J. Phys. Chem. A **1998,** *102,* 6871−6876 **6871**

Molecular Modeling Studies on the Structure and Electronic Properties of Bis(Thiophosphorylamines) and Their Zinc Complexes

John O. Morley*,[†] and Michael H. Charlton[‡]

Chemistry Department, University of Wales Swansea, Singleton Park, Swansea, SA2 8PP, and
Research Centre, Zeneca Specialties, Hexagon house, Blackley, Manchester, M9 8ZS, United Kingdom

Received: April 21, 1998; In Final Form: June 12, 1998

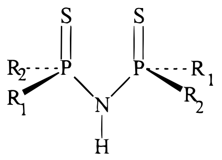
The structures and charge distributions of a number of bidentate bis(disubstituted-thiophosphorylamine) ligands used to extract zinc have been assessed by both semiempirical and ab initio molecular orbital methods and the results compared with crystallographic data where available. At the semiempirical level, the MNDO method gives superior results to either the AM1 or PM3 methods, which give poor charge distributions at the N, P, and S atoms. Five possible conformers of two tautomeric types were calculated for both alkyl and aryl derivatives. The results suggest that ligands containing an α-branched alkyl chain at phosphorus, which are good extractants for zinc, exist predominantly as cis SH tautomers with the acidic hydrogen covalently bonded to one sulfur and hydrogen bonded to the other. In contrast, those ligands containing a primary carbon or oxygen at phosphorus, which are poor extractants for zinc, are predicted to exist as NH tautomers with both sulfur atoms forming a trans arrangement to one another. These structural differences appear to explain the marked difference in the ^{31}P chemical shifts between the α-branched compounds and the other types.

Introduction

The commercial success of processes for the selective solvent extraction of copper from aqueous acidic solutions derived from oxide ores using ring alkylated *o*-hydroxybenzophenone oxime[1] or salicylaldoxime[2] has led to a growing interest in related processes that could be used for the selective solvent extraction of other metals. This interest is particularly true for cases where the required metal is present in much smaller concentration in solution than the main element. Typical examples include attempts to selectively extract gallium from solutions containing high concentrations of aluminum,[3] and zinc from solutions containing high concentrations of iron.[4] In the former, alkylated 8-hydroxyquinoline has been used for solvent extraction,[3] whereas in the latter, dialkyl phosphoric and thiophosphoric acids are known to be effective.[5] Overall, however, none of these reagents have so far achieved the desired selectivity compared with the main metal ion present.

However, in the case of zinc, recent experimental studies have shown that ligands based on bis(dialkylthiophosphoryl)amine (**1**) are not only powerful complexing agents for zinc from aqueous solution but also exhibit good selectivity compared with iron.[6] In this case, the ligand (**1**) is dissolved in an aromatic hydrocarbon such as Escaid (a commercial mixture of alkylated benzenes) and contacted in a countercurrent fashion with an aqueous acidic solution of zinc-containing iron (III) salts. The zinc passes from the aqueous phase to the organic phase to form a soluble complex with the ligand, and the zinc is recovered by treating the separated organic phase with strong acid.[6]

Significantly, when the ligand (**1**) contains α-branched alkyl chains at the phosphorus atom, as in **1d** and **1h**, it is able to form strong complexes with zinc. However, the corresponding analogues, where a primary carbon is bonded to phosphorus, as in **1e** and **1g**, or oxygen is bonded to phosphorus, as in **1f** and **1i**, are generally very poor extractants (Table 1).[6] In addition, the measured ^{31}P NMR chemical shifts exhibit a distinct difference between the straight- and branched-chain types of ligand (Table 1).



(1)

a $R_1 = R_2 = H$
b $R_1 = R_2 = CH_3$
c $R_1 = R_2 = C_6H_5$
d $R_1 = R_2 = i\text{-}C_3H_7$
e $R_1 = R_2 = n\text{-}C_4H_9CH(C_2H_5)CH_2$
f $R_1 = R_2 = C_6H_5O$
g $R_1 = R_2 = n\text{-}C_5H_{11}$
h $R_1 = R_2 = n\text{-}C_3H_7CHCH_3$
i $R_1 = R_2 = C_2H_5O$
j $R_1 = s\text{-}C_4H_{10}$, $R_2 = t\text{-}C_4H_{10}$
k $R_1 = s\text{-}C_4H_{10}$, $R_2 = s\text{-}C_4H_{10}$
l $R_1 = n\text{-}C_4H_{10}$, $R_2 = t\text{-}C_4H_{10}$
m $R_1 = R_2 = n\text{-}C_3H_7$

The explanation for the dramatic change in extraction behavior is not clear. Therefore, the present molecular modeling studies have been carried out to explore the structures and electronic properties of the ligands and metal complexes in an attempt to rationalize their behavior.

Methods of Calculation

Although semiempirical methods are generally unreliable for compounds containing P(V), there are no previous reports of calculations on bis(dialkylthiophosphoryl)amines such as **1**. Initial calculations were carried out, therefore, to assess the accuracy of these methods to reproduce crystallographic data on known derivatives before proceeding with the calculations on the other extractants. The AM1 method[7] of the MOPAC package[8] was used initially at the "precise" level. Although this method has been thoroughly tested against a variety of C-, H-, N-, O-, and F-containing compounds and found to give

---

[†] Chemistry Department.
[‡] Research Centre.

