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Structure of the 1:1 Complex Formed by 4-Nitropyridine *N*-Oxide with 3-Aminophenol

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Abstract. $C_6H_7NO.C_5H_4N_2O_3$, monoclinic, *Cc*, $a = 6{\cdot}988\,(2)$, $b = 20{\cdot}317\,(2)$, $c = 8{\cdot}547\,(2)$ Å, $\beta = 112{\cdot}29\,(1)°$, $M_r = 249{\cdot}23$, $D_m = 1{\cdot}45$ (flotation), $D_x = 1{\cdot}474$ Mg m^{-3}, μ(Cu $K\alpha$) = 0·98 mm^{-1}. The structure was solved by direct methods and refined by full-matrix least-squares calculations. The final *R* was 0·044 for 1034 measured reflections. The complex is formed by hydrogen-bonding of the hydroxyl to the *N*-oxide group, with an O···O distance of 2·696 (3) Å.

Introduction. Despite the great number of studies involving hydrogen-bonded complexes of pyridine *N*-oxide and its derivatives (Golič, Hadzi & Lazarini, 1971; Kreevoy & Chang, 1976; Karayannis, Pytlewsky & Mikulski, 1973), there are few results concerning the molecular parameters in such complexes. A knowledge of these would make it possible to establish correlations between some characteristic properties of the hydrogen bond, for instance the *A*H and *A*H···*B* distances, the frequency shifts in the IR region and the substituent effects, and to establish theoretical treatments involving those properties.

This work, which follows others in the field (Saffioti & Bueno, 1976; Bueno & Lucisano, 1979), describes the determination of the crystal structure of the 3-aminophenol–4-nitropyridine *N*-oxide complex. Some aspects of the hydrogen bond are discussed.

Well formed purple crystals of the title compound were prepared by slowly evaporating an equimolar solution of 3-aminophenol (Carlo Erba) and 4-nitropyridine *N*-oxide (Aldrich) in acetonitrile.

A crystal of approximate dimensions 0·1 × 0·2 × 0·6 mm was used for the data collection on a Nonius CAD-4 diffractometer. The cell parameters were refined from the setting angles of 25 reflections. The three-dimensional intensity data were collected using graphite-monochromated Cu $K\alpha$ radiation up to $\theta = 75°$. The ω–2θ scanning mode with varying interval was used. Of the 1140 recorded independent reflections, 1034 were considered above background [$I > 3\sigma(I)$, where $\sigma(I)$ was based on counting statistics]. The data were reduced to structure factors without absorption correction.

The structure was solved by application of *MULTAN* 78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) to the 172 reflections with $E > 1{\cdot}38$. All non-H atoms appeared clearly in the *E* map based on the set of phases giving the highest combined figure of merit. The H atoms were placed at their calculated positions, the hydroxyl H atom was located by difference synthesis.

Refinement was carried out by full-matrix least-squares calculations with anisotropic thermal parameters for the non-H atoms and isotropic thermal parameters equal to 6·0 Å^2 for the H atoms. The function minimized was $\sum w_i(|F_o| - |F_c|)^2$ with $w_i^{-1} = \sigma(F_o)^2 + (0{\cdot}05|F_o|)^2$ for the observed and $w_i = 0$ for the unobserved reflections. The atomic scattering factors used were those of Cromer & Waber (1974).

The final unweighted *R* factor, omitting unobserved reflections, was 0·044 and, including them, 0·048.

The final atomic parameters are given in Table 1.*

Discussion. Fig. 1 gives the bond lengths and angles in the 3-aminophenol–4-nitropyridine *N*-oxide complex.

The complex, which is formed by hydrogen bonding of the hydroxyl group to the *N*-oxide group, may be described by essentially three planes, whose equations of the form $AX + BY + CZ - D = 0$ referred to absolute coordinates are: plane 1, through atoms C(1), C(2), C(3), C(4), C(5) and C(6) of the phenyl ring of the 3-aminophenol molecule with $A = 0{\cdot}9721$, $B = 0{\cdot}2289$, $C = -0{\cdot}0512$ and $D = 3{\cdot}4588$, exact within standard deviations; plane 2, through atoms N(2), C(7), C(8), C(9), C(10) and C(11) of the pyridyl ring of

