PAPER www.rsc.org/njc | New Journal of Chemistry

Computational study of the bonding structure in ylide compounds

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Received (in Montpellier, France) 1st October 2007, Accepted 26th November 2007
First published as an Advance Article on the web 5th December 2007
DOI: 10.1039/b715049k

The ylide compounds $H_mD{=}AH_n$ (DH_m = NH_3, PH_3, OH_2, SH_2; AH_n = CH_2, NH, NH_2^+, SiH_2, PH, PH_2^+) were examined using *ab initio* calculations. The main finding is that the geometrical planarity and bond strength of the D=A double bond vary significantly for different carbenoid AH_n adducts. Some rationalization of this interesting observation was provided by the $\Sigma\Delta E_{ST}$ (CGMT model) and the HOMO–LUMO gap of the two bonding fragments. In addition, this study demonstrated that protonated pnictenes behave much like heavy carbenes, with respect to their weak π-bonding character. In contrast, nitrene (HN) and nitrenium (H_2N^+) are predicted to have triplet ground states. Thus, both of these species have strong π-bonding character similar to that in carbene.

Introduction

Ylides are dipolar molecules that contain positive and negative charges on adjacent atoms. The most common compounds are phosphorus and sulfur ylides (eqn (1) and (2)), in which a carbanion is directly attached to a phosphorus or sulfur atom carrying a substantial degree of positively charge.[1] Generally, both types of ylides can be generated from phosphonium ($[R_3PCHR'_2]^+X^-$) or sulfonium salts ($[R_2SCHR'_2]^+X^-$).[2] However, the most direct synthesis of the sulfur ylides involves the addition of a sulfide to a carbene.[3]

$$R_3P^+{-}C^-R'_2 \leftrightarrow R_3P{=}CR'_2 \quad (1)$$

$$R_2S^+{-}C^-R'_2 \leftrightarrow R_2S{=}CR'_2 \quad (2)$$

Phosphonium derivatives are useful in organic synthesis, especially in constructing C=C double bonds. The Wittig reaction, the reaction of a phosphorus ylide with an aldehyde or ketone, is one of the most important organic reactions.[4] Many studies concerning ylide compounds have been conducted by theoretical and experimental chemists. Most were trying to resolve some dispute related to the extent of multiple bonding between the carbon and the heteroatom (P and S) in phosphorus and sulfur ylides.[5] Several computational studies of simple ylidic species have been performed in recent years.[6–10] Bonding studies of phosphorus ylides have focused on the nature of the P–C bond, and have been explained in terms of a resonance hybrid between the dipolar and phosphorane forms (eqn (1)).[11] NBO analysis of the molecules SH_2CH_2 and $(CH_3)_2SCH_2$ shows that there is an intermediate single–double bond character between the carbon and sulfur. In addition, the rotational barrier in sulfur ylides is larger than that in the phosphorus ylides.[12]

To understand the chemical bond in ylides, Dobado *et al.* published several important papers.[8,9] A comparison of H_mXCH_2 (XH_m = NH_3, PH_3, AsH_3, OH_2, SH_2, SeH_2) was performed by means of the electron pair density in conjunction with the atoms in molecules (AIM) theory and the calculated NMR chemical shifts.[8] According to Dobado, the N–C bond is weaker than a single bond (1.563 Å for H_3NCH_2 *vs.* 1.465 Å for H_2NCH_3), but the P–C and As–C bonds are shorter than standard single bonds (1.681 Å for H_3PCH_2 *vs.* 1.872 Å for H_2PCH_3; 1.836 Å for H_3AsCH_2 *vs.* 1.997 Å for H_2AsCH_3).[9,13]. Similarly, the O–C bond is weaker than a single bond (1.772 Å for H_2OCH_2 *vs.* 1.422 Å for CH_3OH), but the S–C and Se–C bonds are shorter than standard single bonds (1.675 Å for H_2SCH_2 *vs.* 1.834 Å for CH_3SH; 1.843 Å for H_2SeCH_2 *vs.* 1.978 Å for CH_3SeH).[8] The AIM and chemical shifts are in good accordance with the above-mentioned bonding schemes.[8]