S1089-5639(98)01923-9 CCC: $15.00

TABLE 1: Experimental Zinc Extraction Data and ^{31}P NMR Shifts for Bis(thiophosphoryl)Amines (1)[a]

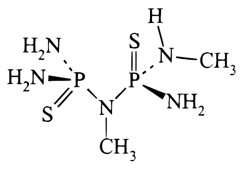
ligand	**1d**	**1e**	**1f**	**1g**	**1h**	**1i**	**1j**	**1k**	**1l**
^{35}P NMR[b]	89	67	47	68	85	56	86	88	89
zinc extracted[c]	—	0	—	0	61.6	—	84.6	50.8	—
zinc extracted[d]	32.8	0	17.0	0	26.9	3.1	59.6	32.8	35.8
relative rate[e]	13	—	2	—	33	—	20	150	—

[a] Data abstracted from ref 6. [b] In ppm. [c] Equilibrium amounts of zinc extracted (%) by a 0.2 M ligand solution either in Escaid from 0.1 M aqueous zinc sulfate solution (6.5 g/L Zn) at initial pH of 2.0. [d] As in *c*, but in chloroform. [e] Time taken to reach 70% of equilibrium position (in minutes).

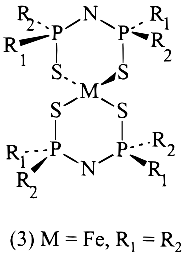
reasonable structures and heats of formation, the treatment of phosphorus and sulfur are both later additions.[9,10] Although AM1 has superseded the older MNDO method,[11] partly because it gives a better treatment of hydrogen bonding (among other factors), the more recent and faster PM3 method[12] is also available to calculate phosphorus- and sulfur-containing systems. Because the AM1 method did not prove to be satisfactory, the two other methods were subsequently evaluated for the bis(thiophosphoryl)amine discussed here. In addition, a series of reference *ab initio* calculations were carried on simpler ligands, **1a** and **1b**, at the 3-21G, 6-31G, 6-31G*,[13a] and TZVP levels[13b] using the GAMESS program.[14] In this study, all calculations were performed in the gas phase. As the ligands used for the experimental extraction of zinc are generally dissolved in solvents of very low dielectric constant, such as chloroform ($\epsilon = 4.70$) or Escaid ($\epsilon = 2.38$), the gas-phase calculations are a valid approximation.

Results and Discussion

1. Reference Calculations. Experimentally, there are limited structural data available on the compounds under consideration here, with the exception of the crystal structures of bis(dimethylthiophosphoryl)amine (**1b**),[15] bis(diphenylthiophosphoryl)amine (**1c**),[16] and the closely related *N,N′*-dimethyl-*N*-(thiophosphorodiamido)thiophosphorotriamide (**2**),[17] all of which are present in the Cambridge Structural Database.[18] There are also crystal structures of a series of related metal complexes present including iron (II) bis(imidotetramethyldithiodiphosphino-*S,S*) (**3**)[19] and nickel (II) bis(imidotetramethyldithiodiphosphino-*S,S*) (**4**).[20] Calculations were carried out at two levels of theory.



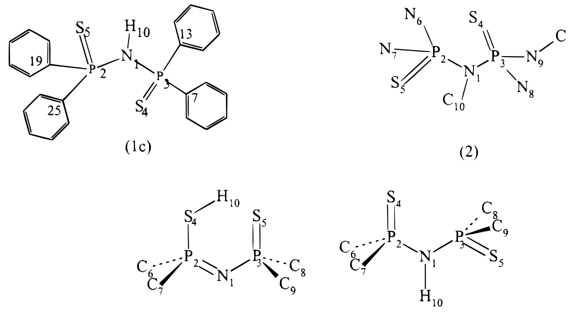
(2)



(3) M = Fe, $R_1 = R_2 = CH_3$
(4) M = Ni, $R_1 = R_2 = CH_3$
(5) M = Zn

1.1 Semi-empirical calculations. Preliminary calculations were carried out to assess the accuracy of the AM1 method to reproduce the bond lengths and angles found in the crystal structures of both the bis(diphenylthiophosphoryl)amine (**1c**) and thiophosphorotriamide (**2**). The atom numbering conventions shown in Scheme 1were adopted for each molecule. The crystal structure of bis(diphenylthiophosphoryl)amine (**1c**)[15] shows the presence of a hydrogen bonded, dimeric form, with the sulfur atoms roughly trans to each other. Optimizations were carried out starting from the crystal structure though it was necessary to remove a number of hydrogen atoms such as those at the N—H and C—H bonds and replace them at more appropriate distances (originally at 0.716 and 0.796 Å, respectively).

