Table 3. *Comparison of selected distances* (Å), *angles* (°) *and torsion angles* (°) *in complexed and uncomplexed* 2,4-*dinitrophenol*

Atomic nomenclature used is that of the present work.

	Title complex	2,4-Dinitrophenol (Iwasaki & Kawano, 1977)
N(18)–O(19)	1·171 (5)	1·240 (6)
O(11)···O(19)	2·596 (5)	2·615 (6)
O(11)–C(12)–C(13)	120·8 (3)	125·6 (4)
C(13)–N(18)–O(19)	121·3 (4)	117·9 (4)
C(13)–N(18)–O(20)	116·7 (3)	119·0 (4)
C(12)–C(13)–N(18)–O(19)	6·2 (5)	1·9 (5)
C(16)–C(15)–N(21)–O(23)	7·7 (5)	−5·2 (4)
C(13)–C(12)–O(11)–H(11)	−176 (2)	−12 (3)

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References

Bandy, J. A., Truter, M. R. & Vögtle, F. (1981). *Acta Cryst.* B**37**, 1568–1571.

Caira, M. R., Watson, W. H., Vögtle, F. & Müller, W. M. (1984). *Acta Cryst.* C**40**, 136–138.

Goldberg, I. (1975). *Acta Cryst.* B**31**, 754–762.

Grossie, D. A., Watson, W. H. Vögtle, F. & Müller, W. M. (1982). *Acta Cryst.* B**38**, 3157–3159.

Iwasaki, F. & Kawano, Y. (1977). *Acta Cryst.* B**33**, 2455–2459.

Johnson, C. K. (1971). *ORTEP*II. Report ORNL-3794, revised. Oak Ridge National Laboratory, Tennessee.

Knochel, A., Kopf, J., Oehler, J. & Rudolph, G. (1978). *J. Chem. Soc. Chem. Commun.* pp. 595–596.

Main, P., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1978). *MULTAN78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

Stewart, J. M., Machin, P. A., Dickinson, C. W., Ammon, H. L., Heck, H. & Flack, H. (1976). The XRAY76 system. Tech. Rep. TR-446. Computer Science Center, Univ. of Maryland, College Park, Maryland.

Trotter, J. & Williston, C. S. (1966). *Acta Cryst.* **21**, 285–288.

Trueblood, K. N., Goldish, E. & Donohue, (1961). *Acta Cryst.* **14**, 1009–1017.

Watson, W. H., Galloy, J., Grossie, D. A., Vögtle, F. & Müller, W. M. (1983). *J. Org. Chem.* Submitted.

Acta Cryst. (1984). C**40**, 493–498

Structures of 2-Cyano-3-(4-diethylaminophenyl)thioacrylamide, $C_{14}H_{17}N_3S$, and 6-Amino-3,5-dicyano-3,4-dihydro-2,4-bis(3-methoxyphenyl)-2*H*-thiapyran-3-carbothioamide* Ethanol Solvate (1:1), $C_{22}H_{20}N_4O_2S_2.C_2H_6O$

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Abstract. $C_{14}H_{17}N_3S$: $M_r = 259{\cdot}4$, monoclinic, $P2_1/n$, $a = 10{\cdot}7555$ (11), $b = 12{\cdot}3646$ (13), $c = 10{\cdot}8680$ (10) Å, $\beta = 104{\cdot}254$ (7)°, $U = 1400{\cdot}8$ (2) Å^3, $Z = 4$, $D_m = 1{\cdot}24$, $D_x = 1{\cdot}230$ Mg m^{-3}, λ(Cu $K\alpha$) = 1·54178 Å, $\mu = 1{\cdot}83$ mm^{-1}, $F(000) = 552$, $T = 291$ (2) K, final $R = 0{\cdot}083$ for 1866 observed reflections. The aryl and thioamide groups occupy *trans* positions across the alkene double bond, whilst the diene fragment C=C—C=S has an *s-trans* geometry. The stereochemical consequences of conjugation in this molecule are successive twists of 8·3 and 18·9° about the single bonds linking aryl and alkene, and alkene and

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* IUPAC name: 6-amino-3,5-dicyano-3,4-dihydro-2,4-bis(3-methoxyphenyl)-2*H*-thiin-3-carbothioamide.

† To whom correspondence should be addressed.

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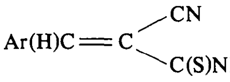
thioalkene, respectively. $C_{22}H_{20}N_4O_2S_2.C_2H_6O$: $M_r = 482{\cdot}6$, triclinic, $P\bar{1}$, $a = 12{\cdot}974\ (2)$, $b = 12{\cdot}6448\ (13)$, $c = 9{\cdot}0253\ (6)$ Å, $\alpha = 100{\cdot}051\ (7)$, $\beta = 69{\cdot}029\ (9)$, $\gamma = 118{\cdot}252\ (10)^\circ$, $U = 1220{\cdot}7\ (3)$ Å^3, $Z = 2$, $D_m = 1{\cdot}31$, $D_x = 1{\cdot}313$ Mg m^{-3}, $\lambda(\mathrm{Cu}\ K\alpha) = 1{\cdot}54178$ Å, $\mu = 2{\cdot}13$ mm^{-1}, $F(000) = 508$, $T = 291\ (2)$ K, final $R = 0{\cdot}102$ for 1770 observed reflections. The thiapyran ring has a distorted half-chair conformation. The stereochemical pattern of the saturated residue C(3)-C(4)C(5) is, respectively, $\mathrm{Ar_{eq}CN_{ax}Ar_{eq}}$, and this has been rationalized on intramolecular steric grounds.

