Structure of 2-Amino-*N*-(3-dichloromethyl-3,4,4a,5,6,7-hexahydro-5,6,8-trihydroxy-3-methyl-1-oxo-1*H*-2-benzopyran-4-yl)propanamide Hydrobromide Dihydrate

By I. Ueda

*College of General Education, Kyushu University, Ropponmatsu, Chuo-ku, Fukuoka 810, Japan*

and T. Munakata and J. Sakai

Research Center, Yoshitomi Pharmaceutical Ind. Ltd, 950 Koiwai, Yoshitomi-cho, Fukuoka 871, Japan

Abstract. $C_{14}H_{21}Cl_2N_2O_6^+ \cdot Br^- \cdot 2H_2O$, monoclinic, $P2_1$, $Z = 2$, $a = 14 \cdot 758$ (4), $b = 6 \cdot 854$ (2), $c = 9 \cdot 929$ (3) Å, $\beta = 90 \cdot 50$ (2)°, $D_m = 1 \cdot 639$, $D_x = 1 \cdot 654$ Mg m^{-3}. The structure was solved by the heavy-atom method; block-diagonal least-squares refinement led to a final R of 0·040 for 2466 observed reflexions. The absolute configuration of the compound was determined by anomalous-dispersion effects. The molecule consists of an isocoumarin ring, a methyl, a dichloromethyl group and an aminopropanamide moiety which is fixed to the ring by a hydrogen bond. A hydrophilic hole is formed by the moiety and the dichloromethyl group. The two water molecules are trapped by strong hydrogen bonds in the hole. The bromide anion is also connected to the surrounding molecules by three strong hydrogen bonds.

Introduction. New antibiotic products which have antitumor activities were isolated from a culture broth of *Pseudomonas yoshitomiensis* Y-12278. The chemical structure of the main product was proposed to be (I) from chemical and spectroscopic studies (Munakata, Sakai, Matsuki & Isagai, 1978). The product was independently found by other researchers (Kondo, Horiuchi, Hamada, Takeuchi & Umezawa, 1979). The compound is one of a new type of actinobolin-group antibiotics and is closely related to actinobolin (Antosz, Nelson, Herald & Munk, 1970). The X-ray diffraction study of the title compound was carried out to confirm the presumed chemical structure and to elucidate the precise molecular conformation.

(I)
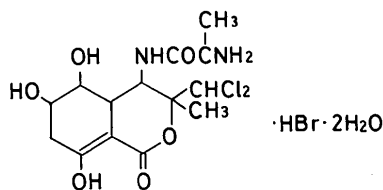
The title compound was recrystallized from water as colorless plates. Preliminary Weissenberg photographs showed systematic absences indicating the space group to be $P2_1$. The unit-cell parameters were refined by a least-squares procedure using the 2θ values of 15 reflexions measured on a Syntex *P*1 four-circle diffractometer with Mo $K\alpha$ radiation. The density was measured by flotation in a carbon tetrachloride–tetrabromoethane mixture. A single crystal used for intensity measurements was manually ground to a sphere of radius 0·176 mm to avoid systematic errors due to absorption effects. 3366 reflexions within a range of $2\theta \le 60°$ were collected by the θ–2θ scan technique with a variable scan rate from 4 to 12° min^{-1} (monochromated Mo $K\alpha$ radiation). 2466 independent reflexions with $I > 2 \cdot 33\sigma(I)$ were considered to be observed and they were used for the analysis. Corrections for Lorentz and polarization effects and for fluctuation of the monitored intensities were applied, but no absorption corrections were made ($\mu r = 0 \cdot 406$).

The structure was solved by the heavy-atom method. The Br and Cl atoms were easily located from the Patterson synthesis. The positions of all nonhydrogen atoms were obtained from a Fourier synthesis phased by the heavy atoms. The real and imaginary dispersion terms of the nonhydrogen atoms were taken into account for further refinement. Block-diagonal least-squares refinement of the atomic coordinates and anisotropic thermal parameters reduced R to 0·052. A difference Fourier synthesis calculated at this stage gave the H peaks except those of the water molecule $W(2)$. Introduction of these H atoms and five cycles of refinement gave an R value of 0·041. A difference Fourier map calculated at this stage gave a diffuse peak (0·7 e Å^{-3}) at a distance 0·5 Å from the O atom of the $W(2)$ molecule. As some heavy and hindered vibrations of the H atoms around the O atom caused this diffuse peak, the H atoms were given an ideal conformation and allocated to the diffuse peak. Five further cycles of refinement gave the final R value of 0·040. Shifts of the

