

The Crystal Structure of Pyridine 1-Oxide

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(Received 12 January 1970)

Pyridine 1-oxide, C_5H_5NO , forms crystals which are orthorhombic, space group $C222_1$, with unit-cell dimensions $a=8.230$ (7), $b=8.221$ (7), $c=13.747$ (8) Å; the cell contains 8 molecules. The observed and calculated densities are 1.34 and 1.358 $g.cm^{-3}$ respectively. A total of 305 unique intensities were obtained photometrically from film exposed to Cu $K\alpha$ radiation in an integrating Weissenberg camera. The structure was determined by statistical methods and refined by least-squares techniques to a conventional R value of 7.8%. The unit-cell contains two crystallographically independent molecules, each of which has the N, O, and one C atom located on an axis of crystal symmetry. The N–O bond length is 1.35 Å.

Introduction

Determination of the crystal structure of pyridine 1-oxide by X-ray diffraction has been undertaken to permit a comparison of its molecular dimensions with those of pyridine 1-oxide and its derivatives as ligands in coordination compounds. The effect of ring substituents on the formation, structure, and physical properties of coordination compounds which have *N*-oxides as ligands has been the subject of considerable interest in this laboratory (Schäfer, Morrow & Smith, 1965; Hatfield, Muto, Jonassen & Paschal, 1965; Hatfield, Copley & Whyman, 1966; Hatfield & Morrison, 1966; Hatfield, Whyman & Copley, 1967). Interatomic distances and angles for pyridine 1-oxide as a ligand are available from crystal structure studies of di- μ -(pyridine 1-oxide)-bis[dichlorocopper(II)] (Sager, Williams & Watson, 1967), bis-(2,4-pentanedionato)bis(pyridine 1-oxide)nickel(II) (Horrocks, Templeton & Zalkin, 1968), tetrakis(pyridine 1-oxide) copper(II) perchlorate and fluoroborate (Lee, Brown & Melsom, 1969), dichlorodimethylbis(pyridine 1-oxide)-tin(IV) (Blom, Penfold & Robinson, 1969), and bis(pyridine 1-oxide)copper(II) nitrate (Šćavničar & Matković, 1969). Two derivatives, 4-nitropyridine 1-oxide (Eichhorn, 1956) and 4,4'-*trans*-azopyridine 1,1'-dioxide (Eichhorn, 1959) have been studied. Information on two methyl derivatives has been obtained from studies of dichlorobis-(2,6-lutidine *N*-oxide)zinc(II) (Sager & Watson, 1968*a*) and a 2-picoline *N*-oxide complex compound, $Cu_3Cl_6.(C_6H_7NO)_2.2H_2O$ (Sager & Watson, 1968*b*). Crystal structure determinations on 1-hydroxypyridinium chloride (Tsoucaris, 1961), phenazine 5-oxide (Curti, Riganti & Locchi, 1961), and phenazine 5,10-dioxide (Namba, Oda & Watanabe, 1963) are helpful in documenting the interrelation between electron density changes and shifts in bond lengths.

Experimental results

Transparent, water-white single crystals of pyridine 1-oxide, C_5H_5NO , were obtained by slow evaporation of a solution of the commercial material (Aldrich Chemical Co.) in ether. The roughly spherical crystals were approximately 1 mm in diameter. Great care had to be exercised in storing, handling, and mounting this extremely hygroscopic material. Protection of crystals from moisture over the period of data collection required the presence of a phosphorus pentoxide packing within the sealed Lindemann glass tubes which held the samples. The desiccant was located so that it did not touch the crystal and was not exposed to the X-ray beam. Preliminary precession photographs showed that the crystals are orthorhombic. Extrapolation of repeat distances obtained from high-angle reflections of the type $h00$ and $0k0$ on zero-level Weissenberg films using Cu $K\alpha$ radiation ($\lambda=1.5405$ Å) and from zero-level precession films gave the following unit-cell dimensions: $a=8.230$ (7), $b=8.221$ (7), $c=13.747$ (8) Å. The density of pyridine 1-oxide was determined by flotation to be 1.34 $g.cm^{-3}$, which indicates the presence of eight molecules per unit cell. The density calculated from $Z=8$ and the unit-cell dimensions is 1.358 $g.cm^{-3}$. The observed systematic absences for $h+k \neq 2n$ for hkl and $l \neq 2n$ for $00l$ indicated space group $C222_1$. The origin is taken to be at 212.