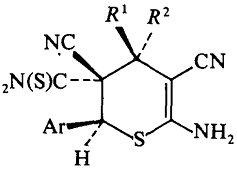
Introduction. Recently, certain 3-aryl-2-cyanothioacrylamides, (1), have been shown to undergo thermally induced Diels–Alder-type dimerizations affording substituted 3,4-dihydro-2*H*-thiapyrans (Brunskill, De & Ewing, 1978).



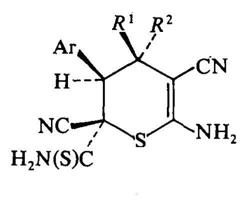
$$\mathrm{Ar(H)C{=}C}\begin{matrix}\diagup\mathrm{CN}\\ \diagdown\mathrm{C(S)NH_2}\end{matrix}$$

(1)

Assuming that the correct stereochemistry of (1) is that with aryl and thioamide groups *trans*, and that the approach of diene and dienophile is suprafacial–suprafacial, ($4_S + 2_S$), four possible dimeric products could have been envisaged: two stereoisomers of 2,4-diaryl derivatives of 6-amino-3,5-dicyano-3,4-dihydro-2*H*-thiapyran-3-carbothioamide, (2) [(2i) Ar, CN, H *cis*; (2ii) Ar, CN, Ar *cis*] and two stereoisomers of 3,4-diaryl derivatives of 6-amino-2,5-dicyano-3,4-dihydro-2*H*-thiapyran-2-carbothioamide, (3) [(3i) CN, Ar, H *cis*; (3ii) CN, Ar, Ar *cis*].



(2i) $R^1 = \mathrm{H}, R^2 = \mathrm{Ar}$
(2ii) $R^1 = \mathrm{Ar}, R^2 = \mathrm{H}$



(3i) $R^1 = \mathrm{H}, R^2 = \mathrm{Ar}$
(3ii) $R^1 = \mathrm{Ar}, R^2 = \mathrm{H}$

However, no evidence of (3) was found from analysis of the ^{1}H NMR spectra, establishing the regioselectivity of the cycloaddition. Furthermore, the reaction appeared totally stereospecific, since only one isomer of (2) is formed for a variety of aryl substituents. Although a frontier-orbital analysis suggested that secondary-overlap considerations slightly favoured an *endo*-transition* state [which leads to (2i)] rather than an *exo*-transition* state [leading to (2ii)], the precise stereochemical nature of (2) remained in doubt particularly as such analyses take no account of steric effects.

Accordingly, we have undertaken single-crystal diffraction experiments on one derivative of each of the compounds (1) and (2), in the former case to confirm the *trans* arrangement of aryl and thioamide functions, and in the latter case to define exactly the product stereochemistry. Suitable crystals were obtained as (1*a*) ($\mathrm{Ar = 4\text{-}Et_2NC_6H_4}$) and as the ethanol solvate (1:1) of (2*b*) ($\mathrm{Ar = 3\text{-}MeOC_6H_4}$).

Experimental. (1*a*): dark-red blocks, $0{\cdot}04 \times 0{\cdot}03 \times 0{\cdot}02$ cm; space group identified by Weissenberg photography; CAD-4 diffractometer; 25 reflections ($25 < \theta < 30^\circ$) centred; graphite-monochromated Cu $K\alpha$ radiation; for data collection $\theta_{\max} = 70^\circ$, ω–2θ scan in 96 steps, ω-scan width $(0{\cdot}75 + 0{\cdot}15\tan\theta)^\circ$; rapid prescan after which reflections with $I \geq 2{\cdot}0\sigma(I)$ remeasured such that final net intensity had $I > 33\sigma(I)$ subject to maximum measuring time of 60 s; no significant crystal decay or movement; 2651 unique reflections; no absorption correction; for structure solution and refinement 1866 amplitudes [$F \geq 2{\cdot}0\sigma(F)$]; Patterson (S) and difference Fourier methods; full-matrix least squares (F); $w^{-1} = [\sigma^2(F) + 0{\cdot}0365(F)^2]$; anisotropic thermal parameters for all non-H atoms, amino-H atoms positionally refined ($U^{*}_{\mathrm{H}} = 0{\cdot}08$ Å^2), methyl functions treated as rigid groups ($U_{\mathrm{H}} = 0{\cdot}10$ Å^2) (see Table 2, deposited), other H atoms idealized (C—H = 1·08 Å, $U_{\mathrm{H}} = 0{\cdot}08$ Å^2); R 0·083, wR 0·111; data:variable ratio 10:1; $(\Delta/\sigma)_{\max}$ in final cycle <0·004; largest residue in final $\Delta\rho$ map 0·38 e Å^{-3}.

