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Effect of intermolecular =C-H...O interaction on the crystal structure and vibrational properties of 2,6-dimethyl-4-nitropyridine N-oxide

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Abstract

The crystal structure of 2,6-dimethyl-4-nitropyridine N-oxide (DMNPO) has been determined at ambient temperature. The compound crystallizes as a monoclinic structure, space group P2/n, with 12 molecules per unit cell. The unit cell contains three non-equivalent formula units. The nitro group is not coplanar with the pyridine ring. Through a system of = $C-H\cdots O$ hydrogen bonds the molecules are arranged into a two-dimensional network of layers parallel to the *axc* plane.

The IR and Raman spectra, measured in the $3500-100 \text{ cm}^{-1}$ region at ambient temperature, are correlated with X-ray structural data. The assignment of IR and Raman bands is given. The appearance of characteristic vibrational features in the spectra of this compound and the observed shifts of the =C-H and N-O IR active stretching modes, when the sample is dissolved in CCl₄, is discussed in terms of the relatively strong =C-H···O hydrogen bonds present in this crystal. © 1998 Elsevier Science B.V.

Keywords: X-ray crystallography; Infrared spectroscopy; Raman spectroscopy; CHO hydrogen bonding; 2,6-dimethyl-4-nitropyridine N-oxide

1. Introduction

4-nitropyridine N-oxide derivatives belong to a class of compounds which are very extensively studied because of their interesting biological and physical properties. These nitro derivatives are, for example, prospective crystals for second-harmonic generation [1-5].

In this paper, part of a systematic investigation of substituted pyridine N-oxide derivatives is reported. In many of these crystals the molecules are connected through intermolecular hydrogen bonds of the type =C-H···O [6,7]. The importance of =C-H···O interactions in various areas of chemistry has frequently been reported [8–10]. These relatively weak but specific interactions may play an important role and be essential for the activity of therapeutic drugs. Vibrational spectroscopy is an excellent tool for studying this type of interaction since the formation of =C-H···O bonding leads to a significant shift of some vibrational bands as well as intensity changes.

In the present work, the X-ray crystal structure of the title compound has been determined and the results obtained have been analysed in respect of

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Table 1

precise assignments of the observed vibrational modes. Special attention has been focused on intermolecular interactions in the crystalline phase. The observed modes have been assigned with reference to previous vibrational studies and normal coordinate analysis of 2,6-dimethylpyridine and 4-nitropyridine N-oxide (NPO) [11–24].

2. Experimental

2.1. Crystal growth

In order to obtain 2,6-dimethyl-4-nitropyridine N-oxide, 0.5 mole of 2,6-dimethylpyridine was dissolved in 100 cm³ of (CH₃CO)₂O. Then 100 cm³ of 30% H₂O₂ was added and the mixture was heated for 3 h at 70-80°C. The acetic acid and water thus formed was distilled off under reduced pressure, then 50 cm³ of water was added and distilled off. The reaction mixture was neutralized with KHCO3 and the reaction product was extracted with chloroform. The 2,6dimethylpyridine N-oxide thus obtained was added to 100 cm^3 of 96% H₂SO₄. The mixture of 2,6dimethylpyridine N-oxide with H₂SO₄ was added to a mixture of $120 \text{ cm}^3 \text{ H}_2\text{SO}_4$ (96%) with 180 cm³ of concentrated HNO₃. The reaction mixture was then heated for 2 h, cooled, poured into 500 g of ice, neutralized with NH4HCO3 and a concentrated NH3 solution (to pH \approx 9). The crystals obtained (melting point 152-153°C, readily soluble in chloroform, hardly soluble in ethanol and acetone) were filtered off and recrystallized from water.

