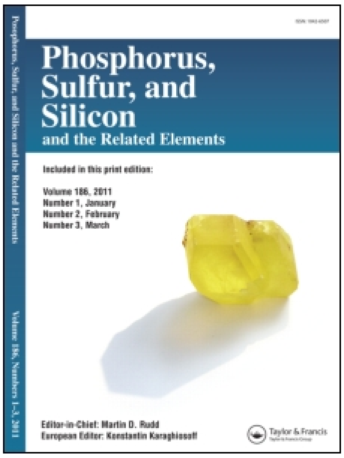

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THE X-RAY CRYSTAL STRUCTURE AND PACKING MODE OF (±)-2-THIONO-2-MERCAPTO-A,A'-DINAPHTHO-(d,f)(1,3,2)-DIOXOPHOSPHEPIN—A CLATHRATE STRUCTURE

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THE X-RAY CRYSTAL STRUCTURE AND PACKING MODE OF (±)-2-THIONO-2-MERCAPTO-a,a'-DINAPHTHO-(d,f)(1,3,2)-DIOXOPHOSPHEPIN— A CLATHRATE STRUCTURE

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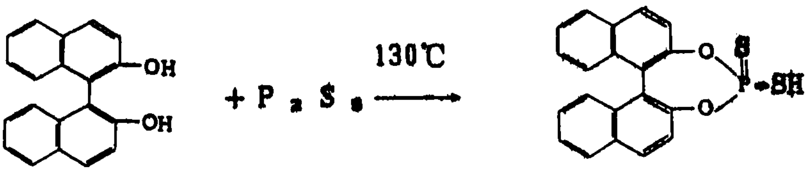
(±)-2-Thiono-2-mercapto-α,α'-dinaphtho-(d,f)(1,3,2)-dioxophosphepin and a number of related compounds which contain a cyclic phosphoric ring all manifested clathrating properties. An X-ray examination of the p-xylene clathrate revealed that the main mode of action in this new class of clathrates is exclusively derived from the topological interaction of the host molecules, the alternating chirality of the binaphthyl unit plays a decisive role in the cavity making.

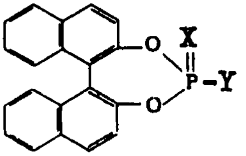
Key words: Dioxophosphepin; clathrate; x-ray crystallography; chirality; binaphthyl.

In the course of systematic studies of chiral properties of cyclophosphoric esters of a biaryl moiety,[1] we found that the reaction product of (±) 2,2'-dihydroxy-1,1'-binaphthyl with phosphorus pentasulfide, exhibited the ability to encapsulate solvent.

The host/guest mol ratios were 2:3, 1:1 or 2:1: the guest molecules were mainly simple aromatics. In order to gain some insight to the packing feature of the clathrate and the structural requirement of the host molecules, a number of com-

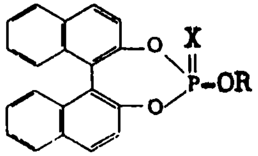


I



II

IIa: X=O, Y=Cl
IIb: X=S, Y=Cl
IIc: X=S, Y=Br



III

IIIa: X=O, R=CH_3
IIIb: X=S, R=CH_3
IIIc: X=S, R=C_2H_5

pounds related to compound **I** were prepared and their clathrating behavior was examined. It was found that racemic 1,1′-2,2′-binaphthyl cyclic phosphoric compounds (**II a – c** and **III a – c**) all manifested the same capability of inclusion.

RESULTS AND DISCUSSION

1. Molecular Structure

Based upon the X-ray crystal structure (Table V, VI, VII, VIII), the molecular structure of the host molecule and its p-xylene clathrate (compound **Ie**) are depicted as Figure 1 and Figure 2.

2. Stoichiometries and Thermal Stability of the Clathrate

The host compound **I** was obtained as an amorphous powder. Recrystallization from various solvents, afforded transparent, dense crystals. They were identified as a solvated species of compound **I** containing various solvent guest molecule in strict 2:3, 1:1 and 2:1 ratios (Table I). Each clathrates with the exception of **Ib** and **Ig**, are almost indefinitely stable upon storage in air or under vacuum drying. Their behavior on heating (crystals turn opaque with release of the solvent at 112 – 145°C, leaving the original compound I) indicated the formation of a clathrate.

