

- International Tables for X-ray Crystallography* (1962). Vol. III, S. 166. Birmingham: Kynoch Press.
- International Tables for X-ray Crystallography* (1969). Vol. I, S. 15, 246, 459. Birmingham: Kynoch Press.
- KRSTANOVIĆ, I. R. (1958). *Acta Cryst.* **11**, 896–897.
- POLECK, T. & THÜMMEL, K. (1883). *Ber. dtsh. chem. Ges.* **16**, 2435–2449.
- PRANDL, W. (1966). *Z. Kristallogr.* **123**, 81–116.
- RAMDOHR, P. (1938). *S.B. Preuss. Akad. Wiss. (phys.-math. Klasse)*, **6**, 71–91.
- REUTER, B. & HARDEL, K. (1960). *Angew. Chem.* **72**, 138–139.
- REUTER, B. & HARDEL, K. (1965). *Z. anorg. allgem. Chem.* **340**, 168–180.
- SCHERINGER, C. (1962). *Verfeinerung nach der Methode der kleinsten Quadrate bei Strukturen mit starren Atomgruppen*. Bonn: Organisch-Chemisches Institut der Universität Bonn.
- SCHULTZE-RHONHOF, E. (1966). *World List of Crystallographic Computer Programs*, 2. Ausgabe, Nr. 5063–5068.
- SCHULTZE-RHONHOF, E. (1972). *Acta Cryst.* **B28**, 1969.
- SCHULTZE-RHONHOF, E. (1973). *Methodicum Chemicum*, Bd. I, Teil 1, 1. Ausgabe S. 546. Stuttgart: Georg Thieme.
- SCHULTZE-RHONHOF, E. & BERGERHOFF, G. (1966). *Z. anorg. allgem. Chem.* **347**, 240–247.
- STAMM, H. & WINTZER, H. (1938). *Ber. dtsh. chem. Ges.* **71**, 2212–2219.
- VAND, V., EILAND, P. F. & PEPINSKY, R. (1957). *Acta Cryst.* **10**, 303.
- WEHE, D. J., BUSING, W. R. & LEVY, H. A. (1962). *World List of Crystallographic Computer Programs*, 1. Ausgabe, Nr. 362.
- WUENSCH, B. J. (1963). *Science*, **141**, 804–805.
- WUENSCH, B. J. (1964). *Z. Kristallogr.* **119**, 437–453.
- WUENSCH, B. J., TAKÉUCHI, Y. & NOWACKI, W. (1966). *Z. Kristallogr.* **123**, 1–20.

Acta Cryst. (1974). **B30**, 2558

Crystal Structure of $C_{33}H_{47}NO_9S$, an Advanced Intermediate in the Synthesis of Talatisamine*

By F. R. AHMED

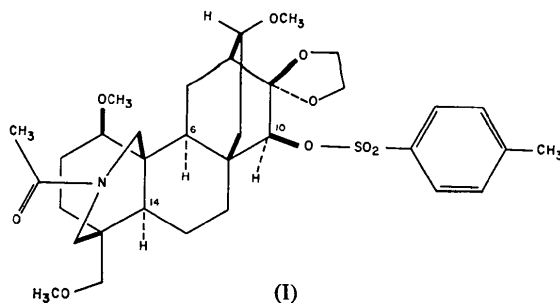
Division of Biological Sciences, National Research Council of Canada, Ottawa, Canada K1A 0R6

(Received 25 June 1974; accepted 27 June 1974)

Crystals of $C_{33}H_{47}NO_9S$ are triclinic, $P\bar{1}$, with $a = 13.556$, $b = 13.907$, $c = 8.675$ Å, $\alpha = 96.80$, $\beta = 93.02$, $\gamma = 101.62^\circ$, and $Z = 2$. The structure has been determined by the direct method, and refined by block-diagonal least-squares calculations to $R = 0.063$ for 3287 observed reflexions. This study has confirmed that the synthesized material is the correct advanced intermediate of talatisamine. Due to close packing in the crystal structure, one of the methyl groups is forced into disorder. The O–S–C angle in the chain part of the tosyl moiety is $97.6(2)^\circ$ as compared to 104.7° in the toluene-*p*-sulphonates. Unequal S–O bonds of lengths 1.579 (3), 1.419 (4), and 1.416 (4) Å are observed.

Introduction

According to Wiesner (1973) the compound $C_{33}H_{47}NO_9S$, (I), is a very advanced intermediate in the total synthesis of talatisamine, an alkaloid of the delphinine type.



By a simple pyrolytic rearrangement which has ample precedents the molecule can be changed to the fully substituted talatisamine system. This intermediate is the product of a long and laborious synthesis, the details of which will be described by Wiesner in a future publication. Its characterization by X-rays was urgently required in order to verify that the synthesized material was in fact that which Wiesner and coworkers set out to produce.

On slow crystallization from methanol-ether, needle-shaped crystals appeared with some fat prisms, but if one did not interrupt at this point some of the prisms became overgrown with needles. The crystalline sample produced by Wiesner contained suitable crystals for the structure determination.

