin—spin coupling between hydrogen atoms H_α and H_β and the signal of H_α appears as a singlet (Fig. 1). Neither the double irradiation of H_α exerts change in the H_β signal, whereas the simplification of multiplets $H_{\beta'}$ and $H_{\beta''}$ brings evidence for a weak long-range interaction between the corresponding hydrogen atoms and H_α . We calculated the theoretical values of coupling constants $J_{H_\alpha H_\beta}$ using the known torsion angles in half-chair ($39, 32, 12, 12, 32^\circ$) and envelope ($37, 23, 0, 23, 37^\circ$) conformations [2] and the Karplus equation referring to the dependence of vicinal coupling constant on the magnitude of the corresponding dihedral angle

$$^3J = 4.22 - 0.5 \cos \Phi + 4.5 \cos 2\Phi.$$

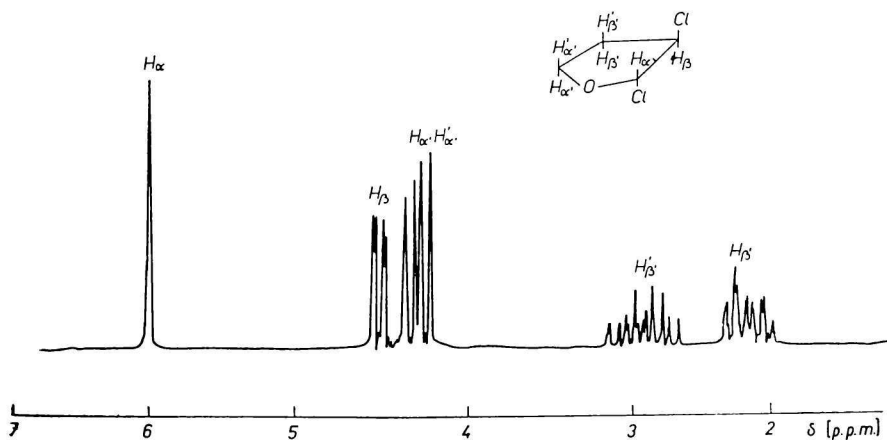
* Presented in part at the 2nd International NMR Symposium, Guildford, England, July 1972.



Scheme 1

Accordance has been found between the experimental value and that of calculated for seven conformers from $\Delta = -36^\circ$ to $\Delta = 180^\circ$ (Fig. 2, curve 2). It follows that puckering of the molecule takes place in the proximity of the place of substitution whereby the substituents occupy axial positions.

Also the signal of H_β , consisting of four virtually equally intense peaks, could be indicative of the conformation of the molecule under investigation. In the first approximation, this signal could be considered the X-part of the spectrum of the ABX system formed by hydrogens H_β , H'_β , H_β . Analysis of this system gave $|J_{H_\beta H_\beta'} + J_{H_\beta H'_\beta}| =$

Fig. 1. The p.m.r. spectrum of *trans*-2,3-dichlorotetrahydrofuran in CCl_4 .

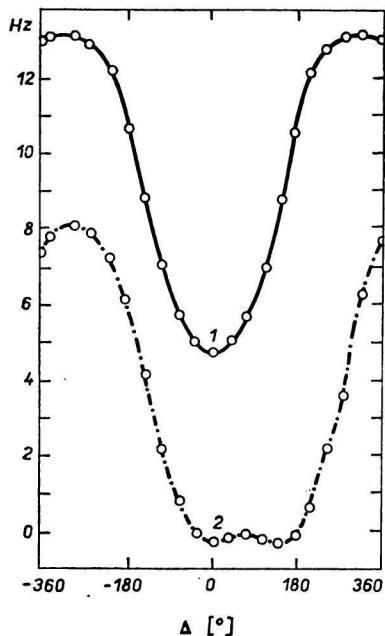


Fig. 2. The dependence of vicinal coupling constants on the phase angle of pseudorotation.

1. $|J_{H\beta H\beta'} + J_{H\beta H\beta}|$; 2. $J_{H\alpha H\beta}$.

