

autour de C(5) confirment une hybridation  $sp^3$  légèrement déformée [ $\text{Fe}-\text{C}(5)-\text{P} = 118,6 (2)^\circ$ ] par une gêne stérique entre les groupements carbonyles et phényles. Des géométries apparentées ont été observées avec un complexe  $\text{Ni}(\text{CO})_3 [\text{P}(\text{C}_2\text{H}_4)(\text{C}_6\text{H}_5)_3]$  (Barnett & Kruger, 1972) et  $\text{Fe}(\text{CO})_4(\text{C}_5\text{H}_8\text{N}_2)$  (Huttner & Gartzke, 1972) mais jamais dans le cas d'un composé méthylène.

**Géométrie au niveau des groupements carbonyles.** Les groupements C(1)–O(1) et C(3)–O(3) sont déformés d'une façon significative [ $\text{Fe}-\text{C}(1)-\text{O}(1) = 172,4 (3)$  et  $\text{Fe}-\text{C}(3)-\text{O}(3) = 177,0 (4)^\circ$ ]. Cette déformation est très probablement due à des interactions intramoléculaires répulsives avec les atomes C(6) et C(11) d'une part, C(22) et C(23) d'autre part. On observe en effet une distance moyenne de 3,2 Å entre C(1)–O(1) et C(6)–C(11) et de 3,3 Å entre C(3)–O(3) et C(22)–C(23). Ceci est particulièrement net dans le cas de l'interaction C(1)–O(1)/C(6)–C(11) qui se caractérise par un allongement à 1,400 (4) Å de la liaison C(6)–C(11). Comme le montre la Fig. 2, ces interactions peuvent être dues à l'empilement des motifs qui met en vis-à-vis les groupements carbonyles de deux molécules.

On peut remarquer enfin que si ces interactions ne semblent pas modifier la planéité des cycles aromatiques, elles permettent de justifier certaines anomalies observées en spectroscopie infra-rouge.

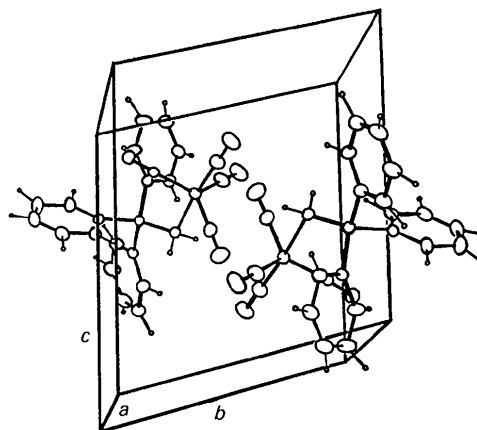


Fig. 2. Empilement des molécules.

#### Références

- BARNETT, B. L. & KRUGER, C. (1972). *J. Cryst. Mol. Struct.* **2**, 271–276.  
 FRENZ, B. A. (1978). *Enraf-Nonius CAD-4 SDP. A Real-Time System for Concurrent X-ray Data Collection and Crystal Structure Determination*. Dans *Computing in Crystallography*, édité par H. SCHENK, R. OLTJOF-HAZEKAMP, H. VAN KONINGSVELD & G. C. BASSI. Delft Univ. Press.  
 HUTTNER, G. & GARTZKE, W. (1972). *Chem. Ber.* **105**, 2714–2725.  
*International Tables for X-ray Crystallography* (1974). Tome IV. Birmingham: Kynoch Press.