SCHEME 1: Numbering Conventions Adopted for the Bis(diphenylthiophosphoryl)Amine (1c), *N,N′*-Dimethyl-*N*-(thiophosphorodiamido)thiophosphorotriamide (2), and the SH and Nh Tautomers of Bis(dimethylthiophosphoryl)amine (1b)



(1c)

(2)

(1b, SH and NH Tautomeric Forms)

TABLE 2: Experimental Versus Calculated Geometries and Heats of Formation for Bis(diphenylthiophosphoryl)amine (1c)[a]

variable	X-ray[b]	MNDO	AM1	PM3
$P_3{-}S_4$	1.936	**1.926**	1.907	1.948
$S_5{-}P_2$	1.951	1.936	1.921	**1.957**
$N_1{-}P_3$	1.683	**1.675**	1.604	1.783
$P_3{-}C_7$	1.800	1.762	1.595	**1.816**
$P_2{-}C_{19}$	1.806	1.762	1.595	**1.818**
$C_7{-}C_8$	1.395	1.411	1.399	**1.393**
$N_1{-}H_{10}$	0.716	1.002	1.018	1.003
$C_{13}{-}P_3{-}C_7$	108.09	109.43	**108.80**	105.59
$C_{13}{-}P_3{-}N_1$	100.01	103.53	109.14	**101.45**
$C_{13}{-}P_3{-}S_4$	113.47	110.28	**111.83**	116.02
$N_1{-}P_3{-}S_4$	115.49	110.41	106.53	**112.91**
$P_3{-}N_1{-}P_2$	132.69	**130.93**	148.95	141.70
$P_2{-}N_1{-}P_1{-}S_4$	62.4	**60.7**	31.2	55.0
$C_{25}{-}P_2{-}N_1{-}P_3$	−10.4	**−12.3**	20.9	−7.7
$C_{19}{-}P_2{-}N_1{-}P_3$	−124.2	**−129.6**	−103.5	−118.4
$S_5{-}P_2{-}N_1{-}H_{10}$	−52.7	−34.5	−31.9	**−51.2**
ΔH_f[c]	154.81	68.22	143.95	

[a] Bold type shows the value closest to the crystal structure. [b] Reference 15; CSD Refcode: BOLGEO. [c] Heat of formation (kcal mol^{-1}).

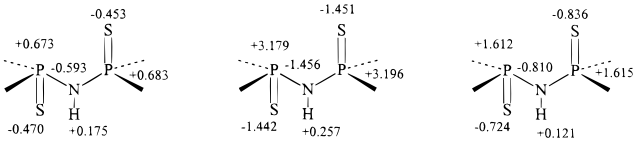
The results from the AM1 calculations are generally poor, and underestimate the P—S, P—N, and P—C bond lengths with values of 1.91, 1.60, and 1.60 Å, respectively, versus values of 1.94, 1.68, and 1.80 Å, respectively, found in the crystal (Table 2). The calculated torsion angle between phosphorus and sulfur ($P_2{-}N_1{-}P_1{-}S_4$) of 31.2° also underestimates the experimental value of 62.4°. Because of these inaccuracies, particularly with respect to the bond lengths, further calculations were carried out using the alternative PM3 and MNDO methods. In contrast to the AM1 results, the PM3 method overestimates the key P—S, P—N, and P—C bond lengths with calculated values of 1.96, 1.78, and 1.82 Å, respectively, though the $P_2{-}N_1{-}P_1{-}S_4$ torsion angle of 55.0° is close to the experimental value (Table 2). However, the best results were obtained with the MNDO method, with calculated bond lengths very close to the experimental data with values of 1.93, 1.68, and 1.76 Å, respectively and a $P_2{-}N_1{-}P_1{-}S_4$ torsion angle of 60.7° (Table 2).

TABLE 3: Experimental Versus Calculated Geometries and Heats of Formation for *N*,*N′*-Dimethyl-*N*−(thiophosphorodiamido)thiophosphorotriamide (2)[a]

variable	X-ray[b]	MNDO	AM1	PM3
C_{11}—N_9	1.423	1.457	**1.422**	1.467
P_3—S_4	1.972	1.926	1.910	**1.955**
P_3—N_1	1.690	**1.677**	1.629	1.787
P_2—S_5	1.958	1.931	1.903	**1.946**
N_8—P_3—N_9	104.15	101.65	112.03	**102.27**
S_4—P_3—N_1	111.37	115.28	103.74	**113.75**
C_{10}—N_1—P_3	117.48	122.02	109.64	**113.85**
C_{11}—N_9—P_3—S_4	64.1	**52.8**	−173.3	160.9
S_4—P_3—N_1—C_{10}	178.1	**−178.2**	156.5	159.7
C_{10}—N_1—P_2—S_5	5.4	**2.9**	38.5	41.2
ΔH_f[c]		+18.81	−96.76	−42.37

[a] Bold type shows the value closest to crystal structure. [b] Reference 16; CSD RefCode: MTHPAM. [c] Heat of formation (kcal mol^{-1}).

SCHEME 2: Charge Distributions in Bis(diphenylthiophosphoryl)amine Calculated Using the MNDO, AM1, and PM3 Methods



A further set of calculations was carried out on the related *N*,*N′*-dimethyl-*N*-(thiophosphorodiamido)thiophosphorotriamide (**2**), again starting from the crystal structure,[16] to check the utility of the semiempirical methods to reproduce the experimental data. In this case, the AM1 method again underestimates the key P−S and P−N bond lengths with respective values of 1.91 and 1.63 Å versus 1.97 and 1.69 Å experimentally, whereas the PM3 method gives values of 1.95 and 1.78 Å. Again the MNDO method gives the best overall results, particularly with respect to the torsion angles (Table 3).

