Journal of Inclusion Phenomena and Molecular Recognition in Chemistry **11**: 41–48, 1991.

Crystal and Molecular Structure of *N,N′,N″*-Tritosyl-5,8,14,17,23,26-hexamethyl-2,11,20-triaza[3.3.3]-paracyclophane 1 : 1 Dichloromethane Clathrate

F. BOTTINO,[a] P. FINOCCHIARO,*[b] J. LIPKOWSKI,*[c] A. MAMO,[b] S. PAPPALARDO,[a] and K. SUWINSKA[c]
[a] *Dipartimento di Scienze Chimiche, Universita' di Catania, Viale A. Doria 8, 95125 Catania, Italy.*
[b] *Istituto Chimico, Facolta' di Ingegneria, Universita' di Catania, Viale A. Doria 6, 95125 Catania, Italy.*
[c] *Institute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01-224 Warsaw, Poland.*

(Received: 13 November 1990; in final form: 14 March 1991)

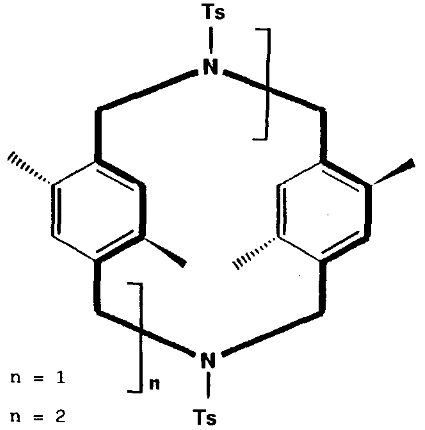
Abstract. The crystal and molecular structure of the title compound, $C_{51}H_{57}N_3O_6S_3 \cdot CH_2Cl_2$ has been determined by single crystal X-ray analysis and refined to an R-value of 0.069 for 1032 reflections. The crystal is trigonal, space group $R3$, with $a = 21.255(7)$, $c = 11.317(4)$, and $Z = 3$. One molecule of dichloromethane used as solvent is enclathrated in the crystal lattice.

Key words. *N*-tosyl azamacrocycles, crystal structure, clathrate formation.

Supplementary Data relevant to this article have been deposited with the British Library as Supplementary Publication No. SUP. 82111 (11 pages).

1. Introduction

We have recently shown that the one-pot condensation of a tosylamide sodium salt (TsNHNa) with bis(halomethyl) compounds offers a practical route to symmetrical *N*-tosyl azamacrocycles [1]. Cyclooligomerization of 1,4-bis(chloromethyl)-2,5-di-



1 n = 1

2 n = 2

Scheme 1.

---

*Authors for correspondence.

methylbenzene with TsNHNa produced the chiral dimer **1**, along with small amounts of the cyclic trimer **2**, which was isolated as a crystalline CH_2Cl_2 adduct [1].

The trigonal symmetry present in **2** is a feature apparent in the molecular structure of a number of important hosts, such as triphenylmethane, *trans,anti, trans,anti,trans*-perhydrotriphenylene, tri-*o*-thymotide, tris(*o*-phenylene dioxy)cyclotriphosphazene, cyclotriveratrylene, and hexa-hosts [2]. Therefore, in order to provide information about the molecular architecture of the three-fold symmetric azamacrocyclic host **2**, as well as elucidating the geometry of the voids available for guest accommodation, single-crystal X-ray structural analysis of the CH_2Cl_2 adduct of **2** was undertaken.

2. Experimental

The title compound was synthesized as described in Ref. 1 and crystallized from dichloromethane.

Intensity data for **2** were collected using a crystal of approximate dimensions 0.20 × 0.20 × 0.30 mm on an Enraf-Nonius CAD4 four-circle diffractometer using MoK_α radiation ($\lambda = 0.71073$ Å) and a graphite monochromator. Crystal data are as follows: $C_{51}H_{57}N_3O_6S_3 \cdot CH_2Cl_2$, $f_w = 989.2$, trigonal $R3$ (hexagonal axes) $a = 21.255(7)$ Å, $c = 11.317(4)$ Å, $V = 4428(4)$ Å^3, $Z = 3$, $D_x = 1.113$ g cm^{-3}, $T = 298$ *K*, μ (MoK_α) $= 1.532$ cm^{-1}. Lattice parameters were determined by the least-squares method from 22 reflections ($8 < 2\theta < 24°$). After 41 h of exposure time the loss of intensity of the standard reflections was 28%. The data collection was interrupted and a new crystal of approximate dimensions 0.20 × 0.30 × 0.30 mm was mounted on the diffractometer. At the end of the experiment the loss of intensity of the standard reflections for the second crystal was 27%. 2816 reflections up to $\theta = 25°$ were measured in the $\omega - 2\theta$ scan mode. Of 1826 unique reflections ($R_{\text{int}} = 0.036$ for the two data sets and 0.034 for equivalent reflections), 1032 had $[F_0 > 1.5\sigma\ (F_0)]$ and were used in the refinement. No absorption or secondary extinction corrections were applied to the data. Complete data were collected for both crystals and all were corrected for intensity decay.

