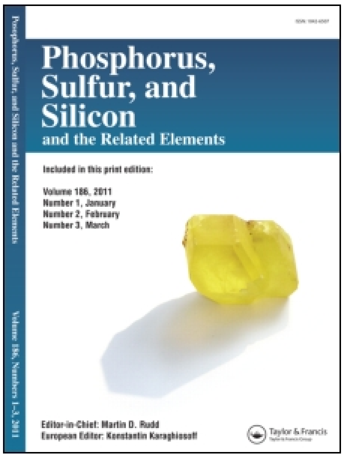

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THE ENANTIOMERISM OF 2-THIONO-2-MERCAPTO-DIBENZO-(d,f)(1,3,2)-DIOXOPHOSPHEPIN

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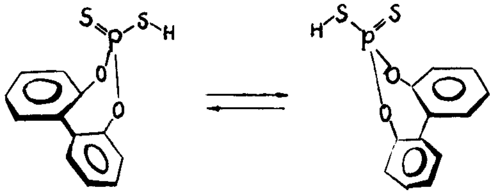
The bridged biphenyl system in the molecule of 2-thiono-2-mercapto-dibenzo-(d,f)(1,3,2)-dioxophosphepin is twisted and dissymmetric. The two enantiomers were resolved by cinchonidine and cinchonine, having $[\alpha]_D^{22} = (+)9.37°$ and $(-)8.94°$ respectively. They are optically stable at 20°C in benzene, but racemized readily in methanol. The U.V. spectra give a torsional angle of the racemic acid as 24.6°.

Key Words: Dioxophosphepin; bridged-biphenyl systems; Enantiomerism; isomeric interconversions; resolution.

Although there have been intensive studies on the subject of stereochemistry of bridged biphenyl systems,[1,2,3,4,5] 2-thiono-2-mercapto-(d,f)(1,3,2)-dioxophosphepin, an O—P—O three atom bridged biphenyl, was prepared only recently.[6] The bridged biphenyl system in the molecule is twisted and dissymmetric. This is unequivocally demonstrated by the resolution of two optical isomers whose interconversion can also be observed.



The two enantiomers were resolved by cinchonidine and cinchoniene. The acids liberated from their salts have $[\alpha]_D^{22} = (+)9.37°$ and $(-)8.94°$ respectively. They are optically active in benzene, ($t_{1/2}^{20}$ is more than 200 h), but racemized readily in methanol ($t_{1/2}^{23}$ is ca. 60 min). When the (±) acid cinchonidine salt is refluxed in benzene for 2 h, the (+) acid-cinchonidine salt was obtained almost quantitatively. The asymmetric transformation obtained by the resolving agent provides further evidence of the existence of the above equilibrium. The proton transfer in this thino-thiol system accounts predominately for the interconversion of the enantiomers. This is evidenced by the fact that they are racemized readily in methanol, but are optically stable in benzene. The rate of racemization in methanol is found to be dependent upon their concentration. This can be

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reasonably explained in that ionization of the acid is facilitated by a protic solvent and the degree of ionization is dependent upon its concentration.

The non-planarity of this biphenyl system is apparent both from its optical resolvability and from its U.V. absorption. It is known that the appearance of a high intensity band at ca. 2500 Å is dependent on conjugation between the diphenyl rings. Reduction of conjugation, as a result of retention of a strainless ring, can be observed from the reduced intensities and slight short-wave length shifts of the conjugation band at ca. 2500 Å.[1] Based on the equation $\cos^2\theta = \varepsilon/\varepsilon^\circ$,[2] spectra data of (±) 2-thiono-2-mercapto-dibenzo-(d,f)(1,3,2)-dioxophosphepin indicate that the interplanar angle is 24.6°.

EXPERIMENTAL

I. The preparation of 2-thiono-2-mercapto-dibenzo-(d,f)(1,3,2)-dioxophosphepin.[6] A mixture of 2,2′-dihydroxybiphenyl (37.0 g, 0.20 mol) and phosphorus pentasulfide (22.0 g, 0.10 mol) were heated with stirring in dried benzene (80 mL), and kept at 70–72°C for 2 h. After the solvent was removed, the product was further heated at 100–110°C for 1 h and filtered while hot. Dark colored crystals collected from the filtrate were recrystallized in cyclohexane with a little Norit: yield 46.0 g (82.5%). Colorless prisms were obtained; m.p. 106–107°C,

Analysis:	C%	H%	P%
Calcd. for $C_{12}H_9O_2PS_2$	51.42	3.24	11.66
Found	51.66	3.30	11.69

^{31}P-NMR: (solvent: DMSO + CCl_4; external 85% H_3PO_4) δ_{ppm} 99.8.

