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## Structure of Solanid-4-en-6-one

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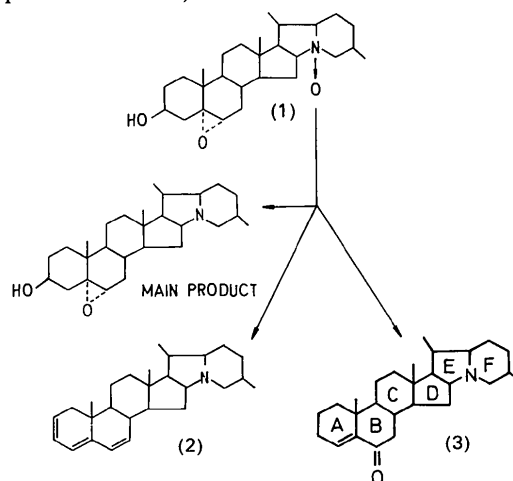
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**Abstract.**  $C_{27}H_{41}NO$ ,  $M_r = 395.6$ , orthorhombic,  $P2_12_12_1$ ,  $a = 31.312$  (4),  $b = 12.400$  (2),  $c = 5.928$  (2) Å,  $V = 2301.7$  (8) Å<sup>3</sup>,  $Z = 4$ ,  $D_{calc} = 1.14$  Mg m<sup>-3</sup>,  $\lambda(Cu K\alpha) = 1.54184$  Å,  $\mu = 0.44$  mm<sup>-1</sup>,  $F(000) = 872$ ,  $R = 0.074$  for 2422 unique observed reflections. The *A*, *B* and *C* rings show the usual conformation of 4-en-6-one structures. Conformational analysis of rings *D*, *E* and *F* confirms that the absolute configuration of the chiral centre at C(22) corresponds to the 22 $\alpha$ (H) isomer.

**Introduction.** In our previous reports (Miljković, Sakač, Gaši, Stanković & Ribár, 1990; Stanković, Miljković, Gaši & Sakač, 1990) some new chemical transformations of solanidine were described. Oxidation of solanidine with monopero-phthalic acid afforded 3 $\beta$ -hydroxy-5 $\alpha$ ,6 $\alpha$ -epoxysolanidan *N*-oxide (1). By thermolysis of (1), solanida-2,4,6-triene (2) and solanid-4-en-6-one (3) were obtained as the

minor products. In this paper, the detailed X-ray determination of compound (3), as final proof of its proposed structure, is described.



**Experimental.** Solanid-4-en-6-one (3) was obtained in addition to solanida-2,4,6-triene (2) and  $3\beta$ -hydroxy- $5\alpha,6\alpha$ -epoxysolanidane (main product) by direct (solventless) heating of (1) at 543 K for 1 min. The crude reaction mixture was separated on a silica gel column (benzene-ethyl acetate), whereupon the main product (18.35%; m.p. 489–491 K) and a mixture of compounds (2) and (3) were obtained. After separation of the mixture on an alumina column (benzene) and purification by recrystallization from acetone, pure crystals of (3) (4.91%; m.p. 505–506 K; calculated for  $C_{27}H_{41}NO$ : C 82.02, H 10.38; found: C 81.90, H 10.23) were obtained.

A transparent colourless well shaped crystal with dimensions  $1.23 \times 1.14 \times 0.62$  mm was mounted on a Siemens AED diffractometer. Data were collected using Ni-filtered Cu  $K\alpha$  radiation. The systematic absences ( $h00$ :  $h = 2n + 1$ ,  $0k0$ :  $k = 2n + 1$ ,  $00l$ :  $l = 2n + 1$ ) correspond to those of the orthorhombic space group  $P2_12_12_1$ . The refined lattice parameters were obtained by a least-squares procedure from the setting angles of 22 reflections with  $10 < \theta < 30^\circ$ . The intensities were collected in the range  $3 \leq \theta \leq 70^\circ$ ;  $\theta$ - $2\theta$  step-scanning mode, minimum scan speed  $0.05^\circ s^{-1}$ ; profile analysis by the method of Lehmann & Larsen (1974); scan amplitude  $\theta - 0.6^\circ \leq \theta \leq \theta - 0.6^\circ + (\Delta\lambda/\lambda)\tan\theta$ ;  $h$  0 to 38,  $k$  0 to 15,  $l$  0 to 7. A standard reflection ( $\bar{1}43$ ) collected after every 50 reflections showed a decrease in intensity of about 25% by the end of the measurements, indicating decomposition of the crystal in its interaction with X-rays, which explains the rather high value of the final  $R$  factor. An automatic rescaling was performed. Of 2539 independent non-zero reflections, 2422 with  $I > 2\sigma(I)$  were considered as observed and used for calculations. Data were corrected for Lorentz and polarization effects but not for absorption.

