envelope conformation with C(2) on the flap, 0·41 Å from plane I (*cf.* Table 3). Force-field calculations performed for a model [*trans*-3-(dimethylamino)-5-(1-methylethenyl)cyclopentene] of the central part of the title compound with the program *MM*2 (Allinger, 1977) indicate that only very little energy (<5 kJmol^{-1}) is needed to change the torsion angle C(3)—C(2)—C(1)—C(8) from the observed ~24° through zero to −20°, and no significant barrier has to be surmounted (*cf.* Fig. 2). This indicates that the molecule is rather flexible and that conformations different from the one observed in the crystal are accessible. The two benzene rings are roughly perpendicular to each other.

The piperazine ring has the normal chair conformation with both exocyclic N—C bonds equatorial. The torsion angle N(11)—C(17)—C(18)—O(19) is 55·3 (5)°. The hydroxyl H atom has no contact with N(11) but is engaged in *inter*molecular H bonding with N(14). The distances from O(19) and H(19) to N(14) are 2·886 (5) and 1·84 Å, respectively, and the angle O(19)—H(19)···N(14) is 176°. H bonds of the type described interlink the molecules in chains (*cf.* Fig. 3). All other *inter*molecular contacts are van der Waals contacts.

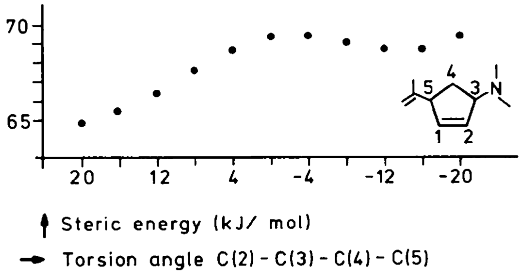

Fig. 2. Results of *MM*2 calculations on the flexibility of a model [*trans*-3-(dimethylamino)-5-(1-methylethenyl)cyclopentene] of the central part of the tefludazine molecule. The torsion angle C(2)—C(3)—C(4)—C(5) of the cyclopentene ring has been varied in steps of 4°. In each step the geometry of the model was fully optimized.

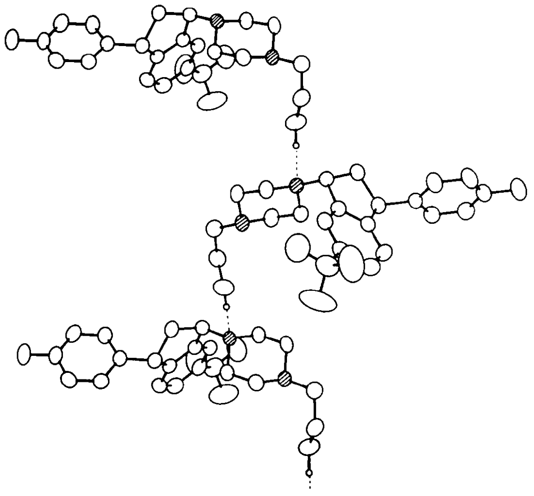

Fig. 3. Hydrogen bonds OH···N interlink the molecules in chains. Nitrogen atoms are shaded.

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trans-2-Isopropyl-*N*,*N*-dimethyl-1,3-dioxane-5-carbothioamide, $C_{10}H_{19}NO_2S$

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Abstract. $M_r = 217·33$, orthorhombic, $P2_12_12_1$, $a = 5·169$ (1), $b = 11·339$ (2), $c = 20·244$ (4) Å, $V = 1186·5$ (2) Å^3, $Z = 4$, $F(000) = 472$, $D_x = 1·22$, $D_m = 1·25$ Mg m^{-3} (flotation at 298 K), $\lambda(\text{Cu } K\alpha) = 1·5418$ Å, $\mu(\text{Cu } K\alpha) = 2·22$ mm^{-1}; final $R = 0·065$ for 1255 observed reflections. The dihedral angle between the least-squares planes of the dioxane ring, which is in a distorted chair conformation, and the dimethylcarbothioamide group is 98·7 (2)°.

