Slow Rotation around Benzene–Oxygen and Benzene–Sulphur Bonds in Aromatic Ethers, Sulphides, and Disulphides

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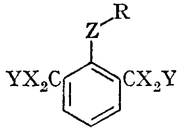
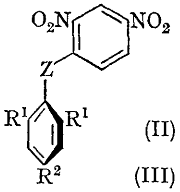
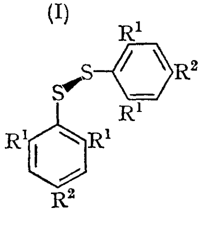
Recently, we have demonstrated the magnetic nonequivalence of the CX_2Y-groups in *ortho*-substituted benzene derivatives (I), if the substituent Z-R is turned out of the plane of the benzene ring and rotation around the benzene–Z bond is slow.[2] We have now investigated the n.m.r. spectra of the hindered ether (II), sulphides (III), (IV), and disulphides (V), (VI). All spectra are temperature-dependent in the CX_2Y-region ($CHMe_2$, CH_2Me). At sufficiently low temperatures magnetic nonequivalence of the X in the *ortho*-alkyl groups was observed. Free enthalpies of activation $(\Delta G)^{\ddagger}_{c}$ were calculated from signal-splitting at low temperatures and from the coalescence temperature by use of the Eyring equation (Table).



(I)



	Z	R¹	R²
(II)	O	Prⁱ	H
(III)	S	Prⁱ	Prⁱ
(IV)	S	Et	H



(V) $R^1 = R^2 = Pr^i$

(IV) $R^1 = Et$, $R^2 = H$

The results allow a correlation between the $\Delta G^{\ddagger}_{c}$ values and the size of Z. Thus the value for $\Delta G^{\ddagger}_{c}$ for the ether (II) is *ca.* 3 kcal./mole higher than that for the corresponding sulphur compound (III). The greater size of the sulphur atom thus reduces the steric interference of the *ortho*-isopropyl groups with the dinitrophenyl group. In agreement with this explanation, in disulphides steric hindrance is at its lowest degree. The dinitrophenyl ring in sulphides shows a larger effect than that of the *S*-aryl group in disulphides.

The higher activation barrier in the oxygen compound compared to the sulphur compound furnishes a good argument against an inversion mechanism with a linear transition state (VII).

Such a mechanism should be more probable for oxygen because of easier hybridisation and also more probable in the case of sulphides than of disulphides.[3] Hence isomerisation must proceed

Free enthalpies of activation of rotation around benzene–Z bonds

Compound	Solvent	Δ (c./sec.)	T_c°	$\Delta G^{\ddagger}_{c}$ [kcal./mole]
(II)	1,2,4-C_6H_3	4·6	+57	17·8
(III)	$CDCl_3$	9·0	+12	15·0
(IV)	$CDCl_3$	2[a]	0[a]	15·1[a]
(V)	CS_2	9·0	−27	12·8
(VI)	CS_2	3·5[a]	−55[a]	11·7[a]

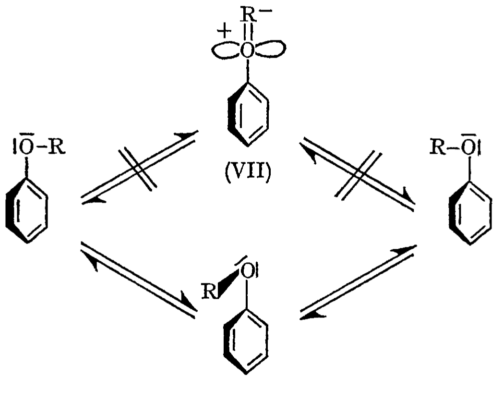
[a] Estimated values

by rotation around the Z–aryl bond (transition state VIII).

There are many examples of hindered rotation around benzene–nitrogen bonds caused by steric effects in aromatic amides,[2,4] amines,[4] and quinone anils.[2] However, hindered rotation around a carbon–sulphur bond has not previously been shown by n.m.r.[5] Slow rotation around the benzene–oxygen bond is found in aryl esters[6] and has been claimed in diaryl ethers.[7]

We thank Professor Dr. Eugen Mueller and the Deutsche Forschungsgemeinschaft for generous support of this work.

(*Received, March 11th, 1968; Com. 290.*)



(VIII)

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[1] Part of the series: Innermolecular motion by n.m.r. spectroscopy; previous part: H. Kessler, *Tetrahedron Letters*, 1968, in the press.

[2] H. Kessler, *Tetrahedron*, 1968, **24**, 1857.

[3] An electronegative substituent such as sulphur on nitrogen stabilizes the pyramidal arrangement of the N (M. Raban, *Chem. Comm.*, 1967, 1017).

[4] T. H. Siddall, tert., and C. A. Prohaska, *J. Amer. Chem. Soc.*, 1966, **88**, 1172; J. Shvo, E. C. Taylor, K. Mislow, and M. Raban, *J. Amer. Chem. Soc.*, 1967, **89**, 4910; B. J. Price, J. A. Eggleston, and I. O. Sutherland, *J. Chem. Soc.* (*B*), 1967, 922 and references cited.

[5] We consider the temperature-dependent n.m.r. spectra of sulphurylides to be caused also by rotation around the sulphur–carbon bond with concurrent rotation around both *C*-acetyl bonds rather than by inversion on sulphur; H. Nozaki, D. Tunemoto, Z. Morita, K. Nakamura, K. Watanabe, M. Takaku, and K. Kondo, *Tetrahedron*, 1967, **23**, 4279.

[6] T. H. Siddall, tert., W. F. Steward, and M. L. Good, *Canad. J. Chem.*, 1967, **45**, 1290.

[7] D. A. Bolon, *J. Amer. Chem. Soc.*, 1966, **88**, 3148.