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THE INTER- AND INTRAMOLECULAR CHARGE TRANSFER ALONG THE POLYMERIC CHAIN OF HYDROGEN-BONDED MOLECULES IN TWO CRYSTAL FORMS OF m-NITROPHENOL

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Abstract The crystal structure of the orthorhombic polymorph of m-nitrophenol (mNPh) is presented and compared with the known structure of the monoclinic one . The inter- and intramolecular interactions previously studied by means of vibrational spectroscopy (IR, Raman) are discussed in terms of the polymeric character of both structures, in which the charge transfer interactions within the molecular chains contrast with the Van der Waals interactions between the chains. The structural instability of the orthorhombic phase is also discussed in terms of different charge transfer along the polymeric chains in the two structures and the considerable anharmonism of the interchain potential in the orthorhombic crystal.

THE COMPARISON OF THE CRYSTAL STRUCTURES OF TWO POLYMORPHIC FORMS OF m-NITROPHENOL

The occurence of two polymorphic modifications of m-nitrophenol (mNPh) having very similar crystal structures were found several years ago[1]. Also the crystal structure of the monoclinic polymorph has been resolved and the space group and the unit cell parameters of another, the orthorhombic polymorph were presented there. We have performed the complete X-ray structure investigation of the orthorhombic mNPh crystal in order to make possible a structural and spectroscopic comparison of the two crystals [2-5].

The purification of the material and the crystal growing were published earlier [2,4]. Collecting of data was performed with aid of an automatic Enraf-Nonius Diffractometer CAD-4 with graphite monochromatized MoKα radiation.

The unit cell parameters are: a=11.328(3) Å, b=6.779(2) Å, c=8.106(3) Å, V_{calc}=622.6(8) Å^3, Z=4, space group $P2_12_12_1$, R=0.031 and they agree with the parameters cited in [1]. The atomic positions and the

anisotropic thermal parameters are shown in Table I and II, respecti-

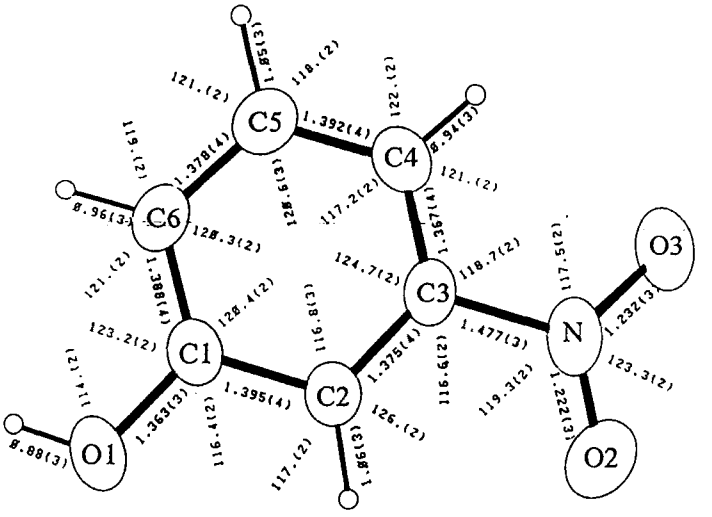

FIGURE 1 The ORTEP[6] view of the mNPh molecule with bond distances in [Å] and angles in [°].

vely. Fig.1 shows the ORTEP view of the mNPh molecule in the orthorhombic crystal with the bond distances and the angles. The comparison with the geometry of the molecule in the monoclinic crystal[1] reveals some differences: the O-H distance is about 0.1 Å longer and the N-O distances are about 0.01 Å longer in the orthorhombic crystal. Also the C_1-O-H_1 and C_3-C_2-H_2 angles are about 7° greater in the orthorhombic crystal.

The similarity of the orthorhombic mNPh crystal to the monoclinic one is well seen in Fig.2 which shows the unit cells of both structures. Belonging to the $P2_12_12_1$ and $P2_1/n$ space groups the two crystals differ only slightly in the arrangement of molecules. The main feature of both structures seems to be their polymeric character realized by infinitive chains of hydrogen-bonded coplanar molecules. Four molecules in the unit cell are engaged in four chains. Two of them are identical in both structures and two other differ by the mirror reflection in the (001) plane. The almost linear hydrogen bonding (HB) links traslationally equivalent molecules along the c crystallographic axis through the OH and NO_2 groups as it is seen in Fig.2. The O-H...O distance is a little shorter in the orthorhombic crystal (2.88 Å) than in the monoclinic one (2.94 Å).

