The Crystal and Molecular Structure of *cis*-1,5-Bis(toluene-*p*-sulfonyl)-3,7-dihydroxyoctahydro-1,5-diazocine*

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Crystals of *cis*-1,5-bis(toluene-*p*-sulfonyl)-3,7-dihydroxyoctahydro-1,5-diazocine are orthorhombic, space group *Pbca*. The unit-cell constants are $a = 12.988$ (2), $b = 21.304$ (3) and $c = 15.299$ (2) Å, $Z = 8$. Three-dimensional intensity data (1797 reflections) were obtained with a CAD-4 automated four-circle diffractometer. The structure was solved by direct methods and refined to a conventional R value of 3.8%. The eight-membered ring has an extended crown conformation and exhibits strain. The hydroxyl groups are definitely *cis*, confirming earlier spectroscopic analysis. The toluene-*p*-sulfonate groups are quite regular and inclined to the mean plane of the eight-membered ring at angles of 161 and 167°. The molecules are held together by hydrogen bonds along the x direction and by van der Waals forces in the other directions.

Introduction

The molecular conformations of cycloalkanes and their oxygen-, nitrogen- and sulfur-containing derivatives have been the subject of several recent theoretical and experimental studies. Theoretical investigations in particular have aimed at determining the geometry corresponding to the minimum energy in medium-sized (six to ten atoms) ring systems (Hendrickson, 1961, 1964, 1967; Bixon & Lifson, 1967; Wiberg, 1965). Knowledge of the most stable conformations under certain circumstances would then help to provide more realistic predictions of the arrangement of atoms in the transition state and of the energy of chemical reactions. In order to determine the most stable conformation of a given molecule, it is necessary to minimize the strain energy with respect to several independent geometrical parameters. The total strain energy for a given conformation is taken as (Hendrickson, 1964):

$$E = \sum E_\theta + \sum E_t + \sum E_{HH}, \tag{1}$$

where E_θ is the bond angle bending strain, E_t is the torsional strain of the dihedral angles about single bonds and E_{HH} is the contribution to the energy from the nonbonded interactions of hydrogen atoms in the carbon skeleton. Thus, by progressive distortion of a given conformation, the most energetically favorable arrangement of atoms may be obtained.

After extensive energy-minimization calculations on rings containing from six to ten carbon atoms, Hendrickson (1967) predicted the boat-chair form of cyclooctane to be the one of lowest strain energy. X-ray diffraction (Dobler, Dunitz & Mugnoli, 1966; Groth, 1965) and n.m.r. (Anet & Basus, 1973) studies appear

to confirm such predictions by proving that, indeed, cyclooctane and its simple derivatives exist predominantly in the boat-chair conformation. However, the introduction of heteroatoms into the eight-membered ring or the attachment of bulky substituents to it may have the effect of making some other conformation lower in energy than the boat-chair form. Crystallographic studies have shown, for example, a twisted crown conformation in *trans-syn-trans*-1,2,5,6-tetrabromocyclooctane (Ferguson, MacNicol, Oberhansli, Raphael & Zabkiewcz, 1968), a crown conformation in 3,7-dimethyl-1,5-dioxa-3,7-diazacyclooctane-2,4,6,8-tetraspirocyclopropane (Schenk, 1971), and the α (Cady, Larson & Cromer, 1963) and β (Choi & Boutin, 1970) forms of octahydro-1,3,5,7-tetranitro-1,3,5,7 tetrazocine, a boat form in 1,3,5,7-tetraceto-1,3,5,7-tetrazacyclooctane (Choi, Abel, Dickens & Stewart, 1973), and a boat-chair conformation in 1,3,5,7-tetrathiocane (Frank & Degen, 1973).

The first functionally substituted perhydro-1,5-diazocine was prepared by Paudler, Gapski & Barton (1966) who found that condensation of 1,3-dibromo-2-propanol with toluene-*p*-sulfonamide anion, followed by addition of a second mole of base, yields a material of molecular formula $C_{20}H_{26}N_2O_6S_2$ (M. W. 454.5). The product proved to be a mixture of two isomers which were separated by silica gel chromatography. These isomers were initially characterized by spectral and chemical means as *cis*- and *trans*-1,5-bis(toluene-*p*-sulfonyl) - 3,7 - dihydroxyoctahydro - 1,5 - diazocine (Fig. 1). The lower-melting isomer (m.p. 207 − 209.5°C) was shown to be the *cis* isomer and the higher-melting one (m.p. 221–222.5°C) the *trans* isomer (Paudler & Zeiler, 1967a). These compounds will be referred to as *cis*- and *trans*-TSD.

