The Conformational Preference of the Isocyanato-group

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As part of a study, by high-resolution n.m.r. spectroscopy, of the conformational equilibrium in *cis*-1,3-di-isocyanatocyclohexane,[1] we wished to know the conformational free energy ($-\Delta G^0$) for the isocyanato-group attached to a cyclohexane system. To obtain the necessary data for isocyanatocyclohexane (I), we have prepared and examined the *cis*- and *trans*-4-t-butyl-1-isocyanatocyclohexanes, (II) and (III) respectively, and now report the results of these measurements.

The procedure follows two routes. The chemical shift of the methine proton in (I) is the weighted mean of the chemical shift of the proton in the axial and equatorial conformations. Assuming that a 4-t-butyl substituent has a negligible effect on the methine proton shift, then (II) and (III) approximate to the two chair conformations of (I), and the equilibrium constant is given by

$$K = \frac{\tau - \tau_{cis}}{\tau_{trans} - \tau}$$

where τ is the observed chemical shift of the methine proton in (I), τ_{cis} and τ_{trans} the shifts in (II) and (III) respectively. The results obtained show that the conformer with equatorial ·NCO is favoured by 0·39 ± 0·02 kcal./mole.

TABLE

Conformational equilibrium of isocyanatocyclohexane n.m.r. signal of methine proton[a]

	Chemical shift[b]	Band width (c./sec.)
(I)	6·576 ± 0·002	24·75 ± 0·6
(II)	6·174 ± 0·003	13·10 ± 0·6
(III)	6·788 ± 0·001	30·10 ± 0·2
K	1·90 ± 0·05	2·18 ± 0·45
$-\Delta G^{\circ}_{\mathrm{NCO}}$ ..	0·39 ± 0·02	0·48 ± 0·15
% Equatorial conformer ..	*ca.* 66	*ca.* 69

[a] Recorded at 100 Mc./sec. in $CDCl_3$ at 35°.
[b] With respect to Me_4Si.

The second method makes use of the coupling constants to the methine proton. The sum of the vicinal coupling constants is given by the distance between the outermost lines in the methine proton multiplet. Again the observed sum is the weighted mean of those in the separate conformations and the equilibrium constant may be expressed as:

$$K = \frac{\mathrm{w} - \mathrm{w}_{cis}}{\mathrm{w}_{trans} - \mathrm{w}}$$

where w is the band width of the methine proton in (I) and w_{cis} and w_{trans} the widths in (II) and (III) respectively.

The value of $-\Delta G^0_{NCO}$ obtained in this manner is 0·48 ± 0·15 kcal./mole, in excellent agreement with the previous result. Errors in the coupling sum may be caused by second-order effects as a result of strong coupling between the geminal protons, but these effects are minimised in the spectra recorded at 100 Mc./sec.

It is clear, therefore, that the $-\Delta G^0_{NCO}$ value obtained represents a preference of the isocyanato-group for the equatorial position to the extent of *ca.* 67% at 35°.

The reference compounds, (II) b.p. 62°/0·9 mm., n_D^{20} 1·4647 and (III), b.p. 57°/0·5 mm. n_D^{20} 1·4618, were prepared from the corresponding acid chlorides[2] (*via* the Curtius reaction) and gave confirmatory analytical and spectral data.

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[1] G. C. Corfield and A. Crawshaw, *Chem. Comm.*, 1966, 85.

[2] H. H. Lau and H. Hart, *J. Amer. Chem. Soc.*, 1959, **81**, 4897.