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* Lists of structure factors, anisotropic thermal parameters and H atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35937 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Fractional atomic coordinates* ($\times 10^4$) *and equivalent isotropic temperature factors* (*Hamilton,* 1959), *with e.s.d.'s in parentheses*

	x	y	z	B_{eq} (Å^2)
3-Aminophenol molecule				
O(1)	3124 (4)	676 (1)	−2872 (3)	4·4 (1)
N(1)	−46 (5)	690 (2)	−8851 (4)	5·0 (1)
C(1)	2143 (1)	1025 (1)	−4301 (1)	2·9 (1)
C(2)	1557 (4)	699 (1)	−5825 (3)	3·1 (1)
C(3)	553 (4)	1024 (1)	−7342 (3)	3·3 (1)
C(4)	95 (4)	1701 (2)	−7309 (4)	3·5 (1)
C(5)	688 (4)	2021 (1)	−5776 (4)	3·6 (1)
C(6)	1697 (4)	1697 (1)	−4258 (4)	3·2 (1)
4-Nitropyridine *N*-oxide molecule				
O(2)	3593 (5)	1449 (1)	−188 (3)	5·3 (1)
O(3)	7725 (5)	1635 (1)	7536 (3)	5·0 (1)
O(4)	8171 (5)	603 (1)	7200 (3)	5·6 (1)
N(2)	4557 (4)	1373 (1)	1410 (3)	3·2 (1)
N(3)	7528 (4)	1148 (1)	6640 (3)	3·4 (1)
C(7)	5416 (4)	781 (1)	2076 (4)	3·4 (1)
C(8)	6394 (4)	702 (1)	3774 (3)	3·0 (1)
C(9)	6517 (3)	1231 (1)	4814 (3)	2·7 (1)
C(10)	5669 (4)	1831 (1)	4162 (3)	2·9 (1)
C(11)	4707 (4)	1892 (1)	2462 (4)	3·3 (1)

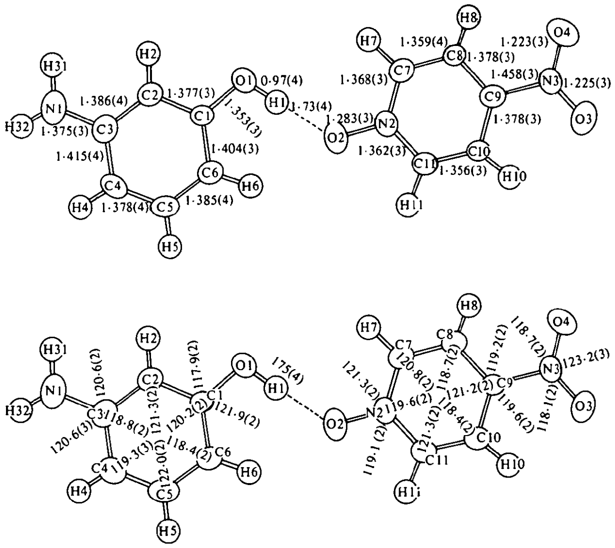

Fig. 1. Representation of the hydrogen-bonding scheme in the complex giving bond lengths (Å), angles (°) and atomic numbering.

the 4-nitropyridine *N*-oxide molecule with $A = 0·9598$, $B = 0·2730$, $C = 0·0646$ and $D = 3·3114$, exact within standard deviations; and plane 3, through atoms N(3), O(3) and O(4) of the nitro group, with $A = 0·9756$, $B = 0·2056$, $C = 0·0764$ and $D = 3·1109$. The dihedral angles between these planes are: 1 to 2, 2·7°, 1 to 3, 2·0° and 2 to 3, 4·0°.

The mean plane through the complex is defined by the constants $A = 0·9682$, $B = 0·2482$, $C = 0·0326$ and $D = 3·3805$, the largest distance to this plane being 0·15 Å for atom O(3). The normal to this mean plane makes an angle of 14·5° with the **a** direction.

The space group requires the free 4-nitropyridine *N*-oxide molecule to be planar (Eichhorn, 1956). The lack of planarity of the molecule in the complex does not greatly affect the molecular parameters when compared with the most recent parameters for the free molecule (Wang, Blessing, Ross & Coppens, 1976). The molecular parameters of the 3-aminophenol molecule also agree fairly well with those of the free molecule (De Rango, Brunie, Tsoucaris, Declercq & Germain, 1974).

