Electronic and Steric Effects on Hindered Rotation about Phenyl–Carbon Bonds

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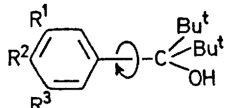
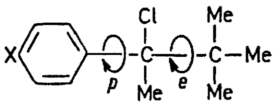
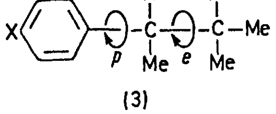
Summary The effect of substituents on rotation about the phenyl–carbon bond in substituted toluenes is reported and discussed in terms of steric and electronic interactions.

CONFORMATIONAL preferences about an sp^3–sp^2 bond have recently been studied,[1] but there has been little consideration of the dynamics of rotation about such bonds. There are few studies of rotation about phenyl–carbon bonds[2] particularly in compounds without *ortho*-substituents, but the barriers to rotation in toluene and similar methylbenzenes are known to be a few cal per mol,[3] while in contrast, the barrier in compounds of type (**1**) is *ca.* 20 kcal mol^{-1}.[2,4]

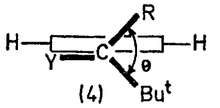

(1)

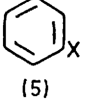

(2)

(a) X = NO$_2$
(b) X = OMe
(c) X = H


(3)

(a) X = NO$_2$
(b) X = OMe


(4)


(5)

(a) X = CH$_2$Bu^t
(b) X = Cl
(c) X = Ph

In (**2a**) and (**2b**) we have found evidence for hindered rotation about the phenyl bond *p* as well as about the ethane bond *e*,† expected from previous work.[5] The n.m.r. spectrum of the phenyl hydrogens in (**2a**) and (**2b**) at room temperature is of the form AA′BB′; below about −60° signals broaden and at about −130° the spectrum is of an ABCD type. Thus at −130° rotation about the phenyl bond *p* is slow on the n.m.r. timescale. An approximate line-shape fit with computer-generated spectra led to the rate constants and barriers to rotation about the phenyl bond given in the Table, the barrier being markedly higher in the nitro-compound.

TABLE

	Rotation	k_{rotation} /s^{-1}	Temperature (t/°C)	$\Delta G^\ddagger$ /(kcal mol^{-1})
(2a)	Ph, *p*	50	−114·0	7·8
(2b)	Ph, *p*	100	−118·4	7·4
(3a)	Ph, *p*	13	−101·0	9·01
(3b)	Ph, *p*	25	−101·0	8·79

To reduce the possibility that changes in dipole interactions affect the barriers (**3a**) and (**3b**) were prepared. The appearance of the aromatic hydrogens is again temperature-dependent, and rate constants and barriers to phenyl rotation derived are shown in the Table. Barriers found for compounds (**3**) are higher than for compounds (**2**) by about 1 kcal mol^{-1}, but in both cases rotation is easier in the *p*-methoxy-compound.

The enhanced barriers for (**3**) are best explained in terms of the ground-state conformation of these compounds, which is expected to be as in (**4**).‡ Y is more or less in the plane of the phenyl ring and when it is a chlorine atom, its interaction with the *ortho*-hydrogen will destabilise the ground state, but will have a considerably smaller effect on the transition state, presumably the conformation with the t-butyl group in the plane of the ring. This destabilisation of the ground state leads to a barrier smaller in (**2**) than in (**3**).

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† As the temperature is lowered, all compounds (**2a**—**2c**, **3a**, **3b**) show changes in the t-butyl signals as expected for rotation about the ethane bond *e* becoming slow on the n.m.r time scale;[5] this aspect is not discussed further here.

‡ For a methyl group attached to an sp^2-centre, it is well established that the preferred conformation has one of the methyl hydrogens in the plane of that centre.[1] This has also been found to hold true for substituted toluenes.[6]

For compounds (**5**) there are no changes in the n.m.r. spectrum even at −150°, indicating barriers to rotation of less than 6 kcal mol^{-1}. These low values and the high barriers for (**1**) are consistent with structure (**4**) and a transition state with a t-butyl group in the plane of the phenyl ring, only if for (**3**) and more so for (**1**), the angle θ, shown in (**4**) is greater than 120° due presumably to steric interactions. Only if this is so will the interaction of the group R with the phenyl ring be greater in the transition state than in the ground state. Thereby R can be the cause of the increase in the barriers along the series (**5**)–(**3**)–(**1**).

The higher barrier in (**3a**) compared with (**3b**), and of (**2a**) compared with (**2b**), suggests an electronic effect on the barrier but further results are necessary before its exact nature can be discussed.

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[1] G. J. Karabatsos and D. J. Fenoglio, *Topics Stereochem.*, 1971, **5**, 167.
[2] See R. E. Gall, D. Landman, G. P. Newsoroff, and S. Sternhell, *Austral. J. Chem.*, 1972, **25**, 109.
[3] A. recent review is given by J. P. Lowe, *Progr. Phys. Org. Chem.*, 1968, **6**, 1.
[4] G. P. Newsoroff and S. Sternhell, *Tetrahedron Letters*, 1967, 2539.
[5] J. E. Anderson and H. Pearson, *Chem. Comm.*, 1971, 871.
[6] G. Tsoucaris, *Acta Cryst.*, 1961, **14**, 909; D. W. J. Cruickshank, *ibid.*, 1949, **2**, 65.