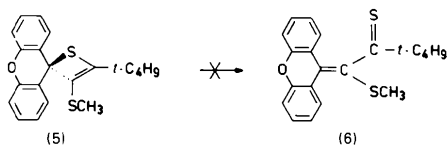


(Brouwer, 1979). In the unbridged dithioester (4c) ($X = -H$ or $-H$) no such interactions take place because the aromatic systems are no longer in one plane. Therefore, it is not surprising that, in solution, (4c) shows no tendency to be in equilibrium with its thiete.

That dithioester (6) is not found to occur in equilibrium with its thiete (5) at room temperature is undoubtedly due to the lack of delocalization energy in the $-C(=S)-tert-C_4H_9$ group.



It is remarkable that the red crystals of dithioester (4b) on storing at 263 K for about a year had crumbled and partially turned yellow. On the basis of infrared spectra, rearrangement into thiete (3b) must have occurred (Brouwer, 1979).

A structural investigation of dithioester (4d) is under way.

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Stereochemical Investigations of Heterocyclic Compounds.

X. The Structure of a Novel Compound: 1,4-Dihydro-3,5-dimethoxy-1-tosylimino-1 λ^4 ,2,4,6-thiatriazine

BY ALAJOS KÁLMÁN AND GYULA ARGAY

Central Research Institute of Chemistry, Hungarian Academy of Sciences, H-1525 Budapest 114, POB 17, Hungary

AND EBERHARD FISCHER AND MARIANNE TELLER

Section of Chemistry, Wilhelm Pieck University of Rostock, Rostock 25, German Democratic Republic

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Abstract

$C_{11}H_{14}N_4O_4S_2$ is monoclinic, space group $P2_1/c$, with $a = 14.415$ (1), $b = 7.534$ (1), $c = 15.473$ (2) Å, $\beta = 120.46$ (1)°, $Z = 4$. Final $R = 0.035$ for 2698 reflexions. As in related compounds the thia(IV)triazine ring is non-planar. The lengths of the $S^{IV}-N$ multiple bonds maintained by S^{IV} situated at the top of a distorted trigonal pyramid are governed by the bond-order rule [Kálmán, Argay, Fischer & Rembarz (1979). *Acta Cryst.* B35, 860–866]. Participation of the *exo* N atom in a strong $NH \cdots N$ hydrogen bond seems to influence the competition between the $S^{IV}-N$ and $S^{VI}-N$

multiple bonds which build up the $RS^{VI}O_2-N=S^{IV}$ moieties (*cf. e.g. N-sulphonylsulphilimines*). The tautomeric proton which maintains a $NH \cdots N$ hydrogen bond was located unambiguously at N(4).

Introduction

A new synthesis (Fischer & Teller, 1979) leads to 1-arylimino-1 λ^4 ,2,4,6-thiatriazines in high yields. Thus the reaction of *O,O*-dimethyldiisobiuret with *N*-tosylsulphinylamine in anhydrous benzene gives 1,4-dihydro-3,5-dimethoxy-1-tosylimino-1 λ^4 ,2,4,6-thiatri-

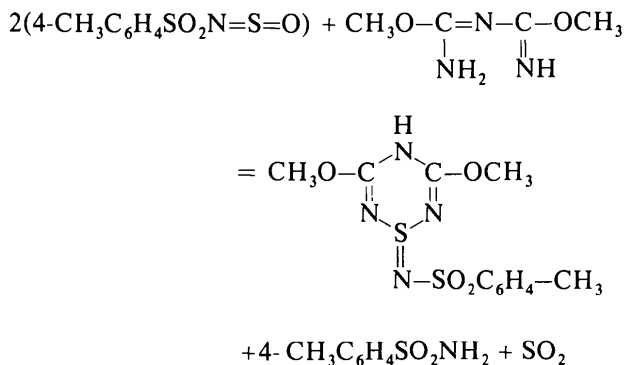
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azine (76%, m.p. 443 K, crystals from methanol) and tosylamide with the elimination of SO_2 .



An identical product is prepared with N,N' -ditosylsulphur diimide as the S precursor (43%). The compound is not hydrolysed in boiling water. It is the first stable cyclic imidothionylamide with non-fixed H. In different aprotic solvents the compound shows marked tautomeric equilibrium observed by different CH_3O signals in the ^1H NMR spectra. To reveal the predominant tautomeric form in the crystal an X-ray analysis of the title compound has been performed. The resemblance between the title compound and 2,5-di-*tert*-butyl-1-tosylimino-1 λ^4 ,2,5-thiadiazolidine-3,4-dione (Gieren, Dederer & Abelein, 1978) offers further study of the bond-order role discussed (Kálmán, Argay, Fischer & Rembarz, 1979) for trigonal-pyramidal $\text{S}^{\text{IV}}\text{N}_3$ moieties.

