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Structure of *N*-Methyl-2-pyridineselone

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Abstract. C_6H_7NSe, $M_r = 172\cdot1$, monoclinic, $P2_1/m$, $a = 7\cdot839\,(1)$, $b = 6\cdot697\,(1)$, $c = 6\cdot979\,(1)$ Å, $\beta = 113\cdot12\,(1)°$, $V = 337\cdot0$ Å^3, $Z = 2$, $D_m = 1\cdot70$, $D_x = 1\cdot696$ g cm^{-3}, $\lambda(\mathrm{Cu}\,K\alpha) = 1\cdot5418$ Å, $\mu = 68\cdot5$ cm^{-1}, $T = 294$ K, $F(000) = 168$; final $R = 0\cdot043$ for 493 reflections, $I \geq 3\sigma(I)$. The whole molecule lies on the mirror planes at $y = 0\cdot25$ and $0\cdot75$, except for two of the methyl H atoms which are on either sides of the mirror. The crystal structure is stabilized by strong stacking interactions of the pyridine ring stacked at a short distance of 3·02 Å.

Introduction. Seleno-substituted heterocyclic compounds are of interest for two basic reasons: (i) similar to the sulfur analogs, 6-selenoguanine, 2-selenouracil and 2-selenocytosine are useful antineoplastic agents (Mautner, Chu & Lee, 1962; Mautner, Chu, Jaffe & Sartorelli, 1963); (ii) the seleno analogs throw light on the chemical and physical properties of their oxygen and sulfur analogs (Cordes, 1974). 2-Pyridone, 2-pyridinethione and 2-pyridineselone and their *N*-methyl analogs have been synthesized as early as 1962 by Mautner and his co-workers (Mautner, Chu & Lee, 1962; Krachov, Lee & Mautner, 1965) who studied them as models of nucleic acid antagonists. These authors studied the ability of the unmethylated compounds to form hydrogen-bonded dimers by means of dielectric constant as a measure of possible DNA antagonist activity. They also studied the *N*-methyl analogs, which cannot form hydrogen bonds, to measure their changes in dipole moments and to relate the dipole-moment changes to the O, S, Se substitution sequence. They concluded that 2-pyridone, 2-pyridinethione and 2-pyridineselone existed in the lactam form rather than the lactim form. As expected the spectrum of 2-pyridineselone is very similar to that of *N*-methyl-2-pyridineselone. The increase in dipole moment from oxo to thio to seleno is presumed to be related to increasing contributions of the polarized forms: 2-pyridinethione and 2-pyridineselone and their *N*-methyl analogs are poorer bases and poorer hydrogen bonders than 2-pyridone. The crystal structure of *N*-methyl-2-pyridineselone has been undertaken to study its structure in the solid state as well as its hydrogen-bonding details.

Experimental. Samples of the title compound were kindly provided by Dr E. Shefter. Crystals were obtained by a slow evaporation from methanol/water and grown as thin needles; density measured by flotation (bromoform/benzene); unit-cell parameters on a CAD-4 diffractometer using reflections with $13 \leq \theta \leq 35°$; crystal, dimensions $0\cdot65 \times 0\cdot45 \times 0\cdot15$ mm, used for three-dimensional data (to the limit of $2\theta_{\max} = 154°$ for Cu $K\alpha$ radiation) by $\omega/2\theta$ scan; scan widths $(0\cdot95 + 0\cdot14\tan\theta)°$; aperture widths $(3\cdot00 + 1\cdot2\tan\theta)$ mm; maximum time spent on any reflection measurement 100s; faster scan used for strong reflections; intensities of three reflections monitored after every hour of exposure; variation in intensity < 6·7% during the complete data collection; orientation matrix checked every 100 reflections; 773 unique reflections measured, out of which 493 had $I \geq 3\sigma(I)$. Lorentz and polarization corrections were applied; the intensities of three reflections at $\chi\sim 90°$ were measured for different values of φ from 0 to 360° and the resultant curve of transmission as a function of φ was used to calculate the anisotropy of absorption for all the reflections; the maximum and minimum transmission factors were 0·99 and 0·67 with an average of 0·89. The distribution of E values was ambiguous and was between those characteristic of the centrosymmetric and non-centrosymmetric space groups. The structure was refined in both space groups, $P2_1$ and $P2_1/m$, before deciding the correct space group. The refinement in $P2_1$ was carried out before that in $P2_1/m$. The position of the Se was determined from a three-dimensional Patterson map and the remaining atoms recovered from a Se-phased Fourier synthesis. Refinement with individual anisotropic thermal parameters for the non-hydrogen atoms, isotropic thermal parameters for the H atoms, and extinction-parameter refinement led to $R = 0\cdot046$ for the 493 reflections; $wR = 0\cdot058$, $S = 1\cdot76$; the quantity minimized was $w[\,|F_o| - (1/k) \times |F_c|\,]^2$ where $w = 4|F_o|^2/\sigma^2(|F_o|^2)$ and $\sigma^2(|F_o|)^2 = [\sigma^2(I) + p^2I^2]/\mathrm{Lp}$; $\sigma(I)$ is the standard deviation in intensity I based upon counting statistics, k is the scale factor and p (= 0·05) is a fudge factor to downweight intense reflections. On inspection of the final refined coordinates of the non-hydrogen atoms, we found that the y coordinates of all the non-hydrogen atoms are