2.2. X-ray diffraction

A single crystal was tested by the usual rotation and Weissenberg technique. The symmetry and systematic absences (h0l: h + l = 2n + 1) indicated one of the monoclinic space groups Pn or P2/n. The quality of the crystal allowed the data collection to be restricted to $\theta = 58.1^{\circ}$ (CuK α radiation), beyond which the intensity faded rapidly. The intensities were corrected for Lorentz polarization effects. Crystal data and experimental details are given in Table 1. The statistical distribution of |E| values, compared with theoretical values expected for the centrosymmetric and acentric structures, gave an indication of the centric

Experimental details	
Crystal data:	
Chemical formula	$C_7H_8N_2O_3$
Molecular weight	168.15
Crystal system	monoclinic
Space group	P2/n
Lattice parameters	a = 17.922(4), b = 3.933(1),
	$c = 34.624(7) \text{ Å}, \beta = 92.58(3)^{\circ}$
V	2438.(1) Å ³
Ζ	12
Radiation wavelength	CuKα, 1.54178 Å
No. of reflections for	39
cell parameters	
θ range for cell parameters	22, 40°
μ	0.91 mm^{-1}
Temperature	294 K
Crystal colour and form	yellow, plate
Crystal size	$0.25 \times 0.15 \times 0.3 \text{ mm}$
D _c	1.374 Mg m ⁻³
Data collection:	
Diffractometer	Kuma KM-4
No. of measured reflections	4509
No. of independent reflections	2930
No. of observed reflections	2081
Observation criterion	$ F_0 ^2 > 2\sigma(F_0)^2$
R int	6.4% for all reflections
$\theta_{\rm max}$ (°)	58.1
Index range	<i>h</i> : - 19, 17; <i>k</i> : - 4, 0; <i>l</i> : - 36, 36
Standard reflections	2, measured every 50 reflections
Intensity variation	0.062%
Refinement:	
Refinement on	F^2
No. of reflections used in	2081
refinement	
Number of parameters varied	350
Final R ₁	0.061
Final <i>wR</i>	0.092
Goodness of fit	1.088
Weight parameters c_1 and c_2	0.07, 2.1
Min., max. residual (eA ⁻³)	- 0.27, 0.26

 $R_{\rm int} = |F_0^2 - F_{\rm filtean}^2|/\Sigma|F_0^2|.$

 $R_{1} = \Sigma ||F_{0}| - |F_{c}|| / \Sigma |F_{0}|.$

 $wR = \{ \sum [w(F_0^2 - F_c^2)^2] / \sum [w(F_0^2)^2] \}^{1/2}.$

 $w = [\sigma^2(F_0^2) + (c_1P)^2 + c_2P]^{-1}, \text{ where } c_1 \text{ and } c_2 \text{ are as in the table,} \\ \text{and } P = [\max(F_0^2) + 2F_0^2)/3].$

Goodness of fit $S = \sum w |F_0| - |F_c| / (n - m)^{1/2}$ (*n* = no. of reflections, *m* = no. of parameters).

structure. The structure was solved by a combination of direct methods and difference Fourier synthesis. The atomic positions were refined by the full-matrix least-squares technique (on F^2) with the SHELXL 93

Table 2

Atomic coordinates (×10⁻⁴) and equivalent isotropic displacement coefficients (Å² × 10⁻³). Equivalent isotropic displacement U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor

	x	у	z	$U_{\rm eq}$
Unit A:				
N(1)	4541(2)	790(7)	6995(1)	34(1)
N(2)	3869(3)	1281(12)	5830(1)	65(1)
O(1)	4751(2)	649(8)	7353(1)	48(1)
O(2)	3310(3)	2864(13)	5739(1)	102(2)
O(3)	4247(2)	- 176(12)	5592(1)	90(1)
C(2)	4985(2)	-605(10)	6724(1)	37(1)
C(3)	4768(2)	- 456(10)	6345(1)	43(1)
C(4)	4094(2)	1115(10)	6237(1)	43(1)
C(5)	3650(2)	2520(10)	6505(1)	42(1)
C(6)	3871(2)	2351(9)	6894(1)	36(1)
C(7)	3447(2)	3811(11)	7213(1)	52(1)
C(8)	5689(2)	- 2207(11)	6871(1)	50(1)
Unit B:				
N(1)	5232(2)	4817(7)	8748(1)	33(1)
N(2)	3292(2)	- 594(8)	8424(1)	45(1)
O(1)	5829(2)	6506(7)	8845(1)	54(1)
O(2)	3167(2)	- 1190(10)	8085(1)	79(1)
O(3)	2893(2)	- 1569(9)	8678(1)	68(1)
C(2)	5091(2)	4017(9)	8364(1)	36(1)
C(3)	4452(2)	2245(10)	8262(1)	37(1)
C(4)	3969(2)	1362(9)	8539(1)	34(1)
C(5)	4107(2)	2161(9)	8919(1)	35(1)
C(6)	4750(2)	3927(9)	9028(1)	33(1)
C(7)	4972(2)	4892(11)	9427(1)	51(1)
C(8)	5656(2)	5039(11)	8090(1)	51(1)
Unit C:				
N(1)	1734(2)	- 3140(8)	10794(1)	35(1)
N(2)	3233(2)	- 1127(10)	9937(1)	50(1)
O(1)	1264(2)	- 3686(8)	11056(1)	58(1)
O(2)	3112(2)	- 2279(12)	9622(1)	86(1)
O(3)	3788(2)	599(10)	10027(1)	79(1)
C(2)	2397(2)	1536(9)	10895(1)	35(1)
C(3)	2901(2)	- 890(10)	10617(1)	36(1)
C(4)	2727(2)	- 1851(9)	10239(1)	34(1)
C(5)	2054(2)	- 3478(10)	10142(1)	39(1)
C(6)	1560(2)	- 4098(10)	10422(1)	36(1)
C(7)	826(2)	- 5735(12)	10345(1)	56(1)
C(8)	2524(3)	- 603(12)	11307(1)	57(1)

program [25]. The check calculations in the space group Pn resulted in numerous strong correlations between the parameters; therefore the space group P2/n has been chosen. The choice was later confirmed by the satisfactory refinement results. All non-hydrogen atoms were refined anisotropically. The H

atoms bound to the pyridine ring were located from a difference Fourier map and refined isotropically, whereas the H atoms belonging to the methyl groups were placed in geometrically calculated positions. The atomic scattering factors for neutral atoms were used as in [26]. The final atomic parameters are reported in Table 2.

2.3. Raman and infrared measurements

The details of IR and Raman measurements have been described previously [7]. Polarized IR reflection spectra of a single crystal, oriented by the X-ray method, were measured with a Perkin–Elmer Auto-IMAGE system microscope connected to a Perkin– Elmer 2000 FTIR spectrometer. The spectra were measured with the incident angle close to 0° and the aperture 100 × 100 μ m. Using standard spectra for Windows software, Kramers–Kronig calculations were carried out on a PC to transform reflection spectra into transmission spectra.

3. Crystal structure determination

The asymmetric unit comprises three formula units A, B and C, shown in Figs. 1–3. Details of the molecular structure geometry are given in Tables 3 and 4. The three nitro groups possess considerable double bond character (average N–O distance = 1.213(4) Å), even though somewhat higher anisotropic displacement amplitudes of these O atoms indicate

Table 3 Bond lengths (Å)

	Unit A	Unit B	Unit C
N(1)-O(1)	1.278(4)	1.291(4)	1.285(4)
N(2)–O(2)	1.209(5)	1.208(4)	1.190(5)
N(2)–O(3)	1.231(5)	1.222(4)	1.233(5)
C(2)–N(1)	1.373(5)	1.377(5)	1.376(5)
C(2)–C(3)	1.351(5)	1.373(5)	1.374(5)
C(2)–C(8)	1.480(6)	1.475(5)	1.480(5)
C(3)–C(4)	1.392(6)	1.368(5)	1.383(5)
C(4)–N(2)	1.450(6)	1.476(5)	1.444(6)
C(5)–C(4)	1.366(6)	1.364(5)	1.392(6)
C(5)–C(6)	1.388(5)	1.384(5)	1.365(5)
C(6)–N(1)	1.380(5)	1.373(5)	1.364(5)
C(6)-C(7)	1.486(6)	1.470(5)	1.478(5)



Fig. 1. Molecular structure showing the labelling of the atoms. Displacement ellipsoids are drawn at the 50% probability level.