Considerable additional work has been done on *cis*- and *trans*-TSD and their derivatives (Paudler & Zeiler, 1967b; Paudler, Zeiler & Gapski, 1969; Paudler &

Zeiler, 1969). Obviously the validity of the initial structural assignment plays a crucial role in all subsequent work based on the assigned structures. Therefore, it was important to establish definitively the structures of the two isomers by X-ray diffraction methods. The structures are also interesting in their own right from a structural viewpoint since eight-membered heterocyclic ring systems with their attendant distortions have not been extensively studied. Therefore they provide additional experimental evidence on eight-membered ring compounds to correlate with the theoretical calculations. In this paper the structure of the *cis*-isomer is reported. Structure determinations of other members in this series are in progress.

Experimental

Crystals of the *cis*-isomer were kindly supplied by Dr W. W. Paudler. They were clear, colorless parallelepipeds bounded by the {100} form. Preliminary survey photographs taken by both the Weissenberg and precession methods revealed an orthorhombic unit cell with the following systematic absences: $hk0$ for $h = 2n + 1$, $h0l$ for $l = 2n + 1$ and $0kl$ for $k = 2n + 1$. These absences are consistent with the space group *Pbca*. A set of unit-cell dimensions was obtained at $24 \pm 1°C$ with the aid of a CAD-4 automated four-circle diffractometer (Enraf–Nonius). 19 reflections at high and moderate Bragg angles were scanned at both $\pm 2\theta$ using a graphite monochromator and 4° take-off angle with Mo $K\alpha$ ($\lambda = 0.7107$ Å) radiation. The Bragg angles were accurately determined by the use of program *DET-CELL* (Enraf–Nonius, 1972) which automatically compensates for wavelength dispersion. Then the initial cell dimensions were subjected to refinement by a least-squares fitting (Smith, 1968) using the accurately determined values of θ_1 and $\lambda = 0.70926$ Å. The results were $a = 12.988(2)$, $b = 21.304(3)$, $c = 15.299(2)$ Å, $V = 4233.2$ Å^3. The density, determined by flotation in an aqueous potassium iodide solution, was found to be

1.436 g cm^{-3}. This compares with a calculated density, with $Z = 8$, of 1.416 g cm^{-3}.

The crystal chosen for data collection measured $0.17 \times 0.1 \times 0.8$ mm and was mounted so that the c or needle axis was parallel to the φ axis of the goniometer but slightly misaligned to avoid Renninger reflections. 12 sets of equivalent reflections were scanned in all octants and their intensities found to agree within 5% in each equivalent set. Data were measured by the θ–2θ scan technique using a variable 2θ scan rate given by:

$$\text{scan rate} = 20.1166 \ X° \ \text{min}^{-1}$$

where X is an integer determined by the intensity of the reflection being scanned. X had a minimum value of 4 for intense reflections and a maximum of 38 for very weak ones. A continuously variable aperture ranging in horizontal width from 2.5 to 9.22 mm with a height of 4 mm was used. The scan width (angular range) was also variable and equal to 3 times $(0.6 + 0.2 \tan \theta)°$. The right and left backgrounds were each scanned at $\frac{1}{4}$ the total scan time. In total, 6321 independent reciprocal-lattice points were scanned in the $+h + k + l$ octant out to a maximum Bragg angle of 45°. Three standard reflections of high, medium and low intensity were scanned every 15 reflections. The fluctuation of the standards was random and amounted to about $\pm 3\%$ overall. The data were corrected for these fluctuations by assuming a linear change in the intensity of the standards between two consecutive measurements (Olson, 1973). Only those reflections whose net counts, determined as $\text{NET} = \text{total counts} - 2(R + L)$ background counts, were greater than or equal to 3σ where $\sigma = [\text{total counts} + \text{background counts}]^{1/2}$ were considered observed. In this way 1797 observed reflections were obtained. These were corrected for Lorentz and double polarization effects (Arndt & Willis, 1966). No correction for absorption was made since μR (Mo $K\alpha$, $\lambda = 0.7107$ Å) ranged from 0.025 to 0.125.
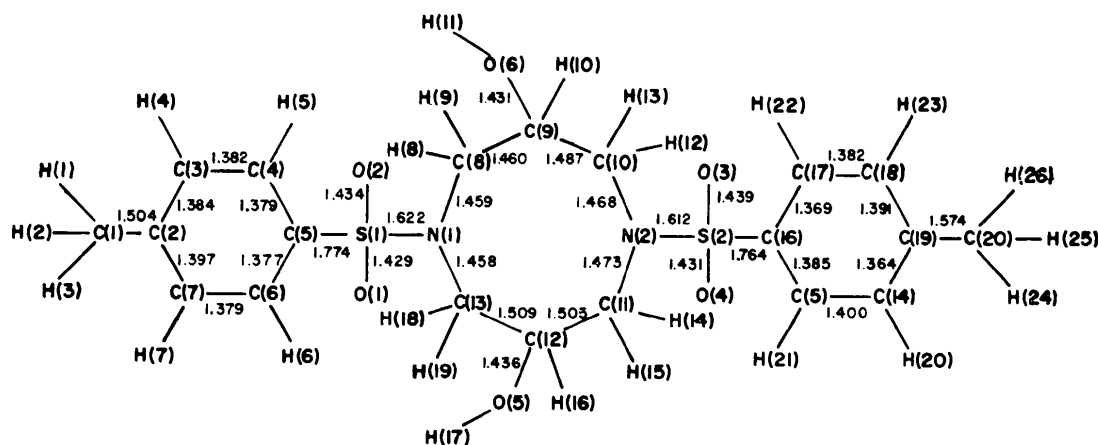