(2*b*) as above with following exceptions: pale-yellow blocks, $0{\cdot}03 \times 0{\cdot}02 \times 0{\cdot}02$ cm; space group identified by E statistics and successful refinement; 19 reflections ($20 < \theta < 30^\circ$) centred; for data collection $\theta_{\max} = 45^\circ$, ω-scan width $(1{\cdot}00 + 0{\cdot}14\tan\theta)^\circ$; after prescan reflections with $I \geq 1{\cdot}0\sigma(I)$ remeasured such that $I > 100\sigma(I)$ at maximum time of 30 s; 1920 unique reflections; for structure solution and refinement 1770 reflections [$F \geq 2{\cdot}0\sigma(F)$]; automatic centrosymmetric direct methods (Sheldrick, 1976); full-matrix least squares (F); $w^{-1} = [\sigma^2(F) + 0{\cdot}00419(F)^2]$; mixed isotropic/anisotropic thermal parameters; H(2), H(4) and amino-H atoms positionally refined ($U_{\mathrm{H}} = 0{\cdot}06$ Å^2), aryl-H and methylene-H atoms idealized (C—H = 1·08 Å, $U_{\mathrm{H}} = 0{\cdot}08$ and 0·15 Å^2, respectively), methoxy-methyl groups treated as rigid ($U_{\mathrm{H}} = 0{\cdot}10$ Å^2) (see Tables 2 and 7, deposited); R 0·102, wR 0·117; data:variable ratio 7:1; $(\Delta/\sigma)_{\max}$ in final cycle <0·4; largest residue 0·70 e Å^{-3}.

Neutral-atom scattering factors for C,N,O,S (Cromer & Liberman, 1970) and H (Stewart, Davidson & Simpson, 1965). No corrections for secondary

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* These terms are used arbitrarily. *endo* corresponds to H of the dienophile approaching S of the diene, whilst *exo* corresponds to Ar of the dienophile approaching S of the diene.

* The isotropic temperature factor is defined as $\exp[-8\pi^2 \times U(\sin^2\theta)/\lambda^2]$.

extinction. Computer programs: *SHELX*76 (Sheldrick, 1976), *XANADU* (Roberts & Sheldrick, 1976), and *ORTEP*II (Johnson, 1976).

Discussion. *Compound* (1*a*). Table 1 lists the fractional coordinates and (where appropriate) equivalent isotropic thermal parameters of the refined atoms; fractional coordinates of idealized H atoms have been deposited as Table 2.* Internuclear distances and interbond angles appear in Table 3. In Table 4 (deposited) we present the results of least-squares-planes' calculations for four molecular fragments. Fig. 1 views a single molecule of (1*a*) projected onto the aryl plane and demonstrates the atomic numbering scheme adopted.

In (1*a*) the aryl and thioamide functions occupy *trans* positions across the double bond C(2)—C(3), 1·361 (8) Å. A *trans* geometry has previously been established for 2-cyanocinnamamide [the oxygen analogue of (1) with Ar = Ph] from its infrared spectrum (Zabicky, 1961) but this technique cannot be confidently employed for stereochemical analysis of compounds (1) because of spectral congestion in the thiocarbonyl absorption region. The aryl and alkene moieties are not coplanar, but inclined at a dihedral angle of 15 (1)°. More relevant is a twist about C(4)—C(3), 8 (1)°, the direction of which is such that, with respect to Fig. 1, H(3) is slightly below, and the C(21)N(21) function slightly above the aryl plane. The origin of this distortion may be traced to two intramolecular repulsive contacts (Table 5, deposited): H(9)···N(21) 2·55 and H(3)···H(5) 2·20 Å. Both are less than the appropriate van der Waals sums by comparable amounts (*ca* 0·15–0·20 Å), but it is likely that in an idealized molecule the former would be considerably more serious, since an idealized geometry would not only involve no twist about C(4)—C(3), but also valence angles of 120° at C(4) and C(3). In the molecular structure found C(9)—C(4)—C(3) is *ca* 7° more, and C(5)—C(4)—C(3) *ca* 4° less than this figure, whilst C(4)—C(3)—C(2) is severely distorted, 133·9 (5)°; indeed, in an idealized molecule H(3) and H(5) would not be in close contact.

In (1*a*) the 4-diethylaminophenyl fragment has effective C_2 symmetry, clearly the preferred stereochemistry of such moieties (Smith & Barrett, 1971; Talberg, 1977; Einstein, Sutton & Vogel, 1978), and one in which the C—N multiple bond, 1·365 (8) Å, is achieved in spite of two very short phenyl-H··· methylene-H contacts [H(6)···H(73) 1·92 and H(8)··· H(71) 1·87 Å in the present compound].

