

C(2), N(3) and C(6). The mean planes through the pyridine rings C(31) to C(36) and C(41) to N(46) form angles of 54.7 (2) and 47.4 (2)°, respectively, with the plane defined by atoms C(9), N(1) and C(8). The direction of this rotation is such that the rings tend to be parallel with the bonds C(9)—C(5) and C(8)—C(7). This orientation of the rings is quite different (approximately perpendicular) to that of the phenyl rings in the comparable chair-chair bicyclononanone (Küppers *et al.*, 1987). Whereas in several similar bicyclononanones the mean planes through the carboxylic groups [C(5), C(12), O(13), O(14) and C(7), C(16), O(17), O(18)] are nearly coplanar with the planes C(5), C(4), N(3) and C(7), C(10), N(3), respectively, (Küppers *et al.*, 1987), in the molecule in this study the planes of the carboxylic groups are tilted by 29.7 (3) and 30.3 (3)°, respectively, from these planes. This is a consequence of the reduction of the carbonyl group to an alcohol and the resulting inclination towards the pyridyl-substituted part of the molecule and the consequential spatial requirements (*cf.* Fig. 2). The distances O(11)···O(14) and O(11)···O(18) are 2.997 (3) and 2.994 (4) Å, respectively.

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Structure of *trans*-1,4,5,8-Tetrathiadecalin (Hexahydro-1,4-dithiino-[2,3-*b*]-1,4-dithiin)

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Abstract. C₆H₁₀S₄, *M_r* = 210.4, monoclinic, *P*2₁/*n*, *a* = 8.587 (2), *b* = 11.813 (2), *c* = 4.519 (1) Å, *α* = 97.65°, *V* = 454.3 (3) Å³, *D_x* = 1.538 g cm⁻³, *Z* = 2, *λ*(Mo *Kα*) = 0.71069 Å, *μ*(Mo *Kα*) = 9.31 cm⁻¹, *F*(000) = 220, *T* = 288 K, *R* = 0.034 for 819 observed reflections. Both six-membered rings are in a chair conformation, with ring dihedral angles of 66.4 (1) (central) and 68.1 (1)° (peripheral). The bond distances and angles are normal. An attractive non-bonded interaction between sulfur atoms in an S—C—S system is suggested by a short S—S distance (2.82 Å) and by a small value of the S—C—S angle (101.4°).

Introduction. 1,4,5,8-Tetraheterodecalins (1)–(3) have attracted the interest of synthetic and structural chemists, since they offer the opportunity of testing the

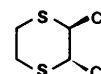
importance and geometrical consequences of anomeric effects.



- (1) x = O
 (2) x = NH
 (3) x = S



(5)



(6)

Table 1. Final atomic coordinates ($\times 10^4$, S $\times 10^5$) and equivalent isotropic thermal coefficients
$$B_{eq} = (8\pi^2/3) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	$B_{eq}(\text{\AA}^2)$
C(1)	4476 (2)	4501 (2)	4464 (5)	2.28 (8)
S(2)	51559 (6)	31767 (4)	62661 (13)	2.91 (3)
C(3)	7071 (2)	3066 (2)	5056 (6)	3.24 (10)
C(4)	8133 (3)	4045 (2)	6148 (6)	3.52 (10)
S(5)	25138 (5)	46225 (5)	55703 (14)	3.17 (3)
H(1)	4365 (31)	4466 (22)	2358 (67)	3.73 (9)
H(3)	6925 (2)	3064 (2)	2645 (6)	3.73 (9)
H(3')	7615 (2)	2282 (2)	5881 (6)	3.73 (9)
H(4)	8148 (30)	4087 (22)	8265 (64)	3.73 (9)
H(4')	9283 (31)	3893 (22)	5675 (58)	3.73 (9)

Table 2. Bond lengths (\AA) and angles ($^\circ$)

S(2)—C(1)	1.823 (2)	C(3)—S(2)	1.806 (2)
S(5)—C(1)	1.826 (2)	C(4)—C(3)	1.514 (3)
C(1)—C(1')	1.523 (4)		
S(5)—C(1)—S(2)	101.4 (1)	S(2)—C(1)—C(1')	112.4 (1)
C(3)—S(2)—C(1)	100.2 (1)	S(5)—C(1)—C(1')	112.3 (1)
C(4)—C(3)—S(2)	112.3 (2)		

Symmetry code: (i) $1-x, 1-y, 1-z$.