When m-xylene, o-xylene or 1,3,5-trimethylbenzene were used as solvents, inclusion compounds also formed, but the host-guest mol ratio was not on integral ratio and unstable. The following compounds did not form inclusion compounds:

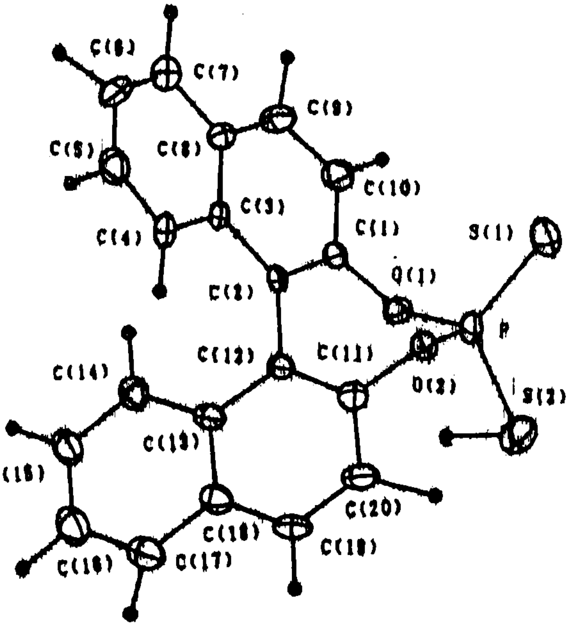


FIGURE 1 Perspective view of the acid in clathrate compound **Ie**.

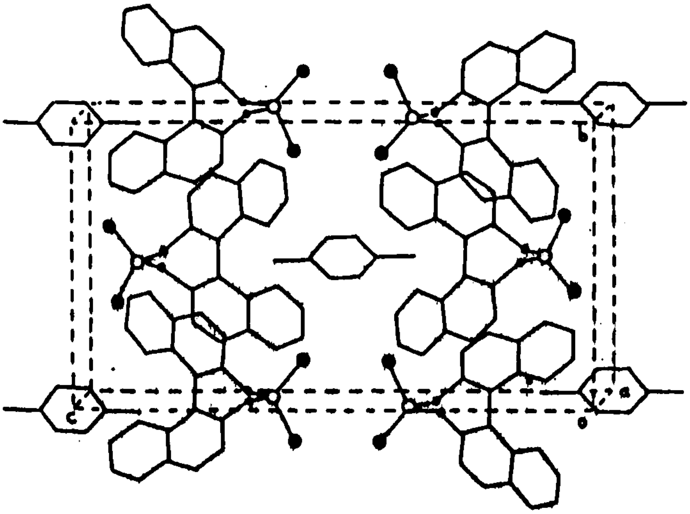


FIGURE 2 Diagram of the molecular packing in compound **Ie**. The origin of the unit cell lies at the lower right corner, with **a** pointing behind plane of papar, **b** pointing upward and **c** pointing left.

DMF, 2,5-dimethylhexadiene-2,4, toluene, ethylbenzene, bromobenzene and nitrobenzene. It was surprising to note that recrystallization from any solvent mixture, for instances, benzene/cyclohexane, benzene/p-xylene, benzene/naphthalene, p-xylene/o-xylene, did not give inclusion compounds, in spite of the fact that they may be well clathrated individually. The clathrating properties of compound **II** and **III** are listed in Table II.

3. *Packing Feature and Host-Guest Interactions*

A common structural feature of clathrates have been mainly represented by the hexa-host type compounds,[2] in which, the linking of the hydroxy-groups of six molecules by a network of —OH . . . O— hydrogen bonds as a hexagon plays a decisive role. It has also been established[3] that the thiol group in the form of —S—H . . . S— hydrogen bonding functions similarly and therefore retains the ability to form clathrates. We have performed a single crystal X-ray diffraction

TABLE I

Stoichiometries and thermal stability of clathrate (**Ia–Ih**)

