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# CONFORMATIONAL EFFECTS IN COMPOUNDS WITH 6-MEMBERED RINGS—VII

## THE PREFERRED CONFORMATION OF 2,4-DIOXABICYCLO(3,3,1)NONANE

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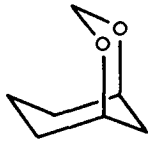
**Abstract**—The 1,3-diozane ring in the preferred conformation of 2,4-dioxabicyclo[3.3.1]nonane II has been shown by dipole moment measurements on the derivatives III to adopt a boat form, in contrast to other heterocyclic analogues of bicyclo(3.3.1)nonane.

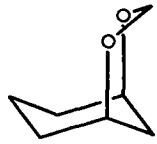
BICYCLO[3.3.1]NONANE I ($Z = CH_2$) and its 3-aza-, 3-azonia-, 3-oxa- and 3-thia-analogues I ($Z = NH$, $\overset{+}{N}H_2$, O or S) have been shown to adopt two-chair conformations.[1–3] The severe interactions between the groups at the 3- and 7-positions are so efficiently relieved by the flexibility of the so-called "rigid" chair rings that the chair-boat and two-boat conformations, in which the principal strains are due to eclipsing along the sides of the "boats", are considerably less stable.[3] The strain in the two-chair conformation IIa of 2,4-dioxabicyclo[3.3.1]nonane II due to the close mutual approach of the endo 3- and 7-hydrogen atoms, whose centres would be only *c* 0·4 A apart in the undistorted molecule, will be even greater than the strain in bicyclo[3.3.1] nonane. The torsional strain in the chair-boat IIb, however, will probably be smaller than in the carbocyclic system because in saturated compounds barriers to rotation are generally smaller about C—O bonds (e.g. in methanol $V_3 = 1{\cdot}07$ kcal/mole,[4] dimethyl ether $V_3 = 2{\cdot}72$ kcal/mole[5]) than about C—C bonds (e.g.) in ethane $V_3 = 2{\cdot}9$ kcal/mole;[6] all saturated derivatives of ethane have higher barriers). We anticipated, therefore, that the chair-boat conformation IIb would be more stable than the two-chair conformation IIa, in contrast to the other [3.3.1]-bridged ring systems. As an essential preliminary to a quantitative study of the difference in stability of the conformations IIa and IIb we have determined the conformational equilibrium qualitatively by measuring the dipole moments of the 1,3-dioxanes III (X = H, Cl or $NO_2$), which were prepared from tricyclo [7.3.1.$O^{2,7}$] tridecane-2,13-diols of known stereochemistry.[3]

8-Phenyltricyclo[7.3.1.$O^{2,7}$]tridecane-*cis*-2,13-diol was converted into its cyclic carbonate and the latter was nitrated and then hydrolysed to give the 8-*p*-nitrophenyl diol, which could not be prepared by the methods available for the 8-phenyl- and

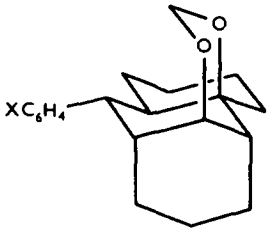

I



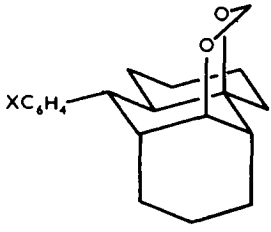
IIa



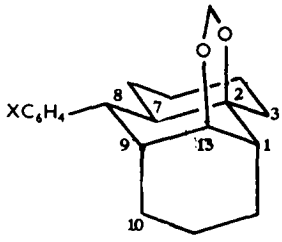
IIb




IIIa




IIIb




IIIc

8-*p*-chlorophenyl-diols,[3,7] nor by nitration of acid sensitive compounds with a free 2-hydroxyl group. The three diols each reacted with dimethoxymethane in the presence of acid to form the 1,3-dioxanes III (X = H, Cl or $NO_2$). The dipole moments were measured in benzene at 25°.