Among the oxygen compounds, only the *cis* isomer (1a) has been prepared (Boeseken, Tellegen & Cohen-Henriquez, 1931) and its crystal structure has been subsequently determined (Fuchs, Goldberg & Shmueli, 1972). On the other hand, the failure of the many fruitless efforts devoted to the preparation of the *trans* isomer (1b) can be explained through the unfavourable conformation, which completely lacks stabilization by anomeric effects of the conceivable transition states leading to it.

In the case of the nitrogen compounds, the parent 1,4,5,8-tetraazadecalin is known exclusively as the *trans* isomer (2b) (Fuchs & Elleneweig, 1979), but the corresponding 1,4,5,8-tetraacetyl derivative exists in both *cis* and *trans* forms, and the crystal structures of both stereoisomers have been determined (Borremans, Anteunis, Shmueli, Schleifer, Shvo & Fuchs, 1984).

Recently the preparation of *trans*-1,4,5,8-tetrathia-decalin (3b) has been reported (Pericàs, Riera & Guilera, 1986). NMR studies indicate that the compound exists in solution as a rigid conformer, with both six-membered rings in the chair form. The outer (peripheral) dihedral angle of the ring was calculated to be 62.3° by the *R*-value method (Lambert, 1971; Lambert & Sun, 1977).

Experimental. Crystals of (3b) suitable for crystallographic study were grown by slow evaporation of a solution of the compound in chloroform. Colourless tabular crystal ($0.2 \times 0.2 \times 0.1$ mm). Philips PW 1100 diffractometer. Unit-cell parameters from 25 reflections ($4 < \theta < 12^\circ$). $\text{MoK}\alpha$, graphite monochromator, ω -scan technique, scan width 0.8° , scan speed $0.03^\circ \text{ s}^{-1}$. Max. $h, k, l = 10, 13, 5$. Three reflections

every 2h as control, significant variations not observed. Lorentz-polarization correction; no absorption or extinction corrections. 1114 unique reflections measured, 819 with $I \geq 2.5\sigma(I)$. The structure was solved by direct methods using *MULTAN80* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). Refinements by full-matrix least-squares method, using *SHELX76* (Sheldrick, 1976) and minimizing $\sum w|F_o| - |F_c|^2$, with $w = [\sigma^2(F_o) + 0.0066|F_o|^2]^{-1}$. Three H atoms from $\Delta\rho$ map, the positions of the remainder being calculated. All H atoms refined with an overall isotropic temperature factor; non-hydrogen atoms refined as anisotropically vibrating; f, f' and f'' were taken from *International Tables for X-ray Crystallography* (1974). Final $R = 0.034$ ($wR = 0.040$). $(\Delta\rho)_{\text{max}}$ for non-hydrogen atoms = 0.04 for U_{23} of C(1). Max. and min. peaks in final $\Delta\rho$ map 0.3 [1.36 \AA from H(C4)] and -0.3 e \AA^{-3} , respectively.

Discussion. Final atomic coordinates and bond lengths and angles are listed in Tables 1 and 2.* A view of the molecule with atom numbering is shown in Fig. 1.