Intensity data were obtained by photometering integrated multiple-film Weissenberg photographs for levels 0–2 on rotation about the b axis and for levels 0–6 on rotation about the c axis. Unfiltered Cu $K\alpha$ radiation was employed. Ilford Industrial G film was used in a Stoe integrating Weissenberg camera. Preliminary interlevel scaling was accomplished by use of the intersection of sets of data from the b and c axis rotations. The scales were later used as variables in the least-squares refinement. Of the 634 unique reflections in the Cu sphere, 466 were observed, but only 305 were strong enough for photometric measurement. Lorentz–polarization corrections but no absorption corrections were applied. Since the crystals were ap-

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proximately spherical with radii 0.05 cm, μR is 0.40. The maximum variation in $|F_o|$ ascribed to absorption would then be 2%. The extremely intense reflection 004 appeared to be suffering badly from extinction, and it was not used in the least-squares refinement. No other allowance was made for extinction.

Structure determination

The non-centrosymmetric symbolic addition method (Karle & Karle, 1966) was selected for use in the phase determination. The pyridine 1-oxide cell was transformed, and the Miller indices of a primitive cell were generated so that the relationships previously worked out for space group $P2_1$ could be used. After the phase determination was completed, the higher symmetry of $C222_1$ was recovered by the appropriate reverse transformation. Normalized structure factor magnitudes $|E|$ were calculated and scaled (Hauptman & Karle, 1953) with $\epsilon=2$ for $00l$ spectra and $\epsilon=1$ otherwise, for $P2_1$. Origin assignment was made by assigning $\phi(110)=0$, $\phi(104)=0$, and $\phi(103)=\pi$. The corresponding E values are 2.94, 1.89, and 1.64 respectively. Enantiomorph selection was made by assigning $\phi(117)=\pi/2$; $|E|$ for 117 was 1.68. One unknown symbol $p=\phi(600)$ with $|E|=2.59$ was assigned. The space group requires that p be 0 or π . Phases for the fifty reflections with $|E|>1$ were determined from the Karle & Karle (1966) relationship:

$$\varphi(\mathbf{h}) \sim \langle \varphi(\mathbf{k}) + \varphi(\mathbf{h} - \mathbf{k}) \rangle .$$

Space group properties restricted the phases of 28 of the reflections to be 0, π , or $\pm\pi/2$, a feature which greatly facilitated the use of the symbolic addition formula. Internal consistency was much more satisfactory for $p=\pi$ than for $p=0$. Use of the former value led to an E map which immediately revealed two crystallographically independent molecules. Molecule I has N(1), O(1), and C(4) located on the twofold axis parallel to the a axis; for molecule II, the corresponding atoms lie on the twofold axis through the point $\frac{1}{2}0\frac{1}{2}$ parallel to the b axis. The special positions 4(a) and 4(b) of the space group are occupied by two sets of atoms, each consisting of an oxygen, a nitrogen, and a carbon atom in the 4-position of the ring. Carbon atoms in the 2- and 3-positions occupy the eightfold general equipoint of the space group which includes by symmetry carbon atoms in the 5- and 6-positions. Eighteen coordinates are variables, if hydrogen atoms are excluded from consideration.

