

L'hypothèse de la délocalisation des charges est confirmée par l'élargissement de l'angle C(2)–N(3)–C(4) jusqu'à une valeur proche de 120°, observée dans les groupements pyridiniums (Dupont, Dideberg & Vermeire, 1974) ainsi que par le raccourcissement des distances C(1)–N(1) et N(2)–C(51) (1,448 et 1,382 Å respectivement) par rapport à la valeur généralement admise pour une liaison simple C–N: 1,47 Å (Pauling, 1960).

Les quatre distances S–C(cycle) sont voisines et en bon accord avec la longueur de 1,768 Å trouvée dans le monohydrate d'éthylthio-2 méthyl-8 inosine (Nagashima & Wakabayashi, 1974). Le même accord se retrouve lorsqu'on compare les distances S–C(chaine) avec celle trouvée dans ce même composé, 1,832 Å.

Il n'existe aucun contact de van der Waals inférieur à 3,5 Å.

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## The Structure of 4-[(*E*)-1,2-Diphenylvinyl]-2,6-diphenyl-1,3,4,5-thiatriazine 1,1-Dioxide

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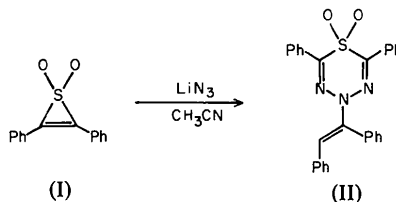
**Abstract.** C<sub>28</sub>H<sub>21</sub>N<sub>3</sub>O<sub>2</sub>S, *M<sub>r</sub>* = 463.6, monoclinic, *P*2<sub>1</sub>/*n*, *a* = 8.580 (2), *b* = 11.174 (3), *c* = 24.592 (7) Å, β = 95.04 (2)°, *Z* = 4, *D<sub>c</sub>* = 1.311 Mg m<sup>-3</sup>; Mo *K*α diffractometer data; final *R* = 0.043. The structure contains the hitherto unknown 1,3,4,5-thiatriazine nucleus, and a *cis*-stilbene moiety. The bond lengths and angles are normal.

**Introduction.** The irreversible reactions of 2,3-diphenylthiurene 1,1-dioxide (I) with nucleophiles have provided a variety of new and interesting compounds (Potts, Elliot & Sorm, 1972; Hayasi, Nakamura & Nozaki, 1973; Rosen & Bonet, 1974; Matsukubo, Kojima & Kato, 1975; Jarvis, Tong & Ammon, 1975). In a continuing investigation of the interaction of nucleophiles with (I), we found that the compound reacted readily with lithium azide to give a bright yellow,

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crystalline sulfone in about 10% yield (Jarvis, Stahly & Ammon, 1978). Aside from the presence of the sulfonyl group, other structural features were not readily apparent in the physical, chemical, or spectral properties of the compound. An X-ray crystallographic analysis was undertaken, which identified the sulfone as the title compound (II).



In a typical experiment, a mixture of 1.0 g (4.13 mmol) of (I) and 1.0 g (20.4 mmol) of finely ground lithium azide in 20 ml of acetonitrile was stirred vigorously at room temperature for 20 h. Removal of

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the solids by filtration, column chromatography (silica gel, 30% dichloromethane in petroleum ether as eluent) of the acetonitrile solubles, and crystallization (dichloromethane-hexane) of the appropriate fraction provided 98 mg of (II), m.p. 454–5–455 K.

A crystal of dimensions 0.08 × 0.24 × 0.58 mm, obtained by slow evaporation of an isooctane solution, was used for all X-ray measurements. Oscillation and Weissenberg photographs (Cu radiation) allowed determination of the Laue symmetry, systematic absences, and rough values of the lattice constants. All lattice parameter and intensity measurements were made with a Picker FACS-I diffractometer with Mo radiation [graphite monochromator,  $\lambda(K\alpha) = 0.71069 \text{ \AA}$ ]. The crystal was aligned to place [100] parallel to the  $\phi$  axis of the instrument. The final unit-cell parameters were obtained by least squares from the Bragg angles of 13 reflections manually centered at  $\pm 2\theta$  (average of  $|2\theta_o - 2\theta_c| = 0.004^\circ$ ).

