

Fig. 2. Comparison of the structures of (a) BaZnF_4 and (b) $\text{Sr}_2\text{Nb}_2\text{O}_7$. Perovskite-type slabs are idealized. The slabs drawn in thick lines are shifted with respect to the others by $a/2$.

$n=6$. The thicknesses of the slabs are $n/2$ times the face-diagonal of the simple perovskite cube in these crystals. $\text{Sr}_2\text{Nb}_2\text{O}_7$ belongs to the family with $n=4$.

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References

- ANDERSSON, S. & GALY, J. (1969). *Acta Cryst.* B25, 847–850.
 BRANDON, J. K. & MEGAW, H. D. (1970). *Phil. Mag.* 21, 189–194.
 COPPENS, S. & HAMILTON, W. C. (1970). *Acta Cryst.* A26, 71–83.
International Tables for X-ray Crystallography (1968). Vol. III, 2nd ed., pp. 201–216. Birmingham: Kynoch Press.
 NANAMATSU, S., KIMURA, M., DOI, K. & TAKAHASHI, M. (1971). *J. Phys. Soc. Japan*, 30, 300–301.
 NANAMATSU, S., KIMURA, M. & KAWAMURA, T. (1975). *J. Phys. Soc. Japan*, 38, 817–824.
 PORTIER, R., FAYARD, M., CARPY, A. & GALY, J. (1974). *Mat. Res. Bull.* 9, 371–378.
 RUDDLESDEN, S. N. & POPPER, P. (1958). *Acta Cryst.* 11, 54–55.
 SCHEUNEMANN, K. & MÜLLER-BUSCHBAUM, H. (1974). *J. Inorg. Nucl. Chem.* 36, 1965–1970.
 SCHNERING, H. G. VON & BLECKMANN, P. (1968). *Naturwissenschaften*, 55, 342–343.
 WUENSCH, B. J. & PREWITT, C. T. (1965). *Z. Kristallogr.* 122, 24–59.

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The Structure of an Adduct of *N*-Methylthiourea and Dimethyl Acetylenedicarboxylate: 2-Imino-3-methyl-5-methoxycarbonylmethylene-1,3-thiazolidin-4-one

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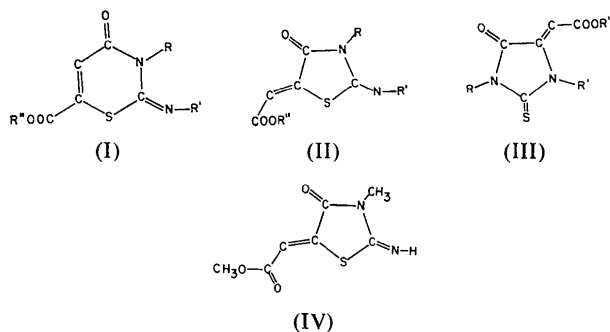
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The structure of an adduct of *N*-methylthiourea and the dimethyl ester of acetylenedicarboxylic acid is shown to be 2-imino-3-methyl-5-methoxycarbonylmethylene-1,3-thiazolidin-4-one ($\text{C}_7\text{H}_8\text{N}_2\text{O}_3\text{S}$) by X-ray crystallographic analysis. The molecule crystallizes in space group $P\bar{1}$, cell dimensions $a=9.275$, $b=12.287$, $c=8.517$ Å, $\alpha=103.62^\circ$, $\beta=96.86^\circ$, $\gamma=100.16^\circ$, with two molecules in the asymmetric unit. The structural model refined to an R of 0.055 with data measured on a four-circle diffractometer. The planar molecules are paired with hydrogen bonds between imine nitrogens and carbonyl oxygens of the carboxyl group; there appears to be sufficient space between packed pairs in the lattice for solvent of crystallization (methanol) to be occasionally included.