Experimental

Crystal data

Formula: $C_{33}H_{47}NO_9S$; F.W. 633.80.
Unit cell: triclinic, $P\bar{1}$, $Z = 2$

* Issued as NRCC No. 14261.

$$\begin{aligned}
 a &= 13.556 (4) \text{ \AA} & \alpha &= 96.80 (5)^\circ \\
 b &= 13.907 (3) & \beta &= 93.02 (5) \\
 c &= 8.675 (3) & \gamma &= 101.62 (5) \\
 D_x &= 1.327 \text{ g cm}^{-3} & V &= 1585.72 \text{ \AA}^3 \\
 D_o &= 1.320 \text{ g cm}^{-3} & & \text{(by flotation in} \\
 & & & \text{aqueous KI solution at } 23^\circ\text{).}
 \end{aligned}$$

Radiation: Cu $K\alpha$ and Ni filter, $\lambda(K\alpha_1) = 1.54050$, $\lambda(K\alpha_2) = 1.54434 \text{ \AA}$, $\mu(\text{Cu}) = 13.53 \text{ cm}^{-1}$

Crystal shape: thin triclinic prism of length 0.45 mm (along c) and a parallelogram cross section of sides 0.067 and 0.052 mm.

Intensities

The intensities were measured on an automatic four-circle diffractometer with the crystal mounted along b^* , by the θ - 2θ scan method, measuring the background at the start and end of each scan. For the range $2\theta \leq 130^\circ$ ($\sin \theta/\lambda = 0.586$), a total of 5392 lattice points were scanned but only 3287 reflexions were observed above threshold. Thus the number of observations per parameter was 5.62. The net counts were corrected for the Lorentz-polarization effect, and for absorption by the Gaussian integration method with grid intervals of $6 \times 6 \times 4$ (Ahmed, 1970).

Structure determination

The distribution statistics of the normalized structure factors, shown in Table 1(a), were in good agreement with those derived by Karle, Dragonette & Brenner (1965) for centrosymmetric space groups. In the first trial of the automated symbolic addition procedure the

sign indications for the four assumed symbols and their cross products were not self-consistent. The corresponding E map showed two images of the molecule, related by a translation vector equal to one of the repeating interatomic vectors in the structure. The correct set of phases, however, was obtained by manually selecting the origin- and symbols-defining reflexions as shown in Table 1(b), so that most of the 30 strongest \sum_2 relations, *i.e.* with the highest $|E_H E_K E_{H-K}|$ were utilized directly in the very early stages of the phasing process. The E map for this second trial revealed all 44 non-hydrogen atoms of the molecule without any ambiguity. The correct position of the molecule was found to be half-way between the two images produced in the first E map. The orientation of the molecule was the same in both maps.

Table 1. The $|E|$ distribution statistics and the starting phases

(a) Statistics of the $|E|$ distribution

	$C_{33}H_{47}NO_9S$	Centric	Non-centric
$\langle E \rangle$	0.822	0.798	0.886
$\langle E ^2 \rangle$	0.988	1.000	1.000
$\langle E^2 - 1 \rangle$	0.922	0.968	0.736
$ E \geq 3.0$	0.37%	0.3%	0.01%
$ E \geq 2.0$	4.02	5.0	1.8
$ E \geq 1.0$	31.57	32.0	37.0

(b) The starting reflexions for the successful trial

Ser. No.	h	k	l	E	
2	-7	10	2	+3.904	Origin-defining
4	8	4	3	+3.425	
9	3	-1	4	+3.126	
1	7	7	2	-4.111	Permuted with \pm signs
3	-3	9	5	-3.611	
10	6	3	0	+3.116	
23	1	0	2	-2.946	B
12	5	7	-5	-3.093	C

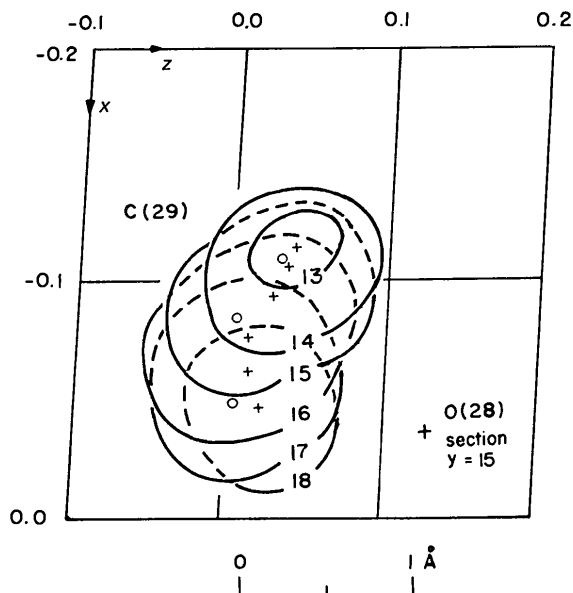


Fig. 1. A composite drawing of the 1 e \AA^{-3} contour lines of the disordered methyl carbon C(29). The y sections are at 0.33 \AA intervals, with $y = \frac{1}{2}$ corresponding to section 20.9. The small circles identify the selected sites for the partial atoms.

