

puckering coordinates are  $Q = 0.446(3) \text{ \AA}$ ,  $\varphi_2 = 351(2)^\circ$  for the sequence O(5), C(1), O(1), C(6), C(5) and  $Q = 0.445(4) \text{ \AA}$ ,  $\varphi_2 = 350(2)^\circ$  for the sequence O(5'), C(1'), O(1'), C(6'), C(5'). The newly formed six-membered heterocycle has an envelope conformation with C(3) displaced  $0.781(2) \text{ \AA}$  from the mean plane through the remaining five atoms.

The central part of the molecule [formed by the atoms N(4), C(2'), C(3'), C(4'), C(1'), C(4), C(2) and C(5')] is planar to within  $\pm 0.016(3) \text{ \AA}$  with the exception of C(5') which is  $0.027(3) \text{ \AA}$  out of the least-squares plane of this eight-atom fragment. The twist angle about the central C(2')—C(3') bond as measured by the angle between the planes [N(4), C(2'), C(1')] and [C(2), C(3'), C(4')] is only  $1.1(2)^\circ$ . On the other hand, the pattern of bond lengths within the alkylideneimine grouping,  $-\text{N}=\text{C}=\text{C}-$ , is entirely consistent with integer bond orders: the N(4)—C(2') and C(3')—C(4') bond distances of  $1.288(3)$  and  $1.330(3) \text{ \AA}$  are in good agreement with the values reported for pure  $\text{C}=\text{N}$  (Schenetti, Taddei, Greci, Marchetti, Milani, Andreotti, Bocelli & Sgarabotto, 1980) and  $\text{C}=\text{C}$  (Bartell, Roth, Hollowell, Kuchitsu & Young, 1965) double bonds, and the C(2')—C(3') bond has a length [ $1.496(3) \text{ \AA}$ ] which is slightly larger than the value of  $1.487(5) \text{ \AA}$  normally accepted for a  $\text{C}(sp^2)\text{—C}(sp^2)$  single bond (Shmueli, Shanan-Atidi, Horwitz & Shvo, 1973). The latter bond length compares quite well with the central bond length in 2,2'-bipyrimidine [ $1.497(4) \text{ \AA}$ ; Fernholt, Rømming & Samdal, 1981] where conjugation is hindered by repulsion. There is, therefore, no evidence for any  $\pi$ -electron delocalization between N(4)=C(2') and C(3')=C(4'). Thus it may be concluded that the planarity of the central portion of the molecule results from rigidity of the polycyclic skeleton rather than from conjugation within the  $\alpha,\beta$ -unsaturated imine function.

The crystal structure of the compound is shown in Fig. 2. Molecules are linked by hydrogen bonds,  $\text{O}(2)\text{—H}\cdots\text{N}(4)(\frac{1}{2}-x, -y, -\frac{1}{2}+z)$  [ $\text{O}\cdots\text{N} = 2.802(3)$ ,  $\text{O—H} = 0.78(3)$ ,  $\text{H}\cdots\text{N} = 2.03(3) \text{ \AA}$ ,  $\text{O—H}\cdots\text{N} = 176(3)^\circ$ ], to form infinite chains running along  $2_1$  screw axes [ $(\frac{1}{4}, 0, z)$  and  $(\frac{3}{4}, \frac{1}{2}, z)$ ]. The chains are packed by van der Waals forces only.

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## Structure of Phenacyl Pentamethylenedithiocarbamate