The structure of the product(s) derived from the reaction of substituted thioureas and acetylenedicarboxylic acid (or esters) has been the subject of some debate (Lown & Ma, 1967). Three ring systems have received support since the original publication by Mushkalo & Yangol (1956). These are the six-membered 1,3-thia-

zines (I) (Lown & Ma, 1967; Winterfeldt & Nelke, 1967; Kishida & Terada, 1968), the five-membered 1,3-thiazolidinone (II) (Mushkalo & Yangol, 1956; Hendrickson, Rees & Templeton, 1964), and the 2-thiohydantoin structure (III) (Sasaki, Sakata & Iwanami, 1964, 1965). Spectral evidence in support of the six-

membered product was strong. More recent papers have accepted and used this formulation (Winterfeldt & Nelke, 1967; Kishida & Terada, 1968), although doubt has been expressed on the validity of this assignment (Cain & Warren, 1971). In view of the uncertainty regarding the structure, we conducted a crystal structure analysis of a key product in this series, namely the isomer (IV), one of two isomers of (II) formed in the reaction of *N*-methylthiourea with dimethyl acetylenedicarboxylate, the other having $R=R'=CH_3$ and $R''=H$. The derived structure fully supports the five-membered 1,3-thiazolidinone structure, the chemical details of which have been published elsewhere (Mercer, Priestley, Warren, Adman & Jensen, 1972). Other investigators have also confirmed this result and have reported the structure of a 2-iminopiperidyl derivative in which *N*-thiocarbamylpiperidine was an initial reactant (Cameron & Hair, 1971).



Experimental

Crystallographic data

Clear lath-like crystals were grown from methanol by evaporation. Weissenberg and precession films indicated a triclinic space group. The cell parameters obtained by least-squares refinement of parameters derived from the diffractometer measurement of three setting angles each for 12 reflections are: $a=9.275$ (2), $b=12.287$ (3), $c=8.517$ (2) Å, $\alpha=103.62$ (2)°, $\beta=96.86$ (2)°, $\gamma=100.16$ (2)°.

The density was measured by flotation on two different crystals, resulting in two values, 1.451 and 1.474 g cm⁻³. The difference is larger than experimental error. The calculated density for a formula weight of 200 and four molecules per unit cell is 1.450 g cm⁻³; thus, the larger density corresponds to an additional 12 Daltons in the unit cell. The probable space group is $P\bar{1}$, with two molecules in the asymmetric unit.

A colorless crystal of dimensions 0.12 × 0.23 × 0.34 mm was chosen for data collection. Data to 50° in 2θ (Nb-filtered Mo $K\alpha$ radiation, $\lambda=0.7107$ Å, pulse height analyzer set to discriminate at approximately 95%) were collected with a computer-controlled automatic four-circle diffractometer, using a $\omega/2\theta$ scan with a tube take-off angle of approximately 3.5°. The limits of the scan were calculated with the use of the expression $A+B \tan \theta$, where $A=1.2$ and $B=1.0$. Back-

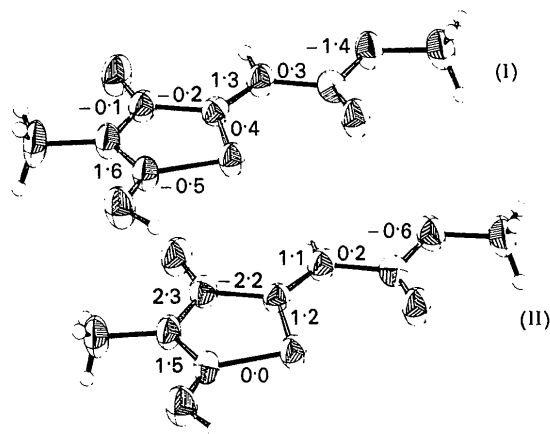


Fig. 1. Plot of thermal ellipsoids for 2-imino-3-methyl-5-methoxycarbonylmethylene-1,3-thiazolidin-4-one. Hydrogens are depicted with a standard sphere of radius 0.1 Å, nonhydrogens with ellipsoids representing 50% probability. Values for some torsion angles (standard deviations are 0.3–0.5°) are also shown to illustrate the planarity of the molecules. For the rings only values for the endocyclic angles are given.

