777. *Hydrogen Bonding of the Thiol Group in Phosphinodithioic Acids.*

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The existence of S–H · · · S hydrogen bonds has been confirmed by infra-red spectroscopy of phosphinodithioic acids. A comparison with thio-carboxylic acids suggests that the highly polar P–S bonds and S–H bonds are responsible for the high degree of association.

THERE is little evidence for the existence of S–H · · · S hydrogen bonds, although the corresponding S–H · · · O and S–H · · · N bonds are fairly common.[1] Recently, however, Menefee, Alford, and Scott [2] in a study of the infrared spectra of two phosphorodithioic acids, $(MeO)_2PS{\cdot}SH$ and $(EtO)_2PS{\cdot}SH$, interpreted the shift in the νSH frequency on passing from the pure liquid to dilute solution in carbon tetrachloride as being due to the

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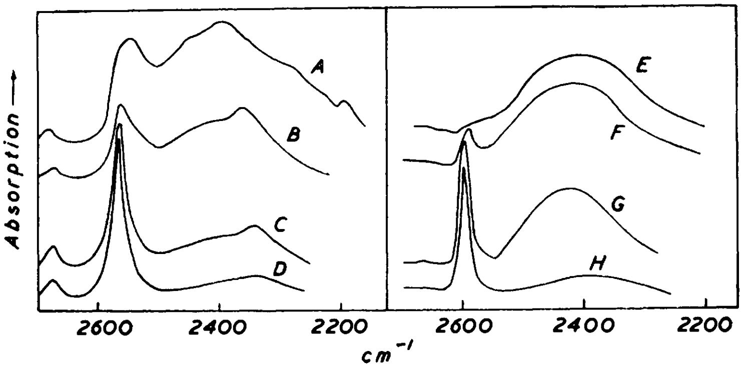
[1] Bellamy, " Infra-red Spectra of Complex Molecules," Methuen, London, 1954, p. 289.

[2] Menefee, Alford, and Scott, *J. Chem. Phys.*, 1956, **25**, 370.

dissociation of S–H ··· S bonds. Since these acids contain alkoxy-groups, the possibility that the observed shift is due to S–H ··· O bonds cannot be excluded, although Menefee *et al.* consider this unlikely both on steric grounds and because the observed νSH shift is significantly larger than that previously reported[3] for S–H ··· O bonding between thiophenol and *iso*propyl ether.

FIG. 1. *Spectra in carbon tetrachloride.*



Diphenylphosphinodithioic Acid.—A, Saturated solution; *B*, 25% soln.; *C*, 5% soln.; *D*, 1% soln. *Diethylphosphinodithioic Acid.—E*, Pure liquid; *F*, 25% soln.; *G*, 5% soln.; *H*, 1% soln.

This assumption can be tested by using a similar molecule in which only S–H ··· S bonds can occur. We have studied the infrared spectra of diethyl- and diphenyl-phosphinodithioic acids, $Et_2PS{\cdot}SH$ and $Ph_2PS{\cdot}SH$, and compared them with those of related thiocarboxylic acids.

RESULTS

Hydrogen Bonding.—The effect of dilution on the νSH absorption bands of $Ph_2PS{\cdot}SH$ and $Et_2PS{\cdot}SH$ is shown in Fig. 1. In the solid, or melt, or in concentrated solutions in inert solvents, $Ph_2PS{\cdot}SH$ shows a broad νSH absorption at 2420 cm.$^{-1}$ while in dilute solution the νSH band is very sharp and lies at 2560 cm.$^{-1}$. The diethyl-acid behaves similarly. This behaviour is characteristic of intermolecular hydrogen bonding. The complexity of the broad band (~2400 cm.$^{-1}$) attributed to νSH ··· S may be due to the presence of a mixture of hydrogen-bonded polymers $(R_2PS{\cdot}SH)_n$, although a similar complex band (of doubtful origin) is observed for νO–H ··· O in dimeric carboxylic acids.

The effect of temperature on the νSH absorption bands is shown in Fig. 2, the degree of association decreasing with rise in temperature as expected. If the equilibrium is assumed to be $(R_2PS{\cdot}SH)_2 \rightleftharpoons 2R_2PS{\cdot}SH$, a hydrogen-bond strength of approximately 1 kcal./mole is indicated.

The capacity of phosphinodithioic acids for hydrogen bonding can be ascribed to the presence of the phosphorus atom rather than to the effect of the substituent phenyl groups, since $Et_2PS{\cdot}SH$ forms hydrogen bonds with equal ease (Fig. 1). Further, little or no hydrogen bonding is observed in pure thioacetic acid (Fig. 3), and only to a minor extent in dithiobenzoic acid (Fig. 4). The νSH absorption of thioacetic acid shows only a slight shift on dilution, and is always found in the position characteristic of a free thiol group. A pure liquid film of dithiobenzoic acid shows a broad νSH band indicating that some hydrogen bonding occurs, but the shift is only half that observed for the phosphinodithioic acids, and in a 20% solution in carbon tetrachloride all evidence of association disappears, leaving a sharp band at 2585 cm.$^{-1}$. The results indicate that the P=S and S–H bonds in

[3] Gordy and Stamford, *J. Amer. Chem. Soc.*, 1940, **62**, 497.

phosphinodithioic acids are intrinsically more polar than the C=S and S–H bonds in thiocarboxylic acids.