Experimental

Crystal data

$\text{C}_{11}\text{H}_{14}\text{N}_4\text{O}_4\text{S}_2$, $M_r = 330.4$, monoclinic, $a = 14.415$ (1), $b = 7.534$ (1), $c = 15.473$ (2) Å, $\beta = 120.46$ (1)°, $V = 1448.5$ Å³, $D_c = 1.515$ Mg m⁻³, $Z = 4$, $F(000) = 688$, $\mu[\lambda(\text{Cu } K\alpha)] = 1.5418$ Å⁻¹ = 3.43 mm⁻¹, space group $P2_1/c$.

Intensities of 2896 independent reflexions were collected on an Enraf-Nonius CAD-4 computer-controlled four-circle diffractometer equipped with a graphite monochromator by an $\omega/2\theta$ scan in the range $\theta_{\text{max}} = 75^\circ$ ($h_{\text{max}} = 18$, $k_{\text{max}} = 9$, $l_{\text{max}} = \pm 19$). Cell constants were determined by least squares from the setting angles of 25 reflexions. Unlike other thiazines studied by us (Kálmán, Argay, Fischer, Rembarz & Voss, 1977; Kálmán, Argay, Fischer & Rembarz, 1979), no decomposition of the sample during data collection could be detected. During 36 h exposure the intensity of the strongest check reflexion showed only $\pm 1.7\%$ fluctuation. After data reduction 2698 reflexions with $I - 4.5\sigma(I) > 0$ were taken as observed. No absorption correction was applied.

The structure was solved by *MULTAN* (Germain, Main & Woolfson, 1971) with 324 normalized structure factors having $E \geq 1.6$. An E map computed from the phase set obtained with the best consistency (ABSFO = 1.08, RESID = 28.72) gave the positions of all non-hydrogen atoms, with $R = 0.30$ for 1388 selected reflexions. Full-matrix least-squares refinement of the positions of these atoms in the anisotropic mode reduced R to 0.051. At this stage the H atoms were located in a difference map. 14 of the 16 strongest peaks with $\rho > 0.15$ e Å⁻³ could be identified as H atoms. The third-strongest peak ($\rho = 0.3$ e Å⁻³) at N(4) could be assigned as the tautomeric H atom. No other maxima were found in the neighbourhoods of

Table 1. Fractional coordinates ($\times 10^5$) and mean temperature factors for non-hydrogen atoms

E.s.d.'s are given in parentheses. $B_{\text{eq}} = 4|B_{11}B_{22}B_{33}|/(a^2b^2c^2)^{1/3}$.

	x	y	z	B_{eq} (Å ²)
S(1)	29333 (3)	239 (7)	24499 (3)	2.47 (1)
N(2)	28130 (12)	8524 (24)	14051 (11)	2.60 (6)
C(3)	36571 (14)	15194 (27)	14582 (13)	2.54 (6)
N(4)	45993 (11)	18796 (25)	23212 (11)	2.72 (5)
C(5)	46507 (14)	17827 (27)	32248 (13)	2.54 (6)
N(6)	39495 (12)	10710 (23)	33945 (10)	2.66 (5)
N(7)	34336 (11)	-19398 (22)	25552 (11)	2.46 (5)
S(8)	25883 (4)	-35513 (7)	22992 (3)	2.75 (2)
O(9)	32201 (14)	-51297 (21)	25047 (12)	3.64 (7)
O(10)	19787 (11)	-33230 (25)	27944 (10)	4.20 (6)
C(11)	16708 (15)	-34208 (27)	10001 (13)	2.68 (6)
C(12)	6640 (16)	-26773 (35)	6461 (15)	3.67 (8)
C(13)	-158 (18)	-24801 (38)	-3818 (18)	3.77 (9)
C(14)	2968 (17)	-29785 (34)	-10535 (16)	3.31 (8)
C(15)	13067 (17)	-37370 (37)	-6799 (15)	3.72 (8)
C(16)	19902 (15)	-39665 (35)	3372 (15)	3.32 (8)
C(17)	-4392 (22)	-27378 (46)	-21598 (19)	4.51 (11)
O(18)	36935 (11)	20120 (23)	6568 (9)	3.30 (5)
C(19)	27393 (20)	16328 (39)	-3043 (15)	3.74 (9)
O(20)	55320 (11)	25334 (21)	39395 (9)	3.09 (5)
C(21)	57147 (20)	24093 (42)	49425 (16)	4.36 (10)