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close to 0·25, which indicated that the correct space group might be $P2_1/m$. Refinement in space group $P2_1/m$ was carried out next. The final R value for 493 reflections was 0·043, $wR = 0·054$, $S = 1·92$.* The maximum and average shift/e.s.d. = 0·2, 0·01; final $|\Delta\rho|_{\max} = 0·3$ e Å^{-3}. Programs and atomic scattering factors from Enraf–Nonius (1979); Fourier and torsion-angle programs by Dr S. T. Rao and *ORTEP* by Johnson (1965).

The correct space group was deduced as $P2_1/m$ for the following reasons. The y coordinates of all the non-hydrogen atoms are close to 0·25 in $P2_1$, which indicated that the correct space group is $P2_1/m$. The hydrogens H1 and H3 of the methyl group are displaced on either sides of the mirror plane. In $P2_1/m$ all the non-hydrogen atoms as well as the H atoms of the pyridine ring lie on the mirror plane at 0·25. As far as the methyl H atoms are concerned, one of them was on the mirror plane and the other two H atoms were on either side of the mirror plane. The pyridine ring was non-planar in space group $P2_1$. The least-squares plane through the atoms N(1), C(2), C(3) and C(6) is given by $0·0003X+0·9998Y-0·01Z = 1·58$ with C(4) and C(6) deviating from this best plane by 0·095 and −0·106 Å respectively. In $P2_1/m$ the molecular geometry of the pyridine ring is planar since all the non-hydrogen atoms are on $y = 0·25$. The final R value for 493 reflections was 0·043 in $P2_1/m$ as against 0·046 in $P2_1$. The estimated standard deviation of an observation of unit weight is 1·92 in $P2_1/m$ as against 1·76 in $P2_1$. From Hamilton's (1965) test and the R values in $P2_1$ and $P2_1/m$ given above, space group $P2_1$ can be rejected at the 0·005 significance level. Hence the correct space group is taken as $P2_1/m$.

Table 1. *Final positional parameters, equivalent isotropic thermal parameters for the non-hydrogen atoms and isotropic thermal parameters for* H *atoms with e.s.d.'s in parentheses*

$$B_{eq} = \tfrac{4}{3}\sum_i \sum_j (\beta_{ij}\mathbf{a}_i\mathbf{a}_j).$$

	x	y	z	B_{eq}/B(Å^2)
Se	0·69384 (8)	0·2500	0·7972 (1)	5·22 (2)
N(1)	0·8354 (6)	0·2500	0·4837 (7)	3·2 (1)
C(2)	0·8767 (7)	0·2500	0·6952 (9)	3·4 (1)
C(3)	1·0665 (8)	0·2500	0·825 (1)	4·4 (2)
C(4)	1·1989 (8)	0·2500	0·743 (1)	5·0 (2)
C(5)	1·1512 (8)	0·2500	0·533 (1)	4·6 (2)
C(6)	0·9701 (8)	0·2500	0·4070 (9)	3·7 (1)
C(7)	0·6407 (8)	0·2500	0·337 (1)	4·7 (2)
HC(3)	1·091 (7)	0·2500	0·972 (9)	4 (2)*
HC(4)	1·33 (1)	0·2500	0·81 (2)	11 (3)*
HC(5)	1·244 (9)	0·2500	0·48 (1)	6 (2)*
HC(6)	0·928 (7)	0·2500	0·268 (8)	3 (1)*
H1C(7)	0·640 (6)	0·301 (8)	0·210 (8)	1 (1)*
H2C(7)	0·576 (8)	0·10 (1)	0·35 (1)	2 (1)*
H3C(7)	0·57 (1)	0·2500	0·37 (2)	13 (3)*

* Atoms refined isotropically.

Discussion. The final positional parameters for all the atoms in the structure are given in Table 1. Bond distances and angles are given in Fig. 1 for bonds not involving H atoms. As can be seen from Table 1 all atoms in the structure lie on $y = 0·25$ or 0·75 except H1C(7) and H2C(7). These two H atoms lie on either side of the mirror.

