

Table 3 (cont.)

|                   |     |                   |     |
|-------------------|-----|-------------------|-----|
| C(27)—C(26)—N(2)  | 125 | H(26)—C(26)—N(2)  | 115 |
| C(26)—C(27)—C(28) | 117 | H(27)—C(27)—C(26) | 119 |
| C(27)—C(28)—C(29) | 120 | H(27)—C(27)—C(28) | 123 |
| C(25)—C(29)—C(28) | 118 | H(28)—C(28)—C(27) | 117 |
| C(25)—C(29)—C(30) | 120 | H(28)—C(28)—C(29) | 121 |
| C(28)—C(29)—C(30) | 122 | H(30)—C(30)—C(29) | 115 |
| C(29)—C(30)—C(31) | 121 | H(30)—C(30)—C(31) | 129 |
| C(23)—C(31)—C(30) | 121 | H(31)—C(31)—C(23) | 104 |
| C(20)—N(1)—C(24)  | 118 | H(31)—C(31)—C(30) | 135 |

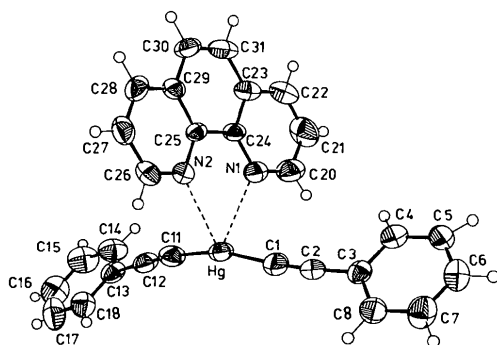


Fig. 1. ORTEP drawing of  $\text{Hg}(\text{C}_6\text{H}_5\text{-C}\equiv\text{C})_2 \cdot \text{C}_{12}\text{H}_8\text{N}_2$  (Johnson, 1965). The labels of the H atoms have been omitted for clarity; their numbering is that of the C atoms to which they are bonded.

interaction cannot be inferred because of the lack of precision in the Hg—N length. However, in our study, a shorter Hg—N distance (2.68 Å) corresponds to a smaller value in the C—Hg—C angle (165°) indicating a weak but clear donor-acceptor interaction between the two moieties.

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### (+)-*trans*-N',O-Cyclohexylidene-N-(2-hydroxycyclohexyl)guanidinium *p*-Toluenesulfonate

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**Abstract.**  $\text{C}_{13}\text{H}_{24}\text{N}_3\text{O}^+ \cdot \text{C}_7\text{H}_7\text{O}_3\text{S}^-$ , FW 409.5, monoclinic,  $P2_1$ ,  $Z = 2$ ,  $a = 10.130$  (5),  $b = 10.593$  (5),  $c = 10.011$  (5) Å,  $\beta = 100.22$  (4)°,  $V = 1057.2$  Å<sup>3</sup>,  $D_x = 1.287$  g cm<sup>-3</sup>.  $R = 0.04$  for 1988 observed structure factors. The complex is formed by the hydrogen bonds between the guanidinium and sulfonate groups which form a helical structure around the screw diad.

**Introduction.** In the course of synthetic studies on dihydrostreptomycin it became necessary to establish the structure of the product obtained by the reaction of

Most of the calculations were performed with the XRAY 70 system (Stewart, Kundell & Baldwin, 1970). Thanks are due to the staff of CPD del MEC for the use of the 1108 Univac computer.

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(+)-*trans*-2-guanidinocyclohexanol with 1,1-dimethoxycyclohexane in order to clarify the unusual reaction of the *trans*-diequatorial guanidino and hydroxyl groups in the streptidine moiety (Takagi, Kawashima, Tsuchiya, Sano & Umezawa, 1976). The guanidino compound was converted to its *p*-toluenesulfonic acid salt in order to make the compound soluble in organic solvents.