Fig. 1. Planar representation of the *cis*-TSD molecule with the numbering scheme used in Table 1 and subsequent representations.

Solution and refinement

The structure was solved by a straightforward application of the $\sum_2$ relationship (Sayre, 1952) in a symbolic-addition procedure. (Hauptman & Karle, 1953). The programs used were those of Ahmed, Hall, Pippy & Huber (1968). The origin-defining reflections were 1,15, 8, 836 and 13,13,3. This choice of origin permitted signs to be assigned to 380 reflections with $E > 1\cdot5$. The resultant E map contained 29 peaks of sufficient density to be considered further. Peaks representing the two sulfur atoms were clearly discernible as they were three times the height of the other peaks. In addition, positional parameters for 11 other nonhydrogen atoms were assigned. The remaining nonhydrogen atoms were located by successive Fourier and difference syntheses. Refinement of the positional parameters, isotropic temperature factors and scale factor by the block-diagonal method (Ahmed, Hall, Pippy & Huber, 1968) reduced the R index,

$$R = \frac{\sum ||F_c| - |F_o||}{\sum |F_o|},$$

from 0·348 to 0·107. Anisotropic refinement of temperature factors further reduced R to 0·071. A difference map now revealed the positions of most of the hydrogen atoms as peaks of maximum density 0·35 to 0·45 eÅ^{-3}. Instead of using the coordinates from the difference map, positional parameters for 24 of the 26 hydrogens were calculated (Stanislowski & Frenz,

1973) assuming a carbon-hydrogen bond length of 0·95 Å and a tetrahedral angle of 109·5° about the eight-membered ring carbons and sp^2 geometry about the aromatic rings. Positional parameters for the two hydroxyl hydrogens were taken from the difference map. All hydrogen atoms were included in subsequent structure-factor calculations with isotropic temperature factors one unit higher than those of the atoms to which they are bonded. Further refinement reduced R to 0·039 and the weighted residual, defined as (Hamilton, 1965)

$$R_w = \left[\frac{\sum w(|F_c| - |F_o|)^2}{\sum w|F_o|^2} \right]^{1/2},$$

to 0·033. The weighting scheme used in the refinement assigned weights as follows:

$$w = \frac{1}{1 + (|F_o| - P_2/P_1)^2}.$$

P_1 and P_2 were finally set at 30 and 85, respectively. The function minimized was $\sum w(|F_o| - |F_c|)^2$. Neutral atom scattering factors, as listed in *International Tables for X-ray Crystallography* (1962), were used. The scattering factor for sulfur was corrected (real part only) for anomalous dispersion. The 'goodness of fit' defined (Hamilton, 1964) as $[\sum w(\Delta|F|)^2/(m-n)]^{1/2}$, where m is the number of observations and n the number of variables refined was calculated to be 0·973 for this structure.

In the last cycle all the shifts for the non-hydrogen

Table 1. *Final least-squares parameters of the non-hydrogen atoms and their e.s.d.'s*

$$T = \exp\left[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl) \times 10^4 \right].$$