The structure was solved by MULTAN 11/82 [3] and refined with the SDP System [4]; final refinement was achieved with SHELX 76 [5]. Weights of each reflection in refinement (on F) were calculated from $w = 2.5/[\sigma^2(F_0) + 0.0001F_0^2]$, $\sigma(F_0)$ being the esd, based on counting statistics, of the observed structure factor. Scattering factors were taken from the *International Tables for X-Ray Crystallography* [6]. All the H atoms included in the refinement are in calculated positions [d(C—H) = 1.08 Å]. The guest molecules were located in channels along a three-fold screw axis of the unit cell at (1/3, 1/3, z). Due to the positional disorder and partial occupancy (the guest molecules were escaping during data collection) the refinement of the guest molecule atoms led to unreasonable geometry. On the basis of Fourier peaks the 'ideal' CH_2Cl_2 molecule was constructed and the rigid-body refinement of the molecule as a whole with variable s.o.f. and isotropic thermal parameters was performed. The final s.o.f. for the guest molecule was 0.54(1). The thermal parameters of the atoms in the guest molecule are much higher than normally found in crystal structures. This is due to positional disorder of the guest molecule mentioned above as there is more space available in the channel than the molecule may occupy. The hydrogen atoms were 'riding' on their carbons and isotropic thermal parameters were refined as common variables for groups. The total number of parameters refined was 216. Refinement resulted in final values of $R = 0.064$, $R_w = 0.055$ and $S = 3.50$; in the last cycle $(\Delta/\sigma)_{\max} < 0.3$. Final max. and min. $\Delta\rho$ were 0.30 and -0.27 e Å^{-3}, respectively. All calculations were performed on a microPDP11/73 and IBM PC computers.

3. Results and Discussion

The atomic fractional coordinates are reported in Table I; Table II shows bond distances and angles, while selected torsion angles are given in Table III. The molecular conformation of host **2** and the atomic numbering scheme, shown for clarity only for one repeating unit, are illustrated in Figure 1.

The solid-state conformation of **2** is attained through the presence of both anticlinal (119.1°) and synclinal (−62.2°) C—N—C—C torsion angles. The conformation of the macrocycle can be referred to the plane determined by the three nitrogen atoms, which is exactly perpendicular to the *z* axis of the crystal. C(1), C(10), and the other three-fold, symmetry-related bridging carbon atoms lie on parallel planes below the reference plane, so that their displacements from this plane can be easily computed by subtracting the orthogonalized *z*-coordinate of each bridging carbon atom to that of nitrogen.

Table I. Final fractional coordinates for $C_{51}H_{57}N_3O_6S_3{\cdot}CH_2Cl_2$.

