

The Crystal Structure of Imidotetra-phenyldithiodiphosphinic Acid, a Compound with an N—H...S Hydrogen Bond

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In recent work, we have used the imidotetra-phenyldithiodiphosphinate anion as a ligand.^{1,2} In the parent acid $H\{N(Ph_2PS)_2\}$, it has been assumed from IR spectral work that the acid proton was bonded to nitrogen rather than to

Table 1. Atomic coordinates for the molecule in fractions of cell edges with estimated standard deviations.

Atom	x	y	z
S1	0.48100(7)	0.76775(8)	0.51748(8)
S2	-0.00376(7)	0.91574(7)	0.35162(7)
P1	0.29746(7)	0.77394(7)	0.59586(7)
P2	0.17583(7)	0.93543(7)	0.34715(7)
N	0.2072(2)	0.8998(2)	0.4978(2)
H	0.162(2)	0.939(2)	0.529(2)
C111	0.2216(3)	0.6188(2)	0.6412(3)
C112	0.0868(3)	0.6172(3)	0.6691(3)
C113	0.0287(3)	0.5015(3)	0.6947(3)
C114	0.1028(4)	0.3861(3)	0.6939(4)
C115	0.2352(4)	0.3862(3)	0.6672(4)
C116	0.2950(3)	0.5014(3)	0.6424(3)
C121	0.2609(2)	0.8133(3)	0.7430(2)
C122	0.3119(3)	0.9297(3)	0.7308(3)
C123	0.2816(4)	0.9693(3)	0.8368(3)
C124	0.2017(4)	0.8925(4)	0.9565(3)
C125	0.1542(4)	0.7781(4)	0.9693(3)
C126	0.1825(3)	0.7369(3)	0.8644(3)
C211	0.2244(3)	1.1084(3)	0.2444(2)
C212	0.1679(3)	1.1917(3)	0.1362(3)
C213	0.2038(4)	1.3249(3)	0.0591(3)
C214	0.2950(4)	1.3756(3)	0.0886(3)
C215	0.3536(3)	1.2933(3)	0.1937(3)
C216	0.3195(3)	1.1600(3)	0.2723(3)
C221	0.2852(3)	0.8245(2)	0.2804(2)
C222	0.4017(3)	0.8682(3)	0.1897(3)
C223	0.4813(3)	0.7798(3)	0.1393(3)
C224	0.4456(3)	0.6493(3)	0.1801(3)
C225	0.3311(3)	0.6054(3)	0.2698(3)
C226	0.2495(3)	0.6936(3)	0.3183(3)

sulfur.³ The present work was undertaken to locate this proton and see if it is involved in hydrogen bonding. Another reason was that the structure of the acid would serve as a reference to further use of its anion as a ligand.

The acid was prepared by published methods³ and recrystallized from CH_2Cl_2 . The crystals are triclinic with $a=10.688(2)$ Å, $b=10.852(2)$ Å, $c=11.192(2)$ Å, $\alpha=64.50(1)^\circ$, $\beta=75.14(1)^\circ$, $\gamma=80.81(1)^\circ$, $Z=2$, $D_m=1.31$ and $D_x=1.32$ g/cm³. Absence of systematic extinctions implies space groups $P1$ or $P\bar{1}$.

Based on 3845 observed reflections [$I>2\sigma(I)$], the structure was solved by direct methods (MULTAN) and refined by full-matrix least squares methods to a final conventional R value of 0.042 ($R_w=0.043$; Table 1). Data collection procedures and programs used in structure determination are similar to those used earlier in this laboratory.⁴ The choice of $P\bar{1}$ as the correct space group was justified by the successful refinement of the structure. All hydrogen atoms were located and refined. Tables of structure factors, temperature factors and phenyl hydrogen coordinates are available from the authors upon request.

Fig. 1. shows the molecule as seen nearly along the normal to the central $P1N1P2$ plane. The S—P—N—P—S backbone of the acid has a *trans* conformation relative to the central —P—N—P—group as opposed to the *cis* conformation found when its anion acts as a bidentate, chelating ligand.¹ This is not unexpected as the non-bonded intramolecular interactions will be reduced in the *trans* as compared to the *cis* conformation. On the other hand, the S—S separation in the anion will be too large in the *trans* conformation if it is to act as a chelating

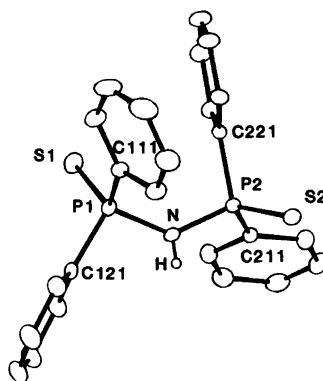


Fig. 1. The imidotetra-phenyldithiodiphosphinic acid molecule as seen along the normal to the C221P2N plane.