*Acta Cryst.* (1984). **C40**, 2058–2061

## The Structure of 3,5-Dichloro-2-hydroxy-4-methoxy-6-*n*-propylbenzoic Acid (Differanisole A), $\text{C}_{11}\text{H}_{12}\text{Cl}_2\text{O}_4$ \*

BY YASUHIRO IIMURA, TOSIO SAKURAI, KEN-ICHI ASAHI AND NOBUTAKA TAKAHASHI

*The Institute of Physical and Chemical Research, Wako-shi, Saitama 351-01, Japan*

AND HIROFUMI OKA

*Meguro Institute of Banyu Pharmaceutical Co. Ltd, Shimo-Meguro, Meguro-ku, Tokyo 153, Japan*

(Received 21 May 1984; accepted 17 July 1984)

**Abstract.**  $M_r = 279.11$ , triclinic,  $P\bar{1}$ ,  $a = 10.242 (1)$ ,  $b = 15.972 (3)$ ,  $c = 7.797 (1)$  Å,  $\alpha = 91.93 (2)$ ,  $\beta = 95.23 (2)$ ,  $\gamma = 98.36 (2)^\circ$ ,  $U = 1255.2 (4)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_m = 1.472$ ,  $D_x = 1.477$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71073$  Å,  $\mu = 0.5154$  mm<sup>-1</sup>,  $T = 296$  K,  $F(000) = 576$ , final  $R = 0.050$  for 3501 unique reflections. The two crystallographically independent molecules are almost identical, except for the direction of the carbox-

ylic groups. There is an intramolecular hydrogen bond between a carboxylic oxygen and the adjacent hydroxy group. The crystal structure consists of centrosymmetric dimers linked by hydrogen bonds.

**Introduction.** To clarify the molecular mechanisms of cell differentiation and development, and to make use of differentiation-inducing substances for the medical treatment of cancer and muscular dystrophy *etc.*, we have studied the endogenous and the exogenous differentiation-inducing substances of animal cells.

\* Studies on the Differentiation Inducing Substances of Animal Cells. IV.

In the course of these studies, a new compound isolated from the cultured broth of a microorganism was found to have a potent differentiation-inducing activity (Oka, Asahi, Morishima, Sanada, Shiratori, Iimura, Iwatare & Takahashi, 1984). This compound, which induces the cell differentiation of murine erythroleukemia (B8) cells into erythrocyte, has been named differanisole A.

**Experimental.** Prismatic faint-yellow crystals (from methanol–water),  $0.3 \times 0.3 \times 0.5$  mm,  $D_m$  by flotation in an aqueous KI solution; great care was necessary to select a crystal that gave no diffraction-spot splitting. Rigaku AFC-4 four-circle diffractometer, graphite-monochromated Mo  $K\alpha$ ; unit-cell dimensions by least-squares analysis of 20 reflections with  $20^\circ < 2\theta < 22^\circ$ ; intensity data within the range  $(\sin\theta)/\lambda < 0.7035 \text{ \AA}^{-1}$  ( $-14 \leq h \leq 14$ ,  $-22 \leq k \leq 22$ ,  $0 \leq l \leq 11$ ) collected by  $\omega$ -scan mode ( $2\theta < 30^\circ$ ) and  $\omega-2\theta$  scan mode ( $2\theta \geq 30^\circ$ ), scan speed  $8^\circ \text{ min}^{-1}$  in  $2\theta$ , scan range  $1.2^\circ + 0.5^\circ \tan\theta$ , background counted for 5 s on either side of the peak; three standard reflections (101, 040 and 004) measured every 100 reflections showed no significant deterioration; Lorentz–polarization corrections, no absorption correction; 7796 reflections measured and 3501 unique reflections obtained with  $F_o \geq 3.0\sigma(F_o)$ , 3821 unobserved reflections. The normalized structure factors were calculated using a small temperature factor,  $B = 3.0 \text{ \AA}^2$ , in the space group  $P1$  (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). The Monte Carlo direct method (Furusaki, 1979) was applied to the 64 initial phases with 200 trial sets and converged to 59 sets. The combined figure of merit (COMBIND FOM) did not indicate the correct set of phases.  $E$ -map synthesis, peak-search and block-diagonal least squares were computed in the order of decreasing COMBIND FOM. The 26th COMBIND FOM (119th trial phase set) gave a low value of  $R = 0.334$  and 53 non-H atoms were obtained among 68 independent atoms. The positions of the remaining non-H atoms were determined from difference Fourier maps. At this stage, atomic coordinates showed that the corresponding atoms of the four molecules were closely related to each other by a center of symmetry. The space group was changed from  $P1$  to  $P\bar{1}$ . Difference Fourier syntheses gave the positions of all the H atoms except the carboxylic H; structure refined by full-matrix least squares based on  $|F_o|$ , anisotropic temperature factors for non-H atoms and isotropic temperature factors for H atoms;  $\sum w(|F_o| - |F_c|)^2$  minimized;  $w = 1/(0.0005|F_o|^2 + 0.016|F_o| + 0.23)$ , final  $R = 0.050$ ,  $R_w = 0.044$ ,  $S = 0.759$ . In final cycle of refinement largest shift/error 0.45 for O(2) of molecule *A*. Max. and min. heights in final difference synthesis 0.37 and  $-0.27 \text{ e \AA}^{-3}$ . Calculations carried out on the FACOM M-380 computer of this Institute using the UNICS-III program system (Sakurai &

