CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY
AND CHEMICAL ENGINEERING,
THE UNIVERSITY OF TEXAS, AUSTIN, TEXAS 78712

The Structure of $(CH_3)_4P_2S_2$

BY A. H. COWLEY AND H. STEINFINK

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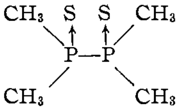
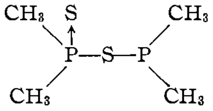
In a recent paper[1] concerned with the proton magnetic resonance spectra of $(CH_3)_4P_2S_2$ and related compounds it was found that the value of J_{PP}, the P–P coupling constant, was an order of magnitude smaller than in other compounds involving a direct phosphorus to phosphorus linkage.[2] This, in turn, has caused the accepted diphosphine disulfide structure (I) to be questioned[1] since a reduction of J_{PP} by the observed magnitude could be caused by the insertion of sulfur atoms between the phosphorus atoms. Structures II, III, and IV must therefore be considered.


I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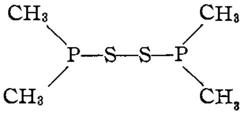
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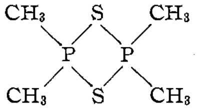
IV

It is of interest to note that the arsenic analog, $(CH_3)_4As_2S_2$, has recently been shown[3] to have structure II.

Experimental

The compound $(CH_3)_4P_2S_2$ was prepared by the procedure of Niebergall and Langenfeld.[4] The crude product was recrystallized twice from 3:1 toluene–ethanol giving long needles, m.p. 223–224°. *Anal.* Calcd. for $(CH_3)_4P_2S_2$: C, 25.80; H, 6.49. Found: C, 25.72, 25.92; H, 6.46, 6.46.

The mass spectra were measured on a CEC 21-102 instrument equipped with a heated inlet system operating at a temperature of 200°. The infrared spectra were recorded on a Beckman IR 7 spectrophotometer using NaCl or CsI optics. The Nujol mulls were run between NaCl or CsI plates and the solutions were run in a 0.1-mm. path length CsI solution cell. The Raman spectra were recorded[5] on a Perkin-Elmer LR 1 laser-excited Raman spectrometer. Ultraviolet spectra were recorded on a Cary Model 14 spectrometer. The X-ray data were obtained with Weissenberg and precession techniques using Cu Kα and Mo Kα radiation, respectively.

Results and Discussion

Strong support for the diphosphine disulfide structure (I) is provided by the mass spectrum (Table I). Two of the most intense peaks (*m/e* 107 and 122) correspond to fragments which have two phosphorus atoms and no sulfur atoms. Since the peak at *m/e* 61 indicates that two methyl groups are attached to each phosphorus atom it is reasonable to assume that the $(CH_3)_4P_2^+$ fragment at *m/e* 122 involves a P–P bond. Additional evidence for a P–P bond are the peaks at *m/e* 62, 75, 76, and 77, which can be assigned to species involving two phosphorus atoms. The presence of a P–P bond would eliminate all structures except I.

TABLE I

MASS SPECTRUM OF $(CH_3)_4P_2S_2$

m/e	Relative abundance	Tentative assignment	*m/e*	Relative abundance	Tentative assignment
186	9.80	$(CH_3)_4P_2S_2^+$	75	15.24	CHP_2^+
171	10.11	$(CH_3)_3P_2S_2^+$	65	16.02	
154	1.87	$(CH_3)_4P_2S^+$	63	15.09	PS^+
139	3.42	$(CH_3)_3P_2S^+$	62	16.17	P_2^+
122	69.52	$(CH_3)_4P_2^+$	61	51.66	$(CH_3)_2P^+$
107	100.00	$(CH_3)_3P_2^+$	59	36.86	$(CH_2)_2P^+$
93	35.92	$(CH_3)_2PS^+$	57	27.06	$(CH_2)P^+$
79	31.57		47	12.44	
77	12.91	$CH_3P_2^+$	46	21.62	CH_3P^+
76	9.18	$CH_2P_2^+$	45	74.96	CH_2P^+
			44	14.62	HCP^+ and/or CO_2^+

TABLE II

INFRARED AND RAMAN SPECTRA OF $(CH_3)_4P_2S_2$

Infrared (solid)[a]	Tentative assignment	Infrared (solution)[c]	Tentative assignment
241 m[b]	CH_3 twist (?)	239 w	CH_3 twist (?)
253 w		279 m	P–C bend (?)
264 w		572 vs	P→S stretch
278 s	P–C bend (?)	732 vs	P–C stretch
568 vs	P→S stretch	746 s	P–C stretch
733 vs	P–C stretch		
747 vs	P–C stretch	825 w	CH_3 rock and wag
824 m	CH_3 rock and wag	858 m	
861 vs		881 vs	
880 vs, br		946 vs	
940 vs, br			

Raman (soln.)[d]	Tentative assignment
185 m	
445 s	P–P stretch
620 s	

[a] Nujol mull. [b] m, medium intensity; w, weak intensity; s, strong intensity; br, broad. All of these intensities are relative. [c] In $CHCl_3$ solution. The spectra were also run in $CHBr_3$ solution in the regions where $CHCl_3$ absorbs. [d] In $CHCl_3$ solution.