The structure consists of discrete molecules linked by van der Waals forces. The individual molecules belong to the C_{2h} point group, the inversion centre being located in the middle of the C(1)—C(1') bond. Some geometrical parameters of the molecular system deserve comment. The C(3)—C(4) distance is very similar to the analogous distance of 1.52 \AA in 2,2'-bis(1,3-dithiolane) (4) (Barricelli-Brahde, 1954), both being slightly longer than the C—C distance in 1,4-dithiane (5) (Marsh & McCullough, 1951). On the other hand, the C(1)—C(1') distance has a coincident value with that of the bond connecting the dithiolane rings in (4). Interestingly, all C—S distances have a similar value. This contrasts with the situation in *trans*-2,3-dichloro-1,4-dithiane (6) (Kalf & Romers, 1965), where anomeric effects are

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44074 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

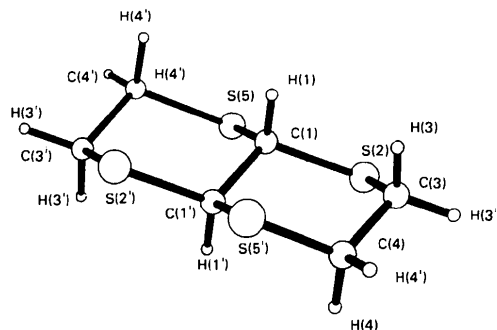


Fig. 1. View of the title compound with atom numbering.

responsible for the shortening of the (Cl)C—S bond (1.79 vs 1.84 Å). The present result confirms that stereoelectronic effects are not appreciable in (3b), a fact that could already be anticipated from the antiperiplanar arrangement of all the S—C—S—C moieties in the molecule. Among the bond angles, the C—S—C values are normal (Abrahams, 1956), as also occurs in (5) and (6). The same applies to the C—C—S angles. However, the S—C—S angle is significantly smaller than the corresponding value in (4) (101.4 vs 104°). If account is taken of the fact that the distance between S(2) and S(5) is only 2.82 Å, much smaller than the sum of van der Waals radii (3.70 Å), the small value of the S—C—S angle may indicate the existence of an attractive non-bonded interaction between the sulfur atoms. However, the possibility that the S—C—S angle could be forced to be small by the small intraannular C—S—C angles cannot be discounted. Finally, both six-membered rings have a slightly skew chair form. The S(2)—C(1)—C(1^b)—S(5ⁱ) dihedral angle has a value of -66.4 (1)°, intermediate between that of 63.5° reported for 1,4-dithiane (5) and that of 70.9° reported for the S—CH₂—CH₂—S moiety of trans-2,3-dichloro-1,4-dithiane, (6). On the other hand, the peripheral S(2)—C(3)—C(4)—S(5ⁱ) dihedral angle has a very similar value of -68.1 (1)°. The discrepancy between this torsion angle and that calculated in solution by the *R*-value method (62.3°), can be attributed to the non-bonded attraction between the sulfur atoms in the crystal, which could be partially mitigated by solvation. It is worth noting that X-ray-measured and *R*-value-calculated torsional angles rarely differ by more than 1–2° over the range from 47 to 69°, so that a difference of 6° cannot be attributed to standard errors (Lambert, 1971). The asymmetry parameters (Duax, Weeks &

Rohrer, 1976) for the rings are $\Delta C_m^1 = 6.1$; $\Delta C_m^2 = 1.0$; $\Delta C_m^3 = 5.9$; $\Delta C_2^{1-2} = 7.5$; $\Delta C_2^{2-3} = 6.9$ and $\Delta C_2^{3-4} = 2.5^\circ$.

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2,2,4,4,6,6-Hexa(1-pyrrolyl)cyclotri(phosphazene)

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Abstract. C₂₄H₂₄N₉P₃, *M_r* = 531.4, monoclinic, *P*2₁/*c*, *a* = 13.683 (2), *b* = 9.474 (1), *c* = 20.789 (3) Å, β = 104.05 (1)°, *V* = 2614 (1) Å³, *Z* = 4, *D_x* = 1.35 g cm⁻³, λ(Mo Kα) = 0.71073 Å, μ = 2.5 cm⁻¹,

F(000) = 1104, *T* = 293 (2) K, *R* = 0.041 for 2711 unique observed reflections. The PN ring is planar within 0.11 (1) Å with average P—N distances of 1.583 (6) Å, P angles of 117.7 (4)° and N angles of

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