Structural Investigations of Ylides. VII.* Crystal and Molecular Structure of a β-Lactam-fused Ylide Derived from Methyl 6β-Phenylacetamidopenicillanate

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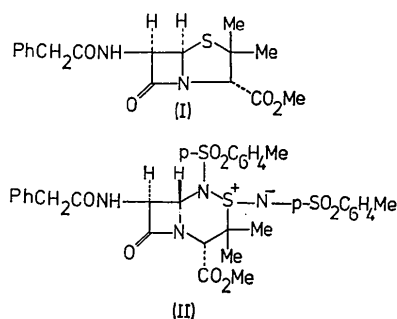
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The structure of the sulphilimine ylide (II) has been determined from 3105 independent intensities collected on a diffractometer. Crystals of (II) are monoclinic, space group $P2_1$, with $Z=2$, $a=15\cdot613$, $b=7\cdot951$, $c=13\cdot840$ Å, $\beta=108\cdot98°$. The structure was solved by direct methods, and refined by least-squares to a final R of $0\cdot048$. S(1)–N(1) and N(1)–S(2) of the ylide moiety have lengths of $1\cdot592$ (5) and $1\cdot613$ (4) Å, respectively, while the S(1)–N(1)–S(2) angle is $116\cdot3$ (2)°.

Introduction

As part of an investigation of the reaction of chloramine *T* with penicillins (Campbell, Johnson, Cameron & Cameron, 1974, 1975), with the objective of chemically modifying the thiazolidine ring and forming β-lactams with possible antibiotic activity, a methanolic solution of methyl 6β-phenylacetoamidopenicillanate (I) was reacted at room temperature with chloramine *T* (2 mol. equiv.) in methanol, to yield white crystals. On the basis of spectroscopic data, three closely related structures were plausible for this crystalline product, but these could not unambiguously be distinguished. One of the possible structures was the unusual ylide (II), and since we have a continuing interest in the detailed geometries and conformations of ylides, we undertook a structure analysis which has both confirmed the structure (II), and has also afforded the opportunity to compare the geometry of (II) with geometries of similar ylide systems.

* Part VI: Cameron, Duncanson, Freer, Armstrong & Ramage, (1975). *J. Chem. Soc. Perkin* II, pp. 1030–1036.

Experimental

Crystal data

$C_{31}H_{34}N_4O_8S_3$, $M=686\cdot8$, monoclinic, $a=15\cdot613$ (2), $b=7\cdot951$ (1), $c=13\cdot840$ (2) Å, $\beta=108\cdot98$ (6)°, $U=1624\cdot7$ Å^3, $Z=2$, $D_m=1\cdot40$ (by flotation), $D_c=1\cdot41$ g cm^{-3}, $F(000)=720$. Space group $P2_1$. Mo $K\alpha$ radiation, $\lambda=0\cdot7107$ Å, μ(Mo $K\alpha$)$=2\cdot94$ cm^{-1}.

Crystallographic measurements

The cell parameters, initially determined from oscillation and Weissenberg photographs taken with Cu $K\alpha$ ($\lambda=1\cdot5418$ Å) radiation and from precession photographs taken with Mo $K\alpha$ ($\lambda=0\cdot7107$ Å) radiation, were refined by least squares prior to the diffractometer data collection. Intensity measurements were made on a Hilger–Watts Y290 diffractometer with Mo $K\alpha$ graphite-monochromated radiation. For a small crystal ($0\cdot3 \times 0\cdot6 \times 0\cdot2$ mm) mounted about *b*, 3105 independent reflexions [$I>2\sigma_I$, $\sigma_I=\sqrt{(I+B_1+B_2)}$] were recorded with the θ, ω scan technique in the range $2\theta=0 \rightarrow 54°$. The intensities were corrected for Lorentz and polarization factors, but absorption effects were ignored.

Structure determination and refinement

The structure was solved with the *MULTAN* suite of programs. An initial E map, based on 397 reflexions with $|E| \geq 1\cdot4$, yielded the positions of the three S atoms. The phases appropriate to these three atomic positions were subjected to a phase-refinement procedure, and from the subsequent E map based on the same set of reflexions, 36 of the non-hydrogen atoms were located. The remaining atomic positions were revealed by conventional structure factor and electron density calculations.