Crystals of the *p*-toluenesulfonate salt grown from ethanol solutions were colorless, transparent prisms elongated along the *b* axis. The lattice constants were

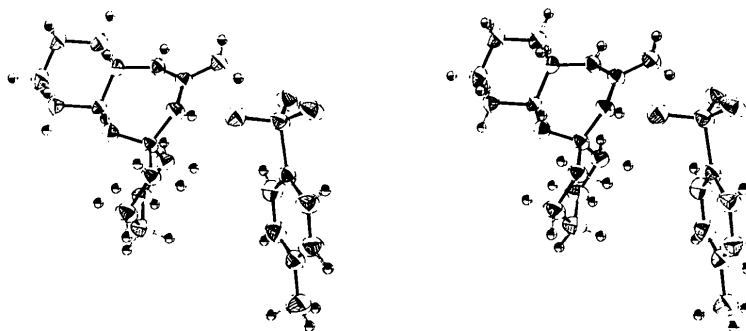


Fig. 1. A stereoscopic view of the complex molecule formed by (+)-*trans*-*N'*,*O*-cyclohexylidene-2-guanidinocyclohexanol and *p*-toluene-sulfonic acid.

calculated from the setting angles of 11 reflexions at  $2\theta > 80^\circ$  on a Philips four-circle diffractometer. Intensities of 1988  $hkl$  and  $\bar{h}\bar{k}l$  reflexions with  $2\theta < 150^\circ$  were measured along with about 300  $h\bar{k}l$  and  $\bar{h}k\bar{l}$  Friedel reflexions.

All the measurements were carried out with Cu  $K\alpha$  radiation monochromated by a graphite plate. The intensities were measured by the  $\theta$ - $2\theta$  scan method. The scan speed was chosen as  $4^\circ (\theta) \text{ min}^{-1}$  and the scans were repeated twice when the total number of counts in the first scan was less than 1000. Back-

ground was measured at each end of the scan for half the total scan time. The observed data were corrected for Lorentz and polarization factors but not for absorption.

The Patterson map showed three prominent peaks on the Harker section assignable to S-S vectors. The  $E$  map calculated by the *MULTAN* program (Germain, Main & Woolfson, 1971) showed many ghost peaks but the one consistent with the Patterson peak was taken as a S atom. A comparison of the electron-density map phased by the S atom with the  $E$  map revealed a partial structure from which the whole structure has been deduced.

The refinement was carried out by the block-diagonal least-squares method to an  $R$  value of 0.05 including 26 H atoms with isotropic temperature factors. The remaining five H atoms were located at the calculated positions. The final least-squares calculations including all the 31 H atoms gave an  $R$  value of 0.04. The weighting system was:  $w = 1$  for  $|F_o| < 15$  and  $\sqrt{w} = 1/|F_o|$  for  $|F_o| > 15$ .

The absolute configuration was determined by taking into account the contributions of  $f'$  and  $f''$  terms of S, O and N atoms for Cu  $K\alpha$  radiation (*International Tables for X-ray Crystallography*, 1974). Comparison of the calculated and observed intensity ratios of 82 Friedel pairs established the configuration shown in Fig. 1, which is in accordance with the chemically assigned absolute configuration for the (+)-*trans*-2-guanidinocyclohexanol moiety. The atomic coordinates are listed in Table 1.\*

**Discussion.** The present X-ray analysis elucidated the seven-membered ring structure which was considered to be the most probable one on the basis of chemical study (Takagi, Kawashima, Tsuchiya, Sano & Umezawa, 1976). The constitution and conformation

