

THE CRYSTAL AND MOLECULAR STRUCTURE OF 3-N-PYRIDYLSYDNONE

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Dedicated to Dr B. Sedláček on the occasion of his 60. birthday.

The title compound studied for its photochromic properties crystallizes in the monoclinic system, the space group $P2_1/c$, $a = 734.3(6)$, $b = 933.3(8)$, $c = 2334.2(2)$ pm, $\beta = 117.71(5)^\circ$, $V = 1.416(2)$ nm³, $Z = 8$, measured and calculated density $D_m = 1.51$, $D_x = 1.53$ Mg m⁻³, $\lambda(\text{CuK}\alpha) = 154.178$ pm, $\mu = 1.0$ mm⁻¹, $F(000) = 672$, $M_r = 163.14$, $T = 296$ K. Final $R = 0.084$ for 1511 significant ($I > 1.96\sigma_I$) reflections. The molecules are roughly parallel with the (100) plane and are stacked so that the sydnone ring of the first independent molecule partly overlaps the pyridyl ring of the second independent molecule. This results in the infinite column of partly overlapping pyridyl and sydnone rings in distances 344(4) and 335(4) pm, parallel with the a axis. Symmetrically independent molecules simulate pseudo 2_1 axis.

The mechanism of photochromy of 3-N-pyridylsydnone, first observed by Tien and Hunsberger¹, has not been satisfactorily explained. The formation of colour centres, similarly to alkali halides, was supposed² basing on a considerable increase of the electric current during the thermal bleaching of coloured crystals³ and basing on the bleaching under the influence of $e.m.f$ ⁴. On the other hand, radiolysis, flash photolysis, and optical absorption experiments⁵ proposed the mechanism of photochromy based on the intermolecular charge-transfer transition.

Also, our experiments with a series of new photochromic 4-alkenyl-3-phenylsydnones⁶⁻⁹ showed no effects which could be expected for materials containing colour centres of the F and F' type. Furthermore, some of these compounds were photochromic in frozen solutions in ethanol, methylpentane, (ether – isopentane – ethyl alcohol mixture, EPA) and in polymeric matrices at low temperatures^{6,7}. Especially,

the 4-(3-methyl-1-buten-2-yl)-3-phenylsydnone was photochromic in frozen solutions, but non-photochromic in the crystalline state.

The crystal and molecular structures of sydnone were studied by us¹⁰⁻¹³ and Hope, Thiessen, Barninghausen, Jellinek, Munnik, Vos¹⁴⁻¹⁶. It seems that the intermolecular interactions are important for the stabilization of the coloured form. In this paper we report the crystal and molecular structure of 3-N-pyridylsydnone determined from crystal X-ray diffraction data.

EXPERIMENTAL

The title compound forms transparent colourless crystals in the dark. The absorption UV spectra at room temperature possess two characteristic bands with maxima at 317 nm (3.49) and 235 nm (3.93) in ethanol, 320 nm (3.86) and 236 nm (4.28) in EPA, 330 nm (3.06) and 238 nm (3.45) in heptane with a shoulder on the long-wavelength part of the second absorption band at 260 to 270 nm (the numbers in parentheses represent the logarithm of the molar absorption coefficient). The diffusion reflection spectrum yields maxima at 237, 270 (weak), and 320 nm. The colour change of the crystalline phase is observed immediately after irradiation with light of a wavelength shorter than 430 nm. This new reversible broad absorption band with the maximum at ~ 630 nm is shown in Fig. 1. The crystals of the title compound do not become coloured at the temperature of liquid nitrogen when irradiated, but the subsequent increase of temperature leads to blue colouration already without irradiation. No colour change was observed in frozen solutions. Bleaching of the coloured material occurs *via* a thermal, nearly monomolecular process with the half-time ~ 6000 s in the dark at 293 K. This process may be accelerated by irradiation with visible and infra-red light with $\lambda > 500$ nm.