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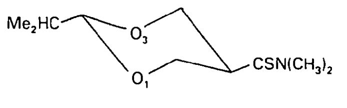
Introduction. The present paper is the third in a series of our study on crystal structures and conformations of 2-isopropyl-5-substituted-1,3-dioxanes (Shoja & White, 1979; Shoja & Kaloustian, 1983). The structure presented here was investigated to determine the effect of a *trans*-5-dimethylcarbothioamide group (I) on the conformation of the dioxane ring.



(I)

Experimental. The title compound crystallizes from ethyl acetate in the form of colorless plates.

Enraf–Nonius CAD-4 automated diffractometer, monochromated Cu $K\alpha$ radiation, crystal $0{\cdot}15 \times 0{\cdot}20 \times 0{\cdot}20$ mm; unit-cell parameters determined by least-squares fit of the angular settings for 15 high-angle reflections (244, $\bar{3}1\bar{7}$, $\bar{2}11$, $25\bar{2}$, 304, 232, $04\bar{3}$, 053, 241, 322, 433, 180, 414, 1,7,11, 188); ω–2θ scanning mode, $\theta \leq 73°$, $0 \leq h \leq 6$, $0 \leq k \leq 14$, $0 \leq l \leq 25$; systematic absences $h00$, $h = 2n+1$, $0k0$, $k = 2n+1$ and $00l$, $l = 2n+1$ uniquely defined $P2_12_12_1$; relative ranges of intensity variation for the standard reflections 020 and 013 were 6·7 and 5·2% respectively; intensities were corrected for Lorentz–polarization effects, but not for absorption; 1414 possible independent reflections, 1255 of which were accepted as observed $[I > 1{\cdot}5\sigma(I)]$. Heavy-atom method, Fourier and block-diagonal least-squares refinement methods; H atoms from difference electron density map. All positional parameters, anisotropic thermal parameters for the non-H atoms and isotropic thermal parameters for the H atoms refined. In final cycle H atoms were assigned isotropic thermal parameters equal to those of the bonded C atoms; function minimized: $\sum w(|F_o| - k|F_c|)^2$, with w from counting statistics for the observed reflections and $w = 0$ for the unobserved reflections; final $R = 0{\cdot}065$ and $R_w = 0{\cdot}053$ for the observed reflections only, mean and maximum shift/e.s.d. 0·29 and 0·50, $S = 0{\cdot}74$, maximum and minimum peak heights in the final difference Fourier synthesis 0·21 and $-0{\cdot}53$ e Å^{-3}, the latter in the region of the S atom; scattering factors for the non-H atoms from *International Tables for X-ray Crystallography* (1968), that for H from Stewart, Davidson & Simpson (1965). All structural calculations were performed with the NRC system (Ahmed, Hall, Pippy & Huber, 1973). The atomic coordinates and equivalent isotropic B's for the non-H atoms (Willis & Pryor, 1975) are given in Table 1.*

Discussion. The bond distances (uncorrected for thermal vibrational effects) are shown in Fig. 1, and the experimental bond angles are given in Table 2. The bond angles in the ring are, within the estimated errors, normal (108·7–112·6°) relative to the tetrahedral angle.

The dioxane ring has a distorted chair conformation with the puckering parameters (Cremer & Pople, 1975) $q_2 = 0{\cdot}028$, $q_3 = -0{\cdot}561$, $Q = 0{\cdot}562$ Å, $\varphi_2 = 193{\cdot}0°$ and $\theta = 177{\cdot}1°$. The mean differences between C(4)–C(5), C(5)–C(6) and O(1)–C(2), C(2)–O(3) bonds are 0·041 (6) and 0·064 (4) Å, respectively.