Also the O-H...O angles differ slightly: 168° and 178° in the orthorhombic and monoclinic polymorph, respectively. The anisotropic parameters of atomic displacements of the orthorhombic crystal (Table II) and of the monoclinic one[1] indicate that the thermal agitation is bigger in the directions perpendicular to the HB axis than along it. The structu-

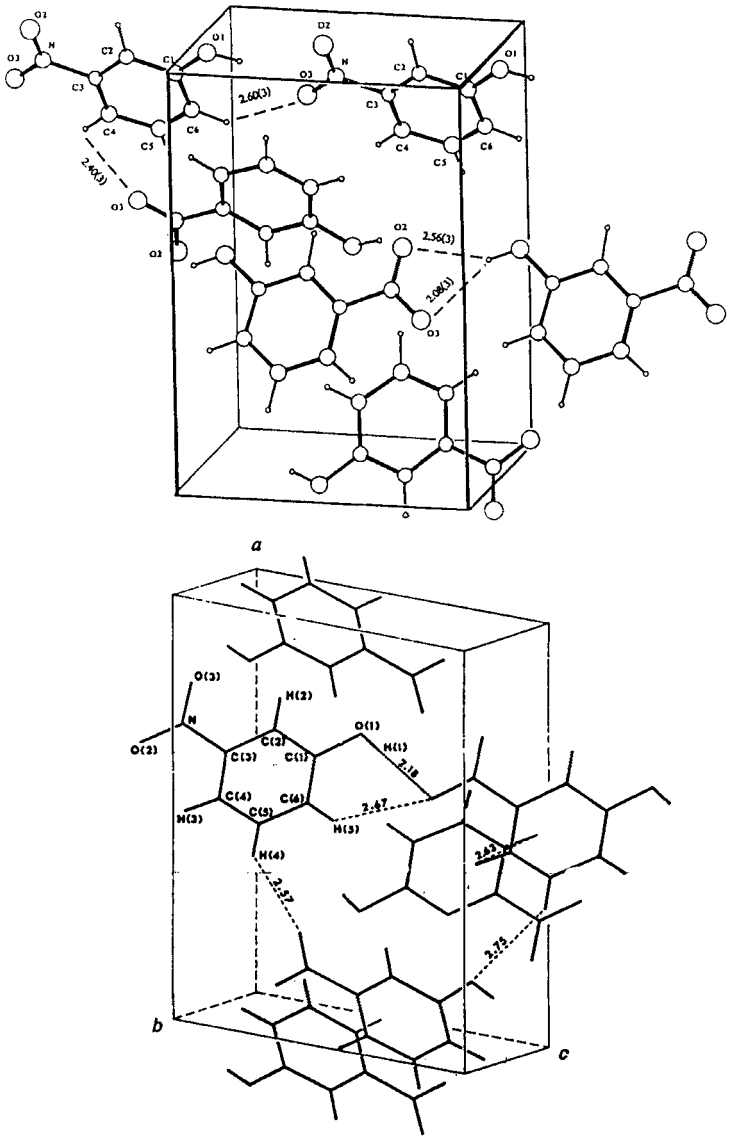

FIGURE 2 The orthorhombic (top) and monoclinic (bottom, acc. to[1]) unit cells of mNPh. All the distanances in [Å].

TABLE I The positional parameters and their estimated standard deviations.

ATOM	X	Y	Z	B(A2)
O1	0.4646(2)	0.0484(3)	-0.0185(2)	4.38(5)
O2	0.5019(2)	0.0284(4)	0.5821(2)	5.27(5)
O3	0.3561(2)	0.1920(4)	0.6765(2)	4.98(5)
N	0.4137(2)	0.1215(4)	0.5618(3)	3.46(5)
C1	0.3985(2)	0.1187(4)	0.1059(3)	3.03(5)
C2	0.4378(2)	0.0823(4)	0.2662(3)	3.07(5)
C3	0.3716(2)	0.1603(4)	0.3924(3)	2.81(5)
C4	0.2718(3)	0.2711(4)	0.3715(3)	3.34(5)
C5	0.2354(3)	0.3065(4)	0.2102(4)	3.73(6)
C6	0.2979(2)	0.2308(4)	0.0788(3)	3.33(5)
H'O	0.442(3)	0.079(5)	-0.118(4)	4*
H2	0.522(3)	0.016(5)	0.279(4)	4*
H4	0.227(3)	0.310(5)	0.463(4)	4*
H5	0.158(3)	0.388(5)	0.192(4)	4*
H6	0.269(3)	0.252(5)	-0.031(4)	4*