The refinement of positional, vibrational and overall scale parameters by least squares converged when R

was 0·048. Computing limitations forced the use of an arbitrary blocking strategy in which the parameters of groups of atoms were refined simultaneously (considering all off-diagonal elements within the group), while the remaining parameters were held constant. A complete set of molecular atomic parameters was refined after a round of 3 successive least-squares calculations. Calculated H atom positions were included in all structure factor calculations, but not refined. In the latter stages of the refinement, it was found necessary to apply a weighting scheme of the form [$|F_o| \leq 7 \cdot 5$, then $w = 1$; else $w = (7 \cdot 5/F_o)^2$] to the data.

On convergence of the refinement, calculations of an electron density distribution and difference synthesis revealed no errors in the structure. Final coordinates and thermal parameters are given in Table 1. Table 2 contains bond lengths, interbond angles and pertinent intra- and intermolecular distances, while selected torsion angles are presented in Table 3. The estimated standard deviations quoted in Tables 1–3 are derived from the inverse of the least-squares normal-equation matrix, and are best regarded as minimum values. Details of least-squares planes calculated for various portions of the molecular framework are given in Table 4.*

Discussion

The geometry of the S(1)–N(1)–S(2) ylide moiety of (II) may be compared with the geometries of the similar molecules (IIIa–d) (Kálmán, 1967; Kálmán, Duffin & Kucsman, 1971; Cameron, Hair & Morris, 1973; Kálmán & Sasvári, 1972). Whereas S(1)–N(1) and S(2)–N(1) in the latter four molecules lie in the ranges 1·620 (7)–1·633 (9) Å and 1·581 (10)–1·618 (7) Å respectively, the value observed for S(1)–N(1) [1·592 (5) Å] of (II) is shorter than in (IIIa–d), while S(2)–N(1) [1·613 (4) Å] is comparable with the upper limit of the range for (IIIa–d). The length of S(1)–N(1) in (II) is intermediate between the values observed in (IIIa–d) and the values observed for the corresponding bonds [1·521, 1·524 Å] of the 'double-ylide' (IV) (Gierin & Pertlik, 1974), and, indeed, (II) may be regarded as an S-alkylated, mono-N-alkylated derivative of the ylide system of (IV). It has previously been argued that the S(1)–N(1) and S(2)–N(1) dimensions of (IIIa–d) and the corresponding dimensions of (IV) are consistent with significant levels of S d-orbital participation in delocalized bonding within the ylide systems, and insofar as such arguments are considered valid, the dimensions of the S(1)–N(1)–S(2) system of (II) are compatible with a similar pattern of bonding.
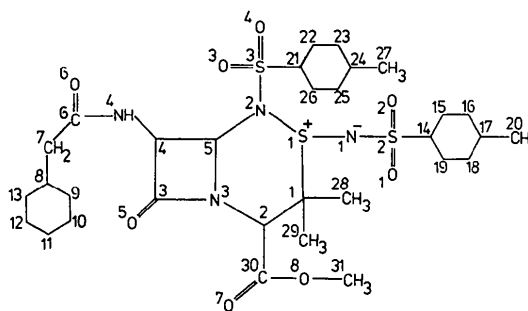
* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31487 (26 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Fig. 1. The atomic numbering scheme used in the X-ray analysis.

Table 1. Atomic fractional coordinates and thermal parameters

(a) Atomic fractional coordinates ($\times 10^5$ for S, $\times 10^4$ for other atoms) with estimated standard deviations in parentheses