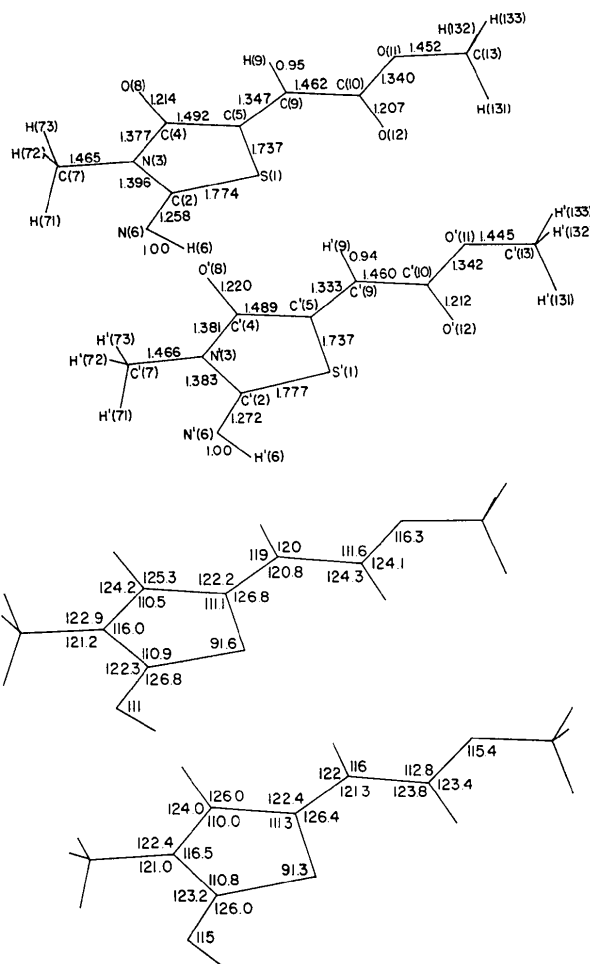


Fig. 2. Schematic plot of the thiazolidinone molecules showing bond lengths and angles.

Table 1. *Final atomic parameters of 2-imino-3-methyl-5-methoxycarbonylmethylene-1,3-thiazolidin-4-one*Thermal parameters are in the form (in units of Å²) exp [-($B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*$)].

	<i>x</i>	<i>y</i>	<i>z</i>	B_{11} or <i>B</i>	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
S(1)	0.1134	0.1655	0.3667	2.87	2.33	3.64	0.08	-0.50	0.46
C(2)	0.1251	0.3140	0.3873	3.07	2.36	3.73	0.33	-0.07	0.55
N(3)	0.2482	0.3791	0.5027	3.46	2.17	3.86	0.21	-0.43	0.36
C(4)	0.3349	0.3184	0.5755	3.32	2.63	3.23	0.30	-0.09	0.37
C(5)	0.2733	0.1927	0.5109	2.83	2.68	2.78	0.23	0.03	0.47
N(6)	0.0379	0.3589	0.3110	4.49	3.37	5.78	0.73	-1.15	1.28
C(7)	0.2799	0.5046	0.5439	5.48	1.93	6.35	0.14	-1.14	-0.17
O(8)	0.4455	0.3621	0.6781	4.01	3.20	4.86	-0.14	-1.72	0.18
C(9)	0.3364	0.1147	0.5647	2.96	2.80	3.49	0.27	-0.10	0.61
C(10)	0.2727	-0.0079	0.4995	3.07	3.02	3.67	0.66	0.60	1.17
O(11)	0.3486	-0.7090	0.5723	3.63	2.62	4.60	0.70	-0.52	0.81
O(12)	0.1631	-0.0473	0.3959	3.73	2.93	4.84	-0.01	-1.23	0.88
C(13)	0.2902	-0.1938	0.5231	4.64	2.70	5.40	0.56	-0.27	1.19
S'(1)	0.1442	0.0637	-0.1190	3.58	2.38	3.40	-0.00	-0.45	0.43
C'(2)	0.1604	0.2124	-0.1022	3.30	2.35	3.40	0.01	0.26	0.34
N'(3)	0.2781	0.2766	0.0182	3.53	2.09	3.63	-0.14	-0.22	0.16
C'(4)	0.3565	0.2165	0.1027	3.51	2.67	3.46	0.20	0.21	0.58
C'(5)	0.2958	0.0912	0.0361	2.74	2.61	2.66	-0.03	0.21	0.23
N'(6)	0.0780	0.2567	-0.1882	4.40	3.47	5.05	0.79	-0.74	1.01
C'(7)	0.3128	0.4020	0.0566	5.03	2.15	5.46	-0.17	-0.38	0.61
O'(8)	0.4603	0.2614	0.2149	4.73	3.34	4.46	-0.36	-1.57	0.32
C'(9)	0.3522	0.0134	0.0951	3.55	2.77	3.27	0.31	-0.11	0.40
C'(10)	0.2895	-0.1090	0.0290	3.86	2.91	3.25	0.81	0.59	0.72
O'(11)	0.3595	-0.1738	0.1052	5.04	2.83	4.11	0.76	-0.81	1.02
O'(12)	0.1846	-0.1482	-0.0816	4.37	2.98	4.37	0.14	-1.19	0.63
C'(13)	0.3007	-0.2958	0.0476	5.82	2.57	5.51	0.72	-0.78	1.06

