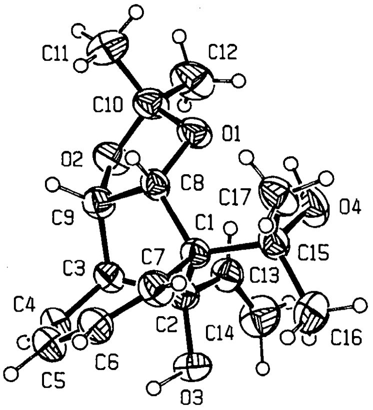

Fig. 1. Perspective drawing of the molecular structure with the crystallographic numbering scheme.

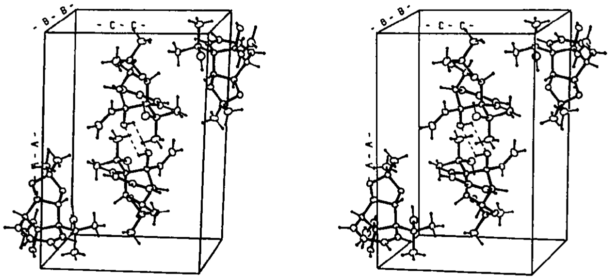

Fig. 2. A stereoview of the molecular-packing diagram for (II); dashed lines indicate O—H···O hydrogen bonds.

C_{sp^3}—C_{sp^3} 1·497 (4)–1·576 (4) [mean 1·535 (4)], C_{sp^3}—C_{sp^2} 1·497 (4)–1·533 (4) [mean 1·511 (4)], C_{sp^2}—C_{sp^2} 1·446 (4), $C_{sp^2}=C_{sp^2}$ 1·311 (4)–1·330 (4) [mean 1·323 (4)], C_{sp^3}—O 1·411 (3)–1·443 (3) [mean 1·426 (3)], and C—H 0·941–1·206 Å. The seven-membered ring C(1)–C(7) has a twisted envelope conformation with C(2) 0·906 (3) Å out of the plane described by the remaining atoms of the ring. The five-membered ring C(1),C(2),C(3),C(8),C(9) has a C(2) envelope conformation with C(2) 0·566 (3) Å out of the best least-squares plane passing through C(1), C(3), C(8) and C(9). The five-membered ring O(1),O(2),C(8),C(9),C(10) has a C(10) envelope conformation with C(10) 0·496 (4) Å out of the plane of the remaining atoms in this ring. The five-membered rings are *cis*-fused to each other.

There is a short intramolecular contact of 2·695 Å between O(1) and O(4) [O(1)···H(O4) 1·972 Å and O(4)—H(O4)···O(1) 129·7°]. The shortest intermolecular contacts in the crystal structure (Fig. 2) involve the hydroxy groups of the adjacent molecules related by an inversion center [O(3)···O(3′) 2·953, O(3′)···H(O3) 2·362 Å, and O(3)—H(O3)···O(3′) 107·2°].

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Structures of 3,6-Dimethoxy-1,2,4,5-tetrazine (V) and 3,6-Bis(1-aziridinyl)-1,2,4,5-tetrazine (VI)

By Claus Krieger, Hans Fischer and Franz A. Neugebauer*

Abteilung Organische Chemie, Max-Planck-Institut für medizinische Forschung, Jahnstr. 29, *D*-6900 *Heidelberg, Federal Republic of Germany*

and Friedemann Gückel and Dieter Schweitzer

Abteilung für Molekulare Physik, Max-Planck-Institut für medizinische Forschung, Jahnstr. 29, *D*-6900 *Heidelberg, Federal Republic of Germany*

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Abstract. (V): $C_4H_6N_4O_2$, $M_r = 142{\cdot}12$, orthorhombic, *Pbca*, $a = 6{\cdot}865$ (3), $b = 13{\cdot}192$ (5), $c = 7{\cdot}013$ (3) Å, $V = 635{\cdot}1$ (7) Å^3, $Z = 4$, $D_x = 1{\cdot}486$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 1{\cdot}139$ cm^{-1}, $F(000) = 296$, $T = 295$ K, $R = 0{\cdot}043$ for 589 unique observed reflections [$I \geq 1{\cdot}96\sigma(I)$]. (VI): $C_6H_8N_6$,

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* To whom correspondence should be addressed.

