THE CRYSTAL STRUCTURE OF THE COMPLEX FORMED BY 4-NITROPYRIDINE N-OXIDE WITH 3-AMINOBENZOIC ACID

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RESUMEN

La estructura cristalina y molecular del complejo formado por enlace de hidrógeno entre la 4-nitropiridina N-oxido y el ácido 3-aminobenzóico fue estudiado por difracción de rayos X. Los cristales fueron obtenidos a partir de una solución equimolecular en acetonitrilo, son monoclínicos $P2_1/c$, con a=7,325(3), b=10,173(1), c=16,701(7)Å, ß=101,74(3)°, V=1219(1)Å^3, e Dc=1,511 g cm^{-3} para Z=4. La estructura fue resuelta por métodos directos y afinada por mínimos cuadrados con $I \geq 2\sigma(I)$, obteniendose un coeficiente de discordancia R=0.0504 y R_w= 0.0485. Las moléculas que forman el complejo presentan un enlace de hidrógeno fuerte entre el grupo carboxilo y el grupo N-óxido con una distancia o···o igual a 2.539(7)Å. El ángulo dihedro formado por los planos medios de sus anillos es igual a 44.5(2)°. Las moléculas de 4-nitropiridina N-óxido y del ácido 3-aminobenzóico presentan superposición en la dirección [100], con una distancia media de 3.25(4) y 3.42(4)Å. Es discutido también el efecto de la substitución meta en el ácido 3-aminobenzóico sobre el empaquetamiento molecular.

ABSTRACT

The crystal structure of the hydrogen-bonded complex formed by 4-nitropyridine N-oxide and 3-aminobenzoic acid has been examined by X-ray diffraction. Crystals grown from an equimolecular solution in acetonitrile, are monoclinic, space group $P2_1/c$ with a=7.325(3), b= 10.173(1), c= 16.701(7)Å, β = 101.74(3)°, V=1219(1)Å^3, and Dc=1.511 g cm^{-3} for Z= 4. The structure was solved by direct methods. Refinements were carried out by least-squares with $I \geq 2\sigma(I)$ to give R= 0.0504 and R_w = 0.0485. The molecules forming the complex are help together by a strong hydrogen bond between the carboxyl and the N-oxide groups with an o···o distance equal to 2.539 (7)Å and the dihedral angle between the mean planes through their rings is equal to 44.5(2)°. The alternate stacking of 4-nitropyridine N-oxide and 3-

aminobenzoic acid molecules results in piles oriented in the [*100*] direction with mean interplanar distances between the overlapped rings equal to 3.25(4) and 3.42(4)Å.

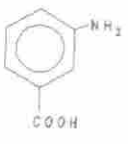
The effect of meta substitution in 3-aminobenzoic acid on the molecular packing of the complex is discussed.

INTRODUCTION

The growing interest in the study and development of organic materials as nonlinear media is clearly demonstrated by the extensive publications about this subject (1,2,3). Much of this interest is due to the exceptionally large second order nonlinear optical properties verified in some classes of organic compounds. Besides the requirement of lack of center of symmetry at molecular and crystal level, two other factors have been identified as responsible for the enhancement of nonlinear response which are the presence of a conjugated system and a high intramolecular chargetransfer (4). If on one hand the molecular criteria can be optimized by application of the rules of organic chemistry and testing molecular models for their second order hyperpolarizability tensors by calculation (5), on the other, there is still practically no control on the mutual arrangement of the molecules in the crystal i.e. on the molecular packing. The usual two approaches for designing suitable packings are the substitution of the target molecule at random as in the case of 3-methyl-4-nitropyridine N-oxide (6) and test of lack of center of symmetry in the derivatives by detection of the second harmonic generation signal on powder samples (7) and the second one is to introduce a chiral center in the molecule in order to ensure non centrosymmetric packing as in the case of N-(4-nitrophenyl)-(L)-prolinol (8).

In previous reports it has been shown that another useful approach is to complex the target molecule with hydrogen bond donors. In this way non centrosymmetric complexes of 4-nitropyridine N-oxide (NPNO) with 3-aminophenol (9) and 2-aminobenzoic acid (10) and 4-nitrophenol (11) were obtained. This crystal structure determination is part of an ongoing study of the effect of substitution on the packing of the complexes formed by 4-nitropyridine N-oxide and hydrogen bond donors.

