Effect of Intermolecular Hydrogen Bonding on the Molecular and Electronic Structure of Hydroxybenzenes

Aldo Domenicano,[a,b,*] István Hargittai,[c,*] Gustavo Portalone[d] and György Schultz[c]

[a]Department of Chemistry, Chemical Engineering and Materials, University of L'Aquila, Via Assergi 4, I-67100 L'Aquila, Italy, [b]Institute of Structural Chemistry, CNR, I-00016 Monterotondo Stazione, Italy, [c]Structural Chemistry Research Group of the Hungarian Academy of Sciences, Eötvös University, Puskin utca 11–13, Pf. 117, H-1431 Budapest, Hungary and [d]Department of Chemistry, University of Rome "La Sapienza", Città Universitaria, I-00185 Rome, Italy

Dedicated to Professor Otto Bastiansen on his 70th birthday

The interaction of a substituent with a molecular framework should not be considered as a merely intramolecular effect. Intermolecular forces in the condensed phase may appreciably perturb the substituent–framework interaction. This is more likely to occur when a π-donor or π-acceptor functional group is attached to an aromatic system, since π electrons are more easily polarized than σ electrons by interactions with adjacent molecules.

In substituted benzene derivatives the presence of a substituent gives rise to small but measurable geometrical distortions of the carbon skeleton. These have been extensively investigated,[1–8] and it is now possible to study the nature of the ring-substituent interaction by accurately measuring the distortion of the ring geometry with respect to unsubstituted benzene. The influence of intermolecular interactions on substituent effects may be studied by comparing the geometry of the benzene ring in the free molecule with that in the crystal molecule.[9–11] The comparison should preferably involve bond angles rather than bond distances, as they are less affected by the various systematic errors inherent in each technique of

structure determination and are thus more easily transferred from one experiment to another.[3]

Using this approach, we have investigated the effect that intermolecular hydrogen bonding in the solid state has on the molecular and electronic structures of hydroxybenzenes.

Origin of the structural data

The structural data used in the present study originate from various sources; they have been critically examined and should all be considered as accurately determined.

The ring angles of the free molecules are taken from our electron diffraction studies of phenol,[12] *p*-dihydroxybenzene[13] and *sym*-trihydroxybenzene.[14] They are accurate to within ±0.2°.

The ring angles of the crystal molecules have been derived indirectly: they are calculated from the so-called "angular parameters" of the hydroxyl group. These parameters express the angular deformation of the benzene ring caused by a functional group,[6] and are defined as $\Delta\alpha = \alpha - 120°$, $\Delta\beta = \beta - 120°$, $\Delta\gamma = \gamma - 120°$; $\Delta\delta = \delta - 120°$ (see Fig. 1 for the labelling of the ring angles). In the case of the hydroxyl group, two sets of angular parameters are available; both have

---
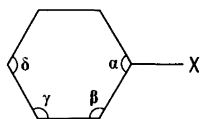
*To whom correspondence should be addressed.

Fig. 1. Labelling of the C-C-C angles in monosubstituted benzene rings. C_{2v} symmetry has been assumed.

been calculated by regression from many accurate structural data on polysubstituted benzene rings *in the solid state,* assuming that the distortions caused by the various substituents are independent and can be superimposed.[6,7] The two groups of authors made use of different data in their regression procedures. The ring angles of phenol, *p*-dihydroxybenzene and *sym*-trihydroxybenzene calculated from the two sets of angular parameters agree to within 0.2°, which may be taken as indicative of their accuracy.

In the case of *p*-dihydroxybenzene, an accurate value of the C-C(OH)-C angle of the crystal molecule has also been determined by averaging many observations from X-ray diffraction studies of *p*-dihydroxybenzene itself and of its molecular complexes.[15] The value obtained is virtually the same as that calculated from the angular parameters for the hydroxyl group.

Discussion

In Table 1 we compare the values of the internal ring angles at the place of substitution, C-C (OH)-C, as obtained from our electron diffraction studies of the free molecules, with the corresponding values for the crystal molecules. These

angles are quite sensitive to the electronic properties of the substituent, and are particularly well suited for revealing their changes.[1-5]

The C-C(OH)-C angles of Table 1 show a characteristic variation on moving horizontally from phenol to *sym*-trihydroxybenzene, irrespective of whether they refer to the free molecule or to the crystal molecule. This is merely an effect of the different patterns of substitution in the molecules considered. In a polysubstituted derivative of benzene, the actual value of a C-C(X)-C angle depends not only on the nature of X but also on the pattern of substitution, due to the superposition of distortional effects from the various substituents.[6,7] In the case of the hydroxyl group, the angular parameters of Refs. 6 and 7 consistently indicate that the γ angle is several tenths of a degree larger, and the δ angle about as much smaller, than the ideal value of 120°. The same indication is given by two different experimental studies of the molecular structure of phenol in the gaseous phase.[12,16] This explains straightforwardly the horizontal variation in the angles of Table 1.
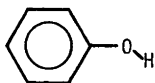
More intriguing is the vertical variation in these angles. The values obtained from gas-phase studies are seen to be invariably larger (by 0.9–1.2°) than the corresponding values from solid-state studies. Although small, the effect is well beyond experimental error and is certainly real.