The vibrational spectroscopic data (Table II) suggest that the molecule has a center of symmetry[6] since neither of the strong Raman bands at 445 and 620 cm.$^{-1}$ has a counterpart in the infrared. The presence of a center of symmetry would eliminate structure II.

The strong infrared band at 568 cm.$^{-1}$ is assigned to P→S stretching on the basis that the P→S stretch of $(CH_3)_3P{\rightarrow}S$ occurs[7] at 570 cm.$^{-1}$. Furthermore we have found that $(C_2H_5)_4P_2S_2$, which has been shown[8] to have a diphosphine disulfide structure, has a band of similar appearance at 549 cm.$^{-1}$. Also, a band is observed in the ultraviolet spectrum of $(CH_3)_4P_2S_2$ at 2440 Å. Since $(C_2H_5)_4P_2S_2$ also absorbs in the same region (2475 Å.) the band may be due to an n → π^* transition involving a nonbonding orbital on a sulfur

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[1] R. K. Harris and R. G. Hayter, *Can. J. Chem.*, **42**, 2282 (1964).

[2] The J_{PP} value for $(CH_3)_4P_2S_2$ was 18.7 c.p.s. [ref. 1]. By contrast J_{PP} is 108.2 c.p.s. for diphosphine [R. M. Lynden-Bell, *Trans. Faraday Soc.*, **57**, 888 (1961)] and 480 c.p.s. for the diphosphite anion [C. F. Callis, J. R. Van Wazer, J. N. Shoolery, and W. A. Anderson, *J. Am. Chem. Soc.*, **79**, 2719 (1957)].

[3] N. Camerman and J. Trotter, *J. Chem. Soc.*, 219 (1964).

[4] H. Niebergall and B. Langenfeld, *Chem. Ber.*, **95**, 64 (1962).

[5] The authors are very grateful to Dr. R. C. Gore of the Perkin-Elmer Corporation for the Raman data.

[6] The same conclusion was reached by P. J. Christen, L. M. Van der Linde, and F. N. Hooge, *Rec. trav. chim.*, **78**, 161 (1959), and J. Goubeau, H. Reinhardt, and D. Bianchi, *Z. physik. Chem.* (Frankfurt), **12**, 387 (1957).

[7] R. A. Zingaro, *Inorg. Chem.*, **2**, 192 (1963).

[8] S. N. Dutta and M. M. Woolfson, *Acta Cryst.*, **14**, 178 (1961).

atom and a π^* molecular orbital of the $P \rightarrow S$ bond, although it is important to realize that $(CH_3)_4P_2$ absorbs in the same region.[9] The presence of a $P \rightarrow S$ bond would therefore eliminate structures III and IV, leaving I as the correct structure.

Further spectroscopic evidence for structure I is the strong Raman band at 445 cm.$^{-1}$. This band can be assigned to P–P stretching on the basis that it is very close to the value assigned to this vibration in P_2H_4 (437 cm.$^{-1}$),[10] $(C_2H_5)_4P_2$ (424 cm.$^{-1}$),[11] and $(C_4H_9)_4P_2$ (419 cm.$^{-1}$).[11] Structure I is the only one that would exhibit a P–P stretching frequency.

The infrared bands at 773 and 747 cm.$^{-1}$ are close to the P–C asymmetric stretch in $(CH_3)_3P$ and related molecules[12] and are therefore assigned to this vibration. The P–C bending mode and the modes involving the CH_3 groups are also tentatively assigned by comparison with analogous CH_3-substituted phosphorus compounds.[12]

