

Table 2. Bond distances (Å), angles (°), and selected torsion angles (°)

C1 C2 1.459 (2)	C1 C5 1.459 (2)	C1 C6 1.342 (2)
C2 C3 1.327 (3)	C3 C4 1.451 (3)	C4 C5 1.337 (3)
C6 C7 1.506 (2)	C6 C11 1.510 (2)	C7 C8 1.529 (2)
C7 C12 1.533 (3)	C8 C9 1.532 (3)	C9 C10 1.526 (3)
C9 C15 1.528 (3)	C10 C11 1.522 (3)	C11 C14 1.541 (3)
C12 C13 1.531 (3)	C13 C14 1.526 (3)	C13 C15 1.519 (3)
C2 C1 C5 104.8 (2)	C2 C1 C6 127.9 (2)	C5 C1 C6 127.2 (2)
C1 C2 C3 109.1 (2)	C2 C3 C4 108.6 (2)	C3 C4 C5 109.1 (2)
C1 C5 C4 108.3 (2)	C1 C6 C7 124.3 (2)	C1 C6 C11 124.2 (2)
C7 C6 C11 111.5 (2)	C6 C7 C8 109.7 (1)	C6 C7 C12 108.3 (2)
C8 C7 C12 109.4 (2)	C7 C8 C9 109.5 (2)	C8 C9 C10 108.8 (2)
C8 C9 C15 109.2 (2)	C10 C9 C15 109.6 (2)	C9 C10 C11 110.3 (2)
C6 C11 C10 109.2 (2)	C6 C11 C14 108.2 (2)	C10 C11 C14 109.2 (2)
C7 C12 C13 109.6 (2)	C12 C13 C14 108.7 (2)	C12 C13 C15 109.7 (2)
C14 C13 C15 109.8 (2)	C11 C14 C13 109.6 (2)	C9 C15 C13 109.9 (2)
C5 C1 C6 C7 -0.3 (4)	C2 C1 C6 C11 0.5 (4)	
C1 C6 C7 C8 -123.0 (2)	C1 C6 C7 C12 117.7 (2)	
C11 C6 C7 C8 58.6 (2)	C11 C6 C7 C12 -60.8 (2)	
C1 C6 C11 C10 123.2 (2)	C1 C6 C11 C14 -118.1 (2)	
C7 C6 C11 C10 -58.4 (2)	C7 C6 C11 C14 60.4 (2)	

compound are given in Table 1. Fig. 1 is a line drawing and Fig. 2 is a perspective drawing showing the atom numbering. Bond distances, angles, and selected torsion angles are presented in Table 2.*

Related literature. The structures of dimethylfulvene at 248 K (Norman & Post, 1961) and the difulvene, 1,4-bis(2,4-cyclopentadien-1-ylidene)cyclohexane (McLaughlin, Cronan & Fronczek, 1988), exhibit the

* Lists of H-atom coordinates and isotropic thermal parameters, anisotropic thermal parameters, bond distances and angles involving H, structure-factor amplitudes, torsion angles and least-squares planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51722 (21 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Structure of 6-Tosyl-1,6,11,17,18-pentaazatricyclo[12.2.1^{1,4}.1^{8,11}]octadeca-2,4(17),8(18),9-tetraene

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Abstract. C₂₀H₂₅N₅O₂S, *M_r* = 399.51, triclinic, *P* $\bar{1}$, *a* = 10.7373 (5), *b* = 9.4581 (5), *c* = 10.8159 (4) Å, α = 74.012 (4), β = 98.504 (3), γ = 77.587 (3)°, *U* = 1005.8 (1) Å³, *Z* = 2, *D_x* = 1.319 Mg m⁻³, graphite-

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expected single–double bond alternation within the fulvene ring system like the title compound. The bond angle C7–C6–C11 = 111.5 (2)° of the title compound compares with the analogous bond angles of dimethylfulvene, 114.0 (6)°, and 1,4-bis(2,4-cyclopentadien-1-ylidene)cyclohexane, 112.71 (9)°.

The adamantane ring system has been extensively characterized including the parent hydrocarbon by Nordman & Schmitkons (1965) and refined by Donohue & Goodman (1967). The geometry about the double bond of adamantylideneadamantane (Swen-Walstra & Visser, 1971) is similar to that of the title compound.