Compound (**I**)	Guest	Host/Guest mol ratio	Dec. Temp. (°C)
a	benzene	1:1	130
b	chlorobenzene	1:1	25 (slowly)
c	methoxybenzene	2:1	135
d	benzylchloride	2:1	135
e	p-xylene	2:1	145
f	o-dichlorobenzene	2:1	130
g	flurobenzene	2:3	25 (slowly)
h	thiophene	1:1	112

TABLE II

The stoichiometries and thermal stability of clathrate **II** and **III**

Compound	Guest	Host/Guest mol ratio	Dec. Temp. (°C)
IIa	benzene	1:1	113
IIb	benzene	1:1	110
IIc	benzene	1:1	98
IIIa	benzene	1:1	99
IIIb	benzene	1:1	125
IIIc	benzene	2:1	122

analysis of compound **Ie**. In this clathrate, the atomic distance between two intramolecular sulfur is 3.39Å and the shortest distances between two intermolecular sulfur are 7.26Å and 7.50Å (Table VII) which are much longer than 3.86Å and 3.76Å, the observed —S . . . H—S distance in H_2S^4 and in 4-p-mercaptophenyl-2,2,4-trimethyl chroman,[3] respectively. The outstanding fact emerges from these data is the non-existence of hydrogen bonding in this clathrate, which was unexpected. The formation of **IIa, IIb, IIc, IIIa, IIIb** and **IIIc** preclude unequivocally the prerequisite of the hydrogen bonding in these clathrates. All experimental findings lead to the conclusion that the main mode of action in this lattice-type clathrate is exclusively derived from the topological interaction of the host molecules, the alternating chirality of the bulky binaphthyl rings forms cavity which takes up guest molecule. It appears in Figure 2 that the molecules are oriented so that the naphthalene groups C_1—C_{10} are stacked on the naphthalene groups C_{11}—C_{20} of adjacent 2_1 screw related molecules. These stacking interactions would form infinite chains of molecules alone b. The guests lie on inversion centers between chains. Two different inversion related pairs of naphthalene groups (parallel to each other) define the major boundaries of the cavities. Recently, several cases of binaphthyls bearing hydroxy or/and carboxyl groups which manifested clathrating properties have been reported.[5-8] According to Weber,[6] however, they are complex or coordinatoclathrate. To the best of our knowledge, this new family of "true" clathrates has not been reported in the literature.[9]

EXPERIMENTAL

Melting points were determined on a Yanaco apparatus. ^1H NMR data were recorded with a Joel FX-900 spectrometer, using TMS as an internal standard, ^{31}P NMR data were recorded using 85% H_3PO_4 as an external standard. Mass spectra were taken on a FINNIGAN MAT 4510 mass spectrometer. The values of specific rotation were measured on a polartronic D. Schmidt + Haensch polarimeter. All solvents used were carefully dried according to literature method.

A. Preparation of the host compound:

*1. Preparation of (±)-***I** *and R-(−)-***I**. A mixture of 2,2'-dihydroxy-1,1'-binaphthyl (28.6 g, 0.10 mol) and phosphorus pentasulfide (11.1 g, 0.050 mol) were refluxed in dry xylene (200 ml). After the P_2S_5 dissolved completely, the reaction mixture was refluxed an additional 0.5 hr and then allowed to stand for 48 hr at room temperature. The pale yellow colored crystals were collected and recrystallized from dry toluene. Colorless prisms were obtained. (32.3 g, 85% yield). mp 232–234°C; ^{31}P NMR ($CDCl_3$) 97.03 ppm; the ^{31}P NMR of its cinchoniene salt (two diastereoisomeric salts), 129.56 ppm and 129.89

ppm; ^{1}H NMR ($CDCl_3$) δ 3.18 (s, SH, 1H), 7.26 – 7.84 (m, Ar—H, 8H), 7.96 – 8.38 (m, Ar—H, 4H).
Anal. Calcd. for $C_{20}H_{13}O_2S_2P$: C, 63.14; H, 3.45.
Found: C, 63.29; H, 3.31. ms M$^+$ + 1 = 381.
R-(−)-**I** was prepared from R-(+)-2,2′-dihydroxy-1,1′-binaphthyl ([α]$^{20}_{D}$ = +35.2°, O.P. 100%) in the same manner. The crude product was recrystallized from dry CCl_4. A pale yellow amorphous powder was obtained in 70% yield. mp 234 – 237°C; ^{31}P NMR ($CDCl_3$) 97.03 ppm, ^{31}P NMR of its cinchoniene salt, 129.56 ppm; ^{1}H NMR ($CDCl_3$), δ 3.22 (s, SH, 1H), 7.30 – 7.90 (m, Ar—H, 8H), 7.98 – 8.32 (m, Ar—H, 4H): [α]$^{18}_{D}$ = −225.0° (C = 0.15, dioxane); ms M$^+$ + 1 = 381.