the presence of librations perpendicular to the ring plane, causing the N–O distance to be shortened. The double bond character is less evident for the N-oxide group (average (N–O) = 1.285(4) Å). The nitro ligand is not coplanar with the pyridine ring; it has pyramidal character. In each of the three subunits the two O atoms lie below and above the least-square plane passing through the pyridine ring. In units A and C the effect is twice as strong as in B. The corresponding distances of the O(2) and O(3) atoms from the plane are: 0.101(3) and -0.084(3) Å in the A subunit, -0.0735(20) and 0.043(2) Å in subunit B, and finally the two oxygen atoms in C are distant from the ring by -0.099(2) and 0.171(3) Å, respectively.

The N(1)-C bonds (average: 1.377(5), 1.370(5)

and 1.373 (5) Å in A, B and C, respectively) are considerably shorter than the N(2)–C distance (1.459(7) Å). Each oxygen atom of the three N-oxide groups is involved in intermolecular hydrogen bond interactions of the type =C–H…O (Table 5 and Fig. 3). This bond system causes the molecules to lie in layers perpendicular to the *b* axis with an interplanar distance ~3.93 Å (Fig. 3). However, in contrast to the previously described 3-chloroand 3-bromo-2,6-dimethyl-4-nitropyridine N-oxide [6], where the molecules are ordered in anti-parallel stacks of pairs suggesting some kind of dipole interaction between the pairs, in the present structure the hydrogen bonded layers are arranged in parallel.



Fig. 2. Mutual orientation of the subunits A, B and C. For clarity, the H atoms are omitted.

Table 4 Bond angles (°)

	Unit A	Unit B	Unit C
O(1)-N(1)-C(2)	119.5(3)	119.1(3)	118.9(3)
C(6)-N(1)-C(2)	121.8(3)	118.9(3)	121.7(3)
O(1)-N(1)-C(6)	118.7(3)	121.9(3)	119.5(3)
O(2)-N(2)-O(3)	122.8(5)	123.4(5)	123.5(3)
O(2)-N(2)-C(4)	117.8(5)	118.7(5)	119.6(4)
O(3)-N(2)-C(4)	119.4(5)	118.0(4)	116.8(3)
N(1)-C(2)-C(3)	119.8(4)	118.7(3)	119.6(3)
N(1)-C(2)-C(8)	116.3(3)	117.2(3)	116.9(3)
C(3)-C(2)-C(8)	123.8(4)	124.1(3)	123.5(4)
C(2)-C(3)-C(4)	119.3(4)	119.6(4)	119.0(4)
C(5)-C(4)-C(3)	121.3(4)	121.8(4)	120.7(3)
C(3)-C(4)-N(2)	118.8(4)	118.7(4)	120.6(4)
C(5)-C(4)-N(2)	119.8(4)	119.5(4)	118.7(3)
C(6)-C(5)-C(4)	119.4(5)	119.4(4)	119.6(4)
C(5)-C(6)-N(1)	118.4(3)	118.6(3)	119.5(3)
C(5)-C(6)-C(7)	124.8(4)	124.9(3)	123.5(4)
N(1)-C(6)-C(7)	116.8(3)	116.5(3)	117.0(3)

4. Vibrational assignment and discussion

The IR and Raman spectra (Figs. 4–8) consist of fewer bands than expected because no factor group splitting is observed. Moreover, although in the unit cell three crystallographically non-equivalent molecules are present and therefore each vibrational band should be split, in principle, into three components, for the majority of bands no splitting is observed.

It is therefore convenient to take into consideration all the vibrations of a single molecule and to explain the observed splitting of some bands as a result of molecular interactions in the crystal. There are 54 internal modes for a free molecule consisting of 20 atoms. Eighteen of them describe the methyl groups, six the nitro group and the remaining 30 the pyridine ring vibrations. The proposed assignment of the vibrational modes is presented in Table 6.



Fig. 3. Packing diagram of the structure. Intermolecular hydrogen bonds are marked by dashed lines.