Structure factors calculated from the E map coordinates, the Wilson scale, and a uniform isotropic thermal factor $B=3.0$ produced a conventional $R=\sum||F_o|-S|F_c||/\sum|F_o|$ of 59%. With the aid of a series of electron density and difference density calculations using all reflections, R was reduced to 21%. Isotropic full-matrix least-squares refinement, using the *ORFLS* program (Busing, Martin & Levy, 1962), converged at $R=10.4\%$. The function minimized was $\sum w(|F_o|-S|F_c|)^2$. The weight, w , given by the formula $w^{-1}=0.355+0.070|F_o|+0.00355|F_o|^2$, was selected so that $\langle w\Delta^2 \rangle$ varied little with changing $|F_o|$. The nine

Table 1. Final atomic coordinates and thermal parameters for non-hydrogen atoms in pyridine 1-oxide

Thermal factors are
 $\exp [-2\pi^2(U_{11}a^*2h^2 + U_{22}b^*2k^2 + U_{33}c^*2l^2 + U_{12}a^*b^*hk + U_{13}a^*c^*hl + U_{23}b^*c^*kl)] .$

Standard deviations, given in parentheses, refer to the least significant digits.

	10^4x	10^4y	10^4z	10^3U_{11}	10^3U_{22}	10^3U_{33}	10^3U_{12}	10^3U_{13}	10^3U_{23}
O(1)	1757 (10)	0	0	36 (4)	62 (6)	69 (8)	0	0	-1 (8)
N(1)	146 (11)	0	0	39 (5)	35 (5)	32 (5)	0	0	2 (9)
C(2)	4323 (11)	3910 (11)	540 (7)	50 (5)	31 (4)	36 (4)	1 (4)	3 (4)	4 (6)
C(3)	2660 (11)	3918 (11)	540 (8)	51 (5)	33 (5)	46 (5)	-6 (4)	8 (4)	-3 (6)
C(4)	3194 (14)	0	5000	32 (5)	48 (8)	48 (8)	0	0	6 (9)
O(2)	5000	1776 (12)	2500	58 (6)	45 (6)	65 (8)	0	1 (6)	0
N(2)	5000	110 (17)	2500	41 (4)	41 (6)	27 (4)	0	-1 (4)	0
C(12)	1103 (10)	4340 (14)	3052 (8)	33 (4)	53 (6)	37 (4)	-5 (4)	-3 (4)	11 (7)
C(13)	1101 (10)	2665 (13)	3068 (7)	33 (4)	54 (6)	34 (4)	4 (4)	-3 (4)	19 (7)
C(14)	0	1792 (19)	2500	57 (7)	49 (8)	43 (8)	0	15 (7)	0

