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X-RAY AND IR STUDIES ON CRYSTAL AND MOLECULAR STRUCTURE OF 4-NITRO-2,6-DIPHENYLPHENOL. STEREOCHEMISTRY OF BIFURCATED OH···π HYDROGEN BONDS

Shinichi Ueji*
Department of Chemistry, College of General Education, Kobe University,
Tsurukabuto, Nada, Kobe 657, Japan
Kazumi Nakatsu,* Hiroshi Yoshioka, and Kenji Kinoshita
Department of Chemistry, Faculty of Science, Kwansei Gakuin University,
Uegahara, Nishinomiya, Hyogo 662, Japan

Abstract: The crystals of the title compound contain both intra- and intermolecular OH···π hydrogen bonds (the first example of bifurcated OH···π bonds), the stereochemistry of which has been elucidated by an X-ray structure analysis; this bifurcated bond is also supported by the observations based on the IR spectrum of the crystals.

Little is known about the stereochemistry of the hydrogen bonds between hydroxyl groups and π electrons of aromatic systems in the crystalline state.[1-3] In order to elucidate the stereochemistry of the OH···π hydrogen bond, we have undertaken an X-ray crystallographic analysis of 4-nitro-2,6-diphenylphenol **1**.[4] Here, we present the first example of the structure which contains the OH···π bond bifurcated into the intra- and inter-molecular π electrons.

Crystal data: $C_{18}H_{13}NO_3$, $\underline{M}_r$ = 291.31; monoclinic, space group $\underline{C2/c}$; $\underline{a}$ = 21.983(3), $\underline{b}$ = 9.259(1), $\underline{c}$ = 14.208(2) Å, $\underline{\beta}$ = 95.32(2)°; $\underline{Z}$ = 8, $\underline{D}_x$ = 1.3440(3) g cm^{-3}. The structure was solved by an application of the direct method, and refined by the block-diagonal least-squares method on the basis of 2040 observed $[|\underline{F}_o| > 3\underline{\sigma}(\underline{F})]$ reflections collected on an automated diffractometer. Anisotropic thermal vibrations were assumed for the non-hydrogen atoms. All the H atoms including phenolic H atom, H(1), that is important in the present study, were found quite unambiguously from a difference Fourier map and refined isotropically. The isotropic temperature factor of H(1) was $\underline{B}$ = 6.8(6) Å^2. In the final least-squares cycles the weighting scheme used was $1/\underline{W} = \underline{\sigma}^2(\underline{F}_o) + 0.00025|\underline{F}_o|^2$. The final residuals were $\underline{R} = \Sigma(|\underline{F}_o| - |\underline{F}_c|)/\Sigma|\underline{F}_o|$ = 0.051 and $\underline{R}_w = [\Sigma\underline{W}(|\underline{F}_o| - |\underline{F}_c|)^2/\Sigma\underline{W}(\underline{F}_o)^2]^{1/2}$ = 0.047. The atomic scattering factors for C, N, and O were those of Cromer and Waber[5]; for H the factors of Stewart, Davidson, and Simpson[6] were used . The final e.s.d.'s for the atomic positions, $(\underline{\sigma}_x^{\ 2} + \underline{\sigma}_y^{\ 2} + \underline{\sigma}_z^{\ 2})^{1/2}$, were less than 0.005 Å for the C atoms, 0.003 Å for the N and O atoms, and 0.04 Å for the H atoms. The e.s.d's for the bond lengths range from 0.002 to 0.004 Å for the C-C, C-N, C-O, and N-O lengths, and from 0.017 to 0.026 Å for the C-H and O-H lengths. See reference 7 for additional crystallographic details.

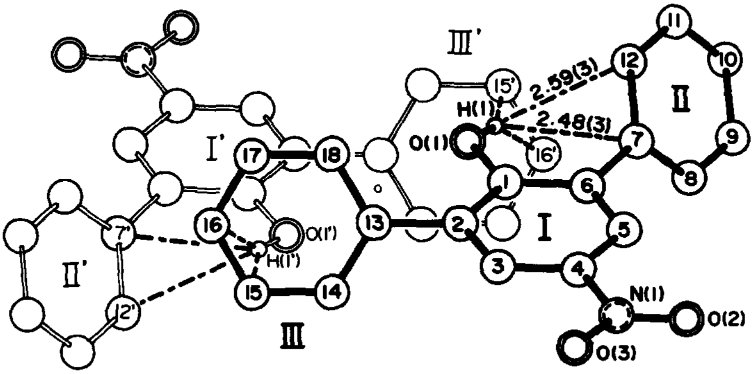


Figure 1. A portion of the crystal structure showing intra (— -)- and inter(- -)-molecular OH···π hydrogen bonds. The smallest circle indicates the center of symmetry relating the molecules. C(1)-O(1) = 1.356(2) Å, O(1)-H(1) = 0.75(2) Å, and C(1)-O(1)-H(1) = 110(2)°.

