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3-Phenyl-2-phenylimino-1,3-thiazetidine

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Abstract. $C_{14}H_{12}N_2S$, FW 240·3, monoclinic, space group $P2_1/c$, $a = 13\cdot688$ (5), $b = 7\cdot128$ (3), $c = 13\cdot093$ (5) Å, $\beta = 108\cdot09$ (5)°; $V = 1214\cdot3$ Å³, $Z = 4$, $D_c = 1\cdot312$, $D_m = 1\cdot305$ g cm⁻³, Cu $K\alpha$ radiation, Ni filtered, μ(Cu $K\alpha$) = 6·1 cm⁻¹. Intensities were collected with the $\theta/2\theta$ scan mode and a scintillation counter. The structure was solved by symbolic addition methods from single-crystal diffractometer data to a final $R(F)$ of 0·031. The heterocycle of 1,3-thiazetidine is almost planar with an extremely small angle of 74·3° at S which introduces considerable strain into the ring. The three-coordinated N in the heterocycle has a tendency to adopt a pyramidal configuration which is reflected by a bend in the connexion between heterocycle and the adjacent benzene ring. Oxidation with H_2O_2/glacial acetic acid gives an enlargement of the ring to 1-oxo-1-λ^4-1,2,4-thiadiazolidin-3-one.

Introduction. The synthesis of 1,3-thiazetidine derivatives by various methods has been studied extensively over the last few years (see, for example, Mösinger, 1977). The title compound was obtained from a reaction of 1,3-diphenylthiourea with diiodomethane (Ried, Merkel & Mösinger, 1973). Oxidation of the thiazetidine ring results surprisingly in an enlargement to a five-membered ring (Ried, Mösinger

& Schuckmann, 1976). The structure of the oxidation products is described in a second paper (Schuckmann, Fuess, Mösinger & Ried, 1978). The study of the structure of the thiazetidine system should cast some light on the nature of this oxidation reaction.

The compound was obtained in a 30% yield. Recrystallization from *n*-hexane gave colourless crystals.

Table 1. *Atom coordinates* $(\times 10^4)$, *with standard deviations in parentheses*

	x	y	z
C(1)	2965 (2)	2582 (3)	5270 (2)
C(2)	3394 (2)	3226 (4)	3838 (2)
C(3)	4870 (2)	2401 (3)	5528 (2)
C(4)	5202 (2)	2000 (4)	6622 (2)
C(5)	6214 (2)	1601 (4)	7129 (2)
C(6)	6919 (2)	1597 (4)	6575 (2)
C(7)	6599 (2)	2000 (4)	5503 (2)
C(8)	5585 (2)	2401 (3)	4975 (2)
C(9)	1841 (2)	1928 (4)	6198 (2)
C(10)	1209 (2)	3474 (5)	6093 (2)
C(11)	223 (3)	3235 (8)	6171 (2)
C(12)	−114 (3)	1517 (8)	6354 (2)
C(13)	510 (3)	−17 (8)	6462 (2)
C(14)	1485 (2)	199 (5)	6394 (2)
N(1)	3842 (1)	2806 (3)	4981 (1)
N(2)	2858 (1)	2084 (3)	6152 (1)
S	2107 (1)	3138 (1)	3976 (1)

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Space group and unit-cell dimensions were determined by precession photographs. The cell dimensions were subsequently refined on a Hilger & Watts computer-controlled, four-circle diffractometer. Data were corrected for background by line-profile analysis (Bartl & Schuckmann, 1966). Of the 1528 independent reflexions 1327 had intensities larger than $2\sigma(I)$ above background. Lorentz–polarization corrections were applied in the usual way and the structure amplitudes were derived. No absorption correction was made.

A Wilson plot gave good centric statistics and E values were derived. The structure was solved by symbolic addition methods with the programs *SINGEN* and *PHASE* from the XRAY system (Stewart, Kruger, Ammon, Dickinson & Hall, 1972). All subsequent calculations were carried out by the various programs of the system. The form factors used for C, S and N were those calculated by Cromer & Mann (1968) from Hartree–Fock wavefunctions, those for H from Stewart, Davidson & Simpson (1965). An anomalous dispersion correction of $f' = 0.3$ and $f'' = 0.6$ was applied for S. The heavy atoms were refined anisotropically and at later stages H atoms were included from a careful inspection of difference Fourier maps. Isotropic thermal parameters were given to the H atoms which were refined subsequently. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$ with weights $w = 1/\sigma^2(F)$. In the final stages of refinement, extinction effects were apparent in the data and an isotropic extinction parameter g was introduced (Larson, 1967). The refined value is $g = 1.61$. The final $R(F)$ and $R_w(F) = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{1/2}$ for the 1327 reflexions with $I > 2\sigma(I)$ were 0.031 in both cases. The atomic positional parameters are given in Tables 1 and 2.*