Experience of the determination of this fairly large structure by the direct method leads to the following two conclusions: (1) as stated by Schenk (1973), it is important to utilize most of the 10 or 20 triples with the highest $|E_H E_K E_{H-K}|$ products in the very early stages of phasing; (2) as reported by Bürgi & Dunitz (1971), O'Connor (1973), and Huber (1974), when two images of the molecule are produced in a given E map there is a good chance that the correct structure is the average of the two images.

Refinement

R for the first trial structure was 0.26. The refinement was carried out by block-diagonal least-squares calculations, minimizing $\sum w(\Delta F)^2$, where $w = 1/\{1 + [(|F_o| - 25)/25]^4\}$ and $3.1 \leq |F_o| \leq 136.5$, and excluding unobserved reflexions. During the refinement, the disorder of atom C(29) and its associated H atoms was suspected, since the O(28)-C(29) bond length re-

mained below 1.29 \AA instead of the expected value of 1.42 \AA . The electron-density distribution of C(29) was then examined in a difference map from which all the other non-hydrogen atoms were subtracted. A composite drawing of the $1 e \text{ \AA}^{-3}$ contour lines in this map at C(29) is given in Fig. 1. For best fit, C(29) was represented by three fractional atoms as shown in Fig. 1, and refined by successive difference maps, but its associated H atoms were excluded from the calculations. All other H atoms were unambiguously determined from a difference map, and refined isotropically. Their peak heights were $0.3\text{--}0.6 e \text{ \AA}^{-3}$. For the final cycle, $R=0.063$, $R_w=0.066$, $\langle \Delta/\sigma \rangle=0.25$, $(\Delta/\sigma)_{\max}=1.1$, and $|\Delta\rho|_{\max}<0.2 e \text{ \AA}^{-3}$ except in the neighbourhood of C(29).

The scattering factors were those of Hanson, Herman, Lea & Skillman (1964) for C, N, O, S, and of Stewart, Davidson & Simpson (1965) for H. All calculations were carried out on the IBM 360 with the programs of Ahmed, Hall, Pippy & Huber (1966).

Results

A perspective view of the molecule showing its conformation and the numbering system is presented in Fig. 2. The refined atomic parameters and their estimated standard deviations are listed in Table 2. The structure-factor table corresponding to this set of parameters is available.* There are no individual high discrepancies in the 3287 observed reflexions, and only 7 of the 2105 unobserved reflexions are calculated higher than 1.5 times their threshold amplitudes. The bond lengths and valency angles, not corrected for thermal vibration, are given in Tables 3 and 4. The C-H lengths are in the range $0.83\text{--}1.18 (4) \text{ \AA}$, and their mean is 0.995 \AA .

* This table has been deposited with the British Library Lending Division, as Supplementary Publication No. SUP 30547 (24 pp, 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

