Table 2. *Endocyclic torsion angles* (°)

Central bond	This work*	Experimental half-chair†	Calculated sofa‡
C(1)–C(2)	−0·2	0	−5·7
C(2)–C(3)	−17·9	−16	0
C(3)–C(4)	46·6	46	32
C(4)–C(5)	−60·6	−63	−58
C(5)–C(6)	41·6	46	51
C(6)–C(1)	−12·1	−16	−20

* Standard deviations are ~0·6°.
† Scharpen, Wollrab & Ames (1968).
‡ Bucourt (1974).

The best plane through selected atoms shows that C(6), C(1), C(2), C(3) are coplanar within 0·001 Å, C(4) and C(5) deviating by −0·45 (1) and 0·30 (1) Å respectively. This plane is nearly perpendicular to the planes through atoms C(5), C(4), C(11) [88·8 (4)°] and C(4), C(5), C(13) [84·5 (4)°]; the dihedral angle between these planes is −172·4 (5)°. This shows that the two cyano groups are in axial positions, in agreement with theory.

The endocyclic torsion angles reported in Table 2 show that the molecule is more half-chair (Scharpen, Wollrab & Ames, 1968) than sofa (Bucourt, 1974). However, the *gauche* interaction between the *tert*-butyl and the 4-cyano substituents in the *cis* relationship provides a stereochemical evolution from half-chair to sofa (Viani & Lapasset, 1978).

Thus, the fact that our molecule does not adopt an intermediate conformation may be ascribed to the 1,3-*syn*-diaxial interaction between the second cyano group and H(31); these develop a strong non-bonded interaction, the H···C distance being 2·67 Å, which is shorter than the sum (3·35 Å) of the van der Waals radii (Allinger, 1976).

All intermolecular distances between atoms are greater than the sum of the van der Waals radii.

The ring conformation of the title compound is half-chair because of the cyano group on C(5) which prevents the *gauche* interaction between the *tert*-butyl and the cyano group from producing a sofa, the main interaction being a 1,3-*syn*-diaxial one between the cyano group and the pseudoaxial H(31).

We are grateful to Professor H. Bodot for his stimulating contribution to this work and to Dr J. P. Aycard (Laboratoire de Chimie Organique Structurale, Université de Provence, Marseille, France) for kindly providing the sample and for helpful discussions. We wish to thank the Laboratoire de Cristallographie, Université du Languedoc, Montpellier, France, for placing the CAD-3 diffractometer at our disposal.

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7,8-Dihydro-2,5-diphenylimidazo[1,2-*f*]-1,3,4,6-thiatriazepine

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Abstract. $C_{17}H_{14}N_4S$, orthorhombic, $Pca2_1$, a = 16·62 (2), b = 8·17 (2), c = 11·15 (2) Å, Z = 4, D_m = 1·305, D_x = 1·340 Mg m^{-3}. The structure, which was solved by the application of direct methods to difference Fourier coefficients, was refined to R = 0·090. Crystal Structure Search Retrieval (CSSR) was used to compare the ring conformations with those of related molecules. The seven-membered ring exists in the usual

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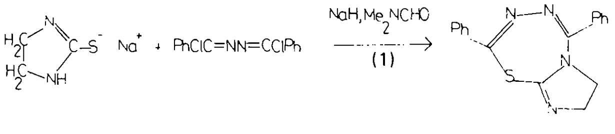
boat conformation (slightly distorted), and the ring fusion does not appear to strain the five-membered ring.

Introduction. Treatment of 1,4-dichloro-1,4-diphenyl-2,3-diaza-1,3-butadiene with the sodium salts of cyclic thioureas has yielded the new type of product shown below (Moss & Taylor, 1980).



This structure determination was undertaken in order to confirm reaction (1) and to investigate the exact nature of the product, a previously unknown type of annelated thiatriazepine.

A crystal of maximum dimensions 0·30 × 0·25 × 0·25 mm was chosen from a batch grown by slow evaporation from alcoholic solution. The unit-cell parameters (see *Abstract*) were determined from Weissenberg photographs. Conditions limiting possible reflexions in the orthorhombic system were observed to be *h*0*l*, $h = 2n$; 0*kl*, $l = 2n$; *i.e.* space groups $Pca2_1$ or *Pcam* (alternative setting of *Pbcm*). The former non-centrosymmetric space group was established by later statistical tests and confirmed during the structure determination. The density, which was measured by flotation, was 1·305 Mg m^{-3}, compared with a calculated value of 1·340 Mg m^{-3} ($Z = 4$).