Table 1. *Fractional atomic coordinates* ($\times 10^4$) *and equivalent isotropic B values*

$$B_{eq} = \tfrac{4}{3}\textstyle\sum_i \sum_j \beta_{ij} \mathbf{a}_i . \mathbf{a}_j.$$

	x	y	z	B_{eq} (Å^2)
S	1414 (3)	501 (1)	2047 (1)	4·8 (1)
N	4729 (8)	2269 (3)	1963 (2)	3·6 (2)
O(1)	3345 (7)	900 (2)	−167 (1)	4·0 (2)
C(2)	4019 (10)	−337 (4)	−169 (2)	3·5 (2)
O(3)	6031 (7)	−552 (3)	263 (1)	4·2 (2)
C(4)	5357 (13)	−300 (4)	935 (2)	4·4 (2)
C(5)	4540 (11)	1008 (4)	988 (2)	3·5 (2)
C(6)	2513 (12)	1254 (4)	474 (2)	4·5 (3)
C(7)	3689 (10)	1322 (4)	1675 (2)	3·3 (2)
C(8)	3996 (14)	2594 (5)	2638 (2)	5·8 (3)
C(9)	6795 (12)	2989 (4)	1667 (2)	4·8 (3)
C(10)	4700 (11)	−682 (4)	−866 (2)	3·7 (2)
C(11)	5346 (15)	−2018 (5)	−875 (3)	5·8 (3)
C(12)	7041 (12)	9 (5)	−1129 (3)	4·7 (3)

Table 2. *Bond angles* (°)

S–C(7)–N	122·2 (4)	O(3)–C(4)–C(5)	108·9 (4)
S–C(7)–C(5)	119·3 (4)	O(3)–C(2)–C(10)	111·8 (4)
N–C(7)–C(5)	118·5 (4)	O(1)–C(2)–C(10)	108·2 (4)
C(7)–C(5)–C(4)	111·8 (4)	C(2)–C(10)–C(11)	108·4 (4)
C(7)–C(5)–C(6)	113·2 (4)	C(2)–C(10)–C(12)	112·1 (4)
C(5)–C(6)–O(1)	111·6 (4)	C(11)–C(10)–C(12)	108·9 (4)
C(6)–O(1)–C(2)	110·5 (4)	C(8)–N–C(7)	120·3 (4)
C(4)–C(5)–C(6)	108·7 (4)	C(9)–N–C(7)	124·2 (4)
O(1)–C(2)–O(3)	110·6 (4)	C(8)–N–C(9)	115·3 (4)
C(2)–O(3)–C(4)	112·6 (4)		

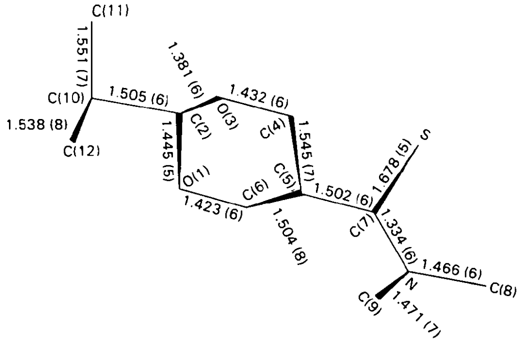


Fig. 1. Bond distances (Å) for the non-hydrogen atoms.

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* Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38528 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

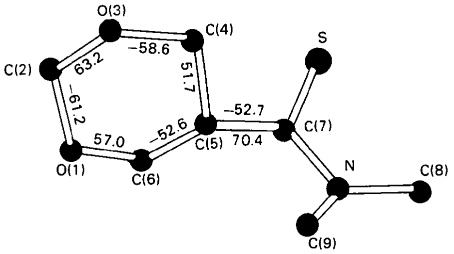

Fig. 2. Torsion angles (°) in the 1,3-dioxane ring. The e.s.d.'s are all in the range 0·3–0·4°.