Atom	*x*/*a*	*y*/*b*	*z*/*c*	*U*(eq)
S(1)	0.1382(1)	0.3727(1)	0.4075(0)	0.0687(13)
O(1)	0.1061(4)	0.3785(3)	0.5158(7)	0.0860(41)
O(2)	0.1967(3)	0.3585(3)	0.4133(8)	0.0955(41)
N(1)	0.1685(4)	0.4492(3)	0.3380(9)	0.0704(42)
C(1)	0.2149(4)	0.4615(4)	0.2347(10)	0.0617(46)
C(2)	0.2944(5)	0.5112(4)	0.2635(11)	0.0581(49)
C(3)	0.3202(5)	0.5344(5)	0.3752(12)	0.0670(53)
C(4)	0.3951(5)	0.5777(5)	0.4013(14)	0.0712(56)
C(5)	0.4421(4)	0.5963(5)	0.3055(14)	0.0646(56)
C(6)	0.4168(5)	0.5746(6)	0.1961(13)	0.0779(63)
C(7)	0.3433(5)	0.5328(5)	0.1698(12)	0.0675(52)
C(8)	0.4178(6)	0.6000(8)	0.5268(13)	0.1059(82)
C(9)	0.3175(7)	0.5089(9)	0.0443(13)	0.1324(89)
C(10)	0.5255(4)	0.6378(4)	0.3242(11)	0.0758(54)
C(11)	0.0681(5)	0.3033(4)	0.3245(10)	0.0575(48)
C(12)	−0.0023(5)	0.2858(5)	0.3398(11)	0.0677(55)
C(13)	−0.0555(6)	0.2312(7)	0.2691(12)	0.0843(70)
C(14)	−0.0419(10)	0.1952(6)	0.1877(14)	0.0924(83)
C(15)	0.0284(9)	0.2132(6)	0.1730(15)	0.1032(81)
C(16)	0.0833(6)	0.2660(6)	0.2394(12)	0.0869(64)
C(17)	−0.1008(9)	0.1381(8)	0.1160(14)	0.1419(88)
C(18)	0.3530(16)	0.3614(10)	0.2637(25)	0.1419(71)
Cl(1)	0.2933(16)	0.3167(10)	0.1469(25)	0.1419(42)
Cl(2)	0.3738(16)	0.3023(10)	0.3300(25)	0.1419(42)

Table II. Bond distances (Å) and angles (deg).

Host			
S(1)—O(1)	1.437(8)	C(3)—C(4)—C(5)	115.9(12)
S(1)—O(2)	1.420(8)	C(5)—C(4)—C(8)	125.2(11)
S(1)—N(1)	1.621(7)	C(4)—C(5)—C(10)	120.7(13)
S(1)—C(11)	1.755(8)	C(4)—C(5)—C(6)	121.1(11)
N(1)—C(1)	1.466(11)	C(6)—C(5)—C(10)	118.1(13)
C(1)—C(2)	1.514(11)	C(5)—C(6)—C(7)	123.3(13)
C(2)—C(3)	1.368(17)	C(5)—C(6)—H(6)	118.4(14)
C(2)—C(7)	1.392(16)	H(6)—C(6)—C(7)	118.3(15)
C(3)—C(4)	1.415(12)	C(2)—C(7)—C(6)	117.6(12)
C(4)—C(5)	1.391(19)	C(6)—C(7)—C(9)	121.2(12)
C(4)—C(8)	1.498(21)	C(2)—C(7)—C(9)	121.2(11)
C(5)—C(10)	1.336(20)	C(4)—C(8)—H(8)C	116.4(15)