Fig. 4. (a) Polycrystalline and (b) CCl₄ solution mid-IR spectra of DMNPO.

The assignment of most of the observed bands is straightforward and we shall therefore discuss in this paper only some particular points concerning the influence of intermolecular interactions, especially $=C-H\cdots O$ hydrogen bonding, and crystal packing on vibrational spectra.

4.1. The $3200-2800 \text{ cm}^{-1}$ region

In the present study, the =C-H stretch band is split into two weak components in the Raman spectrum,

observed at 3091 and 3058 cm⁻¹, whereas the IR spectrum shows one strong band at 3075 cm⁻¹ with shoulders at 3091 and 3061 cm⁻¹. The IR spectrum in CCl₄ solution (Table 6) shows bands at 3096, 3087 and 3067 cm⁻¹. The 3096 cm⁻¹ mode (in solution) originates from the free =C-H group and, as a result of =C-H…O interaction in the crystal, it shifts to 3075 cm⁻¹. It has been shown previously that interaction between a =C-H group and an oxygen atom results in a shift towards smaller wavenumbers for the C-H stretching vibration and intensity increase if

Proposed hydrogen bonding system						
D–H···A	D-H	Н…А	D-A	<) D-H…A		
$C(5c)-H(17)\cdots O(2a)_i$	0.930(4)	2.490(4)	3.411(5)	166.0(3)		
$C(8a)-H(7)\cdots O(1c)_{ii}$	0.947(4)	2.538(3)	3.447(5)	160.9(3)		
C(3b)-H(9)O(1a)	0.890(5)	2.440(5)	3.276(5)	155.0(4)		
C(8b)-H(14)O(1a)iii	0.981(4)	2.524(3)	3.694(5)	153.1(3)		
$C(3c)-H(18)\cdots O(1b)_{iv}$	0.870(5)	2.590(5)	3.354(5)	147.0(4)		

Symmetry codes:

Table 5

i: 1/2 - x, y - 1, 3/2 - z

ii: -x + 1/2, -1 - y, z - 1/2

iii: x, y + 1, z

iv: 1 - x, 1 - y, 2 + z







Fig. 6. Raman spectrum of DMNPO.



Fig. 7. Polarized IR spectra of DMNPO: (a) $E \parallel b$; (b) $E \perp b$.



Fig. 8. Polarized Raman spectra of DMNPO with (a) both incident and scattered light polarized along the b axis and (b) both incident and scattered light polarized perpendicular to the b axis.

compared with the free =C-H group [27,28]. The appearance of the 3091 cm⁻¹ band in Raman and IR spectra of the polycrystalline sample, which can be assigned to the free =C-H group vibration, indicates that not all pyridine ring hydrogen atoms in the crystal form $=C-H\cdots O$ bonding. The results of the X-ray analysis confirm this conclusion: only in two of three crystallographically non-equivalent molecules is this type of hydrogen bond formed, with the O(1a)-H(9) and O(1b)-H(18) distances 2.440 and 2.590 Å, respectively. The 3067 cm⁻¹ IR band in solution can be assigned to the second free =C-H group vibration. Because the hydrogen atoms H2 and H9 do not interact with the N-O groups, the respective modes in the polycrystalline sample are only slightly moved and are observed at 3058 (RS) and 3061 cm⁻¹ (IR). The remaining bands at 3010-3011 and 2962-2965 cm⁻¹ are assigned to the ν_{as} (CH₃) vibrations. The $\nu_s(CH_3)$ mode is split into a doublet. The component at 2919 cm⁻¹ is clearly visible in the IR and as a shoulder in the Raman spectrum, whereas the second component at 2930 cm⁻¹ is Raman active only. The observed splitting can be explained as a result of intermolecular interaction of the methyl groups in 6-position with the N–O groups. According to the X-ray data, the O…H distances are 2.538 and 2.524 Å.