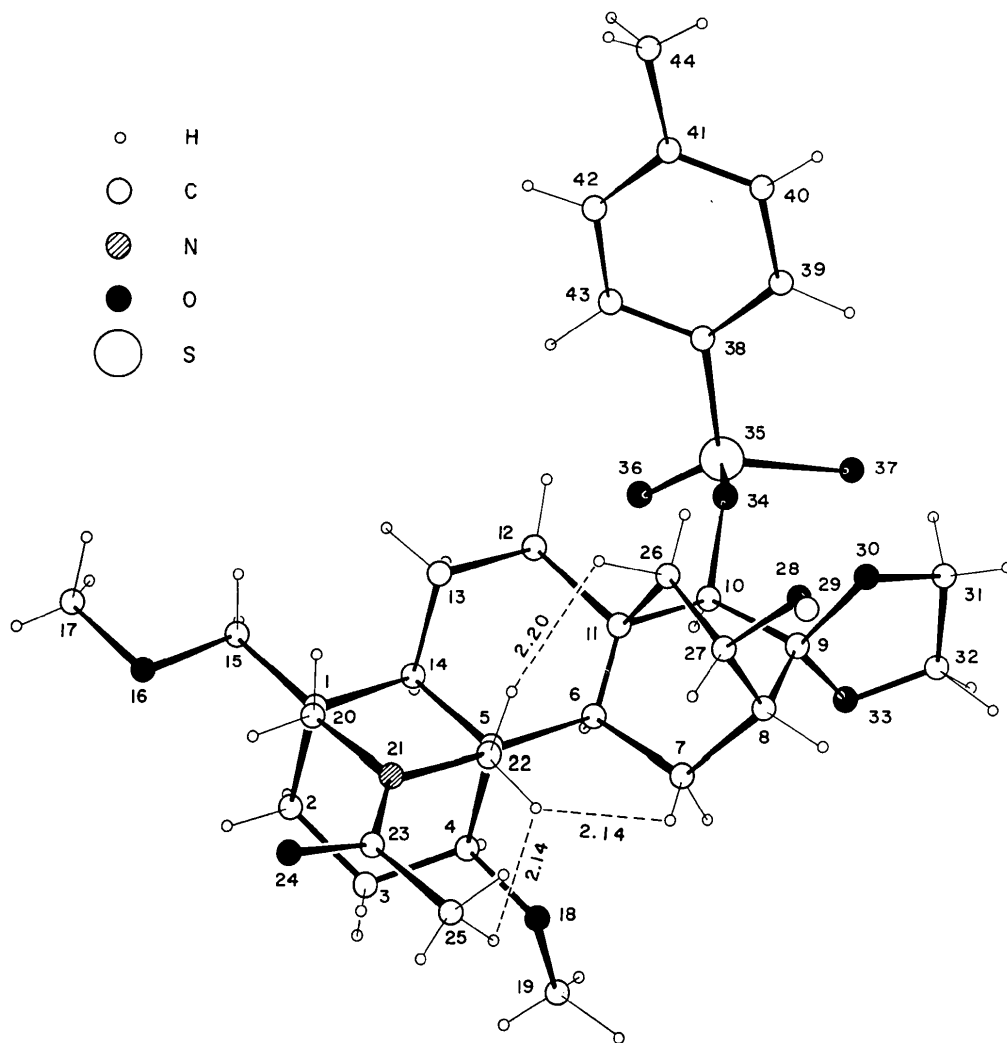


Fig. 2. A perspective view of the $C_{33}H_{47}NO_9S$ molecule, showing the conformation and the numbering system. The $H \cdots H$ distances are in Å .

Discussion

The molecular structure shown in Fig. 2 is consistent with formula (I) which was proposed by Wiesner (1973). The conformation is identical in both, and the three H atoms at C(6), C(10) and C(14) are *cis* as predicted.

Bond lengths and angles

Most of the bond lengths compare reasonably well with the corresponding average values given by Sutton (1965). The largest discrepancies occur in the O(28)–C(29) bond due to the inaccuracy resulting from the pronounced disorder of C(29), and in the C(31)–C(32) and C(32)–O(33) bonds of the five-membered

(dioxolane) ring. The latter two bonds are of lengths 1.470 (9) and 1.377 (8) Å as compared to Sutton's average values of 1.537 ± 0.005 and 1.426 ± 0.005 Å, respectively. Similar short bond lengths in five-membered rings with 2 or 3 CH₂ groups have been reported in several other structures and the abnormality has been attributed to high thermal motion (Braun, Hornstra, Knobler, Rutten & Romers, 1973) and to disorder (Carrell, Gallen & Glusker, 1973) of one of the CH₂ groups. In the present structure, atom C(32) which is common to the short bonds has considerably high thermal parameters which may be an indication of true high thermal motion, or most likely are due to a small degree of disorder of that atom.

Table 2. Fractional coordinates, vibration tensor components (Å^2) for the expression $T = \exp[-2\pi^2(U_{11}a^{*2}h^2 + \dots + 2U_{23}b^*c^*kl + \dots)]$ and their e.s.d.'s (all quantities $\times 10^4$)

The isotropic temperature factors of the H atoms are in Å^2 . The occupancies of C(29, 1), C(29, 2) and C(29, 3) are 0.3, 0.3 and 0.4, respectively.