However, the calculations using the AM1 method give resultant atomic charges at sulfur and phosphorus that are far too high, implying that the ligands are highly ionic in character. A similar picture emerges for the PM3 method, although here the charges are less pronounced and the molecule is less ionic (Scheme 2). However, the MNDO charge distribution is more realistic and corresponds to that of a covalently bound compound of this type. Although both the AM1 and PM3 methods reproduce the experimental data for molecules containing either phosphorus or sulfur, neither is sufficiently accurate for compounds containing both elements bonded together. This deficiency almost certainly arises because of the omission of this type of compound in the original parametrization process.

SCHEME 3: Conformations of SH and NH tautomers of bis(thiophosphoryl)amine (1a)

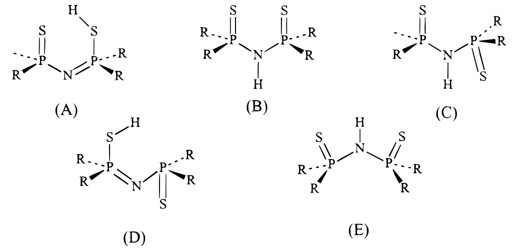


TABLE 4: Relative Energies, Atomic Charges, and Geometries of the Tautomers of Bis(thiophosphoryl)amine (1a) Calculated by Semiempirical and Ab Initio Methods

method	tautomer	relative energy[a]	atomic charges P2	P3	S4	S5	P—N bond[b]	P—N—P angle[c]	SP..PS torsion[c]
MNDO	**A**	3.803	0.38	0.38	−0.24	−0.27	1.643	118.5	−5.7
	B	1.323	0.51	0.48	−0.39	−0.38	1.669	120.8	126.0
	C	0.000	0.56	0.57	−0.37	−0.40	1.649	126.4	175.2
AM1	**A**	0.000	3.03	3.03	−1.21	−1.21	1.466	156.4	0.5
	B	39.734	2.71	2.71	−1.19	−1.19	1.591	136.2	99.9
	C	35.131	2.72	2.72	−1.21	−1.20	1.590	141.4	178.8
PM3	**A**	0.000	1.81	1.82	−0.79	−0.79	1.674	137.7	1.0
	B	10.404	1.76	1.77	−0.79	−0.80	1.785	138.6	−177.8
	C	10.371	1.76	1.77	−0.79	−0.80	1.784	138.7	174.1
TZVP	**A**	18.955	0.66	0.74	−0.22	−0.54	1.543	145.0	−7.9
	B	2.001	0.65	0.61	−0.43	−0.43	1.701	127.6	124.8
	C	0.000	0.65	0.67	−0.46	−0.44	1.699	128.5	169.6
STO-3G	**A**	3.415	0.57	0.57	−0.21	−0.21	1.781	110.7	−7.3
	B	1.086	0.69	0.68	−0.37	−0.35	1.743	121.2	123.0
	C	0.000	0.70	0.71	−0.36	−0.36	1.743	121.2	168.8
3-21G	**A**	45.251	0.86	0.98	−0.28	−0.54	1.645	137.9	−7.7
	B	3.811	0.80	0.80	−0.44	−0.42	1.728	126.4	124.7
	C	0.000	0.82	0.82	−0.44	−0.43	1.722	126.9	173.8
6-31G	**A**	47.291	0.85	0.94	−0.20	−0.51	1.671	136.2	−7.7
	B	2.794	0.82	0.82	−0.40	−0.39	1.749	127.0	125.2
	C	0.000	0.83	0.84	−0.42	−0.40	1.744	127.0	174.2

[a] In kcal mol^{-1}. [b] In Å. [c] In degrees.

1.2 Ab initio calculations. The presence of low-lying d-orbitals on both the phosphorus and sulfur atoms usually preclude the use of ab initio methods on a routine basis for structural evaluation, except for relatively small systems, because of the large number of basis functions required to generate reliable results. For this reason ab initio calculations were carried out on the parent bis(thiophosphoryl)amine (**1a**) rather than the much larger bis(diphenylthiophosphoryl)amine (**1c**). In principle, the simple ligand can exist in two different tautomeric forms with the acidic hydrogen atom either bonded at one sulfur atom to form an intramolecular hydrogen bond with the other sulfur atom (**A**), or bonded at the nitrogen atom where the two sulfur atoms can adopt either a cis (**B**) or trans (**C**) conformation to one another. Two other possibilities, where either the acidic hydrogen atom is bonded to one sulfur atom only (**D**), or the two sulfur atoms adopt a cis conformation to the NH group (**E**), are unlikely to be favored because of the loss of an intramolecular hydrogen bond in the former and the inability of the ligand to form metal complexes by bonding both at sulfur and nitrogen in the latter (Scheme 3).

Accordingly, the three most relevant structures (**A**, **B**, and **C**) were calculated at the STO-3G, 3-21G, 6-31G, and TZVP levels and the relative energies and their geometrical features were then compared with those from MOPAC calculations.