Although ylides are organic compounds, the concept can be extended to inorganic molecules with a zwitterionic structure, where carbon is replaced by a heteroatom. In addition, the main differences in the pnictogen and chalcogen ylide series need to be clarified and analyzed to understand their respective bonding to carbon. The aim of this work is to provide a systematic theoretical study of the equilibrium structures and bond dissociation energies (BDEs) of the heteroatom analogues H_mDAH_n (DH_m = NH_3, PH_3, OH_2, SH_2; AH_n = CH_2, NH, NH_2^+, SiH_2, PH, PH_2^+). The primary purpose of this study is to systematically elucidate the changes in the properties of the ylide compounds involving elements in the first two rows of the periodic table because of their varied ability to fill their valence shells. We would like to demonstrate that the geometries and BDEs of H_mDAH_n can be correlated with the $\Sigma\Delta E_{ST}$ (sum of ΔE_{ST} for the two fragments in the complexes) and the HOMO–LUMO gap of the two bonding fragments. These results will provide insight into the nature of the bonding interactions in ylide compounds.

Methodology

The geometries of the ylide compounds were fully optimized, and vibrational frequencies were calculated using the Møller–Plesset perturbation theory terminated at second order

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Table 1 Optimized geometries (bond lengths in Å) and ΔE_{ST} (kcal mol^{-1})[a] of the fragments DH_m (D = NH_3, PH_3, OH_2, SH_2) and AH_n (AH_n = CH_2, NH, NH_2^+, SiH_2, PH, PH_2^+) at MP2/aug-cc-pVTZ level of theory

	d(D–H)	d(A–H)	ΔE_{ST}
NH_3	1.012	—	124.28
PH_3	1.412	—	78.58
H_2O	0.961	—	152.96
H_2S	1.336	—	99.42
NH_2^+	—	1.028	−35.75
CH_2	—	1.074	−14.13
PH_2^+	—	1.418	13.27
SiH_2	—	1.515	16.87
NH	—	1.031	−52.80
PH	—	1.420	−34.48

[a] ΔE_{ST} = E(triplet) − E(singlet).

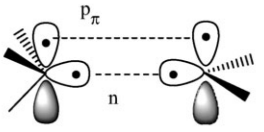
(MP2).[14] The correlation consistent triple-ζ basis sets, augmented by a set of diffuse functions (aug-cc-pVTZ), were used for all calculations.[15,16] True minima were confirmed by frequency analysis. All calculations were performed with the GAUSSIAN 03 package.[17] Zero-point vibrational energies (ZPE) were included in the reported energies.

Orbital energies were determined at the HF/aug-cc-pVTZ level of theory. It is known that the HF results are a useful reference for comparing the experimental results according to Koopmans' theorem.[18,19] In addition, the orbitals and charges were analyzed by means of the natural bond orbital (NBO) scheme.[20]

Results and discussion

The optimized geometries of the fragments DH_m (DH_m = NH_3, PH_3, OH_2, SH_2), AH_n (AH_n = CH_2, NH, NH_2^+, SiH_2, PH, PH_2^+) and their complexes at MP2/aug-cc-pVTZ level of theory are summarized in Tables 1–3. As can be seen in Tables 2 and 3, the calculated geometries of H_mDAH_n complexes agree quite well with previously reported theoretical data.[6–10,21–33] For the H_mDAH_2 complexes (A = C, N^+, Si, P^+), there is a reasonable correlation between the τ-angle, which measures the degree of planarity at the A atom, and the $\Sigma\Delta E_{ST}$ values (ΔE_{ST} is the energy difference between the singlet and triplet electronic states for DH_m and AH_n.