Besides the O(1)···O(3) contact of 2·696 (3) Å responsible for the formation of the complex, there is no other short intermolecular contact. The closest intermolecular contacts of the N(1) atom of the amino group are with N(2) ($x, y, -1 + z$) of the pyridyl group of 3·432 (4) Å and with O(1) ($x, -y, -1 - z$) of the hydroxyl group of 3·449 (4) Å.

The hydrogen bond is asymmetric and its strength may be classified as intermediate (Novak, 1974). For R(O···O) equal to 2·696 Å, the expected OH bond length and ν(OH) frequency are respectively 0·980 Å and 3100 cm^{-1}. The observed ν(OH) frequency occurs at 3150 cm^{-1} and the estimated hydrogen-bond force constant is $0·3 \times 10^{-8}$ N Å^{-1}.

All calculations, unless otherwise mentioned in the text, were performed in this Institute on a PDP11/45 computer using the Nonius SDP crystallographic programs (Frenz, 1978). This work has received the support of FAPESP, CNPq and FINEP which is hereby gratefully acknowledged.

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Ethyl 2-Cyano-5-phenyl-(2*E*,4*E*)-pentadienoate

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Abstract. $C_{14}H_{13}NO_2$, tetragonal, $I4_1/a$, a = 33·278 (4), c = 4·608 (1) Å, M_r = 227·27, Z = 16, D_m = 1·17 (flotation), D_x = 1·183 (1) Mg m^{-3}, μ(Cu $K\alpha$) = 0·65 mm^{-1}, m.p. 383–384 K. The structure was solved by direct methods and refined by full-matrix least-squares calculations. The final R was 0·042 for 1061 observed reflections. The molecule is planar, the carbonyl group being *s-trans* with respect to the cyano group.

Introduction. The title compound was synthesized by the Knoevenagel reaction (Cope, 1937) of ethyl cyanoacetate on cinnamaldehyde (Sá & Pitta, 1979).

Pale-yellow prismatic crystals were obtained by slowly evaporating a solution of the compound in ethanol. A crystal of approximate dimensions 0·1 × 0·2 × 0·2 mm was used for the data collection on a Nonius CAD-4 diffractometer. The cell parameters were refined from the setting angles of 25 reflections. The three-dimensional intensity data were collected using graphite-monochromated Cu $K\alpha$ radiation up to 2θ = 120°. The ω–2θ scanning mode with varying interval was used. Of the 1717 recorded independent reflections, 1061 were observed above background [$I > 3\sigma(I)$, where $\sigma(I)$ was based on counting statistics]. The data were reduced to structure factors without absorption correction. The structure was solved by application of *MULTAN* 78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978).

All the non-H atoms appeared clearly on the E map based on the set of phases giving the highest combined figure of merit. All the H atoms were placed at their calculated positions and were included in the refinement. Refinement was carried out by full-matrix least-squares calculations with anisotropic thermal parameters for the non-H atoms and for H atoms the thermal parameters of the atoms to which they are attached. The function minimized was $\sum w_i(k|F_o| - |F_c|)^2$ where $w_i = |\sigma(F_o)^2 + (0{\cdot}05F_o)^2|^{-1}$ for the observed and $w_i = 0$ for the unobserved reflections. The atomic scattering factors used were those of Cromer & Waber (1974). The final refinement cycle gave R = 0·058 for all reflections and R = 0·042 for the observed reflections only.

The final atomic parameters are given in Table 1.*

Discussion. Bond lengths and angles in ethyl 2-cyano-5-phenyl-(2*E*,4*E*)-pentadienoate are given in Fig. 1, with the atomic numbering.

Although the dihedral angle between the phenyl-ring and the pentadiene-chain planes is 6·4°, the molecule may be described by a mean plane through all non-H atoms whose equation referred to absolute coordinates is $-0{\cdot}1827\,X + 0{\cdot}6527\,Y - 0{\cdot}7352\,Z = 0{\cdot}0175$. The largest distances to this mean plane are observed for the C atoms of the phenyl ring in *ortho* and *meta* positions to the carbon C(6) bonded to the pentadiene chain, for the O atom of the carbonyl group and for the C atoms of the ethyl group and are respectively C(7) −0·124 (2), C(8) −0·127 (3), C(10) 0·101 (3), C(11) 0·087 (3), O(1) −0·120 (2), C(13) −0·113 (3) and C(14) −0·163 (3) Å.

The inclination of the phenyl and ethoxycarbonyl groups with respect to the mean plane of the penta-

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