Effects of Carbon Chain Substituents
on the P···N Noncovalent Bond

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Abstract

The effects of carbon chains placed on the electron-accepting P atom of a P···N bond are examined via ab initio calculations. Saturated alkyl groups have a mild weakening effect, regardless of chain length. In contrast, incorporation of double bonds into the chain strengthens the interaction, C≡C triple bonds even more so. These effects are only slightly enhanced by additional conjugated double bonds or an aromatic ring. Placing F atoms onto the carbon chains strengthens the P···N bond, but only by a small amount, which wanes as the F atom is displaced further from the P along the chain.

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INTRODUCTION

The H-bond is one of the most venerated and well studied sorts of molecular interaction [1-3]. The attractive nature of this bond is due in large part to a transfer of charge from the lone pair of the proton-acceptor molecule to the A-H σ^* antibond of the proton donor. Later observations have shown that such a transfer can also take place to a C-X antibond in which X represents atoms Cl, Br, or I, known more commonly as a halogen bond [4-12]. Other work [13-17] suggested that chalcogens (e.g. S and Se) might be able to replace halogens, which has been confirmed more recently [18-20] (although there remains some lingering question about S···S bonds [21]).

Following up on some earlier indications [22-26], our own group considered the possibility that pnicogens such as P and N might also participate in noncovalent interactions of a similar type. It was found, for example, that the PH_3/NH_3 heterodimer [27] contains a direct interaction between the electronegative P and N atoms, relying upon charge transfer from the N lone pair into the σ^* antibond of the P-H bond that is turned away from the N. It was later shown [28] that interaction is magnified if the pertinent H atom of the phosphine is replaced by a more electronegative group. The ability of a substituent to strengthen the attraction permitted even two electronegative N atoms to attract one another, as in the case of $FH_2N\cdots NH_3$ which is bound by 4 kcal/mol [29]. The pnicogen bond is persistent enough to represent the dominant form of interaction in clusters of relevant molecules [30]. Surprisingly, and in striking contrast with H-bonding, double or triple halogenation does not further amplify this interaction [31]. This noncovalent interaction is not limited to electron donor N, as O and S can also participate, and electron density may also be extracted from the C-C π bonds of alkenes, alkynes and conjugated systems such as benzene. The strength of the interaction is fairly insensitive to the nature of the electron-acceptor atom [32], whether P, S, Cl, or As.

Computations since that time have verified many of the above conclusions. The attractive nature of the P···P pnicogen bond was confirmed [33] at high levels of theory, as was the ability of electron-

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withdrawing substituents to strengthen the bond. The potency of FH_2P to serve as electron acceptor, and the importance of induction energy, was verified by Del Bene et al [34,35] as was the correlation between the binding energy and the intermolecular distance. Buhl et al [36] have extended the concept of a pnicogen P⋯P bond to an intramolecular context.

Most of the substituents that have been added to the electron-accepting pnicogen atom to this point have been fairly electronegative, e.g. F, NO_2, and Cl. From a practical standpoint, it is anticipated that the pnicogen will commonly be bonded to carbon-containing chains. However, the only such groups that have been considered to this point are the methyl groups. There thus remain a number of unanswered questions. How might the pnicogen bond be affected if the alkyl chain is lengthened, e.g. ethyl, propyl, etc? What would be the effects of unsaturated chains which contain double or triple bonds? How might addition of halogen atoms to the carbon chain alter the pnicogen bond?

The present work is an attempt to answer the above questions. The base system considered contains the pnicogen bond formed between RPH_2 and an electron donor (NH_3). As the R group, methyl, ethyl, and propyl allow us to monitor the pnicogen bond in terms of the length of the chain. Double and triple bonds are considered via $-CH=CH_2$ and $-C≡CH$, with elongations considered by adding methyl groups to the growing chain. The possibility of conjugation is taken into account via the butadienyl $-CH=CH-CH=CH_2$ group, and aromaticity via a phenyl group. In each case, F atoms were added at various locations on the chain so as to provide information about how the proximity of these atoms affects the system.

COMPUTATIONAL METHODS

The Gaussian 09 package [37] was used to perform all calculations. Geometries were optimized at the ab initio MP2/aug-cc-pVDZ level which has been shown to be of high accuracy, especially for weak intermolecular interactions of the type of interest here [11,38-41] where the data are in close accord with CCSD(T) values with larger basis sets [28,42,43] and in excellent agreement with experimental

energetics [44]. Interaction energies were computed as the difference in energy between the dimer, and the sum of the optimized energies of the isolated monomers, corrected for basis set superposition error by the counterpoise procedure [45]. Natural bond orbital (NBO) analysis [46,47] was carried out via the procedures contained within Gaussian.

RESULTS

RH_2P was taken as the electron acceptor in complexes with NH_3 as the common electron donor. The R designation refers to a number of different sorts of carbon chains of varying length. Saturated alkyl groups considered were methyl, ethyl, and propyl. A double bond was introduced into the chain via vinyl and $-CH=CHCH_3$. Similarly, triple bonds were considered via $-C\equiv CH$ and $-C\equiv CCH_3$. Conjugated systems of π bonds were studied via $-CH=CH-CH=CH_2$ and full aromaticity by a phenyl ring. The optimized structures of representative samples of each complex are illustrated in Fig 1 which indicate the near linearity of the $C-P\cdots N$ bond. As shown in previous studies, this sort of arrangement permits optimal charge transfer from the N lone pair to the C-P σ^* antibonding orbital, an important ingredient of the attractive force.

