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trans-*N*-[3-Methyl-2-*p*-toluenesulphonimido-3-azatricyclo[8.5.0.$0^{4,9}$]pentadeca-4(9),5,7-trien-10-yl]-*p*-toluenesulphonamide, $C_{29}H_{33}N_3O_4S_2$

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Abstract. $M_r = 551\cdot7$, triclinic, $P\bar{1}$, $a = 14\cdot67$, $b = 13\cdot00$, $c = 8\cdot25$ Å, $\alpha = 99\cdot9$, $\beta = 109\cdot0$, $\gamma = 101\cdot9°$, $V = 1406\cdot2$ Å^3, $Z = 2$, $D_m = 1\cdot312$, $D_x = 1\cdot303$ g cm^{-3}, λ(Cu $K\alpha$) = 1·54178 Å, $\mu = 19\cdot22$ cm^{-1}, $F(000) = 584$, $T = 295$ K. Final $R = 0\cdot0754$ for 1375 unique reflections. The compound has *trans* stereochemistry. Hydrogen bonds of 2·960 Å link N(1) of one molecule to O(3) of another. The seven-membered ring has the chair conformation. The sulphonyl S—N(imino) distance [1·60 (1) Å] is shorter than the sulphonyl S—N(amino) distance [1·64 (1) Å]. The S—O distances in each sulphonyl group are comparable.

Introduction. The stereochemistry of the title compound is of interest as it was observed (Bailey, 1977) that the related six-membered-ring compound on reaction with 1,5-diaza[4.3.0]bicyclonon-5-ene in base shows *cis* stereochemistry, since elimination of the TosNH group by base does not occur. However, hydrolysis and elimination takes place after boiling the related six-membered sulphone with 1,5-diaza[4.3.0]-bicyclonon-5-ene in alcohol for about 24 hours to form the 10-aza compound.

One would expect the compound containing a seven-membered ring and prepared by a route analogous to that used for the six-membered ring (Bailey & Seager, 1974) also to contain a *cis* junction, since a dramatic change in the mechanistic pathway was not envisaged. However, after boiling the compound for five minutes in ethanol with 1,5-diaza[4.3.0]-bicyclonon-5-ene the TosNH group is eliminated suggesting the seven-membered-ring homologue might have *trans* stereochemistry.

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Table 1. *Atomic parameters* ($\times 10^4$) *with e.s.d.'s in parentheses*

$U_{eq} = (U_{11} + U_{22} + U_{33})/3.$

	x	y	z	U_{iso}/U_{eq}(Å^2)
C(1)	6593 (9)	2077 (10)	583 (15)	309 (30)
C(2)	5959 (11)	1065 (12)	−352 (19)	506 (40)
C(3)	5273 (11)	944 (13)	−2124 (20)	555 (42)
C(4)	5286 (12)	1796 (13)	−2844 (20)	583 (43)
C(5)	5917 (12)	2799 (13)	−1944 (21)	620 (45)
C(6)	6587 (12)	2968 (13)	−154 (18)	460 (37)
C(7)	4573 (14)	1654 (16)	−4755 (24)	945 (64)
C(8)	7570 (9)	−1990 (10)	203 (15)	288 (31)
C(9)	6675 (13)	−1837 (13)	162 (22)	681 (49)
C(10)	5778 (13)	−2664 (16)	−767 (23)	788 (55)
C(11)	5773 (12)	−3637 (14)	−1662 (21)	588 (44)
C(12)	6693 (12)	−3778 (14)	−1599 (20)	625 (45)
C(13)	7578 (12)	−2977 (12)	−688 (19)	562 (42)
C(14)	4793 (14)	−4540 (15)	−2598 (25)	1003 (62)
C(15)	9278 (18)	2519 (9)	2621 (14)	224 (28)
C(16)	9964 (9)	3259 (11)	4433 (16)	348 (33)
C(17)	11070 (10)	3738 (11)	4579 (18)	420 (36)
C(18)	11756 (11)	3068 (11)	5341 (18)	473 (38)
C(19)	11582 (10)	1927 (11)	4234 (18)	429 (37)
C(20)	10463 (9)	1186 (10)	3422 (16)	342 (33)
C(21)	9789 (8)	1609 (9)	2010 (14)	213 (27)
C(22)	8993 (9)	816 (10)	402 (15)	251 (28)
C(23)	7804 (10)	605 (11)	−2620 (17)	430 (37)
C(24)	8691 (9)	2433 (10)	−618 (16)	299 (31)
C(25)	9009 (9)	3071 (10)	1164 (15)	271 (29)
C(26)	9087 (10)	4169 (11)	1350 (17)	379 (33)
C(27)	8859 (10)	4650 (11)	−62 (17)	454 (37)
C(28)	8550 (11)	4035 (12)	−1749 (20)	533 (41)
C(29)	8469 (10)	2912 (11)	−2024 (17)	380 (33)
S(1)	7362 (3)	2260 (3)	2803 (4)	385 (21)
S(2)	8683 (3)	−968 (3)	1446 (4)	343 (30)
O(1)	7671 (7)	3410 (7)	3586 (11)	437 (59)
O(2)	6823 (6)	1497 (8)	3490 (10)	498 (59)
O(3)	8511 (7)	−371 (7)	2938 (10)	461 (58)
O(4)	9500 (7)	−1486 (8)	1830 (13)	543 (67)
N(1)	8344 (7)	1845 (9)	2796 (12)	346 (62)
N(2)	8722 (8)	−239 (7)	83 (12)	299 (61)
N(3)	8553 (7)	1279 (8)	−872 (11)	261 (58)