Table 1. Comparison of the ratios of structure factors in Bijvoet pairs

h k l	$|F(hkl)|/|F(h\bar{k}l)|$ Calc.	Obs.	h k l	$|F(hkl)|/|F(h\bar{k}l)|$ Calc.	Obs.
0 1 1	0·841	0·758	4 1 3	0·956	0·934
2 1 $\bar{4}$	1·089	1·142	4 1 7	0·810	0·777
2 1 0	1·220	1·399	5 1 $\bar{2}$	0·938	0·900
2 1 4	1·164	1·293	5 1 5	0·891	0·859
3 1 $\bar{5}$	0·836	0·749	7 1 $\bar{3}$	1·131	1·219
3 1 1	1·070	1·116	7 1 1	0·825	0·730
3 1 4	0·922	0·901	11 1 $\bar{1}$	1·068	1·113
4 1 $\bar{1}$	0·902	0·853			

Fig. 1. A stereoview of the molecular conformation.

Table 2. Final atomic coordinates with their e.s.d.'s in parentheses

	x	y	z	$B_{eq.}$ (Å²)
Br	0·13701 (5)	0·7500 (2)	0·23350 (6)	4·02
Cl(1)	0·44716 (9)	1·1134 (2)	0·6445 (2)	3·33
Cl(2)	0·32931 (11)	0·8678 (2)	0·4845 (1)	3·64
C(1)	0·3875 (3)	0·7556 (10)	0·9873 (5)	2·55
C(2)	0·3773 (3)	0·7676 (9)	0·7410 (4)	2·00
C(3)	0·2924 (3)	0·6358 (7)	0·7510 (4)	1·88
C(4)	0·3103 (3)	0·4779 (7)	0·8556 (4)	1·82
C(5)	0·2297 (3)	0·3445 (7)	0·8802 (4)	2·02
C(6)	0·2592 (4)	0·1936 (7)	0·9808 (5)	2·33
C(7)	0·2793 (4)	0·2868 (9)	1·1173 (5)	2·89
C(8)	0·3299 (3)	0·4752 (8)	1·1047 (5)	2·59
C(9)	0·3435 (3)	0·5668 (7)	0·9866 (5)	2·11
C(10)	0·3566 (3)	0·9448 (7)	0·6515 (5)	2·23
C(11)	0·4610 (3)	0·6548 (8)	0·6973 (6)	2·81
C(12)	0·1338 (3)	0·7304 (8)	0·7179 (4)	2·13
C(13)	0·0586 (3)	0·8657 (8)	0·7658 (5)	2·38
C(14)	0·0024 (4)	0·7698 (13)	0·8744 (5)	3·47
N(1)	0·2125 (2)	0·7532 (8)	0·7824 (3)	1·92
N(2)	0·0003 (3)	0·9137 (7)	0·6468 (4)	2·62
O(1)	0·4148 (3)	0·8368 (7)	1·0896 (4)	3·79
O(2)	0·3966 (2)	0·8566 (5)	0·8714 (3)	2·41
O(3)	0·2026 (2)	0·2468 (7)	0·7596 (3)	2·59
O(4)	0·1924 (3)	0·0440 (6)	0·9901 (4)	2·94
O(5)	0·3579 (3)	0·5423 (7)	1·2239 (4)	3·41
O(6)	0·1186 (2)	0·6076 (7)	0·6308 (4)	3·30
W(1)	0·1111 (3)	1·0972 (7)	0·4510 (4)	3·69
W(2)	0·2422 (3)	1·3882 (8)	0·4539 (4)	4·69
H(C3)	0·281 (4)	0·565 (10)	0·656 (6)	1·7 (1·4)
H(C4)	0·357 (3)	0·397 (8)	0·823 (5)	0·2 (1·0)
H(C5)	0·174 (4)	0·419 (9)	0·911 (6)	0·9 (1·2)
H(C6)	0·315 (4)	0·142 (9)	0·945 (5)	0·9 (1·2)
H(1C7)	0·224 (4)	0·313 (10)	1·157 (6)	1·8 (1·4)
H(2C7)	0·309 (4)	0·198 (9)	1·177 (6)	1·7 (1·4)
H(C10)	0·306 (4)	1·013 (10)	0·687 (6)	1·3 (1·3)
H(1C11)	0·444 (4)	0·560 (11)	0·615 (7)	2·6 (1·6)
H(2C11)	0·512 (4)	0·753 (14)	0·669 (6)	2·7 (1·4)
H(3C11)	0·486 (5)	0·569 (12)	0·778 (7)	3·0 (1·7)
H(C13)	0·081 (4)	0·993 (10)	0·791 (6)	1·6 (1·4)
H(1C14)	−0·022 (5)	0·631 (13)	0·838 (7)	3·3 (1·7)
H(2C14)	0·044 (4)	0·747 (15)	0·962 (6)	3·5 (1·6)
H(3C14)	−0·053 (5)	0·860 (12)	0·899 (7)	3·6 (1·8)
H(N1)	0·219 (4)	0·839 (10)	0·850 (6)	1·5 (1·3)
H(1N2)	−0·050 (4)	1·018 (11)	0·678 (6)	2·6 (1·6)
H(2N2)	0·042 (4)	0·974 (12)	0·571 (6)	2·8 (1·7)
H(3N2)	−0·032 (4)	0·786 (13)	0·609 (6)	2·7 (1·6)
H(O3)	0·185 (4)	0·347 (11)	0·701 (6)	2·7 (1·6)
H(O4)	0·197 (5)	−0·001 (12)	1·077 (7)	3·1 (1·7)
H(O5)	0·375 (5)	0·672 (12)	1·205 (7)	3·5 (1·8)
H(1W1)	0·116 (5)	1·009 (13)	0·383 (7)	3·7 (1·9)
H(2W1)	0·165 (5)	1·170 (12)	0·450 (7)	3·7 (1·9)
H(1W2)	0·306 (5)	1·395 (14)	0·461 (8)	4·8 (2·2)
H(2W2)	0·231 (5)	1·436 (14)	0·368 (8)	5·1 (2·2)