	x	y	z
S(1)	11300 (7)	−23955 (19)	43001 (8)
S(2)	1079 (8)	−9498 (26)	25161 (9)
S(3)	21765 (7)	−53880 (—)	41281 (9)
O(1)	−378 (3)	−2508 (9)	2450 (3)
O(2)	−388 (4)	613 (10)	2462 (4)
O(3)	1292 (3)	−5997 (5)	4030 (4)
O(4)	2952 (3)	−6056 (6)	4898 (3)
O(5)	4549 (2)	−389 (6)	6182 (3)
O(6)	4119 (3)	104 (5)	3693 (4)
O(7)	3238 (3)	59 (6)	7321 (2)
O(8)	2333 (2)	2200 (4)	6620 (2)
N(1)	993 (3)	−868 (7)	3521 (3)
N(2)	2131 (3)	−3337 (6)	4385 (3)
N(3)	3008 (2)	−1023 (5)	5280 (3)
N(4)	4402 (2)	−2604 (6)	4163 (3)
C(1)	1530 (3)	−1267 (7)	5542 (3)
C(2)	2328 (3)	−59 (6)	5545 (3)
C(3)	3943 (3)	−1139 (7)	5580 (4)
C(4)	3875 (3)	−2620 (7)	4838 (4)
C(5)	2834 (3)	−2116 (6)	4394 (3)
C(6)	4490 (3)	−1224 (6)	3633 (4)
C(7)	5123 (4)	−1492 (9)	3007 (4)
C(8)	4921 (3)	−385 (7)	2091 (4)
C(9)	4248 (4)	−706 (10)	1166 (5)
C(10)	4130 (5)	327 (12)	311 (5)
C(11)	4692 (5)	1647 (12)	379 (5)
C(12)	5335 (5)	2038 (11)	1270 (6)
C(13)	5457 (4)	1044 (9)	2134 (4)
C(14)	555 (4)	−881 (9)	1498 (4)
C(15)	69 (4)	−1646 (10)	596 (5)
C(16)	388 (5)	−1625 (10)	−223 (5)
C(17)	1185 (5)	−787 (10)	−166 (5)
C(18)	1656 (5)	0 (10)	733 (6)
C(19)	1359 (5)	−37 (10)	1573 (5)
C(20)	1503 (7)	−747 (14)	−1092 (6)
C(21)	2360 (4)	−5434 (8)	2965 (5)
C(22)	1707 (5)	−4820 (10)	2105 (5)
C(23)	1874 (5)	−4800 (11)	1176 (5)
C(24)	2684 (6)	−5409 (11)	1112 (5)
C(25)	3326 (5)	−6069 (12)	1957 (6)
C(26)	3170 (4)	−6093 (10)	2904 (5)
C(27)	2835 (9)	−5325 (18)	84 (7)
C(28)	708 (3)	−245 (10)	5569 (5)
C(29)	1795 (4)	−2634 (9)	6355 (4)
C(30)	2710 (3)	708 (6)	6611 (3)
C(31)	2571 (4)	3013 (8)	7607 (4)

Table 1 (cont.)

(b) Anisotropic thermal parameters ($\text{Å}^2 \times 10^3$)

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S(1)	332	533	488	−39	188	−59
S(2)	369	929	473	63	122	−15
S(3)	497	420	692	−63	291	−42
O(1)	504	1426	619	−375	163	−40
O(2)	742	1565	660	612	235	25
O(3)	626	578	1289	−240	556	−167
O(4)	691	538	674	72	250	135
O(5)	386	680	709	−148	183	−46
O(6)	960	574	1178	232	775	246
O(7)	695	862	493	212	32	−60
O(8)	657	490	504	18	261	−59
N(1)	488	627	489	−1	111	−3
N(2)	403	427	674	−73	266	−95
N(3)	322	444	521	−38	190	−90
N(4)	465	512	734	21	360	14
C(1)	369	581	494	−43	245	−59
C(2)	348	465	390	35	178	−29
C(3)	350	460	661	−10	268	36
C(4)	371	465	629	−20	282	−13
C(5)	396	459	547	−50	306	−45
C(6)	535	532	786	82	423	68
C(7)	691	841	863	286	573	241
C(8)	473	692	630	42	307	−42
C(9)	594	941	1006	−77	256	−231
C(10)	819	1197	583	206	12	−130
C(11)	871	1111	816	104	415	149
C(12)	857	1041	932	−65	387	128
C(13)	669	871	612	−125	230	−59
C(14)	439	592	441	25	157	20
C(15)	428	650	549	−46	92	−30
C(16)	636	638	498	−28	176	−32
C(17)	731	574	621	65	291	109
C(18)	617	624	711	−78	290	46
C(19)	585	649	558	−110	149	−123
C(20)	995	995	692	−56	469	−136
C(21)	409	454	633	17	165	−135
C(22)	507	685	632	157	119	−87
C(23)	675	746	623	251	107	−59
C(24)	827	643	579	32	234	−188
C(25)	648	848	715	97	309	−190
C(26)	476	693	637	184	166	−26
C(27)	1755	1220	612	350	607	22
C(28)	383	814	798	41	260	−229
C(29)	567	685	600	−83	308	100
C(30)	427	572	467	−27	218	−6
C(31)	682	698	554	−68	269	−162