Table 1. *Atomic coordinates* (×10⁴, *for* S ×10⁵, *for* H ×10³), *with e.s.d.'s in parentheses, for refined atoms in the monomer* (1*a*), *together with equivalent isotropic thermal parameters* (×10³) *for non-hydrogen atoms*

$$U_{\rm eq} = \tfrac{1}{3}\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	*y*	*z*	$U_{\rm eq}$(Å^2)
S	4489 (17)	16537 (12)	−8675 (16)	60·3 (10)
C(1)	994 (5)	658 (4)	−1638 (6)	45 (3)
N(1)	919 (7)	−380 (4)	−1324 (6)	67 (4)
H(1)	134 (6)	−78 (7)	−156 (8)	
H(2)	60 (8)	−54 (7)	−64 (8)	
C(2)	1575 (5)	865 (4)	−2696 (5)	45 (3)
C(21)	2010 (6)	1961 (5)	−2794 (6)	50 (3)
N(21)	2370 (6)	2806 (4)	−2940 (6)	74 (4)
C(3)	1653 (5)	106 (4)	−3580 (6)	47 (3)
C(4)	2229 (5)	82 (4)	−4630 (5)	44 (3)
C(5)	1977 (7)	−848 (5)	−5415 (6)	59 (4)
C(6)	2481 (7)	−985 (5)	−6436 (6)	63 (4)
C(7)	3331 (5)	−218 (5)	−6732 (5)	47 (3)
C(8)	3617 (6)	713 (5)	−5946 (6)	53 (3)
C(9)	3075 (6)	845 (4)	−4936 (6)	52 (4)
N(7)	3873 (5)	−370 (4)	−7731 (5)	59 (3)
C(71)	4775 (5)	413 (5)	−8046 (6)	54 (4)
C(711)	4103 (8)	1260 (7)	−8974 (8)	76 (5)
C(72)	3502 (6)	−1294 (6)	−8607 (6)	61 (4)
C(721)	4295 (10)	−2281 (7)	−8139 (11)	87 (6)

Table 3. *Bond distances* (Å) *and angles* (°), *with e.s.d.'s in parentheses, in the monomer* (1*a*)

S—C(1)	1·674 (6)	C(5)—C(6)	1·360 (9)
C(1)—N(1)	1·366 (7)	C(6)—C(7)	1·409 (8)
N(1)—H(1)	0·75 (9)	C(7)—C(8)	1·421 (8)
N(1)—H(2)	0·91 (8)	C(8)—C(9)	1·374 (8)
C(1)—C(2)	1·460 (8)	C(9)—C(4)	1·406 (7)
C(2)—C(21)	1·445 (7)	C(7)—N(7)	1·365 (8)
C(21)—N(21)	1·139 (8)	N(7)—C(71)	1·470 (8)
C(2)—C(3)	1·361 (8)	C(71)—C(711)	1·509 (10)
C(3)—C(4)	1·427 (8)	N(7)—C(72)	1·478 (8)
C(4)—C(5)	1·418 (8)	C(72)—C(721)	1·504 (11)

S—C(1)—N(1)	121·9 (5)	C(5)—C(4)—C(9)	116·2 (5)
S—C(1)—C(2)	122·4 (4)	C(4)—C(5)—C(6)	122·4 (6)
N(1)—C(1)—C(2)	115·8 (5)	C(5)—C(6)—C(7)	120·9 (6)
C(1)—N(1)—H(1)	118 (7)	C(6)—C(7)—N(7)	121·1 (5)
C(1)—N(1)—H(2)	118 (5)	C(6)—C(7)—C(8)	117·7 (5)
H(1)—N(1)—H(2)	121 (8)	N(7)—C(7)—C(8)	121·2 (5)
C(1)—C(2)—C(21)	115·6 (5)	C(7)—C(8)—C(9)	120·4 (5)
C(1)—C(2)—C(3)	123·2 (5)	C(8)—C(9)—C(4)	122·4 (5)
C(21)—C(2)—C(3)	121·2 (5)	C(7)—N(7)—C(71)	122·0 (5)
C(2)—C(21)—N(21)	175·7 (6)	C(7)—N(7)—C(72)	121·2 (5)
C(2)—C(3)—C(4)	133·9 (5)	C(71)—N(7)—C(72)	116·6 (5)
C(3)—C(4)—C(5)	116·2 (5)	N(7)—C(71)—C(711)	112·2 (5)
C(3)—C(4)—C(9)	127·5 (5)	N(7)—C(72)—C(721)	111·6 (6)

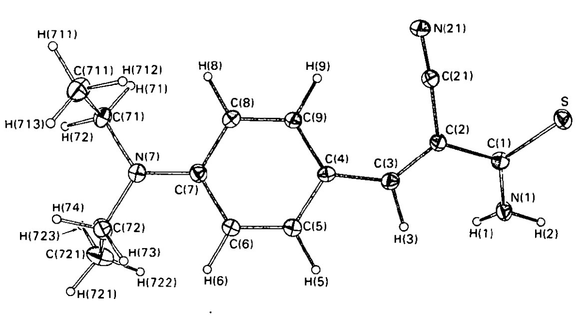

Fig. 1. Perspective view of (1*a*). In all figures, atoms (except H) are drawn with 30% probability ellipsoids (Johnson, 1976). H atoms are given an artificial radius of 0·1 Å for clarity.

