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Insignificance of P−H···P Hydrogen Bonding: Structural Chemistry of Neutral and Protonated 1,8-Di(phosphinyl)naphthalene

Stephan A. Reiter,[†] Stefan D. Nogai,[†] Konstantin Karaghiosoff,[‡] and
Hubert Schmidbaur*,[†]

Contribution from the Department Chemie, Technische Universität München, Lichtenbergstrasse 4, 85747 Garching, Germany, and Department Chemie und Biochemie, Ludwig-Maximilians-Universität München, Butenandtstrasse 5-13 (D), 81377 München, Germany

Received July 28, 2004; E-mail: H.Schmidbaur@lrz.tum.de

Abstract: While there is extensive information on 1,8-di(amino)naphthalene (i.e., the parent compound of the "proton sponge" series), the corresponding phosphorus compound has not been described. A high-yield synthesis of 1,8-di(phosphinyl)naphthalene (**9**) and the 1-naphthylphosphine reference compound (**4**) is now reported. Thermal decomposition of **9** leads to intramolecular dehydrogenative P−P coupling to afford 1,2-dihydro-1,2-diphosphaacenaphthene (**10**). Protonation of **9** and **4** with CF_3SO_3H gives quantitative yields of the monophosphonium salts **11** and **5**, respectively. With excess acid and traces of moisture, the hydronium salt $[C_{10}H_6(PH_2)(PH_3)]^+[H_3O]^+2[CF_3SO_3]^-$ (**13**) is obtained. The structures of **9**, **11**, and **13** have been determined. Molecules of **9** have a planar naphthalene skeleton, $C_{10}H_6P_2$, with the two $-PH_2$ groups in a transoid conformation. The molecules form loose dimers in the crystal, the individual chiral enantiomers of which are related by a center of inversion. In contrast to the situation for the amino analogue, and despite the proximity of the two $-PH_2$ functions, there is no intra- or intermolecular hydrogen bonding. Solutions of **9** (in CD_2Cl_2) show equivalent P-bound hydrogen atoms due to conformational fluctionality. By analysis of the $ABCD_2XX'D'_2C'B'A'$ spin system, it was shown that, in **9**, there are strong through-space pericouplings [$^nJ(P_XP_{X'}) = 221.6$ Hz, $^nJ(P_XH_{D'}) = 31.7$ Hz, $^nJ(H_DH_{D'}) = 3.9$ Hz]. In the cations of **11**, the $C_{10}H_6P_2$ skeleton is also planar (by C_s symmetry), with the $-PH_2$ and $-PH_3^+$ groups in a conformation which rules out any P−H···P hydrogen bonding. The hydronium cation and the two triflate anions in **13** are associated into an anionic network through extensive hydrogen bonding surrounding stacks of the phosphonium cations. In solution, the cations of **11** and **13** show separate ^{31}P resonances for the two phosphorus atoms with fully resolved $^1J(PH)$ couplings, which indicate that there is no intra- or intercationic proton exchange. By contrast, the NMR spectra of solutions of $[C_{10}H_6(NH_2)(NH_3)]^+X^-$ salts show proton scrambling equilibrating all five N-bound hydrogen atoms, and in the crystal, the conformations of the cations feature intramolecular N−H···N hydrogen bonding.

Introduction

For almost half of a century, peridisubstituted naphthalenes have received unabating interest.[1] Their unique stereochemistry gives rise to many unusual properties, of which the behavior as "proton sponges"[2−4] or the action as "anion pincers" are most prominent.[5−7] Functional groups in the 1,8-positions of naphthalene are held in proximity and experience significant steric strain as their size is increased beyond that of hydrogen (in naphthalene itself).[1] The consequences are readily discernible from peculiar structural details of the molecular geometries, from spectroscopic properties, and from the striking differences in reactivity of peridisubstituted as compared to 1-monosubstituted naphthalenes.

The extensive literature on 1,8-disubstituted naphthalenes has detailed information on all prototypes of formulas **A** and **B**. The directly bonded element in functions X can be taken from almost any group of the s- and p-block elements. In the first octet period, with substituents for type **A** ranging from X = F to X = Li,[8] the classes of compounds include simple diols and ethers (X = OR),[9] diamines (X = NR_2),[2] dialkyls (X = R),[10−13]

[†] Technische Universität München.

[‡] Ludwig-Maximilians-Universität München.

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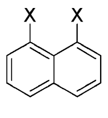
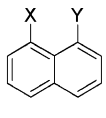
diboryls (X = BR$_2$), and their derivatives.[5] (There is only a blank for beryllium, and generally for X representing a group 2 element, but a few magnesium[14] and mercury compounds[7] have been described.)



A
A1 X = NH$_2$
A2 X = NMe$_2$



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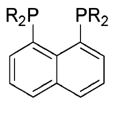
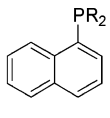


C
C1 R = H
C2 R = Me



D
D1 R = H
D2 R = Me

For a long time, research has focused mainly on the diamines, for which drastic changes of the Brönsted basicity were observed as the substitution pattern was gradually changed from the free diamine to the tetraalkylated species.[2−4,15] While 1,8-diaminonaphthalene (**A1**) exhibits about the same basicity as 1-aminonaphthalene (or aniline), the p*K* of 1,8-bis(dimethylamino)-naphthalene (**A2**) is increased by 7 orders of magnitude as compared to 1-(dimethylamino)naphthalene. This strongly enhanced proton affinity (proton sponge behavior) of **A2** as compared to that of **A1** is caused by the introduction of the four substituents, but clearly not only through the standard inductive effect of alkyl groups, which is also operative in 1-(dimethylamino)naphthalene. It is rather the steric congestion in the tetraalkylated compounds which forces the lone pairs of electrons at the two nitrogen atoms into the "bay region" of the molecule. Relief of the strongly repulsive interactions in this region[1] (the "peristress") by protonation is the main reason for the extreme proton affinity of perinaphthalene proton sponges. For highly strained **A2**, the incoming proton is accommodated in a central position between the two nitrogen atoms,[2] while for the less-strained unsubstituted prototype **A1**, the proton is attached to one of the two nitrogen atoms and forms a hydrogen bond with the neighboring $-NH_2$ group.[16,17]

Phosphines are much poorer Brönsted bases than amines, and strong acid (HZ = HI or HClO$_4$) is required to convert PH$_3$ or primary phosphines, RPH$_2$, into the corresponding phosphonium salts $PH_4^+Z^-$ and $RPH_3^+Z^-$, respectively. Because of this low proton affinity of phosphines, the protonation equilibria of these compounds have received only limited interest, and the proton sponge effect in polyphosphines has not yet been a major issue. In an earlier investigation carried out in our laboratory, bis(dimethylphosphinyl)naphthalene (**C2**) and 1-(dimethylphosphinyl)naphthalene (**D2**) were prepared, and some of their fundamental reactions were studied;[18] however, the simple primary phosphines **C1** and **D1** were not available, and no direct comparison could be made.

In the period since 1980, the chemistry of 1,8-disubstituted naphthalenes of type **C**, with two phosphorus substituents, has grown enormously, and there is a vast literature dealing mainly with the elusive periinteractions between two phosphorus atoms in various oxidation states and with a variety of substitution patterns.[19,20] Yet, the simple prototype, 1,8-di(phosphinyl)-naphthalene **C1**, has not been prepared. We therefore recently resumed our studies in this field and are now able to present some results which provide information on the fundamental structural characteristics of this molecule. The protonation of **C1** with trifluoromethanesulfonic acid has been studied, and the structure of the corresponding phosphonium salt has been determined.

The work presented in this account also complements earlier studies on the related 1,8-di(silyl)naphthalenes, which included determination of the molecular structure of 1,8-$(H_3Si)_2C_{10}H_6$ (**A**, X = SiH$_3$).[21] There is extensive literature on derivatives with triorganosilicon, -germanium, and -tin substituents.[22] The new results thus fill the gap between this disilane and the dithiole 1,8-$(HS)_2C_{10}H_6$ (**A**, X = SH). Similar to this dithiol,[23] the new diprimary phosphine **C1** is an interesting, and yet unexplored, chelating ligand of extreme rigidity which can be transformed into many other disecondary and ditertiary phosphine derivatives with diverse stereochemistry.

Preparative and Analytical Results

As a test run for the preparation of the target molecule (**C1**), 1-naphthylphosphine **D1** has been obtained as a suitable reference compound (**4**, Scheme 1). For its synthesis, 1-naphthyllithium (**1**) was treated with bis(diethylamino)chlorophosphine in tetrahydrofuran to give bis(diethylamino)(1-naphthyl)-phosphine (**2**).[24] This product was readily converted into dichloro(1-naphthyl)phosphine (**3**)[24,25] upon treatment of its solution in hexane with dry hydrogen chloride (83% yield) and finally into 1-naphthylphosphine in the reaction with lithium aluminum hydride in diethyl ether (90% yield). **4** was prepared previously by dearylation of tri(1-naphthyl)phosphine, but no details were given.[26] It is a colorless, distillable liquid (bp$_{0.9}$ 87 °C), which crystallizes upon cooling at −26 °C. Its ^{1}H-coupled ^{31}P NMR spectrum (in CD$_2$Cl$_2$) shows a sharp triplet of doublets for the $-PH_2$ group at δ −133.5 ppm [$^1J(PH) = 203.5$ Hz, $^3J(PH) = 8.0$ Hz]. Other details are given in the Experimental Section.