4.2. The $1650-1100 \text{ cm}^{-1}$ region

In this region interesting features are observed for the NO₂ symmetric stretch, the NO stretch and the band around 1100 cm⁻¹. The NO₂ symmetric stretching mode is split into a doublet (1344 and 1335 cm^{-1}) due to the existence of non-equivalent molecules in the unit cell. In principle, the $v_s(NO_2)$ band should be split into three components. However, in only one molecular unit (A) does the NO_2 group interact with the neighbouring H13 atom, forming hydrogen bonding. The two other nitro groups (in units B and C), for which no NO₂ H interaction exists, may have very similar properties and therefore the $\nu_s(NO_2)$ modes of these groups are observed as only one band. The polarization measurements enable us to distinguish which band originates from the NO₂ vibration of molecule A and which of molecules B and C. Since the molecules B and C are almost parallel to the ac plane, the $\nu_s(NO_2)$ vibrations of these molecules should lead to strong dipole moment changes in the ac plane and very weak ones along the b axis. The opposite behaviour is expected for A, oriented almost perpendicular to the B and C units (Fig. 2). The IR spectrum, recorded with light polarized in the ac plane, shows a strong band at 1341 and a weak one at 1334 cm⁻¹, whereas for the $E \parallel b$ polarization the 1334 band is more intense than the 1341 cm^{-1} one. Similar behaviour is observed in the Raman spectra: when both incident and scattered light are polarized along the b axis the strongest line is observed at 1336 cm⁻¹, whereas for polarization perpendicular to the *b* axis the 1344 cm^{-1} line becomes the most intense. The measured spectra clearly show that the 1344–1341 cm⁻¹ lines may be assigned to the $\nu_s(NO_2)$ modes of units B and C and that the second component at 1336–1334 cm⁻¹, attributed to molecule A, is moved towards lower wavenumbers due to the hydrogen-type interaction of the NO₂ group with the hydrogen atom of the pyridine ring. No $\nu_s(NO_2)$ splitting was previously observed for NPO [18], 3-methyl-4-nitropyridine N-oxide (POM) [24] and 3-halo-2,6dimethyl-4-nitropyridine N-oxides [6], where these modes are located in the $1335-1350 \text{ cm}^{-1}$ region.

The 1108 cm⁻¹ band is substituent dependent and was observed at 1180-1173 cm⁻¹ for 3-halo-2,6-dimethyl-4-nitropyridine N-oxides [6] and 1125 cm⁻¹ for NPO [18]. Former studies of pyridine and pyridine N-oxide derivatives showed that the only vibration above 1000 cm⁻¹, which can be observed in a broad wavenumber range, is in-plane ring deformation (ν_{12} in Wilson notation [29]). This mode was observed at 1025 cm^{-1} for pyridine N-oxide [30], 1271 cm⁻¹ for 2,6-dimethylpyridine [31] and 1010 cm^{-1} for POM [24]. Joyeux and Dao [18] showed by means of normal coordinate analysis that this band is not a pure ν_{12} ring deformation but should rather be assigned as a coupled v_{12} ring deformation and ν (C–NO₂) stretching mode.

The N–O stretch is the most interesting mode in this region and gives much information about the nature of intra- and intermolecular interactions. The aromatic N-oxides show moderate double bond character in their N–O bond and the stretching frequency varies as its π -bond order. The two main mesomeric forms of DMNPO are presented in Fig. 9. In the present study the ν (NO) mode was observed at 1281 cm⁻¹ with a shoulder at 1275 cm⁻¹ (IR) and at 1276 cm⁻¹ with a shoulder at 1281 cm⁻¹ in the Raman