Both AM1 and PM3 predict that the hydrogen-bonded tautomer (A) is favored over the others by at least 35 kcal mol^{-1} for the former and ~10 kcal mol^{-1} for the latter (Table 4) with the overall trend in stability for both cases showing $\mathbf{A} \gg \mathbf{B} \geq \mathbf{C}$. In contrast, MNDO predicts conformer **C** to be favored by a small margin over the others with the overall trend in this case showing $\mathbf{C} > \mathbf{B} > \mathbf{A}$. The cis-conformer **B** as written, however, is twisted substantially by the AM1 optimization to give a structure where one sulfur atom is positioned orthogonally to the other with the actual true representation an average of **A** and **B**. At the MNDO level, the torsion at the sulfur atom increases further, and at the PM3 level, the optimization moves the cis conformer **B** completely to the trans conformer **C**. In tautomer **A**, all three methods give planar conformations and show strong hydrogen bonds with the hydrogen atom almost equidistant between the two sulfur atoms, with average distances of 1.55, 1.68, and 1.65 Å for the MNDO, AM1, and PM3 methods, respectively.

The ab initio results all show conformer **C** to be favored by a small margin over the cis form **B** with both substantially lower

TABLE 5: Selected Geometries and Atomic Charges of Bis(dimethylthiophosphoryl)amine (1b) Calculated by Semiempirical and Ab Initio Methods

variable	3-21G	6-31G	6-31G*	PM3	AM1	MNDO
S_5-P_2	2.149	2.135	2.102	2.057	1.997	1.973
P_2-N_1	1.671	1.698	1.542	1.679	1.471	1.650
P_2-C_6	1.849	1.858	1.809	1.820	1.625	1.795
S_4-H_{10}	1.638	1.368	1.335	1.652	1.681	1.525
$S_4-P_2-N_1$	117.04	117.53	114.73	113.95	106.07	120.40
$P_3-N_1-P_2$	140.54	138.73	151.18	135.96	157.06	121.93
$C_7-P_2-C_6$	104.49	104.77	104.51	103.35	104.69	108.10
$S_4-P_2-N_1-P_3$	−1.1	−0.6	−5.3	0.2	−3.9	−6.4
$C_7-P_2-N_1-P_3$	123.4	124.1	115.7	124.6	114.1	117.1
			atomic charges			
S_5	−0.124	−0.488	−0.582	−0.696	−1.308	−0.290
H_{10}	+0.086	+0.135	+0.190	+0.267	+0.437	+0.170
P_3	+1.149	+1.113	+0.983	+1.514	+3.179	+0.303
N_1	−1.176	−1.222	−0.783	−1.109	−1.931	−0.607

in energy than the hydrogen bonded form **A** at the 3-21G, 6-31G, and TZVP levels. At the STO-3G level, the energy differences are less pronounced. However, the sulfur atom of the cis-conformer **B** is twisted by 120° in line with the semiempirical results to give a lower energy conformation that is nearer to the trans conformation (Table 4). Although all the ab initio methods give essentially planar conformations in tautomer **A**, the STO-3G method gives similar results to the semiempirical methods and suggests that the acidic hydrogen atom is bonded almost equally with the two sulfur atoms at distances of 1.587 and 1.575 Å, respectively. However, the more accurate methods show distinct hydrogen bonds in conformer **A**, with the H−S distances at 1.34 and 2.61 Å using TZVP, 1.36 and 2.53 Å using 3-21G, and 1.37 and 2.54 Å using the 6-31G basis set.

The ab initio and semiempirical calculations were next extended to bis(dimethylthiophosphoryl)amine (**1b**) initially in its SH tautomeric form, to assess the effect of carbon atoms bonded to phosphorus, particularly on the atomic charges at sulfur and phosphorus. Because of the increased size of this structure, a 6-31G* optimization was performed in place of the TZVP basis set used on the parent structure with polarization functions on sulfur and phosphorus only. The results obtained with the numbering system already shown (Table 5), are broadly similar to those calculated for the parent (**1a**) with the AM1 and PM3 methods, producing large charges at phosphorus. Surprisingly, the ab initio results also show similar trends for the two smaller basis sets, though the magnitude of the charge is somewhat smaller than the semiempirical values. These results show the necessity of using a large basis set coupled with polarization functions to produce reasonable charges at phosphorus and nitrogen.

The crystal structure of the tetramethyl ligand (**1b**),[15] however, exists in the NH tautomeric form (Scheme 3, B). Calculations were carried out using the three semiempirical methods and the same three basis sets, but the results again show that none of the methods is consistently close to the experimental structure (Table 6). At the ab initio level, the best results are obtained with the 6-31G* basis set with MNDO giving superior results to the other semiempirical methods (Table 6).

Overall, the results of these studies show that of the three semiempirical methods, the MNDO method gives a reasonable description of the geometries of two known structures, it produces sensible charges at sulfur, phosphorus, and nitrogen, and reproduces the tautomeric conformational preference of the more accurate ab initio methods. For these reasons, therefore, the MNDO method was used subsequently for the structure optimization of ligands used for zinc extraction (Table 1).