positional and thermal parameters of the nonhydrogen atoms were almost less than one tenth of their standard deviations. A final difference Fourier map had no peaks > 0.4 e Å^{-3} except at the midpoints of some bonds and in the vicinity of the Br atom. An electron cloud

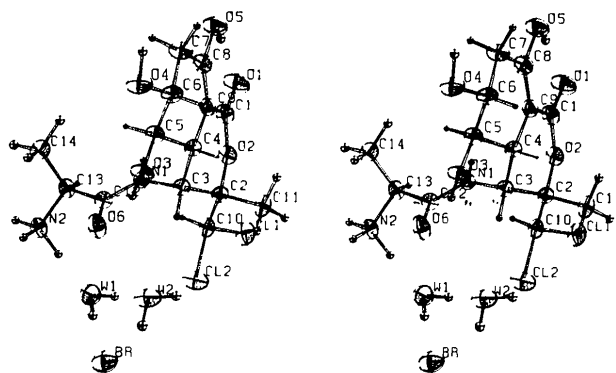(~ 1.0 e Å^{-3}) in a ring around the Br atom was revealed which pointed in the [103] direction. This electron cloud may be caused by a statistical distribution of the Br atom around the mean position rather than by large thermal vibrations. Refinement of the enantiomeric structure was carried out to determine the absolute configuration. The final R factor was 0·048. On the basis of the final R values, the former configuration was chosen. Further confirmation was obtained on comparison of the Bijvoet pairs which gave the highest difference between $F_c(hkl)$ and $F_c(h\bar{k}l)$. The observed relationships confirmed the correctness of the model as shown in Table 1. The absolute configuration is shown in Fig. 1 and Table 2.*

Unit weights for the observed reflexions were adopted in the least-squares refinement. Atomic scattering factors and anomalous-dispersion factors were taken from *International Tables for X-ray Crystallography* (1974). All calculations were performed on the FACOM M200 computer in the Computer Centre of Kyushu University with the *UNICS* II program system (Sakurai, Iwasaki, Watanabe, Kobayashi, Bando & Nakamichi, 1974).

Discussion. Fig. 1 shows a stereoview of the molecular conformation along the *b* axis drawn with *ORTEP* (Johnson, 1965), together with the atom-numbering scheme. The bond lengths and angles are respectively shown in Tables 3 and 4. Intermolecular distances shorter than the sums of the van der Waals radii are shown in Table 5.