The structure was solved by direct methods using *MULTAN80* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). The best  $E$  map gave 13 non-H atoms ( $R = 0.51$ ). Subsequent structure-factor and Fourier calculations gave the positions of all non-H atoms. Full-matrix least-squares refinement with *SHELX76* (Sheldrick, 1976), anisotropic for all non-H atoms yielded  $R = 0.122$ . 22 H atoms were located in the difference map and treated isotropically in the final refinement. All the methyl H atoms were generated as well as those connected to C(3), C(15), C(16), C(22) and C(25). Their positions were not refined.  $\sum w(\Delta F)^2$  minimized,  $w$  for all reflections = 1.0; 375 parameters refined (divided into two cycles). Refinement was terminated at  $R = 0.074$ ,  $wR = 0.074$ ,  $R_{tot} = 0.075$ ; max. and min. peak heights in final  $\Delta\rho$  map were 0.26 and  $-0.23 e \text{ \AA}^{-3}$ ;  $(\Delta/\sigma)_{max} = 0.66$ . Scattering factors were taken from *International Tables for X-ray Crystallography* (1962, Vol. III). All calculations were

Table 1. Fractional atomic coordinates and equivalent isotropic temperature factors for the non-H atoms

$$U_{eq} = \frac{1}{3}(U_{11} + U_{22} + U_{33}).$$

	x	y	z	$U_{eq}(\text{\AA}^2)$
O	0.6642 (1)	0.0215 (3)	0.7925 (8)	0.076 (2)
N	0.5233 (1)	0.5318 (3)	0.9993 (6)	0.045 (2)
C(1)	0.7734 (2)	0.2964 (5)	0.8901 (11)	0.063 (3)
C(2)	0.8071 (2)	0.2065 (5)	0.9117 (13)	0.071 (4)
C(3)	0.7964 (2)	0.1132 (5)	0.7556 (13)	0.075 (4)
C(4)	0.7497 (2)	0.0904 (4)	0.7501 (10)	0.060 (3)
C(5)	0.7190 (1)	0.1515 (4)	0.8380 (8)	0.047 (2)
C(6)	0.6745 (1)	0.1169 (4)	0.8066 (9)	0.052 (3)
C(7)	0.6400 (1)	0.2030 (4)	0.7810 (10)	0.053 (3)
C(8)	0.6485 (1)	0.3068 (4)	0.9137 (8)	0.043 (2)
C(9)	0.6954 (1)	0.3443 (4)	0.8726 (7)	0.042 (2)
C(10)	0.7281 (1)	0.2589 (4)	0.9521 (7)	0.045 (2)
C(11)	0.7041 (2)	0.4585 (4)	0.9636 (10)	0.053 (3)
C(12)	0.6705 (1)	0.5422 (4)	0.8876 (9)	0.051 (3)
C(13)	0.6258 (1)	0.5067 (3)	0.9497 (7)	0.039 (2)
C(14)	0.6177 (1)	0.3956 (3)	0.8358 (8)	0.042 (2)
C(15)	0.5697 (1)	0.3797 (3)	0.8608 (9)	0.052 (2)
C(16)	0.5517 (1)	0.4938 (3)	0.8215 (8)	0.048 (2)
C(17)	0.5898 (1)	0.5737 (3)	0.8383 (7)	0.044 (2)
C(18)	0.6207 (2)	0.5009 (4)	1.2058 (7)	0.052 (2)
C(19)	0.7247 (2)	0.2399 (5)	1.2096 (9)	0.067 (3)
C(20)	0.5719 (1)	0.6738 (4)	0.9588 (9)	0.050 (3)
C(21)	0.5814 (2)	0.7789 (4)	0.8334 (12)	0.074 (3)
C(22)	0.5241 (1)	0.6486 (3)	0.9833 (8)	0.049 (2)
C(23)	0.5010 (2)	0.6972 (4)	1.1818 (11)	0.069 (3)
C(24)	0.4552 (2)	0.6529 (5)	1.1923 (13)	0.075 (4)
C(25)	0.4545 (1)	0.5294 (4)	1.1937 (10)	0.063 (3)
C(26)	0.4800 (1)	0.4871 (4)	0.9918 (9)	0.055 (3)
C(27)	0.4088 (1)	0.4844 (5)	1.1900 (12)	0.081 (4)

