of a triangle of Cl atoms from three separate anions, N–H=0·9, H···Cl=2·9 Å; the latter distance seems too long for significant hydrogen-bond interaction.

The studies were undertaken as a result of interest in the phase transition ($\Delta S = R\ln 2$) at 262K for the K salt (Morfee, Staveley, Walters & Wigley, 1960). The structure adopted by A_2BX_6 compounds of this type appears to depend on the ratio of the size of the A cation to the hole available for it in the BX_6 lattice (Brown, 1964); thus a small A cation results in distortion from cubic to tetragonal or lower symmetry. Ratios greater than 0·98 result in cubic structures at any temperature [for $(NH_4)_2SnCl_6$ the ratio is 0·99], ratios less than 0·89 give structures of lower symmetry at room temperature, while ratios in the range 0·89 to 0·98 yield structures which are cubic at room temperature but transform to lower symmetry at lower temperatures (for K_2SnCl_6 the ratio is 0·92).

The thermal parameters of the Cl atom for both the K and NH_4 salts are larger normal to the Sn–Cl bonds (Table 1) but not excessive, so that the structures appear to be truly cubic at room temperature with libration of the $SnCl_6^{2-}$ ions, rather than a superposition of lower-symmetry structures. On cooling in a stream of nitrogen gas, crystals of the NH_4 compound remained cubic, but the K salt underwent a phase change at about 260K. A Weissenberg film exhibited splitting of spots and the appearance of a 035 reflexion (cubic indices), which suggested lower symmetry. Since the low-temperature specimen was no longer a single crystal, determination of the exact symmetry was difficult, but the structure could possibly be like that of tetragonal room-temperature K_2SnBr_6 (*Strukturbericht*, **6**, 121) (Fig. 2), which is cubic above 400K (*Struct. Rep.* **27**, 462), the cation/hole ratio being 0·86.

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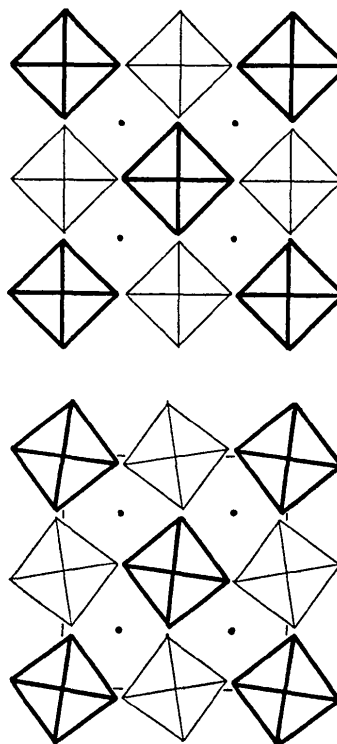

Fig. 2. Structure of room-temperature K_2SnCl_6 (top) and K_2SnBr_6 (bottom).

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N-Vinyl-2-thiopyrrolidone

By Alajos Kálmán and Gyula Argay

Central Research Institute for Chemistry, Hungarian Academy of Sciences, H-1525-Budapest, P.O.B. 17, Hungary

and Ferenc Cser

*Research Institute for Plastics Industry, Hungária krt. 114, H-1950-Budapest XIV, Hungary*

Abstract. C_6H_9NS, monoclinic, $C2/m$ (from refinement); $a=12\cdot316$ (3), $b=6\cdot909$ (2), $c=7\cdot930$ (2) Å, $\beta=98\cdot14$ (2)°; $Z=4$; $V=668\cdot0$ Å^3; $D_c=1\cdot264$ g cm^{-3}; μ(Mo $K\bar{\alpha}$, $\lambda=0\cdot7107$ Å)$=3\cdot27$ cm^{-1}. The structure of NVTP was solved by heavy-atom and Fourier techniques. An R of 0·056 was obtained for 781 observed

reflexions after least-squares refinement. The coplanar molecules lie on mirror planes. The shortest intermolecular vinyl C(5)···C(5') distance is 3·86 Å.

Introduction. NVTP was prepared and provided by Dr M. A. Morsi. The reaction of N-vinyl-2-pyrrolidone with P_2S_5 in a mixture of xylene and pyridine (Shostakowskii, Sidelkowskaya, Avetisyan, Zelenskaya & Lopatin, 1963) furnished NVTP with a yield of 20%. The crude product had to be recrystallized several times from petroleum spirit in order to free NVTP from by-products. At the beginning of this procedure a by-product, separated from NVTP in crystalline form, was thought by Morsi to be NVTP. Its structure analysis (Cser, Argay & Kálmán, 1976) based on low-quality Weissenberg data, however, revealed two saturated monomers to be linked by a S atom.
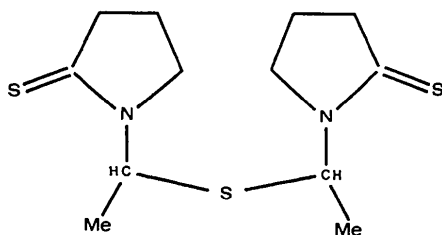
The purified NVTP, m.p. 68·5°C [m.p. of the product of Shostakowskii et al. (1963) was 60–61°C] was then dissolved in heptane. From this solution well-developed crystals suitable for X-ray analysis were obtained by evaporation.