The molecule consists of an isocoumarin ring with three hydroxyl groups, a methyl group, a dichloromethyl group and an aminopropanamide moiety. One side of the ring [C(1), C(7), C(8), C(9), O(1), O(2),

$$C_{14}H_{21}Cl_2N_2O_6^+ \cdot Br^- \cdot 2H_2O$$

Table 3. *Intramolecular distances* (Å)

Cl(1)–C(10)	1·769 (5)	C(4)–C(9)	1·514 (6)	C(10)–H(C10)	0·95 (6)	C(14)–H(3C14)	1·06 (8)
Cl(2)–C(10)	1·783 (5)	C(4)–H(C4)	0·94 (5)	C(11)–H(1C11)	1·07 (7)	N(1)–H(N1)	0·90 (6)
C(1)–C(9)	1·448 (8)	C(5)–C(6)	1·500 (7)	C(11)–H(2C11)	1·05 (8)	N(2)–H(1N2)	1·08 (7)
C(1)–O(1)	1·223 (7)	C(5)–O(3)	1·426 (5)	C(11)–H(3C11)	1·06 (7)	N(2)–H(2N2)	1·06 (6)
C(1)–O(2)	1·351 (6)	C(5)–H(C5)	1·02 (6)	C(12)–C(13)	1·525 (7)	N(2)–H(3N2)	1·06 (8)
C(2)–C(3)	1·549 (7)	C(6)–C(7)	1·525 (7)	C(12)–N(1)	1·331 (5)	O(3)–H(O3)	0·94 (7)
C(2)–C(10)	1·534 (7)	C(6)–O(4)	1·426 (7)	C(12)–O(6)	1·226 (6)	O(4)–H(O4)	0·92 (7)
C(2)–C(11)	1·524 (7)	C(6)–H(C6)	0·97 (6)	C(13)–C(14)	1·516 (8)	O(5)–H(O5)	0·94 (8)
C(2)–O(2)	1·457 (5)	C(7)–C(8)	1·497 (8)	C(13)–N(2)	1·492 (6)	W(1)–H(1W1)	0·91 (8)
C(3)–C(4)	1·521 (6)	C(7)–H(1C7)	0·93 (6)	C(13)–H(C13)	0·97 (7)	W(1)–H(2W1)	0·94 (8)
C(3)–N(1)	1·463 (6)	C(7)–H(2C7)	0·95 (6)	C(14)–H(1C14)	1·08 (9)	W(1)–H(1W2)	0·94 (7)
C(3)–H(C3)	1·07 (6)	C(8)–C(9)	1·347 (7)	C(14)–H(2C14)	1·07 (6)	W(2)–H(2W2)	0·93 (8)
C(4)–C(5)	1·522 (6)	C(8)–O(5)	1·332 (6)				

Table 4. *Bond angles* (°)