$\sum\Delta E_{ST}$ is the sum of ΔE_{ST} for the two fragments in the complexes). As shown in Fig. 1, when DH_m = NH_3, $\angle\tau = -0.5317\sum\Delta E_{ST} + 164.68$ (R^2 = 0.9783 from linear regression). When DH_m = PH_3, $\angle\tau = -1.3221\sum\Delta E_{ST} + 214.21$ (R^2 = 0.9286). When DH_m = OH_2, $\angle\tau = -0.3788\sum\Delta E_{ST} + 153.24$ (R^2 = 0.8814). When DH_m = SH_2, $\angle\tau = -1.0736\sum\Delta E_{ST} + 218.22$ (R^2 = 0.8076). A smaller $\sum\Delta E_{ST}$ value corresponds to a larger τ-angle. That is, decreasing the value of $\sum\Delta E_{ST}$ of the two bonding fragments increases the planarity on AH_2. Such a geometrical trend is anticipated from the Carter–Goddard–Malrieu–Trinquier (CGMT) model.[34] According to the CGMT model, ΔE_{ST} is the promotion energy from the singlet state with the lone pair n^2 to the triplet state with the configuration $n^1p_\pi^1$, the correct valence state for double bond formation, as shown in structures **1** (DH_m = NH_3, PH_3) and **2** (DH_m = OH_2, SH_2).



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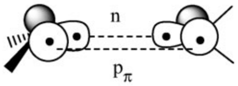

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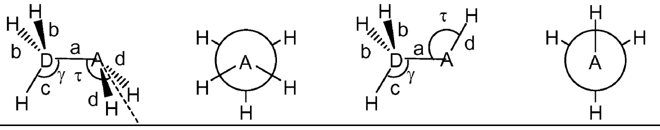
Alternatively, H_3DAH_2 bonding can also be described as the interaction of H_3D with an n^2 singlet AH_2 (as shown in structure **3**), or with a p_π^2 singlet excited AH_2 (as shown in structure **4**);[34] specifically, an ylidic bond can be viewed as a

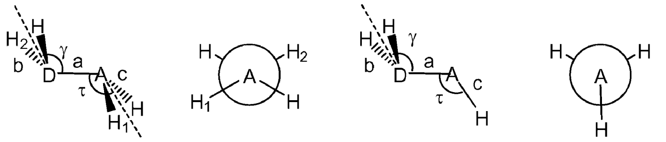
Table 2 Optimized geometries (bond lengths in Å and bond angles in degrees) and $\sum\Delta E_{ST}$ (kcal mol^{-1})[a] of the complexes H_3DAH_n (D = N, P; AH_n = CH_2, NH, NH_2^+, SiH_2, PH, PH_2^+) at MP2/aug-cc-pVTZ level of theory



	a	b	c	d	$\angle\gamma$	$\angle\tau$	$\sum\Delta E_{ST}$
$H_3N–NH_2^+$	1.440	1.023	1.026	1.016	115.8	116.1	88.53
$H_3N–CH_2$	1.544 (1.548;[b] 1.550[c])	1.015 (1.014)[b]	1.025 (1.027)[b]	1.096 (1.098)[b]	118.9 (120.2)[b]	108.6 (113.6)[b]	110.15
$H_3N–PH_2^+$	1.876	1.022	1.021	1.410	113.9	92.2	137.55
$H_3N–SiH_2$	2.041	1.014	1.014	1.520	112.0	88.0	141.15
$H_3N–NH$	1.452	1.026	1.016	1.022	105.2	102.4	71.48
$H_3N–PH$	1.927	1.015	1.015	1.418	107.5	89.1	89.80
$H_3P–NH_2^+$	1.631	1.392	1.398	1.011	117.6	150.0	42.83
$H_3P–CH_2$	1.678 (1.678;[b] 1.669[c])	1.400 (1.402)[b]	1.432 (1.438)[b]	1.082 (1.084)[b]	128.6 (129.4)[b]	142.2 (148.4)[b]	64.45
$H_3P–PH_2^+$	2.198	1.396	1.397	1.415	117.2	90.1	91.85
$H_3P–SiH_2$	2.320	1.402	1.407	1.519	125.2	85.1	95.45
$H_3P–NH$	1.574	1.416	1.395	1.014	108.9	114.7	25.78
$H_3P–PH$	2.082	1.410	1.399	1.421	109.9	88.4	44.10

[a] ΔE_{ST} = E(triplet) − E(singlet). $\sum\Delta E_{ST}$ is the sum of ΔE_{ST} for the two fragments (DH_3 and AH_n) in the complexes. [b] Ref. 8: MP2/6-311+G*//MP2/6-311+G* values. [c] Ref. 30: MP2/6-311++G** values.