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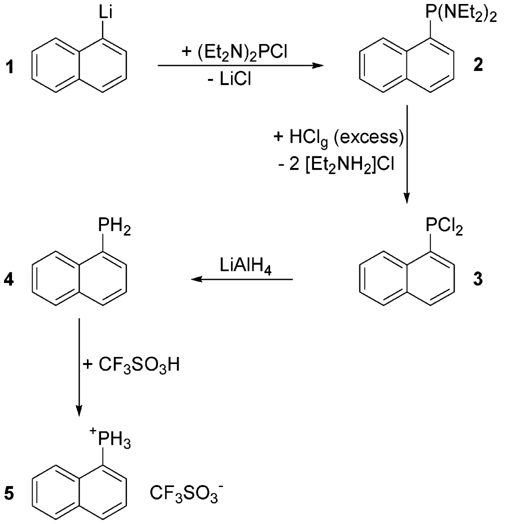
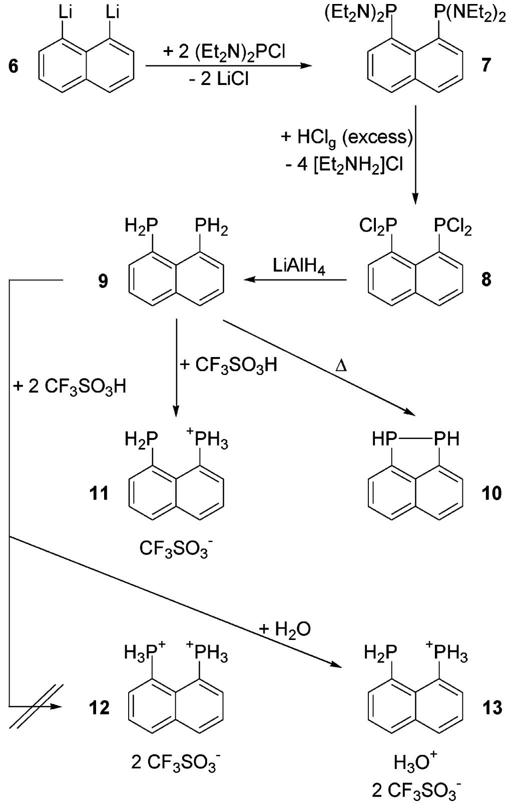
Scheme 1. Preparation of 1-Naphthylphosphines (**D**)



Scheme 2. Preparation of 1,8-Di(phosphinyl)naphthalenes (**C**)



Treatment of **4** with equimolar quantities of trifluoromethanesulfonic acid in dichloromethane gave almost quantitative yields of the corresponding phosphonium triflate $[(1\text{-}C_{10}H_7)PH_3]^+[CF_3SO_3]^-$ (**5**). Its ^{31}P resonance in the ^1H-coupled spectrum in CD_2Cl_2 is a quartet shifted downfield quite drastically to δ −53.4 ppm, with the coupling constant, $^1J(PH)$, rising from 203.5 Hz in **4** to no less than 546.9 Hz, indicating the significant increase in the s-character of the phosphorus orbitals to sp^3.

A similar reaction sequence (Scheme 2), starting with 1,8-dilithionaphthalene (**6**), affords 1,8-bis[bis(diethylamino)phosphinyl] (**7**) and bis(dichlorophosphinyl)naphthalene (**8**, 82% yield).[27] While previous attempts to obtain **C1** by $LiAlH_4$ reduction of bis(dimethoxyphosphinyl)- or bis(dimethoxyphosphoryl)naphthalene were not successful,[28] the same reduction of $1,8\text{-}(Cl_2P)_2C_{10}H_6$ in diethyl ether gave a 78% isolated yield of **9** as a crystalline solid (mp 82 °C, from dichloromethane solution). Solutions of **9** in CD_2Cl_2 at 25 °C show a singlet resonance in the ^1H-decoupled ^{31}P NMR spectrum at δ −104.9 ppm. In the ^1H-coupled form, the spectrum is exceedingly complex (Figure 1), as expected for the X-part (P) of an $ABCD_2$-$XX'D'_2C'B'A'$ spin system, where A/A′, B/B′, and C/C′ denote the (magnetically nonequivalent) protons of the hydrogen atoms in the 2,7-, 3,6-, and 4,5-positions of the naphthalene, respectively, and D/D′ the hydrogen atoms bound to the phosphorus atoms. The ^1H and $^{13}C\{^1H\}$ NMR spectra which yield additional, very significant information have also been recorded and analyzed and are discussed in some detail below.

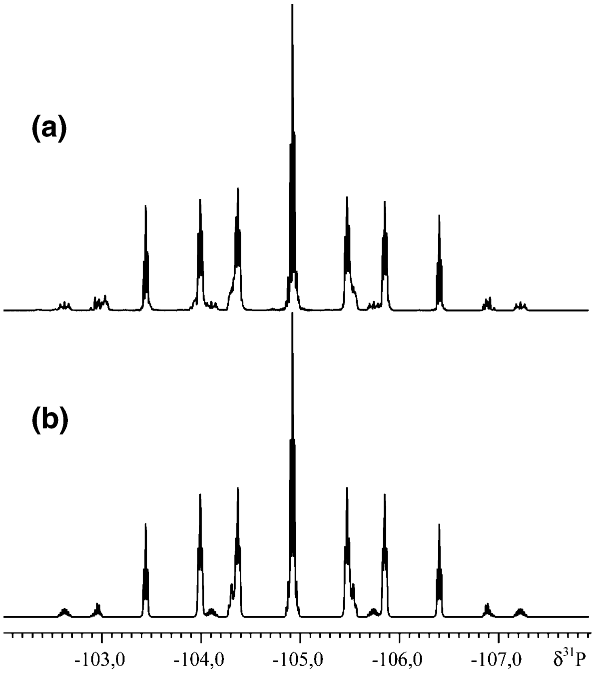


Figure 1. ^{31}P NMR spectrum of compound **9**. (a) Experimental spectrum (in CD_2Cl_2 at 25 °C) and (b) calculated spectrum. (For details, see Table 1.)

Table 1. ^1H NMR Data (δ [ppm], J [Hz]) of Compound **9** (simulated as an $[ABCD_2X]_2$ spin system, $\delta_X = \delta_P$)

δ_A	7.83; $\Delta_{1/2} = 0.6$ Hz	$J_{AX'} = J_{A'X}$	−0.4(1)
δ_B	7.31; $\Delta_{1/2} = 0.8$ Hz	J_{BC}	8.2(1)
δ_C	7.77; $\Delta_{1/2} = 1.0$ Hz	J_{BX}	0.7(1)
δ_D	4.58; $\Delta_{1/2} = 1.1$ Hz	J_{CX}	−1.2(1)
J_{AB}	7.0(1)	$J_{DD'}$	3.8(1)
J_{AC}	1.4(1)	J_{DX}	207.7(1)
J_{AD}	1.0(1)	$J_{DX'} = J_{D'X}$	31.7(1)
$J_{AD'} = J_{A'D}$	0.2(1)	$J_{XX'}$	−221.6(1)
J_{AX}	−6.1(1)		

The NMR spectra of the crude reaction product (prior to recrystallization of **9**) indicated that a byproduct was present in the reaction mixture, which was identified as *trans*-1,2-dihydro-1,2-diphosphaacenaphthene, **10** [δP −103.7 ppm, in CD_2Cl_2]. It is the product of dehydrogenative P−P coupling, which may occur upon successive substitution of the chloride by hydride substituents. It was noted that **10** is also formed during the GC−

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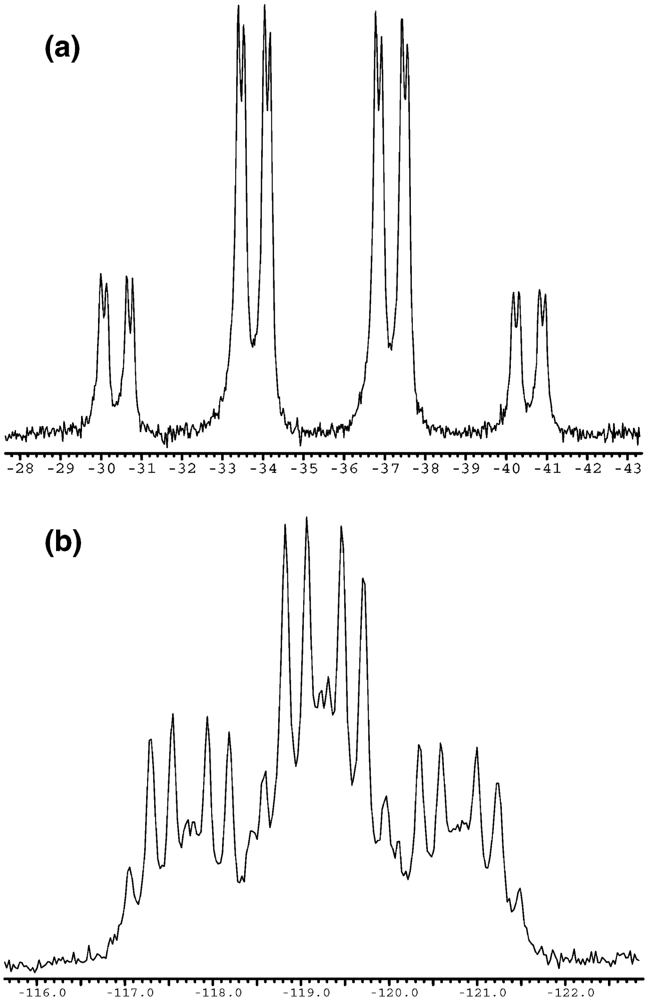

Figure 2. ^{31}P NMR spectrum of **11** (in CD_2Cl_2 at −80 °C). (a) PH_3^+ signal and (b) PH_2 signal. (For details, see Experimental Section.)

