

Fig. 3. Projection de la structure selon l'axe *c*.

deux groupements méthyles adjacents en position 5 et 6.

L'organisation de la structure est représentée sur la Fig. 3.

L'élément de base de cet édifice cristallin est l'existence de piles infinies dans la direction *c*. Il faut noter que ces piles sont formées par la superposition de

molécules homologues par le plan de glissement: les plans moyens des molécules font entre eux un angle de 2° . La surface de recouvrement entre les noyaux ellipticine est importante et la distance moyenne interplanaire est alternativement de 3,50 et 3,55 Å le long d'une pile (Fig. 3).

La cohésion entre les piles est réalisée par de faibles contacts de van der Waals: $C(8)(x,y,z) \cdots C(9)(-x,-y,-z) = 3,79(1)$; $C(9)(x,y,z) \cdots C(9)(-x,-y-z) = 3,81(1)$; $C(7)(x,y,z) \cdots N(2)(-1+x, \frac{1}{2}-y, \frac{1}{2}+z) = 3,45(1)$ Å.

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anti-8-*tert*-Butoxy-*exo*-3,3-diphenyl-2-(*p*-toluenesulfonamidomethyl)-tricyclo[3.2.1.0^{2,4}]octane

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Abstract. $C_{32}H_{37}NO_3S$, $M_r = 515.2$, monoclinic, $P2_1/c$, $a = 14.8226(6)$, $b = 10.7633(4)$, $c = 18.5221(8)$ Å, $\beta = 99.71(1)^\circ$, $V = 2912.7(3)$ Å³, $Z = 4$, $D_c = 1.176$, $D_m = 1.17(1)$ Mg m⁻³. The structure was solved by direct methods and converged to a conventional R of 0.074 for the 335 parameters varied and 3391 reflections used in the refinement. With respect to the tricyclooctane portion of the molecule the *tert*-butoxy group at bridgehead position 8 is *anti* to the phenyl group at position 3, and the contact distance between a bridgehead C and the nearest phenyl carbon C(20) capable of participating in a long-range aryl migration is 2.916(6) Å.

Introduction. The title compound is a member of a series being investigated in a kinetics study of solvolysis reactions involving long-range aryl migration accompanied by electrocyclic ring openings (Wilt, Malloy, Mookerjee & Sullivan, 1974). The compound was prepared by treatment of the corresponding amine with *p*-toluenesulfonyl chloride in aqueous dimethylform-

amide, and large crystals were obtained upon cooling a hexane/chloroform solution of the solid (courtesy of Dr V. A. Curtis). The structure determination was undertaken to identify molecular parameters which could influence the mechanism of reaction in the long-range aryl-migration process.

A fragment of approximate dimensions 0.37 × 0.33 × 0.26 mm was cut from a larger crystal and mounted nearly parallel to the *b* axis. The crystal has systematic absences ($0k0$, k odd; $h0l$, l odd) characteristic of space group $P2_1/c$. ω scans of several intense reflections taken with a small take-off angle and an open detector displayed band widths at half-height of less than 0.1° . Cell constants were determined by a least-squares fit of 12 reflections ($68 < |2\theta| < 76^\circ$) measured at 21° with Cu $K\alpha$ radiation [$\lambda(\text{Cu } K\alpha_1) = 1.54050$, $\lambda(\text{Cu } K\alpha_2) = 1.54433$ Å]. The density was estimated from neutral buoyancy in a chlorobenzene/1,2-dichlorobenzene mixture.

Intensities were measured with a Picker FACS-I automated diffractometer and Ni-filtered Cu radiation

(40 kV, 12 mA, take-off angle = 1.5°). Data were collected using the coupled $\theta:2\theta$ technique from 2 to 120°, with a scan rate of 2° min⁻¹ and range of 2.4(1 + 0.4 tan θ)°, and with 10 s background measurements at both extremities of the scan. A total of 4512 reflections were measured of which 3391 having $|F_o| > 3\sigma(F_o)$ were used in the structure solution and refinement; $\sigma^2(F_o) = 1/w = (F_o/2I_n)^2 [I_s + (t_s/t_b)^2 I_b + (0.02I_n)^2]$, where I , t , s , n and b refer to intensity (counts), time (s), scan, net and background respectively. Three standard reflections measured after every 50 data reflections showed an average intensity decrease of 2.4% and no correction for crystal decay was deemed necessary. Intensities, which were corrected for absorption as a function of ϕ [linear $\mu = 1.14$ mm⁻¹; maximum/minimum transmission (calculated) = 1.18, (observed) = 1.16] and Lorentz-polarization effects in the usual manner, were converted to normalized structure magnitudes.