Average estimated standard deviations

Atom type	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S	5	7	6	5	5	6
O	22	30	24	23	19	25
N	18	22	22	18	16	19
C	35	43	34	34	28	33

Table 2. Bond lengths (Å), valency angles (°), and pertinent intra- and intermolecular non-bonded distances (Å)

(a) Bonded distances (Å)

S(1)−N(1)	1·592 (5)	N(4)—C(6)	1·351 (7)
S(1)−N(2)	1·702 (4)	C(1)—C(2)	1·573 (7)
S(1)−C(1)	1·858 (5)	C(1)—C(28)	1·530 (8)
S(2)−N(1)	1·613 (4)	C(1)—C(29)	1·522 (8)
S(2)−O(1)	1·440 (7)	C(2)—C(30)	1·528 (6)
S(2)−O(2)	1·453 (8)	C(3)—C(4)	1·543 (7)

Table 2 (cont.)

S(2)—C(14)	1·764 (5)	C(3)—O(5)	1·197 (6)
S(3)—N(2)	1·676 (5)	C(4)—C(5)	1·591 (6)
S(3)—O(3)	1·428 (4)	C(6)—C(7)	1·525 (7)
S(3)—O(4)	1·431 (4)	C(6)—O(6)	1·220 (7)
S(3)—C(21)	1·724 (6)	C(7)—C(8)	1·491 (8)
N(2)—C(5)	1·462 (6)	C(17)—C(20)	1·517 (11)
N(3)—C(2)	1·450 (6)	C(24)-C(27)	1·517 (12)
N(3)—C(3)	1·385 (6)	C(30)-O(7)	1·178 (6)
N(3)—C(5)	1·454 (6)	C(30)-O(8)	1·325 (6)
N(4)—C(4)	1·432 (6)	C(31)-O(8)	1·447 (6)

Average (C–C) phenyl bond length 1·385 Å.

(b) Valency angles (°)

C(1)S(1)N(1)	100·9 (2)	C(1)C(2)C(30)	107·9 (3)
C(1)S(1)N(2)	97·0 (2)	N(3)C(2)C(30)	111·6 (3)
N(1)S(1)N(2)	107·6 (2)	N(3)C(3)O(5)	134·0 (3)
N(1)S(2)O(1)	112·1 (3)	N(3)C(3)C(4)	90·6 (4)
N(1)S(2)O(2)	107·6 (3)	C(4)C(3)O(5)	135·4 (4)
N(1)S(2)C(14)	103·8 (2)	C(3)C(4)N(4)	119·8 (4)
O(1)S(2)O(2)	118·2 (3)	C(3)C(4)C(5)	84·7 (3)
O(1)S(2)C(14)	108·2 (3)	N(4)C(4)C(5)	118·5 (3)
O(2)S(2)C(14)	105·9 (3)	N(2)C(5)N(3)	109·8 (3)
N(2)S(3)O(3)	104·1 (2)	N(2)C(5)C(4)	120·4 (3)
N(2)S(3)O(4)	106·7 (2)	N(3)C(5)C(4)	86·3 (3)
N(2)S(3)C(21)	104·5 (3)	N(4)C(6)C(7)	113·2 (4)
O(3)S(3)O(4)	120·2 (2)	N(4)C(6)O(6)	122·2 (3)
O(3)S(3)C(21)	110·6 (3)	C(7)C(6)O(6)	124·6 (4)
O(4)S(3)C(21)	109·4 (3)	C(6)C(7)C(8)	113·8 (4)
S(1)N(1)S(2)	116·3 (2)	C(7)C(8)C(9)	124·2 (5)
S(1)N(2)S(3)	121·0 (2)	C(7)C(8)C(13)	118·9 (4)
S(1)N(2)C(5)	112·3 (3)	S(2)C(14)C(15)	117·9 (3)
S(3)N(2)C(5)	124·4 (2)	S(2)C(14)C(19)	122·3 (3)
C(2)N(3)C(3)	138·2 (3)	C(16)C(17)C(20)	119·6 (5)
C(2)N(3)C(5)	125·2 (3)	C(18)C(17)C(20)	122·0 (5)
C(3)N(3)C(5)	96·0 (3)	S(3)C(21)C(22)	119·8 (3)
C(4)N(4)C(6)	122·8 (3)	S(3)C(21)C(26)	119·5 (3)
S(1)C(1)C(2)	109·0 (2)	C(23)C(24)C(27)	117·9 (6)
S(1)C(1)C(28)	104·3 (2)	C(25)C(24)C(27)	121·6 (6)
S(1)C(1)C(29)	105·6 (3)	C(2)C(30)O(7)	125·4 (4)
C(2)C(1)C(28)	110·2 (4)	C(2)C(30)O(8)	109·3 (3)
C(2)C(1)C(29)	114·1 (3)	O(7)C(30)O(8)	125·3 (3)
C(28)C(1)C(29)	113·0 (4)	C(30)O(8)C(31)	115·4 (3)
C(1)C(2)N(3)	108·7 (3)		