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* Lists of structure factors, anisotropic thermal parameters, and Tables 2,4,5,7,9 and 10 have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39008 (26 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

An important result of the analysis is that in (1*a*) the diene fragment [the sequence S=C(1)–C(2)=C(3)] adopts an *s-trans* geometry in the crystal. The diene atoms are not co-planar: there is a twist of 19 (1)° about the C(1)–C(2) bond, this twist operating in the same sense as that about C(4)–C(3). Once again, the twisting distortion may be traced to a repulsive contact between non-bonded atoms, H(1)···H(3) 2·04 Å.

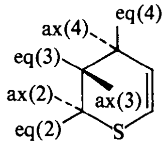
The crystal packing of (1*a*) is reproduced in Fig. 2. Intermolecular H(2)···S hydrogen bonding creates weakly bound dimeric units linked 'head-to-head'. In addition, quasi-graphitic interactions across further symmetry centres are apparent, the aryl ring and its inversion (through $\frac{1}{2}$, 0, $\frac{1}{2}$) related equivalent lying in (necessarily parallel) planes 3·602 Å apart with their ring centroids separated by 4·604 Å, *ca* 0·1 Å less than the critical limit (Welch, 1974). This second feature of the packing aligns parallel molecules 'head-to-tail', and consequently the overall crystal structure consists of infinite chains linked by alternating H bonding and graphitic bonding.

Compound (2*b*). The dimer (2*b*) co-crystallizes (1:1) with ethanol solvent. Positional and isotropic or equivalent isotropic thermal parameters are given in Table 6, whilst bond distances and angles between refined atoms are listed in Table 8. Fig. 3 presents a perspective view of the dimer and establishes the numbering scheme used. Table 7 (deposited) contains the coordinates of idealized H atoms.

The structural study reveals that the stereochemistry of this dimer is of type (2ii), *i.e.* Ar, CN, Ar *cis*. Although the cycloaddition producing (2) affords only one product whatever the aryl substituent it has not yet been established that *the same* stereochemical pathway is followed in all cases. Nevertheless, the observed geometry of (2*b*) is interesting in that the alternative product (2i) was predicted by secondary-overlap arguments. Some least-squares-planes' data, and torsion angles around the heterocyclic ring, are given in Table 9 (deposited). The thiapyran ring has a distorted half-chair conformation [*i.e.* C(2) and C(3) lie on opposite sides of a plane constructed through the atomic sequence C(4)C(5)C(6)S(1)], as might have been expected from the half-chair geometry of cyclohexene (Chiang & Bauer, 1969, and references therein).

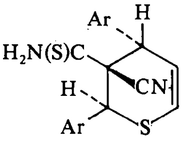
The recognition of a half-chair conformation for the thiapyran ring of (2*b*) allows an empirical discussion of steric factors of possible relevance to its formation. We find the descriptions (2i) Ar, CN, H *cis* [or (2i) H, C(S)NH_2, Ar *cis*] and (2ii) Ar, CN, Ar *cis* [or (2ii) H, C(S)NH_2, H *cis*] to be of limited value in assessing which product is sterically preferred, and shall employ instead the terms axial (ax) and equatorial (eq) for substituents.

For the half-chair thiapyran (4) the geometry is such that the closest intramolecular contact is *not* between substituents on adjacent carbon atoms but rather between ax(2) and ax(4) [furthermore, the C(2)–ax(2) and C(4)–ax(4) vectors are almost parallel].

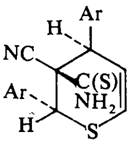


(4)

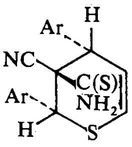
The stereochemistries (2i) and (2ii) may be subdivided [(2i′), (2i″), and (2ii′), (2ii″)], in which each pair is related as mirror images if the conformation at the C(2)C(3)C(4) fragment is inverted. Clearly, product (2ii″) will be favoured on steric grounds since the ax(2)···ax(4) interaction here is only H···H and, indeed, the crystallographically studied dimer (2*b*) described herein has the stereochemistry (2ii″). Table 8 shows that in (2*b*) the angles at C(2) and C(4) are not dramatically altered from the tetrahedral ideal, and so the measured H(2)···H(4) contact distance, 2·22 (11) Å (see Table 10, deposited), may be taken as a reasonable estimate of ax(2)···ax(4) in (4). Such a distance would be very serious (as Ar···H) in either (2i′) or (2i″) (the next most preferable conformers), and molecules with these geometries would presumably undergo significant distortion to relieve this contact, thus incurring valence-angle and/or ring-torsional strain.