The structure was solved through use of the direct-methods program *MULTAN* (Germain, Main & Woolfson, 1971). Of several E maps generated from 300 reflections ($1.87 < |E| < 4.50$), the complete structure was contained in one map with the highest combined figure of merit (2.52). The structure was refined by means of a full-matrix least-squares program which minimized the function $\sum w(|F_o| - |F_c|)^2$, utilized anisotropic temperature factors and included a correction for secondary extinction. Atomic scattering factors for nonhydrogen atoms were taken from tabulations of Cromer & Waber (1965) and for H atoms the values of Stewart, Davidson & Simpson (1965) were used. A difference Fourier electron density map contained peaks near all 37 expected H atom positions. H atoms with a calculated C-H separation of 1.0 Å and $B = 4.0$ Å² were included in the model structure and held fixed. Refinement converged to $R = [\sum (|F_o| - |F_c|) / \sum |F_o|] = 0.074$ and $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w(F_o)^2]^{1/2} = 0.084$. There were no shifts in the final cycle of refinement and the maximum peak in the final difference Fourier electron density map was 0.6 e Å⁻³. Fig. 1 is a stereoview of the molecule and Fig. 2 shows the atom numbering scheme and bonding distances and angles (atom numbers with-

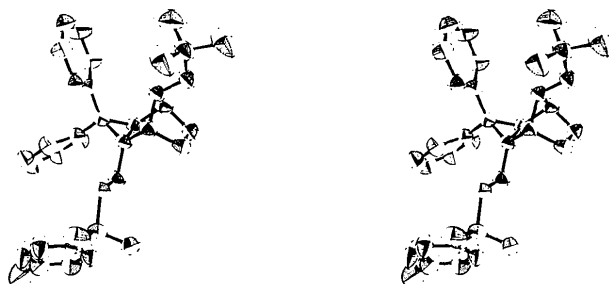


Fig. 1. A stereoview of the C₃₂H₃₇NO₃S molecule (Johnson, 1965).

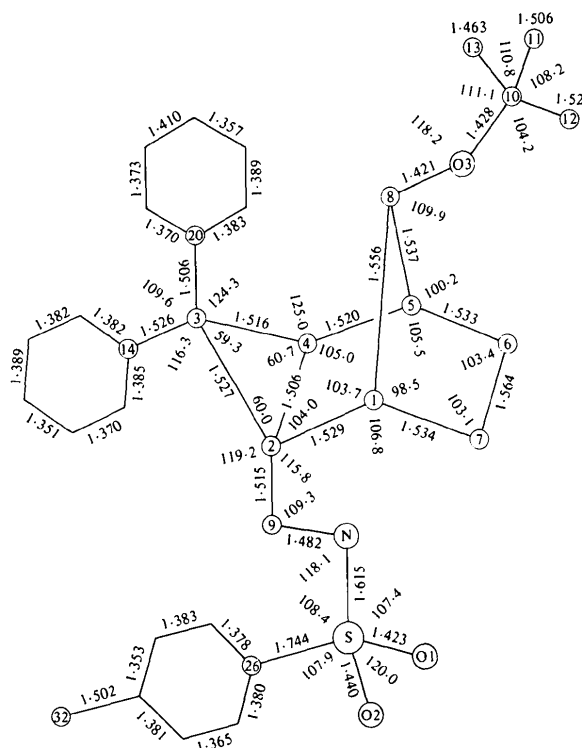


Fig. 2. A diagrammatic representation of the C₃₂H₃₇NO₃S molecule showing bond distances (Å) and angles (°). Atom numbers without elemental symbols are understood to be C atoms. Bond angles not shown in the diagram are listed in Table 2.

out elemental symbols are understood to be C atoms throughout the text). Atomic coordinates are listed in Table 1 and Table 2 lists bond angles not shown in Fig. 2. E.s.d.'s in parentheses have been calculated from the least-squares matrix and are less than 0.008 Å for bond distances and 0.5° for bond angles. E.s.d.'s in square brackets have been calculated by way of the expression [e.s.d.] = $\{[\sum (m_i - m_{ave})^2 / (i - 1)]^{1/2}\}$.

Discussion. In the tricyclooctane ring system the average C-C bond distance is 1.532 [17] Å, the longest bond distance is between atoms C(6) and C(7) which belong to only one ring, and the shortest occurs between atoms C(2) and C(4) which are common to two rings. In the bicycloheptane portion of the ring-system the 'bridgehead' plane of atoms 1-8-5 is inclined away from the cyclopropane ring; accordingly, the dihedral angles between the 1-8-5 plane of atoms and best-fit planes through atoms 1-2-4-5 and 1-5-6-7 are 129 and 120° respectively. The atoms 2-4-6-7 which define the 'base' of the bicyclo-