Table 2. *Hydrogen-atom coordinates* $(\times 10^3)$, *with standard deviations in parentheses*

	x	y	z
H(1)	351 (2)	221 (3)	339 (2)
H(2)	353 (2)	445 (3)	366 (2)
H(4)	469 (2)	196 (3)	696 (2)
H(5)	641 (2)	127 (3)	784 (2)
H(6)	760 (2)	132 (3)	691 (2)
H(7)	709 (2)	194 (4)	511 (2)
H(8)	534 (2)	273 (3)	425 (2)
H(10)	143 (2)	460 (4)	597 (2)
H(11)	−15 (2)	431 (5)	610 (2)
H(12)	−79 (3)	142 (4)	638 (2)
H(13)	26 (3)	−124 (6)	662 (3)
H(14)	190 (2)	−82 (4)	650 (2)

Discussion. The molecule is shown in Fig. 1, and bond lengths and angles are listed in Tables 3 and 4. The benzene rings are planar (Table 5) and the distances within the ring (mean 1.378 Å) are slightly shorter than the mean distance of 1.390 Å determined by neutron diffraction on crystalline benzene (Bacon, Curry & Wilson, 1964).

The four-membered 1,3-thiazetidine ring shows a peculiarly small C—S—C angle of $74.3°$ which puts

* Lists of structure factors and temperature parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33146 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.
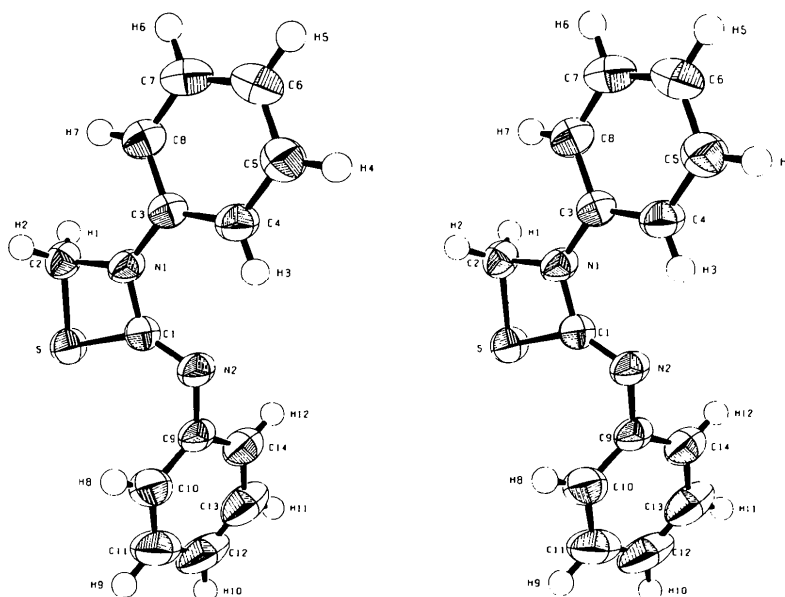

Fig. 1. Stereoscopic view of a single molecule (50% probability for thermal ellipsoids). H spheres are of arbitrary size.

Table 3. *Bond lengths (Å), with standard deviations in parentheses*

C(1)–N(1)	1·375 (3)	C(6)–C(7)	1·365 (4)
C(1)–N(2)	1·260 (3)	C(7)–C(8)	1·375 (3)
C(1)–S	1·780 (2)	C(9)–C(10)	1·382 (4)
C(2)–S	1·826 (3)	C(9)–C(14)	1·379 (4)
C(2)–N(1)	1·460 (3)	C(9)–N(2)	1·415 (3)
C(3)–C(4)	1·392 (3)	C(10)–C(11)	1·395 (5)
C(3)–C(8)	1·388 (4)	C(11)–C(12)	1·356 (8)
C(3)–N(1)	1·396 (3)	C(12)–C(13)	1·368 (7)
C(4)–C(5)	1·367 (3)	C(13)–C(14)	1·374 (5)
C(5)–C(6)	1·375 (4)		