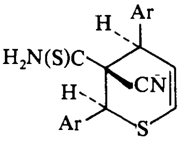
(2i′)



(2i″)



(2ii′)



(2ii″)

Generally, the molecular parameters of (2*b*) are unexceptional. The equatorial C(S)NH_2 moiety is planar [both C–NH_2 functions in (2*b*) are themselves planar with short C–N distances, C(31)–N(31) 1·336 (12) and C(6)–N(6) 1·350 (11) Å, indicative of partial multiple character] and almost perpendicular to the C(5)=C(6) alkene plane. This orientation is clearly determined by the steric influences of the (equatorial) aryl groups [the contacts S(31)···H(26) and S(31)···H(42) are just greater than the van der Waals sum at 3·18 and 3·23 Å respectively] which are also in limiting proximity to the axial C(301)N(301) unit [the four H(22)/H(46)···C(301)/N(301) contacts lie between 2·60 and 2·71 Å].

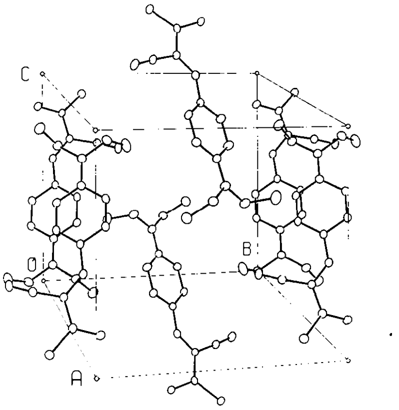


Fig. 2. Molecular-packing diagram of (1*a*).

Table 6. *Positional parameters* (×10⁴, *for* H ×10³) *and isotropic* (*U*) *or equivalent isotropic* (U_{eq}) *thermal parameters* (×10³, *non-hydrogen atoms only*) *of refined atoms in the dimer* (2*b*), *with e.s.d.'s in parentheses*

	x	*y*	*z*	*U* or U_{eq}(Å²)
S(1)	2176 (2)	1205 (2)	9873 (5)	42·3 (15)†
C(2)	2320 (8)	1511 (7)	7895 (9)	29 (5)†
C(3)	2568 (9)	542 (8)	6671 (9)	37 (5)†
C(4)	1370 (8)	−675 (7)	7084 (9)	27 (5)†
C(5)	1014 (7)	−1084 (7)	8771 (9)	27 (5)†
C(6)	1309 (8)	−342 (8)	10003 (9)	37 (5)†
H(2)	146 (7)	138 (7)	796 (8)	
C(21)	3265 (9)	2787 (8)	7548 (10)	39 (2)
C(22)	4431 (9)	3194 (8)	7666 (11)	48 (3)
C(23)	5254 (10)	4425 (9)	7449 (11)	51 (3)
C(24)	4920 (11)	5234 (10)	7149 (12)	64 (3)
C(25)	3768 (11)	4813 (11)	7030 (13)	76 (4)
C(26)	2928 (11)	3608 (10)	7230 (12)	61 (3)
O(23)	6351 (8)	4717 (7)	7620 (9)	80 (2)
C(231)	7198 (14)	6009 (13)	7630 (18)	109 (5)
C(301)	3623 (11)	441 (8)	6768 (10)	35 (6)†
N(301)	4445 (9)	361 (7)	6835 (9)	50 (6)†
C(31)	2809 (9)	887 (8)	4957 (10)	33 (5)†
S(31)	1848 (3)	1201 (2)	4586 (3)	54·8 (17)†
N(31)	3798 (9)	820 (8)	3873 (10)	62 (6)†
H(311)	389 (7)	102 (7)	288 (9)	
H(312)	454 (7)	61 (7)	398 (8)	
H(4)	73 (7)	−49 (7)	707 (9)	
C(41)	1450 (8)	−1672 (7)	5891 (9)	29 (2)
C(42)	735 (8)	−2061 (7)	4921 (10)	38 (2)
C(43)	771 (9)	−3006 (8)	3846 (11)	45 (3)
C(44)	1505 (9)	−3533 (8)	3759 (10)	43 (3)
C(45)	2225 (9)	−3118 (9)	4718 (11)	52 (3)
C(46)	2195 (9)	−2185 (8)	5811 (10)	43 (2)
O(43)	−18 (7)	−3345 (6)	2936 (8)	64 (2)
C(431)	−296 (11)	−4499 (10)	2122 (14)	73 (3)
C(501)	239 (9)	−2296 (8)	9092 (10)	42 (6)†
N(501)	−419 (10)	−3308 (8)	9377 (10)	68 (6)†
N(6)	969 (9)	−741 (8)	11476 (10)	50 (5)†
H(61)	130 (7)	−32 (7)	1224 (9)	
H(62)	64 (9)	−123 (8)	1170 (10)	
‡O(98)	4724 (12)	1394 (11)	584 (14)	138 (4)
‡C(98)	5984 (19)	2112 (19)	−208 (26)	162 (7)
‡C(99)	6818 (18)	2320 (17)	572 (24)	149 (6)

† $U_{eq} = \frac{1}{3}\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i . \mathbf{a}_j$.