Experimental. Density determined by flotation in saturated potassium iodide. Crystals of regular shape, ~0·3 × 0·3 × 0·3 mm. Intensities of 1576 reflections estimated by automated densitometry from equi-inclination Weissenberg photographs, h −17 to 15, k −15 to 15, l 0 to 10. Data corrected for Lorentz and polarization effects but not for absorption. 1375 unique reflections, R_{int} from merging equivalent reflections 0·0886 given by the SRC Microdensitometer Service.

The positions for the two S atoms in space group $P\bar{1}$ were determined from the cross vectors of the S atoms from a sharpened three-dimensional Patterson function. The positions of the other non-H atoms were located from successive difference Fourier syntheses phased on the S-atom positions. The phenyl groups were refined with the rigid-body constraint for hexagonal rings (Sheldrick, 1976).

Using the coordinates of the difference Fourier syntheses the structure was isotropically refined. To refine the structure as a complete unit would involve more than the maximum 120 parameters permitted by the program. Hence the atoms were blocked into 'subunits' of 60 or less parameters and refined in permutations of pairs, *e.g.* (1,3,5,7), (2,4,6,8), (1,4,5,8), (2,3,6,7). The resulting R factor converged to 0·1015 after eight cycles of refinement, *i.e.* four cycles for each variable. This was followed by eight cycles of refinement (in permutation pairs) with anisotropic temperature factors (on F^2) for the non-C atoms, giving an R factor of 0·0904.

The hydrogen atoms were classified as: (i) benzene type; (ii) methyl type, $-CH_3$; (iii) methylene type, $>CH_2$; or (iv) tertiary hydrogen type, and then included in a final refinement attached by fixed geometry to C or N atoms, with standard deviations not greater than 2·0°. The H atoms were given individual isotropic temperature factors and after four cycles the R factors converged to 0·0754. The isotropic temperature factors of the H atoms were not refined and unit weights were used throughout the refinement procedure.

Final difference map revealed no regions of residual electron density greater than 0·39 e Å^{-3} and less than −0·43 e Å^{-3}. There were no unusual features in the difference synthesis at this stage. All calculations computed on the New University of Ulster's 1903A computer with Cameron's (1973), *CRYSTALS* (Carruthers, 1975) or Sheldrick's (1976) computing system.

Discussion. Table 1 provides a listing of coordinates and isotropic thermal parameters.* The interatomic distances and interbond angles are given in Table 2, the torsional angles are given in Table 3* and the interplanar angles are given in Table 4.* Fig. 1 gives the atom-numbering system used, and Fig. 2 is a projection showing the packing of the molecules in the unit cell.

The individual molecules are held together by a hydrogen bond linking N(1) of one molecule to O(3) of another by a contact distance of 2·960 Å. This intermolecular distance is less than the sum of the van der Waals radii of the atoms involved.

The torsional angle N(1)C(15)C(21)/C(15)C(21)-H(25) between the planes around the fused ring junction confirms a *trans* stereochemistry. The seven-membered ring adopts a chair-like conformation. It may be noted that the angles of the ring system open up to give 119° from the normal sp^3 carbon angle of 109°.