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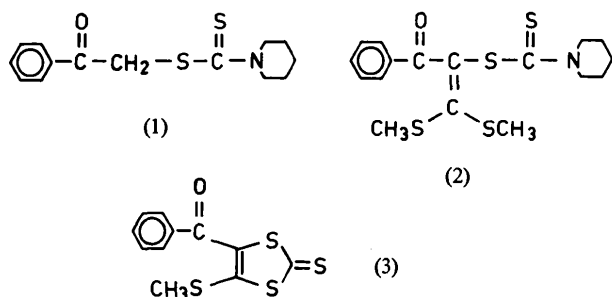
**Abstract.**  $\text{C}_{14}\text{H}_{17}\text{NOS}_2$ ,  $M_r = 279.4$ , monoclinic,  $P2_1/n$ ,  $a = 15.186(2)$ ,  $b = 9.510(2)$ ,  $c = 9.765(2) \text{ \AA}$ ,  $\beta = 95.71(2)^\circ$ ,  $V = 1403.3(5) \text{ \AA}^3$ ,  $Z = 4$ ,  $D_x = 1.32$ ,  $D_m = 1.33 \text{ Mg m}^{-3}$ ,  $\lambda(\text{Mo K}\alpha) = 0.71069 \text{ \AA}$ ,  $\mu =$

$0.32 \text{ mm}^{-1}$ ,  $F(000) = 592$ ,  $T = 293 \text{ K}$ , final  $R = 0.043$  for 1150 observed reflections. The molecule of the title substance (1) has normal bond lengths and angles. The nearly planar phenacyl group is approximately perpendicular to the dithiocarbamate group. The conformation of (1) is discussed with regard to

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its role as a synthon in organosulfur chemistry. The molecules are linked in the crystal by van der Waals forces only.

**Introduction.** Recently we have been able to show that the product obtained by the dithiocarboxylation of phenacyl pentamethylenedithiocarbamate (1) depends on the reaction conditions (Dölling, Khoudary, Augustin, Baumeister & Hartung, 1988). Reaction of (1) with carbon disulfide followed by methylation gives, under phase-transfer conditions, 1-benzoyl-2-bis(methylthio)vinyl pentamethylenedithiocarbamate (2) but in the presence of a strong base (e.g. sodium hydride) heterocyclization takes place and a substituted 1,3-dithiole-2-thione (3) is formed.



The stability of (2) against cyclization subsequent to its formation can be explained by its molecular geometry determined by X-ray analysis (Dölling *et al.*, 1988). The unexpected molecular conformation of (2), unfavorable for cyclization, is stabilized by an attractive dipole-dipole interaction between the carbonyl and the thiocarbonyl group of the compound. The crystal structure of (1) presented in this paper has been investigated in order to obtain a better insight into the mechanism of dithiocarboxylation. Especially, we were interested in a conformational comparison between (1) and (2).

**Experimental.** The title compound was prepared by adaption of the method described by Campaigne & Jacobsen (1964). Colorless clear crystals (m.p. 398–399 K) by recrystallization from methanol, density measured by flotation in aqueous KI solution. Dimensions of crystal for data collection 0.25 × 0.28 × 0.42 mm, Syntex P2<sub>1</sub> diffractometer, graphite-monochromatized Mo K $\alpha$  radiation. Lattice parameters by least-squares refinement from the setting angles of 15 reflections 12.2 >  $\theta$  > 2.7°; intensity data measurement:  $\theta/2\theta$  scan, bisecting mode,  $2\theta_{\max} = 48^\circ$ ,  $hkl$  ranges 17/17, 0/10 and 0/11, largest intensity fluctuations 2.5% (022) and 5.5% (022), corrections for Lorentz and polarization effects, no absorption correction. 2115 unique reflections, 1150 (= 54.4%) with  $I \geq 1.96\sigma(I)$  considered observed. Struc-

ture solved by Patterson and Fourier methods, all H atoms located in a difference map, full-matrix least-squares refinement on  $F$  with anisotropic thermal parameters for non-H atoms, H atoms refined isotropically, unit weights, empirical secondary-extinction correction  $F_{\text{corr}} = F_c(1 - 10^{-7}\chi F_c^2/\sin\theta)$  where  $\chi$  refined to 5.6 (2), 5.0 reflections/parameter in the final cycle,  $(\Delta/\sigma)_{\max} = 0.53$ ,  $-0.21 \leq \Delta\rho \leq 0.20 \text{ e \AA}^{-3}$  in final difference map, final  $R = 0.043$ . All calculations carried out using an ESER 1040 computer and programs SHELX76 (Sheldrick, 1976), SHELXS86 (Sheldrick, 1986), PRARA (Jaskólski, 1980) and EDIT (Jaskólski, 1982). Atomic scattering factors from the SHELX system.