Effects of Alkoxy-groups.—The absence of monomeric νSH bands in ethereal solutions of $Ph_2PS{\cdot}SH$ (Fig. 5) indicates extensive hydrogen bonding which might be due to either S–H ··· S or S–H ··· O. The former can be ruled out since the broad band observed at 2420 cm.$^{-1}$ is unaffected by dilution. Therefore although S–H ··· S bonds probably predominate in alkylphosphorothiolothionic acids of the type $(RO)_2PS{\cdot}SH$, it is obviously difficult to distinguish them spectroscopically from S–H ··· O bonds, since S–H ··· O bonding would give a band coincident with that due to S–H ··· S, contrary to the assumption of Menefee *et al.*[1]

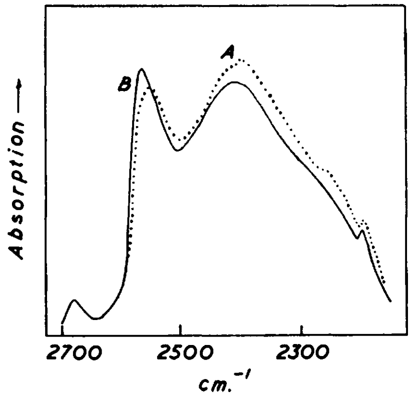


FIG. 2. *Temperature dependence of* νSH *bands of diphenylphosphinodithioic acid in carbon tetrachloride.*

A, 26°; B, 62°.

FIG. 3.

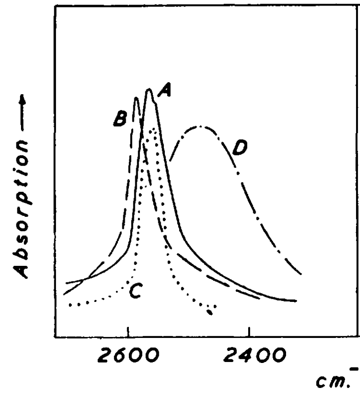


FIG. 4.

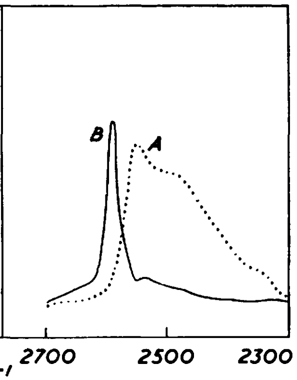


FIG. 3. *Spectra of thioacetic acid.*
A, Pure liquid; *B*, 1% soln. in CCl_4; *C*, 1% soln. in C_6H_6; *D*, 1% soln. in Et_2O.

FIG. 4. *Spectra of dithiobenzoic acid.*
A, Pure liquid; *B*, 20% soln. in CCl_4.

Effect of Solvent.—In the νSH region the spectra indicate that the degree of association does not change significantly in the solvents carbon tetrachloride, *cyclo*hexane, carbon disulphide, and chloroform (Fig. 6), but is much lower in benzene solution at the same concentration. In addition, the half band width of the monomeric νSH band in a 2·5%

benzene solution is approximately twice as great as that of the corresponding band in carbon tetrachloride or carbon disulphide at the same concentration, and the band appears at 2525 cm.$^{-1}$, *i.e.* 25—30 cm.$^{-1}$ lower than in the other solvents. These distinguishing features indicate a greater degree of interaction between benzene and the solute, possibly giving a π-electron complex of the type $Ph_2PS{\cdot}SH \cdots Ph$. A similar effect has been observed in hydroxylic compounds by Mecke,[4] and there is thermodynamic evidence that carboxylic acids form analogous complexes in benzene solution. This effect does not appear to be related to the capacity of the acid to form hydrogen bonds, since in Figs. 3 and 6 thioacetic and the phosphinodithioic acid show a similar displacement of νSH on passing from carbon tetrachloride to benzene solution.

FIG. 5

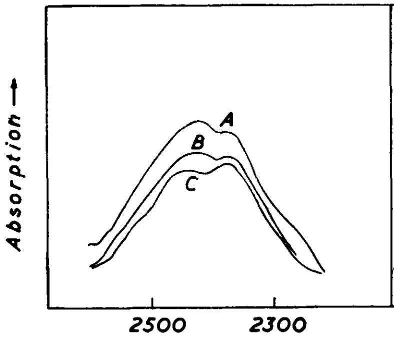


FIG. 5. νSH *for diphenylphosphinodithioic acid in ether solution.* *A*, 25%; *B*, 5%; *C*, 1%.

FIG. 6.

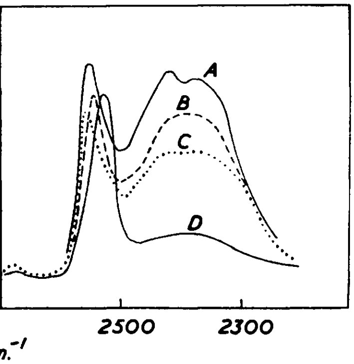


FIG. 6. *Effect of solvent on degree of association of diphenylphosphinodithioic acid in* 20% *solution.* *A*, $CHCl_3$; *B*, CS_2; *C*, CCl_4; *D*, C_6H_6.

EXPERIMENTAL

Materials.—Diphenylphosphinodithioic acid, prepared by Higgins, Vogel, and Craig's method,[5] had m. p. 56—57°; its diethyl analogue was prepared by Malatesta and Pizzotti's method.[6] Dithiobenzoic acid was prepared from potassium sulphide and ωωω-trichlorotoluene by Houben's method.[7] A B.D.H. sample of thioacetic acid was used.

Spectra.—A Perkin-Elmer Model 21 infrared spectrophotometer, with rock-salt and fluorite optics, was used.

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[4] Mecke, *Discuss. Faraday Soc.*, 1950, **9**, 161.
[5] Higgins, Vogel, and Craig, *J. Amer. Chem. Soc.*, 1955, **77**, 1864.
[6] Malatesta and Pizzotti, *Gazzetta*, 1946, **76**, 167.
[7] Houben, *Ber.*, 1906, **39**, 3224.