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MOLECULAR STRUCTURE OF r-2-(p-TRIFLUOROMETHYLPHENYL)-TRANS-4, TRANS-6-DIMETHYL-1,3-DIOXANE

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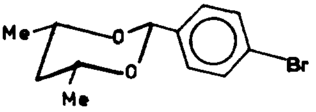
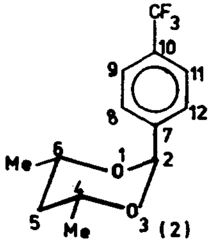
In an earlier communication[1] the problem concerning conformational equilibria of 2-substituted 1,3-dioxanes have been discussed and the crystal and molecular structure of the equatorially aryl-substituted 1,3-dioxane (1), studied in this context, was reported. The X-ray analysis of an axially aryl-substituted analogue, the title compound (2)[2], is reported here and discussed in the context of the preceeding paper.



(1)



(2)

Single crystals of (2), obtained by slow evaporation of petroleum ether solutions, were triclinic with space group P $\bar{1}$ and cell dimensions: a=13.798 Å, b=4.758 Å, c=11.120 Å, α=85.73°, β=112.35°, γ=1o1.66°. X-ray diffraction data were collected on an automatic three-circle Siemens diffractometer controlled by a Siemens 305 on-line computer. The structure was solved by direct methods using a multisolution technique[3]. The CF_3 group appeared to be statically disordered Altogether nine distinct fluorine peaks appeared in successive difference maps from which, also, the locations of all hydrogen atoms were obtained. Refinement with anisotropic temperature factors for all heavy atoms, occupancy factors of .4, .4,and .3 for three sets of CF_3 groups, and isotropic temperature factors for hydrogenatoms with 2748 independant reflections yielded a final agreement factor of R=.065.

The 1,3-dioxane ring which has a non-crystallographic C_m symmetry - as expected - appears in the chair conformation with both methyl groups occupying equatorial positions. The axial phenyl group is oriented in a perfect "perpendicular" conformation (see Fig. 1, nomenclature of ref. 4).

The crystal structure of (2) confirms the qualitative results in solution, namely that despite its relatively low ΔG^o value, axial phenyl in the 2-positioncauses substantial distortions of the 1,3-dioxane ring geometry[2]. Thus (2) appears to be initially sterically more strained than its 2-methyl analogue which nevertheless has the higher ΔG^o value.

Deformations in the 1,3-dioxane ring[5] which minimize the existing strain in (2) are apparent from ring torsional angles (cf. Fig. 1), the orientation of the phenyl group and from changes in bond angles (cf. Fig. 2).

While in (1) the dioxane ring consists of a puckered (O-C-O: $\bar{\omega}$ = 61.4°) and a flattened (C-C-C: $\bar{\omega}$ = 53.3°) moiety, this distinction is lost in (2) which shows about equal torsional angles ranging from 53.7° ($\bar{\omega}_{C-C-C}$) to 54.4° (all ω_{C-O}). The major change is seen in the O-C-O region; the torsional angles in the C-C-C moiety remain virtually uneffected by the axial substitution.

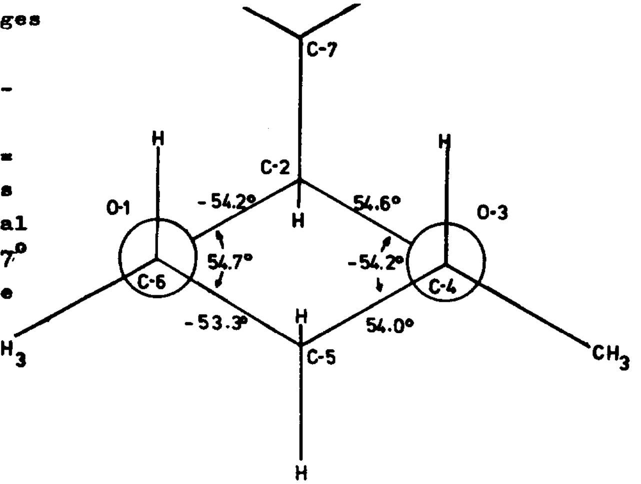


Fig. 1. Ring torsional angles of (2).

The phenyl group is bent outward appreciably as was already suggested by dipole moment calculations[2], but the bending is not as extensive as was assumed earlier. If one takes the position of H-1 in (1) as the true and undistorted axial position at C-2 of the 1,3-dioxane chair then the bending-out amounts to about 7°. This bending-out is reflected in the widening of valency angles O-C-2-C-7 from 108° in (1) to 112.5° in (2). Such bending has previously been observed in r-2-(p-bromophenyl)-2,4,4,trans-6-tetramethyl-1,3-dioxane[7]. Over and above this effect the carbon atom C-2 is displaced significantly out of the plane formed by the six coplanar carbon atoms of the phenyl ring (maximal deviation .01 Å). This deviation corresponds to a 6.5° angle between the C-2-C-7 bond vector and the plane of the phenyl so that the total bending amounts to ca. 13-14°.

The experimental bond angles of (2) (cf. Fig. 2) compare well with those of (1) as far as the C-C-C moiety and the methyl substituents are concerned. The only significant changes are observed for the C-O-C angles which are widened from 111.1° in (1) to 113.8° which clearly is connected with the flattening in this part of the dioxane ring, as is the earlier discussed change in the O-C-2-C-7 angles.

