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THE CONTRASTING CONFORMATIONAL BEHAVIOUR OF 5-ARYL-5-METHYL-1,3-DIOXANES AND 1-ARYL-1-METHYLCYCLOHEXANES

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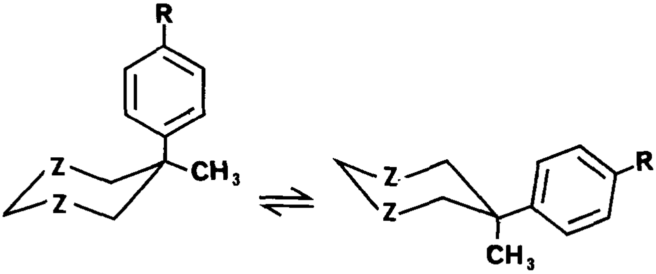
Summary. The chair ⇌ chair equilibrium of 5-aryl-5-methyl-1,3-dioxanes, unlike that of 1-aryl-1-methylcyclohexanes, is remarkably sensitive to the nature of substituents on the aromatic ring. An interaction involving the the aromatic group and the dioxane oxygen atoms or C-O bonds is proposed.

1-Methyl-1-phenylcyclohexane, (**1a**), exists predominantly as conformer **X** in which the substituent with the larger A-value (Ph) is axial.[1] This apparent contradiction, a prime example in conformational analysis of non-additivity of A-values, can be rationalised in terms of a Me....ortho C-H interaction in conformer **Y** which prevents the equatorial phenyl group lying in the bisector plane of the cyclohexane ring, the favoured orientation in phenylcyclohexane. Somewhat surprisingly the conformational behaviour of (**1a**) does not appear to find parallels in other ring systems. Indeed, Eliel and Enanoza[2] showed that the thermodynamically more stable diastereoisomer of 5-methyl-5-phenyl-2-*iso*-propyl-1,3-dioxane is that with the 5-Ph group equatorial. They were unable to pinpoint the exact cause of the different behaviour of the carbocyclic and heterocyclic systems but commented that it must be related to the absence of compression by *syn* axial hydrogens in the latter.[2] In this note we investigate this difference in behaviour further and identify the hitherto unrecognised involvement of an interaction between the phenyl group and components of the dioxane ring.



X **Y**

(**1**) Z = CH_2
a. R = H
b. R = NEt_2
c. R = OCOMe
d. R = COMe
e. R = NO_2

(**2**) Z = O
a. R = H
b. R = Et
c. R = I
d. R = COMe
e. R = NO_2

Table 1. Conformational Equilibria in Compounds of Series (1) and (2) in $CFCl_3$

		Series 1						**Series 2**			
No	Subst R	Temp °K	X:Y a	K	ΔG° kJ/Mole	No	Subst R	Temp °K	X:Y b	K	ΔG° KJ/Mole
1a	H	189	73:27	0.31	1.6	2a	H	173	21:79	3.76	-1.9
1b	NEt_2	193	74:26	0.35	1.7	2b	Et	173	20:80	4.00	-2.0
1c	OCOMe	193	75:25	0.33	1.8	2c	I	173	42:58	1.38	-0.5
1d	COMe	193	72:28	0.39	1.5	2d	COMe	173	48:52	1.08	-0.1
1e	NO_2	180	72:28	0.39	1.4	2e	NO_2	173	71:29	0.41	1.3

[a] Data from 400 MHz spectra (Bruker WH 400, SERC Service), [b] data from 200 MHz spectra (Bruker CXP 200)

Evidence for the interaction follows from a low temperature ^{1}H-nmr study of the conformational equilibria of the 5-aryl-5-phenyl-1,3-dioxanes (**2a**) - (**2e**). Signals for conformers **X** and **Y** are well separated and assigned[3] by comparison with data for conformationally locked compounds.[2] Integration of signals gives the conformer ratios listed in table 1. Also tabulated are data for some 1-aryl-1-methylcyclohexanes (**1a**) - (**1e**).[3]

5-Methyl-5-phenyl-1,3-dioxane (**2a**) favours conformer **Y** in accord with the results obtained from equilibration of configurational isomers.[2] However, we find the equilibrium **X**$\rightleftarrows$**Y** in this series is sensitive to para substitution. Electron withdrawing groups steadily reduce the value of K (= [**Y**]/[**X**]) and, indeed, **X** becomes the substantially preferred conformer of the nitro compound (**2e**). This enhanced population of the gauche arrangement of aryl group and C-O bonds upon introduction of electron withdrawing para substituents finds a parallel in the conformational behaviour of 2-aryl-1-methoxypropanes and 2-arylpropyl acetates.[4]

The variations in K in series (**2**) are consistent with a non-steric interaction involving the aromatic ring. In view of the relative insensitivity of K in the carbocyclic series, (**1**), we surmise that it also involves the dioxane oxygen atoms or the polar C-O bonds. Although the precise nature of the interaction is uncertain, we note that Log K for series (**2**) varies linearly with σ, (ρ = -1.06; corr. coeff. 0.969). This would seem to imply that the interaction is sensitive to variations in electron density at the aryl carbon bonded to C(5) and/or to the polarisation of the aryl-C(5) bond.

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