^{13}C-NMR: (solvent: DMSO-d_6) δ_{ppm} (J, Hz): (1, 1′) 149.67d (12.7), (2, 2′) 123.08d (3.9), (3, 3′) 129.54s, (4, 4′) 126.64s, (5, 5′) 129.75s, (6, 6′) 130.36s.

II. The resolution of 2-thiono-2-mercapto-dibenzo-(d,f)(1,3,2)-dioxophosphepin. (1) Resolution of the racemic mixture with cinchonidine To a (±) mixture (2.80 g, 0.01 mol) in benzene (50 mL), 2.90 g (0.01 mol) of cinchonidine were added in portions with shaking. Yellow crystals were collected, yield 3.80 g (66.7%); m.p. 158–164°C. Recrystallization from 70% ethanol afforded 1.5 g of colorless crystals; m.p. 165–167°C, $[\alpha]_D^{18} = (-)89.9°$ ($c = 0.3$, absolute alcohol), $[\alpha]_D^{10} = (-)85.8°$ ($c = 0.3$, methanol).

Analysis:	C%	H%	N%
Calcd. for $C_{31}H_{31}N_2O_3PS_2$	64.79	5.44	4.87
Found	64.70	5.51	4.44

The above cinchonidine salt was warmed with 10 mL of 18% HCl and 15 mL of benzene for 15 min. The benzene layer was separated and dried over anhydrous sodium sulfate. After evaporation under reduced pressure, 0.5 g (+) acid were obtained (yield 66.7%), m.p. 107°C, ^{31}P-NMR (external 85% H_3PO_4) $\delta_{ppm} = 99.8$.

$$[\alpha]_D^{10} = (+)9.40°(c = 0.6, \text{methanol})$$

$$[\alpha]_D^{22} = (+)9.37°(c = 0.26, \text{methanol})$$

To the above filtrate, a few crystals of the (+) acid-cinchonidine salt were added and kept at room temperature for 24 h. A second crop of crystals was collected, 0.3 g. After removal of the solvent from the filtrate, 1.8 g of white powder were obtained: m.p. 188–189°C (dec.) $[\alpha]_D^{23} = (+)110.2°$ ($c = 0.28$, absolute alcohol). The salt was acidified in warm 18% HCl (10 mL) and benzene (15 mL) was added. After being thoroughly shaken, the benzene layer was separated and evaporated under reduced pressure. Recrystallization from cyclohexane afforded colorless crystals: m.p. 107°C, $[\alpha]_D^{22} = (-)8.4°$ ($c = 0.27$, methanol).

(2) Resolution of the racemic acid with cinchonine. The racemic acid 2.80 g (0.01 mol) was dissolved in 50 mL of benzene with shaking. Cinchonine 2.90 g (0.01 mol) was added in portions. Light yellow

TABLE I

Resolution of 2-thiono-2-mercapto-dibenzo-(d,f)(1,3,2)-dioxophosphepin

Resolving agent	Solvent	Salt of Cinchonidine or Cinchonine				(+) Acid or (−) Acid		
		salt	$[\alpha]_D^{22}$	m.p.°C	yield	$[\alpha]_D^{22}$	m.p.°C	yield
Cinchonidine II	70%	(+) A.II	−89.9	165-7	66.7	+9.37	107	66.7
	ethanol	(−) A.II	+110.2	189-90	/	−8.4	107	
Cinchonine III	70%	(−) A.III	−112.0	168-9	75.3	−8.94	108	53.3
	ethanol	(+) A.III	+91.8	185 (dec)	/	+8.5	108	

crystals (4.3 g) were obtained (yield 75.3%). After washing with chloroform and recrystallization of the crude salt from 70% ethanol, colorless crystals were obtained 1.6 g (yield 74.4%); m.p. 168–169°C, $[\alpha]_D^{22} = (-)112.0°$ ($c = 0.17$, methanol).

Analysis:	C%	H%	N%
Calcd. for $C_{31}H_{31}N_2O_3PS_2$	64.79	5.44	4.87
Found	64.54	5.63	4.59

The above salt (1.5 g) was acidified with 10 mL of 18% HCl in 15 mL of warm benzene with continuous shaking. The benzene layer was separated, washed with water, and dried over anhydrous sodium sulfate. After removal of the solvent, the residue was recrystallized from cyclohexane and