Table 6			
Vibrational	wavenumbers	for	DMNPO

	IR			Raman			Assignment
Polycrystalline	CCl_4	<i> b</i>	$\perp b$	Polycrystalline	bb	$\perp bb$	—
3091sh	3096w			3091w	3093w	3088w	ν(C-H)
_	3087vw			_			overtone or combination band
3075s	_			_			ν (C–H)
3060sh	3067vw			3058w	3064w	3059w	ν(C-H)
3011w	3005w			3010w	3008w	3009w	$\nu_{as}(CH_3)$
2965vw	2962w			2962w	2966w	2960w	$\nu_{\rm as}(\rm CH_3)$
_	_			2930w	2930m	2931w	$\nu_{\rm s}(\rm CH_3)$
2919vw	2921w			2919sh			$\nu_{\rm s}(\rm CH_3)$
1615m	1618w			1616m	1616m	1616m	ν_{s_0} ring stretch
1591w				_			ν_{ob} ring stretch
1538sh	1537w						
1521s	1524s	15198	15198	1524w	1524vw	1524vw	$\nu_{\rm el}(\rm NO_2)$
1463m	1456m	10195	10195	15210	1456vw	1467vw	v_{10} ring stretch
1437w		1435w		1438vw	1439vw	1438vw	y_{191} ring stretch
1420w	1/18w	1/18w		1450VW	14570	14500 W	δ (CH ₂)
1300w	1410w	1410w		1401m	1401m	1402m	δ (CH ₂)
1399w	1370		1381w	1401111 1377xv	1401111 1377m	1377m	$\delta_{s}(CH)$
1363ww	1360w		1301w	1365w	1365	1365w	$\delta_{s}(CH_{3})$
1303VW	1300w	1240m	1241	1303w	1303vw	1305w	$\sigma_{\rm s}({\rm CH}_3)$
15458	155578	134011	13418	13448	134011	134478	$\nu_{\rm s}(\rm NO_2)$
		13308	1334W	15558	13308	13308	$\nu_{\rm s}(\rm NO_2)$
1001	1002	1070	1001	130/W	1308W	1306W	ν_{14} ring in-plane deformation
12818	1293vs	12/9m	12818	1281sn	1282sh	1281sh	$\nu(N-O)$
	1005	12/38	12/4m	1276m	12/6m	1276w	$\nu(N-O)$
	1285w	1010	1000	1010			overtone or combination band
1211m	1218w	1218w	1208w	1210vw			δ(C-H)
1108m	1099m	1109w	1108w	1108w	1109w	1108w	$\nu_{12}^* \nu(C-NO_2)$
1039m	1035w	1039vw	1039vw	1041vw			CH ₃ rock
1004w	997w			1003w	1003vw	1002vw	CH ₃ rock
959vw				959vw			ν (C–CH ₃)
944m	945m	943w	943w	944w	944w	945w	ν_1
924vw		921w		—			γ (C–H)
912m	896m	910w					γ (C–H)
820vw				819vw			$\delta(NO_2)$
749s		749s	748w	749m	749m	749m	$\gamma(NO_2)$
_				620vw		620vw	$ u_{6b}$
559m				558vw		560vw	ν_{6a}
543s				545m	545w	545w	$\rho(\text{NO}_2)$
444w				444w	447vw	444vw	ν_{16a}
377w				381w		381vw	δ(N–O)
364vw				364w	365vw	363w	$\delta(C-CH_3)$
302w				300w		296w	$\gamma(NO)$
				251w	248w	250w	γ (C-CH ₃), δ (C-NO ₂)
201w						· ·	$\tau(CH_3)$
128m							libration or translation
128m							noration or translation



Fig. 9. The two main mesomeric forms of the DMNPO molecule.

spectrum. The respective IR band in non-polar CCl₄ solution was located at 1293 cm⁻¹. The observed shift towards smaller wavenumbers of the $\nu(NO)$ band in a crystal, compared with CCl₄ solution, is due to the =C-H...O interactions. These interactions diminish the intramolecular charge transfer and the π -bond order of the N-oxide moiety, and finally lead to lowering of the $\nu(NO)$ mode wavenumber. A similar shift was observed for the NPO: in non-polar solvents the N–O group absorbs at about 1300 cm^{-1} [32] and in the crystal at 1269 cm⁻¹ [18]; i.e., in the solvent the molecule is best described by the form II and in the crystal by the form I. In the case of DMNPO the situation is similar; i.e., the main resonance form in the crystal is form I. However, for this crystal the observed shift is only 12 cm⁻¹. This conclusion is consistent with the results of X-ray analysis which show that the nitro groups are twisted. The lowering of the ν (N–O) wavenumber in CCl_4 from 1300 cm⁻¹ in the case of NPO to 1293 cm⁻¹ in the present study of DMNPO can be explained as a result of lower π -bond order of a free molecule due to the presence of two electronreleasing CH₃ groups. The higher N–O π -bond order for pyridine N-oxide derivatives was predicted by Kulkarni et al. [33] for compounds with electronwithdrawing substituents rather than for compounds with electron-releasing substituents. This effect explains also why, in the case of 4-chloro-2,6dimethyl-3-iodopyridine N-oxide (without the electron-withdrawing NO₂ group), the ν (NO) band observed by us is moved to 1231 cm^{-1} [7].