MS analysis of pure **9**, owing to pyrolysis in the hot GC columns. The P,P′-diphenylated 1,2-dihydro-1,2-diphospha-acenaphthene derivative has recently been described,[29] and the 1,2-dihydro-1,2-disilaacenaphthene is also known.[30]

Equimolar quantities of the diprimary phosphine **9** and triflic acid in dichloromethane were shown to form high yields (86%) of the corresponding monophosphonium monotriflate **11**. The ^{1}H-decoupled ^{31}P NMR spectrum of this product (in CD_2Cl_2 at −80 °C) shows two separate doublet resonances of equal intensity at δ −119.3 and −35.5 ppm [^4J(PP) = 107.0 Hz], which are readily assigned to the $-PH_2$ and $-PH_3^+$ groups, respectively, as suggested by the data of the reference compounds **4** and **5**. In the ^{1}H-coupled spectrum (under similar conditions), the two resonances have the first-order tdq and qdd multiplicities, as expected for the X,Y-part of an AD_2XYE_3F spin system, with X and Y denoting the two phosphorus nuclei, D and E the P-bound hydrogen nuclei, and F and A the nuclei of the hydrogen atoms in the 2,7-positions of the naphthalene (Figure 2; note that this labeling is not identical with that used for **9** because of the lower symmetry).

This result clearly indicates that in CD_2Cl_2 solution, salt **11** features a 1-(8-phosphinylnaphthyl)-substituted monophosphonium cation (i.e., only one of the two phosphinyl groups has been protonated). The extra proton is not in a symmetrical position between the two P atoms, and any quite conceivable proton exchange between the two P atoms is slow on the NMR time scale (at −80 °C). Line broadening observed at higher temperatures is evidence that such an exchange is becoming more rapid, which leads to coalescence at room temperature. An estimation of the activation energy for the exchange process was not made because of limited reproducibility of the experiments, which is due to the extreme sensitivity of the system to any traces of moisture.

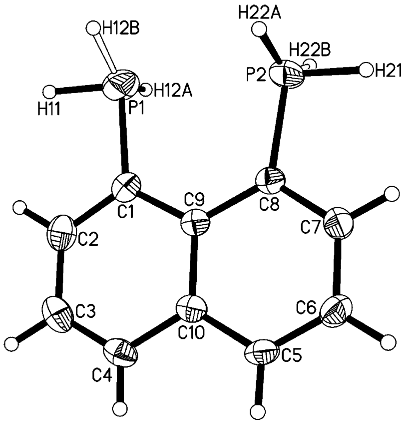

Figure 3. Molecular structure of compound **9** with atomic numbering (ORTEP, 50% probability ellipsoids). Hydrogen atoms H12 and H22 are disordered over two positions each.

Attempts to prepare the 1,8-diphosphonium salt by using 2 equiv of rigorously dried triflic acid in dichloromethane at room temperature did not afford a well-defined product (**12**). However, if residual water was present in the triflic acid, or water was added deliberately, high yields (89%) of a product could be crystallized, which was shown to have the stoichiometry of a monohydrate of the expected bis(phosphonium) bistriflate (**13**). Even though the NMR spectra of its solutions (in CD_2Cl_2 at −80 °C) showed severe line broadening, the overall pattern suggested that the compound contains the same cation as monotriflate **11**. This result was confirmed by the single-crystal X-ray diffraction analysis which revealed the presence of a hydronium cation, $[H_3O]^+$, and two triflate anions along with the 1-(8-phosphinylnaphthyl)phosphonium cation already identified as a constituent of **11** (vide infra). The stoichiometry is therefore best represented by the formula $[1\text{-}(8\text{-}H_2PC_{10}H_6)PH_3]^+\text{-}[H_3O]^+2[CF_3SO_3]^-$ (**13**); it appears that the diprimary phosphine **9** can only be monoprotonated, and the incoming proton is strictly localized at one of the phosphorus atoms.

Crystal and Molecular Structure of 1,8-Di(phosphinyl)-naphthalene. Crystals of 1,8-di(phosphinyl)naphthalene (**9**) are monoclinic, with space group $P2_1/n$ and $Z = 4$ formula units in the unit cell (at 143 K). The molecules have no crystallographically imposed symmetry, but they approach quite closely to a point group C_2 geometry. While one hydrogen atom of each phosphinyl group is readily localized in the reference plane of the hydrocarbon unit, the second one is disordered over two positions above and below this reference plane (Figure 3). The molecule has the conformation designated as “all-eclipsed” in previous studies of substituted analogues, referring to the relative orientation of the hydrogen atoms at C2/C7 and one of the hydrogen atoms at P1/P2.[27a,31] Strictly speaking, the disorder

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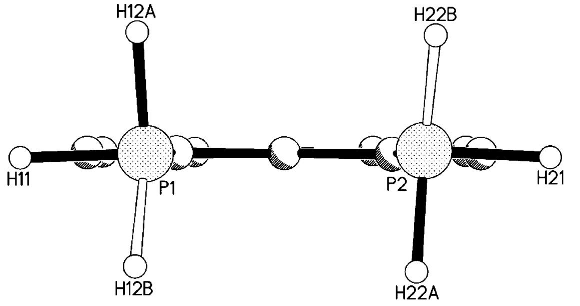

Figure 4. Projection of the structure of molecule **9** along the C9−C10 axis (arbitrary radii, atomic numbering as in Figure 1), showing a superposition of the two enantiomeric transoid conformations (which are disordered in the crystal).

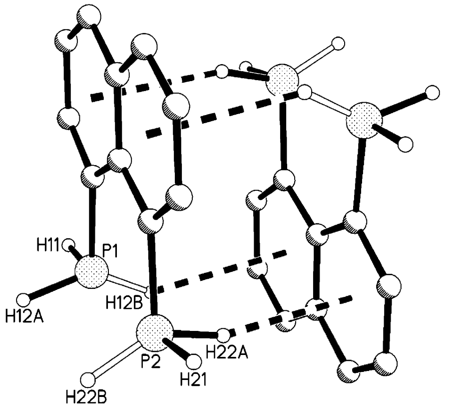

Figure 5. Pairs of enantiomeric molecules **9** in the crystal (arbitrary radii). Hydrogen atoms H22A are in a "phenyl-embraced" orientation. (Note the disorder of hydrogen atoms H12 and H22.)

of a pair of hydrogen atoms (H12 and H22) over four positions, with about equal probability, precludes the decision about a cisoid (point group C_s) or transoid arrangement (point group C_2) of these hydrogen atoms. The latter has tentatively been chosen for the presentation in Figure 4, referring to the geometry of several P,P′-disubstituted derivatives (**C**, R = Cl, Ph, NMe_2, and so forth),[19,27b,32,33] for which the transoid structure has been confirmed by single-crystal X-ray diffraction studies.

Quantum chemical calculations have also shown unambiguously that the transoid conformation (C_2) is lower in energy than the cisoid conformation (C_s), while the C_{2v} conformation (with overlapping lone pairs of electrons at the two P atoms) is a high-energy transition state for the rotation of the $-PH_2$ groups about their P−C axes.[31] With H12 and H22 in transoid positions, the molecules are chiral, and the crystals of **9** contain both enantiomers.

The naphthalene unit shows only very minor deviations from planarity [the maximum C−C−C−C torsional angle is −1.2(1)° for C1−C9−C10−C5], and the two phosphorus atoms reside almost exactly in the plane of the hydrocarbon unit as indicated by the small torsional angles P1−C1−C9−C8 [−0.2(2)°] and P2−C8−C9−C1 [1.7(2)°] (Figures 3 and 4). However, there is considerable distortion of the bay area geometry within the reference plane, which is best demonstrated by the bond angles P1−C1−C2 = 116.9(1)° and P2−C8−C7 = 116.6(1)°. Thus, the P−C bonds are tilted by ~3° in opposite directions in order to minimize steric repulsion between the two $-PH_2$ groups ("perispace crowding").