Table 2. Fractional coordinates ($\times 10^4$) for H atoms

E.s.d.'s are given in parentheses.

	x	y	z	B (Å ²)
H(4)	5110 (15)	2242 (30)	2277 (14)	2.74
H(12)	375 (17)	-2318 (31)	1065 (15)	3.64
H(13)	-658 (16)	-2126 (32)	-610 (15)	3.77
H(15)	1565 (16)	-4060 (32)	-1097 (14)	3.69
H(16)	2672 (15)	-4483 (32)	595 (14)	3.40
H(171)	-147 (18)	-2868 (34)	-2501 (17)	4.40
H(172)	-1105 (18)	-3119 (33)	-2418 (16)	4.40
H(173)	-656 (18)	-1508 (33)	-2372 (16)	4.40
H(191)	2889 (16)	1877 (32)	-743 (15)	3.70
H(192)	2518 (16)	403 (32)	-346 (14)	3.70
H(193)	2131 (17)	2314 (33)	-336 (16)	3.70
H(211)	6384 (18)	2934 (33)	5332 (16)	4.45
H(212)	5201 (18)	2956 (34)	4972 (16)	4.45
H(213)	5772 (17)	1154 (34)	5117 (16)	4.45

Table 3. *Interatomic distances (Å) with their e.s.d.'s in parentheses*

S(1)—N(2)	1.658 (1)	S(8)—O(10)	1.439 (1)
S(1)—N(6)	1.653 (2)	S(8)—C(11)	1.762 (1)
S(1)—N(7)	1.617 (2)	C(11)—C(12)	1.383 (3)
N(2)—C(3)	1.280 (2)	C(11)—C(16)	1.383 (2)
C(3)—N(4)	1.365 (2)	C(12)—C(13)	1.390 (2)
C(3)—O(18)	1.321 (1)	C(13)—C(14)	1.378 (2)
N(4)—C(5)	1.364 (1)	C(14)—C(15)	1.388 (3)
C(5)—N(6)	1.283 (2)	C(14)—C(17)	1.499 (3)
C(5)—O(20)	1.316 (2)	C(15)—C(16)	1.380 (2)
N(7)—S(8)	1.621 (2)	O(18)—C(19)	1.453 (3)
S(8)—O(9)	1.432 (2)	O(20)—C(21)	1.439 (1)

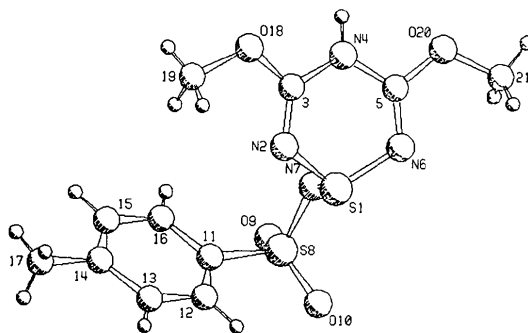


Fig. 1. A perspective view of the molecule. Numbers are for C atoms unless indicated otherwise. H atoms are numbered according to the atoms to which they are linked.

Table 4. *Bond angles (°) with their e.s.d.'s in parentheses*

N(2)—S(1)—N(6)	106.9 (1)	O(9)—S(8)—C(11)	108.9 (1)
N(2)—S(1)—N(7)	105.3 (1)	O(10)—S(8)—C(11)	107.0 (1)
N(6)—S(1)—N(7)	101.4 (1)	S(8)—C(11)—C(12)	120.3 (2)
S(1)—N(2)—C(3)	117.3 (2)	S(8)—C(11)—C(16)	119.3 (2)
N(2)—C(3)—N(4)	125.7 (3)	C(12)—C(11)—C(16)	120.2 (3)
N(2)—C(3)—O(18)	122.6 (3)	C(11)—C(12)—C(13)	119.1 (3)
N(4)—C(3)—O(18)	111.7 (2)	C(12)—C(13)—C(14)	121.6 (3)
C(3)—N(4)—C(5)	120.1 (2)	C(13)—C(14)—C(15)	118.2 (3)
N(4)—C(5)—N(6)	126.4 (3)	C(13)—C(14)—C(17)	121.0 (3)
N(4)—C(5)—O(20)	111.5 (2)	C(15)—C(14)—C(17)	120.7 (3)
N(6)—C(5)—O(20)	122.2 (3)	C(14)—C(15)—C(16)	121.2 (3)
S(1)—N(6)—C(5)	117.1 (2)	C(11)—C(16)—C(15)	119.7 (3)
S(1)—N(7)—S(8)	114.8 (1)	C(3)—O(18)—C(19)	116.0 (3)
N(7)—S(8)—O(9)	104.7 (1)	C(5)—O(20)—C(21)	116.7 (3)
N(7)—S(8)—O(10)	111.5 (1)		
N(7)—S(8)—C(11)	105.9 (1)		
O(9)—S(8)—O(10)	118.2 (1)		

