DIPHOSPHINE DERIVATIVES

Part VIII*. Tetraphenyldiphosphine dioxide and tetraphenyldiphosphine disulphide: structure and skeletal vibrations. Preparation of diphenylphosphinodiselenoic anhydroselenide, $Ph_2P(Se)SeP(Se)Ph_2$

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ABSTRACT

The X-ray powder diffraction pattern for tetraphenyldiphosphine dioxide $Ph_2P(O)P$ -(O)Ph₂ can be satisfactorily indexed on the assumption that the compound is isomorphous with tetraphenyldiphosphine disulphide. Calculated crystal data for the dioxide are: monoclinic, $P2_1/c$, a = 9.44(1), b = 15.62(3), c = 13 37(3) A, $\beta = 98.0(1)^\circ Z = 4$. The P-P stretch is assigned in the Raman spectrum of the disulphide at 536 cm⁻¹ and in the dioxide at the unusually high frequency of 601 cm⁻¹. The reaction of tetraphenyldiphosphine with KSeCN in acetonitrile leads to oxidation of the phosphorus and selenium insertion into the P-P bond, yielding $Ph_2P(Se)SeP(Se)Ph_2$, diphenylphosphinodiselenoic anhydroselenide, previously only identified in solution.

INTRODUCTION

In the crystal, tetraphenyldiphosphine disulphide, $Ph_2P(S)P(S)Ph_2$, has a centrosymmetric *trans* molecular structure [1], as originally predicted by Cowley and White [2] from their analysis of the IR spectrum. The molecular point group is C_i and the only IR-active skeletal S-P-P-S stretching vibration is $\nu_{as}PS(A_u)$. No Raman data are available and $\nu_sPS(A_g)$ and $\nu PP(A_g)$ have not been identified. Information on the P-P mode is particularly desirable because the X-ray data [1] show that the P-P bond in Ph_2P(S)P(S)Ph_2 (2.263 Å) is significantly longer than those in related tetraalkyl compounds (approx. 2.21 Å).

Tetraorganodiphosphine disulphides are relatively easily prepared and have been quite extensively studied, but the corresponding oxides are less stable

^{*}For part VII, see ref. 1. The title compounds are more correctly, but less conveniently, called tetraphenyl-1,2-dioxo(dithioxo)-di- λ^{5} -phosphane.

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and less thoroughly characterised. Until very recently [3, 4] the diselenides were unknown. In this paper we discuss structural and vibrational data for tetraphenyldiphosphine dioxide and tetraphenyldiphosphine disulphide, and report an attempt to prepare the corresponding diselenide.

EXPERIMENTAL

Tetraphenyldiphosphine dioxide

The dioxide was prepared from the reaction of dry oxygen with tetraphenyldiphosphine in dry toluene at 40°C [5, 6]. Found (Calc.): C, 71.6 (71.6)%; H, 4.9 (5.0)%; P, 14.8 (15.4)%. The product was stored under dry nitrogen: it is stable in dry oxygen or oxygen-free water but decomposes rapidly, yielding diphenylphosphinic acid, on exposure to moist air or moist solvents. Traces of diphenylphosphinic acid can be removed by washing with deoxygenated 5% aqueous KOH [5].

Tetraphenyldiphosphine disulphide

This compound is readily prepared from the reaction of tetraphenyldiphosphine with sulphur in refluxing toluene [5, 6].

Selenation of tetraphenyldiphosphine

The reaction of tetraphenyldiphosphine with elemental selenium in toluene under reflux is reported to yield the triselenium compound $Ph_2P(Se)SeP(Se)Ph_2$ [4]. This product was identified from its ⁷⁷Se and ³¹P NMR spectrum, but was not isolated. An alternative selenation technique for arylphosphines, using KSeCN in acetonitrile, has been described by Nicpon and Meek [7]: this reaction takes place at room temperature and seemed to be more likely to lead to the simple diselenide $Ph_2P(Se)P(Se)Ph_2$. A suspension of tetraphenyldiphosphine (1.5 g, 0.004 mol) and dry, finely ground potassium selenocyanate (1.15 g, 0.008 mol) in dry acetonitrile (30 ml) was stirred vigorously for 24 h, and then at intervals for several weeks. The reaction mixture was protected from air, moisture and light at all times. Insoluble material was removed by centrifugation and the acetonitrile solution evaporated to dryness. The resulting solid was extracted with chloroform, and the chloroform-soluble material recrystallised from a 1:1 chloroform: petroleum ether $(40-60^{\circ})$ mixture, yielding a white hygroscopic product which rapidly developed an offensive odour and liberated red selenium on exposure to the atmosphere. The compound also tended to decompose in strong light, but could be stored without difficulty at room temperature in subdued light under a dry nitrogen atmosphere. The analytical data [Found (Calc. for $C_{24}H_{20}P_2Se_3$: C, 48.0 (47.4)%; H, 3.4 (3.3)%; P, 9.8 (10.2)%; Se, 38.0 (39.0)%] identify this product as the same triselenium compound $P_2Ph_4Se_3$ as that

obtained by McFarlane et al. [3] from the direct reaction. Reactions carried out over shorter periods occasionally yielded products with Se:P ratios less than 3:2, but the results were not reproducible and no intermediate monoselenide or diselenide could be isolated.