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monochromated Cu *K* α radiation, λ = 1.5418 Å, μ = 1.599 mm⁻¹, *F*(000) = 424, *T* = 293 K, *R* = 0.059 for 2903 observed reflexions [*I* > 3 σ (*I*)]. The pyrazole rings, which are quite similar, are inclined at different

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Table 1. Final atomic coordinates and equivalent isotropic thermal parameters ($\text{\AA}^2 \times 10^4$)
$$U_{eq} = \frac{1}{3} \sum U_{ij} a_i^* a_j^* \cos(\mathbf{a}_i, \mathbf{a}_j).$$

	x	y	z	U_{eq}
S	0.23454 (6)	0.22656 (8)	0.30002 (7)	415 (3)
O(1)	0.2726 (3)	0.3399 (4)	0.2062 (2)	681 (12)
O(2)	0.3261 (2)	0.0850 (3)	0.3765 (3)	656 (10)
N(1)	0.1779 (2)	0.3070 (2)	0.4010 (2)	385 (8)
C(2)	0.1570 (3)	0.2109 (3)	0.5250 (3)	376 (9)
C(3)	0.2603 (2)	0.1905 (3)	0.6427 (2)	347 (8)
N(4)	0.2274 (2)	0.2521 (3)	0.7334 (2)	414 (8)
N(5)	0.3400 (3)	0.2132 (3)	0.8253 (2)	466 (9)
C(6)	0.4400 (3)	0.1305 (4)	0.7925 (3)	518 (11)
C(7)	0.3932 (3)	0.1108 (3)	0.6760 (3)	469 (10)
C(8)	0.3429 (5)	0.2776 (5)	0.9334 (3)	649 (16)
C(9)	0.3177 (5)	0.4489 (5)	0.8840 (4)	795 (20)
C(10)	0.4138 (4)	0.5038 (5)	0.8060 (4)	643 (15)
C(11)	0.3851 (5)	0.6740 (5)	0.7492 (5)	723 (17)
C(12)	0.2652 (4)	0.7532 (5)	0.6365 (5)	732 (17)
N(13)	0.2634 (3)	0.6868 (3)	0.5296 (3)	516 (10)
N(14)	0.1692 (2)	0.6172 (3)	0.5042 (3)	461 (9)
C(15)	0.1985 (3)	0.5595 (3)	0.4106 (3)	406 (9)
C(16)	0.3124 (3)	0.5911 (4)	0.3749 (4)	596 (13)
C(17)	0.3496 (4)	0.6723 (4)	0.4528 (4)	630 (14)
C(18)	0.1146 (3)	0.4717 (3)	0.3584 (3)	436 (10)
C(19)	0.1037 (3)	0.1827 (3)	0.2127 (3)	377 (9)
C(20)	0.0771 (3)	0.0425 (3)	0.2581 (3)	480 (11)
C(21)	-0.0279 (4)	0.0127 (4)	0.1899 (3)	527 (12)
C(22)	-0.1074 (3)	0.1203 (4)	0.0762 (3)	481 (11)
C(23)	-0.0784 (4)	0.2587 (4)	0.0317 (3)	593 (13)
C(24)	0.0255 (4)	0.2902 (4)	0.0986 (3)	552 (12)
C(25)	-0.2233 (5)	0.0888 (7)	0.0022 (5)	721 (18)

angles with respect to the tosyl substituent. The N(1) atom is slightly pyramidal [the surrounding angles total $358.0(2)^\circ$]. The molecule has an approximate mirror plane through N(1) and C(10), the sequence of torsion angles being: $(ga)^- - (ga)^+ - a^+ - a^+ - g^- - g^- - a^+ - g^- - g^- - (ga)^+ - a^- - a^+ - (ga)^- - (ga)^+$, where $g^{+/-}$, $a^{+/-}$ and $(ga)^{+/-}$ denote angles in the ranges ± 75 , 180 ± 30 and $\pm 75-150^\circ$, respectively [Urbanczyk-Lipkowska, Krajewski, Gluzinski, Andreotti & Bocelli (1981). *Acta Cryst. B37*, 470-473].