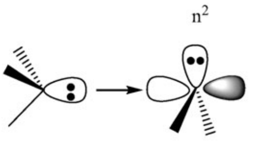
Table 3 Optimized geometries (bond lengths in Å and bond angles in degrees) and $\sum\Delta E_{ST}$ (kcal mol^{-1})[a] of the complexes H_2DAH_n (D = O, S; AH_n = CH_2, NH, NH_2^+, SiH_2, PH, PH_2^+) at MP2/aug-cc-pVTZ level of theory



	a	b	c	∠γ	∠τ	∠H_1ADH_2	$\sum\Delta E_{ST}$
$H_2O–NH_2^+$	1.470	0.980	1.019	126.9	111.2	102.4	117.21
$H_2O–CH_2$	1.741	0.968	1.100	101.1	96.3	179.1	138.83
	(1.734)[b]						
$H_2O–PH_2^+$	1.840	0.973	1.408	143.4	93.4	108.5	166.23
$H_2O–SiH_2$	2.079	0.966	1.518	121.3	87.8	91.1	169.82
	(2.113;[c] 2.090[d])	(0.974)[d]	(1.515)[d]				
$H_2O–NH$	1.600	0.968	1.023	104.8	95.1	—	100.15
$H_2O–PH$	1.980	0.966	1.414	117.1	87.8	—	118.48
$H_2S–NH_2^+$	1.640	1.350	1.012	108.4	139.0	65.1	63.67
$H_2S–CH_2$	1.663	1.367	1.078	118.5	145.5	60.1	85.29
	(1.663;[e] 1.680[f])	(1.354)[e]	(1.081)[e]	(124.0)[e]	(148.0)[e]		
$H_2S–PH_2^+$	2.227	1.347	1.412	103.4	93.6	80.2	112.69
$H_2S–SiH_2$	2.423	1.340	1.516	108.1	89.0	77.0	116.29
$H_2S–NH$	1.599	1.362	1.019	107.9	102.7	—	46.62
$H_2S–PH$	2.118	1.350	1.415	110.2	86.2	—	64.94

[a] ΔE_{ST} = E(triplet) − E(singlet). $\sum\Delta E_{ST}$ is the sum of ΔE_{ST} for the two fragments (DH_2 and AH_n) in the complexes. [b] Ref. 21: MP2/6-311++G** values. [c] Ref. 24: MP2/6-31+G* values. [d] Ref. 25: MP2/6-31G(d) values. [e] Ref. 8: MP2/6-311+G*//MP2/6-311+G* values. [f] Ref. 22: MP2/DZ* values.

dative bond. When the energy required to obtain the p_π^2 configuration is large (the singlet-ground-state AH_2 with positive ΔE_{ST}), a bent geometry is preferred so that the n^2 configuration can be preserved. In contrast, when AH_2 has a small and negative ΔE_{ST}, a planar or quasi-planar geometry with a large τ-angle is preferred. Similarly, bonding in H_2DAH_2 can also be described as shown in structures **5** or **6**.[34]



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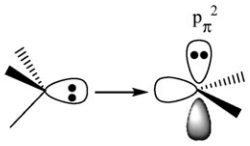

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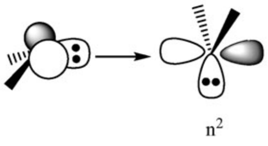

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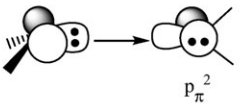