**Discussion.** Final atomic parameters are listed in Table 1.\* The essential structural features of the phenacyl pentamethylenedithiocarbamate molecule are given in Fig. 1 and Table 2. The observed bond lengths and angles in (1) are in good agreement with corresponding values given in the literature in general and with those in (2) in particular. Therefore their discussion can be limited to a few aspects. Just as in (2), the C(2)—N distance of 1.336 (6) Å is markedly shorter than the normal C—N single bond [1.47 Å (Testa, 1983)]. This indicates strong participation of the N lone pair in the  $\pi$  system of the thiocarbonyl group and a substantial contribution from the zwitterionic resonance form (piperidinium structure) to the overall structure. The C(2)—S(1) distance of 1.653 (4) Å is within the rather wide range of values given in the literature for the standard C=S bond length [e.g. 1.63 Å (Rademacher, 1987); 1.70 Å (Testa, 1983)].

In contrast to the general agreement with regard to the bond lengths and angles the conformation of (1) differs considerably from that observed in (2). The essential conformational features are characterized by the torsion angles given in Table 2. The benzene ring and acyl group in (1) are closely coplanar (the interplanar angle is 2.9°) whereas they are markedly twisted by 17.7° in (2). The exact planarity of the dithiocarbamate group is common to both compounds but a striking difference is exhibited in the values for the torsion angle S(2)—C(1)—C(3)—O: 5.2 (4)° in (1) and 43.0 (3)° in (2). As a surprising result an intramolecular S(1)⋯C(3) contact distance of 3.090 (3) Å was found in (2), considerably shorter than the normal S⋯C van der Waals contact [3.50 Å (Bondi, 1964)]. It indicates an intramolecular interaction (dipole-dipole force) and

\* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51984 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Positional parameters and equivalent isotropic temperature factors ( $\text{\AA}^2$ ) of non-H atoms with *e.s.d.*'s in parentheses

	$x$	$y$	$z$	$U_{eq}$
S(1)	0.1453 (1)	0.1252 (1)	0.2470 (1)	0.0636 (5)
S(2)	0.1192 (1)	0.3088 (1)	-0.0063 (1)	0.0594 (5)
C(1)	0.1255 (3)	0.4305 (5)	0.1347 (4)	0.059 (2)
C(2)	0.1249 (2)	0.1423 (5)	0.0784 (4)	0.047 (2)
C(3)	0.0382 (3)	0.4602 (5)	0.1921 (4)	0.047 (2)
C(4)	0.0966 (3)	0.0476 (5)	-0.1620 (4)	0.057 (2)
C(5)	0.1782 (3)	-0.0013 (5)	-0.2250 (4)	0.058 (2)
C(6)	0.2011 (3)	-0.1513 (5)	-0.1824 (5)	0.059 (2)
C(7)	0.2079 (3)	-0.1665 (4)	-0.0275 (5)	0.060 (2)
C(8)	0.1260 (3)	-0.1129 (5)	0.0318 (4)	0.055 (2)
C(9)	0.0382 (3)	0.5716 (4)	0.2982 (4)	0.040 (2)
C(10)	-0.0400 (3)	0.5992 (5)	0.3567 (4)	0.050 (2)
C(11)	-0.0445 (3)	0.7025 (5)	0.4542 (4)	0.056 (2)
C(12)	0.0300 (3)	0.7813 (5)	0.4947 (5)	0.064 (2)
C(13)	0.1079 (3)	0.7547 (5)	0.4407 (5)	0.066 (2)
C(14)	0.1125 (3)	0.6507 (5)	0.3426 (4)	0.052 (2)
N	0.1117 (2)	0.0354 (4)	-0.0100 (4)	0.049 (2)
O	-0.0284 (2)	0.3972 (3)	0.1507 (3)	0.066 (1)