The density of crystals of 3-N-pyridylsydnone was measured by flotation in aqueous NaCl solution. Intensity measurements were performed with the Syntex P2₁ diffractometer, graphite monochromator, CuK α radiation, on a crystal grounded to a sphere with $r = 0.7$ mm. The unit

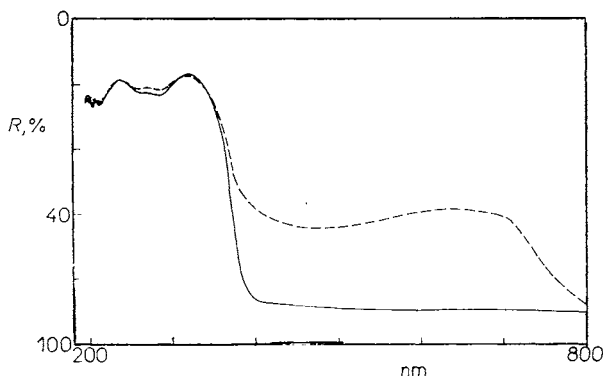


FIG. 1

Diffusion reflection spectra of crystalline 3-N-pyridylsydnone: — in the dark, ---- irradiated for 15 s with light of 400 to 480 nm

cell parameters were refined from 22 reflections with 2θ from 16 to 26° . Systematic absences $h0l: l = 2n + 1$. Almost exact (within 3 e.s.d.'s) absences of $0k0: k = 2n + 1$ reflections were caused by pseudo 2_1 screw axes. Reflected intensities were measured up to $\sin \theta/\lambda = 5.5 \text{ nm}^{-1}$ with $\theta - 2\theta$ scan. The crystals slowly deteriorated during the measurement (45 kV, 20 mA, 180 hours). Four standard reflections showed a decrease of about 13%. A few maxima with intensities from 5 to 12 e.s.d.'s in positions of systematically absent and pseudo-absent reflections decreased to less than 4 e.s.d.'s when checked by ψ scan. Intensity measurements were made by variable scan rate with the minimal rate 1.4 grad/min. 400 reflections were classified as unobserved according to the criterion $I < 1.96\sigma_1$. Absorption and extinction corrections were not applied. An anisotropic Wilson plot showed that the set of observed structure factors suffered from highly anisotropic effects.

Structure Determination and Refinement

Initially, the extinctions $0k0: k = 2n + 1$ caused by a pseudo 2_1 axis were taken as systematic absences and the space group was assumed to be $P2_1/c$. Direct methods, MULTAN¹⁷ and SIMPLE¹⁸, produced one well-defined, almost planar molecule but the pattern of the second one was in all cases disordered around the centre of symmetry.* All attempts to find the remainder of the structure by repeated Fourier syntheses and DIRDIF¹⁹ failed. However, strengthened translation functions²⁰ gave the null-vector with very high correlation factors showing that the molecule was correctly positioned with respect to the $P2_1/c$ symmetry elements. We then decided to run DIRDIF in space group $P1$, using the original input molecule, and reflection data expanded to triclinic symmetry. The procedure for the scaling of the difference structure factors²¹ showed anomalies in the separate temperature factors for the known atoms and for the remainder of the structure. This may be caused either by the anisotropy of the data or by errors in the geometry of the input molecule, especially the planarity of the model. Therefore we imposed a $\sin \theta/\lambda$ cutoff (4.6 nm^{-1}) and used the DIRDIF results with care. Although eight molecules were recognized in the DIRDIF-Fourier map, only 23 new peaks were selected from the highest peaks, with preference given to atoms with the largest deviations from planarity. The 35 atoms were used in DIRDIF for a second run in space group $P1$, which resulted in the determination of eight well-defined molecules. A few missing atoms were located by a weighted Fourier synthesis.

All eight molecules are paired by a well-defined c-glide plane, but they are divided into two groups, each of them forming a sub-structure in $P2_1/c$, explaining thus the $0k0$ absences. However, the two sub-structures are related by a two-fold rotation axis, and the space group was thus found to be $P2/c$. The initial R -value, after transformation and averaging according to the space group symmetry, was 0.33. Full matrix least-squares refinement based on F magnitudes²² was used with default scattering factors^{23,24}. Non-hydrogen atoms were refined anisotropically and hydrogen atoms (located from the difference map) isotropically to $R = 0.084$ for 257 refined parameters and 1 511 reflections. The final difference map gave no significant features, the maximum peak height being $32 \text{ e} \text{ pm}^{-3}$.