	x	y	z	U_{11}	U_{22}	U_{33}	$2U_{23}$	$2U_{13}$	$2U_{12}$
C(1)	4249(4)	2057(3)	-598(5)	533(31)	558(29)	474(27)	-19(44)	153(45)	309(49)
C(2)	4387(4)	1020(4)	-381(5)	595(33)	671(32)	539(30)	-53(49)	160(50)	675(54)
C(3)	3495(4)	287(3)	-228(6)	707(36)	452(27)	621(31)	23(46)	55(52)	627(52)
C(4)	2714(4)	719(3)	869(5)	635(32)	391(24)	443(25)	90(39)	43(45)	432(45)
C(5)	2612(3)	1795(3)	695(5)	598(30)	345(22)	371(23)	63(36)	135(42)	386(43)
C(6)	2047(3)	2156(3)	2120(5)	510(28)	315(21)	398(23)	26(35)	92(41)	318(40)
C(7)	914(3)	1651(3)	2184(5)	545(30)	359(23)	515(27)	-22(40)	134(45)	191(43)
C(8)	285(3)	2428(3)	2575(5)	462(28)	417(25)	518(27)	-78(41)	46(44)	259(43)
C(9)	650(4)	3014(3)	4166(5)	605(32)	437(25)	448(26)	115(41)	327(45)	500(47)
C(10)	1795(4)	3386(3)	4191(5)	677(33)	313(22)	413(25)	-43(37)	13(45)	368(43)
C(11)	2152(3)	329(3)	2530(5)	581(31)	307(22)	426(25)	4(36)	147(43)	188(42)
C(12)	3259(4)	3823(3)	2508(5)	780(37)	322(23)	541(29)	-47(41)	210(52)	216(47)
C(13)	3722(4)	3542(3)	1009(6)	516(31)	452(27)	597(30)	-63(45)	236(48)	46(46)
C(14)	3496(3)	2426(3)	793(5)	535(29)	422(25)	439(25)	-41(39)	145(43)	292(43)
C(15)	5289(4)	2731(4)	-596(6)	657(38)	750(37)	665(34)	-94(57)	289(58)	362(51)
O(16)	5855(3)	2324(3)	-1723(4)	628(26)	995(30)	858(28)	-146(46)	486(42)	300(45)
C(17)	6802(5)	2939(6)	-1805(8)	582(43)	345(17)	1075(54)	-253(95)	368(75)	80(85)
C(18)	1729(2)	85(2)	654(4)	663(23)	421(16)	478(33)	1198(55)	427(70)	181(31)
C(19)	1419(5)	-729(4)	1493(8)	1213(60)	459(32)	421(27)	175(46)	434(90)	135(71)
C(20)	3649(4)	2095(4)	-2135(5)	603(33)	559(32)	421(27)	175(46)	268(47)	300(53)
N(21)	2404(3)	1571(3)	-2205(4)	554(27)	547(23)	407(21)	-18(35)	35(37)	424(40)
C(22)	2050(3)	1841(3)	-880(5)	813(29)	479(26)	387(24)	38(40)	161(42)	464(45)
C(23)	2190(4)	934(4)	-3495(5)	839(40)	645(32)	413(27)	-64(46)	-170(51)	687(59)
Q(24)	2679(3)	835(3)	-4642(4)	1047(33)	1192(34)	495(22)	-388(43)	166(43)	697(54)
C(25)	1136(4)	349(4)	-3492(6)	732(39)	743(37)	604(34)	-308(56)	-272(58)	264(62)
C(26)	1448(4)	3749(3)	1504(5)	726(35)	334(23)	489(27)	72(39)	155(48)	445(46)
C(27)	397(4)	3103(3)	1302(5)	626(33)	558(29)	477(27)	-57(44)	67(48)	608(52)
O(28)	-363(3)	3684(3)	1311(4)	1134(34)	1265(35)	564(22)	-65(44)	-134(43)	1805(60)
O(30)	115(3)	3766(2)	4450(3)	755(24)	501(18)	538(19)	143(30)	407(34)	658(34)
C(31)	-182(4)	3803(4)	6003(6)	853(42)	750(36)	523(30)	120(53)	568(57)	658(63)
C(32)	-163(6)	2803(5)	6376(7)	1624(69)	947(47)	845(44)	779(75)	1578(93)	1222(94)
O(33)	436(3)	2400(2)	5358(4)	1004(29)	549(20)	612(21)	411(33)	631(40)	674(40)
C(34)	2080(2)	4429(2)	4886(3)	782(24)	359(17)	449(19)	-125(26)	-61(32)	364(32)
S(35)	2792(1)	4725(1)	6441(1)	749(9)	363(6)	372(6)	-54(9)	-50(12)	228(12)
C(36)	3613(3)	4234(2)	6350(4)	960(29)	565(21)	774(25)	55(36)	-438(43)	742(41)
O(37)	2198(3)	4614(2)	7729(4)	1124(33)	611(22)	439(19)	99(32)	250(39)	59(42)
C(38)	3210(4)	5970(3)	6250(5)	589(32)	454(26)	430(25)	-22(41)	39(45)	310(46)
C(39)	2584(4)	6638(4)	6250(5)	589(32)	454(26)	430(25)	-22(41)	39(45)	310(46)
H(40)	2543(5)	7619(4)	6429(7)	854(44)	489(30)	821(38)	-49(53)	393(59)	217(53)
C(41)	3878(4)	7936(3)	5905(6)	924(43)	443(28)	564(31)	25(47)	26(58)	111(55)
C(42)	4482(4)	7256(4)	5557(6)	631(36)	626(32)	665(34)	6(53)	210(56)	16(55)
C(43)	4146(4)	6278(4)	5722(6)	645(35)	550(30)	506(28)	-132(46)	121(50)	261(52)
C(44)	4252(6)	9003(4)	5664(9)	1592(76)	514(37)	1153(59)	209(75)	319(105)	80(84)