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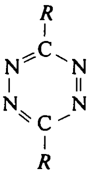
$M_r = 164{\cdot}18$, monoclinic, $C2/m$, $a = 9{\cdot}660\,(2)$, $b = 9{\cdot}077\,(1)$, $c = 4{\cdot}294\,(1)$ Å, $\beta = 91{\cdot}07\,(1)°$, $V = 376{\cdot}5\,(2)$ Å^3, $Z = 2$, $D_x = 1{\cdot}448$ g cm^{-3}, $\lambda(\text{Mo}\,K\alpha) = 0{\cdot}71069$ Å, $\mu = 0{\cdot}952$ cm^{-1}, $F(000) = 172$, $T = 295$ K, $R = 0{\cdot}037$ for 405 unique observed reflections $[I \geq 1{\cdot}96\sigma(I)]$. (V) and (VI) are centrosymmetric, with planar 1,2,4,5-tetrazine rings slightly compressed in the C···C direction (N—C—N $\simeq$ 126°). The remarkably short exocyclic C—O [1·328 (2) Å] and C—N [1·385 (1) Å] bond distances indicate that the methoxy and aziridinyl substituents act as π donors to the electron-deficient 1,2,4,5-tetrazine system.

Introduction. In the evaluation of spectroscopic results concerning the triplet state, T_1, in single crystals of various 1,2,4,5-tetrazines (Gückel, Schweitzer, Hausser & Neugebauer, 1982), the crystal structures, particularly the molecular packing, were required for the compounds studied. Structures are already known for the parent compound 1,2,4,5-tetrazine (I) (Bertinotti, Giacomello & Liquori, 1956) and for three 3,6-disubstituted derivatives [(II), Huffman, 1981; (III), Ahmed & Kitaigorodsky, 1972; (IV), Krieger, Fischer & Neugebauer, 1987]. This paper reports the crystal structures of 3,6-dimethoxy-1,2,4,5-tetrazine (V) (Neugebauer & Fischer, 1982) and 3,6-bis(1-aziridinyl)-1,2,4,5-tetrazine (VI) (Fischer & Neugebauer, 1987, unpublished results). Compound (VI) shows substantial cytotoxic activity which attracts further specific interest.



	(I)	(II)	(III)	(IV)	(V)	(VI)
R	H	CH_3	C_6H_5	NH_2	OCH_3	N◁

Experimental. (V): Needle-shaped red crystals grown from ligroin by slow evaporation at room temperature; approximate crystal dimensions 0·2 × 0·85 × 0·4 mm. Syntex $P2_1$ four-circle diffractometer, graphite-monochromated Mo $K\alpha$ radiation; $\theta/2\theta$ scanning technique. Lattice parameters determined from least-squares fit with 15 reflections (θ range: 10–12·5°); 794 unique reflections measured in the range $2 \leq \theta \leq 28{\cdot}6°$, max. $(\sin\theta)/\lambda = 0{\cdot}676$ Å^{-1}, $0 \leq h \leq 8$, $0 \leq k \leq 17$, $0 \leq l \leq 9$; 589 $[I \geq 1{\cdot}96\sigma(I)]$ used for structure solution and refinement. Three standard reflections, 3% intensity variation. Lorentz and polarization corrections were applied. The structure was solved by direct methods using *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). Full-matrix least squares minimized $\sum w(\Delta F)^2$. H atoms refined with isotropic temperature factors, all other atoms refined anisotropically for 58 variables. $R = 0{\cdot}043$, $wR = 0{\cdot}042$, $w = [\sigma^2(F) + 0{\cdot}005\sigma(F^2)]^{-1}$, max. $\Delta/\sigma = 0{\cdot}05$; residual electron density in final difference map $-0{\cdot}14 < \Delta\rho < 0{\cdot}15$ e Å^{-3}. Atomic scattering factors and anomalous-dispersion corrections taken from *International Tables for X-ray Crystallography* (1974); programs used were those of B. A. Frenz & Associates Inc. (1982). (VI): Red needles from methanol approximately 0·08 × 0·10 × 0·30 mm. Enraf–Nonius CAD-4 four-circle diffractometer, graphite-monochromated Mo $K\alpha$ radiation; $\theta/2\theta$ scanning technique. Lattice parameters determined from least-squares fit with 30 reflections (θ range: 12–15°); 530 unique reflections measured in the range $1{\cdot}5 \leq \theta \leq 29°$, max. $(\sin\theta)/\lambda = 0{\cdot}682$ Å^{-1}, $0 \leq h \leq 13$, $0 \leq k \leq 12$, $-5 \leq l \leq 5$; 405 $[I \geq 1{\cdot}96\sigma(I)]$ used for structure solution and refinement. Three standard reflections, 2% intensity variation. Lorentz and polarization corrections were applied. The structure was solved by direct methods (*MULTAN*80). Full-matrix least squares minimized $\sum w(\Delta F)^2$. H atoms refined with isotropic temperature factors, all other atoms refined anisotropically for 39 variables. $R = 0{\cdot}037$, $wR = 0{\cdot}038$, $w = [\sigma^2(F) + 0{\cdot}003\sigma(F^2)]^{-1}$, max. $\Delta/\sigma < 0{\cdot}001$; $-0{\cdot}09 < \Delta\rho < 0{\cdot}08$ e Å^{-3}. For further details see compound (V).