* Lists of anisotropic thermal parameters, H atom coordinates and structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36052 (21 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Final positional parameters and equivalent isotropic thermal parameters

	x	y	z	B _{eq} [†] (Å ²)
S	0.56437 (8)	0.30204 (13)	0.50683 (6)	4.0
O(1)	0.5742 (2)	0.1819 (3)	0.5392 (2)	5.2
O(2)	0.5823 (2)	0.4112 (3)	0.5519 (2)	5.7
O(3)	0.1061 (2)	0.1553 (3)	0.4651 (2)	5.3
N	0.4592 (2)	0.3159 (3)	0.4671 (2)	4.0
C(1)	0.2655 (3)	0.2193 (4)	0.4575 (2)	4.0
C(2)	0.3184 (3)	0.2356 (4)	0.3940 (2)	3.6
C(3)	0.2777 (3)	0.2995 (4)	0.3223 (2)	3.8
C(4)	0.2641 (3)	0.1614 (4)	0.3327 (2)	4.0
C(5)	0.1863 (3)	0.1043 (5)	0.3654 (3)	4.5
C(6)	0.2313 (4)	0.0062 (5)	0.4199 (3)	5.3
C(7)	0.2821 (3)	0.0855 (5)	0.4850 (3)	5.0
C(8)	0.1644 (3)	0.2049 (4)	0.4188 (3)	4.3
C(9)	0.4213 (3)	0.2198 (4)	0.4131 (2)	4.0
C(10)	0.0459 (4)	0.2384 (5)	0.4938 (4)	6.1
C(11)	0.0975 (5)	0.3441 (6)	0.5352 (4)	8.9
C(12)	0.0039 (5)	0.1595 (6)	0.5481 (4)	9.1
C(13)	-0.0252 (5)	0.2853 (8)	0.4357 (5)	10.8
C(14)	0.3449 (3)	0.3342 (4)	0.2715 (2)	4.0
C(15)	0.3970 (4)	0.4407 (5)	0.2853 (3)	5.0
C(16)	0.4595 (4)	0.4727 (6)	0.2409 (3)	6.4
C(17)	0.4690 (4)	0.4001 (7)	0.1807 (3)	6.4
C(18)	0.4165 (5)	0.2976 (6)	0.1665 (3)	6.6
C(19)	0.3543 (4)	0.2652 (5)	0.2101 (3)	5.6
C(20)	0.2022 (3)	0.3945 (5)	0.3154 (3)	4.2
C(21)	0.1294 (4)	0.3848 (5)	0.2582 (3)	5.9
C(22)	0.0593 (4)	0.4720 (7)	0.2490 (3)	7.7
C(23)	0.0625 (4)	0.5703 (7)	0.2953 (4)	7.7
C(24)	0.1363 (4)	0.5797 (5)	0.3541 (3)	6.3
C(25)	0.2049 (3)	0.4927 (5)	0.3628 (3)	4.6
C(26)	0.6342 (3)	0.3081 (5)	0.4400 (2)	3.8
C(27)	0.6577 (4)	0.2009 (5)	0.4069 (3)	5.6
C(28)	0.7079 (4)	0.2068 (6)	0.3506 (3)	6.3
C(29)	0.7368 (4)	0.3169 (7)	0.3276 (3)	6.7
C(30)	0.7138 (5)	0.4235 (6)	0.3618 (4)	8.5
C(31)	0.6635 (4)	0.4209 (5)	0.4172 (3)	6.7
C(32)	0.7919 (6)	0.3258 (8)	0.2668 (4)	11.5

[†] $B_{eq} = \frac{1}{3} \sum_i \sum_j B_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$. E.s.d.'s are 0.1–0.6 Å².

heptane ring are quite planar as evidenced by an average deviation of only 0.022 [1] Å from the best-fit plane through them. The cyclopropane ring is inclined 121° away from the best-fit plane through atoms 1–2–4–5. Angles internal to the cyclopropane ring are essentially equal and have an average value of 60.0 [7]°. Bonding parameters in this portion of the molecule are comparable to those reported for similar polycyclic compounds (MacDonald & Trotter, 1965*a,b*; Hitchcock & Beheshti, 1979).

The three phenyl rings in the molecule are planar to within experimental error and the average aromatic

Table 2. Bond angles in the C₃₂H₃₇NO₃S molecule which are not shown in Fig. 2 (e.s.d.'s ≤ 0.5°)

O(1)–S–26	107.6°	4–5–8	103.2°
O(2)–S–N	105.0	1–8–O(3)	113.3
1–2–3	122.8	1–8–5	94.3
4–2–9	120.3	11–10–O(3)	111.5
2–3–20	123.9	12–10–13	110.8
4–3–14	115.6		

C–C bond distance is 1.377 [14] Å. The phenyl ring nearest the bridgehead C(8) is active in the long-range aryl-migration reaction, and it has intramolecular nonbonded contacts to C(8) ranging from 2.916 (6) Å for C(20) to 4.671 (8) Å for C(23). The dihedral angle between the best-fit plane through this phenyl group (atoms 20–25) and the 1–8–5 plane is 23°.

Bond distances and angles about the S atom are comparable to those known for other XYSO₂ groups of atoms (Wells, 1962). In particular, all angles about S are nominally tetrahedral angles except for the O(1)–S–O(2) value of 120.0 (3)°. The S–O(2) bond distance is significantly longer than the S–O(1) distance in accord with the role of O(2) as an acceptor atom in a hydrogen bond. The separation between hydrogen-bonded atoms N(x,y,z) and O(2)(1–x, 1–y, 1–z) is 3.010 (5) Å and the N–H···O(2) angle is 147.3 (2)°. This hydrogen bond is the only intermolecular feature of consequence in the crystal.

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