Estimated standard deviations are as follows:

S	0.0001	0.0001	0.0001	0.04	0.04	0.05	0.03	0.03	0.03
N	0.0003	0.0002	0.0004	0.15	0.13	0.17	0.11	0.12	0.12
C	0.0004	0.0003	0.0005	0.19	0.15	0.20	0.13	0.15	0.14
O	0.0002	0.0002	0.0003	0.12	0.11	0.13	0.09	0.10	0.10
H	0.0045	0.0037	0.0055	1.35					

grounds were measured by stationary counting at each limit of the scan. Three standards were monitored every 200 reflections, and the data were scaled accordingly. There was no over-all decay indicated. Lorentz and polarization factors were calculated and applied; no corrections for coincidence loss, absorption or extinction were made. Of the 4176 independent data within the limiting sphere, 1402 intensities were less than $2\sigma_I$ and were coded as unobserved where $\sigma_I = [(T+B) + k(T-B)^2]^{1/2}$ (T =total counts, B =background counts, k =a factor set equal to 0.01 to account for instrumental instability).

Solution of the structure and refinement

The largest reflection in the data set was $20\bar{2}$, while $10\bar{1}$ was unobserved, indicating that the molecules lie almost completely in planes separated by the $(20\bar{2})$ spacing, an observation verified by the Patterson vector map. Consideration of the distribution of heights of vector peaks in these planes indicated that the centers of symmetry in the unit cell lay between planes of molecules rather than on them. With this assumption, two single-weight sulfur-sulfur self-vector peaks and two double-weight sulfur cross-vector peaks were readily identified and the positions of the two sulfur atoms in

Table 1 (cont.)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>
H(6)	-0.043	0.299	0.234	6.9
H(9)	0.430	0.140	0.650	3.5
H(71)	0.333	0.532	0.455	18.2
H(72)	0.188	0.530	0.574	9.4
H(73)	0.340	0.528	0.639	8.9
H(131)	0.277	-0.228	0.403	9.9
H(132)	0.359	-0.229	0.594	8.1
H(133)	0.187	-0.212	0.545	9.2
H'(6)	0.000	0.200	-0.274	6.0
H'(9)	0.436	0.034	0.179	4.3
H'(71)	0.334	0.419	-0.032	7.9
H'(72)	0.395	0.421	0.116	7.7
H'(73)	0.217	0.432	0.067	6.7
H'(131)	0.355	-0.326	0.110	8.4
H'(132)	0.187	-0.317	0.052	7.1
H'(133)	0.313	-0.326	-0.068	7.3
C(M1)	0.043	0.590	0.324	6.0
O(M1)	0.052	0.552	0.190	8.0
C(M2)	0.013	0.520	0.116	6.0
O(M2)	0.081	0.580	0.255	8.0

the asymmetric unit obtained. An F_{obs} Fourier synthesis using phases from these positions revealed 22 of the 26 remaining non-hydrogen atoms; a difference synthesis using phases calculated with the new positions revealed the four remaining atomic sites.

The atom types were assigned upon examination of

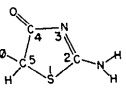
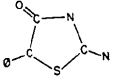
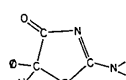
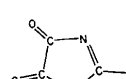
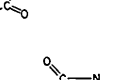
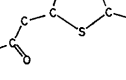
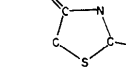
bond lengths calculated after one cycle of refinement* in which nitrogen scattering factors for all non-hydrogen atoms except sulfur were used. Two additional cycles of refinement using isotropic thermal parameters

* Full-matrix least-squares refinements were used until computer storage capacity necessitated refinement in two passes. The sulfur and hydrogen atomic parameters were refined in both passes; the remaining parameters of the unprimed molecule refined in the first pass, those of the primed molecule in the second. Scattering factors for S were those of Dawson (1960); for O, Berghuis *et al.* (1955); for N and C, McWeeny (1951); and for H, Stewart, Davidson & Simpson (1965). The quantity minimized was $\sum_{hkl} w(|F_o| - |F_c|)^2$ in which weights were defined as follows: $1/v^2 w = \sigma_F = \sigma_l / 2(ILp)^{1/2}$ where l = net intensity, Lp = Lorentz and polarization correction.