performed on an IBM PS/2 M80 computer with the *CRYRULER* package (Rizzoli, Sangermano, Cales-tani & Andreetti, 1987).

**Discussion.** The final atomic positions and equivalent isotropic temperature factors for non-H atoms are given with their e.s.d.'s in Table 1.\* Bond lengths and angles are listed in Table 2. A perspective view of the molecule with the atomic nomenclature is shown in Fig. 1. Bond lengths and angles have the usual values for steroid molecules. The slight variations are a property of this type of compound, but the valence angles of C(8)—C(14)—C(15) =  $119.9(6)$  and C(14)—C(13)—C(7) =  $99.9(5)^\circ$  are in excellent agreement with the average values for 91 steroid molecules of  $119.3 \pm 1.9$  and  $99.2 \pm 2.2^\circ$ , respectively (Duax, Weeks & Rohrer, 1976). This severe strain is a result of the fusion of five- and six-membered rings at the C(13)—C(14) bond.

The conformations of rings *A*, *B* and even *C*, shown clearly in Fig. 2, correspond to the 4-en-6-one structure (Nassimbeni, Russel & Gragg, 1977). According to the  $sp^2$  hybridization of C(4) and C(5),

\* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53436 (18 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Bond distances (Å) and bond angles (°) with *e.s.d.*'s in parentheses