The angles between the plane formed by the terminal phenyl rings and the plane formed by respective N, S and C atoms are 97° and 129°, which implies that the orientation is decided by packing requirements.

The molecule contains two *p*-toluenesulphonyl groups, one bonded to an amino and the other to an imino N atom. In the sulphonyl group bonded to the imino nitrogen the S(2)—N(2) [1·60 (1) Å] is shorter than the corresponding bond length between the other S

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* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates, selected H-atom bond distances and angles, Tables 3 and 4 and two perspective views of the molecule have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42195 (20 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

atom and the amino nitrogen S(1)–N(1) [1·64 (1) Å]. S(1)–O(2) [1·45 (1) Å] and S(1)–O(1) [1·43 (1) Å] are comparable and similarly for S(2)–O(3) [1·46 (1) Å] and S(2)–O(4) [1·47 (1) Å] even though O(3) is linked to N(1) of another molecule to form a dimer.

Comparison of this compound with related compounds (Cameron, Prout, Denton, Spagna & White, 1975) shows that the S–N bond length appears to be unaffected by the possibility of π-electron delocalization from sulphur through nitrogen to the aromatic system but hybridization of the N atom imposes restrictions on the relative orientations of the C–N–S and O–S–O planes. The angles between these planes are 128° for sp^3 and 63° for sp^2 hybridizations in the title compound. For related compounds the converse is observed with 87° for sp^2 and 58° for sp^3 N atoms. The presence of the seven-membered ring may have a profound effect on the geometry of the title compound.

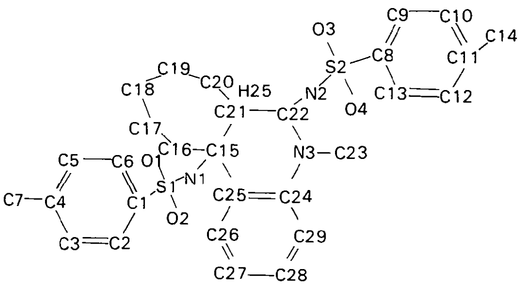

Fig. 1. Atom-numbering scheme.

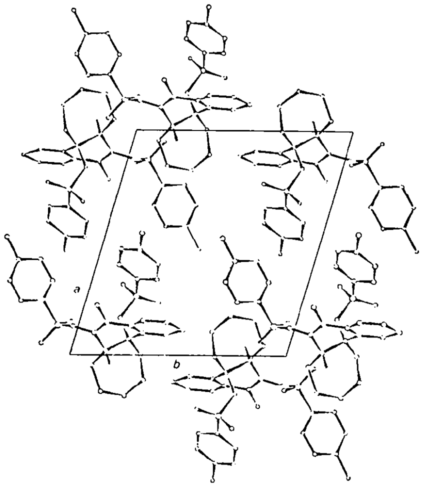

Fig. 2. Projection showing the packing of the molecules in the unit cell.

Table 2. *Interatomic distances* (Å) *and interbond angles* (°) *with e.s.d.'s in parentheses*

