Conformational Analysis of *ortho*-Substituted Toluenes. The δ Effect and ^{13}C Chemical Shifts

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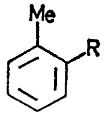
Summary The ^{13}C chemical shift of the methyl group in *ortho*-substituted toluenes is related to the conformation of the *ortho*-substituent.

THE 2·0 p.p.m. upfield shift of the methyl group of toluene (**1**) on substitution of a methyl group to give *o*-xylene (**2**) has been explained in terms of the steric perturbation of the C–H bonds and is a classic example of the γ effect.[1] A bigger *ortho*-alkyl group might be expected to increase steric perturbation and cause the methyl group to shift to even higher field. The Table presents chemical shift data for some such compounds and the δ effects of the substituents. It is clear that increased crowding does not necessarily cause shifts to higher field; a rationalisation of these data requires consideration of the stereochemical dependence of the δ effects.[2]

Examples of significant δ effects are few, although Kroschwitz *et al.*[3] invoked a deshielding δ effect some years ago. Grover and his co-workers[4] observed large downfield shifts in cyclic systems when the interacting groups, one of which was hydroxyl, are *syn*-axial and hence sterically perturbed. More recently Batchelor[5] has demonstrated that such shifts are not a peculiar property of cyclic systems and hydroxyl interactions but that they also occur in acyclic hydrocarbons. The fact that δ effects in acyclic systems, particularly where Me–Me interactions might be involved, are small reflects the fact that conformations with *syn*-axial interactions are little populated.

TABLE. Tolyl methyl shifts in



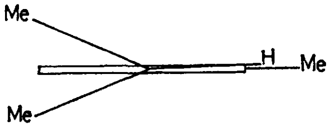
	R	Chemical shift[a]	δ Effect[b]
(**1**)	H	21·4	
(**2**)	Me	19·4	
(**3**)	Et	19·0	−0·4
(**4**)	Pr^i	19·2	0·2
(**5**)	Bu^t	23·2	4·0
(**6**)	CH_2OH	18·4	−1·0
(**7**)	CH(OH)Me	18·8	0·4
(**8**)	$C(Me)_2OH$	22·1	3·3

[a] In p.p.m. from internal Me_4Si for $CDCl_3$ solutions. [b] Tolyl methyl shift in compound − tolyl methyl shift in compound with one less substituent.

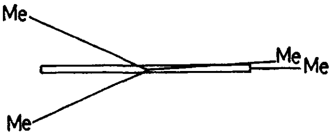
Since knowledge of the conformations about aryl–carbon bonds is much more scant than in simple aliphatic systems, the shifts caused by the *ortho*-groups are particularly interesting.[6] Exchanging a hydrogen for a methyl in *o*-xylene to give *o*-ethyltoluene shifts the tolyl methyl only slightly upfield. Further substitution to give *o*-isopropyltoluene also causes little change in shift. However, in *o*-t-butyltoluene the methyl group is shifted dramatically downfield; addition of the third δ methyl causes a 4·0 p.p.m. downfield shift.

These data suggest that in (**3**) the methyl of the ethyl group is remote from the tolyl methyl, likewise the isopropyl methyls in (**4**). This would give a favoured conformation as in (**9**) in the latter case. The shift in (**5**) is at much lower field since severe steric interactions are unavoidable. It is unlikely that a coplanar interaction as in (**10**) is present; a conformation such as (**11**) is more probable.

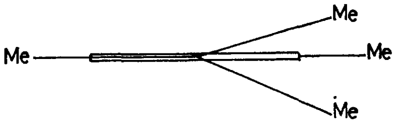
In (**8**) where there are again three δ substituents on the *ortho*-grouping one being hydroxyl, there is again a large downfield shift. In *o*-methylbenzyl alcohol (**6**), the tolyl methyl is shifted 1 p.p.m. upfield by the δ hydroxyl group. Upfield shifts of this magnitude have been observed in cyclohexane[7] and norbornane[2] systems when the groups involved are at maximum separation. Therefore in (**6**) both the absence of a downfield shift and the small upfield shift observed, indicate that the OH is '*anti*' to the tolyl methyl.



(**9**)



(**10**)



(**11**)

The results for this system where the molecular architecture is completely different from those studied previously, further validate the generality of the downfield δ effect and indicate that useful conformational information may be obtained.

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[1] For a discussion see, J. B. Stothers, 'Carbon 13 NMR Spectroscopy,' Academic Press, New York, 1972.

[2] For a recent review see, N. K. Wilson and J. B. Stothers, *Topics in Stereochemistry*, 1974, **7**, 1.

[3] J. I. Kroschwitz, M. Winokur, H. J. Reich, and J. D. Roberts, *J. Amer. Chem. Soc.*, 1969, **91**, 5927.

[4] S. H. Grover, J. P. Guthrie, J. B. Stothers, and C. T. Tan, *J. Magnetic Resonance*, 1973, **10**, 227.

[5] J. G. Batchelor, *J. Magnetic Resonance*, 1975, **18**, 212.

[6] For a recent discussion of the conformations about aryl–carbon bonds see J. E. Anderson and H. Pearson, *J.C.S. Perkin II*, 1974, 1779.

[7] T. Pehk and E. Lippmaa, *Org. Magnetic Resonance*, 1971, **3**, 679.