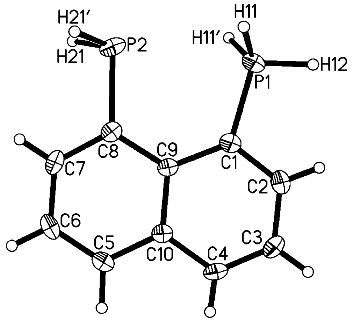

Figure 6. Structure of the cation of compound **11** (mirror symmetry, ORTEP, 50% probability ellipsoids) with atomic numbering.

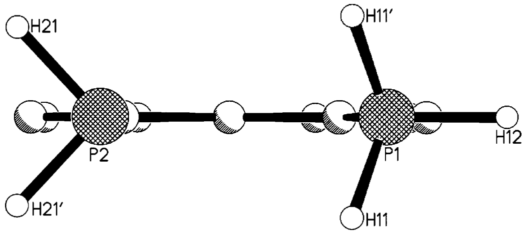

Figure 7. Projection of the structure of the cation in compound **11** along the C9−C10 bond (arbitrary radii, atomic numbering as in Figure 6).

The packing of the molecules of **9** in the crystal is *not* governed by intermolecular hydrogen bonds. It rather features pairs of enantiomers with the molecular planes parallel (the two molecules being related by a center of inversion). The two components of these dimeric units show no $\pi-\pi$ stacking (the naphthalene parts are not facing each other) but have each H22−P bond pointing toward a center of a benzene ring of a neighboring naphthalene unit (Figure 5). The H22 centroid distance of 2.534 Å may indicate very weak hydrogen bonding of the "phenyl embrace"-type.[34]

There is still a paucity of structural data for the supramolecular chemistry of primary arylphosphines. In a previous structural study of primary phenylphosphines, we have shown that there is no evidence for significant hydrogen bonding in the crystals of 1,3,5-chlorophosphinylbenzene molecules, $[C_6H_3Cl_x(PH_2)_{3-x}]$, and the present results support the conclusions drawn from these earlier findings.[35]

Crystal and Molecular Structures of the 1-(8-Phosphinylnaphthyl)phosphonium Trifluoromethanesulfonates (11 and 13). Crystals of triflate salt **11** are orthorhombic, with a space group *Pbcm* and $Z = 4$ formula units in the unit cell, and contain $[C_{10}H_6(PH_2)(PH_3)]^+$ cations and $[CF_3SO_3]^-$ anions, which have no unusually short interionic contacts. The naphthalene unit and the P atoms ($C_{10}H_6P_2$) are coplanar by symmetry, with the crystallographically imposed mirror plane relating the two hydrogen atoms at P2 and two of the three hydrogen atoms at P1 (Figure 6). Referring to the conformation of the di(phosphinyl)naphthalene precursor, molecule **9**, in the crystal, we notice that one $-PH_2$ group has been protonated, resulting in a quasi-tetrahedral coordination of this P atom (P1)

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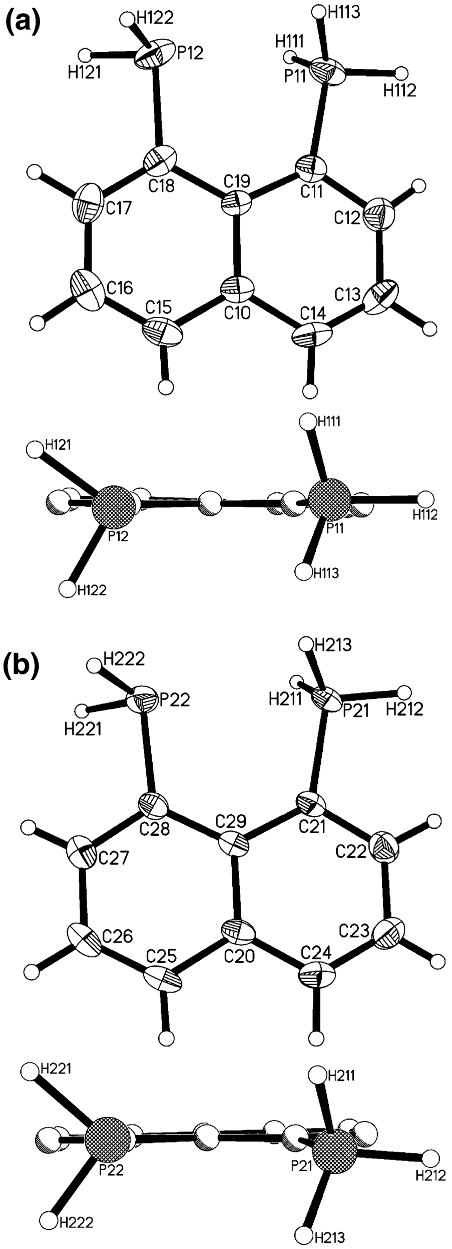


Figure 8. (a and b) Structures of the two independent phosphonium cations in compound **13** (ORTEP, 50% probability ellipsoids) with atomic numbering. In the lower parts, the projections along the bonds C19−C10 and C29−C20 are shown, respectively.

in **11**, and this group is in an eclipsed conformation as related to the hydrogen atom at C2 (Figure 7). Consequently, the nonprotonated $-PH_2$ group has rotated into a staggered conformation as related to the hydrogen atom at C8, which places the vector of the lone pair at P2 in the molecular plane bisecting the angle H11−P1−H11′. In this reorganization, the distortion of the angle P1−C1−C2 [112.0(2)°] has increased very significantly (from an average of 116.5° in **9**), while the angle P2−C8−C7 has increased from 116.5 to 119.1(2)°, indicating an almost strain-free "upright" position of the $-PH_2$ group.

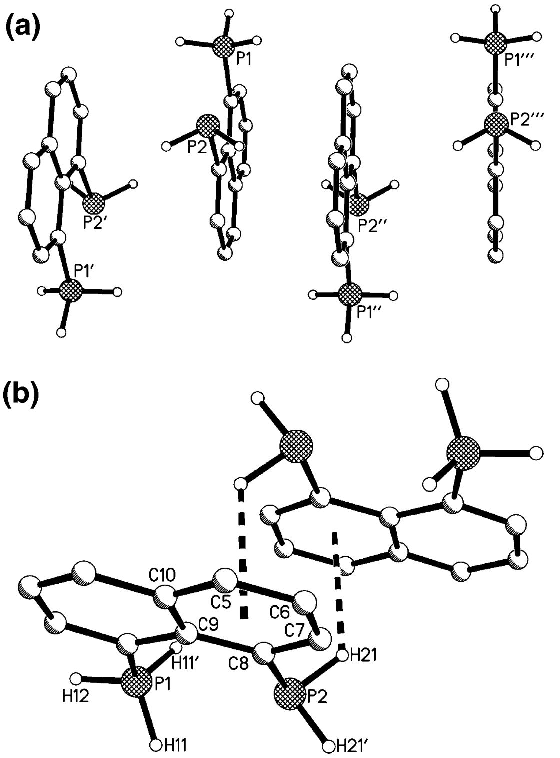


Figure 9. (a) Stacking of the cations in crystals of compound **11**. (b) A pair of adjacent cations showing the weak "phenyl-embrace" type interactions with hydrogen atoms H21 (no $\pi-\pi$ stacking).

Crystals of bistriflate **13** are monoclinic, with the space group $P2_1/n$ and $Z = 8$ formula units in the unit cell. The asymmetric unit contains two sets of crystallographically independent components, including the cations also present in **11**, hydronium cations $[H_3O]^+$, and triflate anions. The geometrical details of the two sets are very similar, and no separate treatment is necessary. The $[C_{10}H_6(PH_2)(PH_3)]^+$ cations have no crystallographically imposed symmetry, but their conformation approaches quite closely to that described for **11** (Figure 8). With an entirely different environment of these cations in **11** and **13**, this result suggests that the conformation represents the true, intrinsic ground state, which is not greatly influenced by crystal packing or other external directional forces. This is particularly obvious from the small angles, P11−C1−C2 = 111.5(2)° and P21−C21−C22 = 111.6(2)° that are observed for the $-PH_3^+$ groups, and the "upright" orientation of the $-PH_2$ groups, with angles of P12−C18−C17 = 120.0(2)° and P22−C28−C27 = 119.0(2)°. It is obvious that this orientation rules out any conventional hydrogen bonding between the two phosphorus atoms in the cations of **11** and **13**.

In the unit cells of **11** and **13**, the phosphonium cations show a different stacking pattern. In the former, along the column of (equivalent) cations, no arene $\pi-\pi$ stacking is observed since the nonpolar $C_6H_3PH_2$ groups lie on top of each other in a head-to-tail arrangement (i.e., with the $-PH_2$ group on top of a benzene ring) (**11**, Figure 9). In the latter, there is alternating $\pi-\pi$ stacking of the $C_6H_3PH_2$ parts of the two nonequivalent cations (**13**, Figure 10). In both types of columns (**11** and **13**), the cationic functions of $-PH_3^+$ are located in the periphery, where they are close to the anions.