The torsion angles in the dioxane ring of the title compound are shown in Fig. 2. The dioxane ring, as expected, is puckered in the O—C—O region, the mean of the torsional angles for O—C—O—C being 62·3 (3)°. The torsion angles for C(12)—C(10)—C(2)—O(1) and C(11)—C(10)—C(2)—O(1) are 61·4 (3) and −178·3 (3)°, respectively. The torsion angle for S—C(7)—C(5)—C(6) is 70·4 (3)°, in contrast to 28(1)° found in a *trans*-substituted-5-carbothioamide (Shoja & Kaloustian, 1983). The dimethylcarbothioamide group is at a dihedral angle of 98·7 (2)° with respect to the plane of the dioxane ring. The equation of this plane calculated with respect to orthogonal coordinates is $(0{\cdot}8055)X + (0{\cdot}5376)Y + (-0{\cdot}244)Z - (1{\cdot}7954) = 0$.

There are no intermolecular distances less than 3·0 Å.

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Structure of a Racemic Compound: The Dicyclohexylammonium Salt of (2*R*,4*R*,2*S*,4*S*)-*cis*-4-Methyl-2-oxido-1,3,2-dioxaphosphorinane 2-Sulphide, $C_{12}H_{24}N^+.C_4H_8O_3PS^-$

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Abstract. $M_r = 349{\cdot}5$, monoclinic, $P2_1/c$, $a = 20{\cdot}621$ (6), $b = 11{\cdot}592$ (2), $c = 18{\cdot}182$ (5) Å, $\beta = 115{\cdot}63$ (2)°, $V = 3918{\cdot}5$ Å^3, $Z = 8$, $D_m = 1{\cdot}171$ (10), $D_x = 1{\cdot}184$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 0{\cdot}22$ mm^{-1}, $F(000) = 1520$, $T = 293$ K, $R = 0{\cdot}0712$, $R_w = 0{\cdot}0797$ for 2928 observed reflections $[F_o \geq 3\sigma(F_o)]$. The salt consists of discrete cations $[C_{12}H_{24}N]^+$ and anions $[C_4H_8O_3PS]^-$ bonded by strong hydrogen bonds to form tetramers. Both the 1,3,2-dioxaphosphorinane and the cyclohexane rings exist in a more or less distorted chair conformation.

Introduction. During a systematic study of the stereochemistry of organophosphorus cyclic compounds, Mikołajczyk & Łuczak (1972) investigated the geometrical isomerism in cyclic five- and six-membered phosphorus monothioacid derivatives which occurs when the molecule contains at least one asymmetric centre at a ring carbon atom. The dicyclohexylammonium (hereafter DCHA) salts of *cis*- and *trans*-4-methyl-2-oxido-1,3,2-dioxaphosphorinane 2-sulphide (the dioxaphosphorinane ring hereafter DOPN) were obtained as diastereoisomerically pure compounds using several different synthetic routes, starting from 2-hydroxy-4-methyl-1,3,2-dioxaphosphorinane 2-sulphide or its sodium salt (Mikołajczyk, 1969 *a*,*b*; Mikołajczyk & Schiebel, 1969; Mikołajczyk & Łuczak, 1972). Here we present the crystal structure of the *cis* isomer (m.p. 481–484 K) which was studied to investigate the conformation of the DOPN ring when present in the crystal as an anion linked to a bulky positively charged DCHA group. This is a continuation of earlier work on the crystal structure of 4-methyl-1,3,2-dioxaphosphorinanes (Bartczak, Christensen, Kinas & Stec, 1975, 1976). The crystal structure of a similar compound, the ammonium salt of *cis*-4-methyl-2-oxido-1,3,2-DOPN 2-sulphide, has also been solved (Bartczak, Wolf & Cameron, 1983). These are probably the first two examples of crystal structures containing ionic forms of 4-methyl-1,3,2-dioxaphosphorinane rings. The convention is used throughout this paper, following Mikołajczyk &

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