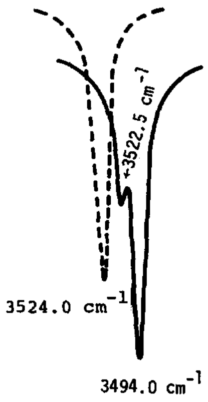


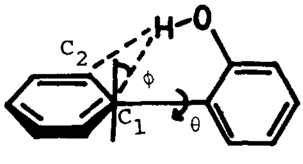
Figure 2. The νOH absorption spectra of the crystals of 1 (——) and 2 (---).

Figure 1 shows the dimeric arrangement of the molecules 1 in the crystals. The *ortho* phenyl rings, II and III, are twisted in opposite directions by 58 and 52°, respectively, from the phenol ring I. The hydroxyl group is almost coplanar with the ring I. The hydroxyl H(1) atom approches C(7) and C(12) with the distances of 2.48(3)[H(1)···C(7)] and 2.59(3) Å [H(1)···C(12)], which are considerably shorter than the sum of the van der Waals radii for hydrogen (1.2 Å) and carbon (1.7 Å). The distance between H(1) and the midpoint of the bond C(7)-C(12) is 2.44 Å. Thus, it is evident that an intramolecular OH···π bond, similar to that found in 2,6-diphenylphenol 2,[3] is formed between H(1) and the π electrons on both C(7) and C(12); the corresponding distances found in 2 are 2.43(4) and 2.40(4) Å.[3]

Additionally, the intermolecular short contacts are also found between H(1) and both C(15') and C(16') of the neighboring molecule(see Fig. 1). The H(1)···C(15')[2.85(2) Å] and H(1)··· C(16')[2.89(2) Å] distances are almost equal to the van der Waals distance. The distance between H(1) and the midpoint of the C(15')-C(16') bond is 2.79 Å. This contact suggests the presence of a weak intermolecular OH···π bond.[8] The presence of such bifurcated OH···π bonds is also supported by the observations based on the IR spectrum of the crystals (see below).

The most interesting feature of the crystal structure of 1 is the stereochemistry of the bifurcated OH···π bonds. In particular, the intermolecular OH···π bond is of interest, because the spatial arrangement of the hydroxyl group and the proton acceptor ring is not fixed in the same molecule. In both OH···π bonds, the H(1) atom is situated almost on top of the center of the C=C bond of the proton acceptor ring (see Fig. 1). This stereochemistry is consistent with that found in the crystal of benzene – Ag^+ complex,[11] but is different from that found in the crystal of tributylammonium tetraphenylborate monohydrate, where each water H atom approaches near the sixfold axis of the benzene ring.[2] The former stereochemistry may be rationalized in terms of the mode of the HOMO(electron donor) — LUMO(acceptor) interaction based on molecular orbital theory,[12] because the HOMO — LUMO overlap is efficient. Consequently, both the OH···π bonds found in **1** can be classified as a weak charge-transfer complex, and may not arise as a result of crystal-packing forces. This observation is consistent with the spectroscopic result of Ōki and Iwamura.[13]