The hydronium cations, $[H_3O]^+$, and the triflate anions, $[CF_3SO_3]^-$ (in a 1:2 ratio), in crystals of **13** are associated through strong hydrogen bonds to give an anionic network around the columns of the phosphonium cations. Two of the triflate anions are in bridging positions between two hydronium cations, while of the other two, each one is attached to only one of the two $[H_3O]^+$ cations. Each $[H_3O]^+$ cation is attached

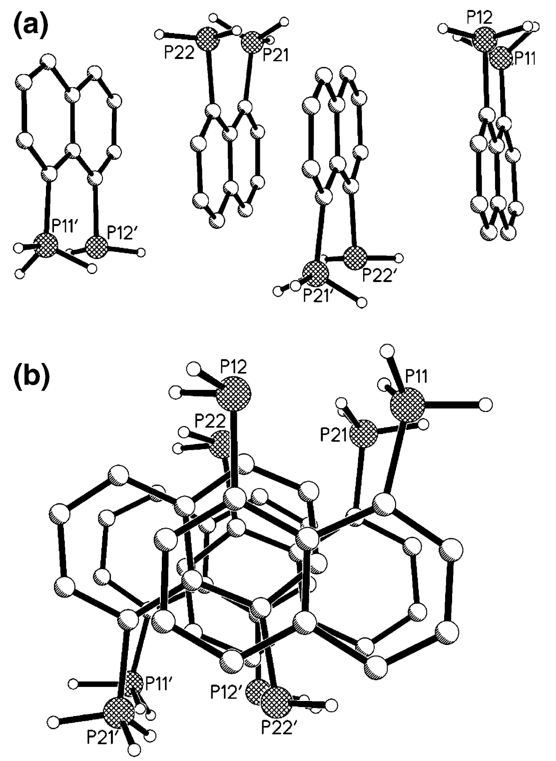


Figure 10. (a) Stacking of the cations in crystals of compound **13**. (b) Projection along the stacking axis showing the position of the $-PH_3^+$ groups in the periphery where these functions are exposed to the anion substructure.

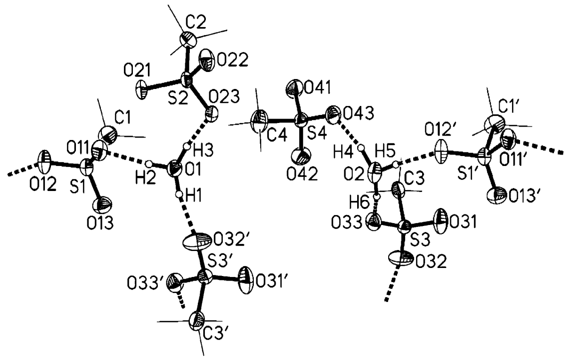


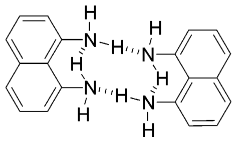
Figure 11. Hydrogen bonding network of hydronium cations $[H_3O]^+$ and triflate anions $[CF_3SO_3]^-$ (1:2 ratio) in crystals of compound **13**.

Table 2. Hydrogen Bonding in the $[H_3O]^+2[CF_3SO_3]^-$ Substructure of Compound **13**

O–H···O	d(O–H) [Å]	d(H···O) [Å]	d(O···O) [Å]	<(OHO) [deg]
O(1)−H(2)···O(11)	0.86(4)	1.79(4)	2.633(3)	169(4)
O(1)−H(3)···O(23)	1.05(5)	1.47(5)	2.502(2)	168(4)
O(1)−H(1)···O(32)′	0.88(4)	1.70(4)	2.577(3)	169(4)
O(2)−H(4)···O(43)	0.99(5)	1.52(5)	2.497(3)	169(4)
O(2)−H(6)···O(33)	1.30(7)	1.30(7)	2.587(3)	170(5)
O(2)−H(5)···O(12)′	0.80(5)	1.83(5)	2.606(3)	164(4)

to three triflate anions (Figure 11). A list of the data for the six hydrogen bonds is presented in Table 2. A similar connectivity pattern has been reported for the monohydrate of sulfuric acid, $H_2SO_4(H_2O)$, which is to be formulated as $[H_3O]^+[SO_4H]^-$,[36] and there are many more examples of structurally characterized hydronium salts, $[H_3O]^+X^-$. It therefore appears that compound **13** is a true hydronium salt. The structure shows no intercation

Scheme 3. Representation of the Dimerization of 1,8-Di(amino)naphthalene (**A1**) through Intra- and Intermolecular Hydrogen Bonding[16,37]



affinity, for example, between $[C_{10}H_6(PH_2)(PH_3)]^+$ and $[H_3O]^+$, which would indicate hydrogen bonding.

Discussion

The present study has shown that 1,8-di(phosphinyl)naphthalene **9** can be readily prepared in high yield as a crystalline solid, which is soluble in many common organic solvents. This simple prototype thus allows an investigation of the ground-state structure, molecular dynamics, and reactivity of 1,8-di(phosphinyl)naphthalenes **C**, with the smallest possible and least-polarizing substituents at the phosphorus atoms (R = H) in the solid state and in solution.

In the crystal, the compound is present as pairs of enantiomeric molecules with individual C_2 symmetry, related by a center of inversion. There is no intermolecular hydrogen bonding, and the aggregation into dimers is based on parallel head-to-tail stacking with only very weak centroid phenyl embrace interactions between P−H functions and benzene rings (Figure 5). This mode of aggregation is entirely different from that found for 1,8-di(amino)naphthalene (**A1**), where pairs of molecules are formed via intermolecular hydrogen bonding. Together with two intramolecular hydrogen bonds, the four amino groups share hydrogen atoms to give an eight-membered ring $(NH)_4$ (Scheme 3).[16,37]

The C_2 symmetry of the individual molecule **9** in the crystal arises from a conformation of the $-PH_2$ groups, which is referred to in the literature as the transoid or biseclipsed arrangement (Figure 4).[19] This conformation places one hydrogen atom of each $-PH_2$ group in the molecular plane, while the other two are positioned perpendicular to this plane, above and below. The same structure was also found for **C** (R = Cl, Ph, NMe_2, and so forth) and therefore appears to be the intrinsic ground state of this family of molecules, as confirmed by quantum chemical calculations for **9** and a $(PH_3)_2$ model system.[31] In the transoid conformation of **9**, any intramolecular hydrogen bonding (P−H···P′) is excluded for geometrical reasons. The same conclusion was drawn from the structural data of $[C_{10}H_6(PPh_2)(PPh_2H)]^+[CF_3SO_3]^-$, in which the cation has an analogous conformation.[38] By contrast, as already noted, the conformation of the 1,8-di(amino)naphthalene molecule (**A1**) in the crystal allows for intramolecular hydrogen bonding (Scheme 3).[16,37]

With the small substituents of $-PH_2$ in **9**, there is no major distortion of the naphthalene scaffold, and the phosphorus atoms are found in the molecular plane and are only tilted slightly in opposite directions (by ~3°) to minimize the peristress in the bay region of the molecule. In the nitrogen analogue with its smaller $-NH_2$ groups, this distortion leads to N−C−C angles

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of only 1.5° away from the ideal 120°.[16,37] Conversely, with the more bulky $-SiH_3$ groups in di(silyl)naphthalene (**A**, X = SiH_3), the distortions are much larger, as shown by symmetrical in-plane Si−C tilts of as much as 10°.[21]

The structure of **9**, as it is found in the crystal, must be fluctional in solution. The hydrogen atoms of the $-PH_2$ groups are equivalent on the NMR time scale, both at room temperature and at −80 °C (in CD_2Cl_2). The equivalence is determined by both the ^{31}P-coupled ^{1}H and the ^{1}H-coupled ^{31}P NMR spectra. This result implies that there must be rapid rotational movement of the $-PH_2$ groups about the P−C bonds with ~90° amplitude. [Dissociative−associative mechanisms for proton exchange can be excluded at low temperature since, even in the protonated forms (**11** and **13**), there is no rapid proton exchange and the two phosphorus atoms are inequivalent in solution. Note also that the P−H couplings with large ^{1}J(PH) constants are retained in **9**, **11**, and **13**.] The rotational movement of the $-PH_2$ groups can be random or concerted (dis- or conrotatory, of the cogwheel-type), possibly involving the conformer of maximum symmetry (point group C_{2v}) as a transition state.[31]

The fully coupled ^{1}H and ^{31}P NMR spectra of compound **9** (in CD_2Cl_2 at 25 °C) show complex multiplets for the $ABCD_2$-$XX'D'_2C'B'A'$ spin system. The experimental and calculated spectra are presented in Figures 1 and 12.