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The orbital interactions considered also provide insight into the origins of the geometric distortions in the DH_2 fragments in H_2DAH_2. Each of these interactions will lead to distortion of DH_2 to maximize two-electron stabilization. Fig. 2 shows secondary overlap of H_2SCH_2 and $H_2SNH_2^+$. For H_2SCH_2, this secondary overlap will cause the HSH plane to tilt away from C and cause the HCH plane to maintain its planarity with respect to S, so as to increase the stabilization. Since the π_C orbital, as compared to the π_N orbital, is much closer to the π_S* orbital, a stronger secondary overlap is expected for H_2SCH_2. The angular distortion resulting from this effect leads to ∠γ = 118.5° (H_2SCH_2) > 108.4° ($H_2SNH_2^+$) and ∠τ = 145.5° (H_2SCH_2) > 139.0° ($H_2SNH_2^+$) at MP2/aug-cc-pVTZ level of theory. An additional consequence of this secondary interaction is lengthening of the S–H bonds of H_2SCH_2. Inspection of Table 3 reveals that this effect amounts to *ca.* 0.02 Å, the S–H bond of H_2SCH_2 being longer than those of $H_2SNH_2^+$.

Because phosphinidene (RP) and phosphonium (R_2P^+) have important differences in their respective π-bonding capabilities,[35] we optimized the H_mDAH complexes (DH_m = NH_3, PH_3, OH_2, SH_2; A = N, P) to observe the geometrical variations. At the MP2/aug-cc-pVTZ level of theory, ∠DPH was found to be near 90° for the H_mDPH complexes (89.1° for DH_m = NH_3; 88.4° for DH_m = PH_3; 87.8° for DH_m = OH_2; 86.2° for DH_m = SH_2). Because PH has two singly-occupied p orbitals, *i.e.*, ground triplet state, it has the correct valence

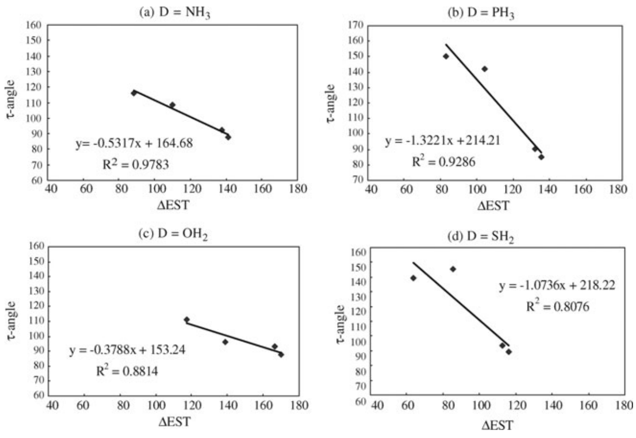


Fig. 1 The correlation between τ-angle and $\sum\Delta E_{ST}$ of H_mDAH_2 (A = C, N^+, Si, P^+) complexes at MP2/aug-cc-pVTZ level of theory.

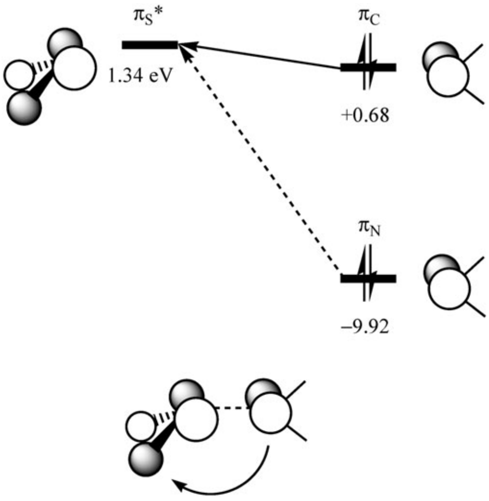
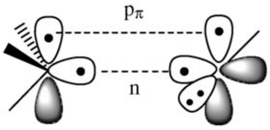


Fig. 2 Secondary orbital interactions between the frontier orbitals of SH_2 and AH_2 (A = C, N^+) fragments.

state to form a stable double bond as shown in structure **7** (DH_m = NH_3, PH_3) and **8** (DH_m = OH_2, SH_2). Alternatively, we can also describe the bonding in H_mDAH complexes as the interaction of the ground-state H_mD with a singlet excited AH as shown in structure **9** (DH_m = NH_3, PH_3) and **10** (DH_m = OH_2, SH_2).