O—C(6)	1.229 (6)	C(13)—C(14)	1.555 (5)
C(1)—C(2)	1.540 (9)	C(13)—C(17)	1.548 (5)
C(1)—C(10)	1.537 (7)	C(13)—C(18)	1.528 (6)
C(2)—C(3)	1.519 (9)	C(14)—C(15)	1.523 (4)
C(3)—C(4)	1.490 (9)	C(15)—C(16)	1.541 (5)
C(4)—C(5)	1.330 (7)	C(16)—C(17)	1.554 (5)
C(5)—C(6)	1.470 (5)	C(16)—N	1.457 (5)
C(5)—C(10)	1.521 (7)	C(17)—C(20)	1.538 (6)
C(6)—C(7)	1.526 (6)	C(20)—C(22)	1.536 (5)
C(7)—C(8)	1.532 (7)	C(20)—C(21)	1.530 (8)
C(8)—C(9)	1.560 (5)	C(22)—C(23)	1.507 (8)
C(8)—C(14)	1.535 (6)	C(22)—N	1.452 (5)
C(9)—C(10)	1.547 (6)	C(23)—C(24)	1.537 (9)
C(9)—C(11)	1.540 (7)	C(24)—C(25)	1.532 (8)
C(10)—C(19)	1.548 (7)	C(25)—C(26)	1.531 (7)
C(11)—C(12)	1.545 (7)	C(25)—C(27)	1.536 (5)
C(12)—C(13)	1.513 (5)	C(26)—N	1.465 (5)
C(2)—C(1)—C(10)	113.2 (9)	C(14)—C(13)—C(17)	99.9 (5)
C(1)—C(2)—C(3)	110.5 (9)	C(14)—C(13)—C(18)	111.9 (6)
C(2)—C(3)—C(4)	112.0 (9)	C(17)—C(13)—C(18)	111.9 (6)
C(3)—C(4)—C(5)	126.3 (9)	C(8)—C(14)—C(13)	113.7 (6)
C(4)—C(5)—C(6)	118.0 (7)	C(8)—C(14)—C(15)	119.9 (6)
C(4)—C(5)—C(10)	122.5 (7)	C(13)—C(14)—C(15)	103.5 (5)
C(6)—C(5)—C(10)	119.3 (6)	C(14)—C(15)—C(16)	103.1 (6)
O—C(6)—C(5)	122.6 (7)	C(15)—C(16)—C(17)	107.2 (5)
O—C(6)—C(7)	118.7 (7)	C(15)—C(16)—N	114.3 (6)
C(5)—C(6)—C(7)	118.6 (7)	C(17)—C(16)—N	102.5 (5)
C(6)—C(7)—C(8)	114.4 (7)	C(13)—C(17)—C(16)	104.1 (5)
C(7)—C(8)—C(9)	109.5 (6)	C(13)—C(17)—C(20)	120.0 (6)
C(7)—C(8)—C(14)	109.8 (6)	C(16)—C(17)—C(20)	105.3 (5)
C(9)—C(8)—C(14)	109.3 (6)	C(17)—C(20)—C(22)	103.6 (6)
C(8)—C(9)—C(10)	111.8 (6)	C(17)—C(20)—C(21)	113.0 (7)
C(8)—C(9)—C(11)	112.7 (6)	C(22)—C(20)—C(21)	114.1 (7)
C(10)—C(9)—C(11)	113.9 (6)	C(20)—C(22)—C(23)	117.4 (7)
C(1)—C(10)—C(5)	109.4 (7)	C(20)—C(22)—N	103.1 (6)
C(1)—C(10)—C(9)	109.3 (7)	C(23)—C(22)—N	109.9 (6)
C(1)—C(10)—C(19)	110.2 (7)	C(22)—C(23)—C(24)	109.7 (8)
C(5)—C(10)—C(9)	109.9 (6)	C(23)—C(24)—C(25)	111.8 (9)
C(5)—C(10)—C(19)	107.0 (6)	C(24)—C(25)—C(26)	109.3 (7)
C(9)—C(10)—C(19)	111.0 (6)	C(24)—C(25)—C(27)	112.1 (8)
C(9)—C(11)—C(12)	113.3 (7)	C(26)—C(25)—C(27)	110.5 (7)
C(11)—C(12)—C(13)	111.3 (7)	C(25)—C(26)—N	109.2 (6)
C(12)—C(13)—C(14)	107.6 (5)	C(16)—N—C(22)	105.4 (5)
C(12)—C(13)—C(17)	114.4 (6)	C(16)—N—C(26)	114.9 (6)
C(12)—C(13)—C(18)	110.6 (6)	C(22)—N—C(26)	113.0 (6)

ring *A* is a somewhat distorted half chair, with the  $C_2$  axis intersecting the C(1)—C(2) and C(4)—C(5) bonds dominating the conformation. This can be seen in Table 3 from the ring-puckering coordinates (Cremer & Pople, 1975) and asymmetry parameters (Duax, Weeks & Rohrer, 1976). The usual chair conformation for a saturated *B* ring is not found in the title compound owing to the  $sp^2$  hybridization of C(5) and C(6). Consequently, the mirror symmetry about the plane through C(6) is predominant, forcing the *B* ring into a transitional form between an envelope and a half chair. The *C* and *F* rings exhibit a symmetrical chair conformation with dominant mirror symmetry about the plane through the C(9) and N atoms. The five-membered *D* ring possesses an almost ideal  $13\beta,14\alpha$ -half-chair conformation, while *E* exhibits a transitional form between a half-chair and an envelope conformation with the N atom on the flap. The conformations of the *D*, *E* and *F*

rings are in good agreement with the corresponding ones in solanida-2,4,6-triene (Stanković, Miljković, Gaši & Sakač, 1990). The torsion angles of these rings (Table 4) confirm the absolute configuration of the chiral centre at C(22) as  $\alpha$  (Fig. 3), assuming C(10) and C(13) have their normal conformations. These findings are in accordance with our earlier work (Miljković, Gaši, Kindjer, Stanković, Ribár & Argay, 1985; Stanković, Ribár, Miljković, Gaši & Courseille, 1989), as well as with the work of Höhne, Schreiber, Ripperger & Worch (1966) concerning the absolute-configuration determination of natural solanidine derivatives by X-ray diffraction methods. The  $\beta$  axial C(18) methyl group is almost eclipsed with the C(19) methyl moiety, as shown by the non-bonded torsion angle C(19)—C(10)⋯C(13)—C(18) =  $-3.0(6)^\circ$ . The position of the