Physical measurements

Vibrational spectra were obtained using Perkin-Elmer 457 (IR) and Cary 83 (Raman, 488.0 nm argon-ion laser excitation) spectrophotometers, and mass spectra with an AEI MS30 mass spectrometer. X-ray powder diffraction data were recorded photographically using a standard Hagg-Guinier camera (CuK_{α} radiation, $\lambda = 1.1416$ Å) and the films measured on a prototype microdensitometer developed by the late Mr. B. G. Cooksley of this Department.

RESULTS AND DISCUSSION

Crystal structure of tetraphenyldiphosphine dioxide

The microcrystalline product obtained from the preparation of tetraphenyldiphosphine dioxide is very susceptible to hydrolysis and invariably becomes contaminated with traces of diphenylphosphinic acid during X-ray powder diffraction measurements. Accurate structural data are available for diphenylphosphinic acid [8] and lines arising from this compound are readily identified. The powder pattern was analysed using fifteen lines clearly distinct from those of any possible hydrolysis product: preliminary investigation using the routines of Visser [9] and Taupin [10] indicated the crystal system to be most probably monoclinic with unit-cell dimensions very similar to those in tetraphenyldiphosphine disulphide. The data were successfully indexed by assuming the space group to be the same as that in the disulphide $(P2_1/c)$; unit cell dimensions were obtained by least-squares refinement of the powder diffraction data, using the cell dimensions of the disulphide as starting parameters [11]. All lines in the experimental powder patterns were satisfactorily accounted for: details of the observed and calculated *d*-spacings, and final unit-cell dimensions, are given in Table 1.

These results strongly suggest that tetraphenyldiphosphine dioxide is isomorphous with the disulphide, and has a similar centrosymmetric *trans* structure. Given that the principal directing influence in these molecules must be the O—O or S—S repulsion, it would be surprising if this were not the case.

Skeletal vibrations

Vibrational frequency data for the relevant parts of the IR and Raman spectra of tetraphenyldiphosphine dioxide and tetraphenyldiphosphine

TABLE 1

hki	d _{obs} (Å)	d _{calc} (A)	I/I _o a	
110	8.00	8.02	60	
020	7.79	7.81	21	
Ī11	7.35	7.32	45	
002	6.90	6.87	46	
111	6.58	6.59	10	
012	6.33	6.29	10	
121	5.66	5.68	12	
1 21	5.31	5.32	16	
102	5.20	5.20	45	
122	4.717	4.729	3	
131	4.242	4.233	16	
032} 202}	4.151	4.149) 4.141)	43	
211	4.099	4.100	31	
212	3.994	4.003	100	
222	3.659	3.659	12	
1 14	3.301	3.303	28	

Unit-cell and observed and calculated X-ray powder diffraction data for tetraphenyldiphosphine dioxide. Monoclinic, $P2_1/c$; a = 9.44(1) Å, b = 15.62(3) Å, c = 13.87(3) Å; $\beta = 98.0(1)^\circ$, Z = 4 (esd. in last significant figure)

^aScaled to 100 for most intense line.

disulphide are given in Table 2. There are no significant differences between the crystal and solution spectra. No new IR bands or Raman lines appear in the solution spectra: the *trans* conformation is fully retained in solution and there is no rotation about the P—P bond.

The skeletal S—P—P—S (O—P—P—O) and low-frequency phenyl "Xsensitive" vibrations are non-coincident in the IR and Raman spectra, as the molecular symmetry requires. Vibrations which are effectively internal modes of the phenyl groups are not significantly coupled within the molecule and hence have coincident, or almost coincident, IR and Raman frequencies. The assignments down to 750 cm⁻¹ (apart from ν PO) follow from those for numerous other molecules [12—15] and are not discussed further here. A complete assignment (to 250 cm⁻¹) for tetraphenyldiphosphine has been proposed by Hassler and Hofler [14]. Below 700 cm⁻¹ there are few obvious correlations between the dioxide and disulphide spectra.