The third row of Table 1 indicates this $\theta(C-P\cdots N)$ angle varies within the fairly narrow range of 165° to 173° for the various systems, with the smallest angles occurring for the alkynyl groups. The preceding row indicates a similarly narrow range of intermolecular $R(P\cdots N)$ distances, between 3.1 and 3.3 Å. The shortest distances, like the smaller angles, are associated with the alkynyl groups. The first row of Table 1 indicates the various interaction energies are smallest for the alkyl groups, about 1.3 kcal/mol, and grow as multiple bonds are introduced. The most strongly bound complex in this set is that containing the simple $C\equiv CH$ group, about twice the binding energy as the alkanes. A double bond produces an intermediate effect, but it might be noted that the introduction of additional double bonds, as in the conjugated C_4H_5 and C_5H_6 groups, has very little cumulative effect. With regard to chain

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lengthening, the addition of methyl groups tends to weaken the interaction, albeit by only a small amount.

Previous work has documented the importance of the $N_{lp} \rightarrow \sigma^*(C-P)$ charge transfer to the P···N bond. Several relevant parameters are reported in the next three rows of Table 1. The NBO perturbation energy associated with this charge transfer, E(2), very nearly parallels the total interaction energies. This quantity grows as one progresses from single to double and then to triple bonds. Like ΔE, E(2) also diminishes as the chain grows longer. The conjugated systems on the right side of Table 1 manifest values similar to the unconjugated double bonds, perhaps slightly larger. The NBO measure of the charge transferred, Δq follows an identical pattern. The last row of Table 1 reports the change in the C-P bond length is caused by the formation of the complex with NH_3. Due to the transfer of charge into the corresponding antibond, this bond is expected to lengthen, and approximately in parallel with E(2) and Δq. In fact, this expectation is confirmed. There is a small bond contraction noted for two of the alkyl groups, but this shortening is less than 0.0001 Å.

F-substitution

Earlier work had shown that the introduction of electron-withdrawing substituents like F onto the P atom result in a marked strengthening of the P···N bond. In order to examine how these effects might be attenuated if the F atoms are placed on the R chain, rather than directly on the P atom, one or more F atoms were placed in various locations on the chains.

Table 2 displays the results when the F atom is placed first on the C of propyl adjacent to P, then the next C, and finally on the methyl group that is most remote. The placing of the F on the first C increases the binding energy from -1.28 to -1.70 kcal/mol. This quantity diminishes as the F is moved further from the P, but only slowly, remaining at -1.52 kcal/mol even when the F is three C atoms down. In fact, there is little change upon moving F from the second to the third C, either in ΔE or any of the other data reported in Table 2.

Similar patterns are noted in the F-substitution on the conjugated butadienyl system in Table 3. The interaction energy of -1.62 kcal/mol climbs to -2.38 kcal/mol when the F is placed on the adjacent carbon, and then diminishes slowly as the F is moved further away. There is an interesting "bump" for -CH_2=CH-CF=CH_2 where the displacement of the F from C2 to C3 yields small increases in the various parameters E(2), Δq, and Δr. One might expect a similar attenuation as the F atom is moved further from the P in the monofluorosubstituted phenyl group. In fact, Table 4 shows that this anticipation is confirmed as the F moves from the ortho to meta to para position. A full perfluorosubstitution of the ring produces a larger effect, raising the binding energy from 1.57 to 2.87 kcal/mol, as indicated in the last column of Table 4.

To place these data in a deeper context, it was shown earlier [28] that elimination of all substituents led to a ΔE of -1.43 kcal/mol, greater by 0.10 than the result with a methyl group. So one can say that all the saturated alkyl groups weaken the interaction to a small degree. In another context, placement of F directly on the P atom raised the binding energy to 6.2 kcal/mol [28]. So displacement to even the first C atom severely damps the effects of the F. Adding three F atoms on the first adjacent C led to a binding energy of 3.4 kcal/mol in $CF_3PH_2\cdots NH_3$, considerably larger than the single F-substitution considered here. On the other hand, even pentafluorosubstitution of the phenyl ring yields a fairly small effect, raising the binding energy from 1.57 to 2.87 kcal/mol, smaller than the effect of perfluorosubstitution of a methyl group, even though the latter reflects only 3 F atoms instead of 5. This surprisingly small effect of pentafluorosubstitution of the phenyl ring is consistent with a recent examination [9] of halogen bonds.

In summary, saturated alkyl groups have only a very modest weakening effect upon the P$\cdots$N pnicogen bond, which is virtually insensitive to chain length. Incorporation of C=C double bonds into the chain, on the other hand, has the opposite effect of strengthening the interaction. The addition of several conjugated double bonds yields only a marginal further change, as does an aromatic phenyl ring.