2. *Preparation of* **IIa, IIb** *and* **IIc.** Triethylamine (4.5g, 0.045 mol) was added to racemic 2,2′-dihydroxy-1,1′-binaphthyl (5.7g, 0.02 mol) and $PSCl_3$ (3.7 g, 0.022 mol) in dry CH_2Cl_2 (30 ml) with stirring and was kept at gentle reflux. The reaction mixture was stirred for 24 hr, then washed with water and dried ($MgSO_4$). After removal of the solvent, a pale yellow product (**IIb**) (7.40g, 96.7% yield) was obtained, mp 232 – 234°C; ^{31}P NMR ($CDCl_3$) 74.20 ppm; ^{1}H NMR ($CDCl_3$) δ 7.20 – 7.80 (m, Ar—H, 14H), 7.85 – 8.18 (m, Ar—H, 4H).
Anal. Calcd. for $C_{20}H_{12}O_2SPCl$: C, 62.75; H, 3.17.
Found: C, 63.05; H, 3.46.
Chiral **IIb** was prepared using R-(+)-2,2′-dihydroxy-1,1′-binaphthyl; yield 96%; mp 221 – 222°C; ^{31}P NMR ($CDCl_3$) 74.20 ppm; ^{1}H NMR ($CDCl_3$) δ 7.24 – 7.82 (m, Ar—H, 4H), 7.88 – 8.20 (m, Ar—H, 4H); [α]$^{20}_{D}$ = −536.2° (C = 0.14, dioxane). Compound **IIa** was prepared similar using $POCl_3$ instead of $PSCl_3$; yield 95%; mp 183 – 185°C; ^{31}P NMR ($CDCl_3$) 10.60 ppm; ^{1}H NMR ($CDCl_3$) δ 7.24 – 7.78 (m, Ar—H, 8H), 7.84 – 8.12 (m, Ar—H, 4H).
Anal. Calcd. for $C_{20}H_{12}O_3PCl$: C, 65.50; H, 3.31.
Found: C, 65.77; H, 3.48.
IIc was prepared according to the following procedure: compound **I** (1.9 g, 0.005 mol) in $CHCl_3$ (25 ml) was added to $CHCl_3$ (20 ml) containing Br_2 (0.80g, 0.005 mol), which was cooled in an ice bath with stirring over 0.5 hour and then stirred for an additional 1 hr. After removal of solvent, the crude product was chromatographed using CH_2Cl_2 as an eluent to give 1.0 g of white crystals, 47% yield; mp 256–258°C; ^{31}P NMR ($CDCl_3$) 57.88 ppm; ^{1}H NMR ($CDCl_3$) δ 7.20–7.70 (m, Ar—H, 8H), 7.84–8.16 (m, Ar—H, 4H).
Anal. Calcd. for $C_{20}H_{12}O_2SPBr$: C, 56.22; H, 2.84.
Found: C, 56.39; H, 3.19.

3. *Preparation of* **IIIa, IIIb** *and* **IIIc.** **IIIa** (1.10 g, 0.003 mol) was added to dry CH_2Cl_2 (20 ml) containing methanol (0.11 g, 0.0035 mol) and Et_3N (0.34 g, 0.0034 mol) with stirring and was allowed to stand for 12 hr, then washed with water and dried over anhydrous $MgSO_4$. The crude product was