Intensity data were collected with the  $\theta-2\theta$  scan mode at a rate of  $2^\circ \text{ min}^{-1}$  over a  $2\theta$  range calculated from  $(1.45 + 0.7 \tan \theta)^\circ$ ; 20 s background measurements were made. Intensity variations were monitored by measuring three standard reflections every 100 reflections. The maximum count rate was maintained below 15 000 counts  $\text{s}^{-1}$  by automatic insertion of metal-foil attenuators into the diffracted beam. Measurement to a  $2\theta$  maximum of  $50^\circ$  provided 4879 data of which 4376 (including 256 systematic absences) were unique; 2635 were more than 3 standard deviations above background.

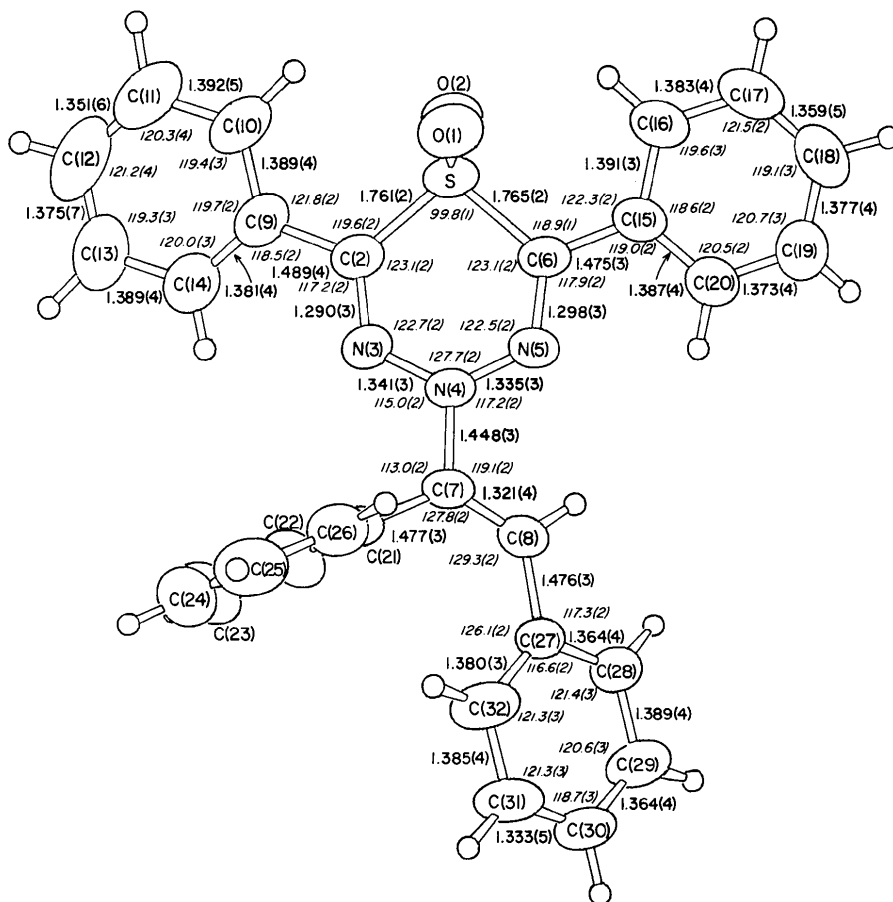
All of the crystallographic calculations were carried out on a Univac 1108 computer with the XRAY 76 system of programs (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976). The structure was solved by the routine application of direct methods, and subsequently refined with the method of full-matrix least squares; the function minimized was  $\sum w(F_o - F_c)^2$ . Unit weights ( $w = 1$ ) were used initially, but  $[1/\sigma(F_o)]^2$  weights were applied in later cycles. Reflections for which  $I_c < 3\sigma(I_o)$  were not included in the calculations. H atoms were located in a difference map. Individual anisotropic temperature factors were used for C, O, N, and S, with isotropic terms for H. Scattering factors for C, N, O, and S were those of Cromer & Mann (1968), and for H those of Stewart, Davidson & Simpson (1965). The final  $R$  ( $\sum |F_o - F_c|/\sum F_o$ ) and weighted  $R$   $\{[\sum w(F_o - F_c)^2/\sum wF_o^2]^{1/2}\}$  factors are 0.043 and 0.036. Fractional atomic coordinates are listed in Table 1.\*