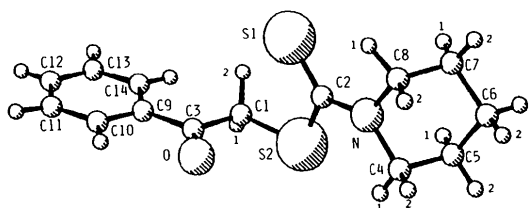


Fig. 1. Molecular structure of (1) with the atomic numbering scheme.

should be one of the factors stabilizing the unusual molecular conformation of (2). In (1) the observed  $S(1)\cdots C(3)$  contact distance of 3.593 (5)  $\text{\AA}$  is quite normal and excludes such a special intramolecular interaction. The different  $S(1)\cdots C(3)$  distances are correlated with the different values for the torsion angle  $C(2)-S(2)-C(1)-C(3)$ :  $-83.8 (3)^\circ$  in (1) and  $59.3 (2)^\circ$  in (2). Also the value for the torsion angle  $S(2)-C(1)-C(3)-C(9)$  in (1) [ $-173.5 (4)^\circ$ ] deviates considerably from that in (2) [ $-138.5 (3)^\circ$ ] but because of a compensation of the described differences in the values of the individual torsion angles, the orientation of the phenacyl and the dithiocarbamate fragment to each other is nearly the same in both compounds, namely approximately perpendicular.

The only difference between (1) and (2) with respect to their chemical composition consists in the substitution of two H atoms by the bis(methylthio)methylene group. Therefore, the described differences between their conformations must be attributed to this substituent. It increases the polarity of the  $C=O$  bond and causes the observed conformational changes. As discussed above the conformation of (2) stabilizes this compound against cyclization to (3). In contrast to that, the conformation of (1) allows its cyclization to (3) to occur by reaction with carbon disulfide.

Table 2. Selected bond lengths ( $\text{\AA}$ ), angles ( $^\circ$ ) and torsion angles ( $^\circ$ )

S(1)—C(2)	1.653 (4)	C(2)—N	1.336 (6)
S(2)—C(1)	1.795 (5)	C(3)—C(9)	1.481 (6)
S(2)—C(2)	1.784 (5)	C(3)—O	1.211 (5)
C(1)—C(3)	1.517 (6)		
C(1)—S(2)—C(2)	102.7 (2)	C(1)—C(3)—O	121.1 (3)
S(2)—C(1)—C(3)	114.9 (3)	C(1)—C(3)—C(9)	116.9 (3)
S(1)—C(2)—S(2)	123.0 (2)	C(9)—C(3)—O	122.0 (3)
S(1)—C(2)—N	124.7 (3)		
N—C(2)—S(2)—C(1)	173.3 (3)	S(2)—C(1)—C(3)—C(9)	-173.5 (4)
S(1)—C(2)—S(2)—C(1)	-7.2 (2)	C(1)—C(3)—C(9)—C(10)	-178.1 (4)
C(2)—S(2)—C(1)—C(3)	-83.8 (3)	O—C(3)—C(9)—C(10)	3.3 (5)
S(2)—C(1)—C(3)—O	5.2 (4)		

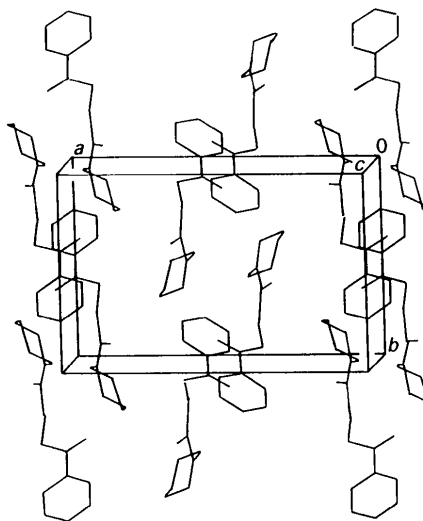


Fig. 2. Crystal structure of (1).

The crystal structure of (1) (Fig. 2) consists of discrete molecules with all intermolecular contacts between non-H atoms greater than the sums of the corresponding van der Waals radii.

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