TABLE III
Elemental analysis data of clathrates **I, II, III**

Compounds	Formula	C%		H%	
		Calcd	Found	Calcd	Found
Ia	$C_{20}H_{13}O_2S_2P\ C_6H_6$	68.10	67.80	4.19	3.94
Ib	$C_{20}H_{13}O_2S_2P\ C_6H_5Cl$	63.34	63.08	3.69	3.36
Ic	$2C_{20}H_{13}O_2S_2P\ C_7H_8O$	64.96	64.75	3.95	3.72
Id	$2C_{20}H_{13}O_2S_2P\ C_7H_7Cl$	63.61	63.71	3.76	3.65
Ie	$2C_{20}H_{13}O_2S_2P\ C_8H_{10}$(p)	66.49	66.26	4.19	4.37
If	$2C_{20}H_{13}O_2S_2P\ C_6H_4Cl_2$(o)	60.85	61.02	3.34	3.22
Ig	$2C_{20}H_{13}O_2S_2P\ 3C_6H_5F$	66.39	65.94	3.95	3.94
Ih	$C_{20}H_{13}O_2S_2P\ C_4H_4S$	62.05	61.84	3.70	3.99
IIa	$C_{20}H_{12}O_3PCl\ C_6H_6$	70.19	70.29	4.09	4.29
IIb	$C_{20}H_{12}O_2SPCl\ C_6H_6$	67.75	67.88	3.94	4.24
IIc	$C_{20}H_{12}O_2SPBr\ C_6H_6$	61.79	61.91	3.60	3.83
IIIa	$C_{21}H_{15}O_4P\ C_6H_6$	73.62	73.51	4.82	4.98
IIIb	$C_{21}H_{15}O_3SP\ C_6H_6$	71.03	71.16	4.65	4.74
IIIc	$2C_{22}H_{17}O_3SP\ C_6H_6$	69.59	69.35	4.68	4.82

(±) 1,1′-2,2′-binaphthyl dithiophosphoric esters (methyl, ethyl, n-propyl, isopropyl, and benzyl) show no clathrating ability. Chiral **I** and chiral **IIb** afford benzene clathrates which was not on integral ratio and with extremely poor stability.

TABLE IV

Crystallographic data for compound **Ie**

formula: $C_{20}H_{13}O_2S_2P \cdot 1/2C_8H_{10}$
crystal system: monoclinic
space group: $P2_{1/u}$
a = 8:907(4)Å
b = 11.684(2)Å
c = 20.910(4)Å
d_{calc} = 1.21 g/cm^3
temperature = 20°C
cryst color = colorless
diffractometer = Nicolet R3
monochromator = graphite
scan speed = 4–29°C/min
octants colled = h,k,±1
observed data = 1839(F_0) > 5σ(F_0))
params refined = 261
R = 0.0955
Rw = 0.0955

V = 2131(1)Å^3
β = 101.61(2)°
Z = 4
μ (MoK α) = 2.92
cryst size = 0.3 × 0.4 × 0.5 (mm)
Dihedral angle (between two naphthyl planes) = 60.1°
radiation = Mo(K α)
scan method = θ/2θ
data limits = 0° > 2θ > 45°

reflens colled = 2926
weighting scheme = 1
data/param ratio = 7.05

TABLE V

Atomic coordinates (× 10^4) and thermal parameters (× 10^3)

Atom	X	Y	Z	U_{eq}
P	4553(3)	194(2)	6284(1)	40(1)
S(1)	4791(3)	1430(2)	5726(1)	63(2)
S(2)	3550(4)	−1287(3)	5857(1)	75(2)
O(1)	3270(6)	434(4)	6750(2)	39(3)
O(2)	6009(6)	−48(6)	6786(2)	41(3)
C(1)	3728(8)	1204(6)	7262(3)	30(4)
C(2)	4796(9)	882(6)	7799(3)	30(4)
C(3)	5309(8)	1762(3)	8284(3)	31(4)
C(4)	6579(10)	1554(8)	8815(3)	40(4)
C(5)	7087(11)	2463(8)	9237(4)	54(5)
C(6)	6464(11)	3503(7)	9163(4)	53(5)
C(7)	5294(12)	3750(8)	8674(4)	58(6)
C(8)	4690(10)	2874(7)	8202(4)	42(4)
C(9)	3513(10)	3108(7)	7661(4)	50(5)
C(10)	3056(10)	2315(8)	7173(4)	48(5)
C(11)	5987(10)	−742(7)	7340(4)	46(5)
C(12)	5445(8)	−329(6)	7839(3)	34(4)
C(13)	5331(9)	−1019(7)	8394(4)	40(5)
C(14)	4649(10)	−684(8)	8912(4)	46(5)
C(15)	4596(11)	−1422(8)	9424(4)	55(5)
C(16)	5252(12)	−2489(9)	9448(5)	64(6)
C(17)	5932(12)	−2869(8)	8955(5)	60(6)
C(18)	5958(10)	−2145(7)	8405(4)	43(5)
C(19)	6591(10)	−2523(7)	7872(5)	46(5)
C(20)	6623(11)	−1850(7)	7347(5)	51(5)
C(21)	971(14)	732(11)	10369(8)	79(8)
C(22)	1061(17)	613(11)	9770(9)	91(9)
C(23)	113(18)	−80(13)	9359(7)	97(9)
C(24)	214(24)	−24(27)	8609(9)	184(19)