Table 1. Fractional atomic coordinates with e.s.d.'s in parentheses

	x	y	z
C(2)	0.7224 (3)	0.2336 (2)	0.49375 (9)
C(6)	1.0052 (3)	0.3306 (2)	0.52288 (8)
C(7)	0.9444 (3)	0.2729 (2)	0.37872 (8)
C(8)	1.0571 (3)	0.3409 (2)	0.36227 (8)
C(9)	0.5597 (3)	0.1914 (2)	0.4988 (1)
C(10)	0.5081 (3)	0.1606 (2)	0.5489 (1)
C(11)	0.3578 (4)	0.1147 (3)	0.5508 (2)
C(12)	0.2633 (5)	0.1002 (3)	0.5044 (2)
C(13)	0.3114 (4)	0.1318 (3)	0.4545 (2)
C(14)	0.4609 (3)	0.1778 (3)	0.4517 (1)
C(15)	1.1352 (3)	0.3822 (2)	0.55854 (8)
C(16)	1.1440 (3)	0.3720 (3)	0.6151 (1)
C(17)	1.2737 (4)	0.4160 (3)	0.6462 (1)
C(18)	1.3931 (4)	0.4698 (3)	0.6227 (1)
C(19)	1.3840 (4)	0.4813 (3)	0.5668 (1)
C(20)	1.2568 (3)	0.4383 (2)	0.5349 (1)
C(21)	0.8446 (3)	0.1869 (2)	0.34609 (9)
C(22)	0.7148 (3)	0.2272 (3)	0.3137 (1)
C(23)	0.6215 (5)	0.1430 (4)	0.2837 (1)
C(24)	0.6603 (6)	0.0247 (4)	0.2865 (1)
C(25)	0.7900 (5)	-0.0141 (3)	0.3173 (1)
C(26)	0.8810 (4)	0.0667 (2)	0.3480 (1)
C(27)	1.1204 (3)	0.3458 (2)	0.30842 (8)
C(28)	1.2188 (3)	0.4382 (3)	0.2993 (1)
C(29)	1.2855 (4)	0.4497 (3)	0.2500 (1)
C(30)	1.2548 (4)	0.3677 (3)	0.2094 (1)
C(31)	1.1556 (4)	0.2787 (3)	0.2171 (1)
C(32)	1.0874 (4)	0.2667 (2)	0.2659 (1)
N(3)	0.7691 (2)	0.2375 (2)	0.44533 (7)
N(4)	0.9113 (2)	0.2771 (2)	0.43541 (7)
N(5)	1.0203 (2)	0.3253 (2)	0.47088 (6)
O(1)	0.8927 (2)	0.1596 (2)	0.58043 (6)
O(2)	0.7733 (2)	0.3593 (2)	0.58446 (6)
S	0.84398 (8)	0.26896 (6)	0.55300 (2)
H(8)	1.112 (2)	0.393 (1)	0.3870 (6)
H(10)	0.582 (3)	0.170 (2)	0.587 (1)
H(11)	0.327 (4)	0.092 (3)	0.590 (1)
H(12)	0.167 (3)	0.067 (2)	0.504 (1)
H(13)	0.250 (4)	0.109 (3)	0.415 (1)
H(14)	0.496 (3)	0.197 (2)	0.4164 (8)
H(16)	1.059 (3)	0.331 (2)	0.6334 (8)
H(17)	1.283 (3)	0.404 (2)	0.6843 (8)
H(18)	1.488 (3)	0.502 (2)	0.6436 (8)
H(19)	1.462 (3)	0.524 (2)	0.5509 (9)
H(20)	1.251 (2)	0.447 (2)	0.4949 (8)
H(22)	0.693 (3)	0.318 (2)	0.3120 (8)
H(23)	0.537 (3)	0.186 (2)	0.263 (1)
H(24)	0.597 (3)	-0.024 (2)	0.264 (1)
H(25)	0.820 (4)	-0.098 (2)	0.319 (1)
H(26)	0.974 (3)	0.039 (2)	0.3724 (8)
H(28)	1.238 (3)	0.503 (2)	0.3273 (9)
H(29)	1.355 (4)	0.519 (3)	0.246 (1)
H(30)	1.301 (3)	0.373 (2)	0.1751 (8)
H(31)	1.130 (3)	0.222 (2)	0.1877 (9)
H(32)	1.028 (3)	0.197 (2)	0.272 (1)

