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CONFORMATIONAL DATA IN Me-SUBSTITUTED 1,3-DIOXADECALANES.

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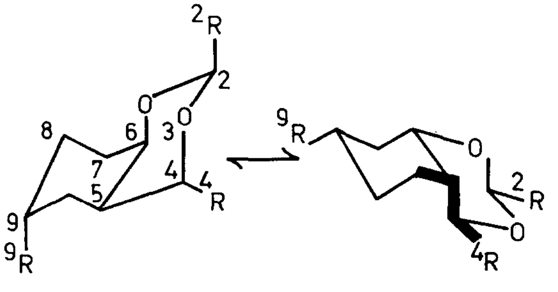
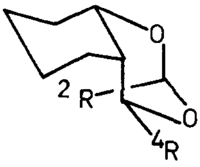
Cis-1,3-dioxadecalane can exist in two conformations (IA ⇀↽ IIA), distinguished as the O-inside (I) and O-outside (II) conformation. We have recently evaluated their difference in enthalpy content to be about 2.35 Kcal/mole by summation of all encountered interactions (1), assuming an additivity-validity. From pmr data of 4-substituted derivatives (I ⇀↽ II; $^{2}R=^{9}R=H$ and ^{4}R = subst.), obtained below and above the coalescence temperature and using the above estimated intrinsic differences between O-in and O-out, values were also obtained for ΔG°, ΔH° and ΔS°. We have now confirmed some of these data on equilibrating chemically at different temperatures 2,9-diMe-cis-1,3-dioxadecalane (IB ⇀↽ IIB) and 2,4-diMe-cis-1,3-dioxadecalane (IC ⇀↽ IIC), both existing as configurational epimerisable isomers.



I O-inside

II O-outside



III

A: $^{2}R=^{4}R=^{9}R=H$

B: $^{4}R=H;^{2}R=^{9}R=Me$

C: $^{9}R=H;^{2}R=^{9}R=Me$

D: $^{4}R=^{9}R=H;^{2}R=H$

The 2-Me group is used as a "blocking" group because the equatorial position is favoured over the axial in 1,3-dioxane for about 4 Kcal/mole (2; cf. 3). Thus forms III may be neglected, the more because here an additional serious 2:6 synaxial interaction exists, which is not present in either an

Table I.

Epimerisation of 2,9-diMe-(O-in ⇌ O-out)-*cis*-1,3-dioxadecalane

IB ⇌ IIB

Temp.(°K)	%(O-out)(a)	K_e = (O-in)/(O-out)	ΔΔG° cal/mole	
273	9.55	9.47	-1214	ΔΔH° = -515 cal/mole
298	10.29	8.72	-1278	ΔΔS° = + 2.6 e.u.
323	10.91	8.16	-1342	r(b) = 1.00
373	12.00	7.33	-1470	

Table II.

Epimerization of 2,4-diMe-(O-in ⇌ O-out)-cis-1,3-dioxadecalane

IC ⇌ IIC

Temp.(°K)	%(O-out)(a)	K_e = (O-in)/(O-out)	ΔΔG°(c) cal/mole	
273	29.36	2.41	$-475._6$	ΔΔH° = -93 cal/mole(c)
298	29.61	2.38	$-511._7$	ΔΔS° = + 1.4 e.u.(c)
333	29.96	2.34	$-560._6$	r = 0.9999
364	30.17	2.31	$-603._5$	

(a) Evaluated by G.C. glass-capillary columns, l = 50 m, ∅ = 0.5 mm Carbowax 20 M, t = 105°C; F.I.-detection; split ratio : 1/60. Electronic integrations.

These values were checked in attaining the equilibrium, starting from both isomers separatedly.

(b) Correlation coefficient.

(c) To be compared with values from PMR-study(1) : ΔΔH° = -495 cal/mole; ΔΔS° = 0.6 e.u.; ΔG°_{298} = -690 cal/mole.

axial Me-4 substitution (IC; $\Delta G^\circ \sim 3$ Kcal/mole (3)) or in an axial Me-9 substitution (IB; $\Delta G^\circ = 1.7$ Kcal/mole) (4)(5)).

The thermodynamic properties related with the O-inside $\rightleftharpoons$ O-outside conversion was obtained by the use of the 2,9-diMe-derivatives (IB $\rightleftharpoons$ IIB). Thus we have introduced in the Me-2eq derivative an additional Me-9ax group, in order to obtain a reasonable equilibrium state (predicted $\Delta\Delta G^\circ$: $2.35 - 1.7 = 0.65$ Kcal/mole). Without the Me-9 substitution a too extreme equilibrium state would have been encountered. Furthermore, the value of ΔH°(Me in cyclohexane) is now very well established (4,5).

Results of the epimerisation in CCl_4 (0.06 molar) with trifluoroacetic acid as a catalyst (0.04 M) are found in tables I and II, together with the extracted thermodynamic quantities (least squares method, correlation coefficient r). From table I ($\Delta\Delta H^\circ$ (IB $\rightleftharpoons$ IIB) = -515 cal/mole) and ΔH°(Me in cyclohexane) = -1,690 cal/mole it follows that ΔH°(IA $\rightleftharpoons$ IIA) = 2.21 Kcal/mole, which is in excellent agreement with our previous estimation (1), although it has been recognised that linear additivity of several accumulating interactions has to be employed with care.

On the other hand it follows from table II, that the thermodynamic quantities differ somewhat with previous evaluated values from PMR-data (cf. footnote c, table II). The total free energy difference is quite analogous, but greater deviations are observed for enthalpy and entropy data. This is a quite common phenomenon, the experimental failures on ΔH° being related to those of ΔS° in a manner as to give still precise ΔG°-values (6). Other factors which might contribute to the deviations observed, are differences in solute-solvent complexation which might give differences for ΔH° of several hundred cal/mole (cf. 7).

The new obtained values of ΔΔH° however still fit quite well the expectations, assuming again that additivity is valid. We can for instance predict with reasonable accuracy what the enthalpy contribution would be, for a Me-4-axial group in a simple m-dioxane system. As form IC seems to be favoured with 93 cal/mole on the one hand and the difference O-in/O-out is now been found to be 2210 cal/mole, (in favour of the O-in conformation) we can compute the value of Me-4 ax in the 1,3-dioxane system. The only unknown contribution is the gauche interaction in the O-outside conformation depicted by the heavy lines in IIC. This however must be very near 850 cal/mole (half of the value for $-\Delta H°$(Et in cyclohexane), cf. (1)) so that it follows that $-\Delta H°$(Me-4,dioxane) = 2210 + 850 - 93 = 2.97 Kcal/mole. This indeed is more than excellent, when compared to values determined through other approximations (3)).

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