Intensities of 781 independent reflexions were collected on a Syntex $P2_1$ computer-controlled four-circle diffractometer with Mo $K\bar{\alpha}$ radiation from a graphite monochromator. All 781 measured reflexions were treated as observed. The sharpened Patterson map revealed the image of the molecule in the plane $(u,0,w)$ and the absence of Harker vectors $(0,v,0)$. This fact together with $Z=4$ excluded space group Cm. A structure factor calculation in space group $C2$ based on the coordinates of S and C(1) and a subsequent Fourier synthesis gave the missing six non-hydrogen atoms $(R=0\cdot31)$. Full-matrix least-squares refinement of the eight atomic positions and isotropic thermal parameters in $C2$ failed, however, to decrease R. Therefore it was decided to change to $C2/m$. Prior
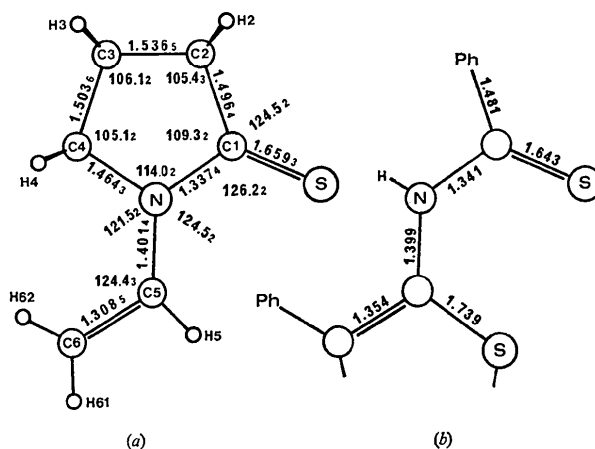

Fig. 1. (a) Bond distances and angles with their e.s.d.'s for the non-hydrogen atoms and the atomic numbering for the title compound. (b) Bond distances for the thiobenzamide group measured in N-(3-phenyl-2-benzo[b]thienyl)thiobenzamide (Argay & Kálmán, 1973).

to the refinement in $C2/m$ the positions of the H atoms (except those belonging to the terminal CH_2 group) were generated assuming regular tetrahedra for C(2), C(3) and C(4), and sp^2 hybridization for C(5) with C–H distances constrained to 1·08 Å. These moieties were treated throughout the refinement as rigid groups. The terminal H atoms, also lying on the mirror plane, were located in a difference map. Further refinement reduced R to 0·059 $[R_G=(\sum w\Delta^2/\sum w|F_o|^2)^{1/2}=0\cdot074]$. The weights were $w=k/[\sigma^2(F_o)+gF_o^2]$ where k and g refined to 0·685 and 0·00294 respectively. A bonded H atom scattering factor was employed (Stewart, Davidson & Simpson, 1965) with complex neutral-atom scattering factors for the remaining atoms (Cromer & Mann, 1968; Cromer & Liberman, 1970). All calculations were performed with SHELX (Sheldrick, 1976) adapted for a CDC 3300 computer. The final coordinates and thermal parameters for the non-hydrogen atoms are given in Table 1, the parameters for the H atoms in Table 2, the bond distances and angles in Fig. 1(a).*

Table 1. *Fractional coordinates* $(y/b=0)$ *and anisotropic thermal* $(U_{12}=U_{23}=0)$ *parameters* $(\times 10^4)$

Estimated standard deviations are given in parentheses. The anisotropic thermal parameters are given in the form $\exp[-2\pi^2 \sum_i \sum_j a_i^* a_j^* h_i h_j U_{ij}]$, with U_{ij} in Å².

	x	z	U_{11}	U_{22}	U_{33}	U_{13}
S	1047 (1)	2932 (1)	434 (5)	1222 (9)	738 (6)	178 (3)
N	2604 (2)	897 (3)	389 (10)	590 (13)	630 (13)	111 (9)
C(1)	2317 (2)	2461 (4)	420 (12)	633 (16)	624 (15)	101 (11)
C(2)	3329 (3)	3751 (4)	483 (15)	919 (23)	716 (19)	27 (13)
C(3)	4292 (3)	2715 (6)	384 (14)	1037 (27)	1048 (27)	13 (16)
C(4)	3790 (2)	873 (5)	398 (13)	684 (18)	891 (20)	203 (13)
C(5)	1860 (2)	−613 (4)	552 (15)	554 (15)	624 (15)	98 (12)
C(6)	2143 (4)	−2142 (5)	852 (24)	826 (23)	667 (18)	157 (17)