NPNO



MABA

MATERIAL AND METHODS

Crystals of the complex were obtained by slow evaporation from an equimolecular solution of NPNO and 3-aminobenzoic acid (MABA) in acetonitrile. Red crystals were obtained with melting point equal to 387±1K.

Experimental data for the structure are collected in Table 1. The intensities were corrected for Lorentz and polarization effects. No absorption correction was applied. Ring H-atoms were placed in their calculated positions (H-atom temperature factor = 6Å^2). H(05) was found from Fourier difference map. Carboxyl and amino groups H-atom positions were refined.

The structure refinement was carried out by full-matrix least squares calculations. The function minimized was $\Sigma\omega(|Fo| - |Fc|)^2$ with $\omega^{-1} = \sigma^2(Fo)$ for observed and $\omega=0$ for unobserved reflections. Refinement was carried out with anisotropic thermal parameters for non-H atoms. Scattering factors (12) for all non-H atoms and their corrections for anomalous dispersion (13) were applied. All calculations were performed on a VAX-6420 computer from the Instituto de Física e Química de São Carlos.

RESULTS AND DISCUSSION

A view of the hydrogen-bonded complex NPNO-MABA giving the adopted atom numbering is shown in fig. 1. Final atomic coordinates and equivalent isotropic temperature factors (14), are listed in Table 2*. Bond lengths and bond angles are given in the Table 3. The complex owes its formation to a strong (18) H-bond between O (3) of the N-oxide group of NPNO and O (5) of the carboxyl group of MABA, with an o···o distance equal to 2.539 (7)Å. The other closest intermolecular contacts are between N(3) and two O(4) atoms belonging to symmetry related MABA molecules (1-x, -1/2+y, 3/2-z; x, 1/2-y, -1/2+z) with distances equal to 3.18(1) and 3.32(1)Å respectively. The complex may be described by two planes which contain respectively the NPNO and MABA molecules with a dihedral angle equal to 44.5(2)°. The alternate stacking of NPNO and MABA molecules results in piles oriented in the [100] direction with mean interplanar distances between the ring planes of 3.25 (4) and 3.42(4)Å and is depicted in Fig 2.

The molecular parameters of NPNO are not significantly affected in the complex when compared with those of the free molecule (19). The molecular parameters of MABA also agree fairly well with those of the free molecule (20). As expected (21), due to the higher acidity of MABA, the hydrogen bond length is shorter than in the corresponding complexes involving 2- and 4-aminobenzoic acids where the o···o distances are 2.629(4) and 2.618(5)Å respectively.

Meta substitution which has for long been recognized as promoting crystallization in non centrosymmetric space groups in the case of disubstituted benzene derivatives (6,22), has also been pointed out as responsible for the formation of the non centrosymmetric complex between NPNO and 3-aminophenol (23).

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* *List of structure factor, anisotropic thermal parameters and H-atom parameters may be obtained from the autors*

Table 1. Crystallographic Data

Crystal shape and size (mm)	Rhombic_shape, 0.05 x 0.15 x 0.50
Diffractometer used and data collection technique	Four-circle diffractometer (Enraf-Nonius CAD-4) ω-2θ
Number and 2θ range (°) of reflections used for measuring latt. param.	25, $16 \leqslant 2\theta \leqslant 32$
Check reflections and intensity variations (%) throughout exp.	0 6 4, -4 0 4, 0 2 8; 2.0,2.0, 1.9
Max. value of sin θ/λ reached in intensity measurements (Å)	0.593
Range in hkl, min.; max.	-7, 0, 0; 7, 10, 17
Total reflections measured	2283
Number of independent reflections	1917
Number of observed reflections	455
Acceptance criterion for obs. refl.	$I \geqslant 2\ \sigma(I)$
Method used to solve structure	Direct methods
Absorption coefficient (mm^{-1})	0.08
Parameters refined [a]	91, 93
Value of R, Rw	0.0504, 0.0485
Max. and min. residual densities (e Å^{-3}) in final diff. Fourier map	+0.278, -0.319
Largest shift/e.s.d in final least-square cycle $(\Delta/\sigma)_{max}$	0.03
Goodness of fit	2.21
Computer programs used	SHELX76(15), SHELXS86(16), ORTEP(17)

[a] *Refinement was done in blocks, with parameters of NPNO and MABA in alternate cycles.*

In the case of the presently studied complex the meta substitution rule fails. Quite interestingly the complexes of NPNO with 2- and 4-aminobenzoic acids exhibit non centrosymmetric packings. In our opinion this failure has to be attributed to the fact that the closer approximation of the two complex moieties, due to the strong hydrogen bond, originates an appreciable twist of their mean planes and cancels out the effect of meta substitution on packing.