Discussion. Final atomic and isotropic thermal parameters are listed in Table 1, and bond distances and angles are presented in Table 2.* Views of the molecules (V) and (VI) with the chosen atom-numbering schemes are presented in Figs. 1 and 2, respectively.

(V) shows C_i symmetry. The ring is exactly planar. The attached O atoms deviate from the ring plane by 0·020 Å. The methyl groups are more displaced (0·153 Å) due to some distortion about C(3)—O(3′) [N(2)—C(3)—O(3′)—C(3″) = 8·8°]. (VI) has C_{2h} symmetry with the mirror plane bisecting the molecule through N(3), C(2), C(2$^{\text{iii}}$) and N(3$^{\text{iii}}$) orthogonal to the planar 1,2,4,5-tetrazine ring. The N atoms of the 1-aziridinyl substituents deviate to some extent from the tetrazine ring plane [N(3): −0·109 Å] yielding 184·3° for the angle between the ring plane and the C(2)—N(3) bond. The angle between this bond and the aziridine ring plane was found to be 124·5°. The slight bending of the aziridinyl N out of the 1,2,4,5-tetrazine plane is apparently caused by intramolecular van der Waals interactions of the aziridinyl methylene groups with C(2) as indicated by the C(4)···C(2) distance of 2·452 Å and the H(4A)···C(2) distance of 2·54 Å.

Bond distances and bond angles in the 1,2,4,5-tetrazine rings in (V) and (VI) agree with those of (I)–(IV) (Table 3). Different N—N—C ($\simeq$ 117°) and

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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 43875 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Fractional atomic coordinates and isotropic (for* H) *or equivalent isotropic (for* C,N,O) *thermal parameters* (Å^2) *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} or B_{iso}
(V) 3,6-Dimethoxy-1,2,4,5-tetrazine				
N(1)	−0·0431 (2)	−0·0991 (1)	0·0327 (2)	3·92 (3)
N(2)	0·1272 (3)	−0·0635 (1)	0·0898 (2)	4·13 (4)
C(3)	0·1637 (3)	0·0343 (1)	0·0546 (2)	3·52 (4)
O(3′)	0·3356 (2)	0·0661 (1)	0·1176 (2)	4·83 (3)
C(3″)	0·3983 (3)	0·1671 (2)	0·0644 (3)	5·01 (5)
H(3*A*)	0·322 (3)	0·217 (2)	0·130 (3)	6·1 (6)
H(3*B*)	0·386 (2)	0·175 (2)	−0·079 (3)	5·8 (5)
H(3*C*)	0·524 (3)	0·176 (2)	0·109 (3)	6·3 (6)
(VI) 3,6-Bis(1-aziridinyl)-1,2,4,5-tetrazine				
N(1)	−0·0514 (1)	0·1307 (1)	0·0992 (2)	2·83 (2)
C(2)	−0·0989 (2)	0·0000	0·1906 (4)	2·36 (4)
N(3)	−0·1989 (1)	0·0000	0·4177 (4)	2·83 (4)
C(4)	−0·3276 (1)	0·0806 (2)	0·3616 (4)	3·83 (3)
H(4*A*)	−0·332 (1)	0·129 (2)	0·161 (3)	5·0 (4)
H(4*B*)	−0·361 (1)	0·131 (2)	0·542 (4)	5·0 (4)

Table 2. *Bond distances* (Å), *angles* (°) *and selected torsion angles* (°) *with e.s.d.'s in parentheses*