Table 2. *Fractional coordinates* ($\times 10^3$) *for the hydrogen atoms with a common isotropic thermal parameter of* $\bar{u} = 0.098$ (4) Å^2

Estimated standard deviations are given in parentheses.

	x	y	z
H(2)	336 (2)	−134 (2)	446 (3)
H(3)	470 (2)	137 (2)	301 (4)
H(4)	396 (3)	−127 (3)	16 (3)
H(5)	102 (1)	0	−38 (6)
H(61)	148 (2)	0	−320 (3)
H(62)	302 (1)	0	−209 (6)

Discussion. In order to explain the kinetics of the polymerization of NVTP in the solid state and the results of elemental analysis, Morsi (1971) assumed that free S atoms were dispersed in the crystal. He came to the conclusion that the vinyl groups should be at favourable distances to react with each other in accordance with the topochemical conditions of solid-state reactions (Cohen & Schmidt, 1961; Hirschfeld & Schmidt, 1964). The structure determination of the by-product $(C_6H_{10}NS)_2S$ (Cser, Argay & Kálmán, 1976) seems to throw light upon the assumption of Morsi concerning the surplus of S atoms in the not fully purified NVTP products. The present work aimed to study not only the topochemical conditions in NVTP crystals by determining the molecular packing, but also to give an accurate geometry of the molecule for further physico-chemical investigations (*e.g.* quantum chemical studies).

The conformation analysis with the force-field method shows that the geometry of NVTP with minimal strain energy is not planar. Therefore the coplanar molecules lying on mirror planes are somewhat strained, which seems to be shown by the short C(3)–C(4) distance of 1·503 (6) relative to the normal C(2)–C(3) sp^3-sp^3 length of 1·536 (5) Å. The other bond distances, however, resemble the corresponding values observed in similar systems, *e.g.* the substituted thiobenzamide group [Fig. 1(*b*)] in *N*-(3-phenyl-2-benzo-[*b*]thienyl)thiobenzamide (Argay & Kálmán, 1973). The length of the $S^{II}-C(sp^2)$ bond indicates a strong, almost localized double bond (Argay, Kálmán, Nahlovski & Ribár, 1975, and references therein).

The coplanar molecules with coordination number 6 (Fig. 2) are close-packed in layers [010]. These layers are separated by 3·45 Å (*b*/2) which fits the requirements of close-packing. Thus the total coordination number is 12. The shortest intermolecular distance within a layer is C(4)···C(4')[1 − *x*, 0, $\bar{z}$] = 3·46 Å. The mean shortest interatomic distance for the overlapping molecular fragments, *i.e.* the C(1)[C(4)]–N–C(5)–C(6) and C(1')[C(4')]–N'–C(5')–C(6') at [$\frac{1}{2}$ − *x*, ±$\frac{1}{2}$,$\bar{z}$], is 3·54 Å. The C(5) and C(5') atoms are at 3·86 Å, which indicates a favourable topochemical condition for polymerization in the solid in accordance with the conclusion of Morsi (1971).

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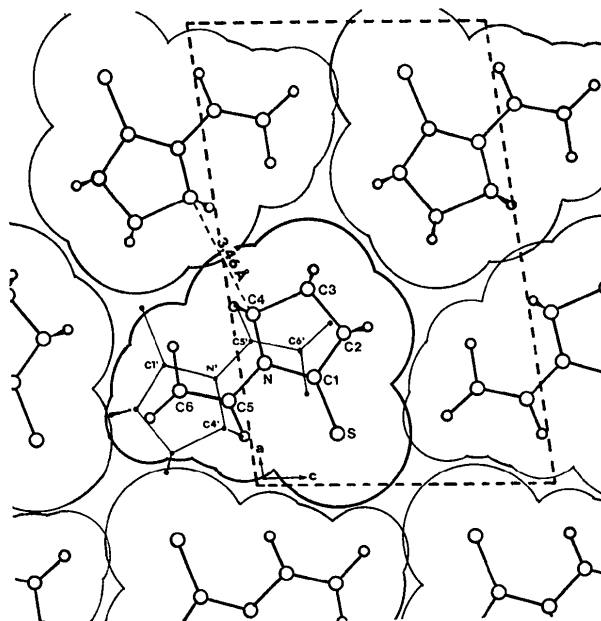

Fig. 2. The close-packing of the molecules in the plane ($x, 0, z$) indicating the van der Waals envelopes surrounding the molecules [van der Waals radii applied: $R_C = 1.85$, $R_H = 1.20$ Å (Cser, 1974), $R_S = 1.91$, $R_N = 1.54$ Å (Allinger, Hirsch, Miller & Tyminski, 1969)]. A molecule lying in the layer (x, ±$\frac{1}{2}$,z) is drawn with thin lines.

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