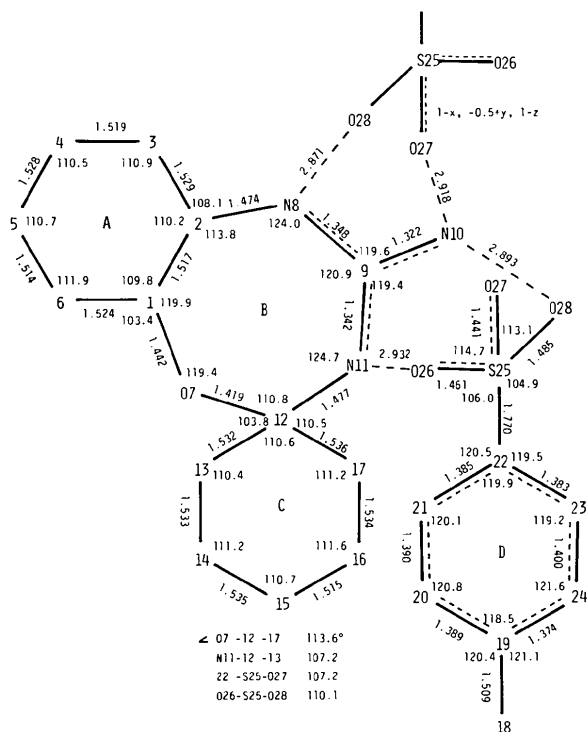


Fig. 2. Bond lengths (Å) and bond angles ( $^\circ$ ) found in the complex. Intermolecular hydrogen bonds are shown by broken lines with associated interatomic distances. Dotted lines indicate that the corresponding bond is involved in conjugation.

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33632 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

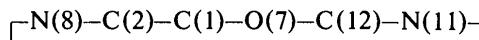
of the structure of the *p*-toluenesulfonate are illustrated in Fig. 1 by an ORTEP (Johnson, 1965) drawing.

All the bond lengths and angles found in both

Table 1. Positional parameters ( $\times 10^4$ ; for H  $\times 10^3$ ) with standard deviations in parentheses

|          | x        | y         | z         |
|----------|----------|-----------|-----------|
| C(1)     | 1060 (3) | -1487 (3) | 3135 (3)  |
| C(2)     | 1756 (3) | -1885 (3) | 4540 (3)  |
| C(3)     | 2015 (4) | -734 (4)  | 5473 (4)  |
| C(4)     | 712 (4)  | -61 (5)   | 5571 (4)  |
| C(5)     | -22 (4)  | 322 (4)   | 4162 (4)  |
| C(6)     | -248 (3) | -812 (4)  | 3230 (4)  |
| O(7)     | 630 (2)  | -2560 (2) | 2282 (2)  |
| N(8)     | 3045 (2) | -2536 (3) | 4555 (2)  |
| C(9)     | 3156 (3) | -3711 (3) | 4068 (3)  |
| N(10)    | 4155 (3) | -4446 (3) | 4636 (3)  |
| N(11)    | 2270 (3) | -4144 (3) | 3009 (3)  |
| C(12)    | 1606 (3) | -3360 (3) | 1867 (3)  |
| C(13)    | 779 (3)  | -4249 (4) | 836 (3)   |
| C(14)    | 111 (4)  | -3510 (4) | -421 (3)  |
| C(15)    | 1155 (4) | -2804 (4) | -1077 (4) |
| C(16)    | 1988 (4) | -1933 (4) | -59 (3)   |
| C(17)    | 2652 (3) | -2649 (4) | 1216 (3)  |
| C(18)    | 3667 (4) | -7171 (6) | -3404 (4) |
| C(19)    | 3690 (3) | -7261 (4) | -1896 (3) |
| C(20)    | 4008 (4) | -6211 (4) | -1071 (4) |
| C(21)    | 4041 (4) | -6287 (4) | 321 (4)   |
| C(22)    | 3742 (3) | -7415 (4) | 899 (3)   |
| C(23)    | 3427 (4) | -8470 (4) | 93 (4)    |
| C(24)    | 3409 (4) | -8377 (4) | -1305 (4) |
| S(25)    | 3677 (1) | -7500 (0) | 2652 (1)  |
| O(26)    | 2416 (2) | -6901 (3) | 2814 (2)  |
| O(27)    | 3787 (3) | -8813 (3) | 3033 (2)  |
| O(28)    | 4831 (2) | -6731 (3) | 3326 (2)  |
| H(C1)    | 164 (3)  | -86 (4)   | 274 (4)   |
| H(C2)    | 115 (3)  | -238 (4)  | 495 (3)   |
| H(C3)    | -265 (4) | -14 (5)   | 516 (4)   |
| H'(C3)   | 248 (4)  | -101 (4)  | 644 (4)   |
| H(C4)    | 88 (5)   | 61 (5)    | 612 (5)   |
| H'(C4)   | 9 (4)    | -70 (5)   | 607 (4)   |
| H(C5)    | 51 (4)   | 99 (5)    | 378 (4)   |
| H'(C5)   | -90 (4)  | 72 (5)    | 421 (4)   |
| H(C6)    | -69 (4)  | -63 (5)   | 235 (4)   |
| H'(C6)   | -88 (4)  | -140 (4)  | 365 (4)   |
| H(N8)    | 369 (3)  | -226 (4)  | 524 (4)   |
| H(N10)   | 470 (4)  | -417 (4)  | 548 (4)   |
| H'(N10)  | 434 (4)  | -510 (5)  | 411 (4)   |
| H(N11)   | 228 (4)  | -493 (4)  | 284 (4)   |
| H(C13)   | 146 (3)  | -487 (4)  | 53 (4)    |
| H'(C13)  | 3 (3)    | -465 (4)  | 129 (3)   |
| H(C14)   | -47 (4)  | -411 (5)  | -115 (4)  |
| H'(C14)  | -53 (4)  | -288 (4)  | -9 (4)    |
| H(C15)   | 178 (5)  | -338 (5)  | -142 (5)  |
| H'(C15)  | 67 (4)   | -234 (5)  | -187 (4)  |
| H(C16)   | 274 (4)  | -156 (5)  | -41 (5)   |
| H'(C16)  | 140 (4)  | -123 (5)  | 23 (4)    |
| H(C17)   | 335 (3)  | -330 (3)  | 97 (3)    |
| H'(C17)  | 318 (3)  | -207 (4)  | 187 (3)   |
| H(C18)   | 314 (5)  | -637 (5)  | -381 (5)  |
| H'(C18)  | 327 (5)  | -794 (5)  | -393 (5)  |
| H''(C18) | 454 (4)  | -699 (4)  | -363 (4)  |
| H(C20)   | 419 (4)  | -539 (4)  | -147 (4)  |
| H(C21)   | 440 (5)  | -561 (6)  | 96 (5)    |
| H(C23)   | 331 (5)  | -940 (5)  | 57 (5)    |
| H(C24)   | 319 (4)  | -917 (5)  | -189 (4)  |