Average (C–C–C) phenyl valency angle 120·0°.
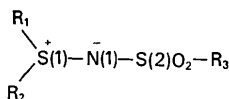
(c) Selected intramolecular non-bonded distances (Å)

S(1) · · · O(1)	2·864	O(7) · · · · O(5)	2·982
S(1) · · · O(3)	2·910	C(14) · · · C(22)	3·574
O(6) · · · C(3)	2·888	C(15) · · · C(22)	3·716
O(6) · · · C(5)	3·058	C(15) · · · C(23)	3·661
O(6) · · · O(5)	3·313	C(16) · · · C(23)	3·549
O(7) · · · C(29)	3·081	C(17) · · · C(23)	3·673

(d) Intermolecular distances < 3·60 Å

O(6)· · · ·C(26^i)	3·39	C(28)· · ·O(3^{iii})	3·40
O(8)· · · ·O(4^i)	3·17	C(31)· · ·O(1^{iii})	3·43
C(2)· · · ·O(4^i)	3·53	O(5)· · · ·C(7^{iv})	3·28
C(31)· · ·C(27^i)	3·57	O(5)· · · ·C(25^{iv})	3·52
O(2)· · · ·C(20^{ii})	3·59	O(5)· · · ·C(26^{iv})	3·42
C(15)· · ·C(23^{ii})	3·54	C(7)· · · ·O(4^{iv})	3·45
C(20)· · ·O(1^{ii})	3·33	C(12)· · ·O(7^{iv})	3·42
O(2)· · · ·C(29^{iii})	3·43	O(5)· · · ·N(4^{iv})	2·88

Roman numerals as superscripts refer to the following equivalent positions which should be applied to the coordinates of the second atom:
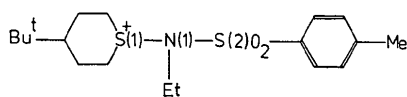
(i)	$x, 1+y, z;$	(iii)	$-x, \frac{1}{2}+y, 1-z$
(ii)	$-x, \frac{1}{2}+y, -z;$	(iv)	$1-x, \frac{1}{2}+y, 1-z$

R₁
\ + ̄
 S(1)—N(1)—S(2)O₂—R₃
/
R₂

(a) R₁=R₂=R₃=Me

(b) R₁=R₂=Ph, R₃=p–totyl

(c) R₁=R₂=Me, R₃=p–totyl

(d) R₁=Ph, R₂=C₃H₇, R₃=p–totyl (III)

(III)

Me—⟨benzene⟩—SO₂—N⁻—S⁺⁺—N⁻—SO₂—⟨benzene⟩—Me

(IV)

Buᵗ—⟨benzene⟩—S⁺(1)—N(1)—S(2)O₂—⟨benzene⟩—Me
                         |
                         Et
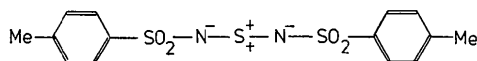
(V)

The S(1)–N(2)–S(3) system of (II) is quite different from the S(1)–N(1)–S(2) system, and may be compared with the N-alkylated derivative (V) (Cook, Glick, Rigau & Johnson, 1971). S(1)–N(2) [1·702 (4) Å] of (II) is significantly longer than the corresponding bond [1·644 (5) Å] of (V), although the S(3)–N(2) lengths of the two molecules, respectively 1·676 (5) and 1·681 (5) Å, are not only experimentally equal, but are also very similar to the values observed for the corresponding

bonds [1·683, 1·686 Å] of (IV). The value of 1·702 (4) Å for S(1)–N(2) of (II) is intermediate between the values observed in molecules such as (IIIa–d) and (V), and the value observed for sulphamic acid [1·772 (1) Å] (Cameron & Duncanson, 1975), a feature which suggests minimal double-bond character for S(1)–N(2) in (II).