\* Lists of structure factors, temperature factors, and all bond lengths and angles involving H have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35217 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

**Discussion.** An ORTEP II (Johnson, 1971) drawing of (II) including bond lengths and angles is shown in Fig. 1. (II) is a member of the previously unknown class of thiatriazine 1,1-dioxides, with N atoms at positions 3, 4, and 5. The thiatriazine ring is slightly boat shaped; the angles between the bottom plane [N(3)-N(5)-



S—O(1)	1.440 (2)	C(21)—C(22)	1.385 (4)	C(23)—C(24)	1.363 (7)	C(25)—C(26)	1.375 (5)
S—O(2)	1.438 (2)	C(22)—C(23)	1.402 (5)	C(24)—C(25)	1.361 (6)	C(26)—C(21)	1.378 (4)
O(1)—S—O(2)	117.6 (1)	O(2)—S—C(6)	109.6 (1)	C(26)—C(21)—C(22)	120.3 (2)	C(23)—C(24)—C(25)	121.3 (4)
O(1)—S—C(2)	108.9 (1)	C(7)—C(21)—C(22)	119.9 (2)	C(21)—C(22)—C(23)	118.5 (3)	C(24)—C(25)—C(26)	119.6 (4)
O(2)—S—C(2)	110.8 (1)	C(7)—C(21)—C(26)	110.8 (2)	C(22)—C(23)—C(24)	120.0 (3)	C(25)—C(26)—C(21)	120.3 (3)
O(1)—S—C(6)	108.8 (1)						

Fig. 1. An ORTEP drawing viewed normal to the six-atom thiaziazine ring; the C, N, O, and S atoms are drawn as 50% ellipsoids and the H atoms are shown as 0.1 Å spheres. Bond lengths (Å), angles (°) and e.s.d.'s (in parentheses) are shown for all non-hydrogen atoms. Each H atom bears the number of the C to which it is attached.

C(2)—C(6)] and the two end planes [N(3)—N(4)—N(5) and C(2)—S—C(6)] are 4.7 and 8.4°, respectively. As is typical of sulfones, the O atoms are symmetrically disposed about the plane defined by S and the C atoms adjacent to it. The phenyl substituents bonded to C(2) and C(6) are somewhat twisted (*ca* 10°) with respect to the thiaziazine ring, presumably to minimize steric interactions between the ring and the closest phenyl H atoms. In particular, H(10) and H(16) are equidistant from the sulfonyl O atoms and the H(14)—N(3) and H(20)—N(5) distances at 2.43 (2) Å are slightly less than the sum of the van der Waals radii of N and H (*ca* 2.5 Å).

*sp*<sup>2</sup> hybridization for N(4) is suggested by the angle sum of 359.9 (2)°. The thiaziazine ring is twisted with respect to the plane of the olefin [dihedral angle about

N(4)—C(7) is *ca* 20°] so that its convex face is nearest to H(8). The aromatic substituents on C(7) and C(8) are also not coplanar with the olefin; the former is twisted *ca* 80° and the latter *ca* 10°. Relief of steric strain clearly is the reason for the severe twist of the C(7) aromatic ring. The resulting C(21)⋯H(32) distance of 2.52 (3) Å is less than the *ca* 2.7 Å van der Waals contact for an aromatic ring and a proton.