TABLE 6: A Comparison of the Calculated Geometries of the NH Tautomer of Bis(dimethylthiophosphoryl)amine (1b) Versus Experimental Data[a]

variable	3-21G	6-31G	6-31G*	PM3	AM1	MNDO	X-ray[b]
S_4-P_2	2.130	2.114	1.959	**1.949**	1.881	1.921	1.939
P_2-N_1	1.720	1.743	**1.692**	1.778	1.595	1.661	1.680
P_2-C_6	1.852	1.856	1.818	1.826	1.622	**1.797**	1.798
N_1-H_{10}	1.008	1.002	1.003	1.005	1.015	**0.999**	0.800
$S_4-P_2-N_1$	113.36	**114.37**	114.72	112.16	106.01	112.09	113.97
$P_3-N_1-P_2$	132.48	**133.03**	135.05	139.84	142.62	131.89	133.14
$C_7-P_2-C_6$	106.41	106.69	**105.04**	102.23	105.29	107.80	104.88
$S_4-P_2-N_1-P_3$	−2.5	−2.6	**−2.8**	**−2.8**	−2.4	−1.5	−3.2
$C_7-P_2-N_1-P_3$	121.1	121.4	**122.0**	124.0	120.1	120.8	122.2
rms[c]	1.74	0.71	0.71	2.55	4.20	1.43	

[a] Calculated value closest to X-ray structure data is highlighted in bold print. [b] Reference 15. [c] Root mean square deviation between X-ray and calculated values.

TABLE 7: Heats of Formation of the Conformers of the Bis((disubstituted)thiophosphoryl)amines (1) and Their Corresponding Bis(imido(tetrasubstituted)dithiodiphosphino-*S,S*) Zinc Complexes (5)[a]

structure	ligand conformer (**1**)					^{35}P NMR shift[b]	zinc complex (**5**)
	A	**B**	**C**	**D**	**E**		
d	**−5.41**	−1.46	−2.34	9.29	4.41	89	−18.77
e	−73.00	−67.79	**−74.85**	−52.39	−51.38	67	−153.09
f	−32.32	−28.46	**−40.73**	−38.53	−40.21	47	−
g	−60.46	−54.35	**−65.79**	−46.14	−55.75	68	−142.32
h	**−31.12**	−22.47	−29.61	−13.82	−13.02	85	−79.81
i	−184.6	−195.8	**−196.1**	−186.9	−195.4	56	−
j	**3.28**	4.78	8.02	11.34	24.28	86	−
m	−23.56	−13.50	**−28.23**	−12.17	−19.64	−	−68.17

[a] In kcal mol^{-1}; bold type shows the favored conformer. [b] In ppm (see Table 1).

2. Calculations on Experimental Bis(disubstitutedthiophosphoryl)amines (1). *2.1 Conformations of the Free Ligands.* The five possible tautomeric and conformational forms of the experimental ligands (Table 1) were identified for each structure, and full geometry optimizations were performed using the MNDO method. The results for the simple *iso*propyl ligand (**1d**) show that conformer **A** is most stable with a heat of formation of −5.41 kcal mol^{-1}, followed by conformers **C** and **B**, with energies of −2.34 and −1.47 kcal mol^{-1}, respectively; conformers **D** and **E** are the least favored (Table 7). Calculations were also carried out on the *n*-propyl derivative (**1m**), which would be expected to be a poor extractant, so as to provide a meaningful comparison between a simple α-branched ligand and its corresponding straight-chain analogue. In this case, **C** is the preferred conformer, with a heat of formation of −28.2 kcal mol^{-1} versus −23.6 and −19.6 for conformers **A** and **E**, respectively (Table 7). Significantly, the remaining two α-branched ligands (**1h**) and (**1j**) show a preference for the hydrogen bonded S−H tautomer (**A**), whereas all the others analogues prefer the trans conformation of the N−H tautomer **C** (Table 7).

Of the five conformers considered in these studies, only two **A** and **B** are correctly orientated to facilitate the formation of the zinc bis(chelate) (**5**) by a single-step mechanism, with the latter producing a coordinate complex only in the first instance. It follows that conformer **A** is likely to be the active chelating agent, with Zn^{2+} replacing the acidic hydrogen at sulfur. This feature may explain the highly selective performance of the α-branched ligands (**1d**, **1h**, and **1j**) that are good extractants and exist in the favored SH tautomeric cis orientation (**A**), and all of the other types that are weak extractants and are predicted to exist in the unfavored NH tautomeric trans arrangement (**C**). These structural differences also appear to explain the observed

TABLE 8: Calculated Geometries of Bis(imido(tetrasubstituted)Dithiodiphosphino-*S,S*) Zinc (5) Calculated by the MNDO Method and Experimental Geometries of the Related Iron (3) and Nickel (4) Complexes

	MNDO results			X-ray data	
geometric parameter[a]	**5d**	**5m**	**5c**	**3**[b]	**4**[c]
M	Zn	Zn	Zn	Fe	Ni
M−S	2.307	2.299	2.298	2.360	2.283
P−S	1.972	1.972	1.976	2.020	2.024
N−P	1.646	1.642	1.643	1.592	1.580
P−C	1.847	1.828	1.767	1.806	1.826
S−M−S	105.3	104.2	106.3	109.0	107.9
P−S−M	117.1	114.6	114.3	99.5	104.5
S−P−N	118.7	121.1	119.0	116.8	116.5
P−N−P	125.7	124.8	124.6	132.3	128.4
C−P−C	109.7	109.8	104.9	105.7	107.2
P−S−M−S	84.4	84.6	80.8	88.1	80.5