‡ These atoms define the molecule of ethanol of solvation.

Table 8. *Bond distances* (Å) *and angles* (°), *with e.s.d.'s in parentheses, in the dimer* (2*b*)

S(1)–C(2)	1·818 (8)	C(31)–S(31)	1·626 (10)
C(2)–C(3)	1·575 (11)	C(31)–N(31)	1·336 (12)
C(3)–C(4)	1·565 (12)	N(31)–H(311)	0·93 (8)
C(4)–C(5)	1·532 (10)	N(31)–H(312)	1·16 (9)
C(5)–C(6)	1·366 (11)	C(4)–H(4)	0·98 (9)
C(6)–S(1)	1·737 (9)	C(4)–C(41)	1·528 (11)
C(2)–H(2)	1·04 (8)	C(41)–C(42)	1·366 (11)
C(2)–C(21)	1·497 (11)	C(42)–C(43)	1·411 (12)
C(21)–C(22)	1·387 (13)	C(43)–C(44)	1·374 (12)
C(22)–C(23)	1·411 (13)	C(44)–C(45)	1·361 (12)
C(23)–C(24)	1·383 (14)	C(45)–C(46)	1·409 (12)
C(24)–C(25)	1·369 (14)	C(46)–C(41)	1·375 (12)
C(25)–C(26)	1·390 (15)	C(43)–O(43)	1·403 (11)
C(26)–C(21)	1·408 (13)	O(43)–C(431)	1·458 (12)
C(23)–O(23)	1·350 (11)	C(5)–C(501)	1·392 (12)
O(23)–C(231)	1·479 (15)	C(501)–N(501)	1·167 (11)
C(3)–C(301)	1·466 (15)	C(6)–N(6)	1·350 (11)
C(301)–N(301)	1·141 (12)	N(6)–H(61)	0·90 (8)
C(3)–C(31)	1·562 (12)	N(6)–H(62)	0·59 (8)

C(6)–S(1)–C(2)	102·7 (4)	C(31)–N(31)–H(312)	132 (4)
S(1)–C(2)–H(2)	106 (4)	H(311)–N(31)–H(312)	117 (7)
S(1)–C(2)–C(21)	106·4 (6)	C(3)–C(4)–H(4)	104 (5)
S(1)–C(2)–C(3)	110·8 (6)	C(3)–C(4)–C(41)	113·1 (7)
H(2)–C(2)–C(21)	112 (5)	C(3)–C(4)–C(5)	112·1 (7)
H(2)–C(2)–C(3)	105 (4)	H(4)–C(4)–C(41)	110 (5)
C(21)–C(2)–C(3)	116·6 (7)	H(4)–C(4)–C(5)	107 (4)
C(2)–C(21)–C(22)	121·2 (8)	C(41)–C(4)–C(5)	110·3 (7)
C(2)–C(21)–C(26)	119·2 (9)	C(4)–C(41)–C(42)	117·9 (8)
C(22)–C(21)–C(26)	119·4 (9)	C(4)–C(41)–C(46)	121·4 (8)
C(21)–C(22)–C(23)	118·8 (9)	C(42)–C(41)–C(46)	120·7 (8)
C(22)–C(23)–C(24)	121·8 (10)	C(41)–C(42)–C(43)	118·6 (9)
C(22)–C(23)–O(23)	113·4 (9)	C(42)–C(43)–C(44)	121·5 (9)
C(24)–C(23)–O(23)	124·7 (10)	C(42)–C(43)–O(43)	113·5 (8)
C(23)–C(24)–C(25)	118·5 (11)	C(44)–C(43)–O(43)	125·0 (8)
C(24)–C(25)–C(26)	121·7 (12)	C(43)–C(44)–C(45)	119·0 (9)
C(25)–C(26)–C(21)	119·7 (11)	C(44)–C(45)–C(46)	120·5 (10)
C(23)–O(23)–C(231)	116·7 (9)	C(45)–C(46)–C(41)	119·8 (9)
C(2)–C(3)–C(4)	107·8 (7)	C(43)–O(43)–C(431)	117·0 (8)
C(2)–C(3)–C(301)	109·7 (7)	C(4)–C(5)–C(6)	125·1 (7)
C(2)–C(3)–C(31)	109·9 (7)	C(4)–C(5)–C(501)	116·7 (7)
C(4)–C(3)–C(301)	111·1 (8)	C(6)–C(5)–C(501)	118·0 (7)
C(4)–C(3)–C(31)	107·3 (7)	C(5)–C(501)–N(501)	179·2 (10)
C(301)–C(3)–C(31)	110·9 (7)	C(5)–C(6)–S(1)	124·9 (7)
C(3)–C(301)–N(301)	179·6 (6)	C(5)–C(6)–N(6)	123·1 (8)
C(3)–C(31)–S(31)	120·5 (7)	S(1)–C(6)–N(6)	112·0 (6)
C(3)–C(31)–N(31)	114·2 (9)	C(6)–N(6)–H(61)	126 (5)
S(31)–C(31)–N(31)	125·2 (7)	C(6)–N(6)–H(62)	126 (9)
C(31)–N(31)–H(311)	111 (5)	H(61)–N(6)–H(62)	108 (11)