Six film packs were exposed to Cu *Kα* radiation (λ = 1·5418 Å) on a Pye Unicam Weissenberg camera (*h*0*l*–*h*4*l* and cross level *hk*0). Intensity measurements, performed by the SRC microdensitometer service with an Optronics film scanner, produced 1395 reflexions, 430 of which were unique and were used in the structure determination. Lorentz and polarization corrections were applied, but absorption corrections were deemed unnecessary (μ = 1·8 mm^{-1}). *MULTAN* 78 (Germain, Main & Woolfson, 1971) was used in the conventional manner to attempt solution but succeeded only in locating the S atom (at approximately $\frac{1}{2}$,0,0). The remaining atoms were obscured by false symmetry elements generated by the strong scatterer at $\frac{1}{2}$,0,0 which taken alone conforms to a special position in the centrosymmetric space group *Pcam*, and contributes only to reflexions with *h* and *l* both equal to 2*n*. A further seven atoms were located when *MULTAN* 78 was applied to difference Fourier coefficients. Our method was influenced by, but did not directly use, the procedure employed by Hark, Prick & Beurskens (1976). The ΔF coefficients were derived by removing the S scattering from the structure factors to which it contributed, namely those reflexions with *h* and $l = 2n$. Coefficients for the remaining reflexions remained unchanged. For the strong reflexions the scattering from the S and the remainder of the cell contents was assumed to be in phase, while the weaker reflexions with *h* and *l* even were discarded. With eight atomic locations then available for generating starting phases, the remaining non-hydrogen atoms were located when *MULTAN* 78 was applied to the original data set.

SHELX (Sheldrick, 1976) was used for full-matrix least-squares refinement of the structure, with *z*(S) fixed to define the origin. Individual isotropic temperature factors were used throughout except for S, which was treated anisotropically. The phenyl C atoms were constrained to be regular hexagons, as were the phenyl H atoms which were assigned vibrational parameters matched to those of their C neighbours. The H atoms bonded to the five-membered ring were constrained to their formal sp^3 positions and given the vibrational parameters of their carbons. Scattering factors were taken from *International Tables for X-ray Crystallography* (1974). Unit weights were used throughout.

The final *R* was 0·090 with electron density fluctuations not exceeding $\pm\frac{1}{2}$e in the difference Fourier synthesis. All computations were performed on the

Table 1. *Fractional coordinates and isotropic vibrational parameters with standard deviations in parentheses*

	x	*y*	*z*	*U* (Å^2)
S(1)	0·5005 (6)	0·0102 (13)	1·0000	*
C(1)	0·5373 (14)	0·1343 (38)	0·8824 (24)	0·0247 (67)
C(2)	0·4001 (15)	0·3248 (37)	0·9829 (27)	0·0402 (82)
C(3)	0·4937 (13)	0·1697 (38)	1·1115 (20)	0·0191 (62)
C(4)	0·4538 (17)	0·4224 (36)	1·1885 (26)	0·0336 (77)
H(1)	0·3937 (17)	0·4458 (36)	1·2211 (26)	= *U*(C4)
H(2)	0·4826 (17)	0·5370 (36)	1·1663 (26)	= *U*(C4)
C(5)	0·4995 (22)	0·3234 (47)	1·2766 (32)	0·0641 (104)
H(3)	0·5517 (22)	0·3926 (47)	1·3037 (32)	= *U*(C5)
H(4)	0·4634 (22)	0·2951 (47)	1·3543 (32)	= *U*(C5)
C(6)	0·3171 (7)	0·3692 (27)	1·0058 (18)	0·0228 (59)
C(7)	0·2796 (10)	0·4742 (28)	0·9243 (16)	0·0350 (75)
C(8)	0·1999 (11)	0·5220 (29)	0·9427 (17)	0·0524 (99)
C(9)	0·1550 (8)	0·4508 (29)	1·0347 (18)	0·0397 (87)
C(10)	0·1914 (8)	0·3396 (26)	1·1127 (17)	0·0316 (71)
C(11)	0·2734 (8)	0·3051 (24)	1·1017 (17)	0·0312 (73)
H(5)	0·3149 (17)	0·5322 (73)	0·8546 (44)	= *U*(C7)
H(6)	0·1721 (19)	0·6096 (71)	0·8831 (46)	= *U*(C8)
H(7)	0·0916 (10)	0·4773 (53)	1·0428 (34)	= *U*(C9)
H(8)	0·1556 (14)	0·2761 (72)	1·1788 (47)	= *U*(C10)
H(9)	0·3019 (14)	0·2213 (46)	1·1634 (30)	= *U*(C11)
C(12)	0·6165 (8)	0·1046 (29)	0·8337 (16)	0·0270 (73)
C(13)	0·6762 (10)	0·0267 (31)	0·9007 (16)	0·0324 (74)
C(14)	0·7545 (9)	0·0160 (32)	0·8562 (18)	0·0589 (83)
C(15)	0·7739 (8)	0·0895 (29)	0·7471 (19)	0·0444 (85)
C(16)	0·7138 (9)	0·1637 (31)	0·6786 (17)	0·0494 (89)
C(17)	0·6347 (9)	0·1676 (28)	0·7207 (16)	0·0243 (65)
H(10)	0·6583 (24)	−0·0536 (169)	0·9750 (74)	= *U*(C13)
H(11)	0·8007 (17)	−0·0447 (68)	0·9079 (34)	= *U*(C14)
H(12)	0·8354 (15)	0·0898 (125)	0·7159 (53)	= *U*(C15)
H(13)	0·7284 (14)	0·2166 (67)	0·5927 (30)	= *U*(C16)
H(14)	0·5893 (22)	0·2353 (124)	0·6714 (56)	= *U*(C17)
N(1)	0·4995 (13)	0·2678 (32)	0·8448 (18)	0·0270 (55)
N(2)	0·4198 (12)	0·2901 (30)	0·8770 (21)	0·0314 (59)
N(3)	0·4512 (12)	0·3033 (29)	1·0870 (19)	0·0232 (54)
N(4)	0·5217 (10)	0·1648 (35)	1·2163 (18)	0·0274 (64)