S(1)–O(1)	1·43 (1)	C(8)–C(13)	1·37 (2)
S(1)–O(2)	1·45 (1)	C(9)–C(10)	1·40 (3)
S(1)–N(1)	1·64 (1)	C(10)–C(11)	1·35 (3)
S(1)–C(1)	1·75 (1)	C(11)–C(12)	1·38 (2)
S(2)–O(3)	1·46 (1)	C(11)–C(14)	1·52 (3)
S(2)–O(4)	1·47 (1)	C(12)–C(13)	1·37 (2)
S(2)–N(2)	1·60 (1)	C(15)–C(16)	1·52 (2)
S(2)–C(8)	1·74 (1)	C(15)–C(21)	1·62 (2)
N(1)–C(15)	1·53 (2)	C(15)–C(25)	1·49 (2)
N(2)–C(22)	1·30 (2)	C(16)–C(17)	1·57 (2)
N(3)–C(22)	1·35 (2)	C(17)–C(18)	1·52 (2)
N(3)–C(23)	1·48 (2)	C(18)–C(19)	1·53 (2)
N(3)–C(24)	1·44 (2)	C(19)–C(20)	1·58 (2)
C(1)–C(2)	1·37 (2)	C(20)–C(21)	1·53 (2)
C(1)–C(6)	1·40 (2)	C(21)–C(22)	1·49 (2)
C(2)–C(3)	1·44 (2)	C(24)–C(25)	1·43 (2)
C(3)–C(4)	1·34 (2)	C(24)–C(29)	1·39 (2)
C(4)–C(5)	1·35 (2)	C(25)–C(26)	1·39 (2)
C(4)–C(7)	1·54 (3)	C(26)–C(27)	1·39 (2)
C(5)–C(6)	1·43 (2)	C(27)–C(28)	1·36 (2)
C(8)–C(9)	1·36 (2)	C(28)–C(29)	1·41 (2)
O(1)–S(1)–O(2)	121·8 (6)	C(10)–C(11)–C(12)	117 (2)
O(1)–S(1)–N(1)	109·7 (6)	C(10)–C(11)–C(14)	120 (2)
O(1)–S(1)–C(1)	105·6 (6)	C(12)–C(11)–C(14)	123 (2)
O(2)–S(1)–N(1)	105·1 (6)	C(11)–C(12)–C(13)	123 (2)
O(2)–S(1)–C(1)	106·8 (6)	C(8)–C(13)–C(12)	120 (1)
N(1)–S(1)–C(1)	107·3 (6)	N(1)–C(15)–C(16)	108 (1)
O(3)–S(2)–O(4)	118·3 (6)	N(1)–C(15)–C(21)	103 (1)
O(3)–S(2)–N(2)	109·7 (6)	N(1)–C(15)–C(25)	112 (1)
O(3)–S(2)–C(8)	106·0 (6)	C(16)–C(15)–C(21)	110 (1)
O(4)–S(2)–N(2)	112·6 (6)	C(16)–C(15)–C(25)	116 (1)
O(4)–S(2)–C(8)	107·4 (6)	C(21)–C(15)–C(25)	107 (1)
N(2)–S(2)–C(8)	101·1 (6)	C(15)–C(16)–C(17)	114 (1)
S(1)–N(1)–C(15)	125·3 (9)	C(16)–C(17)–C(18)	112 (1)
S(2)–N(2)–C(22)	128·6 (9)	C(17)–C(18)–C(19)	118 (1)
C(22)–N(3)–C(23)	121 (1)	C(18)–C(19)–C(20)	116 (1)
C(22)–N(3)–C(24)	124 (1)	C(19)–C(20)–C(21)	112 (1)
C(23)–N(3)–C(24)	115 (1)	C(15)–C(21)–C(20)	119 (1)
S(1)–C(1)–C(2)	118 (1)	C(15)–C(21)–C(22)	106 (1)
S(1)–C(1)–C(6)	120 (1)	C(20)–C(21)–C(22)	118 (1)
C(2)–C(1)–C(6)	121 (1)	N(2)–C(22)–N(3)	119 (1)
C(1)–C(2)–C(3)	118 (1)	N(2)–C(22)–C(21)	128 (1)
C(2)–C(3)–C(4)	121 (2)	N(3)–C(22)–C(21)	114 (1)
C(3)–C(4)–C(5)	122 (2)	N(3)–C(24)–C(25)	117 (1)
C(3)–C(4)–C(7)	120 (2)	N(3)–C(24)–C(29)	123 (1)
C(5)–C(4)–C(7)	117 (2)	C(25)–C(24)–C(29)	120 (1)
C(4)–C(5)–C(6)	119 (2)	C(15)–C(25)–C(24)	118 (1)
C(1)–C(6)–C(5)	119 (1)	C(15)–C(25)–C(26)	127 (1)
S(2)–C(8)–C(9)	120 (1)	C(24)–C(25)–C(26)	115 (1)
S(2)–C(8)–C(13)	121 (1)	C(25)–C(26)–C(27)	124 (1)
C(9)–C(8)–C(13)	119 (1)	C(26)–C(27)–C(28)	120 (1)
C(8)–C(9)–C(10)	121 (2)	C(27)–C(28)–C(29)	118 (1)
C(9)–C(10)–C(11)	121 (2)	C(24)–C(29)–C(28)	122 (1)

The C(15)–C(21) [1·62 (2) Å] bond length is longer than the corresponding C–C bonds in the seven-membered ring and may be postulated as being a consequence of the steric interaction due to the seven-membered ring.

The bond lengths and bond angles in the rest of the molecule are as would be expected.

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