TABLE VI

Atom-atom bond length (Å)

P—S(1)	1.918(4)	C(8)—C(9)	1.406(11)
P—S(2)	2.039(4)	C(9)—C(10)	1.378(12)
P—O(1)	1.598(6)	C(11)—C(12)	1.325(12)
P—O(2)	1.586(5)	C(11)—C(20)	1.413(12)
O(1)—C(1)	1.394(8)	C(12)—C(13)	1.434(11)
O(2)—C(11)	1.417(10)	C(13)—C(14)	1.406(13)
C(1)—C(2)	1.370(9)	C(13)—C(18)	1.427(11)
C(1)—C(10)	1.426(11)	C(14)—C(15)	1.381(12)
C(2)—C(3)	1.452(10)	C(15)—C(16)	1.374(14)
C(2)—C(12)	1.526(10)	C(16)—C(17)	1.371(16)
C(3)—C(4)	1.437(9)	C(17)—C(18)	1.431(13)
C(3)—C(8)	1.408(11)	C(18)—C(19)	1.417(14)
C(4)—C(5)	1.397(12)	C(19)—C(20)	1.356(13)
C(5)—C(6)	1.332(13)	C(21)—C(22)	1.278(25)
C(6)—C(7)	1.336(12)	C(22)—C(23)	1.348(20)
C(7)—C(8)	1.449(12)	C(23)—C(24)	1.589(26)

TABLE VII

Atom-atom bond length between sulfur (Å)

S1—S2	3.39	S1A—S2C	8.69
S1—S1A	8.91	S2A—S1B	12.00
S1—S2A	12.16	S2A—S1C	12.24
S1—S1C	12.42	S2A—S2C	9.49
S1—S2C	12.68	S1B—S2B	3.39
S2—S1A	12.16	S1B—S1C	9.10
S1A—S2A	3.39	S1B—S2C	7.50
S1A—S1B	10.80	S2B—S1C	7.50
S1A—S2B	12.00	S2B—S2C	7.26
S1A—S1C	10.86	S1C—S2C	3.39

chromatographed (CCl_4), giving a colorless solid **IIIa** 0.63 g; yield 58%; mp 211-213°C; ^{31}P NMR ($CDCl_3$) 3.74 ppm; ^{1}H NMR ($CDCl_3$) δ 3.96 (*d*, CH_3, 3H; *J* = 11 Hz), 7.20-7.64 (m, Ar—H, 8H), 7.84-8.12 (m, Ar—H, 4H).

IIIb and **IIIc** were prepared similarly and the work-up was the same as above.

IIIb: yield 57%; mp 210-212°C; ^{31}P NMR ($CDCl_3$) 76.29 ppm; ^{1}H NMR ($CDCl_3$) δ 3.96 (*d*, CH_3, 3H; *J* = 10Hz), 7.18-7.70 (m, Ar—H, 8H), 7.84-8.04 (m, Ar—H, 4H).

IIIc: yield 62%; mp 152-154°C; ^{31}P NMR ($CDCl_3$) 74.65 ppm; ^{1}H NMR ($CDCl_3$) δ 1.40 (*t*, CH_3, 3H; *J* = 6 Hz), 4.24-4.64 (m, CH_2, 2H), 7.20-7.68 (m, Ar—H, 8H), 7.80-8.12 (m, Ar—H, 4H).