C(5)—C(10)	1.549(10)	C(4)—C(8)—H(8)B	109.1(14)
C(6)—C(7)	1.389(13)	C(4)—C(8)—H(8)A	102.6(14)
C(7)—C(9)	1.515(19)	C(7)—C(9)—H(9)C	119.3(16)
C(10)—N(1)′	1.543(10)	C(7)—C(9)—H(9)B	113.5(15)
C(11)—C(12)	1.360(15)	C(7)—C(9)—H(9)A	94.3(14)
C(11)—C(16)	1.384(18)	C(5)—C(10)—N(1)′	108.1(8)
C(12)—C(13)	1.397(14)	C(5)—C(10)—H(10)B	123.8(9)
C(13)—C(14)	1.318(23)	C(5)—C(10)—H(10)A	124.2(10)
C(14)—C(15)	1.354(28)	H(10)B—C(10)—N(1)′	123.7(10)
C(14)—C(17)	1.476(19)	S(1)—C(11)—C(16)	120.7(9)
C(15)—C(16)	1.369(17)	S(1)—C(11)—C(12)	121.1(8)
		C(12)—C(11)—C(16)	118.1(10)
Guest		C(11)—C(12)—C(13)	118.5(11)
C(18)—Cl(1)	1.749(37)	C(11)—C(12)—C(12)	121.2(12)
C(18)—Cl(2)	1.752(44)	H(12)—C(12)—C(13)	120.4(13)
		C(12)—C(13)—C(14)	124.1(15)
N(1)—S(1)—C(11)	109.1(5)	C(12)—C(13)—H(13)	118.3(14)
O(2)—S(1)—C(11)	108.1(5)	H(13)—C(13)—C(14)	117.6(15)
O(2)—S(1)—N(1)	106.5(5)	C(13)—C(14)—C(17)	121.3(17)
O(1)—S(1)—C(11)	106.8(5)	C(13)—C(14)—C(15)	116.9(13)
O(1)—S(1)—N(1)	107.2(4)	C(15)—C(14)—C(17)	121.8(16)
O(1)—S(1)—O(2)	118.8(5)	C(14)—C(15)—C(16)	122.1(16)
S(1)—N(1)—C(10)″	114.2(6)	C(14)—C(15)—H(15)	119.1(16)
S(1)—N(1)—C(1)	117.4(6)	H(15)—C(15)—C(16)	118.8(19)
C(1)—N(1)—C)10)″	115.2(8)	C(11)—C(16)—C(15)	120.2(14)
N(1)—C(1)—C(2)	111.7(9)	C(15)—C(16) – H(16)	119.7(15)
N(1)—C(1)—H(1)B	109.1(10)	C(11)—C(16)—H(16)	120.0(13)
N(1)—C(1)—H(1)A	108.7(9)	C(14)—C(17)—H(17)C	125.1(17)
H(1)B—C(1)—C(2)	109.0(9)	C(14)—C(17)—H(17)B	100.1(15)
H(1)A—C(1)—C(2)	108.9(10)	C(14)—C(17)—H(17)A	102.1(18)
C(1)—C(2)—C(7)	117.0(10)		
C(1)—C(2)—C(3)	123.8(10)	*Guest*	
C(3)—C(2)—C(7)	119.1(10)	Cl(2)—C(18)—H(18)B	109.3(29)
C(2)—C(3)—C(4)	123.0(12)	Cl(2)—C(18)—H(18)A	109.4(24)
C(2)—C(3)—H(3)	118.2(12)	Cl(1)—C(18)—H(18)B	109.5(26)
H(3)—C(3)—C(4)	118.8(14)	Cl(1)—C(18)—H(18)A	109.6(29)
C(3)—C(4)—C(8)	118.9(11)	Cl(1)—C(18)—Cl(2)	109.3(15)