Kobayashi, 1979), best planes calculated with  $BP70$  (Ito, 1982). Atomic scattering factors, including anomalous-scattering corrections, from *International Tables for X-ray Crystallography* (1974).

**Discussion.** The final atomic coordinates are shown in Table 1.\* The atomic numbering, thermal ellipsoids and intramolecular hydrogen bonds are shown in Fig. 1. The bond lengths, angles and torsion angles are given in Table 2. The benzene ring has many substituents. The methoxy and propyl planes are nearly perpendicular to the benzene ring. An intramolecular hydrogen bond is formed between the carboxylic O(1) and the 2-hydroxy group. The geometry of the hydrogen bond is close to those found in 2-hydroxy-5-methylbenzoic acid and 2,5-dihydroxybenzoic acid (Haisa, Kashino, Hanada, Tanaka, Okazaki & Shibagaki, 1982) and salicylic acid (Bacon & Jude, 1973). The two crystallographically independent molecules, *A* and *B*, are almost identical, except for the direction of the carboxylic plane relative to the benzene ring. The dihedral angles between the carboxylic group and the benzene ring are  $11.6(2)$  and  $8.4(1)^\circ$  for molecules *A* and *B* respectively. However, the torsion angles C(2)–C(1)–C(7)–O(1) and C(2)–C(1)–C(7)–O(2) are  $10.8(4)$  and  $-167.9(3)^\circ$  for molecule *A* and  $-7.2(5)$  and  $172.3(3)^\circ$  for *B*. Therefore, the carboxylic groups tilt in opposite directions to one another. The torsion angles C(6)–C(9)–C(10)–C(11) in the propyl group are also different in molecules *A* and *B*,  $170.7(4)$  and  $-166.3(5)^\circ$  respectively. Some of the carbon bond angles in the benzene ring deviate about  $4^\circ$  from  $120^\circ$ . This occurs at C(1) and C(2) because of the intramolecular hydrogen bond, and at C(5) and C(6) to reduce the crowding of the substituent groups including the bulky propyl group. The nearest-neighbor intramolecular distance between O(2) and the propyl group is  $\text{O}(2)\cdots\text{H}(\text{C}92) = 2.28 \text{ \AA}$  in molecule *B*. To reduce the steric hindrance, the angle C(1)–C(6)–C(9) of molecule *B* [ $125.7(3)^\circ$ ] is slightly larger than that of molecule *A* [ $123.9(3)^\circ$ ]. C(2)–C(5) is  $1.733(4)$  and  $1.745(4) \text{ \AA}$  and C(1)–C(3) is  $1.718(3)$  and  $1.719(4) \text{ \AA}$  in molecules *A* and *B* respectively. The angles C(4)–O(4)–C(8) are  $115.4(3)$  and  $116.0(3)^\circ$  respectively. The analogous angle for 2,3,5,6-tetrachloro-1,4-dimethoxybenzene (Wieczorek, 1980) is  $115.2(3)^\circ$ . Table 3\* shows the planarity of the benzene ring. The  $\chi^2$  values are 132.9 and 243.3 in molecules *A* and *B* respectively. The value of  $\chi^2$  at 99.9% for three degrees of freedom is 16.27, showing that the benzene ring is nonplanar. The crystal structure projected along

\* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, distances and angles involving the H atoms and least-squares planes (Table 3) have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39644 (27 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

the *a* axis is shown in Fig. 2. It consists of centrosymmetric dimers linked by hydrogen bonds between the carboxylic groups like that found in salicylic acid. The hydrogen-bond distance O(1)⋯O(2')=O(2)⋯O(1') is 2.632 (3) Å for molecule *A* and 2.679 (3) Å for molecule *B*. The dimers are stacked along [014] by van der Waals contacts to form a column in which the shortest contact is 3.238 (6) Å for O(4) (molecule *A*)⋯C(8') (molecule *B'* at  $-x, 1-y, 1-z$ ).

Table 1. Atomic coordinates ( $\times 10^5$ ) with estimated standard deviations in parentheses and equivalent isotropic temperature factors

$$B_{\text{eq}} = \frac{4}{3} \sum_i \sum_j B_{ij} a_i \cdot a_j$$

Molecule A	<i>x</i>	<i>y</i>	<i>z</i>	$B_{\text{eq}}(\text{\AA}^2)$
Cl(1)	6056 (10)	16461 (6)	14173 (13)	6.4
Cl(2)	55443 (12)	9897 (6)	12322 (17)	7.7
O(1)	37182 (23)	42914 (13)	44536 (34)	5.5
O(2)	57583 (23)	41978 (15)	39692 (39)	6.6
O(3)	18125 (24)	32202 (16)	30745 (37)	5.7
O(4)	27174 (28)	6750 (14)	5688 (29)	6.1
C(1)	41152 (30)	30141 (17)	30736 (37)	3.9
C(2)	27389 (31)	27521 (18)	27003 (38)	4.1
C(3)	22812 (32)	19582 (19)	18820 (39)	4.5
C(4)	31636 (37)	14336 (18)	14325 (38)	4.8
C(5)	45110 (36)	16976 (19)	18121 (42)	4.9
C(6)	50359 (33)	24669 (18)	26660 (39)	4.3
C(7)	45146 (30)	38743 (17)	38884 (39)	4.1
C(8)	23667 (70)	-187 (25)	16297 (67)	7.2
C(9)	65125 (37)	26612 (23)	31794 (50)	5.2
C(10)	72548 (41)	31109 (30)	17967 (56)	6.3
C(11)	86839 (50)	34199 (52)	24775 (91)	9.2

Molecule B	<i>x</i>	<i>y</i>	<i>z</i>	$B_{\text{eq}}(\text{\AA}^2)$
Cl(1)	-45978 (12)	89093 (6)	38961 (13)	6.9
Cl(2)	3019 (11)	81853 (7)	34358 (15)	7.5
O(1)	-51838 (27)	58293 (15)	11121 (37)	6.6
O(2)	-32775 (28)	55433 (16)	4107 (41)	7.2
O(3)	-54556 (30)	72626 (19)	23861 (39)	6.5
O(4)	-16703 (29)	91896 (14)	43606 (29)	6.4
C(1)	-32987 (34)	68648 (18)	19325 (39)	4.6
C(2)	-41272 (37)	74267 (20)	24988 (40)	4.9
C(3)	-35701 (39)	82251 (19)	32443 (39)	5.0
C(4)	-22131 (40)	84446 (19)	35074 (39)	5.2
C(5)	-14045 (37)	78746 (20)	29932 (43)	5.3
C(6)	-18923 (37)	70931 (19)	21470 (41)	5.1
C(7)	-39748 (38)	60424 (19)	11253 (42)	4.9
C(8)	-14769 (73)	99058 (26)	33318 (71)	7.7
C(9)	-8877 (45)	65496 (24)	15665 (51)	5.9
C(10)	-4913 (57)	59835 (32)	29589 (65)	7.3
C(11)	7445 (90)	55989 (65)	25651 (135)	10.1