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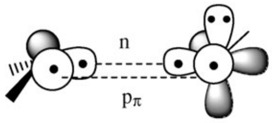

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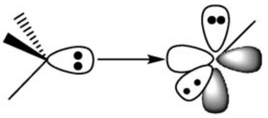

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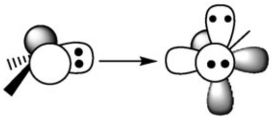

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After protonation, the PH_2^+ is isolobal to carbene with a stable lone pair n^2. Thus, a significant n → p_π promotion is required for double bond formation. In addition, the τ-angle value for $H_mDPH_2^+$ is similar to the corresponding H_mDSiH_2. It is interesting to examine the ΔE_{ST} value for the protonated species AH_2^+ and those of the carbene analogues of group 14 elements. The original difference ($\Delta E_{ST}(PH) - \Delta E_{ST}(NH)$) at the MP2/aug-cc-pVTZ level of theory between PH and NH is 18.32 kcal mol^{-1}. After protonation, this energy difference ($\Delta E_{ST}(PH_2^+) - \Delta E_{ST}(NH_2^+)$) significantly increases to a value of 49.02 kcal mol^{-1} between PH_2^+ and NH_2^+. This situation resembles the occurrence of the largest ΔE_{ST} gap between SiH_2 and CH_2 for the group 14 elements ($\Delta E_{ST}(SiH_2) - \Delta E_{ST}(CH_2)$ = 31.00 kcal mol^{-1}). The distinction in the π-bonding capability between PH_2^+ and NH_2^+ therefore resembles that between SiH_2 and CH_2. Interestingly, nitrenium (NH_2^+) has a persistent π-bonding tendency with a negative ΔE_{ST} = −35.75 kcal mol^{-1}, compared with −52.80 kcal mol^{-1} for NH. Therefore, both of these moieties resemble carbene and we observed that the τ-angle values for $H_mDNH_2^+$ and H_mDCH_2 are similar.

Table 4 Calculated bond dissociation energies (BDE, kcal mol^{-1}),[a] ΔIP (eV),[b] D–A bond distances (*d*(D–A), Å) and NBO charge (*q*) for the H_mDAH_n complexes (DH_m = NH_3, PH_3, OH_2, SH_2; AH_n = CH_2, NH, NH_2^+, SiH_2, PH, PH_2^+) at MP2/aug-cc-pVTZ level of theory

H_mDAH_n	BDE	ΔIP	*d*(D–A)	*q*(D)	*q*(A)
$H_3P–NH_2^+$	178.1	−0.48	1.631	1.29	−1.18
$H_3N–NH_2^+$	143.0	−1.67	1.440	−0.49	−0.57
$H_3P–NH$	118.6	−10.69	1.574	1.33	−1.37
$H_3P–CH_2$	67.50	−11.08	1.678	1.05	−1.21
$H_3N–NH$	60.78	−11.88	1.452	−0.51	−0.87
$H_3N–CH_2$	35.53	−12.27	1.544	−0.68	−0.68
$H_3P–PH_2^+$	86.51	−1.89	2.198	0.60	0.30
$H_3N–PH_2^+$	86.05	−3.08	1.876	−0.95	0.73
$H_3P–PH$	60.68	−9.50	2.082	0.61	−0.40
$H_3N–PH$	41.84	−10.69	1.927	−0.92	−0.17
$H_3N–SiH_2$	25.43	−11.51	2.041	−1.00	0.44
$H_3P–SiH_2$	23.73	−10.32	2.320	0.42	0.20
$H_2S–NH_2^+$	136.7	+1.16	1.640	0.85	−0.99
$H_2O–NH_2^+$	90.92	−1.69	1.470	−0.54	−0.36
$H_2S–NH$	79.15	−9.05	1.599	0.79	−1.19
$H_2S–CH_2$	42.11	−9.44	1.663	0.57	−1.02
$H_2O–NH$	26.36	−11.90	1.600	−0.15	−0.57
$H_2O–CH_2$	11.11	−12.29	1.741	−0.77	−0.43
$H_2S–PH_2^+$	66.82	−0.25	2.227	0.19	0.49
$H_2O–PH_2^+$	57.77	−3.10	1.840	−0.89	0.87
$H_2S–PH$	39.25	−7.86	2.118	0.16	−0.29
$H_2O–PH$	22.00	−10.71	1.980	−0.86	−0.06
$H_2S–SiH_2$	14.38	−8.68	2.423	−0.03	0.34
$H_2O–SiH_2$	13.12	−11.53	2.079	−0.91	0.53