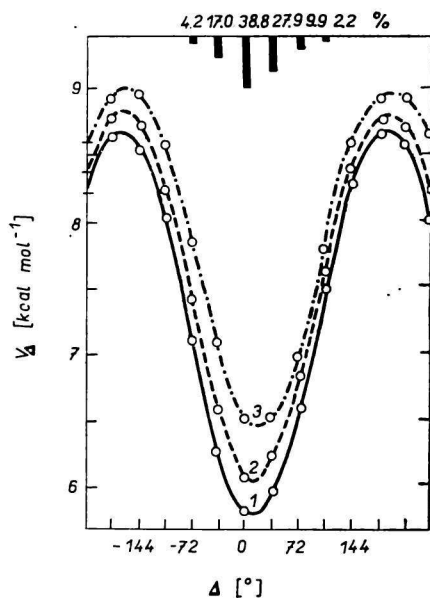


Fig. 3. Energy barrier to pseudorotation and the population of conformers.

$V_{\max} - V_{\min}$: 1. 2.90 kcal mol⁻¹; 2. 2.73 kcal mol⁻¹; 3. 2.52 kcal mol⁻¹.

= 4.6 Hz. Similarly as in the foregoing case, theoretical values of the sum of coupling constants (see Fig. 2, curve 1) were calculated for particular conformers. The calculated value for $\Delta = 0^\circ$, i.e. 4.64 Hz, is nearest to that obtained from the spectrum indicating thus the half-chair conformer, possessing this phase angle of pseudorotation, to be the most probable. Considering the approximative character of the Karplus equation, it is necessary also to take into account the envelope conformers $\Delta = -36$ and 36° .

Induced shifts of p.m.r. signals, due to addition of shift reagent tris(dipivalomethanato)europium to the measured sample of *trans*-2,3-dichlorotetrahydrofuran, could provide further information on geometry of the molecule. Since the coordination of europium to halogen atoms is negligible [6, 7], the only expected place for labile complex — substrate — shift reagent — formation is oxygen. The magnitudes of the induced shifts of p.m.r. signals of the particular protons at the given concentration of the substrate and shift reagent, characterized [8] by the shift parameter S (1), depend on the vector distance [9] of the corresponding hydrogen atom from the atom of europium in the moment of coordination (2)

$$S = (\delta_{Eu} - \delta) \frac{[\text{substrate}]}{[\text{Eu(DPM)}_3]}, \quad (1)$$

$$S = \frac{k(3 \cos^2 \Phi - 1)}{r^3}. \quad (2)$$

Table 1

Calculated and experimental values of the shift parameter S

H	$\Delta [^\circ]$								$S_{\text{exptl.}}$
	-36	0	36	180	324	360	396	540	
H_α	1.285	1.254	1.250	1.255	1.285	1.296	1.304	1.335	1.34
H_β	0.631	0.616	0.626	0.651	0.802	0.842	0.888	0.734	0.59
$H_{\beta'}$	0.888	0.842	0.802	0.651	0.626	0.616	0.631	0.734	0.70
$H_{\beta''}$	0.626	0.616	0.631	0.734	0.888	0.842	0.802	0.651	0.61
$H_{\gamma'}$	1.250	1.254	1.285	1.335	1.304	1.296	1.285	1.255	1.32
$H_{\gamma''}$	1.304	1.296	1.285	1.255	1.250	1.254	1.285	1.335	1.32

Experimental values S obtained using eqn (1) are correlated in Table 1 with those calculated according to eqn (2) for some conformers of *trans*-2,3-dichlorotetrahydrofuran. To calculate hydrogen—europium distance (r) and angle H—Eu—O (Φ) we used published coordinates of half-chair and envelope models of cyclopentane [10] and the most used distance O—Eu equal to 2.35 Å. The constant k was chosen so that the sum of all experimental values S was equal to the sum of parameters S calculated for fundamental conformation $\Delta = 0^\circ$. The disagreement in absolute values S calculated (eqn 2) and measured (eqn 1) indicates that the cyclopentane model for calculation has not been selected properly. It can be, of course, assumed from the relative comparison ($S_{H\beta'} > S_{H\beta} \doteq S_{H\beta''}$) that also in the substrate—shift reagent complex the favoured conformations of tetrahydrofuran derivative are in the region of pseudorotational cycle characterized by phase angles of pseudorotation $\Delta = -36, 0$, and 36° .