The polarized IR spectra show two components of the ν (NO) stretching mode at 1274 and 1281 cm⁻¹.

The former is more intense for polarization along the *b* axis and the latter for polarization in the *ac* plane. In a similar way as was presented above for the $\nu_s(NO_2)$ mode, the 1274 cm⁻¹ band can be attributed to the $\nu(NO)$ vibration of molecule A and the 1281 cm⁻¹ mode to molecules B and C. This assignment is consistent with the X-ray analysis since stronger C–H…O hydrogen bonding is observed for the N–O group of molecule A than for those of molecule B or C.

4.3. The $1100-100 \text{ cm}^{-1}$ region

The two strongest IR lines in this region, at 749 and 543 cm⁻¹, can be unambiguously assigned to the $\gamma(NO_2)$ and $\rho(NO_2)$ modes. The $\delta(NO_2)$ vibration gives rise to a very weak band at 820–819 cm⁻¹ and the twist $\tau(NO_2)$ mode was not detected in the present studies since it is situated below 100 cm^{-1} [24]. The medium intensity IR band at 912 cm⁻¹ and the weak one at 924 cm^{-1} (absent in the Raman spectrum) show considerable shift towards smaller wavenumbers, i.e. to 896 cm⁻¹ in CCl₄ solution. Since a shift towards higher wavenumbers is expected for the out-of-plane C-H bending [27] forming the =C-H...O bond in a crystal these bands can be assigned to the γ (C3b–H9) and γ (C3c-H18) modes. The line at 944 cm⁻¹ does not show any shift in CCl₄ solution and therefore originates from the v_1 ring-stretching mode. The polarized IR spectra support our conclusion. The in-plane ν_1 vibration should be more intense for polarization in the *ac* plane than for light polarized along the *b* axis since the two molecules (B and C) give rise to a transition moment in the *ac* plane but only one (A) does along the b axis. This type of behaviour is observed for the 944 cm⁻¹ band. For the out-ofplane vibrations, higher intensity is expected for $E \| b \|$ than for $E \perp b$ polarization. The only bands increasing their intensity for polarization along the b axis are those at 749 ($\gamma(NO_2)$), 910 and 921 cm⁻¹. The two latter bands are therefore assigned to the γ (C–H) modes.

5. Conclusions

Our study of the infrared and Raman spectra of 2,6dimethyl-4-nitropyridine N-oxide allows us to make a

- at least two non-equivalent molecules are present in the unit cell;
- relatively strong =C-H···O-N hydrogen bonds are present in this crystal. There are the following spectroscopic proofs of existence of the =C-H···O hydrogen bonds:
- a shift towards smaller wavenumbers of the =C-H and N-O stretch vibrations;
- a shift towards higher wavenumbers of the =C-H out-of-plane vibrations;
- the relative intensity increase of the =C−H stretch in the polycrystalline sample as compared with the CCl₄ solution.X-ray analysis confirmed the presence of both nearly free =C−H groups and strong intermolecular =C−H…O bonds.The crystal studied is an interesting example of application of polarized light in the determination of the origin of observed bands even if the symmetry of a crystal is low. The polarized measurements enabled us to:
- discriminate between in-plane and out-ofplane vibrations, especially in locating unambiguously ν₁ and γ(C–H) modes situated close to each other;
- attribute the two components of the observed $\nu_s(NO_2)$ and $\nu(NO)$ doublets to the two groups of molecules (A and B + C) and explain the observed differences in their frequencies as a result of intermolecular interactions.

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