residues are in the usual range as shown in Fig. 2. As is clearly shown in Fig. 1, the guanidino group is protonated whereas the sulfonic acid group is deprotonated. The bond lengths and angles of these groups are in good agreement with those found in L-arginine dihydrate (Karle & Karle, 1964) and ammonium acid *o*-carboxybenzenesulfonate (Okaya, 1967). Fig. 2 also shows the lengths of the intermolecular hydrogen bonds. As seen in the figure, all the available electronegative atoms are participating in hydrogen bonding. The conformation of the ring is illustrated in Fig. 3 showing the endocyclic torsion angles along the bonds involved in each ring. The rings *A* and *C* adopt a quite regular chair conformation and the ring *B*, a seven-membered heterocyclic ring fused to the *A* ring in the *trans* orientation, also adopts a chair-like conformation. In this ring *B*, the guanidinium group takes an almost completely planar conformation. Therefore, the endocyclic torsion angle about the line connecting the atoms N(11) and N(8) was calculated [C(12)—N(11)—N(8)—C(2) = 54° as given in Fig. 3] which shows that the ring



adopts a nearly regular chair conformation.

The crystal is composed of the cationic molecule C<sub>13</sub>H<sub>24</sub>N<sub>3</sub>O<sup>+</sup> and the *p*-toluenesulfonate anion C<sub>7</sub>H<sub>7</sub>O<sub>3</sub>S<sup>-</sup> which are bound to each other by hydrogen bonds between the guanidinium and sulfonate groups. As is shown in Fig. 2, each guanidinium group is hydrogen bonded to two sulfonate groups around the