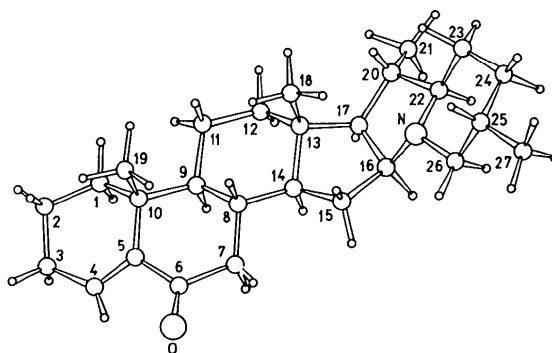


Fig. 1. A perspective view of the molecule showing atomic labeling. The bare numbers are C atoms.

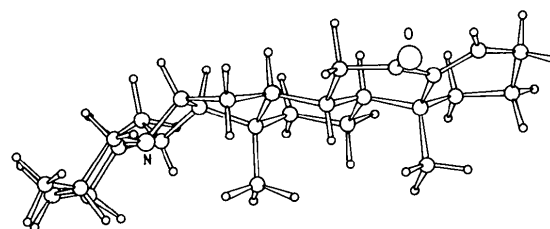


Fig. 2. The conformation of the steroid skeleton.

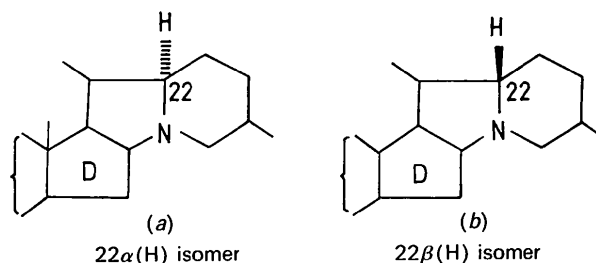


Fig. 3. The possible absolute configurations of the chiral centre at C(22).

Table 3. Ring-puckering coordinates and asymmetry parameters

Ring	$Q$ (Å)	$\varphi$ (°)	$\theta$ (°)	$\Delta C_1$ (°)	$\Delta C_2$ (°)
Six-membered					
A	0.373 (8)	203 (1)	128.5 (9)	17.7 [C(1)]	6.0 [C(1)—C(2)]
B	0.234 (6)	44 (1)	153.3 (7)	5.9 [C(6)]	7.5 [C(5)—C(6)]
C	0.075 (6)	69 (5)	172.5 (6)	1.8 [C(9)]	4.6 [C(9)—C(11)]
F	0.028 (8)	174 (15)	177.2 (8)	0.5 (N)	4.0 [N—C(22)]
Five-membered					
D	0.465 (5)	17.6 (7)	—	—	0.9 [C(16)]
E	0.419 (5)	317.3 (7)	—	6.5 (N)	14.4 [C(17)]

Table 4. Torsion angles (°) in D, E and F rings

Column I refers to the title compound, II to solanida-2,4,6-triene and III to 21,27-bisnordemissidine.