DISCUSSION

The final positional and thermal parameters of non-hydrogen atoms are given in Table I, and for hydrogen atoms in Table II. The numbering of atoms, interatomic

* In the correct space group, the programs MULTAN and SIMPEL revealed both independent molecules at their correct positions.

distances, and interbond angles are given in Fig. 2. Projection of the crystal structure along a axis is shown in Fig. 3. Including the title compound, ten independent determinations of sydnone ring were found in the literature. The title compound has extremal values of the following intramolecular parameters: Both bonding distances N(3)–C(4) 133.0(6) and 132.3(6) pm are the shortest ones, the angles C(4)–C(5)–O(6) 136.7(2) and 138.1(2) are the widest and the adjacent angles O(1)–O(5)–O(6)

TABLE I

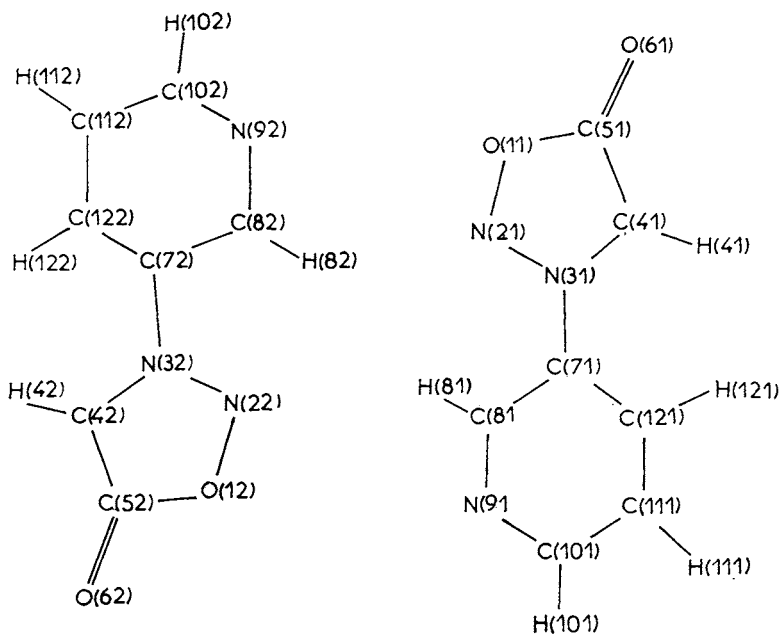
Final positional parameters with their estimated standard deviations ($\cdot 10^4$) and U_{eq} values ($\cdot 10^{-1}$ pm²) of the non-H atoms

Atom	x/a	y/b	z/c	U_{eq}
Molecule (1)				
O(11)	2 300(6)	440(3)	5 835(2)	94(2)
N(21)	2 228(7)	1 718(4)	5 524(2)	86(2)
N(31)	2 497(6)	2 693(4)	5 962(2)	73(2)
C(41)	2 696(9)	2 174(5)	6 520(2)	83(3)
C(51)	2 584(8)	684(5)	6 459(2)	83(3)
O(61)	2 688(7)	— 341(4)	6 800(2)	109(3)
C(71)	2 532(7)	4 182(5)	5 798(2)	73(3)
C(81)	3 045(10)	4 536(6)	5 324(3)	94(4)
N(91)	3 128(7)	5 903(5)	5 156(2)	97(3)
C(101)	2 581(9)	6 910(6)	5 446(3)	86(3)
C(111)	1 984(10)	6 629(6)	5 912(3)	98(4)
C(121)	1 924(9)	5 205(6)	6 087(3)	91(3)
Molecule (2)				
O(12)	2 158(7)	4 571(4)	3 396(2)	103(2)
N(22)	2 036(8)	3 295(5)	3 677(2)	102(3)
N(32)	2 497(6)	2 337(4)	3 362(2)	73(2)
C(42)	2 867(10)	2 851(6)	2 895(3)	92(4)
C(52)	2 695(9)	4 333(6)	2 898(2)	90(3)
O(62)	2 853(7)	5 354(5)	2 601(2)	122(3)
C(72)	2 537(7)	858(5)	3 550(2)	72(3)
C(82)	2 729(9)	558(6)	4 156(3)	91(4)
N(92)	2 721(8)	— 795(6)	4 346(2)	106(3)
C(102)	2 571(9)	—1 849(7)	3 945(3)	94(4)
C(112)	2 366(10)	—1 629(6)	3 333(3)	92(4)
C(122)	2 370(8)	— 221(6)	3 134(2)	81(3)

TABLE II

Final positional parameters with their estimated standard deviations ($\cdot 10^4$) and U values ($\cdot 10^{-2} \text{ pm}^2$) of the H atoms