The most intriguing feature of the NMR spectra of compound **9** is the large coupling constant, $^{n}J(PP')$ = 221.6 Hz [corresponding to $^{n}J(XX')$ in the above spin system; *n* denotes the unknown number of bonds, if any, between the coupling nuclei]. This coupling has previously been reported for only one other symmetrical compound (**C**, R = Ph, $^{n}J(PP')$ = 199 Hz, determined in the solid state by MAS experiments).[32] Data are known for several asymmetrically $P^{III}-P^{III}$-substituted compounds, including the results of very recent measurements on 1-bis(dimethylamino)phosphinyl-8-[(dimethylamino)(methoxy)-phosphinyl]naphthalene [$^{n}J(P_XP_Y)$ = 246 Hz].[39]

It appears to be generally accepted that this coupling, $^{n}J(PP')$, should be assigned to a through-space spin−spin interaction transmitted via the lone pairs of electrons at the phosphorus atoms. These lone pairs are forced into (repulsive) overlap in the periregion, and the extent of overlap depends strongly on the conformations and their intramolecular dynamics. The P−P′ coupling obviously is very efficient, as illustrated by a comparison with coupling constants for true $P^{III}-P^{III}$ and $P^{III}-H$ single bonds, which are in the same order of magnitude. An internal reference parameter of **9** is ^{1}J(PH) = 207.7 Hz [^{1}J(XD) in the above spin system].

In **9**, there are even large $^{1+n}J(H_DP_{X'})$ couplings (31.7 Hz) and significant $^{2+n}J(H_DH_{D'})$ couplings (3.8 Hz) “across the bay”, which were both measured here for the first time. By contrast, the “regular” $^{3}J(H_AP_X)$, $^{4}J(H_BP_X)$, and $^{5}J(H_AP_{X'})$ couplings, following the “bond tracks”, are all very small at 6.1, 0.7, and 0.4 Hz, respectively.

These strong coupling effects are probably associated with the high s-character of lone-pair electrons at P^{III} centers, which is evident from the small bond angles at these centers, even though these data are of limited accuracy [e.g., C1−P1−H11 = 95(1)°, H11−P1−H12A = 90(3)°, C1−P1−H12A = 105(3)°, C8−P2−H21 = 95(1)°, C8−P2−H22A = 103(3)°, and H21−P2−H22A = 92(3)°]. [Note also that in PH_3, the H−P−H angles are close to 90° (gas phase and matrix experiments).][40]

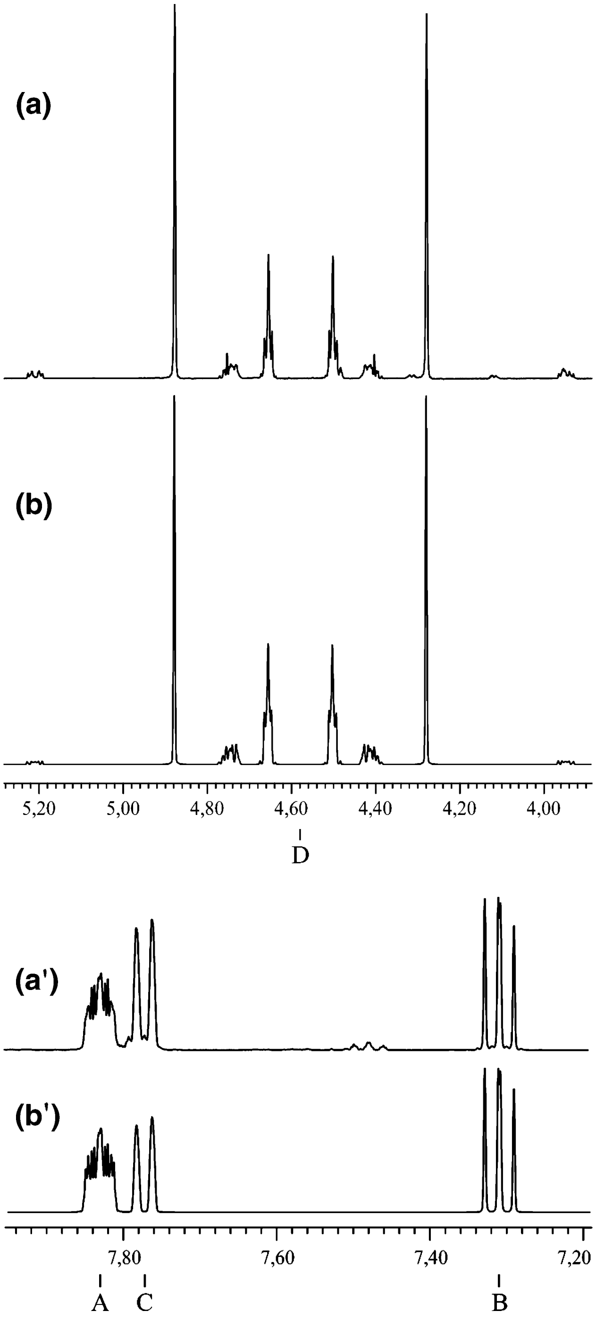

Figure 12. ^{1}H NMR spectrum (phosphinyl and aryl region) of compound **9**. (a/a′) experimental (in CD_2Cl_2 at 25 °C), (b/b′) calculated spectrum. (For details see Table 1.)

Interestingly, the ^{1}H NMR spectrum of compound **9** shows a small but significant temperature dependence in the range from 20 to −90 °C. Apart from the common minor shift in the δ value, the line spacings in the multiplet of the $-PH_2$ hydrogen atoms (which reflect sums and differences of coupling constants, *J*) follow major trends. The spacing of the two most-intense lines (Figure 12) increases steadily from 239.9 (at 20 °C) to 249.5 Hz (at the experimental limit of −90 °C). This effect may indicate a slowing down of the rotational movement of the $-PH_2$ groups, but the low-energy barriers probably associ-

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ated with these movements preclude any detailed analysis of the data for the accessible temperature region.

Upon protonation of **9** with triflic acid, monocations are formed, which could be crystallized as triflate **11** or hydronium bis(triflate) salt **13**. The structure of the cations, including their conformation, is the same in both salts. (Moreover, in **13**, two almost identical crystallographically independent cations are present.) The most important structural result is the absence of any intra- or intermolecular P−H···P hydrogen bonding. The mutual, rotational orientation of the $-PH_2$ and $-PH_3^+$ groups places the remaining lone pair of electrons of the former in a staggered position between two H atoms of the latter (Figure 7).

It should be noted that, by contrast, in the structure of the cation resulting from the monoprotonation of the corresponding 1,8-di(amino)naphthalene **A1** (determined for the hydrogenmaleate salt), the incoming proton occupies an asymmetric position between the two nitrogen atoms, which still indicates significant intracationic N−H···N hydrogen bonding.[17] In crystals of the di- and trichloroacetate salts, the hydrogen bonding pattern is more complex due to stronger interactions between cations and anions.[16] The cations, $[C_{10}H_6(NH_2)(NH_3)]^+$, therefore do not feature C_s or C_{2v} symmetry, attainable for asymmetrical or symmetrical hydrogen bonding, respectively, but are significantly distorted because of these N−H···O hydrogen bonds.

The absence of hydrogen bonding in the cations of **11** and **13** is corroborated by the NMR spectra of solutions of the compounds (in CD_2Cl_2 at −80 °C). Separate ^{31}P and ^{1}H signals are observed for $-PH_2$ and $-PH_3^+$ groups, which rules out any rapid proton exchange mediated by hydrogen bonding. (The ^{31}P and ^{1}H chemical shifts and the $^{1}J(PH)$ coupling constants for the $-PH_2$ and $-PH_3^+$ groups are very similar to those of the reference compounds, **4** and **5**.)

This observation is again in notable contrast to the behavior of the nitrogen analogues. In three different solvents, the $[C_{10}H_6(NH_2)(NH_3)]^+$ cations show only one proton signal for the five N-bound hydrogen atoms, suggesting rapid proton exchange.[16,17]

Conclusions

The present work is a contribution to the discussion of the significance of hydrogen bonding between the phosphorus atoms of primary arylphosphines and the corresponding arylphosphonium salts. It has been demonstrated, by studies of the crystal and the solution state, that even in cases where $-PH_2$ and $-PH_3^+$ functions are held in proximity (as in the peripositions of naphthalene in **9**, **11**, and **13**), there is no evidence for hydrogen bonding between phosphorus atoms ($-PH_2$ and $-PH_2$ or $-PH_2$ and $-PH_3^+$) or for proton exchange between the two functions. This is also true for the packing of molecules (**9**) or cations (**11** and **13**) in the crystal, which is clearly not governed by such intermolecular interactions. It thus appears that hydrogen bonding between primary (RPH_2) or secondary arylphosphines (R_2PH) and their phosphonium salts plays no significant role in the molecular or supramolecular chemistry of these molecules.[35] Literature data for arylamines and arylammonium salts show that hydrogen bonding in these N-analogues may be weak, but it is still discernible from molecular structures in the condensed phase and from molecular dynamics in solution.[2] The present account leads to the very general conclusion that hydrogen bonding of the type P−H···P is insignificant regarding its effects in structural chemistry of phosphines and phosphonium salts, even if the functions are held in proximity, thus minimizing entropy losses. The inherent low polarity of P−H bonds, which is comparable to that of most C−H bonds, reduces their affinity for potential electron donor centers (D) to a degree that this type of contact, P−H···D, is associated with only very minor gains in energy.