* Anisotropic vibrational parameters for sulphur: U_{11} = 0·0416 (19), U_{22} = 0·0417 (19), U_{33} = 0·0421 (30), U_{23} = 0·0160 (59), U_{13} = 0·0217 (43), U_{12} = −0·0018 (56).

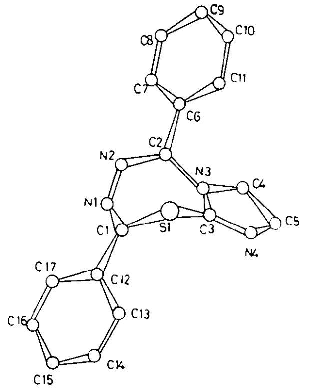


Fig. 1. The molecular skeleton showing the atom-numbering scheme.

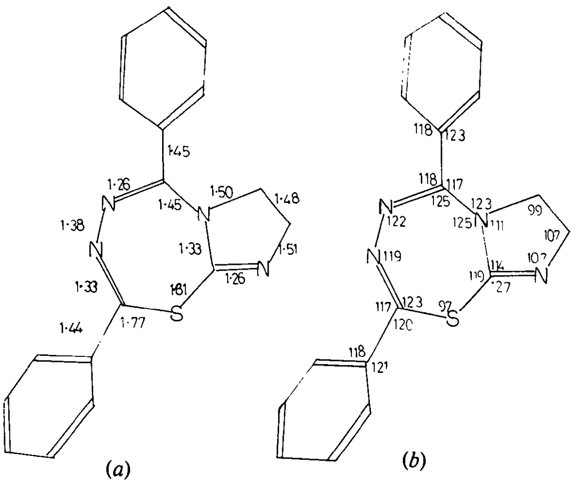
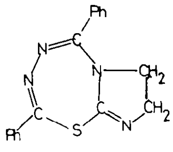


Fig. 2. (*a*) Bond lengths (Å). The average e.s.d. is 0·03 Å, excluding phenyl-ring atoms. The phenyl parameters are C—C = 1·396 (1), C—H = 1·08 (3) Å. (*b*) Bond angles (°). The average e.s.d. for the angles is 2°.

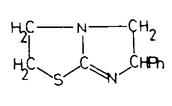
CDC 7600/1906A system at the University of Manchester Regional Computer Centre. The final positional and thermal parameters are given in Table 1.[*] Fig. 1 shows the molecular skeleton, the atom numbering, and the perspective of the ring system corresponding to the coordinates in Table 1. The bond lengths and angles are given in Fig. 2.

Discussion. The present molecule possesses an entirely new fused 7,5 ring system (Moss & Taylor, 1980) so that fragmentary comparisons only may be made with structural data for other molecules. We have made exhaustive searches for related ring fragments with the aid of the computerized Crystal Structure Search Retrieval (1980) (CSSR) system. These interactive searches were run on the DEC-10 computer at Edinburgh University, by means of the link from UMIST. The CSSR system accesses the Cambridge Crystallographic Database (CCD). We ignored conference papers throughout the searches.