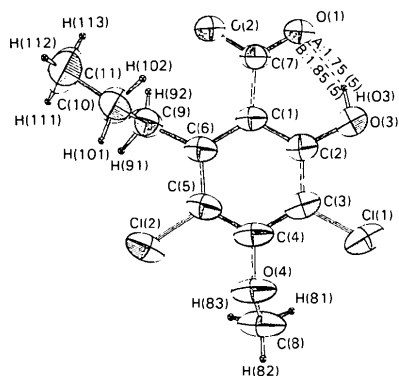


Fig. 1. Atomic numbering of the molecule. The thermal ellipsoids are at 50% probability for non-H atoms (H atoms are arbitrarily scaled). Distances are in Å.

Table 2. Intramolecular bond distances (Å), angles ( $^\circ$ ) and important torsion angles ( $^\circ$ ) for molecules *A* and *B* with e.s.d.'s in parentheses

	<i>A</i>	<i>B</i>		<i>A</i>	<i>B</i>
Cl(1)—C(3)	1.718 (3)	1.719 (4)	C(1)—C(7)	1.480 (4)	1.484 (4)
Cl(2)—C(5)	1.733 (4)	1.745 (4)	C(2)—C(3)	1.398 (4)	1.403 (4)
O(1)—C(7)	1.228 (4)	1.235 (5)	C(3)—C(4)	1.378 (5)	1.378 (6)
O(2)—C(7)	1.298 (4)	1.290 (5)	C(4)—C(5)	1.385 (5)	1.389 (5)
O(3)—C(2)	1.337 (4)	1.342 (5)	C(5)—C(6)	1.389 (4)	1.395 (4)
O(4)—C(4)	1.363 (4)	1.362 (4)	C(6)—C(9)	1.513 (5)	1.528 (6)
O(4)—C(8)	1.429 (5)	1.420 (5)	C(9)—C(10)	1.516 (6)	1.501 (7)
C(1)—C(2)	1.411 (4)	1.408 (5)	C(10)—C(11)	1.516 (7)	1.536 (12)
C(1)—C(6)	1.425 (5)	1.427 (5)			

	<i>A</i>	<i>B</i>
C(4)—O(4)—C(8)	115.4 (3)	116.0 (3)
C(2)—C(1)—C(6)	120.5 (3)	120.5 (3)
C(2)—C(1)—C(7)	116.0 (3)	116.2 (3)
C(6)—C(1)—C(7)	123.5 (3)	123.3 (3)
O(3)—C(2)—C(1)	124.2 (3)	124.9 (3)
O(3)—C(2)—C(3)	116.3 (3)	115.2 (3)
C(1)—C(2)—C(3)	119.6 (3)	119.9 (3)
Cl(1)—C(3)—C(2)	119.3 (3)	119.3 (3)
Cl(1)—C(3)—C(4)	120.2 (2)	120.5 (2)
C(2)—C(3)—C(4)	120.5 (3)	120.2 (3)
O(4)—C(4)—C(3)	120.4 (3)	120.3 (3)
O(4)—C(4)—C(5)	120.2 (3)	120.2 (3)
C(3)—C(4)—C(5)	119.4 (3)	119.3 (3)
Cl(2)—C(5)—C(4)	116.2 (2)	116.6 (2)
Cl(2)—C(5)—C(6)	120.5 (3)	120.1 (3)
C(4)—C(5)—C(6)	123.4 (3)	123.4 (3)
C(1)—C(6)—C(5)	116.7 (3)	116.5 (3)
C(1)—C(6)—C(9)	123.9 (3)	125.7 (3)
C(5)—C(6)—C(9)	119.4 (3)	117.8 (3)
O(1)—C(7)—O(2)	119.5 (3)	119.5 (3)
O(1)—C(7)—C(1)	122.7 (3)	121.6 (3)
O(2)—C(7)—C(1)	117.8 (3)	118.9 (3)
C(6)—C(9)—C(10)	112.3 (3)	111.2 (4)
C(9)—C(10)—C(11)	110.4 (4)	111.3 (6)