Experimental Section

General. All of the chemicals used as starting materials were commercially available, except bis(diethylamino)chlorophosphine,[41] which was prepared according to the literature. All of the reactions were carried out routinely in an atmosphere of dry and pure nitrogen. All of the solvents were distilled from an appropriate drying agent and stored over molecular sieves (4 Å) and under nitrogen. Glassware was oven dried and filled with nitrogen. Mass spectra were recorded on an HP 5971A (Hewlett-Packard) spectrometer using EI at 70 eV as an ionization method. NMR spectra were obtained at room temperature and at −80 °C on JEOL JNM-GX-400 or JEOL 400 Eclipse spectrometers. Chemical shifts are reported in δ values relative to the residual solvent resonance of CD_2Cl_2 (^{1}H and ^{13}C). ^{31}P and ^{19}F NMR spectra are referenced to external aqueous H_3PO_4 (85%) and $CFCl_3$, respectively. Assignments were supported by 2D NMR experiments (HH COSY, HC HMQC, and HC HMBC). Simulation of spin systems was carried out using the PERCH program package.[42] Signs of coupling constants were chosen following reference data.[43] GC−MS analyses of the reaction mixtures were carried out on an HP 5890 Series II (Hewlett-Packard) gas chromatograph with an HP 5971A mass-selective detector.

Bis(diethylamino)(1-naphthyl)phosphine, 2. The preparation of 1-naphthyllithium **1** was based on a modified literature procedure.[44] A solution of *n*-BuLi (75 mL, 120 mmol, 1.6 M in hexane) was diluted with diethyl ether (80 mL) at −20 °C, and subsequently, 1-bromonaphthalene (20.70 g, 100 mmol) was added at the same temperature. The reaction mixture was allowed to warm to 10 °C and stirred continuously at this temperature for 15 min. The white suspension was cooled to −20 °C, and after letting the mixture stand for about 10 min, the clear supernatant solution was removed via cannula. Hexane (250 mL) was added, and after the mixture was swirled, the suspension was recooled to −20 °C. After the mixture was left to stand for about 10 min, the clear solution was removed via cannula. These operations were repeated twice, and **1** was then suspended in THF (150 mL). Bis(diethylamino)-chlorophosphine (24.05 g, 114 mmol) was slowly added at −78 °C, and the reaction mixture was allowed to warm to room temperature and stirred for 12 h. The residue remaining upon evaporation of the solvent in vacuo was extracted with hexane (150 and 50 mL). Evaporation of the combined hexane extracts in vacuo yielded a yellow oily liquid, which contained only small amounts of bis(diethylamino)-chlorophosphine, tris(diethylamino)phosphine, and (diethylamino)(1-naphthyl)chlorophosphine: $^{31}P\{^{1}H\}$ NMR (CD_2Cl_2, 25 °C) δ 94.7 (s); MS (EI) *m*/*z* 302 $[M]^+$.

Dichloro(1-naphthyl)phosphine, 3. A solution of the product (above) in hexane (500 mL) was cooled to 0 °C and saturated with gaseous HCl. The reaction mixture was stirred for 1 h, again saturated with gaseous HCl, and stirred for 1 h. This procedure was repeated until the supernatant solution remained clear upon further addition of HCl. The reaction mixture was then allowed to warm to room

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temperature and stirred for 12 h. The diethylammonium chloride precipitate was separated and extracted with hexane (2 × 100 mL). Evaporation of the combined organic phases in vacuo afforded a white solid, which was recrystallized from hexane at −30 °C, and yielded colorless, plate-shaped crystals: 18.94 g, 82.7% (based on 1-bromonaphthalene); mp 55 °C; ^{31}P{^{1}H} NMR (CD_2Cl_2, 25 °C) δ 164.2 (s); ^{13}C{^{1}H} NMR (CD_2Cl_2, 25 °C) δ 135.7 (d, ^1J(CP) = 61.5 Hz, C1), 134.3 (s), 134.1 (d, ^3J(CP) = 2.3 Hz, C10), 132.7 (d, ^2J(CP) = 19.2 Hz, C9), 131.2 (d, J(CP) = 32.3 Hz), 129.7 (s), 127.8 (d, J(CP) = 2.3 Hz), 127.2 (s), 125.5 (d, J(CP) = 9.2 Hz), 124.8 (d, J(CP) = 23.8 Hz); ^{1}H NMR (CD_2Cl_2, 25 °C) δ 8.63 (dm, ^3J(HH) = 8.2 Hz, 1H, H2), 8.28 (ddd, ^4J(HP) = 11.4 Hz, ^3J(HH) = 7.2 Hz, ^4J(HH) = 1.2 Hz, 1H, H8), 8.09 (d, ^3J(HH) = 8.2 Hz, 1H, H4/5), 7.98 (dm, ^3J(HH) = 7.9 Hz, 1H, H5/4), 7.65 (m, 3H, H3/6/7); MS (EI) m/z 228 [M]$^+$. Anal. Calcd for $C_{10}H_7Cl_2P$ (229.04): C, 52.44; H, 3.08; P, 13.52. Found: C, 52.42; H, 3.19; P, 13.28. Bp 139−149 °C (1 Torr),[24] bp 135−137 °C (0.5 Torr), mp 55 °C;[25c] bp 118−120 °C (0.5 Torr), mp 54 °C;[25b] bp 130−131 °C (0.8 Torr), mp 51−54 °C.[25a]

1-Naphthylphosphine, 4. A solution of **3** (18.00 g, 78.6 mmol) in diethyl ether (100 mL) was added slowly to a stirred suspension of $LiAlH_4$ (12.00 g, 316.2 mmol) in diethyl ether (400 mL) at −78 °C. The reaction mixture was then allowed to warm to room temperature and stirred for 12 h. For workup, degassed water (70 mL) was added dropwise at 0 °C, and the mixture stirred at room temperature for 1 h. The precipitate was separated and extracted with diethyl ether (2 × 100 mL), and the combined organic phases were dried over $MgSO_4$. Evaporation of the solvent and distillation of the residue in vacuo yielded a colorless liquid: 11.35 g, 90.2%; bp 87 °C (0.9 mbar), mp −26 °C; ^{31}P{^{1}H} NMR (CD_2Cl_2, 25 °C) δ −133.5 (s); ^{31}P NMR (CD_2Cl_2, 25 °C) δ −133.5 (td, ^1J(PH) = 203.5 Hz, ^3J(PH) = 8.0 Hz); ^{13}C{^{1}H} NMR (CD_2Cl_2, 25 °C) δ 135.8 (d, ^2J(CP) = 8.5 Hz, C9), 134.9 (d, ^2J(CP) = 16.9 Hz, C2), 133.8 (d, ^3J(CP) = 2.3 Hz, C10), 129.9 (s, C4/5), 129.1 (s, C5/4), 127.4 (d, ^1J(CP) = 11.5 Hz, C1), 126.9 (d, ^3J(CP) = 10.8 Hz, C8), 126.8 (s, C6/7), 126.4 (s, C7/6), 125.8 (d, ^3J(CP) = 6.1 Hz, C3); ^{1}H (CD_2Cl_2, 25 °C) δ 8.21 (dd, ^3J(HH) = 8.2 Hz, ^4J(HH) = 0.7 Hz, 1H, H8), 7.92 (d, ^3J(HH) = 7.2 Hz, 1H, H4/5), 7.89 (d, ^3J(HH) = 8.2 Hz, 1H, H5/4), 7.82 (m, 1H, H2), 7.61 (m, 2H, H6/7), 7.44 (m, 1H, H3), 4.26 (d, ^1J(HP) = 203.4 Hz, 2H, PH_2); MS (EI) m/z 160 [M]$^+$. Anal. Calcd for $C_{10}H_9P$ (160.15): C, 75.00; H, 5.66; P, 19.34. Found: C, 74.86; H, 5.72; P, 19.22. [^{31}P NMR ($CDCl_3$) δ −134.0 (t, ^1J(PH) = 200 Hz).][26a]

1-Naphthylphosphonium Trifluoromethanesulfonate, 5. Trifluoromethanesulfonic acid (0.78 mL, 8.78 mmol) was added to a stirred solution of **4** (1.40 g, 8.74 mmol) in CH_2Cl_2 (80 mL) at room temperature. After the mixture was stirred for 0.5 h, the solution was concentrated in vacuo and stored at −30 °C and yielded colorless, needle-shaped crystals: 2.54 g, 93.7%; mp 91 °C; ^{31}P{^{1}H} NMR (CD_2Cl_2, −80 °C) δ −53.4 (s); ^{31}P NMR (CD_2Cl_2, −80 °C) δ −53.4 (q, ^1J(PH) = 546.9 Hz); ^{19}F{^{1}H} NMR (CD_2Cl_2, −80 °C) δ −79.1 (s). Anal. Calcd for $C_{11}H_{10}F_3O_3PS$ (310.23): C, 42.59; H, 3.25; P, 9.98. Found: C, 42.71; H, 3.24; P, 10.12.