The crystals of $(CH_3)_4P_2S_2$ are usually acicular and frequently clump together forming hollow cylinders. Most crystals are twinned, but X-ray diffraction photographs from single crystal fragments show that the diffraction symbol is $^{2}/_{m}C$, a = 18.82 Å., b = 10.64 Å., c = 6.74 Å., β = 94.4°. Diffraction spectra, *hkl*, are present only when $h + k = 2n$ so that the three space groups C2, Cm, and $C^{2}/_{m}$ are consistent with the diffraction data. The *hk*0 zone shows strong pseudo-hexagonal character and spectra are present only for $h = 3n$; the relationship $a \simeq \sqrt{3}b$ exists also for the monoclinic unit cell. The c axis is the needle axis and most crystals display parallel extinction between crossed polaroids as well as orthorhombic diffraction symmetry because of the twinning in the a,b plane. There are six formula weights in the unit cell and the calculated density 1.38 g./cc. is near values reported for similar compounds.[8] The pseudo-hexagonal cell contains three molecules and the c axis is approximately equal to the length of the molecule of formula I, further strengthening the conclusion that it is the correct choice. The centers of the six molecules can be located in one twofold and one fourfold site in each of the three possible space groups. The twofold locations in C2, Cm, and $C^{2}/_{m}$ require a molecular symmetry of 2, m, or $^{2}/_{m}$, respectively, and our infrared data as well as the structure of $(C_2H_5)_4P_2S_2$ (8) indicate that the most probable molecular symmetry is $^{2}/_{m}$.

In summary the above data make it fairly conclusive that the structure of $(CH_3)_4P_2S_2$ is I. We have repeated the spectrum of $(CH_3)_4P_2S_2$ at 100 Mc. (it was formerly done at 60 Mc.[1]) and find good agreement on the line separations as reported by Harris and Hayter.[1] This indicates that the spectrum is due to spin–spin splitting rather than a chemical shift difference. The reason for the variation in magnitude of J_{PP} between directly bonded phosphorus nuclei in the few known cases is not clear.

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(9) L. R. Grant, Jr., and A. B. Burg, *J. Am. Chem. Soc.*, **84**, 1834 (1962).

(10) M. Baudler and L. Schmidt, *Z. anorg. allgem. Chem.*, **289**, 219 (1957).

(11) E. Steger and K. Stopperka, *Chem. Ber.*, **94**, 3029 (1961).

(12) M. Halmann, *Spectrochim. Acta*, **16**, 407 (1960), and references quoted therein.

CONTRIBUTION FROM THE GORGAS LABORATORY,
ROHM & HAAS COMPANY, REDSTONE ARSENAL
RESEARCH DIVISION, HUNTSVILLE, ALABAMA

The Fluoro-O-fluorosulfatomethanes

BY MAX LUSTIG

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The new compounds difluorobis(O-fluorosulfato)-methane, $F_2C(OSO_2F)_2$, and fluorotris(O-fluorosulfato)-methane, $FC(OSO_2F)_3$, were prepared by the reaction of peroxydisulfuryl difluoride, $S_2O_6F_2$, with dibromodifluoro- and tribromofluoromethane, respectively.

$$CBr_2F_2 + S_2O_6F_2 \longrightarrow F_2C(OSO_2F)_2 + Br_2$$

$$CBr_3F + {}^{3}/_{2}S_2O_6F_2 \longrightarrow FC(OSO_2F)_3 + {}^{3}/_{2}Br_2$$

The fluoropoly(O-fluorosulfato)methanes are the first examples of compounds containing more than one O-fluorosulfate group attached to a single carbon atom. A similar reaction employing CBr_4 did not yield the tetrakis compound, but, rather, a compound tentatively identified as $O{=}C(OSO_2F)_2$.

The first member of the series of fluoro-O-fluorosulfatomethanes, F_3COSO_2F, was first prepared in small yield by the reaction of sulfur dioxide and trifluoromethyl hypofluorite[1] and later in high yield by combining CF_3I,[2] CF_3Br, or CF_3Cl[3] with $S_2O_6F_2$. However, the reaction of CCl_4 with the latter gives $S_2O_5F_2$, $COCl_2$, and/or CO_2 as the products,[4] rather than mixed chloro(O-fluorosulfato)methanes.

Experimental

Reagents.—Peroxydisulfuryl difluoride[4] and the bromofluoromethanes[5] were made by literature methods. Tetrabromomethane was distributed by Baker and Adamson Products, Allied Chemical Corp.

General Procedure.—Transfer of gaseous substances was accomplished by use of a standard Pyrex vacuum apparatus. The reactor used for the preparation of $F_2C(OSO_2F)_2$ and $FC(OSO_2F)_3$ was a 100-ml. Pyrex bulb with a side arm attached through a stopcock. The $S_2O_6F_2$ was measured into the bulb and then condensed into the side arm and the stopcock was closed. The appropriate bromofluoromethane was then placed into the bulb. The peroxide was allowed to warm to room temperature and then the stopcock was opened, permitting it to diffuse slowly into the bulb and react with the appropriate substrate.

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(2) M. Lustig, Thesis, University of Washington, 1962.

(3) C. T. Ratcliffe and J. M. Shreeve, *Inorg. Chem.*, **3**, 631 (1964).

(4) J. M. Shreeve and G. H. Cady, *J. Am. Chem. Soc.*, **83**, 4521 (1961).

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