(V) 3,6-Dimethoxy-1,2,4,5-tetrazine			
N(1)—N(2)	1·322 (2)	N(2)—N(1)—C(3^{i})	117·3 (1)
N(1)—C(3^{i})	1·338 (2)	N(1)—N(2)—C(3)	116·9 (1)
N(2)—C(3)	1·337 (2)	N(1^{i})—C(3)—N(2)	125·8 (1)
C(3)—O(3′)	1·328 (2)	N(1^{i})—C(3)—O(3′)	120·0 (1)
O(3′)—C(3″)	1·450 (2)	N(2)—C(3)—O(3′)	114·2 (1)
C(3″)—H(3*A*)	0·955 (20)	C(3)—O(3′)—C(3″)	117·9 (1)
C(3″)—H(3*B*)	1·016 (19)		
C(3″)—H(3*C*)	0·925 (21)	N(2)—C(3)—O(3′)—C(3″)	8·8 (2)

Symmetry code: (i) $-x, -y, -z$.

(VI) 3,6-Bis(1-aziridinyl)-1,2,4,5-tetrazine			
N(1^{ii})—N(1)	1·320 (1)	N(1^{ii})—N(1)—C(2)	117·2 (1)
N(1)—C(2)	1·334 (1)	N(1)—C(2)—N(1^{i})	125·6 (1)
C(2)—N(3)	1·385 (1)	N(1)—C(2)—N(3)	117·1 (1)
N(3)—C(4)	1·458 (1)	C(2)—N(3)—C(4^{i})	119·2 (1)
C(4)—C(4^{i})	1·464 (2)	C(4)—N(3)—C(4^{i})	60·2 (1)
C(4)—H(4*A*)	0·969 (9)	N(3)—C(4)—C(4^{i})	59·9 (1)
C(4)—H(4*B*)	0·963 (9)		
		N(1^{ii})—N(1)—C(2)—N(3)	174·9 (1)
		N(1)—C(2)—N(3)—C(4)	57·3 (2)
		C(2)—N(3)—C(4)—C(4^{i})	108·9 (2)

Symmetry code: (i) $x, -y, z$; (ii) $-x, y, -z$; (iii) $-x, -y, -z$.

Table 3. *Observed bond lengths* (Å) *and angles* (°) *for the* 1,2,4,5-*tetrazine ring in* (I) *and in the* 3,6-*disubstituted derivatives* (II)–(VI)

	R	N—N	C—N	N—N—C	N—C—N
(I)	H	1·321	1·345 1·323	116·2 115·4	127·2
(II)	CH_3	1·326	1·343 1·335	118·2 118·0	123·8
(III)	C_6H_5	1·314	1·353 1·338	120·6 117·5	121·8
(IV)	NH_2	1·328 1·314	1·348 1·347	118·3 118·0	123·7
(V)	OCH_3	1·322	1·338 1·337	117·3 116·9	125·8
(VI)	N	1·320	1·334	117·2	125·6

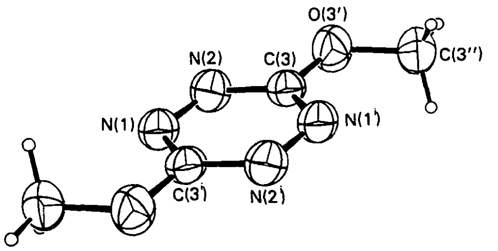

Fig. 1. *ORTEP* drawing (Johnson, 1976) of (V) with the atom-numbering scheme and thermal ellipsoids at the 50% probability level.

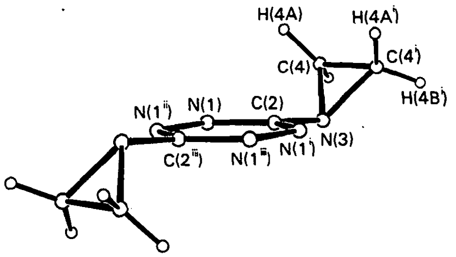

Fig. 2. Perspective view of (VI) with the atom-numbering scheme.

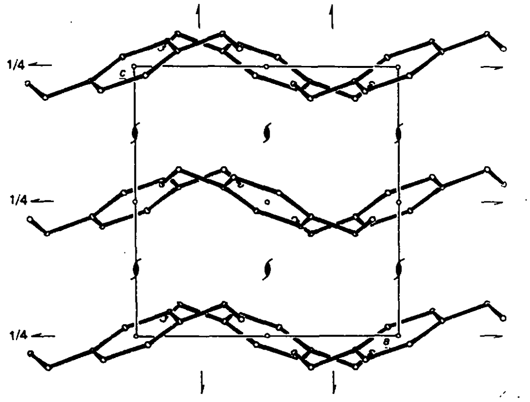

Fig. 3. Packing arrangement of (V) as viewed along **b**.