the three other N atoms. In further refinement of the non-hydrogen parameters, the H coordinates were refined isotropically with fixed individual isotropic temperature factors. The H atoms were assigned the isotropic temperature factors of the atoms to which they are bound. The final $R = 0.035$ for the 2698 observed reflexions [$R_w = \sum w^{1/2} \Delta / \sum w^{1/2} |F_o| = 0.050$ where $w = (\sigma F_o^2)^{-1}$]. The greatest shift/error for positional parameters of the non-hydrogen atoms was 0.10. Scattering factors were from *International Tables for X-ray Crystallography* (1962). All calculations were performed on a PDP 11/34 minicomputer with the SDP-34 system provided by Enraf-Nonius (Delft). The final coordinates of the non-hydrogen atoms are given in Table 1, parameters for H atoms in Table 2 and bond distances and angles in Tables 3 and 4.*

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35620 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Discussion

The bonding of the thiatriazine ring exhibits almost perfect mirror symmetry through S(1) and N(4) (Fig. 1). Nevertheless, the endocyclic torsion angles (Table 5) reveal an asymmetric puckering of the hetero ring which is somewhat more pronounced than in related compounds (Kálmán, Argay, Fischer, Rembarz & Voss, 1977; Kálmán, Argay, Fischer & Rembarz, 1979). S^{IV} is the bowsprit of a flattened boat and is 0.41 Å out of the best plane of the other five atoms of the hetero ring (Table 6). The exocyclic N(7) atom is linked pseudo-axially. The plane of the S^{VI}—N—S^{IV} moiety is perpendicular (91.3°) to the plane of the hetero ring. The angle between the best planes of the phenyl and the hetero rings is 47.1°.

The conformation of the *N*-tosyl group is depicted in the Newman projection (Fig. 2) perpendicular to S^{VI}—N(7). Comparison of this conformation with those of other *N*-tosyl and *N*-mesyl groups (Kálmán, Párkányi & Kucsman, 1980; Kálmán, Párkányi & Schwartz, 1977) suggests that the *exo* N(7) is three- rather than two-coordinated with its lone pair donated to an intermolecular hydrogen bond [N...N = 2.884 (2), H...N = 2.08 (2) Å, NH...N = 169.5 (30)°]. The other end of the hydrogen bond is maintained by the tautomeric proton linked to N(4). Accordingly, from the three tautomers *A*, *B* and *C* which are claimed by ¹H NMR to take part in an equilibrium in solution, *A* predominates in the crystal.