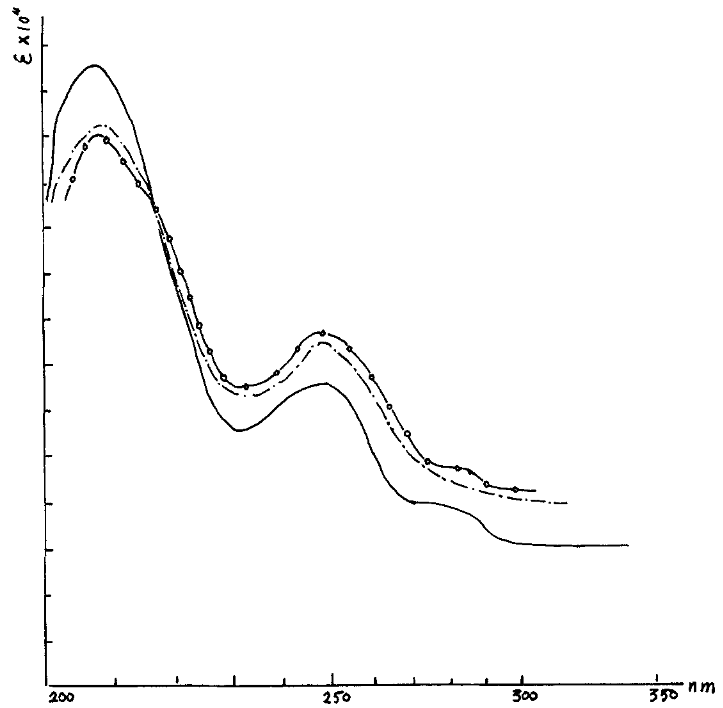


FIGURE 1 The U.V. spectra of racemic acid, biphenyl and 2:7-dihydro-3:4,5:6-dibenzoxepin. Solvent: 95% ethanol, $c = 3.5 \times 10^{-5}$ mol

—○— biphenyl

—·— 2:7-dihydro-3:4,5:6-dibenzoxepin

—— 2-thiono-2-mercapto-dibenzo-(d,f)(1,3,2)-dioxophosphepin

0.4 g (yield 53.3%) of (−) acid was obtained: m.p. 108°C, ^{31}P-NMR (external 85% H_3PO_4) $\delta_{ppm} = 99.8$.

$$[\alpha]_D^{20} = (-)8.72°(c = 0.40, \text{methanol})$$

$$[\alpha]_D^{22} = (-)8.94°(c = 0.48, \text{methanol})$$

After the above filtrate was concentrated to half its volume, a few crystals of (−) acid-cinchonine salt were added. Colorless crystals (2.1 g) were collected after 72 h. After evaporation to dryness, the filtrate afforded 0.8 g of white powder; m.p. 185°C (dec.).

$$[\alpha]_D^{19} = (+)91.80°(c = 0.28, \text{methanol})$$

When the above salt was acidified and extracted with benzene, the benzene layer gave 0.4 g of colorless micro-crystals: m.p. 108°C, $[\alpha]_D^{18} = (+)8.5°(c = 0.2, \text{methanol})$.

The resolution is summarized in Table I.

(*3*) *Racemization.* The (+) or (−) acid in methanol lost half of its optical activity at 23°C in 60 min in a 0.72% solution, in 87 min in a 1.16% solution, and in 103 min in a 2.14% solution. In benzene at 20°C, only 5.9% of its optical activity was reduced after 20 h.

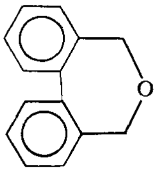
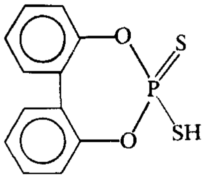
When equal moles of (±) acid and cinchonidine were refluxed in benzene for 2 h, a nearly quantitative yield of crude (+) acid-cinchonidine salt resulted; m.p. 156–162°C. Recrystallization of the crude salt with 70% aqueous alcohol afforded 85.7% pure (+) acid cinchonidine salt; m.p. 166°C, $[\alpha]_D^{22} = (-)88.2°$ ($c = 0.24$, methanol).

II. Ultraviolet spectra of the (±) *acid.* As expected, the U.V. spectrum of 2-thiono-2-mercapto-dibenzo-(d,f)(1,3,2)-dioxophosphepin has a typical biphenyl absorption at 249 nm, showing a similar shape to that of biphenyl and 2:7-dihydro-3:4,5:6-dibenzoxepin[1] (Figure 1).

Their torsional angles were calculated as shown in Table II.

TABLE II

U.V. Spectra and Torsional Angles

Compound	λ_{max} (nm)	ε_{max}	$\varepsilon/\varepsilon°$	θ
Biphenyl	249	18 000	0.947	13.3°$^{(1)}$
	250	16 500	0.868	21.3°$^{(1)}$
(±) 	248.8	15 700	0.826	24.6°

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