While the above comparisons reveal minor, but significant differences between the bond lengths of (II) and those of the other examples, more striking differences are revealed on examination of the molecular conformation. It has previously been noted (Cameron, Hair & Morris, 1973) that the S(1)–N(1)–S(2)=O(cis) torsion angles of (IIIa–c) lie within a relatively narrow range [31–37°], the subsequent analysis of (IIId) revealing a value of 33·9° which is in accord with this observation. However, the corresponding S(1)–N(1)–S(2)= O(cis) angle of (II) is −5·3°, such that this grouping of atoms deviates little from coplanarity. Moreover, whereas a value of ca 50° is observed for the S(1)–N(2)–S(3)=O(cis) torsion angle of (V), the corresponding angle in the present molecule is −9·2°. The conformations of both the S(1)–N(1)–S(2)=O(cis) and S(1)–N(2)–S(3)=O(cis) systems of (II) are thus quite different from those of previous examples. In seeking an explanation for this apparently anomalous behaviour of (II), we note that there are close contacts between the phenyl rings of the two tosyl groups, both within one molecule and also between screw-axis related molecules. Moreover, an examination of a molecular model reveals that any attempt to adjust the conformation to mimic the conformations of (IIIa–d) and (V) would worsen the interactions between the phenyl rings to an impossible extent, given that no

Table 3. *Selected torsion angles* (°)

(a) Ylide moiety

C(1)S(1)N(1)S(2)	−139·6 (3)	O(2)S(2)C(14)C(19)	82·8 (6)
N(2)S(1)N(1)S(2)	119·4 (3)	N(1)S(1)N(2)S(3)	−123·3 (3)
S(1)N(1)S(2)O(1)	−5·3 (4)	S(1)N(2)S(3)O(3)	−9·2 (3)
S(1)N(1)S(2)O(2)	126·3 (4)	S(1)N(2)S(3)O(4)	−137·3 (3)
N(1)S(2)C(14)C(15)	151·7 (5)	O(3)S(3)C(21)C(22)	46·6 (6)
N(1)S(2)C(14)C(19)	−30·4 (6)	O(3)S(3)C(21)C(26)	−133·5 (5)
O(1)S(2)C(14)C(15)	32·5 (6)	O(4)S(3)C(21)C(22)	−178·9 (5)
O(1)S(2)C(14)C(19)	−149·6 (5)	O(4)S(3)C(21)C(26)	1·1 (6)
O(2)S(2)C(14)C(15)	−95·1 (6)		

(b) Six-membered ring

N(2)S(1)C(1)C(2)*	59·2 (3)	C(30)C(2)N(3)C(3)	−20·4 (7)
N(1)S(1)C(1)C(28)	67·4 (4)	C(2)N(3)C(5)N(2)*	−54·0 (6)
N(1)S(1)C(1)C(29)	−173·3 (4)	C(3)N(3)C(5)C(4)	11·9 (4)
S(1)C(1)C(2)N(3)*	−52·9 (4)	N(3)C(5)N(2)S(1)*	61·5 (4)
C(28)C(1)C(2)C(30)	72·1 (5)	C(4)C(5)N(2)S(3)	−38·5 (6)
C(29)C(1)C(2)C(30)	−56·3 (5)	C(5)N(2)S(1)C(1)*	−64·1 (4)
C(1)C(2)N(3)C(5)*	51·2 (5)	S(3)N(2)S(1)N(1)	−123·3 (3)

(c) Four-membered ring

C(5)N(3)C(3)C(4)*	−12·3 (4)	C(3)C(4)C(5)N(3)*	−10·7 (3)
C(2)N(3)C(3)O(5)	−3·0 (10)	N(4)C(4)C(5)N(2)	117·3 (5)
N(3)C(3)C(4)C(5)*	11·2 (3)	C(4)C(5)N(3)C(3)*	11·9 (4)
O(5)C(3)C(4)N(4)	−49·5 (8)	N(2)C(5)N(3)C(2)	−54·0 (6)

* Endocyclic values.