reduced R ($= \sum_{hkl} ||F_o| - |F_c|| / \sum_{hkl} |F_o|$) to 0.15, and the fol-

lowing cycle with anisotropic thermal parameters reduced R to 0.095. A difference synthesis revealed the 16 hydrogen atom positions. These were included with isotropic thermal parameters in the next cycle and R decreased to 0.089. However, a broad peak spread over a volume of approximately 5 \AA^3 representing about eight electrons was also observed in the difference synthesis in a region between methyl groups of neighboring molecules. The electron density can be accounted for in a reasonable way by two disordered methanol molecules. This model was refined by difference syntheses resulting in an occupancy of 0.20 and thermal parameters of 6 and 8 \AA^2 for carbon and oxy-

Table 2. Comparison of some bond lengths in substituted thiazolinones and thiazolidinones

Com- pound †	C(1)–C(2) C(2)–N(3) N(3)–C(4) C(4)–C(5) C(5)–S(1)						C(2)–N(6) C(5)–C(9) C(4)–O(8)			Ref.‡
	S(1)–C(2)	C(2)–N(3)	N(3)–C(4)	C(4)–C(5)	C(5)–S(1)		C(2)–N(6)	C(5)–C(9)	C(4)–O(8)	
1	1.755	1.337	1.357	1.542	1.812		1.316	1.506	1.224	<i>a</i>
	1.737	1.342	1.354	1.531	1.813		1.323	1.518	1.234	
2	1.756	1.336	1.349	1.535	1.841		1.303	1.512	1.233	<i>b</i> *
	1.771	1.338	1.357	1.527	1.839		1.301	1.509	1.223	
3	1.754	1.323	1.353	1.542	1.818		1.309	1.505	1.225	<i>c</i>
	1.782	1.324	1.340	1.509	1.718		1.314	1.356	1.223	
4	1.73	1.36	1.41	1.52	1.86		1.36	1.57	1.24	<i>e</i> *
	1.78	1.34	1.37	1.55	1.77		1.31	1.57	1.24	
5	1.764	1.388	1.357	1.537	1.808		1.257	NA	1.207	<i>g</i>
	1.764	1.377	1.368	1.521	1.814		1.273	1.202		
6	1.777	1.383	1.381	1.489	1.737		1.272	1.333	1.220	This work
	1.774	1.396	1.377	1.492	1.737		1.258	1.347	1.214	

* These structures were refined without the inclusion of hydrogen atom positions.

† Compound names are as follows: (1) 2-amino-5-phenyl-4-thiazolinone; (2) 2-amino-5-phenyl-4-thiazolidinone; (3) 2-imino-5-phenyl-4-thiazolidinone; (4) 2-piperidino-5-methoxycarbonylmethylene-4-thiazolinone; (5) 2-amino-5-acetyl-4-thiazolidinone; (6) 2-imino-4-thiazolidinone; (7) 2-phenylimino-3-methyl-5-phenyl-4-thiazolidinone; (8) 2-imino-3-methyl-5-methoxycarbonylmethylene-4-thiazolidinone.

‡ References: (a) Mornon & Bally (1972). (b) Mornon & Raveau (1971). (c) Plastas & Stewart (1969). (d) Cameron & Hair (1971). (e) Amirthaligam & Muralidharan (1972a). (f) Amirthaligam & Muralidharan (1972b). (g) Bally & Mornon (1972).

gen respectively, reducing R to 0.072. The final R after two additional cycles of least-squares refinement in which all parameters of the methanols were kept fixed is 0.055.

Results

The atomic parameters are listed in Table 1.* Fig. 1 is a plot of the atomic positions showing the thermal ellipsoids at a 50% probability level. Fig. 2 shows the bond distances and angles and confirms the structure proposed by Mushkalo & Yangol. (Standard deviations in bond lengths are 0.003, 0.004, 0.0045, 0.0042, 0.03, 0.04, 0.05 Å for S–C, O–C, N–C, C–C, H–C, H–N and H–C methyl respectively. Standard deviations are 0.25° for endocyclic bond angles except for that at the sulfur atom which is 0.15°; the average is 0.29° for exocyclic bond angles, and those involving hydrogen are 2–3°.) Bond distances and angles involving methyl hydrogens are normal and are not included.

Discussion

Molecular geometry

In general, the bond lengths in the two molecules agree very well. The heterocyclic-ring bond lengths are intermediate in length between those of single and double bonds. The differences between comparable bond lengths in each ring are not statistically significant, although taken at face value they may indicate slightly different delocalization around C(2), which is of some interest with respect to the molecule's character as a thiazolinone or thiazolidinone.