Table 4. *Bond angles (°), with standard deviations in parentheses*

N(1)–C(1)–N(2)	130·2 (2)	C(10)–C(9)–N(2)	121·8 (3)
N(1)–C(1)–S	95·0 (1)	C(14)–C(9)–N(2)	119·1 (3)
N(2)–C(1)–S	134·8 (2)	C(9)–C(10)–C(11)	119·1 (4)
N(1)–C(2)–S	90·2 (2)	C(10)–C(11)–C(12)	120·9 (4)
C(4)–C(3)–C(8)	118·6 (2)	C(11)–C(12)–C(13)	120·3 (4)
C(4)–C(3)–N(1)	121·8 (2)	C(12)–C(13)–C(14)	119·5 (4)
C(8)–C(3)–N(1)	119·6 (2)	C(9)–C(14)–C(13)	121·3 (3)
C(3)–C(4)–C(5)	120·0 (2)	C(1)–N(1)–C(2)	100·4 (2)
C(4)–C(5)–C(6)	121·1 (2)	C(1)–N(1)–C(3)	131·4 (2)
C(5)–C(6)–C(7)	119·2 (2)	C(2)–N(1)–C(3)	127·2 (2)
C(6)–C(7)–C(8)	120·9 (3)	C(1)–N(2)–C(9)	117·6 (2)
C(3)–C(8)–C(7)	120·2 (2)	C(1)–S–C(2)	74·3 (1)
C(10)–C(9)–C(14)	119·0 (3)		

Table 5. *Atomic deviations from the least-squares planes (Å)*

P1 heterocycle		P2		P3		P4	
C(1)	−0·017	C(1)	0·000	C(3)	−0·002	C(9)	−0·006
C(2)	−0·015	C(2)	0·000	C(4)	0·001	C(10)	0·003
N(1)	0·020	C(3)	0·000	C(5)	−0·000	C(11)	0·000
S	0·013	N(1)*	0·083	C(6)	−0·000	C(12)	0·000
N(2)*	−0·093	C(4)*	0·076	C(7)	−0·000	C(13)	−0·003
C(3)*	−0·135			C(8)	0·001	C(14)	0·006
				C(2)*	−0·027	N(2)*	0·028
				N(1)*	−0·006		

Angles (°) between normals to planes

P1	P3	8·6
P1	P4	67·4
P3	P4	68·5

* Atom not included in least-squares calculation.

considerable strain on the ring. Krebs & Beyer (1969) found an angle of 83·9° in the four-membered ring of dithiophosgene chloride. It seems that this small angle might achieve a compromise between an optimal orbital overlap and a possible repulsion of the lone pairs on S. It might be interesting to study the deformation density

Table 6. *Conformation angles (°) in the heterocyclic ring*

N(2)–C(1)–S–C(2)	5	S–C(2)–N(1)–C(3)	8
N(2)–C(1)–N(1)–C(2)	5	S–C(1)–N(1)–C(3)	9
S–C(1)–N(2)–C(9)	1	C(4)–C(3)–N(1)–C(2)	1
N(1)–C(1)–N(2)–C(9)	2	C(4)–C(3)–N(1)–C(1)	13

in this ring system and compare it with the deformation density of 1,3,5-dimercaptothiadiazole (Bats, 1976). A least-squares calculation of the thiazetidine ring ($P1$ in Table 5) results in a fairly planar configuration despite the fact that three of the four distances within the ring show single-bond character. Only the C(1)–N(1) distance near to the imino group has a shortened bond (1·374 Å) corresponding to almost 20% double-bond character (Wheatley, 1955). This partial double bond may be due to a conjugation of the p_π electrons of the N atom with the benzene ring or of an interaction with the imino group. It has in fact been shown (Bats & Coppens, 1975) that non-planar distortions of amino groups do not prevent a partial overlap of π electrons.

The plane through the three C atoms C(1), C(2) and C(3) reveals, however, that N(1) deviates from that plane by nearly 0·1 Å, indicating the tendency of three-fold coordinated N to adopt a pyramidal structure (see plane $P2$ in Table 5). The small deviations from planarity in the heterocycle and its vicinity are further shown by the torsion angles listed in Table 6. Non-bonded distances correspond to van der Waals contacts. A comparison between the thiazetidine ring and the 1,2,4-thiadiazolidine (Schuckmann *et al.*, 1978) shows that the part of the ring far from the imino group is similar in both systems and hence is not involved in the oxidation reaction.