Experimental. Colourless prism, $0.27 \times 0.33 \times 0.47$ mm, used for data collection and determination of lattice constants (Cu $K\alpha$, 91 reflexions up to $\theta = 45^\circ$); the low values of the standard deviations reflect the precision in the fit, not the accuracy of the values. Philips PW 1100 diffractometer, Cu $K\alpha$, graphite monochromator, bisecting geometry, $\omega/2\theta$ scan mode, 3414 independent reflexions up to $\theta = 65^\circ$, hkl range $-12, 12; -11, 11; 0, 12$. Two standard reflexions were measured every 90 min, no decay observed. The structure was solved by direct methods (MULTAN80, Main *et al.*, 1980). Empirical absorption correction (Walker & Stuart, 1983) gave max. and min. transmission factors of 1.255 and 0.659, respectively. H atoms, located in a difference synthesis, included isotropically in last cycles of refinement. Empirical weights so as to give no trends in $\langle w\Delta F^2 \rangle$ versus $\langle |F_o| \rangle$ and $\langle (\sin \theta) / \lambda \rangle$. $R = 0.059$, $wR = 0.070$, $S = 1.09$. Max. and average $\Delta/\sigma = 0.92$ and 0.07 . Final

Table 2. Selected geometrical parameters (\AA , $^\circ$)

N(1)-C(2)	1.477 (3)	N(1)-C(18)	1.469 (3)
C(2)-C(3)	1.497 (4)	C(18)-C(15)	1.499 (5)
C(3)-N(4)	1.325 (4)	C(15)-N(14)	1.322 (4)
C(3)-C(7)	1.404 (3)	C(15)-C(16)	1.402 (5)
N(4)-N(5)	1.356 (3)	N(13)-N(14)	1.355 (4)
N(5)-C(6)	1.340 (4)	N(13)-C(17)	1.342 (5)
C(6)-C(7)	1.363 (5)	C(16)-C(17)	1.360 (6)
N(5)-C(8)	1.459 (5)	C(12)-N(13)	1.459 (6)
C(8)-C(9)	1.508 (6)	C(11)-C(12)	1.524 (6)
C(9)-C(10)	1.514 (7)	C(10)-C(11)	1.500 (6)
S-O(1)	1.434 (3)	S-O(2)	1.424 (2)
S-N(1)	1.612 (3)	S-C(19)	1.764 (3)
S-N(1)-C(2)	119.1 (2)	S-N(1)-C(18)	121.0 (2)
N(1)-C(2)-C(3)	112.9 (2)	N(1)-C(18)-C(15)	112.9 (2)
C(2)-C(3)-C(7)	129.5 (3)	C(18)-C(15)-C(16)	128.7 (3)
C(2)-C(3)-N(4)	118.8 (2)	C(18)-C(15)-N(14)	120.3 (3)
N(4)-C(3)-C(7)	111.7 (2)	N(14)-C(15)-C(16)	111.0 (3)
C(3)-N(4)-N(5)	104.5 (2)	C(15)-N(14)-N(13)	105.6 (2)
N(4)-N(5)-C(8)	119.2 (3)	N(14)-N(13)-C(12)	119.5 (3)
N(4)-N(5)-C(6)	111.7 (2)	N(14)-N(13)-C(17)	110.7 (3)
C(6)-N(5)-C(8)	128.6 (3)	C(17)-N(13)-C(12)	129.6 (3)
N(5)-C(6)-C(7)	107.8 (3)	N(13)-C(17)-C(16)	108.1 (3)
C(3)-C(7)-C(6)	104.2 (3)	C(15)-C(16)-C(17)	104.6 (3)
N(5)-C(8)-C(9)	111.6 (3)	C(11)-C(12)-N(13)	113.4 (4)
C(8)-C(9)-C(10)	114.2 (4)	C(10)-C(11)-C(12)	116.4 (4)
C(2)-N(1)-C(18)	117.9 (2)	C(9)-C(10)-C(11)	114.8 (4)
N(1)-S-C(19)	107.4 (1)	O(2)-S-C(19)	106.8 (2)
O(2)-S-N(1)	107.5 (1)	O(1)-S-C(19)	106.9 (1)
O(1)-S-N(1)	106.6 (2)	O(1)-S-O(2)	120.9 (2)
C(18)-N(1)-C(2)-C(3)	-92.2 (3)	C(15)-C(18)-N(1)-C(2)	90.3 (3)
N(1)-C(2)-C(3)-N(4)	112.8 (3)	N(14)-C(15)-C(18)-N(1)	-108.0 (3)
C(2)-C(3)-N(4)-N(5)	179.7 (2)	N(13)-N(14)-C(15)-C(18)	179.4 (3)
C(3)-N(4)-N(5)-C(8)	173.0 (3)	C(12)-N(13)-N(14)-C(15)	-175.4 (3)
N(4)-N(5)-C(8)-C(9)	-63.2 (4)	C(11)-C(12)-N(13)-N(14)	114.7 (4)
N(5)-C(8)-C(9)-C(10)	-58.4 (5)	C(10)-C(11)-C(12)-N(13)	-52.0 (5)
C(8)-C(9)-C(10)-C(11)	176.4 (4)	C(9)-C(10)-C(11)-C(12)	-70.0 (5)
O(2)-S-C(19)-C(20)	24.2 (3)	O(1)-S-C(19)-C(24)	-26.1 (3)
O(2)-S-N(1)-C(2)	-36.1 (2)	O(1)-S-N(1)-C(18)	29.5 (3)
S-N(1)-C(2)-C(3)	103.8 (2)		