	x	y	z	β_{11}	β_{22}	β_{33}	$2\beta_{12}$	$2\beta_{13}$	$2\beta_{23}$
S(1)	0·46516 (9)	0·42253 (5)	0·17314 (6)	62·8 (7)	21·6 (3)	27·9 (4)	2·5 (9)	−1·8 (11)	−3·2 (7)
S(2)	0·07286 (9)	0·08290 (5)	0·35166 (6)	61·8 (7)	18·2 (2)	32·0 (4)	8·1 (9)	−13·8 (11)	−5·2 (7)
N(1)	0·3495 (3)	0·4382 (2)	0·2078 (2)	61 (3)	19 (1)	25 (2)	16 (3)	6 (3)	1 (2)
N(2)	0·1743 (3)	0·0433 (2)	0·3250 (2)	61 (3)	18 (1)	26 (2)	8 (3)	7 (4)	0 (2)
O(1)	0·0135 (2)	0·3856 (1)	0·2601 (2)	76 (3)	36 (1)	36 (1)	34 (3)	24 (3)	−5 (2)
O(2)	0·0106 (3)	0·4810 (1)	0·3534 (2)	87 (3)	26 (1)	42 (2)	−31 (3)	−11 (4)	10 (2)
O(3)	0·0026 (2)	0·0390 (1)	0·3918 (2)	55 (2)	25 (1)	61 (2)	−15 (2)	7 (3)	−10 (2)
O(4)	0·0421 (3)	0·1175 (1)	0·2755 (2)	110 (3)	24 (1)	38 (2)	35 (3)	−53 (4)	1 (2)
O(5)	0·2770 (3)	0·3877 (1)	0·4293 (2)	154 (4)	23 (1)	35 (2)	−46 (3)	45 (4)	2 (2)
O(6)	0·2921 (2)	0·0712 (1)	0·1056 (2)	76 (2)	29 (1)	36 (1)	−22 (3)	24 (3)	11 (2)
C(1)	0·4097 (4)	0·2346 (2)	0·3464 (3)	75 (4)	33 (2)	49 (3)	4 (4)	−4 (6)	31 (3)
C(2)	0·4255 (3)	0·1959 (2)	0·4278 (3)	42 (3)	24 (1)	36 (2)	0 (4)	7 (5)	12 (3)
C(3)	0·4418 (4)	0·1316 (2)	0·4219 (3)	66 (4)	24 (1)	32 (2)	−1 (4)	10 (5)	5 (3)
C(4)	0·4545 (3)	0·0955 (2)	0·4964 (3)	79 (4)	18 (1)	31 (2)	1 (4)	15 (5)	0 (2)
C(5)	0·4514 (3)	0·3758 (2)	0·0775 (2)	52 (3)	19 (1)	26 (2)	10 (3)	11 (4)	−10 (2)
C(6)	0·4371 (4)	0·3118 (2)	0·0858 (3)	69 (4)	20 (1)	38 (2)	14 (4)	16 (5)	6 (3)
C(7)	0·4234 (4)	0·2236 (2)	0·5109 (3)	67 (4)	16 (1)	53 (2)	1 (4)	12 (6)	5 (3)
C(8)	0·2821 (4)	0·4751 (2)	0·1508 (3)	82 (4)	22 (1)	33 (2)	23 (4)	−24 (5)	−5 (3)
C(9)	0·2223 (4)	0·0428 (2)	0·1666 (3)	104 (5)	30 (1)	34 (2)	−36 (4)	49 (6)	−15 (3)
C(10)	0·2427 (4)	0·0677 (2)	0·2561 (3)	82 (4)	23 (1)	30 (2)	−7 (4)	4 (5)	−8 (3)
C(11)	0·2860 (4)	0·4952 (2)	0·3859 (3)	78 (4)	20 (1)	28 (2)	−5 (4)	24 (5)	−9 (2)
C(12)	0·3264 (4)	0·4299 (2)	0·3690 (2)	84 (4)	22 (1)	29 (2)	−13 (4)	14 (4)	2 (3)
C(13)	0·3044 (3)	0·4023 (2)	0·2798 (3)	74 (4)	18 (1)	34 (2)	−8 (3)	18 (5)	−5 (2)
C(14)	0·1296 (4)	0·3340 (2)	0·0831 (3)	74 (4)	27 (1)	24 (2)	−18 (4)	5 (5)	3 (3)
C(15)	0·1000 (3)	0·3787 (2)	0·0206 (3)	64 (4)	17 (1)	36 (2)	−9 (3)	12 (5)	−7 (3)
C(16)	0·1080 (3)	0·1379 (2)	0·4330 (2)	52 (3)	16 (1)	28 (2)	9 (3)	−6 (4)	−8 (2)
C(17)	0·1424 (4)	0·1961 (2)	0·4080 (3)	69 (4)	18 (1)	34 (2)	5 (4)	17 (5)	2 (3)
C(18)	0·1713 (3)	0·2394 (2)	0·4711 (3)	70 (4)	17 (1)	51 (3)	−6 (4)	17 (5)	−5 (3)
C(19)	0·1650 (3)	0·2759 (2)	0·0596 (3)	54 (4)	52 (1)	42 (2)	−6 (3)	−4 (5)	15 (3)
C(20)	0·1945 (4)	0·2280 (2)	0·1286 (3)	103 (5)	33 (2)	57 (3)	4 (5)	−26 (6)	48 (4)