Since the inception of this work a number of thiazolinone and thiazolidinone structures have been studied; Table 2 is a summary of some pertinent bond lengths

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30987 (19 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

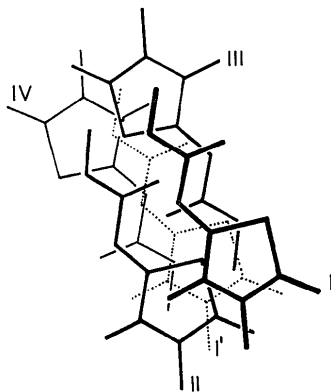
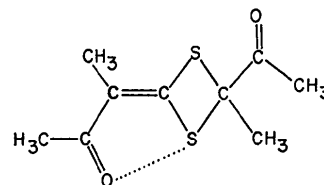


Fig. 3. View through five planes of molecules projected onto the $(10\bar{1})$ plane showing the stacking interactions. Close contacts between planes are given in Table 3.

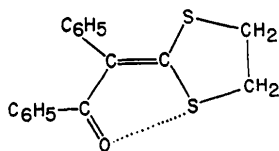
for comparison. A thiazolinone is a five-membered heterocycle with one endocyclic double bond, whereas a thiazolidinone has no endocyclic double bond. Which is which is not readily apparent from examination of the relevant bond lengths C(2)–N(3) and C(2)–N(6) since the presumed endocyclic double bond is longer than the exocyclic 'single' bond, probably because of delocalization in the ring. Compounds 1–4 (1 and 3 are two independent determinations of the same structure; 2 is another crystal form of 1, however not all hydrogen atom positions were found for it) appear to be aminothiazolinones by virtue of having no substituent at N(3) (therefore a possibility of an internal double bond) and two substituents (H or others) on N(6). Compounds 7 and 8 are then clearly iminothiazolidinones inasmuch as they are substituted at N(3) and C(2)–N(6) is considerably shortened. The hydrogen positions for compounds 5 and 6 have not been ascertained, and it is not readily apparent from bond lengths if these are thiazolinones or thiazolidinones. Other changes in ring bond lengths as a result of substitution of different groups at C(5) are entirely as expected: a trigonal carbon in this position has a shorter bond length associated with it than a tetrahedral carbon, *i.e.*, 1.49 Å for C(4)–C(5) in this work and 1.53 Å for compound 7.

Torsion angles given in Fig. 1 illustrate the planarity of the molecule. The unprimed five-membered ring is not significantly nonplanar, while the five-membered ring of the primed molecule is probably significantly nonplanar. S(1) is the furthest from the plane of the other four atoms, while C'(4) is 0.039 Å from a 'best' plane of the other four atoms in its ring. The nonplanarity is significant in that the carbonyl oxygen attached to C'(4) overlaps the ring beneath it (see Fig. 3) and is displaced toward that ring, probably to minimize crowding from adjacent methyl groups (see *Molecular packing*).

In both molecules the atoms S(1)–C(5)–C(9)–C(10)–O(12) are coplanar. However, the S(1)···O(12) distances within these planes of 2.795 and 2.780 Å, while less than the sum of van der Waals radii, do not indicate any intramolecular interaction such as in a thiathiophene derivative in which an S···O distance of 2.38 Å is observed (Hordvik, Sletten & Sletten, 1969). The distance is, in fact, somewhat longer than that observed for two similar arrangements: 2.64 Å for a 2-methylene-1,3-dithiacyclobutane



(Kapecki, Baldwin & Paul, 1968) and 2.70 Å for 2-desyldiene-1,3-dithiolane



(Schmidt & Tulinsky, 1967; see Table 10 of Kapecki, Baldwin & Paul for additional comparisons). In the thiacyclobutane derivative the bond angles in the five-membered conjugated system are smaller than the corresponding ones in our compound, particularly at C(9) where ours averages 121° and in their compound it is

115° . Also, the C-C angle is larger in our compound, 124° vs. 122° ; this in addition to the observation that the C=C double-bond distance is longer in the other compound suggests that there is more interaction between the S and O in that compound. The reasons for this undoubtedly have to do with factors other than just the atoms in this group – as is apparent from examination of Table 10 of Kopecki, Baldwin & Paul. S...O distances of 2.89 and 2.96 were reported for compounds 4 and 5 of Table 2; however, the latter has a single bond at C(5)–C(9). In short, substitution at various places in the whole molecule has an effect on this distance; what we have observed here is not unreasonable.