	x	y	z	B	x	y	z	B	
C(29, 1)	-1130(16)	3390(15)	390(24)	7.5(0.7)	H(19, 1)	2029(60)	-1111(57)	1087(90)	14.3(2.5)
C(29, 2)	-880(16)	3730(15)	701(24)	7.5(0.7)	H(19, 2)	825(44)	-1138(43)	1435(68)	9.2(1.7)
C(29, 3)	-540(12)	4130(11)	501(18)	7.5(0.5)	H(19, 3)	1793(57)	-621(56)	2488(89)	13.0(2.4)
H(2, 1)	4777(32)	7701(31)	-1205(49)	4.6(1.0)	H(20, 1)	3584(31)	1861(30)	-2956(47)	4.1(1.0)
H(2, 2)	4830(35)	1069(34)	612(54)	5.6(1.2)	H(20, 2)	3672(36)	2782(35)	-2385(55)	6.2(1.2)
H(3, 1)	3033(32)	60(31)	-1200(48)	4.3(1.0)	H(22, 1)	1356(32)	1375(31)	-937(48)	4.3(1.0)
H(3, 2)	3553(30)	-295(29)	151(46)	3.9(1.0)	H(22, 2)	1890(30)	2531(29)	-996(45)	3.7(0.9)
H(4, 1)	2952(25)	684(24)	1938(38)	2.0(0.7)	H(25, 1)	969(39)	23(37)	-2512(57)	6.3(1.3)
H(5, 1)	2471(28)	1951(27)	3003(42)	2.8(0.8)	H(25, 2)	1051(48)	-138(47)	-4385(73)	9.6(1.8)
H(7, 1)	602(30)	1243(29)	1162(45)	3.8(0.9)	H(25, 3)	630(55)	786(54)	-3479(85)	12.3(2.2)
H(7, 2)	858(30)	1169(29)	2992(46)	3.7(0.9)	H(26, 1)	1421(30)	4398(29)	1983(46)	4.0(0.9)
H(8, 1)	-463(32)	2105(31)	2541(49)	4.2(1.1)	H(26, 2)	1699(34)	3900(33)	396(52)	5.1(1.1)
H(10, 1)	2153(28)	3035(27)	4861(42)	3.0(0.9)	H(27, 1)	275(34)	2623(32)	274(51)	5.5(1.1)
H(12, 1)	3604(32)	3674(31)	3445(49)	4.5(1.0)	H(31, 1)	-858(36)	3968(35)	6052(55)	5.9(1.2)
H(12, 2)	3318(27)	4548(26)	2627(42)	2.9(0.8)	H(31, 2)	375(44)	4357(43)	6781(67)	8.5(1.7)
H(13, 1)	3340(29)	3714(28)	87(45)	3.4(0.9)	H(32, 1)	-935(61)	2444(59)	6190(95)	15.8(2.7)
H(13, 2)	4468(26)	3926(25)	1128(40)	2.4(0.8)	H(32, 2)	-215(34)	2543(33)	7346(51)	5.0(1.1)
H(14, 1)	4041(31)	2260(30)	1795(48)	4.5(1.0)	H(39, 1)	1931(40)	6383(39)	7125(61)	7.1(1.4)
H(15, 1)	5708(31)	2801(30)	444(47)	4.1(1.0)	H(40, 1)	2470(41)	8003(39)	6435(62)	7.2(1.5)
H(15, 2)	5346(32)	3393(31)	-734(49)	4.3(1.0)	H(42, 1)	5170(32)	7441(30)	5193(48)	4.4(1.0)
H(17, 1)	7123(49)	2659(48)	-2448(76)	10.0(1.9)	H(43, 1)	4638(36)	5780(32)	5453(51)	5.1(1.1)
H(17, 2)	7138(56)	3093(54)	-501(85)	13.3(2.3)	H(44, 1)	4363(53)	9135(51)	4701(82)	11.6(2.1)
H(17, 3)	6746(52)	3657(50)	-1864(81)	11.3(2.1)	H(44, 2)	3708(50)	9337(49)	5663(77)	10.6(2.0)
					H(44, 3)	4910(60)	9242(59)	6125(95)	14.3(2.5)

its associated H atoms. As shown in Fig. 1, this atom is close to the centre of symmetry at $(0, \frac{1}{2}, 0)$. Thus, in position C(29, 3) the atom makes short contacts of 2.59

and 3.22 Å to C(29, 3¹) and C(29, 2¹) at $(-x, 1-y, -z)$. Therefore, if the atom occupies the site C(29, 3), the centrosymmetrically related site C(29, 3¹), and probably