[a] BDE is defined as Δ*E* for H_mDAH_n → DH_m + AH_n, where DH_m and AH_n are in the ground singlet states. [b] ΔIP is defined as the difference between the orbital energies of the HOMO of DH_m and the LUMO of AH_n (in the ground singlet state) at the HF/aug-cc-pVTZ level of theory.

Table 4 presents the computed bond dissociation energies (BDEs) for the H_mDAH_n complexes (DH_m = NH_3, PH_3, OH_2, SH_2; AH_n = CH_2, NH, NH_2^+, SiH_2, PH, PH_2^+). The BDEs are calculated as the energy differences between the complexes and the respective optimized fragments DH_m and AH_n in their electronic ground singlet states, *e.g.*, the $^1A_1$ state for CH_2. The MP2/aug-cc-pVTZ method should be the best choice for estimating the bond strength of the ylide compounds because the MP2/aug-cc-pVTZ BDEs are comparable to CBS-QB3 data.[7,13]

The electronic structures of the singlet H_mDAH_n complexes can be formed from either two triplet or two singlet fragments.

As shown in Tables 2 and 3, the promotion energy of the fragments from the respective ground singlet state into two triplet species ($\sum \Delta E_{ST}$) was required in the former case. Thus, the bonding mode, which consists of two singlet fragments, should be favored over the bonding mode that consists of two triplet fragments.

As in the previous discussion on geometry, an ylidic bond can be viewed as a dative bond. Consider the ionization potential for the orbitals involved in the D–A interaction. For example, in $H_3N–CH_2$, the HOMO of the CH_2 fragment is the lone-pair σ orbital and the LUMO is the p_π orbital. The LUMO of the CH_2 is +0.68 eV, with lower magnitude than that of the σ nonbonding ionization energy on the nitrogen of the ammonia molecule, −11.59 eV, as shown in Fig. 3. The IP

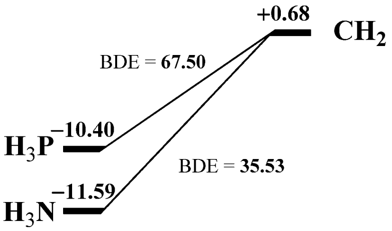


Fig. 3 Orbital energy (in eV) of NH_3 and PH_3 and CH_2 calculated at the HF/aug-cc-pVTZ level of theory. BDE is defined as ΔE for $H_3DCH_2 \rightarrow DH_3 + CH_2$, where DH_3 and CH_2 are in the ground singlet states.

value can be correlated with the orbital energy, which is also an indicator of the ability to attract electrons toward the corresponding orbital. Therefore, the electron-pair on the nitrogen lies closer to the nitrogen relative to the carbon and gives rise to a weaker N–C interaction.

For the complex H_3P–CH_2, the HOMO–LUMO gap is reduced, as compared to H_3N–CH_2. Therefore, the electron-pair from the PH_3 can be donated to CH_2 more efficiently, resulting in a stronger P–C interaction, as indicated by a larger BDE value. As can be seen in Table 4, all H_3P–AH_n interactions are stronger than the H_3N–AH_n interactions with the same AH_n (except for H_3N–SiH_2 since it has a large electrostatic attractive interaction). For the same reason, all H_2S–AH_n interactions are stronger than the H_2O–AH_n interactions with the same AH_n.