Table 2. Hydrogen atom positional parameters and isotropic temperature factors

	x	y	z	B_{iso}
H(1)	0·472	0·268	−0·190	5·35
H(2)	0·399	0·222	−0·141	5·35
H(3)	0·351	0·279	−0·192	5·35
H(4)	0·446	0·387	−0·137	4·88
H(5)	0·462	0·451	−0·007	4·37
H(6)	0·437	0·292	0·143	4·73
H(7)	0·413	0·231	0·016	4·92
H(8)	0·212	0·459	0·155	5·37
H(9)	0·303	0·468	0·090	5·37
H(10)	0·347	0·560	0·156	5·60
H(11)	0·364	0·053	0·117	5·37
H(12)	0·186	0·555	0·270	3·99
H(13)	0·259	0·612	0·255	3·99
H(14)	0·212	0·493	0·382	4·33
H(15)	0·303	0·508	0·445	4·33
H(16)	0·403	0·430	0·381	5·37
H(17)	0·283	0·410	0·484	5·74
H(18)	0·230	0·401	0·272	4·43
H(19)	0·328	0·359	0·276	4·43
H(20)	0·376	0·657	0·646	4·82
H(21)	0·426	0·579	0·537	4·49
H(22)	0·353	0·707	0·346	4·55
H(23)	0·301	0·780	0·454	5·11
H(24)	0·178	0·242	0·186	6·31
H(25)	0·157	0·189	0·118	6·31
H(26)	0·266	0·218	0·126	6·31

atoms were less than one tenth of their corresponding standard deviations. A difference Fourier map was featureless, with maxima and minima ranging from +0·36 to −0·26 e $Å^{-3}$. The final positional and thermal parameters for the non-hydrogen atoms are given in Table 1. Hydrogen atom parameters are presented in Table 2.*

Description of the structure

The molecular structure is shown in Fig. 2 and the numbering scheme identifying the atoms in Fig. 1. From the relative orientation of the hydroxyl groups it is apparent that the molecule is indeed the cis-isomer. The heterocyclic eight-membered ring has an extended crown configuration. This feature of the molecule will be discussed later after a consideration of the bonds and angles in the molecule.

The bond distances are given in Fig. 1. The estimated standard deviations are 0·006 Å for C–C, 0·005 Å for C–N, 0·003 Å for S–O and S–N and 0·004 Å for S–C. It is seen that the eight-membered ring is not quite symmetrical. The bond distances on the C(13)–C(12)–C(11)–N(2)–C(10) side are in general larger than their counterparts in the other half of the ring. However, only the C(8)–C(9) distance is significantly shorter than its counterpart in the other half of the ring, C(11)–C(12), if 3 σ_{DIFF} is considered the real limit of error. Here, σ_{DIFF} is the standard deviation in the bond length difference as defined by Stout & Jensen (1968).

The average C–C bond distance in the eight-membered ring, 1·490(11), is about 0·05 Å shorter than the expected sp^3 value. Nevertheless, this average agrees well with the values found in similar kinds of con-

Fig. 2. A perspective view of the cis-TSD molecule showing the crown configuration of the eight-membered ring and the orientation of the toluene groups. Thermal ellipsoids are at the 50% probability level (Johnson, 1965).
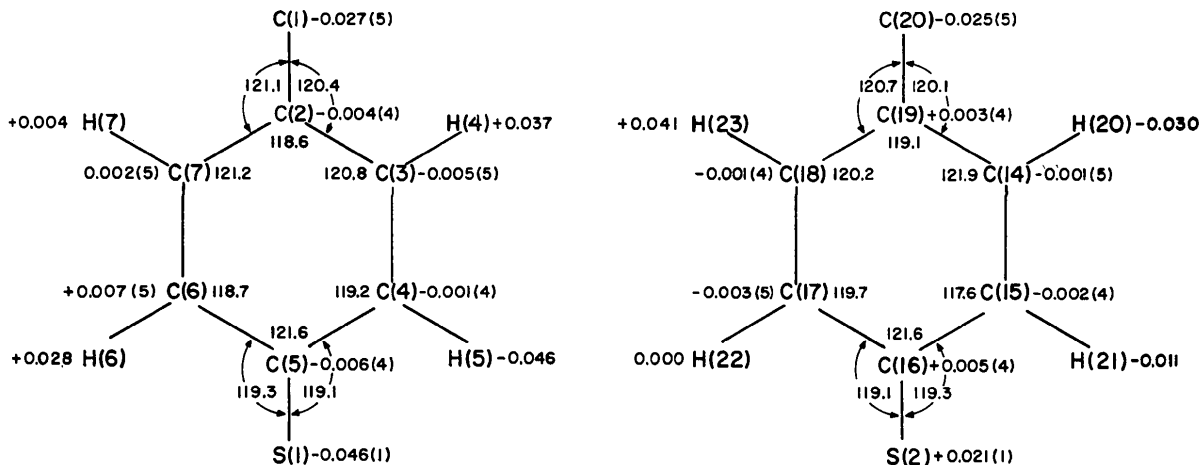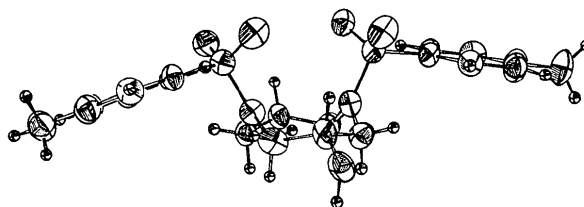