[a] Average value for bond lengths (in Å) and angles (in degrees). [b] Reference 19; CSD Refcode: IMSPFE10. [c] Reference 20; CSD Refcode: IMSPN10.

difference in the ^{31}P chemical shifts between the α-branched compounds and the other types (Table 7). In the former (**A**), the single phosphorus resonance observed at 89 ppm for **1d** and 85 ppm for **1h** is likely to be a time-averaged effect with the acidic SH hydrogen oscillating between the two sulfur atoms. On average therefore, the phosphorus atoms of this tautomer (**A**) form partial double bonds with both sulfur and nitrogen, and in the parent (**1a**), are positively charged with a value of 0.38 (Table 4). In the latter (**C**), the two phosphorus atoms are essentially equivalent, and here the phosphorus atoms form a double bond with sulfur but only a single bond with nitrogen, with an increased positive charge now of 0.58 in the parent (**1a**; Table 4). This difference in charge explains the upfield shift in the resonance of the phosphorus atoms to 67 ppm for **1e** and 68 ppm for **1g**. The replacement of the alkyl groups at phosphorus by phenoxy or ethoxy groups further increases the charge at phosphorus, because the four attached oxygen atoms are more electronegative than carbon, and consequently, the resonance moves further upfield to 47 ppm for **1f** and 56 ppm for **1i**.

2.2 Structure of the Zinc Bis(chelates). The crystal structures of both iron(II) bis(imidotetramethyldithiodiphosphino-*S,S*) (**3**)[19] and nickel (II) bis(imidotetramethyldithiodiphosphino-*S,S*) (**4**)[20] show very similar features in terms of the bond lengths and angles surrounding the phosphorus and sulfur atoms (Table 8). Because zinc also belongs to the first transition series and shows a tetrahedral geometry at the metal atom, the structure of the corresponding zinc bis(chelates) (**5**) at phosphorus and sulfur would be expected to be similar to the iron (**3**) and nickel (**4**) complexes also. Calculations were carried out, therefore, on the zinc chelates (**5**) corresponding to the bis(thiophosphoryl)-amine ligands (**1**) already explored, again using the MNDO method that is parametrized for zinc.[21]

The calculated structures for **5c**, **5d**, and **5m** show a reasonable fit with crystallographic data for the methyl-substituted tetrahedral iron (**3**) and nickel (**4**) chelates, with zinc in an approximately tetrahedral conformation (Table 8). Surprisingly, there is little to choose between the structures of the isopropyl (**5c**) and *n*-propyl (**5m**) chelates with almost identical values for the P−S and N−P bond lengths at 1.97 and 1.64 Å, respectively. However, the P−C bond length is longer in **5c** than that found in **5d**, with values here of 1.85 and 1.83 Å, respectively (Table 8). The angles and torsion angles are also similar for both complexes, with the value for P−S−Zn−S angle at 84° predicted to be similar to the corresponding angles in the iron (**3**) and nickel (**4**) complexes that have values of 88 and 81°, respectively (Table 8). Experimentally, there are a number of structures in the Cambridge Structural Database where zinc is coordinated to an S−P system. Here, the Zn−S bonds range from 2.27 to 2.51 Å, with a mean value of 2.36 Å, which support the calculated values of ∼2.30 Å at the MNDO level. The equivalent experimental values for the S−P bonds range from 1.90 to 2.06 Å, with a mean value of 2.00 Å, again supporting the MNDO value of ∼1.97 Å. Overall, therefore, the MNDO method appears to give a good account of the expected structure of the zinc bis(chelates).

The zinc bis(chelates) formed from both the α-branched ligands and their corresponding straight-chain analogues are predicted to be stable (Table 7), and the explanation for the inability of the latter to form a complex under the experimental conditions reported here must lie therefore with the relative populations of the active complexing conformer (**A**) present for each ligand at the extraction temperature (25 °C). For the straight-chain bis(di-*n*-pentylthiophosphoryl)amine (**1g**), the energy difference between the energetically favored conformer **C** and the active conformer **A**, which is able to form the bis-(chelate) (**5g**), is 5.33 kcal mol^{-1} (Table 7). The Boltzmann distribution for the relative populations of **A** and **C** based on this energy difference at 25 °C yields a ratio 1:8103 in favor of the latter, which partly explains why this ligand does not form the zinc bis(chelate) under the experimental conditions, assuming entropic factors are similar for the two species.

This argument is less convincing for bis(di-*n*-2-ethylhexyl-thiophosphoryl)amine (**1e**) where the energy difference between the energetically favored conformer **C** and the active conformer **A** is only 1.85 kcal mol^{-1} (Table 7), yielding a Boltzmann distribution of 1:22.7 in favor of the former. However, there is no simple mechanism where the acidic hydrogen can move from the nitrogen atom of conformer **C** to the sulfur atom of conformer **A** in aprotic solvents such as Escaid or chloroform. This result may explain why this ligand does not apparently form the zinc bis(chelate) under the experimental conditions though ∼4% would be expected from the simple Boltzmann distribution.