Atom	x/a	y/b	z/c	U_{iso}
Molecule (1)				
H(41)	304(6)	280(5)	691(2)	6(1)
H(81)	374(10)	395(8)	516(3)	15(3)
H(101)	254(6)	787(5)	532(2)	6(1)
H(111)	170(7)	759(7)	616(3)	11(2)
H(121)	146(5)	505(4)	643(2)	6(1)
Molecule (2)				
H(42)	359(9)	231(8)	278(3)	14(2)
H(82)	285(6)	142(5)	446(2)	8(1)
H(102)	244(7)	-279(6)	407(2)	8(1)
H(112)	226(9)	267(8)	302(3)	12(2)
H(122)	213(6)	0(5)	267(2)	7(1)



a

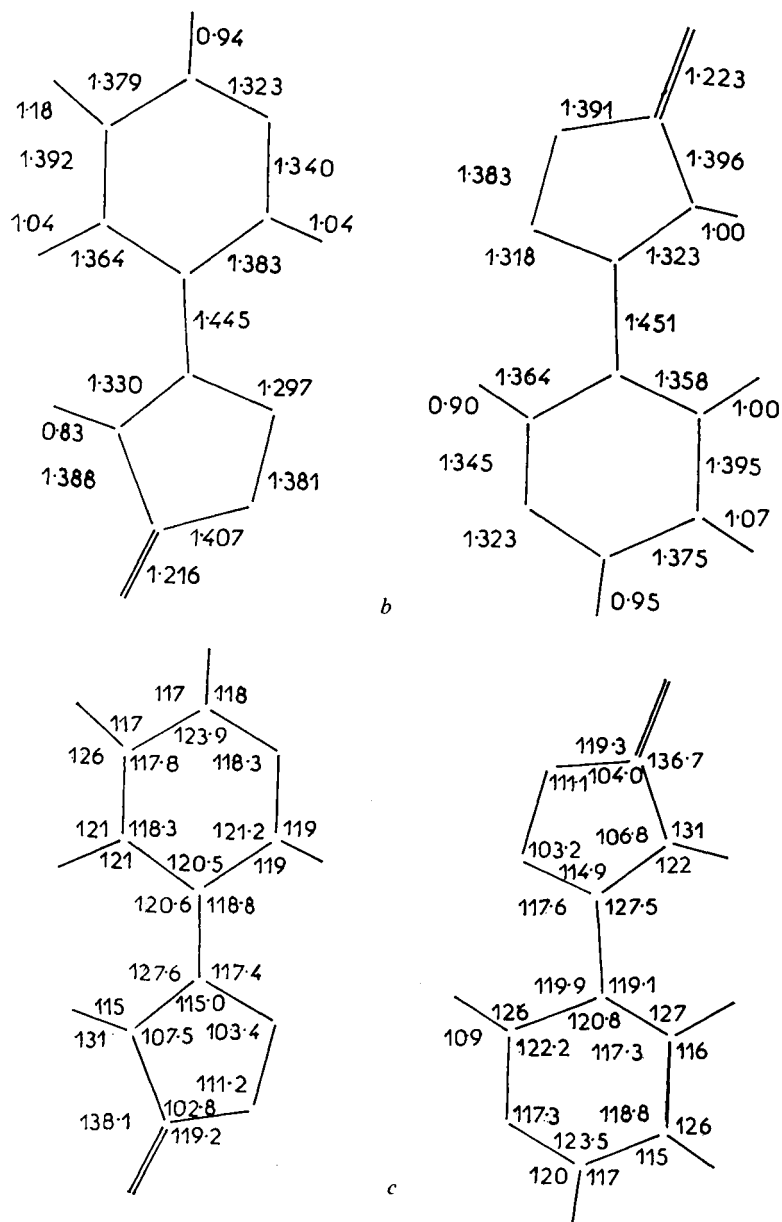


FIG. 2

Projection of the independent part of the unit cell of 3-N-pyridylsydnone perpendicular to the plane going through both pyridyl centres and C(72). *a* Numbering scheme; *b* interatomic distances: e.s.d.'s between non-hydrogen atoms from 0.6–0.8 pm, for hydrogen bonds from 4 to 7 pm; *c* interbond angles; e.s.d.'s of angles involving only non-hydrogen atoms are 0.2–0.4°, e.s.d.'s of angles involving also hydrogen atoms are 1–3°