Fig. 3. Deviations of the atoms from the mean plane through the ring carbon atoms for (a) toluene group 1; (b) toluene group 2.

strained rings (Royer, Schievelbein, Kalyanaraman & Bertrand, 1972; Hussain & Hope, 1969). The average C–N bond length, 1·465(4) compares favorably with the recently reported value of 1·456(2) Å found in 1,3,5,7-tetraceto-1,3,5,7-tetrazacyclooctane (Choi, Abel, Dickens & Stewart, 1973) and the values found in dibenz[c, f]azocines (Hardy & Ahmed, 1974). The C–O bond lengths are also well within the range exhibited by similar bonds (Cox & Jeffrey, 1951; Smith, Fitzgerald, Caughlon, Kerr & Ashore, 1974).

The ring strain is evident in the heterocyclic ring bond angles which are listed in Table 3. These are significantly larger than the ideal tetrahedral angle but

Table 3. *Bond angles* (°) *in the eight-membered ring and associated groups*

C(8)–C(9)—C(10)	120·6 (4)		C(11)–C(12)–C(13)	116·5 (4)
N(1)–C(8)—C(9)	117·1 (4)		N(2)—C(10)–C(9)	115·1 (4)
N(1)–C(13)–C(12)	113·5 (4)		N(2)—C(11)–C(12)	114·2 (3)
C(8)–N(1)—C(13)	119·3 (3)		C(10)–N(2)—C(11)	119·1 (3)
O(6)–C(9)—C(10)	109·6 (4)		O(5)—C(12)–C(11)	108·2 (4)
O(6)–C(9)—C(8)	109·4 (4)		O(5)—C(12)–C(13)	104·5 (4)
S(1)–N(1)—C(8)	117·9 (3)		S(2)—N(2)—C(10)	119·1 (3)
S(1)–N(1)—C(13)	120·5 (3)		S(2)—N(2)—C(11)	119·2 (3)
N(1)–S(1)—O(1)	106·6 (2)		N(2)—S(2)—O(3)	106·5 (2)
N(1)–S(1)—O(2)	107·1 (2)		N(2)—S(2)—O(4)	106·9 (2)
N(1)–S(1)—C(5)	106·9 (2)		N(2)—S(2)—C(16)	108·3 (2)
O(1)–S(1)—O(2)	119·8 (2)		O(3)—S(2)—O(4)	120·2 (2)
O(1)–S(1)—C(5)	108·8 (2)		O(3)—S(2)—C(16)	107·0 (2)
O(2)–S(1)—C(5)	107·1 (2)		O(4)—S(2)—C(16)	107·6 (2)

are comparable with bond angles found in other eight-membered rings (Dobler, Dunitz & Mugnoli, 1966; Ferguson, MacNicol, Oberhansli, Raphael & Zabkiewicz, 1968; Choi, Abel, Dickens & Stewart, 1973). On the other hand bond angles which involve an atom outside the ring (O–C–C) are close to the tetrahedral value.