C(9)–C(1)–O(1)	123·7 (5)	C(4)–C(9)–C(8)	120·7 (4)
C(9)–C(1)–O(2)	120·1 (4)	Cl(1)–C(10)–Cl(2)	108·8 (3)
O(1)–C(1)–O(2)	116·1 (6)	Cl(1)–C(10)–C(2)	113·2 (3)
C(3)–C(2)–C(10)	110·0 (4)	Cl(1)–C(10)–H(C10)	107 (4)
C(3)–C(2)–C(11)	112·4 (5)	Cl(2)–C(10)–C(2)	110·3 (3)
C(3)–C(2)–O(2)	109·8 (3)	Cl(2)–C(10)–H(C10)	109 (4)
C(10)–C(2)–C(11)	113·2 (4)	C(2)–C(10)–H(C10)	109 (4)
C(10)–C(2)–O(2)	102·7 (4)	C(2)–C(11)–H(1C11)	110 (3)
C(11)–C(2)–O(2)	108·2 (4)	C(2)–C(11)–H(2C11)	110 (5)
C(2)–C(3)–C(4)	108·8 (4)	C(2)–C(11)–H(3C11)	110 (4)
C(2)–C(3)–N(1)	110·3 (4)	H(1C11)–C(11)–H(2C11)	110 (5)
C(2)–C(3)–H(C3)	109 (3)	H(1C11)–C(11)–H(3C11)	109 (6)
C(4)–C(3)–N(1)	112·4 (3)	H(2C11)–C(11)–H(3C11)	108 (5)
C(4)·C(3)·H(C3)	108 (4)	C(13)–C(12)–N(1)	114·4 (4)
N(1)–C(3)–H(C3)	108 (3)	C(13)–C(12)–O(6)	120·5 (4)
C(3)–C(4)–C(5)	113·9 (4)	N(1)–C(12)–O(6)	125·0 (5)
C(3)·C(4)–C(9)	110·7 (4)	C(12)–C(13)–C(14)	111·2 (5)
C(3)–C(4)–H(C4)	108 (3)	C(12)–C(13)–N(2)	107·6 (4)
C(5)·C(4)–C(9)	110·6 (3)	C(12)–C(13)–H(C13)	112 (4)
C(5)–C(4)–H(C4)	106 (3)	C(14)–C(13)–N(2)	110·1 (4)
C(9)–C(4)–H(C4)	107 (3)	C(14)–C(13)–H(C13)	113 (4)
C(4)–C(5)·C(6)	107·4 (4)	N(2)–C(13)–H(C13)	102 (4)
C(4)–C(5)–O(3)	111·2 (3)	C(13)–C(14)–H(1C14)	109 (4)
C(4)–C(5)–H(C5)	112 (3)	C(13)–C(14)–H(2C14)	109 (4)
C(6)–C(5)–O(3)	108·2 (4)	C(13)··–H(3C14)	110 (4)
C(6)–C(5)–H(C5)	112 (3)	H(1C14)–C(14)–H(2C14)	109 (7)
O(3)–C(5)·H(C5)	105 (3)	H(1C14)–C(14)–H(3C14)	110 (6)
C(5)–C(6)–C(7)	110·9 (4)	H(2C14)–C(14)··H(3C14)	110 (6)
C(5)·C(6)·O(4)	110·0 (4)	C(3)–N(1)–C(12)	122·3 (4)
C(5)··C(6)–H(C6)	105 (3)	C(3)–N(1)–H(N1)	116 (4)
C(7)–C(6)–O(4)	111·9 (4)	C(12)–N(1)–H(N1)	122 (4)
C(7)· C(6)–H(C6)	109 (3)	C(13)–N(2)–H(1N2)	108 (3)
O(4)–C(6)–H(C6)	111 (4)	C(13)–N(2)–H(2N2)	108 (3)
C(6)–C(7)–C(8)	112·3 (4)	C(13)–N(2)–H(3N2)	111 (4)
C(6)·C(7)–H(1C7)	107 (4)	H(1N2)–N(2)–H(2N2)	111 (5)
C(6)·C(7)·H(2C7)	112 (4)	H(1N2)–N(2)–H(3N2)	110 (5)
C(8)–C(7)–H(1C7)	108 (4)	H(2N2)–N(2)–H(3N2)	109 (5)
C(8)–C(7)–H(2C7)	112 (4)	C(1)–O(2)–C(2)	121·5 (4)
H(1C7)–C(7)–H(2C7)	105 (5)	C(5)–O(3)–H(O3)	105 (4)
C(7)–C(8)·C(9)	123·6 (5)	C(6)–O(4)–H(O4)	105 (5)
C(7)–C(8)–O(5)	112·0 (4)	C(8)–O(5)–H(O5)	103 (4)
C(9)–C(8)–O(5)	124·4 (5)	H(1W1)–W(1)–H(2W1)	106 (7)
C(1)–C(9)·C(4)	120·4 (4)	H(1W2)–W(2)–H(2W2)	103 (7)
C(1) C(9)–C(8)	118·9 (5)		

Table 5. *Intermolecular distances* (Å)