Other systems are being studied at the moment in order to gather more information about the effect of substitution on packing.

Table 2. Fractional atomic coordinates and equivalent isotropic temperature factors with e.s.d.'s in parentheses

Atom	X	Y	Z	B_{eq} (Å^2)*
O(1)	1.0245(9)	0.3068(6)	1.3281(3)	6.5(3)
O(2)	0.9285(9)	0.1071(6)	1.3463(3)	6.3(3)
O(3)	0.6170(9)	0.1651(6)	0.9811(3)	6.8(3)
O(4)	0.3877(8)	0.4064(6)	0.8460(3)	4.8(2)
O(5)	0.5249(8)	0.2165(5)	0.8295(3)	4.2(2)
N(1)	0.943 (1)	0.2027(8)	1.3039(4)	4.1(3)
N(2)	0.692 (1)	0.1778(8)	1.0565(4)	4.5(3)
N(3)	0.325 (2)	0.0920(8)	0.5375(5)	5.4(3)
C(1)	0.849 (1)	0.1970(9)	1.2172(4)	3.1(3)
C(2)	0.759 (1)	0.0833(8)	1.1885(4)	3.0(3)
C(3)	0.680 (1)	0.0735(8)	1.1078(5)	3.5(3)
C(4)	0.791 (1)	0.2891(9)	1.0859(5)	4.5(3)
C(5)	0.867 (1)	0.3012(9)	1.1661(5)	4.0(3)
C(6)	0.417 (1)	0.3167(9)	0.8021(5)	3.8(4)
C(7)	0.344 (1)	0.3144(9)	0.7123(4)	3.0(3)
C(8)	0.369 (1)	0.2033(7)	0.6668(5)	2.9(3)
C(9)	0.298 (1)	0.2023(9)	0.5817(5)	3.6(3)
C(10)	0.210 (1)	0.316 (1)	0.5465(5)	4.3(3)
C(11)	0.184 (1)	0.4231(8)	0.5933(5)	4.2(3)
C(12)	0.249 (1)	0.4247(8)	0.6755(5)	3.4(3)
H(O5)	0.57 (1)	0.240 (6)	0.895 (4)	6.00
H(N31)	0.31 (1)	0.100 (7)	0.480 (4)	6.00
H(N32)	0.37 (1)	0.034 (8)	0.554 (5)	6.00

*$B_{eq} = 8\pi^2/3\ \Sigma_i \Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i \bullet \mathbf{a}_j$

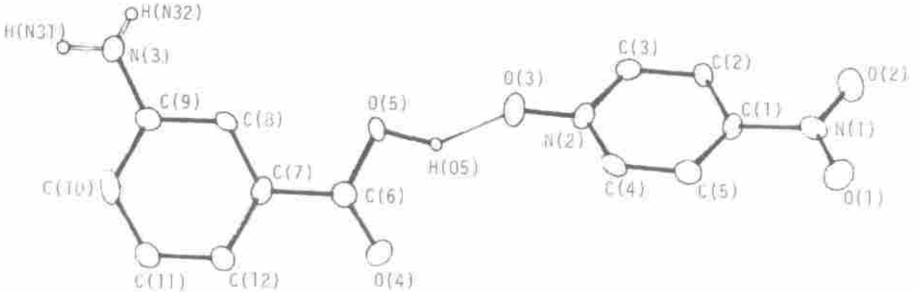

Fig.1. Representation of a hydrogen bonded pair of NPNO and MABA molecules giving atomic numbering