Table 4. *The valency angles (°)*

C(2)—C(1)—C(14)	106.9 (4)	C(1)—C(14)—C(5)	109.6 (4)
C(2)—C(1)—C(15)	108.4 (4)	C(1)—C(14)—C(13)	114.4 (4)
C(2)—C(1)—C(20)	112.7 (4)	C(5)—C(14)—C(13)	112.8 (4)
C(14)—C(1)—C(15)	110.5 (4)	C(1)—C(15)—O(16)	110.6 (4)
C(14)—C(1)—C(20)	110.3 (4)	C(15)—O(16)—C(17)	112.3 (5)
C(15)—C(1)—C(20)	108.2 (4)	C(4)—O(18)—C(19)	114.4 (4)
C(1)—C(2)—C(3)	114.3 (4)	C(1)—C(20)—N(21)	113.3 (4)
C(2)—C(3)—C(4)	112.9 (4)	C(20)—N(21)—C(22)	115.3 (4)
C(3)—C(4)—C(5)	115.6 (4)	C(20)—N(21)—C(23)	119.9 (4)
C(3)—C(4)—O(18)	108.9 (4)	C(22)—N(21)—C(23)	124.7 (4)
C(5)—C(4)—O(18)	109.0 (4)	C(5)—C(22)—N(21)	112.5 (4)
C(4)—C(5)—C(6)	106.8 (3)	N(21)—C(23)—O(24)	120.6 (5)
C(4)—C(5)—C(14)	106.8 (3)	N(21)—C(23)—C(25)	118.5 (5)
C(4)—C(5)—C(22)	111.1 (4)	O(24)—C(23)—C(25)	120.9 (5)
C(6)—C(5)—C(14)	109.7 (3)	C(11)—C(26)—C(27)	110.1 (4)
C(6)—C(5)—C(22)	112.2 (3)	C(8)—C(27)—C(26)	108.9 (4)
C(14)—C(5)—C(22)	110.0 (4)	C(8)—C(27)—O(28)	111.7 (4)
C(5)—C(6)—C(7)	117.7 (3)	C(26)—C(27)—O(28)	111.6 (4)
C(5)—C(6)—C(11)	116.8 (3)	<C(27)—O(28)—C(29)>	119.6 (10)
C(7)—C(6)—C(11)	108.1 (3)	C(9)—O(30)—C(31)	107.9 (4)
C(6)—C(7)—C(8)	110.5 (4)	O(30)—C(31)—C(32)	104.0 (5)
C(7)—C(8)—C(9)	110.2 (4)	C(31)—C(32)—O(33)	107.5 (5)
C(7)—C(8)—C(27)	107.3 (4)	C(9)—O(33)—C(32)	109.1 (4)
C(9)—C(8)—C(27)	111.0 (4)	C(10)—O(34)—S(35)	119.7 (3)
C(8)—C(9)—C(10)	107.8 (4)	O(34)—S(35)—O(36)	110.0 (2)
C(8)—C(9)—O(30)	109.3 (4)	O(34)—S(35)—O(37)	109.2 (2)
C(8)—C(9)—O(33)	110.4 (4)	O(34)—S(35)—C(38)	97.6 (2)
C(10)—C(9)—O(30)	113.4 (4)	O(36)—S(35)—O(37)	117.7 (2)
C(10)—C(9)—O(33)	109.2 (4)	O(36)—S(35)—C(38)	109.8 (2)
O(30)—C(9)—O(33)	106.7 (4)	O(37)—S(35)—C(38)	110.7 (2)
C(9)—C(10)—C(11)	111.1 (4)	S(35)—C(38)—C(39)	120.0 (4)
C(9)—C(10)—O(34)	110.2 (3)	S(35)—C(38)—C(43)	119.2 (4)
C(11)—C(10)—O(34)	108.5 (3)	C(39)—C(38)—C(43)	120.7 (4)
C(6)—C(11)—C(10)	102.2 (3)	C(38)—C(39)—C(40)	118.1 (5)
C(6)—C(11)—C(12)	109.8 (4)	C(39)—C(40)—C(41)	121.6 (5)
C(6)—C(11)—C(26)	114.4 (4)	C(40)—C(41)—C(42)	119.2 (5)
C(10)—C(11)—C(12)	111.6 (4)	C(40)—C(41)—C(44)	121.5 (5)
C(10)—C(11)—C(26)	107.3 (4)	C(42)—C(41)—C(44)	119.3 (5)
C(12)—C(11)—C(26)	111.3 (4)	C(41)—C(42)—C(43)	120.3 (5)
C(11)—C(12)—C(13)	113.4 (4)	C(38)—C(43)—C(42)	119.9 (5)
C(12)—C(13)—C(14)	109.5 (4)		

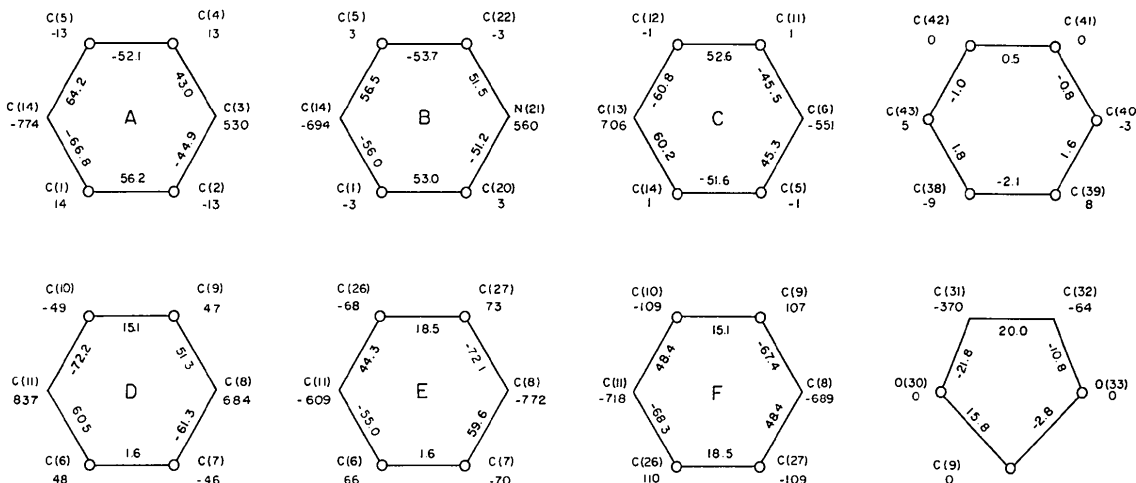
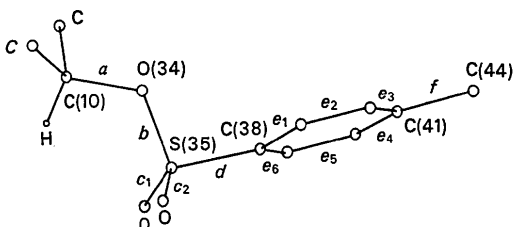


Fig. 3. Schematic drawing of the rings showing the torsion angles ($^{\circ}$) of the bonds, and the deviations (10^3 \AA) of the atoms from the mean planes of the circled atoms.