Table III. Selected torsion angles (deg).

C(10)—N(1)—C(1)—C(2)	119.1(9)
N(1)—C(1)—C(2)—C(3)	7.4(15)
C(4)—C(5)—C(10)—N(1)	−81.5(13)
C(1)—C(2)—C(3)—C(4)	176.5(11)
C(1)—C(2)—C(7)—C(9)	1.4(17)
C(2)—C(3)—C(4)—C(8)	−179.7(12)
C(8)—C(4)—C(5)—C(6)	−179.2(13)
C(10)—C(5)—C(6)—C(7)	175.5(11)
C(11)—S(1)—N(1)—C(1)	−75.1(8)
S(1)—C(11)—C(12)—C(13)	178.5(9)
N(1)—S(1)—C(11)—C(12)	−89.8(10)
O(2)—S(1)—C(11)—C(12)	154.6(9)
S(1)—N(1)—C(1)—C(2)	−101.9(9)
O(2)—S(1)—N(1)—C(1)	41.4(9)
O(1)—S(1)—N(1)—C(1)	169.6(7)

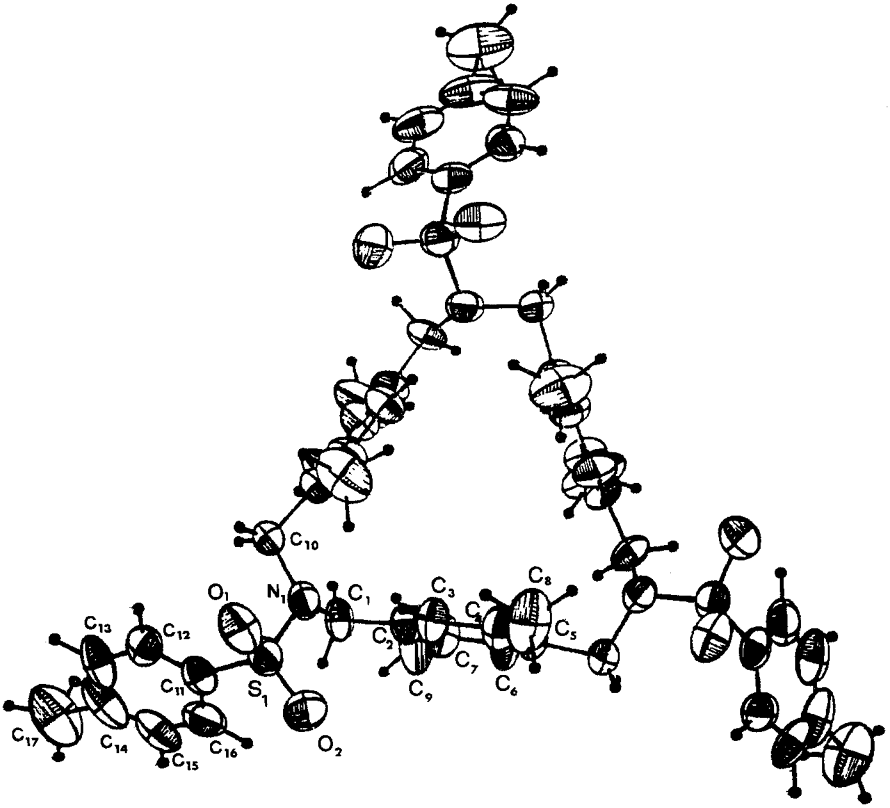


Fig. 1. ORTEP view of the host molecule with atom numbering scheme. The thermal ellipsoids are given at 50% probability.

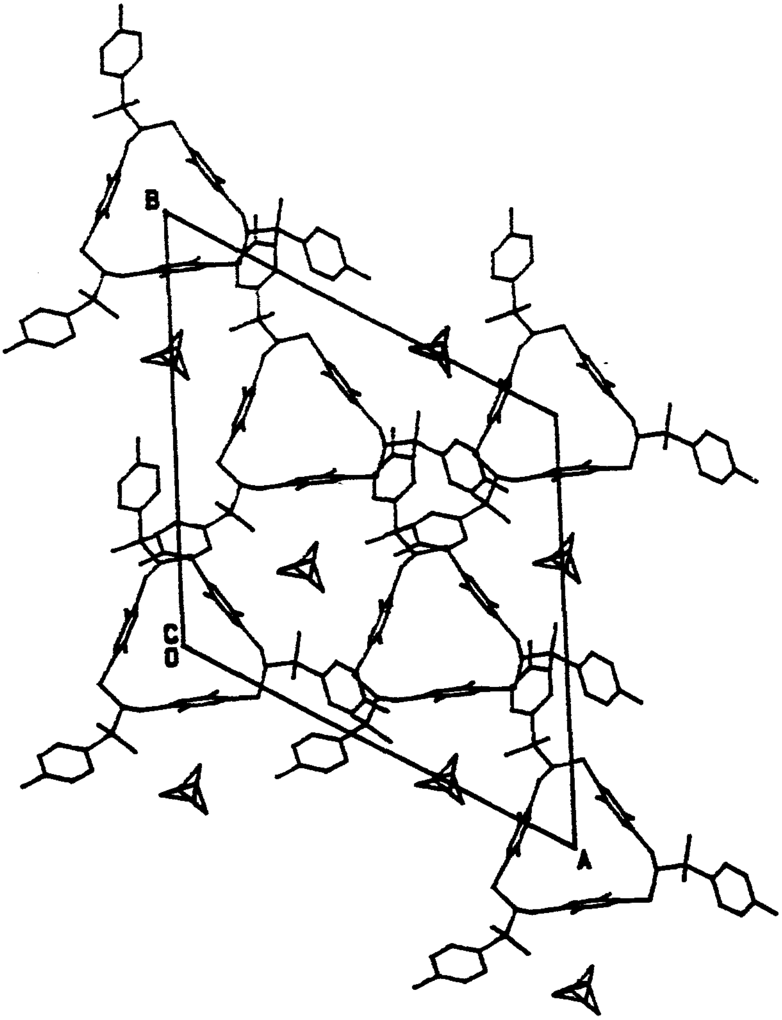


Fig. 2. Packing diagram along the *c* axis showing guest molecules packed in the channels.

The xylylene units are almost perpendicular to the plane of the nitrogen atoms (dihedral angle 94.6°), and form dihedral angles of 118.3 (3)° with each other. The xylylene rings are nearly planar, while the bridgehead C(1) and C(10) atoms are slightly bent out of the best plane of the aromatic ring with average C(1)—C—C—C and C(10)—C—C—C dihedral angles of 176.2° and 175.1°, respectively.

The S—N bond has a length of 1.621(7) Å, and the pyramidal coordination about N is considerably flattened, with angles ranging from 114.2(6)–117.4(6)°. The endocyclic C—C—C angles average 119.9°, but they vary significantly in the xylylene portion. The smallest endocyclic bond angles are found at C(4) [115.9(12)°] and C(7) [117.6(12)°] bearing the methyl substituents, while those at C(3) [123.0(12)°] and C(6) [123.3(13)°] are the largest ones. C—C and C—N bond lengths are normal, whereas the C—N bond is quite elongated.