119.3(2) and 119.2(2) are the lowest among all ten compared structures¹³. Also, the dihedral angles between the sydnone and pyridyl rings in the same molecule, 26.1(2) and 19.8(2)°, correspond just to the two lowest torsions observed between the sydnone ring and its aromatic substituent. Compare with 27.6, 30.0, 54.9, 58.9, and 63.8° for 3-(*p*-bromophenyl)sydnone¹⁴, 3-phenylsydnone¹⁶, 4-(3-methyl-1-buten-2-yl)-3-phenylsydnone¹⁰, 4-bromo-3-pyridylsydnone¹¹, and 4-(cyclohexen-1-yl)-3-phenylsydnone¹², respectively. This observation proposes that the torsion along N(3)–C(7) is principally influenced by the presence of a substituent on C(4). The quasiplanar molecules make possible the stacking of the almost parallel sydnone rings and pyridyl rings (dihedral angles 2.4(2) and 4.0(2)°) so that the alternating symmetrically independent molecules form infinite columns along the *a* direction. The angle between two independent sydnones (including carboxyl oxygen) is 22.2(2)°, and between

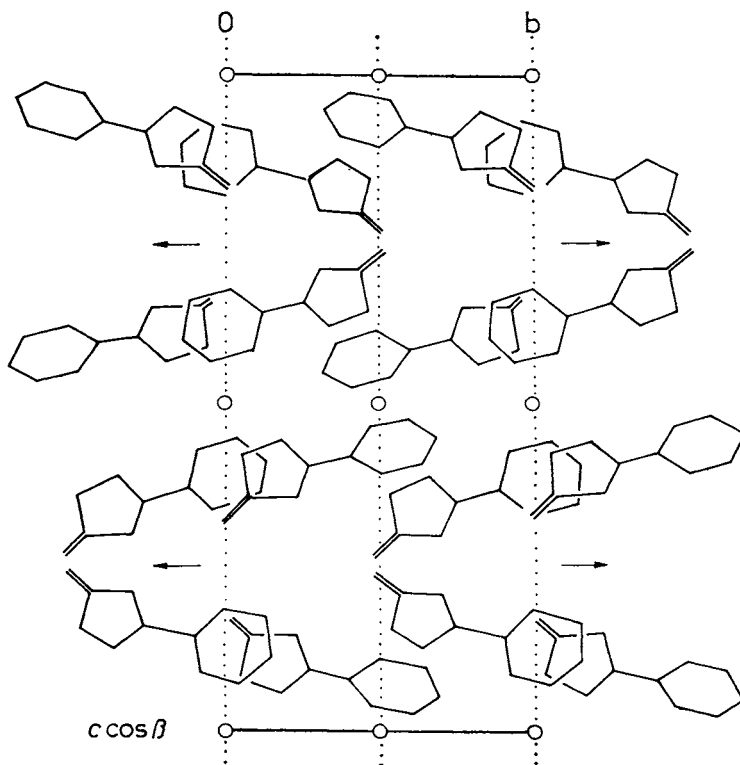


FIG. 3

Projection of the crystal structure of 3-N-pyridylsydnone along *a* axis

pyridyls, $23.7(2)^\circ$. A statistical χ^2 test for the planarity of sydnone and pyridyl rings gives 3.9, 8.4 for the first and 28.8, 3.2 for the second independent molecule. The corresponding ring puckering coordinates^{25,26} are $q = 1.0(6)$, $1.5(6)$ pm and $\varphi = -120(37)$, $-89(22)^\circ$ for sydnone rings and $Q = 3.4(6)$, $1.3(8)$ pm, $\varphi = -166(16)$, $167(89)^\circ$, $\theta = 137(11)$, $22(30)^\circ$ for pyridyl rings. Viewing the structure perpendicularly to the pyridyl rings, the C(51)=O(61) lies approximately under C(112)–C(122) and both bonds make in projection an angle $20(1)^\circ$. The relatively short perpendicular distance of the pyridyl and sydnone planes in the stack (344(4) and 335(4) pm)

TABLE III

The anisotropic thermal coefficients U_{ij} with their estimated standard deviations ($\cdot 10^{-1}$ pm²) for all non-H atoms