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Triple C≡C bonds have the largest effect, producing a pnicogen bond that is roughly twice the strength of the unsubstituted P···N system. Lengthening any of these chains tends to weaken the P···N bond. Fluorosubstitution of the carbon chain strengthens the interaction, although much less than if the F is placed directly on the P atom. Even adding multiple F atoms to the carbon chain is less effective than a single F situated on the P.

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Table 1. Energetic, geometric, and electronic aspects of $RPH_2\cdots NH_3$ complexes.

	alkyl			alkenyl		alkynyl		Conjugated	
	CH_3	C_2H_5	C_3H_7	$CH=CH_2$	$CH=CHCH_3$	$C\equiv C-H$	$C\equiv C-CH_3$	C_4H_5	C_6H_5
ΔE^a, kcal/mol	-1.33	-1.29	-1.28	-1.56	-1.45	-2.54	-2.13	-1.62	-1.57
$R(P\cdots N)$ Å	3.353	3.323	3.330	3.249	3.269	3.112	3.142	3.238	3.232
$\theta(CP\cdots N)$, degs	173	173	173	170	171	165	167	170	170
$E(2)^b$, kcal/mol	0.76	0.90	0.85	1.70	1.37	4.24	3.51	1.83	1.87
Δq^c, me	1.4	1.6	1.5	2.8	2.2	6.9	5.6	3.1	3.3
$\Delta r(C-P)$, mÅ	0.2	-0.8	-0.9	1.2	0.9	9.9	8.5	1.4	0.6

[a]Corrected by counterpoise procedure

[b]NBO perturbation energy corresponding to $N_{lp}\rightarrow\sigma^*(C-P)$ charge transfer

[c]$N_{lp}\rightarrow\sigma^*(C-P)$ charge transfer, computed as $2*(F_{ij}/\Delta\varepsilon_{ij})^2$

Table 2. Energetic, geometric, and electronic aspects of $FC_3H_6-PH_2\cdots NH_3$ complexes.

	$-CHFCH_2CH_3$	$-CH_2CHFCH_3$	$-CH_2CH_2CH_2F$
ΔE, kcal/mol	-1.70	-1.54	-1.52
$R(P\cdots N)$ Å	3.231	3.276	3.262
$\theta(CP\cdots N)$, degs	169	171	170
$E(2)$, kcal/mol	1.84	1.26	1.52
Δq, me	3.31	2.27	2.57
$\Delta r(C-P)$, mÅ	-1.01	0.07	1.23

Table 3. Energetic, geometric, and electronic aspects of $C_4H_5(F)-PH_2\cdots NH_3$ complexes.

	$-CF=CH-CH=CH_2$	$-CH=CF-CH=CH_2$	$-CH=CH-CF=CH_2$	$-CH=CH-CH=CFH$
ΔE, kcal/mol	-2.38	-1.84	-1.85	-1.70
$R(P\cdots N)$ Å	3.141	3.193	3.212	3.230
$\theta(CP\cdots N)$, degs	165	168	168	169
$E(2)$, kcal/mol	3.42	2.45	2.31	1.96
Δq, me	5.76	4.01	3.83	3.30
$\Delta r(C-P)$, mÅ	3.63	3.05	1.99	1.63

Table 4. Energetic, geometric, and electronic aspects of fluorophenyl complexes.

	$o-FC_6H_4$	$m-FC_6H_4$	$p-FC_6H_4$	C_6F_5
ΔE, kcal/mol	-1.96	-1.81	-1.72	-2.87
$R(P\cdots N)$ Å	3.170	3.188	3.219	3.068
$\theta(CP\cdots N)$, degs	167	168	169	162
$E(2)$, kcal/mol	2.79	2.55	2.08	5.02
Δq, me	4.79	4.38	3.62	8.99
$\Delta r(C-P)$, mÅ	3.2	1.54	2.13	11.43

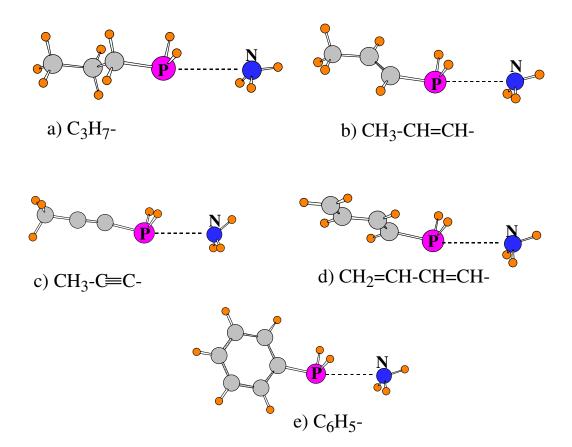o-, m-, and p- refer respectively to ortho, meta and para position of F with respect to $-PH_2$ group.

a) C$_3$H$_7$-

b) CH$_3$-CH=CH-

c) CH$_3$-C≡C-

d) CH$_2$=CH-CH=CH-

e) C$_6$H$_5$-

Fig 1. Optimized RH$_2$P···NH$_3$ complexes with various carbon chains taken as R group.