Table 2. Some bond lengths (Å) and angles (°) with standard deviations.

S1-P1	1.937(1)	S1-P1-N	115.49(9)
S2-P2	1.950(1)	S2-P2-N	114.59(9)
N-P1	1.683(2)	P1-N-P2	132.68(14)
N-P2	1.672(2)	S1-P1-C111	113.37(9)
P1-C111	1.800(3)	S1-P1-C121	113.53(9)
P1-C121	1.808(3)	S2-P2-C211	112.16(9)
P2-C211	1.807(3)	S2-P2-C221	111.20(9)
P2-C221	1.803(2)	N-P1-C111	105.27(12)
N-H	0.711(24)	N-P1-C121	99.97(11)
H...S2'	2.638(25)	N-P2-C211	104.28(11)
N...S2'	3.349(2)	N-P2-C221	106.32(11)
		P1-N-H	117(2)
		P2-N-H	109(2)
		N-H...S2'	178(3)
Torsional angles			
		S1-P1-N-P2	62.4
		S2-P2-N-P1	112.8
		S1-P1-N-H	-133.1
		S2-P2-N-H	-52.7

ligand. A similar behaviour has been observed in oxamide and dithioxamide ligands.⁵ The average P-S and P-N bond lengths are 1.944(9) and

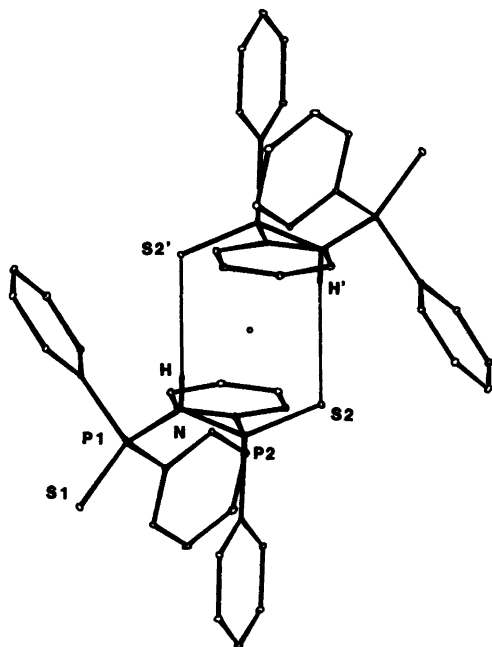
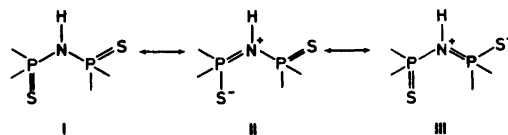


Fig. 2. Pairs of hydrogen bonded molecules seen along the normal to the plane through S2...H' and S2'...H. Primed letters denote atoms in a molecule related to the original one (Table 1) by a center of symmetry in 0,0,1/2.

1.678(8) Å, respectively (Table 2). These lengths may be compared to 2.02 and 1.59 Å which are the corresponding bond lengths found in metal complexes of the anionic ligand.¹ They may also be compared to P=S double bond lengths around 1.95 Å observed in phosphine sulfides⁶ and to a P-N single bond of 1.77 Å.⁴ Thus the P-N bonds have some double bond character. This agrees with the observation that the H-atom bonded to N is only 0.17 Å below the PNP plane, indicating a tendency toward sp^2 hybridization of nitrogen. Consequently it is found that the sum of the nitrogen bond angles is 358.7°. Possible resonance forms of the acid could then be of the types I-III with I dominating.



A positive charge on nitrogen will increase the acidity of the hydrogen bonded to it and enhance the possibility of hydrogen bonding to a partially negative and thus better hydrogen bond accepting sulfur atom. This is also observed in the present investigation where pairs of molecules are bonded together across centers of symmetry by N-H...S2' bonds (Fig. 2). The N...S2' and H...S2' distances of 3.349(2) and 2.64(3) Å, respectively, agree well with previous investigations.⁷ The angle N-H...S2' is 178(3)°. Resonance form III which puts negative charge

on S2, contributes more than II which puts negative charge on S1, the sulphur atom not involved in hydrogen bonding. This is reflected in the observed bond lengths in the SPNPS group (Table 2). Thus hydrogen bonding explains why P2-S2 is longer than P1-S1. Similar effects are observed in thioamides where conjugated systems strengthen hydrogen bonding.⁸⁻¹⁰ An IR spectrum (KBr) of the acid shows absorptions at 2680 (w) and 2623 cm⁻¹ (ms) probably due to N-H... stretch and in this region differs from the first reported spectrum.³ Bonds and angles in the phenyl groups have normal values.

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