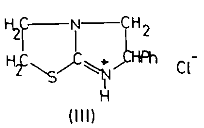
CSSR revealed structural data for numerous molecules in which the five-membered imidazoline ring is imbedded. However, restricting the search to retrieve only structures with S substituted at the C atom of the C=N bond [*i.e.* to N=C(S)—N imidazoline derivatives like the present molecule, (I)] revealed five such structures: three methylthio derivatives (not required) and two molecules with a 5,5-fused-ring system {(II): 2,3,5,6-tetrahydro-6-phenylimidazo[2,1-*b*]thiazole (Spek, 1972), and (III): 2,3,6,7-tetrahydro-6-phenyl-5*H*-imidazo[2,1-*b*]thiazolium chloride (Baker & Pauling, 1973)}.



(I)

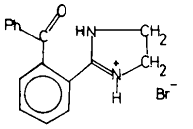


(II)

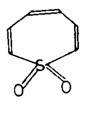


(III)

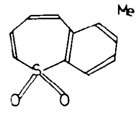
None of the five structures retrieved have imidazoline rings with unsubstituted methylene groups like those in (I). Indeed, only two of all the imidazoline derivatives retrieved possess an unsubstituted $-\mathrm{CH_2}-\mathrm{CH_2}-$ ring fragment; one of these includes the conjugated N=C(N)—N fragment, but in the other [(IV), McKechnie & Paul, 1968] the integrity of the imidazoline ring is intact. Molecule (IV) is 2-(1-imidazolin-2-yl)-benzophenone hydrobromide. The geometries of the imidazoline rings in molecules (I)–(IV) were calculated using the VIEW facility of CSSR. From the torsion angles (Table 2) it is clear that the imidazoline ring in (I) is less puckered than in the related 5,5 fused systems of (II) and (III), where the fusion presumably strains the imidazoline ring. Fusion to the seven-membered ring in (I) and no fusion at all (molecule IV) give similar torsion angles. The bond distances and angles of the imidazoline ring (I) fall within the spread of values found in molecules (II)–(IV). The signs of the torsion angles in Table 2 conform to the convention of Klyne & Prelog (1960).



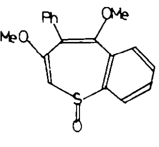
(IV)



(V)



(VI)



(VII)

CSSR searches for seven-membered-ring systems containing S revealed three molecules whose bonding is such that the ring conformations can be compared with

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[*] A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35729 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Ring conformations: comparison of ring torsion angles* (°) *in* (I) *and related molecules*

Molecule	(I)	(II)	(III)	(IV)
CSSR/CCD code	–	PIMTAZ	HPIMTZ	IMABPB
CSSR/CCD registration number	–	17584	11034	11541
Fused-ring system	5,7	5,5	5,5	–
S as N=C(S)–N	Yes	Yes	Yes	No
Unsubstituted $-CH_2-CH_2-$	Yes	No	No	Yes
Ring torsion angle about				
–N=C–	–3	0	8	1
=C–N–	6	–18	6	5
–N–C–	–5	26	–15	–9
–C–C–	3	–27	18	9
–C–N=	0	17	–16	–6

Molecule	(I)	(V)	(VI)	(VII)
CSSR/CCD code	–	THIEPO10	BZTIEP	MBZTPO
CSSR/CCD registration number	–	20632	3690	13095
Fused-ring system	5,7	–	6,7	6,7
N in thiepin ring	Yes	No	No	No
Ring torsion angle about*				
S(1)–C(3)	55	57	59	71
C(3)–N(3)†	8	–8	–10	–2
N(3)–C(2)	–46	–29	–31	–50
C(2)=N(2)	–17	–1	4	1
N(2)–N(1)	71	30	30	51
N(1)=C(1)	–16	9	6	0
C(1)–S(1)	–56	–57	–57	–73

* In molecules (V)–(VII), N(1), N(2) and N(3) are C atoms.

† Position of fusion in fused-ring systems; double bond in (V).

that of (I). No structures at all with the exact hetero-atom pattern of (I) were found. The three structures retrieved are for (V): thiepin 1,1-dioxide (Ammon, Watts & Stewart, 1970), and for the fused-ring molecules (VI): 1-benzothiepin 1,1-dioxide (Yasuoka, Kai & Kasai, 1975) and (VII): 3,5-dimethoxy-4-phenyl-1-benzothiepin 1-oxide (Hofmann, Bohme & Wilhelm, 1978). In Table 2, the ring torsion angles for the seven-membered rings, calculated using the VIEW facility, are compared. All the seven-membered rings adopt the boat conformation, with small torsion angles (<20°) around the double bonds and the site of fusion. The three C_6S rings of (V)–(VII) are almost mirror symmetrical about a plane through S and the opposite double bond. The torsion angles of (I) do not show this symmetry, presumably because of the hetero substitution; the asymmetry is greatest at the end of the molecule remote from sulphur.

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