B. Preparation of the Clathrates.

The host compound (**I**) (0.76 g, 0.002 mol) was dissolved at reflux temperature in dry p-xylene (15 ml) and the solution was cooled slowly in a hot water bath. After 24 hr at 25°C, the crystals were collected and dried. Transparent crystals (0.73 g, 75% yield) were obtained (compound **Ie**); mp 145°C (dec.); ^{1}H NMR ($CDCl_3$) δ 2.36 (s, CH_3, 6H), 3.00 (s, SH, 2H), 7.17 (S, Ar—H, 4H), 7.30-7.90 (m, Ar—H, 16H), 7.98-8.30 (m, Ar—H, 8H). All clathrates were prepared by the same procedure. Elemental analysis data are listed in Table III.

C. Crystallography

A crystal of the compound **Ie** suitable for crystallographic study was obtained as described in section B of the Experimental Section. Diffraction data were collected on a Nicolet R3 four-circle diffractometer

TABLE VIII

Atom-atom-atom bond angle (deg.)

S(1)—P—S(2)	118.0(1)	C(7)—C(8)—C(9)	121.7(8)
S(1)—P—O(1)	116.3(2)	C(8)—C(9)—C(10)	121.7(8)
S(1)—P—O(2)	108.3(2)	C(1)—C(10)—C(9)	117.5(7)
S(2)—P—O(1)	99.6(2)	O(2)—C(11)—C(12)	120.2(7)
S(2)—P—O(2)	110.7(2)	O(2)—C(11)—C(20)	117.4(8)
O(1)—P—O(2)	102.9(3)	C(12)—C(11)—C(20)	122.3(8)
P—O(1)—C(1)	117.0(5)	C(2)—C(12)—C(11)	119.2(7)
P—O(2)—C(11)	119.2(5)	C(2)—C(12)—C(13)	118.6(7)
O(1)—C(1)—C(2)	120.0(6)	C(11)—C(12)—C(13)	122.0(7)
O(1)—C(1)—C(10)	115.9(6)	C(12)—C(13)—C(14)	125.5(7)
C(2)—C(1)—C(10)	124.1(7)	C(12)—C(13)—C(18)	116.1(8)
C(1)—C(2)—C(3)	116.6(6)	C(14)—C(13)—C(18)	118.4(8)
C(1)—C(2)—C(12)	119.5(5)	C(13)—C(14)—C(15)	120.5(8)
C(3)—C(2)—C(12)	123.8(6)	C(14)—C(15)—C(16)	121.1(9)
C(2)—C(3)—C(4)	120.5(7)	C(15)—C(16)—C(17)	121.0(9)
C(2)—C(3)—C(8)	120.5(7)	C(16)—C(17)—C(18)	119.6(9)
C(4)—C(3)—C(8)	118.6(7)	C(13)—C(18)—C(17)	119.2(8)
C(3)—C(4)—C(5)	117.6(8)	C(13)—C(18)—C(19)	119.4(8)
C(4)—C(5)—C(6)	123.1(8)	C(17)—C(18)—C(19)	121.3(8)
C(5)—C(6)—C(7)	121.9(8)	C(18)—C(19)—C(20)	122.2(8)
C(6)—C(7)—C(8)	119.6(9)	C(11)—C(20)—C(19)	117.8(9)
C(3)—C(8)—C(7)	119.1(7)	C(21)—C(22)—C(23)	122.3(15)
C(3)—C(8)—C(9)	119.2(7)	C(22)—C(23)—C(24)	116.8(17)

at room temperature using MoK α radiation and a graphite crystal monochromator by $\theta/2\theta$ scan technique using variable speed scanning rates. Crystal data and experimental details are listed in Table IV. The intensity data were corrected for Lorentz and polarization factors.

The structure was solved by direct and difference Fourier method. Twelve hydrogen atoms were located in a difference Fourier map. Other hydrogen atoms were located theoretically. All calculations were carried out with the MULTAN 84 program. Data are listed in Table IV.

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