STARRED ATOMS WERE REFINED ISOTROPICALLY.
ANISOTROPICALLY REFINED ATOMS ARE GIVEN IN THE FORM OF THE ISOTROPIC EQUIVALENT DISPLACEMENT PARAMETER DEFINED AS:
(4/3) * [A2*B(1,1) + B2*B(2,2) + C2*B(3,3) + AB(COS GAMMA)*B(1,
+ AC(COS BETA)*B(1,3) + BC(COS ALPHA)*B(2,3)]

TABLE II The anisotropic displacement parameters.

NAME	B(1,1)	B(2,2)	B(3,3)	B(1,2)	B(1,3)	B(2,3)	BEQV
O1	5.4(1)	5.6(1)	2.21(6)	1.27(9)	0.39(8)	-0.17(8)	4.38(5)
O2	5.5(1)	7.1(1)	3.25(8)	1.6(1)	-1.23(8)	0.2(1)	5.27(5)
O3	7.0(1)	5.9(1)	2.05(6)	0.5(1)	0.54(9)	-0.41(9)	4.98(5)
N	4.4(1)	3.8(1)	2.21(7)	-0.6(1)	-0.19(8)	-0.03(8)	3.46(5)
C1	3.6(1)	3.2(1)	2.27(8)	-0.0(1)	0.2(1)	-0.01(9)	3.03(5)
C2	3.5(1)	3.2(1)	2.47(8)	0.3(1)	-0.17(9)	-0.02(9)	3.07(5)
C3	3.4(1)	3.0(1)	2.02(8)	-0.4(1)	-0.23(9)	0.09(9)	2.81(5)
C4	3.5(1)	3.7(1)	2.8(1)	0.2(1)	0.4(1)	-0.3(1)	3.34(5)
C5	3.4(1)	4.3(1)	3.6(1)	0.4(1)	-0.2(1)	0.3(1)	3.73(6)
C6	3.6(1)	3.9(1)	2.55(9)	-0.0(1)	-0.42(9)	0.5(1)	3.33(5)

THE FORM OF THE ANISOTROPIC DISPLACEMENT PARAMETER IS:
EXP[-0.25(H2A2B(1,1) + K2B2B(2,2) + L2C2B(3,3) + 2HKABB(1,2) + 2HLACB(1,3)
+ 2KLBCB(2,3))] WHERE A,B, AND C ARE RECIPROCAL LATTICE CONSTANTS.

ral differences between the two polymorphs will be discussed later in

terms of specific interactions along the polymeric chains in the crystals. The lack of centrosymmetry enables the orthorhombic polymorph to reveal weak nonlinear optical properties[7] which is characteristic for nitrobenzenes[8].

THE MOLECULAR INTERACTIONS IN BOTH CRYSTAL FORMS OF m-NITROPHENOL

It is known that a charge transfer (CT) between the electron donating OH group and the electron accepting NO_2 group occures in the mNPh molecule producing a CT band in the electronic spectra of its solutions[9]. In the crystals the molecules are linked by the weak HB and the intramolecular CT competes with the intermolecular HB. The question arises whether these inter- and intra-CT's are identical in both mNPh crystal forms. From the structural data it is seen that the O-H...O distance is shorter and the O-H distance is longer in the orthorhombic crystal. Hence, the intramolecular CT must be weaker and the intermolecular HB stronger in this polymorph in comparison with the monoclinic one.

