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CONFORMATIONAL PREFERENCE OF THE CHLORO-SUBSTITUENT: EQUILIBRATION OF 1- AND 4-CHLORODIAMANTANE

by M.A. McKervey, D.E. Johnston, and J.J. Rooney

Department of Chemistry, The Queen's University, Belfast BT9 5AG

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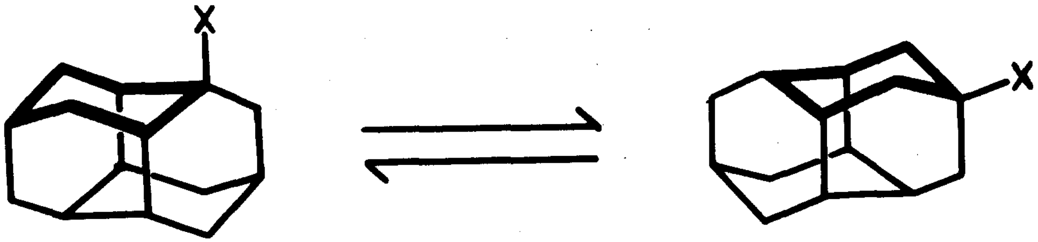
A new approach to the determination of the conformational enthalpy of the hydroxy-substituent in which the diamantyl derivatives Ia and IIa are employed as templates for the cyclohexane chair conformations III and IV was recently described (1).

In view of the complete agreement between $-\Delta H^{o}_{OH}$ obtained in this way and values (for hydrogen-donor solvents) derived from the 4-*t*-butylcyclohexyl system (2), it is desirable to test the reliability of the method by applying it to the determination of the conformational preferences of other substituents, e.g., chlorine.

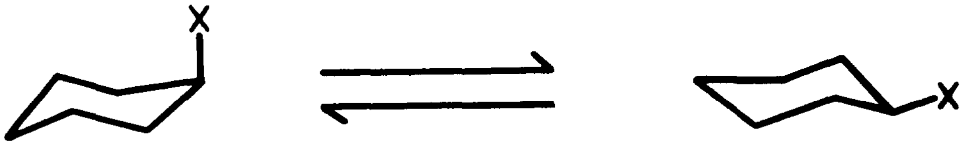


(Ia) X = OH

(Ib) X = Cl

(IIa) X = OH

(IIb) X = Cl



(III)

(IV)

Chlorocyclohexane has been intensively investigated mostly by i.r. and n.m.r. methods and $-\Delta G^{o}_{Cl}$ values ranging from 0.26 to 0.94 kcal mol^{-1} have been reported (3); however, the reliability of some of the n.m.r. methods has been questioned on theoretical grounds (4). There are apparently no recorded chemical determinations of the conformational preference of chlorocyclohexane.

Our approach is a direct chemical method based on the fact that in isomer I the substituent is axially disposed with respect to one cyclohexane ring of the diamantane skeleton whereas in isomer II the substituent is exclusively equatorial. The process of ring inversion whereby the equilibrium III $\rightleftharpoons$ IV is established cannot occur with diamantyl derivatives, but the same overall result can be realised by isomerisation I $\rightleftharpoons$ II, provided of course that a reaction pathway is available.

Alcohols Ia and IIa were brought to equilibrium in 98% sulphuric acid and $-\Delta H^{o}_{OH}$ was measured as 1.1 kcal mol^{-1}. The difference between the experimental entropy change, ΔS, of 3.4 cal deg^{-1} mol^{-1} and a value of 2.18 cal deg^{-1} mol^{-1} calculated on the basis of the different symmetry properties of isomers Ia and IIa was attributed to the entropy of mixing of the various rotational conformations of the substituent; furthermore, there is probably an appreciable solvent effect on ΔS. But the chloro-substituent is symmetrical and in the absence of any solvent effects the measured ΔS for isomerisation IIb $\longrightarrow$ Ib should approach closely the calculated value.

TABLE

Relative equilibrium concentrations of
1-chlorodiamantane (Ib) and 4-chlorodiamantane (IIb)

$T^{o}K$	334	300	274	251	210
isomer Ib	51.95	50.00	46.05	43.65	37.95
isomer IIb	48.05	50.00	53.95	56.35	62.05

1- and 4-Chlorodiamantane, (Ib) and (IIb) (5), were equilibrated at several temperatures in chloroform solution containing aluminium chloride; these equilibrations, like those of alcohols Ia and IIa, probably proceed via an intermolecular hydride transfer mechanism (6). As we were unable to measure accurately the equilibrium concentrations, each mixture was subjected to complete hydrolysis in aqueous dimethylformamide and glc ratios (see Table) were obtained with the corresponding alcohols (7). The thermodynamic data for isomerisation IIb to Ib are derived from the temperature dependence of the equilibrium by a linear least squares analysis: $\Delta H = 0.68 \pm 0.03$ kcal mol^{-1} and $\Delta S = 2.2 \pm 0.1$ cal deg^{-1} mol^{-1}. Thus, there is complete agreement between the measured and calculated ΔS. This result indicates that ΔS for isomerisation III $\rightleftharpoons$ IV (X = Cl) should be close to zero.

The conformational enthalpy of the chloro-substituent obtained with the diamantyl system is to be compared with a value of 0.56 kcal mol^{-1} calculated for chlorocyclohexane by Allinger and co-workers (8) using the Westheimer approach. Of the various measured values for chlorocyclohexane, those derived by the low temperature n.m.r. peak area method are generally regarded as being the most reliable. Using this technique, Reisse (9) recently obtained an enthalpy value of 0.52 kcal mol^{-1}; he noted also that ΔS was essentially zero. This is in accord with earlier work of Jensen and co-workers (4) who obtained a value of 0.53 kcal mol^{-1} for the conformational free energy of the chloro-substituent at -80° (10).

REFERENCES and FOOTNOTES

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(7) 3-Chlorodiamantane was also present in trace amounts at equilibrium with isomers Ib and IIb but it has been excluded from the analysis presented here.

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