Statistical population of the particular conformers of *trans*-2,3-dichlorotetrahydrofuran at room temperature (20°C) was deduced from the potential energy barrier to pseudorotation. The total torsion energy for single phase angles of pseudorotation Δ was calculated using equations and values already reported [2]. This calculation neglects dipole—dipole interactions of substituents, so that energies for half-chair diaxial and diequatorial conformers are equal. As it follows from our experiments, the diequatorial conformer $\Delta = 360^\circ$ and conformations in pseudorotational cycle near to it are unlikely and their population at room temperature is negligible. In these cases, the contribution of the dipole—dipole interaction cannot be neglected when calculating the total energy of the molecule. On the other hand, for diaxial conformers near $\Delta = 0^\circ$ the orientation of dipoles [C-2—Cl, C-3—Cl, C-2—Cl, lone electron pairs of oxygen] favours the anomeric effect, whereas the vicinal interaction is negligible. Therefore the contribution of the dipole—dipole interaction does not substantially alter the general feature of the potential barrier to pseudorotation in the range of pseudorotational cycle with conformations energetically favoured. The value of the barrier to rotation round the CHCl—O bond used for calculation has so far not been published and that is why we employed three various values derived from the barrier to rotation for the $\text{CH}_2\text{—O}$ bond considering the contribution of the chlorine *a*) negligible ($1.07 \text{ kcal mol}^{-1}$); *b*) proportional ($1.38 \text{ kcal mol}^{-1}$) or *c*) additive ($1.87 \text{ kcal mol}^{-1}$). The minimum of the torsion barrier to pseudorotation lies between the half-chair ($\Delta = 0^\circ$) and envelope ($\Delta = 36^\circ$) conformations and slightly shifts to conformation with $\Delta = 36^\circ$ with the enhancement of the barrier to rotation of the CHCl—O bond. Also the depth of the energy barrier undergoes a small change; it decreases with the increasing effect of the chlorine atom

(Fig. 3). The population of the single energetically favoured conformations at 20°C was calculated from the Boltzmann distribution law. The result for case *a* is shown in the upper part of Fig. 3.

The energetically most favoured conformation of *trans*-2,3-dichlorotetrahydrofuran is the half-chair one with the C-3 atom puckered above and C-4 below the C-5—O—C-2 plane. However, the nearest envelope conformations with the C-3 atom above and C-4 below the molecule plane are also present in a relatively considerable extent at room temperature.

Experimental

The p.m.r. spectrum of *trans*-2,3-dichlorotetrahydrofuran was recorded with a Tesla BS 487 C spectrometer at 80 MHz. The sample (39 mg) was dissolved in carbon tetrachloride (0.5 ml) containing 5% of tetramethylsilane as internal reference substance. Chemical shifts of the particular protons, in p.p.m. on the δ scale (Fig. 1), were found to be: $H_\alpha = 6.14$, $H_\beta = 4.57$, $H_{\alpha'}$ and $H_{\beta'} = 4.31$, $H_{\beta'}' = 2.83$, $H_{\beta'}'' = 2.19$. Induced chemical shifts were measured with the respective addition of 20, 40, and 60 mg of tris(dipivalomethanato)europium; no changes either in the magnitude of coupling constants or in the multiplet pattern have been observed. For the calculation of the induced chemical shifts of $H_{\beta'}$ and $H_{\beta'}'$ the corresponding multiplets were reduced to AB quartet. To find out the long-range coupling constants by double-resonance method, the degassed sample was used. The shift reagent — tris(dipivalomethanato)europium was prepared according to [11].

Acknowledgements. The authors are gratefully indebted to Dr M. Kratochvíl for his interest and valuable discussion.

References

1. Altona, C., in *Conformational Analysis — Scope and Present Limitations*. (G. Chiurdoglu, Editor.) P. 1. Academic Press, New York, 1971, and references therein.
2. Buys, H. R., Altona, C., and Havinga, E., *Tetrahedron* **24**, 3019 (1968).
3. Sundaralingham, M., *J. Amer. Chem. Soc.* **87**, 599 (1965).
4. Altona, C. and Sundaralingham, M., *J. Amer. Chem. Soc.* **94**, 8205 (1972).
5. Holík, M., Štern, P., and Kratochvíl, M., *Chem. Zvesti* **25**, 9 (1971).
6. Sanders, J. K. M. and Williams, D. H., *Chem. Commun.* **1970**, 422.
7. Sanders, J. K. M. and Williams, D. H., *J. Amer. Chem. Soc.* **93**, 641 (1971).
8. Cockerill, A. F. and Rackham, D. M., *Tetrahedron Lett.* **1970**, 5149.
9. Briggs, J., Hart, F. A., and Moss, G. P., *Chem. Commun.* **1970**, 1506.
10. Altona, C., Buys, H. R., and Havinga, E., *Rec. Trav. Chim. Pays-Bas* **85**, 973 (1966).
11. Eisentrant, K. J. and Sievers, R. E., *J. Amer. Chem. Soc.* **87**, 5254 (1965).

Translated by Z. Votický