The experimental bond lengths (cf. Fig. 2) compare well with those found for (1) with the exception of the C-2-C-7 bond. In the axial isomer (2) this bond is longer by .2-.3 Å (1.532 compared to 1.511 in (1) and 1.50 Å in p-chlorophenyl-1,3-dioxane[5]). The accepted average value for a C_{sp^3}-C_{sp^2} bond reported by Bastiansen[6] is 1.504 Å. The deviation for the axial isomer seems to be well beyond the limit of error and therefore is probably of significance[+].

[+] In r-2-(p-chlorophenyl)-trans-4-t-butyl-1,3-dioxane (yet unpublished results) the corresponding $C\text{-}C_{aryl}$ bond is 1.521 Å, again significantly longer than the value of Bastianson[6].

Three main processes: flattening of the dioxane ring in the O-C-O region, bending outward of the phenyl substituent, and displacement of C-2 out of the plane of the aromatic ring (Knickung), decrease the *syn*-axial interactions of the phenyl substituent and the hydrogen atoms at C-4 and C-6 (H-2 and H-5) by increasing their intramolecular separations. The experimental distances are: C-7....H-2/H-5 2.75 Å and C-8/C-12....H-5/H-2 2.85 Å. (In an undistorted chair the distance C-7....H-2/H-5 would be about 2.4 Å).

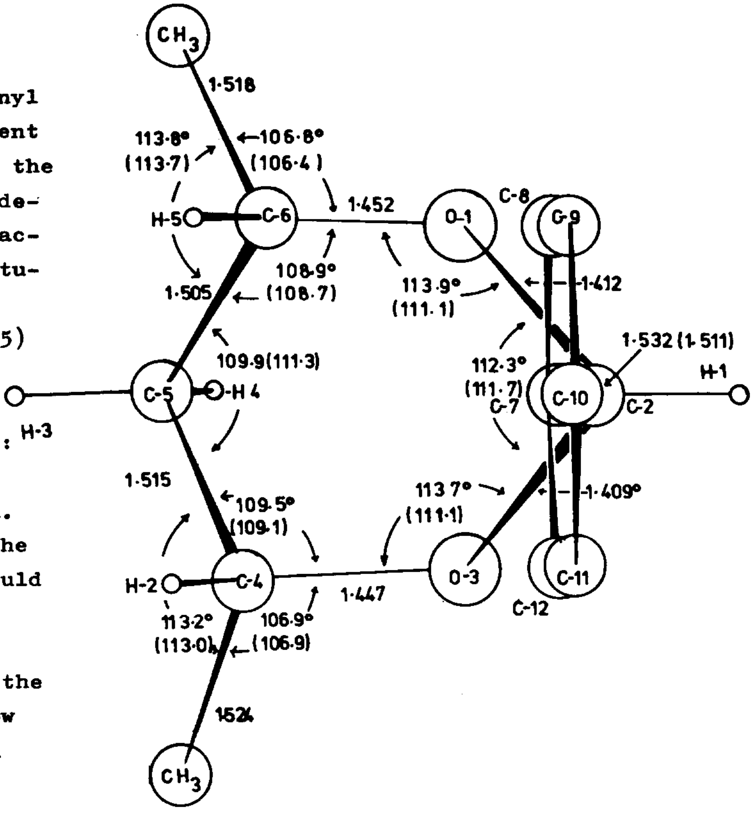


Fig. 2. Bond lengths and bond angles of (*2*) the values in parentheses are those of (*1*).

As a result of these changes in ring geometry, the dipole moment of (*2*) is now calculated to be 2.4 D^{+} in reasonable agreement with the experimental value of 2.7 D[2]. With the ring geometry of (*1*) the axial *p*-trifluoromethyl isomer would have a calculated moment of 1.63 D. Calculation of the equatorial analogue with the geometry of (*1*) leads to 4.55 D in excellent agreement with measurement (4.5 D). Thus one may conclude that the conformation of the 1,3-dioxane ring found in the solid state is similar to that in solution.

In trying to understand the energetic situation discussed previously in detail[2,1] we must explain the following problems: a. The similar conformational energies of axially phenyl substituted cyclohexanes and 2-substituted 1,3-dioxanes, despite closer *syn*-axial contacts in the latter; and b. strong deformations and yet lowered ΔG^{o} for axial phenyl compared to axial methyl. The cyclohexane comparison is readily understood on the basis of the results of calculations by Allinger and Tribble[4]: Much of the steric interactions in axial phenyl-cyclohexanes is due to "ortho-hydrogen/equatorial hydrogen" inter-

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$^{+}$ Using a C-O moment of 1.315 D and a CF_3 moment of 2.56 D.

action. Experimentally this is clearly seen in the crystal structure of cis-p-bromophenyl-4-t-butyl-cyclohexane[8]. Since o-hydrogen/equatorial hydrogen interactions are absent in 2-phenyl-1,3-dioxane or, rather, supplanted by far less severe o-hydrogen/oxygen contacts (O-H....O 2.55 Å in (2)), it is reasonable that the resulting loss in interaction energy about balances the increase in syn-axial repulsion.

By the same token, the absence of the C-H/e-H interaction allows the phenyl ring to bend out substantially and with little resistance, thus further minimizing syn-axial interactions.

Besides the above steric argument we may have to consider electronic factors. The finding of a lengthening of the C-2 - C-7 bond in (2) may indicate the presence of an anomeric effect of the phenyl group which favours the axial position. Similar bond lengthening has been found for 2-halo-1,4-dioxanes by Altona[9] and in 2-halo-glycopyranoses by Jeffrey and Pople[10] and was related to the anomeric effect observed in these compounds[11].

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