Normal values were found for all bond lengths and angles. The N(4)—C(7) distance of 1.448 (3) Å, which is typical of C—N single bonds, suggests that the thiaziazine ring and olefin  $\pi$  systems are isolated. The bottom half of the molecule, therefore, can be viewed as a possible model for *cis*-stilbene. The 1.321 (4) Å C(7)—C(8) distance is close to the 1.31 (1) and 1.339 (7) Å values found in *trans*-stilbene (Finder,

Newton & Allinger, 1974) and 1,2-diphenylcyclopentene (a *cis*-stilbene model) (Bernstein, 1975).

There are no unusual intermolecular distances.

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### Méthoxy-3 Oestratriène-1,3,5(10) Yle-17β Méthanol

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**Abstract.** C<sub>20</sub>H<sub>28</sub>O<sub>2</sub>, orthorhombic, *P*<sub>2</sub><sub>1</sub><sub>2</sub><sub>1</sub>, *a* = 22.873 (6), *b* = 12.155 (4), *c* = 6.051 (3) Å, *Z* = 4, *d*<sub>c</sub> = 1.19 Mg m<sup>-3</sup>. The structure was solved by direct methods and refined to an *R* of 0.059 for 1317 observed reflections measured with an automatic diffractometer. The methanol group [C(97)–O(98)] statistically occupies two positions (50%). The overall conformation of the molecule is slightly disturbed by the presence of the methoxy group on the *A* ring of the steroid.

**Introduction.** Comme annoncé dans un article précédent (Précigoux, Marsau, Leroy & Busetta, 1980), l'étude de quelques dérivés substitués de l'oestradiol a été entreprise pour vérifier une hypothèse concernant les relations structure–affinité pour le récepteur utérin de l'oestradiol. Les cristaux du composé ont été obtenus par une lente évaporation d'une solution acétonique. Les intensités de 1740 réflexions (1317 observées) ont été mesurées à l'aide d'un diffractomètre Siemens en utilisant la radiation Cu *K*<sub>α</sub>. La structure a été résolue par méthodes directes avec le programme *SIR* (Giacovazzo, 1977; Busetta, 1978). L'affinement par moindres carrés des paramètres atomiques a permis de mettre en évidence un désordre statistique pour le groupement méthanol

situé en position 17β. Le facteur d'occupation des sites C(97) et O(98), évalué à 0,5, reste le même après plusieurs cycles d'affinement. Les facteurs de diffusion atomique ont été extraits de *International Tables for X-ray Crystallography* (1974) pour les atomes autres que les atomes d'hydrogène et sont ceux de Stewart, Davidson & Simpson (1965) pour les atomes d'hydrogène. Les derniers cycles d'affinement tenant compte des paramètres d'agitation thermique anisotrope ont conduit à un facteur résiduel *R* de 0,059. Le schéma de pondération utilisé a été le suivant:  $\omega^{1/2} = 1$  si  $F_o < p$  et  $\omega^{1/2} = p/F_o$  si  $F_o > p$  avec  $p = [F_o^2(\max.)/10]^{1/2}$ .

Le Tableau 1 donne les coordonnées atomiques et la Fig. 1 représente les distances et angles de valence et les angles de torsion.\*

**Discussion.** La conformation de la molécule est proche de celle déjà trouvée pour la molécule d'hydroxyméthyle-17β oestratriène-1,3,5(10) ol-3 (Précigoux,

\* Les listes des facteurs de structure, des facteurs d'agitation thermique et des coordonnées des atomes hydrogène ont été déposées au dépôt d'archives de la British Library Lending Division (Supplementary Publication No. SUP 35199: 15 pp.). On peut en obtenir des copies en s'adressant à: The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, Angleterre.