The interatomic distances and angles for the toluene-p-sulfonyl groups are shown in Figs. 1 and 3. Estimated standard deviations in the angles are 0·3° for C–C–S and 0·4° for C–C–C. These bond distances and angles are in excellent agreement with those of recent determinations (Faber & Altona, 1974, and references therein). Mean plane calculations show that the toluene groups are planar. The mean plane equations calculated for the six aromatic carbons in each ring were

Ring 1: ($\chi^2 = 7\cdot01$)
$$0\cdot9878X - 0\cdot1488Y - 0\cdot0466Z - 4\cdot5341 = 0;$$
Ring 2: ($\chi^2 = 2\cdot50$)
$$-0\cdot9360X - 0\cdot3511Y - 0\cdot0256Z + 9\cdot6816 = 0.$$

Deviations from the planes are shown in Fig. 3(a) and (b) for rings 1 and 2, respectively. The ring carbon atoms all lie in the plane within one standard deviation except C(6) which has a slightly higher deviation. The methyl carbon and sulfur atoms show larger deviations from the mean plane but these are still small. The two
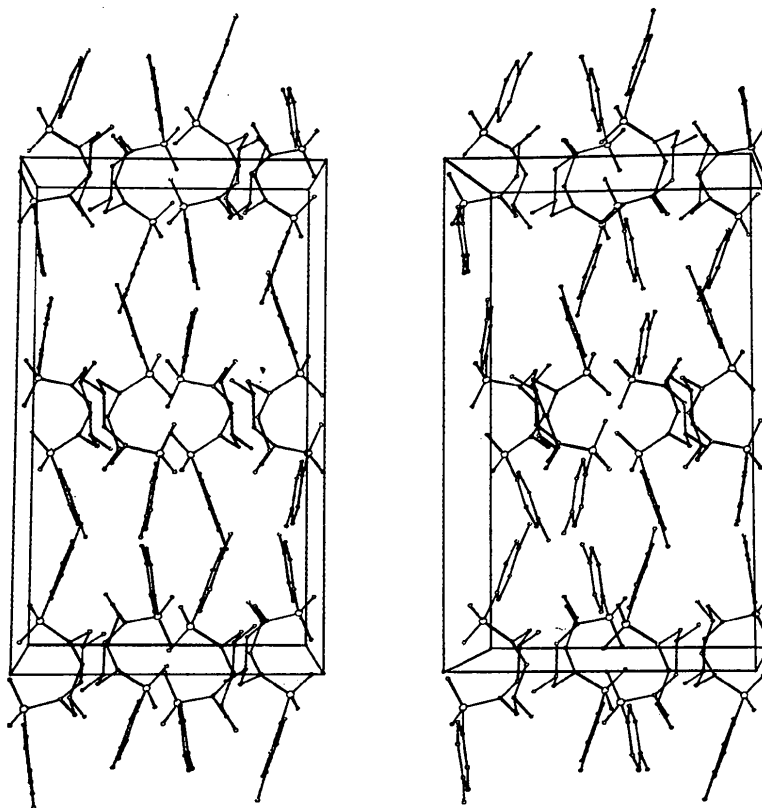

Fig. 4. Stereoscopic view of the unit-cell contents of cis-TSD.

toluene group mean planes make a dihedral angle of 150·6° with each other.

As stated earlier the eight-membered ring has the extended crown conformation, *i.e. CC* in Hendrickson's (1964) notation. This was shown in the following way. A mean plane calculated through atoms C(8), C(10), C(11) and C(13) gave the equation $0.9853X + 0.1674Y - 0.0336Z - 5.1899 = 0$ with $\chi^2 = 82.8$. Deviations of these carbon atoms and their immediate neighbors from the mean plane are given in Table 4. It is seen that the nitrogen atoms are more than 0·7 Å above the plane but the corresponding values for the two remaining carbon atoms of the eight-membered ring are less than half this. Thus, the carbon atoms are extended down towards the plane. As expected for a *cis* compound the hydroxyl oxygens are both about 0·5 Å below the plane. Dihedral angles of 161 and 167° were calculated between the planes of toluene rings 1 and 2, respectively, and the heterocyclic ring mean plane.

Table 4. *Atomic distances (Å) from the best-fit mean plane through* C(8), C(10), C(11), *and* C(13) *of the eight-membered ring*

Atoms in plane		Neighboring atoms	
C(8)	+0·021 (5)	N(1)	+0·720 (3)
C(10)	−0·020 (5)	N(2)	+0·730 (3)
C(11)	+0·020 (5)	C(9)	+0·200 (5)
C(13)	−0·021 (4)	C(12)	+0·313 (5)
		S(1)	+2·156 (1)
		S(2)	+2·150 (1)
		O(5)	−0·500 (4)
		O(6)	−0·561 (3)

The N(1)–N(2) distance is 2·877 Å compared with 3·974 Å for the C(9)–C(12) distance. These unequal lengths produce the oval shape of the eight-membered ring as required for an extended crown (Hendrickson, 1964). The torsional angles are given in Table 5. The ideal torsional angles for the minimum-energy *CC* form are given as $\omega_1 = 77.4$ and $\omega_2 = 104.8°$ (Hendrickson, 1964). This compares with the average observed values for this structure of 56·5 and 104·7°.