As shown in Figure 2, the OH stretching IR absorption (νOH) of the crystals (CsI disc) of **1** appears as a doublet,[14] whereas that of **2** possessing a single intramolecular OH···π bond as a singlet; in CCl_4 solution both the phenols indicate a singlet νOH band due to a single OH···π bond.[15] In the doublet, the bands at 3494.0 and 3522.5 (weak band at higher frequency) cm^{-1} can be assigned to the intra- and inter-molecular OH···π bonded species, respectively, on the following basis. The frequency difference in the ν(intra-)OH···π band of the crystals between **1** and **2** [3524.0 cm^{-1}(**2**) — 3494.0 cm^{-1}(**1**) = 30.0 cm^{-1}], arising mainly from the substituent effects, corresponds fairly well to that observed in CCl_4 solution [3555.7 cm^{-1}(**2**) — 3532.0 cm^{-1}(**1**) = 23.7 cm^{-1}][15b], thus supporting the assignment of the ν(intra-)OH···π band. The small difference (30.0 cm^{-1} — 23.7 cm^{-1} = 6.3 cm^{-1}) on passing from the crystals to CCl_4 solution may be mainly due to the phase effects.[16] On the other hand, the assignment of the ν(inter-)OH···π band is based on the correlation proposed by Ōki and Iwamura,[13] who reported that the strength of the OH···π bond is approximately proportional to the square of the overlap integral between the orbitals of the hydroxyl H atom and the carbon atoms concerned. For the OH···π bond in 2-phenylphenols,[13] a linear correlation between the frequency shifts [$\Delta\nu$ = ν(free)OH — ν(intra-)OH···π] as a measure of the strength of the OH···π bond and the square of the overlap integral [$S(R,\phi)$] is reproduced in Figure 3. The geometrical parameters, R and ϕ, are represented as follows.



$\phi = 90° - \theta$

(θ:dihedral angle)

R = distance H···C atom

The S value contains the contribution of both the C_1 atom (80%) and C_2 atom (20%).[13]
To establish a similar correlation for the OH···π bond in **1**, the S^2 value (0.008)[17] for the intramolecular OH···π bond calculated on the basis of the X-ray result is plotted against the corresponding

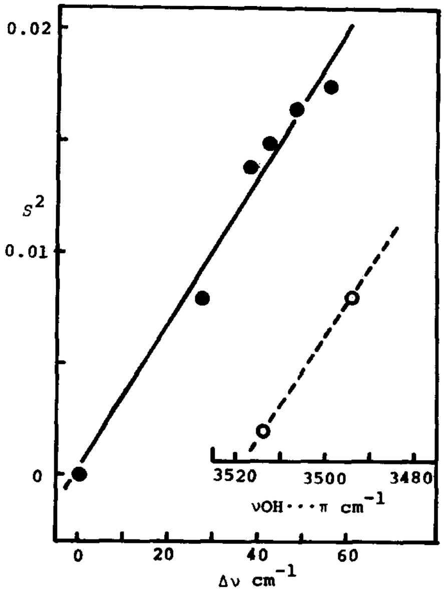


Figure 3. Plots of S^2 values against frequency shifts: 2-phenylphenols (●) and **1** (○).

ν(intra-)OH···π frequency.[18] Thus, the dotted line in Fig. 3 is obtained by assuming that the slope for **1** is the same as that for 2-phenylphenols. For the intermolecular OH···π bond, the S^2 value (0.002) can also be calculated in the same manner; here the angle ϕ is assumed to be 45°, because the distances, H(1)···C(15') and H(1)···C(16'), are almost the same. Thus, the ν(inter-)OH···π frequency (*ca.* 3514 cm^{-1}) corresponding to this S^2 value can be estimated by the use of the dotted line in Fig. 3. Taking the phase effects on the frequency shift stated above (+6.3 cm^{-1}) into consideration, the excellent agreement between the calculated and observed frequency is found.

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(7) The atomic co-ordinates and all the bond lengths and angles have been deposited with the Cambridge Crystallographic Data Centre.

(8) The intermolecular OH···π bond length observed seems to be rather long as compared with those for ordinary hydrogen bonds obtained by X-ray studies. In NMR studies, the rather long H···π hydrogen bond has been often reported, *e. g.*, for chloroform – benzene complex [3.8 Å(ref 9) and 3.1 Å(ref 10)]. This is probably attributed to high polarizability of the delocalized π electron systems.

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(16) For example, in hexane solution, the corresponding frequency difference results in 30.9 cm^{-1} [3560.2 cm^{-1}(**2**) – 3539.3 cm^{-1}(**1**)](ref 15(b)), which agrees well with that (30.0 cm^{-1}) found in the crystals.

(17) The S value was calculated by the same method described by Ōki and Iwamura (ref 13).

(18) For **1**, the νOH···π frequency was adopted as a measure of the strength of the OH···π bond, because **1** has no free hydroxyl group.

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