Ring	I	II	III
Ring D			
C(17)—C(13)—C(14)—C(15)	47.5 (5)	47.2 (4)	45 (2)
C(13)—C(14)—C(15)—C(16)	-38.5 (5)	-36.5 (4)	-46 (2)
C(14)—C(15)—C(16)—C(17)	14.5 (5)	11.2 (4)	28 (2)
C(15)—C(16)—C(17)—C(13)	14.8 (5)	17.5 (4)	2 (2)
C(14)—C(13)—C(17)—C(16)	-37.3 (5)	-38.8 (4)	-26 (2)
Ring E			
C(16)—C(17)—C(20)—C(22)	4.9 (5)	3.6 (4)	3 (2)
C(17)—C(20)—C(22)—N	-29.8 (5)	-28.9 (4)	-43 (2)
C(20)—C(22)—N—C(16)	46.6 (5)	45.9 (4)	46 (2)
C(22)—N—C(16)—C(17)	-41.8 (5)	-42.6 (4)	-31 (2)
N—C(16)—C(17)—C(20)	21.4 (5)	22.9 (4)	24 (2)
Ring F			
N—C(22)—C(23)—C(24)	56.4 (7)	56.8 (5)	61 (2)
C(22)—C(23)—C(24)—C(25)	-54.0 (8)	-53.5 (5)	-54 (2)
C(23)—C(24)—C(25)—C(26)	53.7 (7)	52.4 (5)	52 (2)
C(24)—C(25)—C(26)—N	-55.9 (7)	-54.5 (5)	-51 (2)
C(25)—C(26)—N—C(22)	61.8 (6)	60.0 (5)	54 (2)
C(26)—N—C(22)—C(23)	-62.3 (7)	-61.6 (5)	-61 (2)

C(27) methyl group is equatorial [C(27)—C(25)—C(24)—C(23) = 176.6 (9)°], while C(21) assumes an  $\alpha$  pseudo-equatorial position [C(21)—C(20)—C(17)—C(16) = 128.9 (8)°].

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## Structures of Three Complexes with the Host Diaza-18-Crown-6\*

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**Abstract.** Bis(*p*-nitrobenzaldehyde oxime)-diaz-18-crown-6 (2/1),  $C_{12}H_{26}N_2O_4 \cdot 2C_7H_6N_2O_3$ , (1),  $M_r = 594.63$ , triclinic,  $P\bar{1}$ ,  $a = 4.657$  (1),  $b = 11.197$  (2),  $c = 15.418$  (3) Å,  $\alpha = 104.49$ ,  $\beta = 96.29$  (2),  $\gamma = 98.51$  (2)°,  $V = 760.7$  (3) Å<sup>3</sup>,  $Z = 1$ ,  $D_x = 1.298$  g cm<sup>-3</sup>,  $\lambda(Mo K\alpha) = 0.71073$  Å,  $\mu = 0.94$  cm<sup>-1</sup>,  $F(000) = 316$ ,  $T = 298$  K,  $R = 0.0637$  for 947 reflections. Bis(*N*-hydroxybenzamide)-diaz-18-crown-6 (2/1),  $C_{12}H_{26}N_2O_4 \cdot 2C_7H_7NO_2$ , (2),  $M_r = 536.63$ , monoclinic,  $P2_1/c$ ,  $a = 15.989$  (2) (supercell

$A = 2a$ ),  $b = 5.030$  (1),  $c = 17.929$  (2) Å,  $\beta = 100.88$  (1)°,  $V = 1416.0$  (3) Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 1.258$  g cm<sup>-3</sup>,  $\lambda(Mo K\alpha) = 0.71073$  Å,  $\mu = 0.87$  cm<sup>-1</sup>,  $F(000) = 576$ ,  $T = 298$  K,  $R = 0.0767$  for 1856 reflections. 2,6-Dihydroxynaphthalene-diaz-18-crown-6 (1/1),  $C_{12}H_{26}N_2O_4 \cdot C_{10}H_8O_2$ , (3),  $M_r = 422.53$ , triclinic,  $P\bar{1}$ ,  $a = 7.639$  (1),  $b = 9.648$  (1),  $c = 18.045$  (2) Å,  $\alpha = 80.43$  (1),  $\beta = 80.30$  (1),  $\gamma = 67.84$  (1)°,  $V = 1206.3$  (2) Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 1.163$  g cm<sup>-3</sup>,  $\lambda(Mo K\alpha) = 0.71073$  Å,  $\mu = 0.79$  cm<sup>-1</sup>,  $F(000) = 456$ ,  $R = 0.060$  for 2582 reflections. In complexes (1) and (2), the diaza-18-crown-6 hosts lie on centers of symmetry with a guest molecule on each side of the molecular plane and

\* Diaza-18-crown-6 = 1,4,10,13-tetraoxa-7,16-diazacyclooctadecane.

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