The intermolecular CT is evidenced in the vibrational spectra by very strong bands of HB vibration (far IR)[4] and of the OH stretching vibration (the fundamental IR and Raman)[3] having comparable positions and intensities for both polymorphs. The occurence of the strong ν_{OH} band in the Raman spectra of both polymorphs but only in the (c,c) polarization indicates that the delocalization of π electrons along the planar chains of congugated molecules is considerable. On the other hand the C-N distance has a classic value for nitrobenzenes[10] in both polymorphs. Also the strong band at about 92 cm^{-1} assigned to the nitro group torsion[4] has similar position and intensity as it is in the spectra of other m-substituted nitrobenzenes: m-dinitrobenzene[11], m-chloronitrobenzene[12] and m-nitroaniline[13] in which HB does not occur (the first two crystals) or it may be classified as an extremely weak one (m-nitroaniline)[10]. It seems to indicate that the intramolecular CT through the C-N bonding is not greater than in the above mentioned crystals. Nevertheless the molecular interactions whithin the polymeric chains seem to have predominantly the CT character but its magnitude depends on the polymorph.

In contrast with that the interactions between the chains seem to

be of the Van der Waals type. Fig.3 shows the (a,b) projection of the two mNPh crystal structures. The intermolecular interactions in the plane ought to be besides nearly isotropic. The far IR spectra polarized in the plane show numerous strong bands which may be assigned to

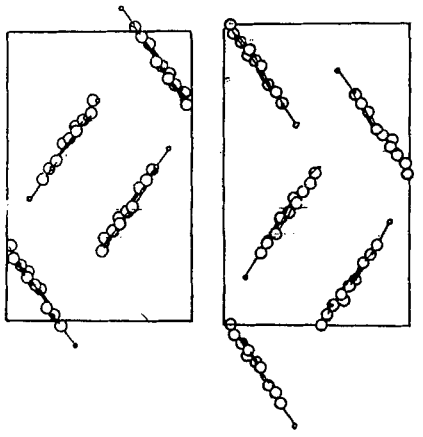

FIGURE 3 The a,b view of the monoclinic (left, acc. to [1]) and orthorhombic (right) unit cells of mNPh

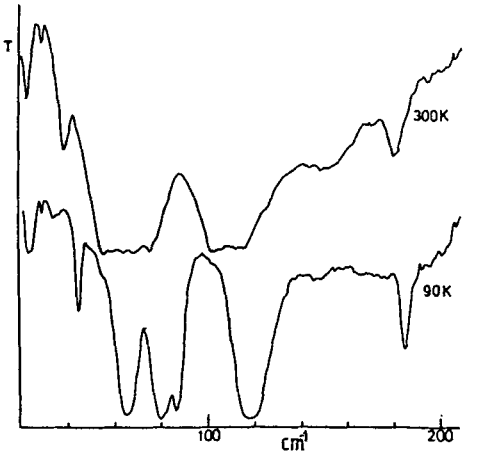

FIGURE 4 The polarized along the b axis far IR spectra of the orthorhombic mNPh crystal at two temperatures

lattice translations and librations[4]. A very strong band at about 117 cm^{-1} originates probably from the torsion of the molecular chains. The considerable intensities of the bands seem to indicate that the amplitudes of lattice vibrations in the (a,b) plane are greater than along the molecular chains. The strong bands of the γ_{OH} and δ_{OH} vibrations in the fundamental frequency IR spectra[3] seem to confirm the statement. However some differences between the IR and Raman spectra which concern out-of-plane vibrations[3,4] agree with the structural results that the mutual contacts between the polymeric chains are different in the two crystals.

STRUCTURAL INSTABILITY OF THE ORTHORHOMBIC CRYSTAL OF m-NITROPHENOL

The small differences of CT along the molecular chains evidenced by the different O-H...O and O-H distances may lie at the origin of the struc-

tural polymorphism of mNPh. This statement seems yet more valuable when we realize the decisive influence of a solvent on the crystallization of one of the polymorphs. At the room temperature the monoclinic crystals grow easily from polar solvents as water and ethanol while the orthorhombic ones are obtained in majority from the unpolar benzene and acetone solutions[1]. The orthorhombic crystals transform into the monoclinic phase at 350K [2,5]. The structural instability of the orthorhombic polymorph seems to correlate with its considerable anharmonism of interactions along the b axis [5]. The frequencies of the maxima of some bands polarized along the b axis shift much more with changing temperature than other bands. It concerns two bands which maxima situated at 65 and 105 cm^{-1} at 300K shift to 80 and 117 cm^{-1} at 90K as it is seen in Fig.5. They seem to originate from some out-of-plane vibrations of mNPh molecule. The vibrations might be expected to couple with a low-energetic electronic transition which has a CT character[3] and to constitute a "driving force" of the phase transition of the orthorhombic crystal into the monoclinic one.

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