Table 3. Intermolecular distances between planes (Å)

Molecules I and II are the primed and unprimed molecules of the asymmetric unit respectively. III is related to II, and IV to I by the symmetry operation $(1-x, -y, 1-z)$. I' is then related to IV by $(1-x, -y, -z)$ or to I by $(x, y, z-1)$.

I-II		II-III	
O'(8) ... C(5)	3.407	All greater than 3.6 Å	
O'(8) ... C(4)	3.377		
O'(8) ... N(3)	3.529		
III-IV*			
S(1) ... C'(4)	3.452	N'(6) ... C(5)	3.337
S(1) ... C'(5)	3.479	N'(6) ... C(4)	3.395
C(2) ... N'(3)	3.567		
C(2) ... C'(4)	3.563		
N(6) ... C'(7)	3.585		
O(12) ... C'(9)	3.422		
O(12) ... C'(10)	3.433		
O(12) ... C'(11)	3.482		
IV-I'			
O'(11) ... C'(4)	3.393		
C'(9) ... C'(9)	3.373		
O'(11) ... O'(8)	3.424		
C'(13) ... O'(8)	3.375		

* Interactions not shown in Fig. 3, between N'(6) in level IV of one stack and C(5) + C(4) of level III of another stack: *i.e.*, the latter molecule is related to the primary molecule (II) of the asymmetric unit by the symmetry operation $(x, y, 1+z)$.

Molecular packing

Fig. 3 illustrates the stacking of the molecules into directions normal to the mean planes of the molecules, which are inclined 5° to each other. As shown in Table 3, no interatomic distances between molecules I and II in Fig. 3 are less than 3.34 Å. The (202) planes near which the molecules lie are 3.34 Å apart. This distance is similar to that between planes of molecules in which charge transfer occurs (Boeyens & Herbstein, 1965), but in the absence of spectral data, a charge-transfer self complex cannot be inferred.

The molecules are held together in a plane (shown in Fig. 4) by two weak hydrogen bonds between N(6)...O'(12) and N'(6)...O(12). The parameters are given in Table 4. A short H-O distance of 2.35 Å reflects some crowding of C(13) and O'(8); and in fact the out-of-plane bending at C'(4) to which O'(8) is bonded may result from that crowding. Otherwise, no other significantly short intermolecular distances appear.

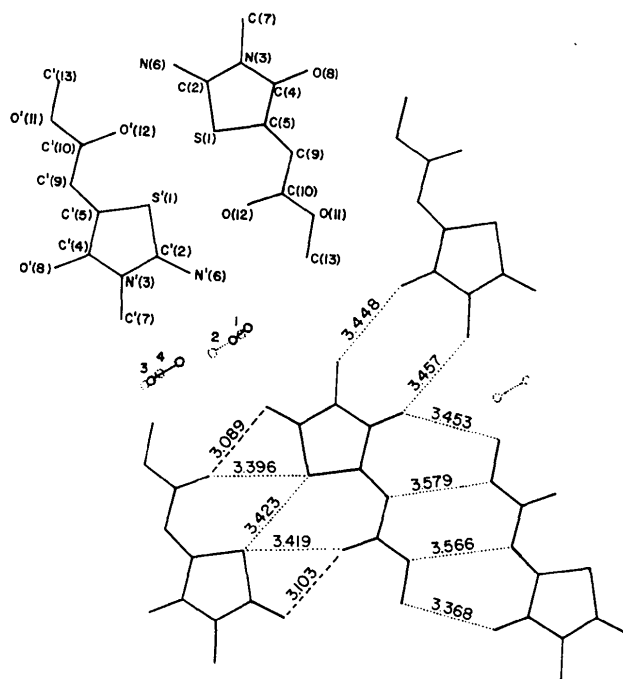


Fig. 4. Projection onto the (10I) plane in which b^* runs from bottom to top and [101] from left to right. The top molecule of Fig. 3 is the lower left molecule of this figure. The figure illustrates the packing of molecules and intermolecular distances (in the plane) and also the sites of disordered methanols. Sites 2 and 4 are related by a center of symmetry as are 1 and 3. Although there is an apparent center of symmetry in this plane between the two molecules of the asymmetric unit, it is not borne out in three dimensions. The true unit-cell centers of symmetry lie between planes of molecules.