	Sym.*	Trans.†	Distance	Dvan.‡
Br–O(4)	1	0,1,–1	3·256 (4)	3·35
Br–W(1)	1	0,0,0	3·238 (5)	3·35
Br–H(2C14)	1	0,0,–1	3·01 (6)	3·15
Br H(O4)§	1	0,1, 1	2·48 (8)	3·15
Br–H(1W1)§	1	0,0,0	2·34 (8)	3·15
Br–H(2W2)	1	0,–1,0	2·88 (9)	3·15
Br–N(2)	2	0,–1,1	3·298 (5)	3·45
Br–H(1N2)	2	0,–1,1	2·23 (7)	3·15
Cl(1)–H(C4)	1	0,1,0	2·95 (5)	3·00
Cl(1)–O(5)	2	1,0,2	3·187 (5)	3·20
C(1)–H(C6)	1	0,1,0	2·89 (6)	2·90
C(6)–H(N1)	1	0,–1,0	2·82 (7)	2·90
C(7)–H(2W2)	1	0,–1,1	2·79 (8)	2·90
N(1)–O(4)	1	0,1,0	2·885 (6)	2·90
N(2)–W(1)	2	0,–1,1	2·885 (7)	2·90
O(1)–H(3C11)	2	1,0,2	2·52 (8)	2·60
O(2)–H(C6)	1	0,1,0	2·41 (6)	2·60
O(3) H(C10)	1	0,–1,0	2·33 (6)	2·60
O(3)–H(C13)	1	0,–1,0	2·52 (6)	2·60
O(4)–H(C13)	1	0,–1,0	2·58 (6)	2·60
O(4)··H(N1)§	1	0,–1,0	2·02 (6)	2·60
O(5)–H(2W2)	1	0,–1,1	2·48 (8)	2·60
W(1)–H(2N2)§	1	0,0,0	1·79 (7)	2·60
W(1)–H(3N2)§	2	0,0,1	1·84 (8)	2·60
W(2)–H(C3)	1	0,1,0	2·41 (6)	2·60
W(2)–H(2W1)§	1	0,0,0	1·88 (8)	2·60
H(C3)–H(1W2)	1	0,–1,0	2·29 (10)	2·40
H(1C7)··H(2W2)	1	0,–1,1	2·26 (10)	2·40
H(3N2)–H(1W1)	2	0,–1,1	2·27 (11)	2·40
H(3N2)–H(2W1)	2	0,–1,1	2·19 (10)	2·40

* Symmetry operations: (1) = *x,y,z*; (2) = –*x*, ½ + *y*, –*z*.
† Translations along the *a*, *b* and *c* axes.
‡ *D*van. = sum of van der Waals radii (Pauling. 1960).
§ Hydrogen bonds.

O(5)] is almost planar and the bond distances are slightly short. These facts are caused by the double bonds C(1)–O(1) and C(8)–C(9), and by the hydrogen bond O(1)···H(O5) [1·72 (8) Å] and their conjugation. Another side of the ring has tetrahedral and puckered connexions. The hydrogen bond O(6)··· H(O3) [2·15 (8) Å] serves to fix the aminopropanamide moiety. The fixed moiety and the dichloromethyl group form a hydrophilic hole as shown in Fig. 1. The two water molecules are trapped in the hole by the strong hydrogen bonds W(1)···H(2N2) and W(2)···H(2W1). The amino group is connected to the

Br atom and the two W(1) atoms, which occupy different sites, by the three strong hydrogen bonds Br···H(1N2), W(1)···H(2N2) and W(1)···H(3N2) as shown in Table 5. The amino group is involved in the antitumor activity of the compound. In fact, a compound with the alanine part removed shows no antitumor activity. The four hydrogen bonds around the water molecule W(1) are fairly short, as shown in Table 5. The Br anion is indirectly connected to the amino group through the water molecule by the hydrogen bonds. Such features were also found by Johnson, Frank & Paul (1973) in the case of the nicotinamide–adenine dinucleotide. The Br anion is also connected to the surrounding three molecules by strong hydrogen bonds Br···H(1W1), Br···H(1N2) and Br···H(O4), respectively. Such a variety of types

of hydrogen bonds plays an important role in building up the crystal structure in a way similar to that in benzylglutamic acid (Ashida, Sasada & Kakudo, 1967).

The present results have confirmed that the conformation of actinobolin proposed by Antosz, Nelson, Herald & Munk (1970) and that of bactinobolin proposed by Kondo, Horiuchi, Hamada, Takeuchi & Umezawa (1979) are essentially correct.

References

ANTOSZ, F. J., NELSON, D. B., HERALD, D. L. J. & MUNK, M. E. (1970). *J. Am. Chem. Soc.* **92**, 4933–4942.

ASHIDA, T., SASADA, Y. & KAKUDO, M. (1967). *Bull. Chem. Soc. Jpn*, **40**, 476–487.