Solvate molecule

O(98)–C(98)	1·413 (20)	O(98)–C(98)–C(99)	117·0 (19)
C(98)–C(99)	1·394 (24)		

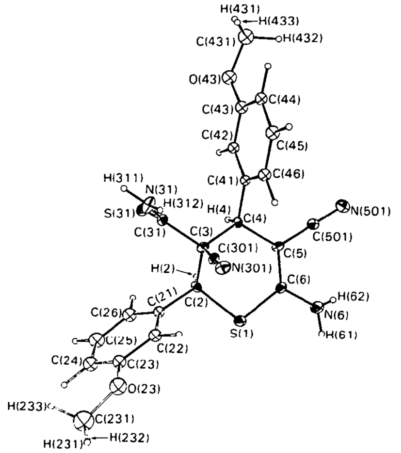


Fig. 3. Perspective view of (2*b*). Hydrogen atoms not labelled carry the same number as the C to which they are attached. H(232) is almost totally obscured by H(231).

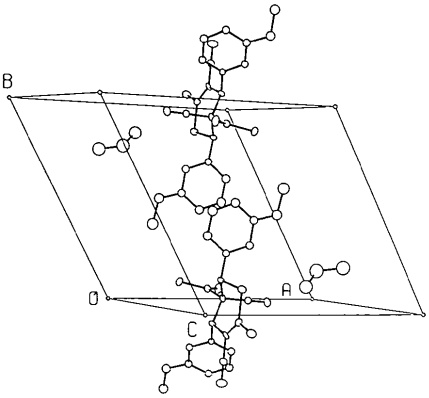


Fig. 4. The crystal structure of (2*b*).

Table 10 (deposited) also provides details of the H bonding. H(311) is H-bonded to O(98) of the ethanol solvent molecule, whilst H(61) makes a contact of 2·66 Å with S(31) of the thiapyran molecule at *x*, *y*, 1 + *z*, this 'head-to-tail' linkage generating infinite chains of (2*b*) parallel to **c**. Fig. 4 is a view of the crystal packing arrangement, and clearly shows a graphitic-like interaction between C(21)—C(26) rings related across $\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$ [these rings occupy (parallel) planes 3·505 Å apart, and the centroid–centroid distance is 4·555 Å] that cross-link pairs of the parallel chains described above.

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References

BRUNSKILL, J. S. A., DE, A. & EWING, D. F. (1978). *J. Chem. Soc. Perkin Trans.* 1, pp. 629–633.
CHIANG, J. F. & BAUER, S. H. (1969). *J. Am. Chem. Soc.* **91**, 1898–1901.
CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.
EINSTEIN, F. W. B., SUTTON, D. & VOGEL, P. L. (1978). *Can. J. Chem.* **56**, 891–895.
JOHNSON, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
ROBERTS, P. & SHELDRICK, G. M. (1976). *XANADU*. Univ. of Cambridge, England.
SHELDRICK, G. M. (1976). *SHELX*. Program for crystal structure determination. Univ. of Cambridge, England.
SMITH, D. L. & BARRETT, E. K. (1971). *Acta Cryst.* B**27**, 2043–2057.
STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
TALBERG, H. J. (1977). *Acta. Chem. Scand. Ser. A*, **31**, 743–751.
WELCH, A. J. (1974). PhD Thesis, p. 192. Univ. of London.
ZABICKY, J. (1961). *J. Chem. Soc.* pp. 683–687.

Acta Cryst. (1984). C**40**, 498–500

3a,6a-Dimethyl-2,3,3a,5,6,6a-hexahydrofuro[3,2-*b*]furan-2,5-dione, $C_8H_{10}O_4$

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Abstract. $M_r = 170{\cdot}2$, orthorhombic, $Fdd2$, $a = 13{\cdot}055$ (2), $b = 20{\cdot}759$ (2), $c = 6{\cdot}080$ (1) Å, $U = 1647{\cdot}6$ Å^3, $Z = 8$, $D_x = 1{\cdot}372$ Mg m^{-3}, $\lambda(\text{Cu } K\alpha) = 1{\cdot}5418$ Å, $\mu = 0{\cdot}95$ mm^{-1}, $F(000) = 720$, $T = 293$ K. Final $R = 0{\cdot}034$ for 296 independent observed reflexions. The molecule consists of two *cis*-fused γ-lactone rings with methyl groups attached to the bridgehead atoms. A crystallographic twofold axis passes through the midpoint of the bridgehead bond. The ring C—O distances are 1·343 (5) and 1·463 (5) Å and the lactone groups are planar. Each five-membered ring thus adopts an envelope form with the flap at the bridgehead atom. This conformation alleviates steric repulsion between the methyl groups.

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