The dipole moment of 1,3-dioxane has been reported as 2·13 ± 0·03 D[8] and as 1·9 D,[9] and has been estimated to be 1·87 D for the boat or chair conformations with $C_S$ symmetry.[10] From the observed moment of III (X = H) and an assumed moment for the alkylbenzene portion of the molecule, it is possible to derive an effective magnitude for the dipole moment of the 1,3-dioxane ring portion if an angle between the two moments can be ascribed. This angle will depend on the conformation of the 1,3-dioxane ring and can be calculated on various assumptions, e.g. for the undistorted chair (IIIa) and boat (IIIb) forms and for a "semi-planar" form (IIIc) in which the C—O—C—O—C chain of atoms is coplanar and which corresponds to the limit of distortion of the chair ring. The moment of the alkylbenzene portion is assumed to have the magnitude of that of toluene, i.e. 0·4 D,[11] and to act along the $C_{alkyl}$–$C_{aryl}$ bond. The directions of the 1,3-dioxane ring moment for the conformations IIIa–c were calculated from accepted bond lengths and angles[12] and on the assumption that each C—O—C moment lies on the bisector of the C—O—C atom plane.

TABLE 1. DIPOLE MOMENTS OF THE 1,3-DIOXANE RING IN THE COMPOUND III (X = H) FOR VARIOUS ASSUMED CONFORMATIONS

| Conformation of the 1,3-dioxane ring | Angle[a] between dipoles | Dipole moment[b] for 1,3-dioxane ring |
|---|---|---|
| Chair, IIIa | 144½° | 2·59 D |
| Boat, IIIb | 74½ | 2·13 |
| Semi-planar, IIIc | 109½ | 2·38 |

[a] ±3°.

[b] ±0·05 D; the dipole moment of toluene is assumed to be 0·4 D.[11]

It is not very profitable to compare these moments with the moments of 1,3-dioxane itself quoted above, but they may be combined vectorially with the moments[11] of *p*-chlorotoluene or *p*-nitrotoluene to estimate the moments of III (X = Cl or $NO_2$) for the three conformations IIIa–c (Table 2). The moments corresponding to distorted chair conformations for the 1,3-dioxane ring will lie between the values for IIIa and IIIc. If the calculations are based on the dipole moments of phenyl- and *p*-chlorophenyl-cyclohexane[13] (the dipole moment of *p*-nitrophenylcyclohexane has not been measured) rather than of toluene and *p*-chlorotoluene then the values calculated for the conformations IIIa–c (X = Cl) are increased by *c* 0·1 D but our conclusion is unchanged.

TABLE 2. MEASURED AND ESTIMATED DIPOLE MOMENTS FOR VARIOUS CONFORMATIONS OF THE COMPOUNDS III (X = H, Cl OR $NO_2$)

| Substituent X | Measured dipole moments | Estimated dipole moments for various conformations of III[a] | | |
|---|---|---|---|---|
| | | IIIa | IIIb | IIIc |
| H | 2·28 ± 0·05 D | | | |
| Cl | 3·11 ± 0·05 | 1·5 ± 0·1 D | 3·3 ± 0·1 D | 2·5 ± 0·1 D |
| $NO_2$ | 5·25 ± 0·05 | 2·8 ± 0·1 | 5·4 ± 0·2 | 4·3 ± 0·2 |

[a] Calculated from the angles and dipole moments given in Table 1 and from the dipole moments of *p*-chlorotoluene (1·96 D)[11] and *p*-nitrotoluene (4·47 D).[11]

The dipole moments establish that the 1,3-dioxane ring in the compounds III is in a boat conformation and by inference that the preferred conformation of 2,4-dioxabicyclo[3.3.1]nonane is IIb. This conclusion is supported by the proton magnetic resonance spectrum of III (X = H), in which there is no detectable spin–spin coupling between either of the methylene ether protons and the 13-hydrogen atom. In simple 1,3-dioxanes which exist in chair conformations there are small but easily detectable couplings between the equatorial 2- and 4- (or 6-) hydrogen atoms.[14]