Table 2. Observed and calculated structure amplitudes, in electrons

h	k	l	$ F_o $	$ F_c $	$ F_o / F_c $	h	k	l	$ F_o $	$ F_c $	$ F_o / F_c $	h	k	l	$ F_o $	$ F_c $	$ F_o / F_c $
0	0	0	100	100	1.00	0	0	0	100	100	1.00	0	0	0	100	100	1.00
0	0	1	80	75	1.07	0	0	1	80	75	1.07	0	0	1	80	75	1.07
0	0	2	27	27	1.00	0	0	2	27	27	1.00	0	0	2	27	27	1.00
0	0	3	11	11	1.00	0	0	3	11	11	1.00	0	0	3	11	11	1.00
0	0	4	5	5	1.00	0	0	4	5	5	1.00	0	0	4	5	5	1.00
0	0	5	3	3	1.00	0	0	5	3	3	1.00	0	0	5	3	3	1.00
0	0	6	2	2	1.00	0	0	6	2	2	1.00	0	0	6	2	2	1.00
0	0	7	1	1	1.00	0	0	7	1	1	1.00	0	0	7	1	1	1.00
0	0	8	1	1	1.00	0	0	8	1	1	1.00	0	0	8	1	1	1.00
0	0	9	1	1	1.00	0	0	9	1	1	1.00	0	0	9	1	1	1.00
0	0	10	1	1	1.00	0	0	10	1	1	1.00	0	0	10	1	1	1.00
0	0	11	1	1	1.00	0	0	11	1	1	1.00	0	0	11	1	1	1.00
0	0	12	1	1	1.00	0	0	12	1	1	1.00	0	0	12	1	1	1.00
0	0	13	1	1	1.00	0	0	13	1	1	1.00	0	0	13	1	1	1.00
0	0	14	1	1	1.00	0	0	14	1	1	1.00	0	0	14	1	1	1.00
0	0	15	1	1	1.00	0	0	15	1	1	1.00	0	0	15	1	1	1.00
0	0	16	1	1	1.00	0	0	16	1	1	1.00	0	0	16	1	1	1.00
0	0	17	1	1	1.00	0	0	17	1	1	1.00	0	0	17	1	1	1.00
0	0	18	1	1	1.00	0	0	18	1	1	1.00	0	0	18	1	1	1.00
0	0	19	1	1	1.00	0	0	19	1	1	1.00	0	0	19	1	1	1.00
0	0	20	1	1	1.00	0	0	20	1	1	1.00	0	0	20	1	1	1.00
0	0	21	1	1	1.00	0	0	21	1	1	1.00	0	0	21	1	1	1.00
0	0	22	1	1	1.00	0	0	22	1	1	1.00	0	0	22	1	1	1.00
0	0	23	1	1	1.00	0	0	23	1	1	1.00	0	0	23	1	1	1.00
0	0	24	1	1	1.00	0	0	24	1	1	1.00	0	0	24	1	1	1.00
0	0	25	1	1	1.00	0	0	25	1	1	1.00	0	0	25	1	1	1.00
0	0	26	1	1	1.00	0	0	26	1	1	1.00	0	0	26	1	1	1.00
0	0	27	1	1	1.00	0	0	27	1	1	1.00	0	0	27	1	1	1.00
0	0	28	1	1	1.00	0	0	28	1	1	1.00	0	0	28	1	1	1.00
0	0	29	1	1	1.00	0	0	29	1	1	1.00	0	0	29	1	1	1.00
0	0	30	1	1	1.00	0	0	30	1	1	1.00	0	0	30	1	1	1.00
0	0	31	1	1	1.00	0	0	31	1	1	1.00	0	0	31	1	1	1.00
0	0	32	1	1	1.00	0	0	32	1	1	1.00	0	0	32	1	1	1.00
0	0	33	1	1	1.00	0	0	33	1	1	1.00	0	0	33	1	1	1.00
0	0	34	1	1	1.00	0	0	34	1	1	1.00	0	0	34	1	1	1.00
0	0	35	1	1	1.00	0	0	35	1	1	1.00	0	0	35	1	1	1.00
0	0	36	1	1	1.00	0	0	36	1	1	1.00	0	0	36	1	1	1.00
0	0	37	1	1	1.00	0	0	37	1	1	1.00	0	0	37	1	1	1.00
0	0	38	1	1	1.00	0	0	38	1	1	1.00	0	0	38	1	1	1.00
0	0	39	1	1	1.00	0	0	39	1	1	1.00	0	0	39	1	1	1.00
0	0	40	1	1	1.00	0	0	40	1	1	1.00	0	0	40	1	1	1.00
0	0	41	1	1	1.00	0	0	41	1	1	1.00	0	0	41	1	1	1.00
0	0	42	1	1	1.00	0	0	42	1	1	1.00	0	0	42	1	1	1.00

scale factors were treated as variables. Scattering factors for C, N, and O were taken from the Tables of Hanson, Herman, Lea & Skillman (1964). Hydrogen scattering factors, used later in the calculations, were those given by Stewart, Davidson & Simpson (1965).

The difference density calculated from the above isotropic refinement showed that the assumption of isotropic thermal behaviour was invalid for N(1), N(2), C(3) and C(13). A modified version of the program *FORDAP* by A. Zalkin was used for the electron density calculations. Five peaks in the synthesis are readily attributable to five of the six crystallographically independent hydrogen atoms. Since the synthesis also contains some error peaks with heights about the same as those in plausible positions for hydrogen atoms, hydrogen atoms were introduced with coordinates fixed at these positions and were not treated as variables in the subsequent refinement. These atoms were assigned an invariant isotropic thermal parameter $B=3.0$. The sixth hydrogen atom, invisible in the difference map, was set 1 Å from its neighboring carbon atom. The introduction of these fixed hydrogen atoms into the isotropic model decreased R to 9.0%. At this point, anisotropic thermal coefficients were assigned to non-hydrogen atoms, and the refinement of this model converged at $R=7.8\%$. In order to determine whether or not the use of anisotropic thermal parameters was justified, the method of Hamilton (1965) was applied to the weighted R indices,