Table 4. Hydrogen-bond parameters

	O...N	O...H	∠H-N-O	∠C-O-N	∠C-N-O	∠O-H-N
O'(12) ... H(6)-N(6)	3.089 Å	2.11 Å	7°	149.4°	102.7°	168°
O(12) ... H'(6)-N'(6)	3.103	2.14	12	149.9	103.2	160

The packing of the hydrogen-bonded pairs is such that methyl groups are found primarily in sheets to which b^* is normal, intersecting the b axis at $(0, \frac{1}{2}, 0)$. The packing of methyl groups results in cavities which appear to be filled by methanol molecules, at least in the crystal under study. An examination of the contact distances of each methanol site shows that while the cavities are large enough to accommodate the solvent only one of the four sites possible is likely to be occupied in any given unit cell (sites 1 and 2 are about 0.6 Å apart; 2 and 4 come within 3.1 Å of each other, the furthest apart of the possible pairs). The values of the occupancy and thermal parameters indicate that occupation of each site is equally probable. The bond lengths of each methanol (1.1 and 1.3 Å), although shorter than the accepted value for a C–O bond are, nevertheless, reasonable in view of the overlap and lack of resolution at the sites. It appears that the methanols are hydrogen bonded to the imine nitrogens, inasmuch as the 2.8 Å O–N distances are valid.

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The plot in Fig. 1 was made with Carroll Johnson's ORTEP program, Report ORNL-3794.

References

- AMIRTHALINGAM, V. & MURALIDHARAN, K. V. (1972a). *Acta Cryst.* **B28**, 2417–2421.
- AMIRTHALINGAM, V. & MURALIDHARAN, K. V. (1972b). *Acta Cryst.* **B28**, 2421–2423.
- BALLY, R. & MORNON, J. P. (1972). *C.R. Acad. Sci. Paris, Sér. C*, **275**, 933–935.
- BERGHUIS, J., HAANAPPEL, IJ. M., POTTERS, M., LOOPSTRA, B. O., MACGILLAVRY, C. H. & VEENENDAAL, A. L. (1955). *Acta Cryst.* **8**, 478–483.
- BOEYENS, J. C. A. & HERBSTEIN, F. H. (1965). *J. Phys. Chem.* **69**, 2160–2176.
- CAIN, E. N. & WARRENER, R. N. (1971). *Aust. J. Chem.* **24**, 785–807.
- CAMERON, A. F. & HAIR, N. J. (1971). *J. Chem. Soc. (B)*, pp. 1733–1736.
- DAWSON, B. (1960). *Acta Cryst.* **13**, 403–408.
- HENDRICKSON, J. B., REES, R. & TEMPLETON, J. F. (1964). *J. Amer. Chem. Soc.* **86**, 107–111.
- HORDVIK, A., SLETTEN, E. & SLETTEN, J. (1969). *Acta Chem. Scand.* **23**, 1377–1388.
- KAPECKI, J. A., BALDWIN, J. E. & PAUL, I. C. (1968). *J. Amer. Chem. Soc.* **90**, 5800–5805.
- KISHIDA, Y. & TERADA, A. (1968). *Chem. Pharm. Bull. (Tokyo)*, **16**, 1351–1359.
- LOWN, J. W. & MA, J. C. N. (1967). *Canad. J. Chem.* **45**, 939–951.
- MCWEENY, R. (1951). *Acta Cryst.* **4**, 513–519.
- MERCER, J. F. B., PRIESTLEY, G. M., WARRENER, R. N., ADMAN, E. & JENSEN, L. H. (1972). *Synth. Commun.* **2**, 35–41.
- MORNON, J. P. & BALLY, R. (1972). *Acta Cryst.* **B28**, 2074–2079.
- MORNON, J. P. & RAVEAU, B. (1971). *Acta Cryst.* **B27**, 95–108.
- MUSHKALO, L. K. & YANGOL, G. Y. (1956). *Chem. Abs.* **50**, 16751a.
- PLASTAS, L. & STEWART, J. M. (1969). *Chem. Commun.* p. 811.
- SASAKI, H., SAKATA, H. & IWANAMI, T. (1964). *J. Chem. Soc. Japan*, **85**, 704–707.
- SASAKI, H., SAKATA, H. & IWANAMI, Y. (1965). *Chem. Abs.* **62**, 14678f.
- SCHMIDT, W. H. & TULINSKY, A. (1967). *Tetrahedron Lett.* pp. 5311–5313.
- STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
- WINTERFELDT, E. & NELKE, J. M. (1967). *Chem. Ber.* **100**, 3671–3678.