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Molecule (1)						
O(11)	151(3)	55(2)	79(2)	-3(2)	75(2)	-1(2)
N(21)	132(4)	58(2)	69(3)	-3(2)	61(3)	2(2)
N(31)	98(3)	58(2)	60(2)	-4(2)	50(2)	3(2)
C(41)	120(4)	61(3)	68(3)	-2(2)	66(3)	-2(2)
C(51)	119(4)	64(3)	67(3)	2(2)	64(3)	2(3)
O(61)	167(4)	66(2)	94(3)	11(2)	91(2)	2(2)
C(71)	97(3)	58(3)	63(3)	-0(2)	49(3)	-0(2)
C(81)	130(5)	70(3)	82(4)	8(3)	74(4)	2(3)
C(101)	118(4)	58(3)	81(3)	-1(3)	59(3)	-7(3)
C(111)	143(5)	65(3)	85(4)	-6(3)	79(4)	-0(3)
C(121)	136(4)	63(3)	74(3)	-6(2)	72(3)	2(3)
Molecule (2)						
O(12)	158(3)	63(2)	89(3)	-1(2)	81(3)	3(2)
N(22)	153(4)	69(3)	84(3)	-4(2)	82(3)	3(3)
N(32)	95(3)	65(2)	58(2)	-6(2)	43(2)	-5(2)
C(42)	133(5)	70(4)	72(3)	5(3)	72(3)	4(3)
C(52)	135(4)	64(3)	70(3)	2(2)	66(3)	-0(3)
O(62)	188(4)	76(3)	103(3)	9(2)	95(3)	-6(3)
C(72)	91(3)	63(3)	63(3)	3(2)	45(2)	8(2)
C(82)	128(4)	76(4)	69(3)	2(3)	61(3)	3(3)
N(92)	159(4)	77(3)	81(3)	8(2)	75(3)	-1(3)
C(102)	122(5)	66(3)	94(4)	5(3)	62(3)	3(3)
C(112)	125(4)	74(4)	78(4)	-2(3)	57(3)	3(3)
C(122)	104(4)	71(3)	68(3)	-6(2)	51(3)	-3(3)

TABLE IV

Intermolecular interactions of hydrogen bond type in 3-N-pyridylsydnone. Estimated standard deviations of distances (pm) and angles ($^{\circ}$) are in parentheses

Contact	A...D	A...H	A...H—D
O ^{iv} (61)...H(42)—C(42)	342·5(8)	279(7)	135(6)
O ^{iv} (61)...H(122)—C(122)	327·3(8)	227(5)	161(4)
O ⁱⁱⁱ (61)...H(111)—C(111)	340·4(7)	240(4)	157(4)
N ⁱⁱ (91)...H(81)—C(81)	150·0(10)	276(9)	140(6)
N ^v (91)...H(102)—C(102)	339·2(9)	266(6)	135(4)
O ⁱ (62)...H(41)—C(41)	338·0(8)	242(5)	162(4)
O ⁱ (62)...H(121)—C(121)	331·3(8)	248(4)	141(3)
O ^v (62)...H(112)—C(112)	340·0(8)	225(8)	165(5)
N ⁱⁱⁱ (92)...H(101)—C(101)	338·0(9)	264(5)	135(4)
O ⁱⁱⁱ (11)...H(101)—C(101)	345·2(7)	273(5)	134(3)

Symmetrically equivalent positions: *i*: $x, 1 - y, z + 1/2$
ii: $1 - x, 1 - y, 1 - z$
iii: $x, 1 + y, z$
iv: $x, -y, z - 1/2$
v: $x, 1 - y, z$

probably influences the stability of the coloured intermediates. The problem will be discussed generally for the structure of the sydnone type in more detail in another paper. The stacking of molecules described above implies that the eight molecules in the unit cell are divided into two groups (each of them containing both symmetrically independent molecules) so that four molecules in one group form approximately the screw axis 2_1 along the *b* direction. This property, implying the non-space group extinction of $0k0$ reflexions, may cause appearance of stacking faults in the crystal structure, which is consistent with the large observed anisotropy (Table III). However, this behaviour was not studied more deeply.

The molecular packing of 3-N-pyridylsydnone in the crystal is a result of numerous hydrogen bonds (Table IV). Nine symmetrically independent hydrogen bonds bound molecules inside the layers perpendicular to *b* axis; four of them are between symmetrically dependent molecules. The layers are inter-connected by the hydrogen bond Nⁱⁱ(91)...H(81)—C(81) between the pyridyl ring of the first molecule and its image related by the centre of symmetry.

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