## EXPERIMENTAL

*8-p-Nitrophenyltricyclo*[7.3.1.$0^{2,7}$]*tridecane*-cis-2,13-*diol*

Carbonyl chloride was bubbled through a warm stirred soln of 8-phenyltricyclo[7.3.1.$O^{2,7}$]tridecane-*cis*-2,13-diol (5 g) in benzene (15 ml) and pyridine (10 ml) for 4 hr. The resulting mixture was left overnight at room temp and the 2,13-*carbonate* was isolated with ether and recrystallized from MeOH in prisms, m.p. 205–206° (Found: C, 76·81; H, 7·80. $C_{20}H_{24}O_3$ requires: C, 76·89; H, 7·74%). A soln of the carbonate (5 g) and $HNO_3$ (d 1·4, 14 ml) in $Ac_2O$ (150 ml) was left (1 day) at room temp, treated with NaOAC (20 g) and then concentrated *in vacuo*. When the pasty residue was taken up in water and ether 8-p-*nitrophenyltricyclo*[7.3.1$O^{2,7}$]*tridecane*-cis-2,13-carbonate (5 g) separated and after crystallization from MeOH formed prisms, m.p. 225–226°. (Found: C, 66·99; H, 6·44; N, 4·01. $C_{20}H_{23}O_5N$ requires: C, 67·21; H, 6·49; N, 3·93%). A mixture of the 8-p-nitrophenyl 2,13-carbonate (2·5 g) and NaOH (5 g) in MeOH (100 ml) was boiled (½ hr), and the *diol* was isolated with ether and recrystallized from MeOH in minute needles (1·7 g), m.p. 208–212° (dec). (Found: C, 68·73; H, 7·65; N, 4·18. $C_{19}H_{25}O_4N$ requires: C, 68·86; H, 7·62; N, 4·23%).

*Preparation of cyclic methylene ethers* III (X = H, Cl or $NO_2$)

An 8-aryl diol (3·5 g) in dimethoxymethane (80 ml) containing conc $HSO_4$ (0·1 ml) was heated at 100° in a sealed tube for 6 hr. The resulting soln was shaken with $BaCO_3$, filtered through alumina, concentrated *in vacuo*, and diluted with petr ether from which the methylene ether immediately crystallized. The ethers

prepared were the 8-*phenyl derivative* III (X = H), m.p. 126–127° (Found: C, 80·23; H, 8·67. $C_{20}H_{26}O_2$ requires: C, 80·49; H, 8·78%), the 8-p-*chlorophenyl derivative* III (X = Cl), m.p. 130–132° (Found: C, 71·96; H, 7·41; Cl, 10·65. $C_{20}H_{25}O_2Cl$ requires: C, 72·16; H, 7·75; Cl, 10·65%), and the 8-p-*nitrophenyl derivative* III (X = $NO_2$), m.p. 144–146° (Found: C, 70·17; H, 7·39; N, 4·28. $C_{20}H_{25}O_4$ requires: C, 69·95; H, 7·33; N, 4·08%).

*Dipole moments*

Dipole moments ($\mu$) were measured in dilute soln in dry benzene at 25°, assuming dielectric constant ($\varepsilon$) 2·2741,[15] and specific volume ($v$) 1·1446[16] for the solvent. The results were calculated by the method of Halverstadt and Kumler.[17] The molar refraction ($R_D$), calculated from tables of bond refractions[18] was used as the distortion polarization because the solutions were too dilute for accurate measurement of refractive index differences; $w$ is the weight fraction of the solute.

| Compound | $10^6w$ | $\varepsilon$ | $v$ |
|---|---|---|---|
| III (X = H) | 356 | 2·2749 | 1·1445 |
| | 1258 | 2·2768 | 1·1443 |
| | 2090 | 2·2785 | 1·1440 |
| | 3823 | 2·2821 | — |
| III (X = Cl) | 587 | 2·2762 | 1·1444 |
| | 1201 | 2·2782 | 1·1443 |
| | 2246 | 2·2816 | 1·1439 |
| | 3612 | 2·2860 | — |
| III (X = $NO_2$) | 493 | 2·2786 | 1·1443 |
| | 1191 | 2·2848 | 1·1442 |
| | 2059 | 2·2926 | 1·1438 |
| | 3632 | 2·3067 | — |

| | $d\varepsilon/dw$ | $dv/dw$ | $T^P2\infty$ | $R_D$ | $R_D$ calc. | $\mu$ (D) |
|---|---|---|---|---|---|---|
| III (X = H) | 2·10 | −0·30 | 192·9 | 85·3 | 86·6 | 2·28 ± 0·05 |
| III (X = Cl) | 3·28 | −0·30 | 289·0 | 97·3 | 91·4 | 3·11 ± 0·05 |
| III (X = $NO_2$) | 8·97 | −0·40 | 655·3 | 87·7 | 92·3 | 5·25 ± 0·05 |

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