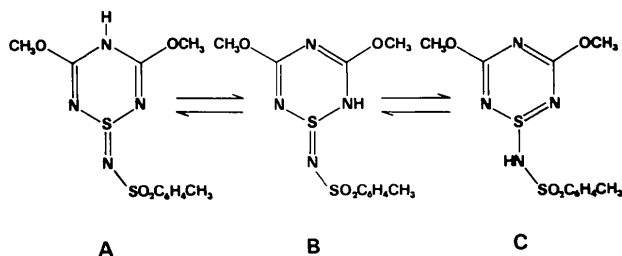


Table 5. Torsion angles ($^{\circ}$) with their e.s.d.'s in parentheses

N(4)–C(3)–N(2)–S(1)	–11.6 (2)	S(8)–N(7)–S(1)–N(2)	–105.9 (2)	C(12)–C(11)–S(8)–O(10)	17.7 (3)
N(4)–C(5)–N(6)–S(1)	5.4 (2)	S(8)–N(7)–S(1)–N(6)	142.9 (2)	C(16)–C(11)–S(8)–N(7)	74.7 (3)
C(5)–N(4)–C(3)–N(2)	–9.9 (3)	O(9)–S(8)–N(7)–S(1)	–176.4 (1)	C(16)–C(11)–S(8)–O(9)	–37.4 (3)
C(5)–N(6)–S(1)–N(2)	–22.9 (2)	O(10)–S(8)–N(7)–S(1)	–47.5 (1)	C(16)–C(11)–S(8)–O(10)	–166.3 (3)
N(6)–S(1)–N(2)–C(3)	25.9 (2)	C(11)–S(8)–N(7)–S(1)	68.6 (1)	C(19)–O(18)–C(3)–N(2)	–4.4 (3)
N(6)–C(5)–N(4)–C(3)	13.6 (3)	C(12)–C(11)–S(8)–N(7)	–101.3 (3)	C(21)–O(20)–C(5)–N(6)	4.3 (3)
N(7)–S(1)–N(2)–C(3)	–81.3 (2)	C(12)–C(11)–S(8)–O(9)	146.6 (3)	H(4)–N(4)–C(3)–N(2)	175.8 (25)
N(7)–S(1)–N(6)–C(5)	87.1 (2)				

Table 6. Equations of planes in the form $AX + BY + CZ - D = 0$, where X , Y and Z are orthogonal coordinates (\AA)

Deviations ($\text{\AA} \times 10^3$) of relevant atoms from the planes are given in square brackets.

Plane (1): N(2), C(3), N(4), C(5), N(6)

$$-0.3750X + 0.9253Y - 0.0570Z + 0.6210 = 0$$

[N(2) 1 (2), C(3) 21 (2), N(4) –49 (2), C(5) 53 (2), N(6) –27 (2), S(1) –414 (1), O(18) 170 (2), O(20) 256 (2), C(19) 212 (3), C(21) 289 (3)]

Plane (2): C(11)–C(16)

$$-0.4157X - 0.9079Y - 0.0536Z - 1.5997 = 0$$

[C(11) –6 (2), C(12) –2 (3), C(13) 9 (3), C(14) –8 (3), C(15) 0 (3), C(16) 7 (3), S(8) –136 (1), C(17) –14 (3)]

Plane (3): S(1), N(7), S(8)

$$0.2839X + 0.0315Y - 0.9583Z + 2.4758 = 0$$

[N(2) 1538 (2), N(6) –977 (1), O(9) –87 (2), O(10) –987 (1), C(11) 1577 (2)]

Angles between planes (e.s.d.'s $\sim 0.3^{\circ}$):

$$(1)-(2) 47.1; \quad (1)-(3) 91.3; \quad (2)-(3) 95.5^{\circ}.$$

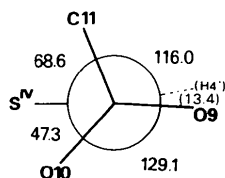


Fig. 2. Newman projection down S(8)–N(7). (Angles are in degrees.)

In principle, the infinite hydrogen-bond helices (Fig. 3) around the screw axes, N(4)–H(4) (x, y, z) \cdots N(7) ($1-x, \frac{1}{2}+y, \frac{1}{2}-z$), may enable a proton migration between donor and acceptor resulting in the formation of tautomer C. Though the hetero ring is puckered, its six- π -electron system is indicated by the multiple bonds which resemble the corresponding ones found in the two symmetrically substituted thiaziazines (Kálmán, Argay, Fischer & Rembarz, 1979). An analysis of the double-bond order of the three S^{IV}–N multiple bonds which form the characteristic S^{IV}N₃ pyramid gives further support to our conclusion that the equilibrium of the bonding around S^{IV} can be best described in

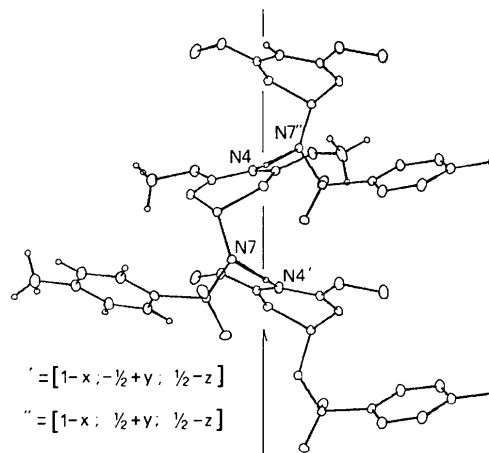


Fig. 3. Hydrogen-bond helices around the crystallographic screw axis $[\frac{1}{2}, y, \frac{1}{2}]$.

terms of the sum of the bond orders (Kálmán, Argay, Fischer & Rembarz, 1979). The accuracy of the refinement permits good agreement between the theoretical (4.0) and the experimental (4.001) sums of the single- and double-bond orders (Coulson, 1939) of these S–N bonds.