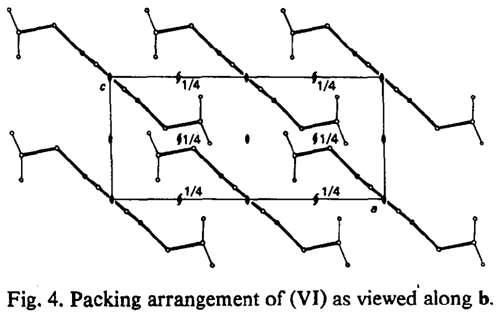

Fig. 4. Packing arrangement of (VI) as viewed along **b**.

N—C—N angles ($\simeq 125°$) produce a compressed six-membered ring in which all bonds (N—N $\simeq$ 1·32 and C—N $\simeq$ 1·34 Å) have partial ($\simeq$ 50%) double-bond character consistent with the resonance structure. The exocyclic bonds, C(3)—O(3′) = 1·328 (2) Å in (V) and C(2)—N(3) = 1·385 (1) Å in (VI), are also remarkably short. As in the case of (IV) we interpret this finding as a result of the strong electron-acceptor property of the 1,2,4,5-tetrazine system. The methoxy and also, surprisingly, the 1-aziridinyl substituents serve as weak π-electron donors. The interaction of the lone pair of electrons at the exocyclic heteroatoms with the electron-deficient π system of the molecule gives the exocyclic C(3)—O(3′) and C(2)—N(3) bonds some double-bond character. Bond distances and angles of the aziridinyl substituents correspond to known data for the aziridine ring (*e.g.* Boese, Rademacher & Treschanke, 1985; Rudchenko, D'yachenko, Zolotoi, Atovmyan, Chervin & Kostyanovsky, 1982).

The molecular packing of (V) viewed along **b** is shown in Fig. 3. The 1,2,4,5-tetrazine moieties are positioned in a herringbone arrangement. (VI) shows layers in the (201) plane in which each 1,2,4,5-tetrazine unit is surrounded by four neighbouring molecules. The packing arrangement of the layers, separated from each other by 3·18 Å and with the shortest intermolecular contact C(2)···C(2)($-x$, y, $1-z$) = 3·244 Å, is illustrated in Fig. 4.

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Structure of 4,5-Di(benzoylthio)-4,5-didehydro-1,3-dithiolane-2-thione

BY X. SOLANS, M. FONT-BARDÍA AND M. FONT-ALTABA

Departamento Cristalografía y Mineralogía, Universidad de Barcelona, Gran Via 585, 08007-*Barcelona, Spain*

AND R. VICENTE AND A. SEGUÍ

Departamento Química Inorgánica, Universidad de Barcelona, Diagonal 645, 08028-*Barcelona, Spain*

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Abstract. $C_{17}H_{10}O_2S_5$, $M_r = 406·6$, monoclinic, $P2_1/a$, $a = 17·369$ (4), $b = 10·687$ (3), $c = 9·695$ (3) Å, $\beta = 93·83$ (3)°, $V = 1796$ (1) Å^3, $Z = 4$, $D_x = 1·50$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, μ(Mo $K\alpha$) = 6·3 cm^{-1}, $F(000) = 832$, $T = 288$ K, $R = 0·070$ for 2815 observed reflections. The structure consists of discrete molecules linked by van der Waals forces. One C_6H_5CO moiety is nearly coplanar with the five-membered ring; the second C_6H_5CO moiety is rotated around the S—C(ring) bond, the C(O)—S—C(ring)—S(ring) torsion angle being 87·9 (4)°. Packing forces may cause the 2-thione S atom to lie 0·178 (5) Å from the plane of the five-membered ring. The C—S bond lengths are generally larger than those observed in metal complexes with 4,5-dimercapto-1,3-dithio-2-thione as ligand.

Introduction. 4,5-Dimercapto-1,3-dithiole-2-thione has been used frequently as a ligand in metal complexes. A study of the variation of the bond lengths of this ligand according to the oxidation state of the metal has been carried out by Valade, Legros, Bousseau, Cassoux, Garbauskas & Interrante (1985) and Kato, Mori, Kobayashi, Sasaki & Kobayashi (1984). We now

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