$$\left[\sum w(|F_o| - S|F_c|)^2 / \sum wF_o^2 \right]^{1/2}$$

on the assumption that their ratio is a sufficiently good approximation to the ratio of the generalized R indices in this instance. The use of anisotropy for the non-hydrogen atoms decreased the weighted R from 0.130 to 0.106, with the insertion of 38 new parameters, and with 229 degrees of freedom. From values in Hamilton's tables one can readily show that α is well below 0.005, so that the use of anisotropic thermal parameters seems quite justified. Final coordinates and temperature factors are listed in Table 1, and a list of observed and calculated structure factors is given in Table 2.

Discussion of the structure

The crystal is composed of discrete molecules, C_5H_5NO . Intramolecular bond distances and angles, calculated from the final coordinates for molecules I and II are shown in Table 3 and Fig. 1. The estimated standard deviations for bond distances and angles in molecule II are somewhat larger than those for molecule I primarily because the distribution of Miller indices in the intensity data favors precision in x over that in y . Bond distances and bond angles in molecules I and II are very similar and are close to corresponding values found in pyridine (Bak, Hansen-Nygaard & Rastrup-Andersen, 1958). Since the standard deviations for bond distances in molecules I and II are 0.015 and 0.020 Å respectively, the standard deviation of the

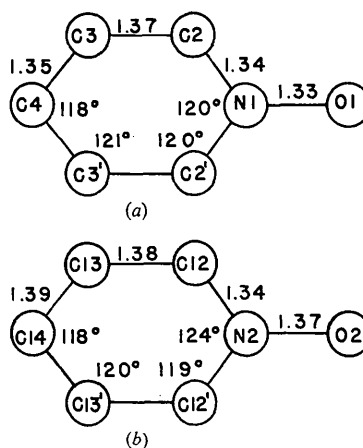


Fig. 1. Bond lengths (Å) and angles ($^{\circ}$) in pyridine 1-oxide. (a) Molecule I, (b) molecule II.

difference between corresponding bond lengths in the two molecules is 0.025 Å. The greatest of such differences is 0.04 Å, which is significant at the 10% level. Since bond lengths in the two molecules do not differ significantly, the weighted average of corresponding lengths should be used in describing pyridine 1-oxide. The average is given as $(\frac{2}{7})(L_I) + (\frac{3}{7})(L_{II})$ to reflect the difference in standard deviations of the two sets of lengths.

Table 3. Bond lengths* and angles† in pyridine 1-oxide

Molecule I			
N(1)—O(1)	1.33 Å	C(3)—C(4)—C(3')	118°
N(1)—C(2)	1.34	C(4)—C(3)—C(2)	121
C(2)—C(3)	1.37	C(3)—C(2)—N(1)	120
C(3)—C(4)	1.35	C(2)—N(1)—C(2')	120
		C(2)—N(1)—O(1)	120
Molecule II			
N(2)—O(2)	1.37 Å	C(13)—C(14)—C(13')	118°
N(2)—C(12)	1.34	C(14)—C(13)—C(12)	120
C(12)—C(13)	1.38	C(13)—C(12)—N(2)	119
C(13)—C(14)	1.39	C(12)—N(2)—C(12')	124
		C(12)—N(2)—O(2)	118

* E.s.d. is 0.015 Å for molecule I and 0.020 Å for II.

† E.s.d. is 0.9° for molecule I and 1.2° for II.