Overall, the driving force of the chelation reaction is almost certainly dominated by the entropy of the process and although there is little experimental data available on the systems considered here, the free energy, enthalpy, and entropy of related chelation reactions is known. For example, in the formation of zinc bis(acetylacetonate) in water, the free energy of chelation of 10.6 kcal mol^{-1} is dominated by an entropy contribution of +7152 e.u. (68%).[21] However, for sulfur containing ligands this appears to rise and in the case of zinc bis(α-mercaptopropanoate), the free energy of chelation of 19.4 kcal mol^{-1} is dominated by the entropy contribution of +16390 eu (85%).[22] This result implies that the orientation of the chelating sulfur atoms in the ligand may be of crucial importance in the entropic process, which results in the displacement of six water molecules from the octahedral $[Zn(OH_2)_6]^{2+}$ complex present in the aqueous phase of the extraction process to give the solvent soluble zinc bis(chelate).

Conclusions

At the semiempirical level, the MNDO method gives atomic charges and geometries for the bis(disubstitutedthiophosphoryl)-amines (**1**) that are superior to either the AM1 or PM3 methods. The MNDO method also gives a good account of the structure of the corresponding zinc bis(chelates) (**5**). The calculations suggest that the different performance of the α-branched ligands (**1d**, **1h**, and **1j**), which are good extractants, and all of the other types, which are weak extractants, arise because the former exist in a favored SH tautomeric cis orientation (**A**), whereas the latter exist in an unfavored NH tautomeric trans arrangement (**C**). These structural differences also appear to explain the observed difference in the ^{31}P chemical shifts between the α-branched compounds and the other types.

References and Notes

(1) U. S. Patent 3428449 (to General Mills Corporation).

(2) U. S. Patent 342449 (to ICI PLC); Dalton, R. F.; Massam, J. P.; Tumilty, J. A. *Advances in Extractive Metallurgy*, Institute of Mining and Metallurgy, London, 1977; p 123.

(3) Leveque, A.; Helgorsky, J. *International Solvent Extraction Conference 1977, Canadian Institute of Mining*, Special Vol. 21, p 439.

(4) *Productivity and Technology in the Metalurgical Industries*; Koch, M.; Taylor, J. C., Eds.; pp 695−703; Caravaca, C.; Alhuacil, F. J. *Hydrometallurgy* **1991**, *27*, 327.

(5) Handley, T. H. *Anal. Chem.* **1963**, *35*, 991.

(6) U. S. Patent 5393431 (to Zeneca Ltd.); Campbell, J.; Dalton, R. F.; Quan, P. M., personal communication.

(7) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. P. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902.

(8) *QCPE Program 455*, Department of Chemistry, Indiana University, Bloomington, Indiana, 47405.

(9) Dewar, M. J. S.; Jie, V. *J. Mol. Struct. (THEOCHEM)* **1989**, *187*, 1.

(10) Dewar, M. J. S.; Yuan, Y.-C. *Inorg. Chem.* **1990**, *29*, 3881.

(11) Dewar, M. J. S.; Thiel, W. J. *J. Am. Chem. Soc.* **1977**, *99*, 4899.

(12) Stewart, J. J. P. *J. Comput. Chem.* **1989**, *8*, 1004.

(13) (a) See for example: Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; John Wiley and Sons: New York, 1986; (b) For a detailed description of the triple-ζ valence polarized basis set see: Dunning, T. H. *J. Chem. Phys.* **1971**, *55*, 716; McLean, A. D.; Chandler, G. S. *J. Chem. Phys.* **1980**, *72*, 5639; Binning, R. C.; Curtiss, L. A. *J. Comput. Chem.* **1990**, *11*, 1206.

(14) GAMESS−UK is a package of ab initio programs written by Guest, M. F.; van Lethe, J. H.; Kendrick, J.; Schoffel, K.; Sherwood, P.; Harrison, R. J., with contributions from Amos, R. D.; Buenker, R. J.; Dupuis, M.; Handy, N. C.; Hiller, I. H.; Knowles, P. J.; Bonacic-Koutecky, V.; von Niessen, W.; Saunders: V. R.; Stone, A. (available form The Daresbury Laboratory, Warrington, UK). The package is derived from the original GAMESS code due to Dupuis, M.; Spangler, D.; Wendoloski, J. NRCC Software Catalogue, Vol. 1, Program No. QG01 (GAMESS), 1980.

(15) Silvestru, C.; Rosler, R.; Haiduc, I.; Cea-Olivares, R.; Espinosa-Perez, G. *Inorg. Chem.* **1995,** *34*, 3352.

(16) Noth, H. *Z. Naturforsch., Chem. Sci.* **1982**, *37*, 1491.

(17) Ziegler, M. L.; Weiss, J. *Z. Anorg. Allg. Chem*. **1968**, *361*, 136.

(18) *Cambridge Structural Database*, Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge, CB2 2EW, UK 11.

(19) Churchill, M. R.; Wormald, J. *Inorg. Chem.* **1971**, *10*, 1778.

(20) Churchill, M. R.; Cooke, J.; Fennessy, J. P.; Wormald, J. *Inorg. Chem.* **1971**, *10*, 1031.

(21) Dewar, M. J. S.; Mertz, K. M. *Organometallics* **1986**, *5*, 1494.

(22) Martell, A. E.; Smith, R.M. *Critical Stability Constants*, Vol. 3; Plenum: New York, 1977; and references therein.