The bond system formed in the $RO_2S^{VI}-N=S \begin{matrix} \diagup N \\ \diagdown N \end{matrix}$

moiety is comparable to that in the analogous 2,5-di-*tert*-butyl-1-tosylimino-1 λ^4 ,2,5-thiadiazolidine-3,4-dione (Gieren, Dederer & Abelein, 1978). In the latter the lone pair of each three-coordinated *endo* N atom is delocalized towards the C=O groups. Accordingly, two weak *endo* S–N multiple bonds (1.691 and 1.693 \AA) are balanced by a strong *exo* S–N multiple bond (1.546 \AA). In the title compound, however, the 3- and 5-methoxy groups have a significantly weaker electron-withdrawing effect on the two-coordinated N atoms bound to S^{IV}. Consequently, to keep the total valence number ($V = 4.0$) constant, these *endo* S–N bonds could gain greater double-bond character only at the expense of the *exo* S^{IV}–N bond. Simultaneously, this weakened (lengthened by 0.07 \AA) *exo* S^{IV}–N bond is balanced in the S^{VI}–N=S^{IV} moiety by a strengthened S^{VI}–N bond (shortened from 1.65 to 1.62 \AA). Similar S–N–S bonding was found in *S*-phenyl-*S*-propyl-

N-*p*-tolylsulphonylsulphilimine (Kálmán & Sasvári, 1972). The fact that in both structures (*i.e.* the title compound and the sulphilimine) there is a somewhat weaker S^{VI}-N bond than in other sulphilimines (Kálmán, Párkányi & Kucsman, 1980, and references therein) seems to corroborate Kálmán's (1974) conjecture that the involvement of the lone pair of a bridging N atom in any intra- or intermolecular contact (*e.g.* hydrogen bonding in the title compound) weakens the S^{VI}-N bond. Theoretical considerations on bond-length controlling factors in these systems have been presented (Náray-Szabó & Kucsman, 1979).

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2-Acetamido-3,6-dioxo-5-isopropyl-10b-methoxy-2-methylperhydro-8*H*-oxazolo[3,2-*a*]pyrrolo[2,1-*c*]pyrazine: a Cyclol Tripeptide Related to Ergot Alkaloids*

BY M. PRZYBYLSKA AND F. R. AHMED

Division of Biological Sciences, National Research Council of Canada, Ottawa, Canada K1A 0R6

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Abstract

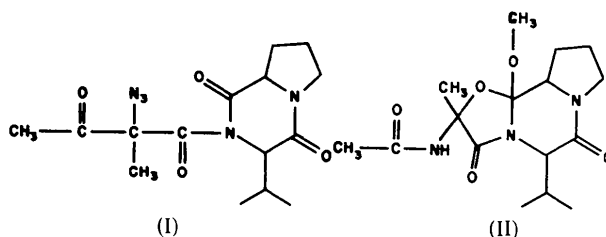
C₁₆H₂₅N₃O₅, *M_r* = 339.40, orthorhombic, *P*2₁2₁2₁, *a* = 13.859 (3), *b* = 16.770 (2), *c* = 7.861 (2) Å, *V* = 1827.0 Å³, *Z* = 4, *D_c* = 1.234, *D_m* = 1.227 Mg m⁻³ (floatation in toluene and CCl₄ mixture). Final *R* = 0.035, *R_w* = 0.040 for 1618 observed reflexions. The stereochemistry of the tripeptide has been found to differ from that in the natural product, ergotamine, by inversions at two asymmetric centres. The molecules are linked by N-H...O hydrogen bonds into continuous spirals along *a*.

Introduction

The peptide portion of the ergot alkaloids has a profound influence on their physiological activity.

Photochemical generation of *N*-acyl imines (Court, Edwards, Grieco, Rank & Sano, 1975) provided a possible synthesis of the cyclol system common to these peptides, distinct from the approach of Stadler, Frey, Ott & Hofmann (1964). Indeed, an appropriately substituted diketopiperazine (I), when irradiated in methanol, with subsequent acid treatment in that solvent, gave a low yield of the crystalline derivative of one such tripeptide with the correct analyses and spectra for (II) (Edwards, 1980).

The present analysis has established that the chemical formula (II) is correct, but that the stereo-



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