The carbon-carbon bond lengths are close to the average of values found in aromatic molecules. The carbon-nitrogen bond length is equal to 1.34 Å, the average for conjugated heterocyclic systems (Sutton, 1965). The N—O bond length (1.35 Å) in pyridine 1-oxide is somewhat shorter than the 1.388 Å for the N—O length in trimethylamine oxide (Caron, Palenik, Goldish & Donohue, 1964) but is significantly longer than the values 1.28 Å in 4,4'-*trans*-azopyridine *N*-oxide (Eichhorn, 1959), 1.26 Å in 4-nitropyridine *N*-oxide (Eichhorn, 1956), and 1.24 Å in phenazine 5-oxide (Curti, Riganti & Locchi, 1961). Horrocks, Templeton & Zalkin (1968) have estimated 10–20% π -bond character for the N—O bond in pyridine 1-oxide. Both

the N–O separation and the C(2)–C(3) separation suggest that quinoid resonance forms are not very important in pyridine 1-oxide. These bond lengths contrast markedly with the corresponding lengths in 4,4'-*trans*-azopyridine *N*-oxide and 4-nitropyridine *N*-oxide (Eichhorn, 1959, 1956). In the latter, the C(2)–C(3) distance is 0.04 Å less and the N–O distance 0.09 Å less than in pyridine 1-oxide. These features emphasize the increase in importance of the quinoid structure which accompanies substitution of the nitro group in the 4-position.

The N–O separation changes very little when pyridine 1-oxide becomes a ligand in complex compounds. The N–O distance of 1.33 Å is observed in bis-(2,4-pentanedionato)bis(pyridine 1-oxide)nickel(II) (Horrocks, Templeton & Zalkin, 1968), and in tetrakis(pyridine 1-oxide)copper(II) perchlorate and fluoroborate (Lee, Brown & Melsom, 1969). The values 1.35, 1.36, 1.36, 1.37 and 1.35 Å found respectively in di- μ -(pyridine 1-oxide)-bis[dichlorocopper(II)] (Sager, Williams & Watson, 1967), 2-picoline *N*-oxide complex compound $\text{Cu}_3\text{Cl}_6(\text{CH}_3\text{C}_5\text{H}_4\text{NO})_2 \cdot 2\text{H}_2\text{O}$ (Sager & Watson, 1968*b*), bis(pyridine 1-oxide)copper(II) nitrate (Šćavničar & Matković, 1969), dichlorodimethylbis(pyridine 1-oxide)tin(IV) (Blom, Penfold & Robinson, 1969), and dichlorobis-(2,6-lutidine *N*-oxide)zinc(II) (Sager & Watson, 1968*a*) are the same as, or very close to, the N–O distance in the free ligand. For these determinations, the standard deviation of the N–O bond length is about 0.02 Å, so that none of the values differs significantly from 1.35 Å. The very small magnitude of the change in N–O bond length on attachment of pyridine 1-oxide to metal supports the suggestion of Blom, Penfold & Robinson (1969) that the accompanying infrared frequency shifts may be due more to the orientation of the aromatic ring than to the electronic nature of the N–O bond. Mirone (1963), in

furnishing a complete vibrational assignment from spectral data, emphasized that, in the three A_1 vibrations at 1252, 837, and 544 cm^{-1} , the motions of nitrogen and oxygen are coupled with those of other atoms so that there is no 'true' N–O stretching frequency. Similarly, Katritzky & Ambler (1963) have pointed out that the band near 1250 cm^{-1} , found in all pyridine *N*-oxides, is extremely sensitive to the molecular environment. Mirone (1963) reports that varying the N–O distance from 1.33 to 1.47 Å made very little difference in the general features of the calculated spectrum, while Berezin (1965) reports good agreement between experimental frequencies and those calculated from a model with an N–O separation of 1.26 Å.

The bond angles in pyridine 1-oxide are very close to those observed in pyridine (Bak, Hansen-Nygaard & Rastrup-Andersen, 1958) and in the derivatives and coordination compounds mentioned above. Pyridine 1-oxide molecules are planar. The plane $0.2248Y - 0.9744Z = 0$, where Y and Z are coordinates in Å, contains the axis on which N(1), O(1) and C(4) lie; C(2) and C(3) are -0.001 and $+0.001$ Å respectively from this plane. The plane $0.6471X - 0.7624Z = 0.0427$ contains the axis on which N(2), O(2) and C(14) lie; the atoms C(12) and C(13) are $+0.009$ and -0.009 Å respectively from this plane. For both molecules these distances from the planes are less than the estimated standard deviations of the atom coordinates.