We have observed a similar angular change in a related molecule, *p*-diaminobenzene, where the C-C(NH$_2$)-C angle was found to decrease by 1.9° in going from the free molecule to the crystal molecule.[11] This remarkable geometrical change was attributed to the formation of $N-H\cdots N$ hydrogen bonds in the solid state.[11] Here, we

Table 1. Values of the C-C(OH)-C angles (°) in some hydroxybenzenes.

	Phenol	*p*-Dihydroxybenzene	*sym*-Trihydroxybenzene
Free molecule[a]	121.4±0.2[b]	120.7±0.2[c]	122.4±0.2[d]
Crystal molecule	120.2[e]	119.6[e]	121.4[e]
	120.2[f]	119.8[f]	121.5[f]
		119.7(1)[g]	

[a]Total errors are given as error limits. [b]Ref. 12. [c]Ref. 13. [d]Ref. 14. [e]Calculated from the angular parameters for the hydroxyl group given in Ref. 6. [f]Calculated from the angular parameters for the hydroxyl group given in Table 5 of Ref. 7. [g]Average of 17 observations obtained by X-ray crystallography for *p*-dihydroxybenzene and its molecular complexes (Ref. 15). The standard deviation of the mean is given in parentheses as units in the last digit.
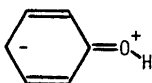
(I)   (II)

suggest that the vertical variation in the C-C(OH)-C angles of Table 1 may originate from a similar effect.

In the solid state, the molecules of phenol and of its substituted derivatives are invariably connected by $O-H \cdots O$ hydrogen bonds. These become stronger as the $O-H$ bond is made more polar by a partial positive charge residing on the oxygen atom[17] (it is well known, for instance, that phenols form stronger hydrogen bonds than alcohols). It follows that the relative contribution of polar canonical forms like (II) should be somewhat greater for the crystal molecules than for the free molecules, which – according to the VSEPR model – is consistent with the direction of the observed angular change.

References

1. Domenicano, A., Vaciago, A. and Coulson, C. A. *Acta Crystallogr., Sect. B 31* (1975) 221.
2. Domenicano, A., Vaciago, A. and Coulson, C. A. *Acta Crystallogr., Sect. B 31* (1975) 1630.
3. Domenicano, A. and Vaciago, A. *Acta Crystallogr., Sect. B 35* (1979) 1382.
4. Domenicano, A., Murray-Rust, P. and Vaciago, A. *Acta Crystallogr., Sect. B 39* (1983) 457.
5. Domenicano, A., Mazzeo, P. and Vaciago, A. *Tetrahedron Lett.* (1976) 1029.
6. Domenicano, A. and Murray-Rust, P. *Tetrahedron Lett.* (1979) 2283.
7. Norrestam, R. and Schepper, L. *Acta Chem. Scand., Ser. A 35* (1981) 91.
8. Bock, C. W., Trachtman, M. and George, P. *J. Mol. Struct. (Theochem.) 122* (1985) 155.
9. Colapietro, M., Domenicano, A., Portalone, G., Schultz, Gy. and Hargittai, I. *J. Mol. Struct. 112* (1984) 141.
10. Colapietro, M., Domenicano, A., Portalone, G., Torrini, I., Hargittai, I. and Schultz, Gy. *J. Mol. Struct. 125* (1984) 19.
11. Colapietro, M., Domenicano, A., Portalone, G., Schultz, Gy. and Hargittai, I. *J. Phys. Chem. 91* (1987) 1728.
12. Portalone, G., Domenicano, A., Schultz, Gy. and Hargittai, I. *Presentation at the 18th Meeting of the Italian Crystallographic Association,* Como, Italy, 27–30 October 1987. Abstracts, p. 54.
13. Domenicano, A., Hargittai, I., Portalone, G. and Schultz, Gy. *Presentation at the 7th European Crystallographic Meeting,* Jerusalem, Israel, 29 August – 3 September 1982. Abstracts, p. 155.
14. Domenicano, A., Portalone, G., Schultz, Gy. and Hargittai, I. *To be published.*
15. Domenicano, A. *Presentation at the 5th Italian-Yugoslav Crystallographic Congress,* Padua, Italy, 3–6 June 1986. Abstract C23.
16. Larsen, N. W. *J. Mol. Struct. 51* (1979) 175.
17. Pimentel, G. C. and McClellan, A. L. *The Hydrogen Bond,* Freeman, San Francisco and London 1960, pp. 280–284.