	<i>A</i>	<i>B</i>
C(8)—O(4)—C(4)—C(3)	-87.0 (4)	87.7 (4)
C(6)—C(1)—C(2)—O(3)	178.5 (3)	-178.6 (3)
Cl(1)—C(3)—C(4)—O(4)	2.0 (4)	3.1 (5)
O(4)—C(4)—C(5)—C(1)	-3.3 (4)	-2.1 (4)
C(1)—C(6)—C(9)—C(10)	-92.2 (4)	-89.8 (5)
C(2)—C(1)—C(7)—O(1)	10.8 (4)	-7.2 (5)
C(2)—C(1)—C(7)—O(2)	-167.9 (3)	172.3 (3)
C(6)—C(9)—C(10)—C(11)	170.7 (4)	-166.3 (5)
C(7)—C(1)—C(2)—O(3)	-1.7 (4)	1.3 (5)

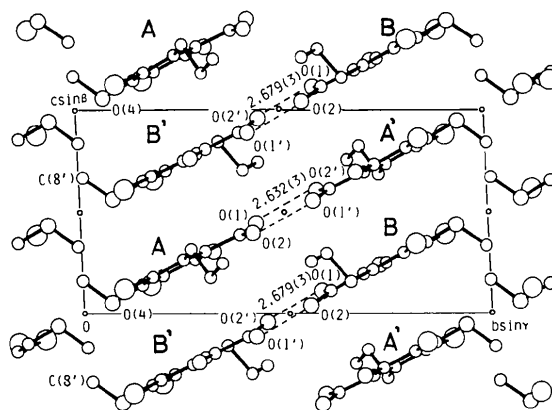


Fig. 2. The crystal structure projected along the *a* axis. H atoms are omitted for clarity. Broken lines show the hydrogen bonds (distances in Å). *A* and *B* indicate the molecules in Table 1. Symmetry code: (*A*), (*B*) *x, y, z*; (*A'*)  $1-x, 1-y, 1-z$ ; (*B'*)  $-x, 1-y, -z$ .

## References

- BACON, G. E. & JUDE, R. J. (1973). *Z. Kristallogr.* **138**, 19–40.  
 FURUSAKI, A. (1979). *Acta Cryst.* **A35**, 220–224.  
 HAISA, M., KASHINO, S., HANADA, S., TANAKA, K., OKAZAKI, S. & SHIBAGAKI, M. (1982). *Acta Cryst.* **B38**, 1480–1485.  
*International Tables for X-ray Crystallography* (1974). Vol. IV, pp. 72–73, 149. Birmingham: Kynoch Press.  
 ITO, T. (1982). *Acta Cryst.* **A38**, 869–870.  
 MAIN, P., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1978). *MULTAN78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.  
 OKA, H., ASAH, K., MORISHIMA, H., SANADA, M., SHIRATORI, K., IIMURA, Y., IWATARE, S. & TAKAHASHI, N. (1984). *J. Antibiot.* Submitted.  
 SAKURAI, T. & KOBAYASHI, K. (1979). *Rikagaku Kenkyusho Hokoku*, **55**, 69–77.  
 WIECZOREK, M. W. (1980). *Acta Cryst.* **B36**, 1515–1517.

*Acta Cryst.* (1984). **C40**, 2061–2064

## Structures of 1,4,10,13-Tetrathia-7,16-diazacyclooctadecane, $C_{12}H_{26}N_2S_4$ , and 7,16-Bis(4-chlorobenzoyl)-1,4,10,13-tetrathia-7,16-diazacyclooctadecane, $C_{26}H_{32}Cl_2N_2O_2S_4$

BY HERMAN L. AMMON, K. CHANDRASEKHAR AND SOVAN K. BHATTACHARJEE

*Department of Chemistry, University of Maryland, College Park, Maryland 20742, USA*