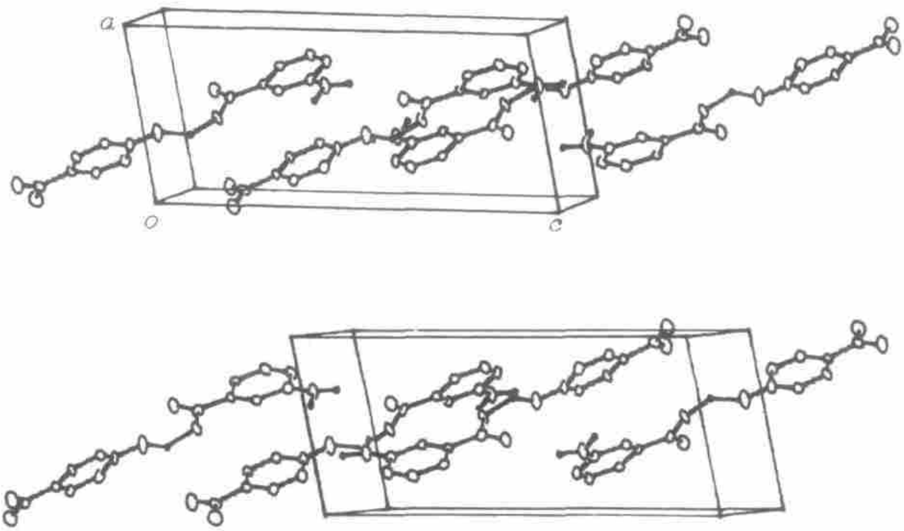

Fig. 2. Representation of the molecular packing of the NPNO - MABA complex along the [100] direction

Table 3. Bond distances (Å)and bond angles (°) with e.s.d.'s in parentheses

O(1)-N(1)	1.24 (1)	O(2)-N(1)	1.23 (1)
O(3)-N(2)	1.274(8)	O(4)-C(6)	1.22 (2)
O(5)-C(6)	1.31 (2)	N(1)-C(1)	1.473(9)
N(2)-C(3)	1.38 (2)	N(2)-C(4)	1.38 (1)
N(3)-C(9)	1.38 (1)	C(1)-C(2)	1.37 (1)
C(1)-C(5)	1.38 (1)	C(2)-C(3)	1.36 (2)
C(4)-C(5)	1.35 (1)	C(6)-C(7)	1.49 (2)
C(7)-C(8)	1.39 (1)	C(7)-C(12)	1.40 (1)
C(8)-C(9)	1.42 (2)	C(9)-C(10)	1.39 (1)
C(10)-C(11)	1.38 (1)	C(11)-C(12)	1.36 (1)
O(5)-H(O5)	1.10 (6)		
O(1)-N(1)-O(2)	125.7(7)	O(1)-N(1)-C(1)	116.8(8)
O(2)-N(1)-C(1)	117.4(8)	O(3)-N(2)-C(3)	117.9(7)
O(3)-N(2)-C(4)	121.6(7)	C(3)-N(2)-C(4)	120.5(7)
N(1)-C(1)-C(2)	118.2(7)	N(1)-C(1)-C(5)	119.5(7)
C(2)-C(1)-C(5)	122.1(7)	C(1)-C(2)-C(3)	119.2(7)
N(2)-C(3)-C(2)	119.6(8)	N(2)-C(4)-C(5)	120.6(8)
C(1)-C(5)-C(4)	118.2(8)	O(4)-C(6)-O(5)	122.6(7)
O(4)-C(6)-C(7)	123.3(8)	O(5)-C(6)-C(7)	114.0(8)
C(6)-C(7)-C(8)	121.6(7)	C(6)-C(7)-C(12)	118.5(8)
C(8)-C(7)-C(12)	121.4(7)	C(7)-C(8)-C(9)	119.6(7)
N(3)-C(9)-C(8)	118.8(7)	N(3)-C(9)-C(10)	123.7(7)
C(8)-C(9)-C(10)	117.6(8)	C(9)-C(10)-C(11)	121.6(7)
C(10)-C(11)-C(12)	121.5(8)	C(7)-C(12)-C(11)	118.4(7)
C(6)-O(5)-H(O5)	102 (3)		

SUPPLEMENTARY MATERIAL

List of the observed and calculated structure factors is available from one of the authors (RMF) upon request.

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