P-P stretching vibrations in diphosphine derivatives usually occur between 400 and about 540 cm⁻¹ [2, 14, 16-23]. The P-P stretch in tetraphenyldiphosphine is found at 530 cm⁻¹ [14] and a corresponding strong Raman line, with no IR active counterpart (the P-P stretch belongs to the A_g symmetry species in the centrosymmetric molecule) appears at 536 cm⁻¹ in the spectrum of the disulphide. The addition of two sulphur atoms thus has little obvious effect on the vibrational behaviour of the P-P bond. In the

TABLE 2

Assignment ^a	Ph ₂ P(O)P(O)Ph ₂		Ph ₂ P(S)P(S)Ph ₂	
	IRb	Raman ^c	IRb	Raman ^c
δCH (a)		1192 w	1191 m	1193 vw
ν _s PO		1182 mw		
vasPO	1176 vvs			
δCH (c)	1161 m	11 62 w	1166 m	1162 vw
• •			1160 m	
X-sens. (a)	{1113 vs	1113 w	1097 vs	1094 ms
	1092 s	1096 m	1091 vw	
/ \	{ 721 vs			715 w
X-sens. (r)	Į	708 w	709 vs	
$\phi CC(v)$	692 vvs		689 vvs	693 w
$\nu_{\rm PS}$				649 m
v_PS			639 vvs	
$\alpha CCC(s)$	619 mw	618 m	614 vs	618 w
"PP		601 vs		538 vs
		585 vvw		
2	(553 m	000 111		
\cdot \mathbf{V}_{comp} (a)		597 w		
A-sens. (y)	513 10/5	021 4	492 vvs	493 w
	188 1015	173 2	474 m	472 w
Name (t)	(450 WS	470 W :	4595	
A-sens. (t)	405 m	400 W	4025	437 m
	407 ab	407 W		407 m
+ CC ()	407 SIL	410 w		208
$\varphi \cup \cup (w)$	3915	354 W	269 -	050 W
V (42)	3105	248	2045	348
Λ -sens. (ι ?)	l	040 W	_	040 W

Vibrational data for Ph,P(O)P(O)Ph, and Ph,P(S)P(S)Ph, (cm⁻¹)

^aNotation for phenyl-group modes as in ref. 11. ^bNujol mulls. ^cPowdered solids.

Raman spectrum of tetraphenyldiphosphine dioxide, there is no line between 400 and 600 cm⁻¹ which can plausibly or even implausibly be assigned to the P--P stretching mode. However, a very strong line, with no counterpart in the IR spectrum, appears at 601 cm⁻¹. The only other vibration to be expected in this region is a C-C-C bending mode ("s" in the Whiffen [12] notation): this is readily identified with a medium-intensity Raman line and corresponding weak IR absorption, at 618 cm⁻¹. Therefore despite its unusually high frequency, we assign the 601 cm⁻¹ Raman line to the P-P stretching mode, or perhaps more correctly to a vibration with predominant P-P stretching character.

The P-P stretching modes in tetraphenyldiphosphine and its derivatives are thus found near or above the upper limit of the frequency range previously observed for these vibrations. In general, P-P stretching vibrations in relatively simple diphosphine derivatives (e.g., P_2H_4 [16], $P_2Me_2H_2$ [17], P_2Me_4 [18] or $P_2Me_4S_2$ [2, 19, 20]) occur roughly in the range 420-450 cm⁻¹,

while in compounds with larger substituent groups (e.g. ethyl, [2, 20, 21] n-propyl, n-butyl [2, 21], and allyl [22] or dialkylamino [23]) the frequency moves to 490-540 cm⁻¹. In the second group, vibrations involving P-C-C or related deformations occur in the 400–550 cm⁻¹ region and may affect the frequency of the P-P mode. In the phenyl-substituted compounds, the X-sensitive "y" and "t" vibrations appear between 400–550 cm⁻¹: the "y" mode is believed to involve a P-C deformation and the "t" mode has substantial P-C stretching character [13-15, 24]. Thus, unlike the alkyl compounds (in which the P-C stretches are found near 700 cm⁻¹) the tetraphenyldiphosphine derivatives have vibrational modes which can be regarded, at least approximately, as P-C stretches near or below the P-P stretching frequency. Mixing of the P-P and P-C motions may therefore lead to an increase in the "P-P" frequency, and the assignment of the vibration at 536 cm^{-1} in tetraphenyldiphosphine disulphide to νPP is not necessarily incompatible with the rather long P-P bond found in this molecule. In the case of tetraphenyldiphosphine dioxide, the X-sensitive modes are likely to be further modified by P-O deformation components [24] and the replacement of $\nu_{\rm s}$ PS at 649 cm⁻¹ (in the disulphide) by $\nu_{\rm s}$ PO at 1182 cm⁻¹ (in the dioxide) will remove any constraint on the further upward movement of ν PP. It should hardly be necessary to add that the representation of the mode at 601 cm^{-1} in tetraphenyldiphosphine dioxide as a "P-P stretch" is at best a partial and highly approximate description of the molecular motion involved in this vibration. Further structural and spectroscopic data for diphosphine dioxides are clearly highly desirable, especially for the tetraalkyl compounds which at present appear to be unknown.