Table 4. *Least-squares planes for various portions of the molecular framework, in the form*
$lX + mY + nZ = d$, *where* X, Y *and* Z *represent an orthogonalized set of axes*

(a) Plane equations

Plane 1: $+0.4345X - 0.8422Y + 0.3193Z = +1.2933$
Plane 2: $-0.3645X - 0.9073Y - 0.2098Z = 2.2618$
Plane 3: $-0.7754X + 0.5704Y + 0.2709Z = -4.6476$
Plane 4: $+0.3628X - 0.4471Y + 0.8176Z = +6.3610$

(b) Deviations (Å) of atoms from planes

Plane 1	C(14)*	+0.005	C(15)*	−0.012	C(16)*	+0.008	C(17)*	+0.001
	C(18)*	−0.007	C(19)*	+0.004	C(20)	+0.002	S(2)	+0.001
Plane 2	C(21)*	−0.015	C(22)*	+0.010	C(23)*	+0.003	C(24)*	−0.011
	C(25)*	+0.006	C(26)*	+0.007	C(27)	−0.044	S(3)	−0.073
Plane 3	C(8)*	−0.017	C(9)*	+0.004	C(10)*	+0.015	C(11)*	−0.019
	C(12)*	+0.005	C(13)*	+0.013	C(7)	−0.119		
Plane 4	C(1)*	−0.013	C(2)*	+0.013	C(5)*	−0.014	N(2)*	+0.014
	S(1)	−0.965	N(3)	+0.500				

* Atoms defining planes.
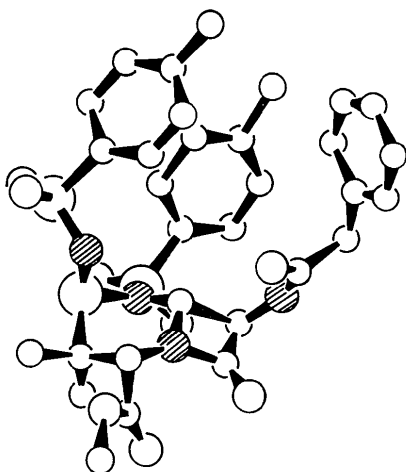
Fig. 2. A projected view of one molecule showing the close proximity of the two toluene-p-sulphonyl groups.

other changes take place. We suggest, therefore, that the unusual conformations of the ylide and N-alkylated ylide moieties of (II) may well have root in the overall steric constraints of the molecule. In this respect, it is of interest to note that (II) undergoes an unusually facile and quantitative thermal rearrangement (Campbell & Johnson, 1974), to form a thiadiazine ring-opened β-lactam, which can then undergo β-lactam cleavage reactions with a variety of nucleophilic reagents to yield dipeptides. It is plausible that the ease of the initial rearrangement may well result from steric interactions similar to those potentially responsible for the unusual conformation.

The S(1)–N(1)–S(2) angle [116·3 (2)°] compares well with the range [113·4 (5)–116·2 (6)°] observed for (IIIa–d), and although the S(1)–N(2)–S(3) angle [121·0 (2)°] is considerably larger than the corresponding angle [114·5°] in (V), the sum of the three angles at

N(2) [357·7°], and the corresponding sum in (V) [356·0°], indicate that in each case the alkylated N atoms adopt almost planar configurations.

Other aspects of the geometry of (II) compare well with literature values for similar bonding situations. The heterocyclic six-membered ring adopts a chair conformation in which S(1) and N(3) are respectively −0·965 and +0·500 Å distant from the plane of C(1), C(2), C(5) and N(2). The pseudo-axial and pseudo-equatorial orientations of S(1)–N(1) and N(2)–S(3) respectively, avoid serious interaction between adjacent ring-bonded atoms, although it is partly as a result of this feature that the inhibiting interactions between the phenyl rings of the toluene-p-sulphonyl groups, which we have noted above, arise. The four-membered ring is significantly non-planar, with an average endocyclic torsion angle modulus of 11·5°.

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