The C=Se bond distance is 1·834 (5) Å. A stereoview of the packing of the molecules in the crystal structure down the a axis is shown in Fig. 2, which shows an edge view of the stacked planar pyridine rings at a distance of 3·02 Å. The crystal structure is

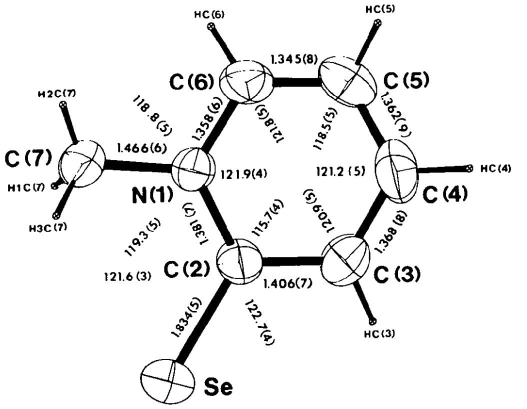

Fig. 1. Bond distances (Å) and bond angles (°) in the title compound. The average e.s.d. in a bond length involving non-hydrogen atoms is 0·009 Å and with H atoms is 0·06 Å; e.s.d. in a bond angle is 0·6°. H thermal parameters were fixed at an arbitrarily small value for the purpose of the drawing only.

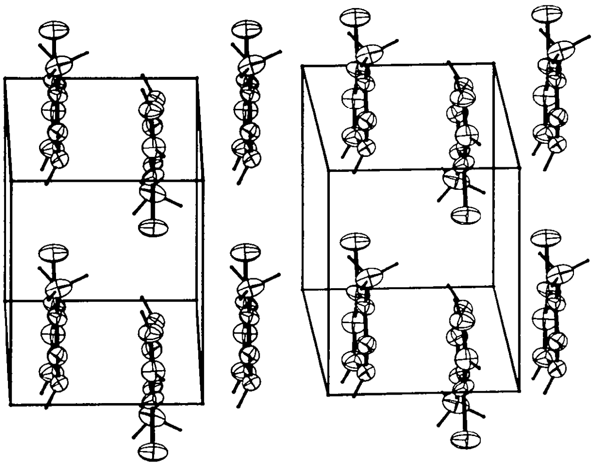

Fig. 2. Stereoview of the packing of the molecules in the unit cell down the a axis showing the stacking of the molecules in the unit cell.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44314 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

stabilized in addition by van der Waals and non-bonded interactions.

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Structure of (3-Isopropyl-1-methyl-4-pyrazolyl)diphenylphosphine Oxide

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Abstract. $C_{19}H_{21}N_2OP$, $M_r = 324\cdot36$, monoclinic, $P2_1/n$, $a = 10\cdot936\,(2)$, $b = 9\cdot431\,(2)$, $c = 17\cdot708\,(3)$ Å, $\beta = 107\cdot62\,(2)°$, $V = 1740\cdot7\,(1\cdot2)$ Å^3, $Z = 4$, $D_x = 1\cdot237$ Mg m^{-3}, $\lambda(\text{Mo}\ K\alpha) = 0\cdot7107$ Å, $\mu(\text{Mo}\ K\alpha) = 0\cdot124$ mm^{-1}, $F(000) = 688$, $T = 296$ K, final $R_F = 0\cdot036$ for 1757 observed independent reflections. The coordination around P is distorted tetrahedral with the P—C bond to the pyrazole ring [1·777 (2) Å] slightly shorter than to the phenyl rings [1·804 (3) and 1·807 (3) Å]. The pyrazole and phenyl rings are planar within 0·03 Å.

Introduction. The method of preparation of the compound has been described by Ben Akacha, Baccar & Ayed (1983). The formula and the conformation of the molecule were established by elemental analysis,* mass spectrometry and ^{1}H, ^{31}P and ^{13}C NMR.

As pyrazole derivatives are used in therapy and the phosphine oxide pyrazoles have interesting properties (Ben Akacha, 1987), we decided to carry out an X-ray structure analysis in order to determine the precise conformation of the molecule and the coordination and the geometry of the ligands around the phosphorus ion.

Experimental. A transparent crystal with irregular shape *ca* 0·13 × 0·33 × 0·36 mm was selected. Precession photographs indicated monoclinic symmetry (Boutiba, 1984). The cell constants were refined from setting angles of 25 reflections. 2747 integrated independent intensities were measured on a CAD-4 diffractometer with graphite-monochromated Mo $K\alpha$ radiation. The range of hkl was $h\,0\rightarrow12$, $k\,0\rightarrow10$, $l\,-19\rightarrow19$ up to $2\theta = 46°$, corresponding to $(\sin\theta)/\lambda = 0\cdot59$ Å^{-1}. $\omega/2\theta$ scan was used. The standard reflections measured every 2·5 h remained stable. The merging of measured reflections gave 1757 with $I > 2\cdot5\sigma(I)$, which were used in the structure analysis. The intensities were corrected for Lorentz–polarization and absorption (empirical by ψ scan). The relative transmission was in the range 0·94–1·0. The structure was solved by *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980) and refinement on F was by *SHELX*76 (Sheldrick, 1976). All H atoms were located in the difference Fourier map and then refined with the same overall isotropic thermal parameter. The maximum and minimum heights in the final difference Fourier synthesis were 0·27 and −0·25 e Å^{-3}. The weighting scheme used was $w(F) = 1/[\sigma^2(F) + 0\cdot00146F^2]$ where $\sigma(F)$ was the estimated standard deviation on F. In the last cycle of refinement

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