Pyridine 1-oxide has a dipole moment of 4.2 debyes (Sharpe & Walker, 1961), and the crystal is held together by a combination of van der Waals forces and dipole-dipole interactions. The crystal may be described as consisting of alternating layers of the crystallographically independent molecules stacked in the c direction. The shortest intermolecular carbon-carbon distance is 3.63 Å. The only intermolecular distances smaller than 3.5 Å are the carbon-oxygen separations listed in Table 4. These contacts determine the packing. Within a layer the molecules are packed so that four neighboring, crystallographically related molecules make contact with a given molecule through the C(3) and O(1) or C(13) and O(2) atoms. The layers above and below make contact with the reference layer through the C(2) and O(2) or C(12) and O(1) atoms. (Fig. 2). A given molecule makes these contacts with two molecules in each of the two neighboring layers, so that each molecule has $\text{C}\cdots\text{O}$ contacts with eight other molecules. Each oxygen atom O(1) is in contact with two C(3) and two C(12) atoms. Molecules in every other layer are related by twofold screw axes parallel to c . An alternative representation is that of columnar stacks of molecules related by a twofold screw axis normal to the symmetry axis of the molecule and passing essentially through the nitrogen atom. The packing of these stacks is determined by the above mentioned carbon-oxygen contacts. The screw axis produces an alternation of the dipole moment directions and minimizes the dipole-dipole interactions in a

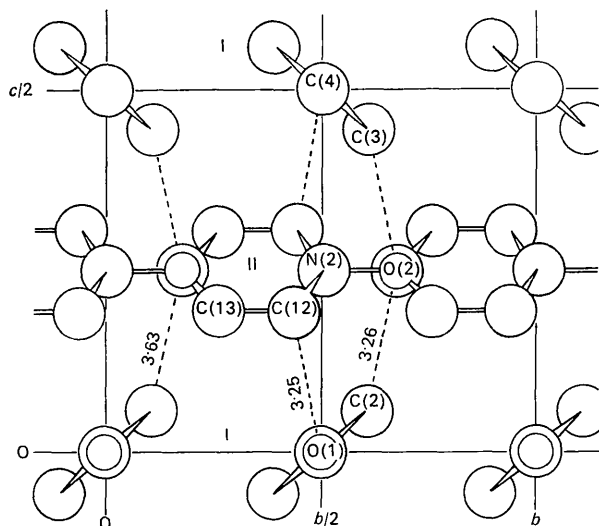


Fig. 2. Projection of the structure on a plane perpendicular to the a axis.

given stack. Trimethylamine *N*-oxide (Caron, Palenik, Goldish & Donohue, 1964), which has a dipole moment larger than that of pyridine 1-oxide, exhibits alternation of dipole orientation in directions parallel to each of the three crystallographic axes. The relative compactness of trimethylamine *N*-oxide permits molecules related by the twofold screw to be separated by only 4.5 Å, which is quite a bit smaller than *c*/2 (6.9 Å) for pyridine 1-oxide. The lowering of energy which is related to the compactness of the trimethylamine *N*-oxide structure is reflected in the melting point of 207°C as compared with 66°C for pyridine 1-oxide.

Table 4. Intermolecular distances less than 3.5 Å

O(1)···C(12)	3.25 Å
O(2)···C(2)	3.26
O(1)···C(3)	3.39
O(2)···C(13)	3.38

IBM 360/75 equipment available through the Computation Center of the University of North Carolina was used to make the calculations. The authors wish to acknowledge financial support for this work under Grant GP-6001 of the National Science Foundation and through the University of North Carolina Materials Research Center from Contract SD-100 with the Advanced Research Projects Agency.

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