CHEMISTRY LETTERS, pp. 1151-1152, 1972. Published by the Chemical Society of Japan

THE CRYSTAL STRUCTURE OF THE MOLECULAR COMPLEX FORMED FROM 4-NITROPYRIDINE N-OXIDE AND HYDROQUINONE IN THE MOLE RATIO 2 : 1

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Crystals of the molecular complex composed of 4-nitropyridine N-oxide (4NPO) and hydroquinone (HQ) with 2 : 1 molecular ratio, $2(C_5H_4N_2O_3)\cdot C_6H_6O_2$, crystallized in monoclinic, space group $P2_1/c$, with two formula units in a cell (a = 5.963, b = 14.606, c = 10.157 Å, β = 105°13'). One HQ is connected to two 4NPO molecules by two hydrogen bonds. Molecular arrangement of a sandwich type was not observed between HQ and 4NPO. It was concluded that charge transfer interactions of the π-π type are not operative in the crystal of the complex.

It has been reported that 1 : 1 π-π charge transfer (CT) molecular complexes of 4-nitropyridine N-oxide (4NPO) or 4-nitroquinoline N-oxide (4NQO) are formed in CH_3CN solution with various π electron donors such as tetramethyl-p-phenylene diamine, dimethyl aniline, hydroquinone (HQ), HQ dimethylether and hexamethylbenzene. Red shift of the end absorptions of 4NPO and 4NQO occurs in a visible region according as the electron donating ability of the donor increases. The values of $K\epsilon$, where K (equilibrium const.) and ϵ (molecular extinction coefficient) cannot be experimentally separated, and ΔH (heat of formation) are so small that 4NPO and 4NQO are considered to be weak π electron acceptors.[1)]

In order to investigate these molecular interactions in further detail, crystal structure analysis was desirable. Crystals were obtained only of HQ complexes of 4NPO and 4NQO. Elementary analysis proved the molecular ratio to be 2 (4NPO or 4NQO) : 1 (HQ). 4NPO-HQ crystallizes in orange crystals of mp 128-130°C and 4NQO-HQ in deep orange crystals of mp 134-135°C.

Crystal structure analysis of 4NPO-HQ was carried out by the x-ray diffraction method. Noting that the HQ molecule is a good proton donor for hydrogen bonding interaction in addition to its well known π electron donor character, it was expected that the above two kinds of molecular interaction would be possible in the 4NPO-HQ crystal, as in the crystal of phenoquinone.[2)] To examine what type of interaction is significant is therefore of some interest. Crystal data: $2(C_5H_4N_2O_3)\cdot C_6H_6O_2$, monoclinic, space group $P2_1/c$, a = 5.963(2), b = 14.606(6), c = 10.157(3) Å, β = 105°13'(1'), D_m = 1.51 gcm^{-3}, Z = 2, D_c = 1.52 gcm^{-3}.

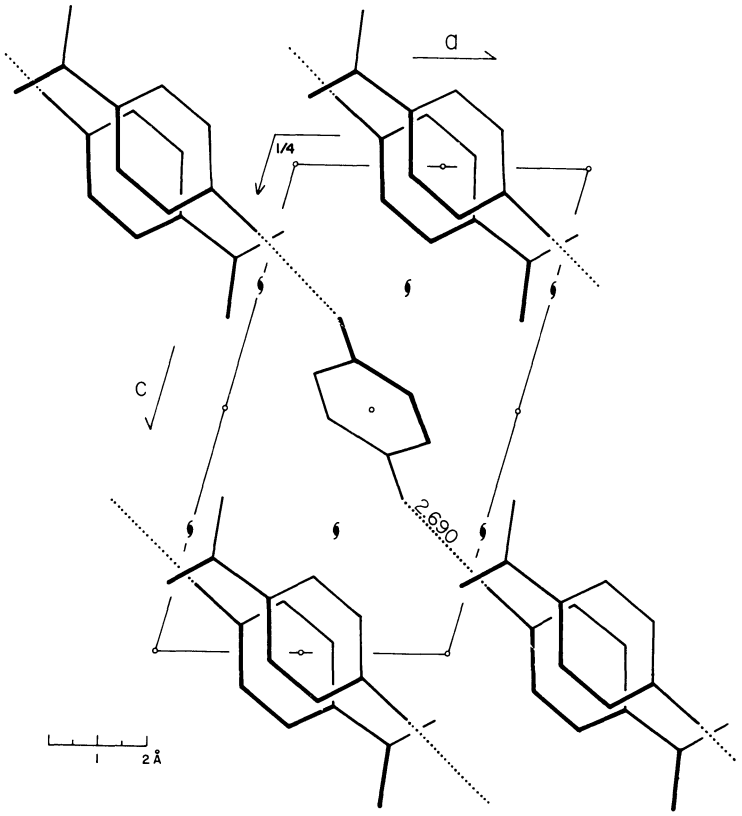
Three-dimensional intensity data were collected on a Hilger and Watts Y-290. Integrated intensities were measured up to θ = 22.5° by the θ-2θ scan technique with Mo-K_α radiation and scintillation counter. A pulse height analyser and a zirconium filter were used. A total of 1178 independent reflections were obtained.

The signs of 137 reflections ($E \geqq 1.2$) were determined by the method of Beurskens,[3)] from which the correct

structure was deduced. The positional and anisotropic temperature parameters were refined by a block-diagonal least squares method and the inclusion of the hydrogen atoms reduced the conventional R-value to 5.2%.

A view of the structure, bound between y = 1/4 and 3/4, is shown in the Figure. One HQ molecule is connected to two 4NPO molecules by two hydrogen bonds (2.690 Å) between the hydroxyl group (HQ) and the N-oxide group (4NPO). The molecular complex, thus combined, has a center of symmetry which coincides with an inversion point of the crystal structure. Different molecules in the complex are not coplanar but have a dihedral angle of 87°. The N→O bond length of the N-oxide is 1.310 Å, while it is 1.260 Å in the crystal of 4NPO itself.[4] The reason for this difference is the presence of an adjacent proton donor in 4NPO-HQ; the lone pair electrons of the N-oxide group oxygen atom are transferred to the anti-bonding orbital of the hydroxyl group of HQ and this lowers the contribution of the intramolecular CT from the N-oxide group to the nitro group of 4NPO resulting in elongation of the N→O bond length in 4NPO-HQ. A similar phenomenon can be seen with one of the two hydroxyl groups of Myxin.[5]

The molecular complexes are packed to form a sheet parallel to the $(\bar{1}02)$ plane. Two kinds of short contacts in the sheet are between the nitro group N and the hydroxyl O atom, 2.831 Å, and between two inversely related 4NPO molecules, 3.32 Å (interplanar distance).



There are also two short CH (in pyridine ring)-O distances between different sheets. Two C-H bonds point to the O atoms of the N-oxide and nitro groups with H···O distances of 2.18 Å and 2.38 Å, respectively. This suggests the formation of intermolecular hydrogen bonds C-H···O.[6] No other short contacts within the sum of van der Waals radii are found.

4NPO-HQ is comparable with phenoquinone in its molecular structure and in the principle of its crystal structure. π-π CT interactions are not found in 4NPO-HQ, though found in phenoquinone. These results support the fact that 4NPO is a weak electron acceptor.

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(Received August 4, 1972)