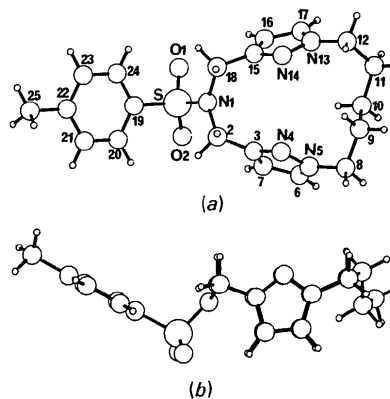


Fig. 1. (a) A view of the molecule showing the atomic numbering. (b) The molecular structure showing the pseudo-mirror plane.

$\Delta\rho = \pm 0.70 \text{ e \AA}^{-3}$; the highest peaks are close to atoms C(8), C(9), C(10) and C(11), which have the highest thermal factors. No extinction correction. Computing with XRAY76 (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976) on a VAX 11/750 computer.

Scattering factors from *International Tables for X-ray Crystallography* (1974). Final atomic coordinates for the non-H atoms and the main geometrical parameters are given in Tables 1 and 2,* according to the numbering scheme given in Fig. 1 (*PLUTO*, Motherwell & Clegg, 1978).

Related literature. The synthesis of the title compound is described in Iturrino, Juanes, Mendoza, Rodriguez-Ubis & Serrano (1989). Similar ring conformations around the SO₂ group have been found in four phenylsulfonyl derivatives by searching the Cambridge Structural Database (Allen *et al.*, 1979). In contrast, no 14-membered rings containing N atoms at similar positions could be found.

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* Lists of structure factors, anisotropic thermal parameters, bond distances, bond angles and torsion angles, H-atom parameters and references for the four phenylsulfonyl derivatives mentioned in *Related literature* have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51759 (24 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Redetermination of the Absolute Configuration of Deoxyprepacifenol, from the Mediterranean Red Alga *Laurencia majuscula*

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Abstract. 3,4'-Dibromo-4-chloro-1',3',3',4-tetramethylspiro(cyclohexane-1,2'-[7]oxabicyclo[4.1.0]hept-4'-ene), C₁₅H₂₁Br₂ClO, *M_r* = 412.6, orthorhombic, *P*2₁2₁2₁, *a* = 11.6520 (14), *b* = 12.079 (2), *c* = 11.606 (3) Å, *V* = 1633.5 (9) Å³, *Z* = 4, *D_x* = 1.678 g cm⁻³, λ(MoKα) = 0.71073 Å, μ = 50.7 cm⁻¹, *F*(000) = 824, *T* = 297 K, *R* = 0.053 for 2288 observations (of 3909 unique data). The original absolute configuration determination has been questioned as based on a small difference in *wR* between enantiomorphous models, 0.085 *vs* 0.088. Our study, on material from a new natural source, confirms the molecular structure and the absolute configuration with

Professor J. Mendoza for suggesting the problem and providing the material.

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correlation to chiroptical data and increases the resolution of the determination.

Experimental. Colorless, tabular crystals of (1) isolated from *Laurencia majuscula*, m.p. 402 K. Crystal size 0.28 × 0.40 × 0.52 mm, space group from systematic