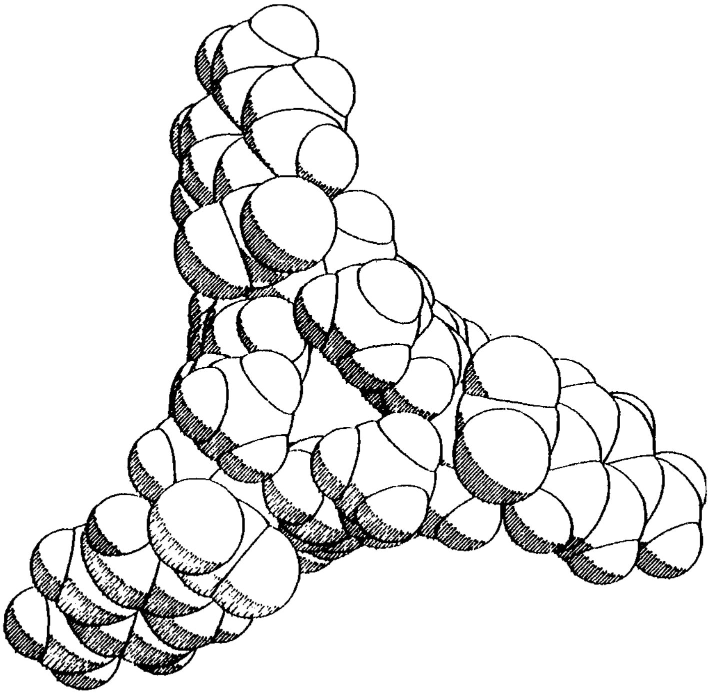


Fig. 3. Space-filling representation of the host molecule.

The molecular packing is consistent with van der Waals interactions, and leaves in the crystal lattice intermolecular voids of suitable size to clathrate the molecule of dichloromethane, as shown in Figure 2. There are no interatomic distances smaller than the van der Waals sum of covalent radii.

The trigonal symmetry of host **2** generates chiral cavities in which guests can be accommodated; thus, in principle, our host can be used to resolve optical antipodes of suitable guests. CPK models of host **2** show that the diameter of the internal cavity is too small for guest accommodation (Figure 3), while it is well known that a cavity of appropriate size for intramolecular inclusion is reached with the larger tetraaza[3.3.3.3]paracyclophanes [7–10].

Acknowledgment

The authors wish to thank Prof. G. D. Andreetti for providing a program for crystal structure determination, and Mr. R. Luboradzki for technical assistance and computational work. Thanks are also due to the Italian Ministry of Education for partial support (MPI funds) of this work.

References

1. F. Bottino, M. Di Grazia, P. Finocchiaro, F. R. Fronczek, A. Mamo, and S. Pappalardo, *J. Org. Chem.* **53**, 3521 (1988).

2. D. D. MacNicol: *Structure and Design of Inclusion Compounds: the Hexa-host and Symmetry Considerations* (Inclusion Compounds Vol. 2, Eds. J. L. Atwood, J. E. D. Davies, D. D. MacNicol), pp. 123–168. Academic Press (1984).
3. P. Main, S. J. Fiske, S. E. Hull, L. Lessinger, G. Germain, J.-P. Declercq, and M. M. Woolfson. *MULTAN* 11/82. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data. University of York, York, England (1982).
4. B. A. Frenz, SDP. *Structure Determination Package.* College Station, Texas, and Enraf-Nonius, Delft Associates Inc. (1985).
5. G. M. Sheldrick, *SHELX76.* Program for Crystal Structure Determination. University of Cambridge, Cambridge, England (1976).
6. *International Tables for X-Ray Crystallography.* Vol. IV. Birmingham: Kynoch Press (1974). Distributed by Kluwer Academic Publishers, Dordrecht.
7. Y. Urushigawa, T. Inazu, and T. Yoshino, *Bull. Chem. Soc. Jpn.* **44**, 2546 (1971).
8. I. Tabushi, H. Sasaki, and Y. Kuroda, *J. Am. Chem. Soc.* **98**, 5727 (1976).
9. I. Tabushi, Y. Kuroda, and Y. Kimura, *Tetrahedron Lett.*, 3327 (1976).
10. S. J. Abbott, A. G. M. Barrett, C. R. A. Godfrey, S. B. Kalindjian, G. W. Simpson, and D. J. Williams, *J. Chem. Soc., Chem. Commun.*, 796 (1982).