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2,3-Epoxy-*trans*-1,3-dimethyl-4a,9a-diaza-1,2,3,4,4a,9,9a,10-octahydroanthracene-9,10-dione*

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Abstract. $C_{14}H_{14}N_2O_3$. Monoclinic, $P2_1/n$, $a = 12.5288$ (11), $b = 8.3247$ (5), $c = 12.0593$ (9) Å, $\beta = 97.46$ (1)°, $Z = 4$, $D_x = 1.37$ g cm^{-3}. The structure has been solved by direct methods and refined to an R value of 0.047 for 1939 observed reflexions. The intramolecular distances are compared, by means of statistical tests, with those of the *cis* compound.

Introduction. Continuing the project on the tetracycline analogues with potential pharmacological ac-

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*Crystal and Molecular Structure of Diazapolycyclic Compounds. II.

tivity mentioned in a previous work (Foces-Foces, Cano & García-Blanco, 1977) we have determined the crystal structure of the title compound. This kind of compound seems to offer a feasible method of obtaining different substituted tetracycline analogues, because of the reactivity of the epoxide group.

A crystal, $0.32 \times 0.36 \times 0.50$ mm, was used in the measurement of the cell dimensions and for the collection of intensities, on a Philips PW 1100 four-circle diffractometer, with graphite-monochromated Cu $K\alpha$ radiation. Cell constants were determined by a least-squares fit to the settings for 85 reflexions. 2121 independent reflexions up to $\theta = 65°$ were recorded in

Table 1. *Final positional parameters* ($\times 10^4$; *for* H $\times 10^3$) *and their standard deviations, with bond distances* (Å) *for the hydrogen atoms*

	x	y	z		x	y	z	C–H bond
C(1)	1936 (1)	2987 (2)	596 (1)	H(1)	182 (2)	199 (2)	20 (2)	0.96 (2)
C(2)	945 (2)	3327 (2)	1123 (2)	H(2)	28 (2)	304 (3)	62 (2)	0.99 (2)
C(3)	941 (2)	3411 (2)	2329 (2)	H(4a)	202 (2)	199 (3)	332 (2)	1.01 (2)
C(4)	1992 (2)	3141 (2)	3054 (1)	H(4b)	205 (2)	382 (3)	371 (2)	0.96 (2)
C(5)	5851 (2)	4076 (2)	3187 (2)	H(5)	585 (2)	467 (3)	392 (2)	1.01 (3)
C(6)	6789 (2)	3657 (3)	2775 (2)	H(6)	745 (3)	394 (3)	320 (2)	0.95 (2)
C(7)	6762 (2)	2684 (3)	1835 (2)	H(7)	742 (2)	241 (3)	156 (2)	0.96 (3)
C(8)	5790 (2)	2131 (3)	1286 (2)	H(8)	577 (2)	146 (3)	61 (2)	0.99 (2)
C(9)	3796 (1)	2109 (2)	1057 (1)	H(15a)	222 (2)	535 (3)	18 (2)	0.98 (3)
C(10)	3872 (2)	3844 (2)	3125 (1)	H(15b)	152 (2)	446 (4)	−79 (2)	1.00 (3)
C(11)	4866 (1)	3531 (2)	2637 (1)	H(15c)	280 (2)	414 (2)	−59 (2)	1.00 (3)
C(12)	4837 (1)	2572 (2)	1689 (1)	H(17a)	−6 (2)	368 (4)	355 (2)	0.98 (3)
N(13)	2919 (1)	3499 (2)	2474 (1)	H(17b)	−3 (2)	190 (4)	317 (2)	1.01 (3)
N(14)	2894 (1)	2694 (2)	1438 (1)	H(17c)	−67 (3)	317 (4)	230 (3)	0.99 (3)
C(15)	2150 (2)	4321 (3)	−208 (2)					
O(16)	905 (1)	4878 (2)	1678 (1)					
C(17)	−40 (2)	3040 (3)	2870 (2)					
O(18)	3873 (1)	4346 (2)	4079 (1)					
O(19)	3724 (1)	1350 (2)	178 (1)					