Table 5. Summary of the bond lengths (Å) and valency angles (°) in the tosyl group of the toluene-*p*-sulphonates and this structure



	Toluene- <i>p</i> -sulphonates		This	
	Range	Mean	structure	Δ
<i>a</i>	1.474–1.490	1.483	1.469 (5)	–0.014
<i>b</i>	1.563–1.567	1.566	1.579 (3)	0.013
$\langle c \rangle$	1.426–1.431	1.429	1.418 (3)	–0.011
<i>d</i>	1.743–1.758	1.752	1.738 (5)	–0.014
$\langle e \rangle$	1.377–1.384	1.381	1.382 (4)	0.001
<i>f</i>	1.493–1.520	1.504	1.511 (8)	0.007

Angles	Toluene- <i>p</i> -sulphonates		This	
	Range	Mean	structure	Δ
<i>ab</i>	119.3–121.5	120.2	119.7 (3)	–0.5
<i>bc</i> ₁	103.7–104.7	104.2	109.2 (2)	5.0
<i>bc</i> ₂	109.8–110.2	109.9	110.0 (2)	0.1
<i>bd</i>	103.9–105.9	104.7	97.6 (2)	–7.1
<i>c</i> ₁ <i>c</i> ₂	118.8–119.5	119.2	117.7 (2)	–1.5
<i>c</i> ₁ <i>d</i>	109.1–110.2	109.6	110.7 (2)	1.1
<i>c</i> ₂ <i>d</i>	107.9–108.5	108.2	109.8 (2)	1.6
<i>de</i> ₁	119.1–120.8	119.9	120.0 (4)	0.1
<i>de</i> ₆	119.5–120.6	120.0	119.2 (4)	–0.8
<i>e</i> ₁ <i>e</i> ₆	119.6–120.3	120.0	120.7 (4)	0.7

C(29, 2¹), must be left vacant. In positions C(29, 1) and C(29, 2) the atom makes short intermolecular contacts of 2.37 and 2.65 Å, respectively, with H(17, 2²) at $(x-1, y, z)$. Also, the C(29, 1) site is only 2.48 Å away from H(39, 1³) at $(-x, 1-y, 1-z)$. Therefore, the disorder of C(29) appears to be forced by its close packing to the neighbouring atoms.

The only other short intermolecular contact in the structure is the O(36)···H(20, 2⁴) = 2.42 (5) Å, where the corresponding van der Waals contact should be 2.6 Å (Pauling, 1960). This may be indicative of a weak hydrogen bond between O(36) at (x, y, z) and C(20⁴) at $(x, y, 1+z)$, especially since the angles O(36)···H(20, 2⁴)–C(20⁴) = 162.4 and O(36)···C(20⁴)–H(20, 2⁴)

= 10.4°. The corresponding O(36)···C(20⁴) distance is 3.398 Å. Such a hydrogen bond would link the molecules into chains parallel to *c*, which is also the direction of fastest growth in the crystals.

The author is grateful to Professor K. Wiesner of the University of New Brunswick for suggesting the problem, to Dr A. D. Hardy for measuring the crystal density, and to Mrs M. E. Pippy for valuable assistance with the computations.

References

- AHMED, F. R. (1970). *Crystallographic Computing*, pp. 55–57. Copenhagen: Munksgaard.
- AHMED, F. R., HALL, S. R., PIPPY, M. E. & HUBER, C. P. (1966). *World List of Crystallographic Computer Programs*. Second ed., Appendix, p. 52. Utrecht: Oosthoek.
- BRAUN, P. B., HORNSTRA, J., KNOBLER, C., RUTTEN, E. W. M. & ROMERS, C. (1973). *Acta Cryst.* B29, 463–469.
- BÜRGI, H. B. & DUNITZ, J. D. (1971). *Acta Cryst.* A27, 117–119.
- CARRELL, H. L., GALLEN, B. & GLUSKER, J. P. (1973). *Acta Cryst.* B29, 2580–2585.
- FABER, D. H. & ALTONA, C. (1974). *Acta Cryst.* B30, 449–458.
- GEISE, H. J., BUYS, H. R. & MIJLHOFF, F. C. (1971). *J. Mol. Struct.* 9, 447–454.
- HANSON, H. P., HERMAN, F., LEA, J. D. & SKILLMAN, S. (1964). *Acta Cryst.* 17, 1040–1044.
- HUBER, C. P. (1974). *Acta Cryst.* In the press.
- JOHNSON, P. L., CHEER, C. J., SCHAEFER, J. P., JAMES, V. J. & MOORE, F. H. (1972). *Tetrahedron*, 28, 2893–2900.
- JOHNSON, P. L., SCHAEFER, J. P., JAMES, V. J. & MCCONNELL, J. F. (1972). *Tetrahedron*, 28, 2901–2908.
- KARLE, I. L., DRAGONETTE, K. S. & BRENNER, S. A. (1965). *Acta Cryst.* 19, 713–716.
- O'CONNOR, B. H. (1973). *Acta Cryst.* B29, 1893–1903.
- PAULING, L. (1960). *The Nature of the Chemical Bond*. Ithaca: Cornell Univ. Press.
- SCHENK, H. (1973). *Acta Cryst.* A29, 503–507.
- STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* 42, 3175–3187.
- SUTTON, L. E. (1965). *Tables of Interatomic Distances and Configuration in Molecules and Ions*, Supplement. Spec. Publ. No. 18. London: The Chemical Society.
- WIESNER, K. (1973). Private communication.