Diphenylphosphinodiselenoic anhydroselenide

Tetramethyldiphosphine diselenide, $P_2Me_4Se_2$, is a perfectly stable molecule, obtainable by standard synthetic methods [3], but our attempts to prepare the tetraphenyl analogue, like those of McFarlane and co-workers [4], have yielded only $P_2Ph_4Se_1$. The NMR spectrum [4] identifies this compound as the selenium bridged species $Ph_2P(Se)SeP(Se)Ph_2$, "diphenylphosphinodiselenoic anhydroselenide". Further, albeit indirect, evidence for this structure can be obtained from the mass spectrum: the molecular ion $P_2Ph_4Se_3^+$ (m/z = 607) cannot be detected, which is not surprising in view of the reactivity of the material and the temperature (approx. 200°C) required to volatilise it, but the partially oxidised species $P_2Ph_4Se_2O^+$ (m/z = 544) and $P_2Ph_4SeO_2^+$ (m/z = 481) are readily identifiable. A rather complex series of peaks between m/z = 260 and m/z = 270 can be resolved into the overlapping isotopic patterns of the fragments Ph_2PSe^+ (m/z = 264) and $PhPSe_2^+$ (m/z= 266). No Raman data could be obtained because the compound decomposed rapidly in the laser beam. Samples for IR examination also tended to decompose rather rapidly, but a strong absorption observed reproducibly at 542 cm⁻¹ is probably associated with a P–Se stretching mode [25].

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REFERENCES

- 1 A. J. Blake, R. A. Howie and G. P. McQuillan, Acta Crystallogr., Sect. B, 37 (1981) 966.
- 2 A. H. Cowley and W. D. White, Spectrochim. Acta, 22 (1966) 1341.
- 3 H. C. E. McFarlane, W. McFarlane and J. A. Nash, J. Chem. Soc., Dalton Trans., (1980) 240.
- 4 I. Colquhoun, H. C. E. McFarlane, W. McFarlane, J. A. Nash, R. Keat, D. S. Rycroft and D. G. Thompson, Org. Magn. Resonance, 12 (1979) 473.
- 5 E. J. Spanier and F. E. Caropreso, J. Am. Chem. Soc., 92 (1970) 3348.
- 6 W. Kuchen and H. Buchwald, Chem. Ber., 91 (1958) 2871.
- 7 P. Nicpon and D. W. Meek, Inorg. Chem., 5 (1966) 1297.
- 8 D. Fenske, R. Mattes, J. Lons and K.-F. Tebbe, Chem. Ber., 106 (1973) 1139.
- 9 J. W. Visser, J. Appl. Crystallogr., 2 (1969) 89.
- 10 D. G. Taupin, J. Appl. Crystallogr., 2 (1969) 179.
- 11 R. A. Howie, Program LRSQ, University of Aberdeen.
- 12 D. H. Whiffen, J. Chem. Soc., (1956) 1350.
- 13 G. B. Deacon and J. H. S. Green, Spectrochim. Acta, Part A, 24 (1968) 845.
- 14 K. Hassler and F. Hofler, Z. Anorg. Allg. Chem., 443 (1978) 125.
- 15 G. B. Deacon and J. H. S. Green, Spectrochim. Acta, Part A, 25 (1969) 355.
- 16 J. D. Odem, C. J. Wurrey, L. Carreira and J. R. Durig, Inorg. Chem., 14 (1975) 2849.
- 17 J. R. Bard, A. A. Sandoval, C. J. Wurrey and J. R. Durig, Inorg. Chem., 17 (1978) 286.
- 18 J. R. Durig and J. S. DiYorio, Inorg. Chem., 8 (1973) 2796.
- 19 G. P. McQuillan and I. A. Oxton, Spectrochim. Acta, Part A, 33 (1977) 233.
- 20 J. R. Durig and M. A. Sens, J. Cryst. Mol. Struct., 7 (1977) 295.
- 21 G. P. McQuillan and I. A. Oxton, Spectrochim. Acta, Part A, 34 (1978) 33.
- 22 A. J. Blake, G. P. McQuillan and I. A. Oxton, Spectrochim. Acta, Part A, 36 (1980) 501.
- 23 D. Troy, J. P. Legros and G. P. McQuillan, Inorg. Chim. Acta, in press.
- 24 S. Milicev, Spectrochim. Acta, Part A, 30 (1974) 255.
- 25 M. G. King and G. P. McQuillan, J. Chem. Soc., A, (1967) 898.