AND SEIJI SHINKAI AND YOSHIHIRO HONDA

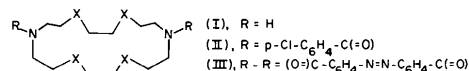
*Department of Industrial Chemistry, Faculty of Engineering, Nagasaki University, Nagasaki 852, Japan*

(Received 22 March 1984; accepted 12 June 1984)

**Abstract.** 1,4,10,13-Tetrathia-7,16-diazacyclooctadecane (I),  $M_r = 326.6$ , monoclinic,  $P2_1/c$ ,  $a = 5.200$  (2),  $b = 14.576$  (7),  $c = 11.203$  (3) Å,  $\beta = 100.95$  (2)°,  $V = 833.7$  Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 1.301$  g cm<sup>-3</sup>,  $\lambda(\text{Cu } K\alpha) = 1.5418$  Å,  $\mu = 49.0$  cm<sup>-1</sup>,  $F(000) = 352$ ,  $T = 295$  K, final  $R = 0.051$  for 1017 observed reflections. 7,16-Bis(4-chlorobenzoyl)-1,4,10,13-tetrathia-7,16-diazacyclooctadecane (II),  $M_r = 603.7$ , monoclinic,  $P2_1/a$ ,  $a = 11.8146$  (4),  $b = 21.6043$  (8),  $c = 11.5440$  (4) Å,  $\beta = 94.255$  (6)°,  $V = 2938.4$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.364$  g cm<sup>-3</sup>,  $\lambda(\text{Cu } K\alpha) = 1.5418$  Å,  $\mu = 48.6$  cm<sup>-1</sup>,  $F(000) = 1264$ ,  $T = 295$  K, final  $R = 0.063$  for 2764 observed reflections. A two-atom fragment of the macro-ring in (II) shows positional disorder. The crown-ring conformations in the two structures are significantly different. (I) incorporates a crystallographic inversion center, has no exo- or endodontate S atoms and no *anti* C–S bonds, while (II) has two exodontate S atoms and three *anti* C–S bonds.

**Introduction.** Macrocyclic polyethers ('crown' ethers) contain intramolecular cavities lined with molecular segments that are capable of binding cations. Ammon, Bhattacharjee, Shinkai & Honda (1984) reported the structure of a capped thia-crown, namely 2,2'-azobenzoyl-capped 1,4,10,13-tetrathia-7,16-diazacyclooctadecane (III), the first of the thia-crowns to exhibit the C–S bond in the *anti* conformation. The present investigation was undertaken to study both the effect of the azobenzene cap or bridge on the structure of the tetrathiadiazacyclooctadecane ring, and the effect of the hy-

bridization of the macrocyclic N atoms on the crown structure. Compound (II) contains  $sp^2$ -hybridized amide-type N atoms similar to that in the capped molecules, whereas the N atom in (I) is an  $sp^3$ -hybridized amino-type.



**Experimental.** Picker FACS-I diffractometer, graphite-monochromatized Cu radiation, cell parameters calculated by least squares from 12/16 reflections automatically centered at  $\pm 2\theta$ , intensity data collected to  $2\theta_{\max}$  of 126°,  $\theta$ - $2\theta$  scan, 10 s backgrounds; four standard intensities measured at 100-reflection intervals showed no significant variations. (I) and (II) prepared by SS and YH (procedure unpublished). (I): crystal  $0.27 \times 0.10 \times 0.07$  mm,  $h,k,l$  range 0–6, 0–16, –13–13, 1643 data measured, 1334 unique excluding systematic absences, 1017  $3\sigma$  above background; (II):  $0.47 \times 0.13 \times 0.10$  mm, 0–13, 0–24, –13–13, 5392 data measured, 4755 unique excluding systematic absences, 2764  $3\sigma$  above background.

Both structures solved with *MULTAN80* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). *E* map with highest combined figure of merit revealed all C, N and S atoms in (I); H atoms attached to C included in calculated positions with C–H = 1.05 Å; H linked to N located from difference map [peak height 0.46 (13) e Å<sup>-3</sup>]. Full-matrix least-squares