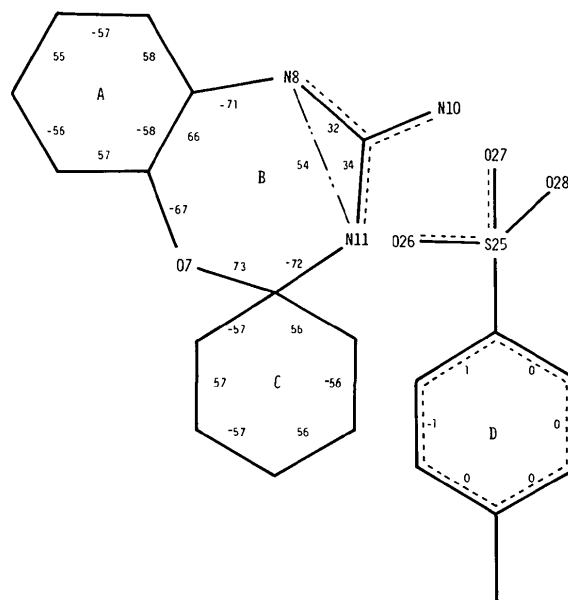


Fig. 3. Endocyclic torsion angles along the bonds involved in each ring. For ring *B*, the torsional angle about the line connecting N(8) and N(11) (indicated by a chain line) is also shown.

screw diad and forms a molecular complex having the open-type helical structure around the screw diad.

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## A Host–Guest-Type Water Adduct of 3,3'-(1,1'-Bi-2-naphthol)-21-crown-5\*

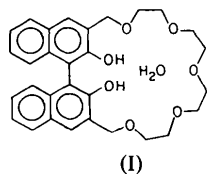
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**Abstract.** C<sub>30</sub>H<sub>32</sub>O<sub>7</sub> · H<sub>2</sub>O, *M<sub>r</sub>* = 522·6, monoclinic, *P*2<sub>1</sub>/*c*, *a* = 12·334 (3), *b* = 10·638 (2), *c* = 21·704 (4) Å, β = 110·81 (2)°, *V* = 2662·0 Å<sup>3</sup>, *Z* = 4, *D<sub>x</sub>* = 1·304 g cm<sup>-3</sup>. The structure was solved by direct and Fourier methods, and refined by block-diagonal least squares with 2640 observations to *R* = 0·065. The component species in the crystal associate *via* hydrogen-bonding interactions; the H<sub>2</sub>O molecule, too small to fit into the macrocyclic cavity, is preferentially coordinated to some of the O atom sites of the ligand. That part of the ring which is not involved in specific interactions with the guest molecule exhibits an irregular conformation and is probably disordered.

**Introduction.** In a recent communication Koenig, Helgeson & Cram (1976) report the synthesis and binding characteristics of macrocyclic polyethers containing phenolic ether groups. They also indicate that incorporation of phenolic substituents into crown ether rings may have a potential influence on the ligand-binding capability. As part of our systematic investigation of ligand–substrate interactions within inclusion compounds, it was of interest to study the nature of the



\* Structure and Binding in Molecular Complexes of Cyclic Polyethers. V.

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association between ligand (I) and water, and to describe the conformational features of the complexed host molecule. Coordination of H<sub>2</sub>O molecules to cyclic polyethers has been previously observed by other workers but not described in sufficient detail (Cradwick & Poonia, 1977; Hughes & Wingfield, 1977).

Crystals of the title compound were kindly supplied by Professor Cram of the University of California at Los Angeles.

Intensity data were collected on a four-circle diffractometer (Syntex P1) with graphite-crystal-monochromatized Cu Kα radiation ( $\lambda_{\text{mean}} = 1·5418$  Å). 3159 unique reflections within  $0 < 2\theta \leq 113^\circ$  ( $\sin \theta/\lambda \leq 0·54$  Å<sup>-1</sup>) were measured by the  $\theta$ - $2\theta$  scan technique at a constant scan rate (2° min<sup>-1</sup>). Each of the three standard reflections 126, 212 and 031 that were recorded after every fiftieth measurement suffered, however, about 30% loss of intensity (in total) during data collection. The data processing was carried out in the usual manner, and included renormalization of the intensities to account for the marked deterioration of the crystal. The structure was solved by a combination of direct methods (*MULTAN*) and Fourier techniques, and refined by least-squares analysis. The H atoms were introduced in calculated positions except for those of the phenolic groups and the H<sub>2</sub>O molecule which were located from a difference Fourier synthesis. The H atom parameters, including isotropic *U* = 0·05 Å<sup>2</sup>, were held constant during refinement. The atomic scattering factors for C and O were those of Hanson, Herman, Lea & Skillman (1964) and for H those given by Stewart, Davidson & Simpson (1965).