Table 5. *Torsion angles for the eight-membered ring* (°)

N(1)—C(8)—C(9)—C(10)	−51·6
C(8)—C(9)—C(10)–N(2)	53·4
C(9)—C(10)–N(2)—C(11)	−104·0
C(10)–N(2)—C(11)–C(12)	105·6
N(2)—C(11)–C(12)–C(13)	−59·4
C(11)–C(12)–C(13)–N(1)	61·5
C(12)–C(13)–N(1)—C(8)	−107·9
C(13)–N(1)—C(8)—C(9)	101·4

The packing diagram is shown in Fig. 4. The molecules form layers which lie roughly parallel to the *XZ* plane. Within the layers the molecules are hydrogen bonded to each other. One of the hydroxyl hydrogens, H(17), bonds to the hydroxyl oxygen, O(6), of another molecule while the other hydroxyl hydrogen, H(11), closely approaches a sulfonyl oxygen, O(3), of a third

molecule. The observed distances for the hydrogen bonds are O(5)–O(6), 2·60 Å and O(3)–O(6), 2·80 Å. The layers stack up along the *Y* direction. There are no hydrogen bonds between layers.

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Rotation Function Studies of Southern Bean Mosaic Virus at 22 Å Resolution

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Approximately 60% of the data to a resolution of 22 Å has been collected for an R32 form of southern bean mosaic virus. The data were used to compute the rotation function for fivefold, fourfold, threefold, and twofold symmetry axes. An orientation of the icosahedral virus was determined consistent with the observed function. This differed from an earlier prediction based on apparent spikes of an *hk*0 photograph.

Introduction

Southern bean mosaic virus (SBMV) is a small spherical plant virus of molecular weight $6·6 \times 10^6$ daltons (Miller & Price, 1946) containing 21% RNA by mass (Ghabrial, Shepherd & Grogan, 1967). The single protein component in the coat (Hill & Shepherd, 1971) has a molecular weight of 29000 daltons consistent with the presence of 180 protein subunits in the virus and $T=3$ icosahedral symmetry (Caspar & Klug, 1962). A number of crystalline forms of SBMV have been obtained. Magdoff (1960) reported an orthorhombic form of space group $C222_1$ with $a=295$, $b=508$, $c=474$ Å. In this laboratory three different crystalline forms have been obtained: type I in space group R32 with $a=542$ Å, $\alpha=116°42'$ (Johnson, Rossmann, Smiley & Wagner, 1974); type II in space group R32 with $a=317$ Å, $\alpha=62°30'$; and type III in space group $C222_1$ with $a=335$, $b=530$, $c=530$ Å (Akimoto, Wagner, Johnson & Rossmann, 1975). In the type I crystal form there are three virus particles in the rhombohedral cell and each particle must therefore have one of its twofold axes directed along a crystallographic a axis of the hexagonal unit cell (Fig. 1). An orientation of the particle about the crystallographic twofold axis was previously suggested on the basis of apparent spikes observed on an *hk*0 precession photograph (Johnson *et al.*, 1974). These conclusions were, however, based on inadequate experimental data.

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Subsequently a data set consisting of approximately 60% of the 22 Å data was collected and used to calculate the rotation function (Rossmann & Blow, 1962).

Reported here are the details of the data collection and a revised particle orientation which was obtained by computing a rotation function with these three-dimensional data.

Experimental

Rhombohedral type I crystals were obtained with techniques previously described (Johnson *et al.*, 1974). The crystal morphology necessitated the placement of the [*hh*0] axis along the camera spindle axis. (Reference to this crystal lattice will be in terms of the hexagonal unit cell with $a=923$, $c=302$ Å.) Data were collected with standard precession techniques and a crystal-to-film distance of 100 mm. However, a layer-line screen with a 3 mm radius hole, rather than an annulus, was used to block upper-layer reciprocal-lattice reflections. The negative reciprocal-lattice levels did not intersect the sphere of reflection at the small precession angles for the chosen zones.

A total of 18 zero level $\mu=2°0'$ precession photographs (Fig. 2) were taken with Ni filtered Cu $K\alpha$ radiation using a 0·2 mm collimator. Intensity measurements were made with an Optronics photoscan film scanner. The film scanner procedure (Ford, 1974) calculated the intensity of a reflection by a profile-fitting method. Different films within one film pack, symmetry-related reflections within one plane and different film planes were successively scaled together by the method of Hamilton, Rollett & Sparks (1965).