International Tables for X-ray Crystallography (1974). Vol. IV, pp. 72–98. Birmingham: Kynoch Press.

JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.

JOHNSON, P. L., FRANK, J. K. & PAUL, I. C. (1973). *J. Am. Chem. Soc.* **95**, 5377–5385.

KONDO, S., HORIUCHI, Y., HAMADA, M., TAKEUCHI, T. & UMEZAWA, H. (1979). *J. Antibiot.* **32**, 1069–1071.

MUNAKATA, T., SAKAI, J., MATSUKI, H. & ISAGAI, K. (1978). Patent pending.

PAULING, L. (1960). *The Nature of the Chemical Bond*, 3rd ed. Ithaca: Cornell Univ. Press.

SAKURAI, T., IWASAKI, H., WATANABE, Y., KOBAYASHI, K., BANDO, Y. & NAKAMICHI, Y. (1974). *Rikagaku Kenkyusho Hokoku*, **50**, 75–91 (in Japanese).

Octaméthylène-3,4;3',4' Tétrathia-2,2',5,5' Fulvalène–Diméthoxy-2,5 Tétracyano-7,7,8,8 p-Quinodiméthane (OMTTF–DIMEOTCNQ)

PAR DANIEL CHASSEAU ET CHRISTIAN HAUW

Laboratoire de Cristallographie et Physique Cristalline associé au CNRS, Université de Bordeaux I, 351 cours de la Libération, 33405 Talence, France

Abstract. $C_{14}H_{16}S_4 \cdot C_{14}H_8N_4O_2$, monoclinic, $P2_1/c$, $a = 7 \cdot 097$ (2), $b = 9 \cdot 426$ (2), $c = 21 \cdot 266$ (4) Å, $\beta = 93 \cdot 92$ (5)°, $V = 1419 \cdot 3$ Å^3, $Z = 2$, $F(000) = 600$, $M_r = 576$, $d_c = 1 \cdot 348$ Mg m^{-3}, μ(Cu $K\alpha$) = $3 \cdot 22$ mm^{-1}. The structure was solved by the heavy-atom method and refined to an R of $0 \cdot 071$ for the 2477 independent diffractometer-observed reflections. OMTTF and DIMEOTCNQ are alternately stacked along the [100] direction, the average perpendicular separation between the molecular planes is $3 \cdot 53$ Å. Bond lengths in DIMEOTCNQ show that the constituent molecules in this compound are essentially neutral. The electrical conductivity of this compound measured on single crystals is $\sigma = 6 \times 10^{-8}$ Ω^{-1} mm^{-1}.

Introduction. Les cristaux d'OMTTF–DIMEOTCNQ ont été préparés au Laboratoire de Chimie Structurale Organique de l'Université de Montpellier; la synthèse de OMTTF a été réalisée selon un schéma réactionnel classique dans ce type de composé substitué, celle de DIMEOTCNQ selon la méthode décrite par Wheland & Martin (1975); le complexe a été cristallisé par combinaison de diffusion et évaporation. L'échantillon utilisé pour la mesure par diffraction X est un

monocristal de couleur noire de dimensions 0,35 × 0,2 × 0,15 mm.

Les intensités de 3149 réflexions indépendantes (2477 observées) ont été mesurées sur diffractomètre automatique Nonius CAD-4 muni d'un monochromateur au graphite, en utilisant la radiation Cu $K\alpha$. Ces intensités ont été corrigées des facteurs de Lorentz et polarisation, mais aucune correction d'absorption n'a été effectuée. Les facteurs de diffusion des atomes S, O, N et C sont extraits des *International Tables for X-ray Crystallography* (1974) tandis que pour les atomes d'hydrogène ont été retenues les valeurs de Stewart, Davidson & Simpson (1965).

La structure a été résolue par la méthode de l'atome lourd, l'analyse de la fonction de Patterson ayant permis de placer les atomes de soufre. L'affinement de la structure a été conduit de la façon suivante: affinement avec agitation thermique isotrope ($R = 0,15$) puis anisotrope ($R = 0,08$) des positions des atomes S, N, O, C (les atomes de carbone des groupes méthylènes présentent un désordre de position; seuls les parametres de position, d'agitation thermique isotrope ainsi que le taux d'occupation ont été affinés), introduction des atomes d'hydrogène du