1,8-Bis(dichlorophosphinyl)naphthalene, 8. Compound **8** was prepared by a modification of the procedure reported by Schmutzler et al.[27a] A solution of **7** (11.34 g, 23.8 mmol) in diethyl ether (250 mL) was cooled to 0 °C and saturated with gaseous HCl. The reaction mixture was stirred for 1 h, and was again saturated with gaseous HCl and stirred for 1 h. This procedure was repeated until the supernatant solution remained clear upon further addition of HCl. The reaction mixture was then allowed to warm to room temperature and stirred for 12 h. The diethylammonium chloride precipitate was separated and extracted with diethyl ether (2 × 50 mL). Evaporation of the combined organic phases in vacuo left a residue, which was recrystallized from CH_2Cl_2 at −30 °C, and yielded pale yellow, block-shaped crystals: 6.41 g, 81.7%. For analytical data, see refs 27a and 27b.

1,8-Di(phosphinyl)naphthalene, 9. A solution of **8** (6.00 g, 18.2 mmol) in diethyl ether (50 mL) was added slowly to a stirred suspension of $LiAlH_4$ (5.50 g, 144.9 mmol) in diethyl ether (200 mL) at −78 °C. The reaction mixture was then allowed to warm to room temperature and stirred for 12 h. For workup, degassed water (30 mL) was added dropwise at 0 °C, and the mixture was stirred at room temperature for 1 h. The precipitate was separated and extracted with diethyl ether (2 × 50 mL), and the combined organic phases were dried over $MgSO_4$. Evaporation of the solvent in vacuo yielded a white solid. Repeated recrystallization from CH_2Cl_2 at −30 °C gave colorless, block-shaped crystals: 2.71 g, 77.6%; mp 82 °C; ^{31}P{^{1}H} NMR (CD_2Cl_2, 25 °C) δ −104.9 (s); ^{31}P NMR (CD_2Cl_2, 25 °C) δ −104.9 (X-part of an $[ABCD_2X]_2$ spin system); ^{13}C{^{1}H} NMR (CD_2Cl_2, 25 °C) δ 139.0 (t, ^2J(CP) = 17.3 Hz, C9), 138.2 (s, C2/7), 135.1 (t, ^3J(CP) = 4.6 Hz, C10), 130.6 (t, A-part of an AXX′ spin system, $N = J_{AX} + J_{AX'}$ = 1.8 Hz, C4/5), 128.7 (t, A-part of an AXX′ spin system, $N = J_{AX} + J_{AX'}$ = 20.2 Hz, C1/8), 125.3 (s, C3/6); ^{1}H NMR (CD_2Cl_2, 25 °C), $ABCD_2$-part of the $[ABCD_2X]_2$ spin system, δ 7.83 (A, 2H, H2/7), 7.31 (B, 2H, H3/6), 7.77 (C, 2H, H4/5), 4.58 (D, 4H, PH_2). For coupling constants, see Table 1. MS (EI) m/z 192 [M]$^+$, 191 (100) [M − H]$^+$, 190 [M − 2H]$^+$, 189 [M − 3H]$^+$, 188 [M − 4H]$^+$, 159 [M − PH_2]$^+$, 128 [$C_{10}H_8$]$^+$, 127 [$C_{10}H_7$]$^+$, 126 [$C_{10}H_6$]$^+$. Anal. Calcd for $C_{10}H_{10}P_2$ (192.13): C, 62.51; H, 5.25; P, 32.24. Found: C, 62.49; H, 5.21; P, 31.98.

Table 3. Crystal Data, Data Collection, and Structure Refinement for Compounds **9**, **11**, and **13**

	9	11	13
empirical formula	$C_{10}H_{10}P_2$	$C_{11}H_{11}F_3O_3P_2S$	$C_{12}H_{14}F_6O_7P_2S_2$
M	192.12	342.20	510.29
crystal system	monoclinic	orthorhombic	monoclinic
space group	$P2_1/n$	$Pbcm$	$P2_1/n$
a (Å)	8.4840(1)	10.5319(2)	14.1998(2)
b (Å)	12.8058(2)	18.0050(5)	13.4147(1)
c (Å)	9.7203(2)	7.3227(1)	21.2356(3)
β (deg)	115.0878(7)	90	98.0005(5)
V (Å^3)	956.43(3)	1388.58(5)	4005.73(9)
ρ_{calc} (g cm^{-3})	1.334	1.637	1.692
Z	4	4	8
F(000)	400	696	2064
T (K)	143	143	143
reflns measured	25895	32396	91685
reflns unique	1736	1345	7259
parameters/restraints	153/6	144/0	635/0
R1 [$I \geq 2\sigma(I)$]	0.0391	0.0374	0.0389
wR2[a]	0.0990	0.0947	0.0950
weighting scheme	a = 0.0480 b = 0.7188	a = 0.0476 b = 1.4323	a = 0.0366 b = 5.0076
σ_{fin}(max/min) (e Å^{-3})	0.354/−0.514	0.316/−0.364	0.643/−0.468

[a] $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (ap)^2 + bp]$; $p = (F_o^2 + 2F_c^2)/3$.

1,2-Dihydro-1,2-diphosphaacenaphthene, 10. ^{31}P{^{1}H} NMR (CD_2Cl_2, 25 °C): δ −103.7 (s). MS (EI) m/z 190 (100) [M]$^+$, 189 [M − H]$^+$, 188 [M − 2H]$^+$.

1-(8-Phosphinylnaphthyl)phosphonium Trifluoromethanesulfonate, 11. Trifluoromethanesulfonic acid (0.13 mL, 1.46 mmol) was added to a stirred solution of **9** (280.0 mg, 1.46 mmol) in CH_2Cl_2 (30 mL) at room temperature. After the mixture was stirred for 0.5 h, the solution was concentrated in vacuo, stored at −30 °C, and yielded colorless, needle-shaped crystals: 429.7 mg, 86.2%; mp 135 °C; ^{31}P{^{1}H} NMR (CD_2Cl_2, −80 °C) δ −35.5 (d, ^4J(PP) = 107.0 Hz, PH_3^+), −119.3 (d, ^4J(PP) = 107.0 Hz, PH_2); ^{31}P NMR (CD_2Cl_2, −80 °C) δ −35.5 (qdd, ^1J(PH) = 546.9 Hz, ^4J(PP) = 107.0 Hz, ^3J(PH) = 23.8 Hz, PH_3^+), −119.3 (tdq, ^1J(PH) = 245.7 Hz, ^4J(PP) = 107.0 Hz, ^5J(PH) = 39.6 Hz, PH_2); ^{19}F{^{1}H} NMR (CD_2Cl_2, −80 °C) δ −79.2 (s). Anal. Calcd for $C_{11}H_{11}F_3O_3P_2S$ (342.21): C, 38.61; H, 3.24; P, 18.10. Found: C, 38.52; H, 3.31; P, 17.94.

1-(8-Phosphinylnaphthyl)phosphonium Hydronium Bis(trifluoromethanesulfonate), 13. Trifluoromethanesulfonic acid (0.25 mL, 2.82

mmol) and degassed water (25.3 μL, 1.40 mmol) were added to a stirred solution of **9** (270.0 mg, 1.41 mmol) in CH_2Cl_2 (30 mL) at room temperature. After the mixture was stirred for 0.5 h, the solution was concentrated in vacuo, stored at −30 °C, and yielded colorless, block-shaped crystals: 635.4 mg, 88.6%; mp 74 °C. Anal. Calcd for $C_{11}H_{11}F_3O_3P_2S{\cdot}CF_3SO_3H{\cdot}H_2O$ (510.31): C, 28.24; H, 2.77; P, 12.14. Found: C, 28.19; H, 2.86; P, 12.03. The NMR parameters (in CD_2Cl_2 at −80 °C) are similar to those of **11**, but feature broader signals.

Determination of the Crystal Structures. Specimens of suitable quality and size of **9**, **11**, and **13** were mounted on the ends of quartz fibers in inert perfluoropolyalkyl ether and used for intensity data collection on a Nonius DIP2020 diffractometer, employing graphite monochromated Mo Kα radiation. The structures were solved by a combination of direct methods (SHELXS-97) and difference Fourier syntheses and were refined by full-matrix least-squares calculations on F^2 (SHELXL-97).[45] The thermal motion was treated anisotropically for all non-hydrogen atoms.

The "in plane" P−H hydrogen atom of each $-PH_2$ group in the structure of **9** and all hydrogen atoms in **11** and **13** were localized and refined with isotropic displacement parameters. The disordered P−H hydrogen atoms of both $-PH_2$ units in **9** were assigned to peaks of the residual electron density of similar height and orientation (above and below the reference plane of the hydrocarbon unit), with a site occupation factor of 0.5 for each position. The corresponding P−H distances were refined with a similarity restraint placed on the four bond lengths.

Further information on crystal data, data collection, and structure refinement is summarized in Table 3.

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Supporting Information Available: X-ray crystallographic files for **9**, **11**, and **13**. Crystal data, data collection, structure refinement, thermal parameters, and complete tables of interatomic distances and angles for **9**, **11**, and **13**. This material is available free of charge via the Internet at http://pubs.acs.org.

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