In addition, from the results in Table 4, we can state that during complexation, the charge transfer between PH_3 and AH_n and between H_2S and AH_n are much more significant than between NH_3 and AH_n and between H_2O and AH_n, respectively, because $q(\mathrm{P}) = 0.18e$ in the isolated PH_3 and $q(\mathrm{N}) = -1.02e$ in the isolated NH_3. For example, $q(\mathrm{N}) \cong -0.68e$ in H_3N–CH_2, thus, $\Delta q(\mathrm{N}) \cong +0.34e$. The charge on the P atom of PH_3 moiety in the H_3P–CH_2 is $+1.05e$, that is, $\Delta q(\mathrm{P}) \cong +0.87e$. Similarly, $q(\mathrm{S}) = -0.22e$ in the isolated H_2S and $q(\mathrm{O}) = -0.93e$ in the isolated H_2O. When in H_2O–CH_2, $q(\mathrm{O}) \cong -0.77e$ and thus $\Delta q(\mathrm{O}) \cong +0.21e$, and the charge on the S atom of H_2S moiety in the H_2S–CH_2 is $+0.57e$, that is, $\Delta q(\mathrm{S}) \cong +0.79e$. This information gives an important suggestion concerning the electronic structures and bonding nature in the singlet ylide compounds: PH_3 is a stronger donor than NH_3, and thus the heteroatom in the AH_n portion bears a greater negative charge (or a less positive charge). In addition, H_2S is a stronger donor than H_2O, and the heteroatom in the AH_n part bears a more negative charge (or a less positive charge). Therefore, we conclude that the main factor that determines the bond strength of a donor–acceptor bond is the difference between orbital energies (ΔIP = HOMO(DH_m) − LUMO(AH_2)) of the orbitals involved in the H_mD–AH_n interaction.

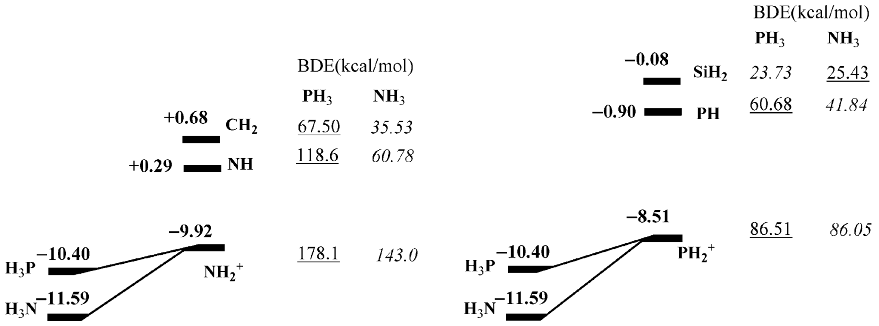
Furthermore, we compared the BDE for ylide compounds involving elements in the first two rows of the periodic table. In each series, as seen in Table 4 and Fig. 4 and 5, the more negative the ΔIP, the smaller the BDE. Specifically, there is a reasonable correlation between the ΔIP and the BDE values of H_mD–AH_n. A less negative ΔIP value results in a stronger D–A interaction indicated by a larger BDE value.

Conclusions

For the H_mDAH_2 complexes (DH_m = NH_3, PH_3, OH_2, SH_2; A = C, N^+, Si, P^+), the τ-angle, which measures the degree of planarity at the A atom, correlates well with $\sum \Delta E_{ST}$.

Decreasing the value of $\sum \Delta E_{ST}$ of the two bonding fragments increases the planarity at AH_2; hence, we can predict the π-bonding contribution of the H_mDAH_2 complexes from its τ-angle value. These results can be interpreted in terms of the CGMT model.

As for the bond dissociation energy (BDE) of the D–A bond in H_mDAH_n (DH_m = NH_3, PH_3, OH_2, SH_2; AH_n = CH_2, NH, NH_2^+, SiH_2, PH, PH_2^+) complexes, our calculations demonstrate that all H_3P–AH_n interactions are stronger than the corresponding H_3N–AH_n interactions. PH_3 is a stronger donor than NH_3. Similarly, all H_2S–AH_n interactions are stronger than the corresponding H_2O–AH_n interactions. Thus, H_2S is a stronger donor than H_2O. In summary, it appears that one important parameter for the bonding strength of the H_mD–AH_n system is the difference between the orbital energies ΔIP [HOMO(DH_m) − LUMO(AH_n)]. The IPs refer to the orbitals involved in the H_mD–AH_n interaction. A less negative ΔIP value reflects a stronger D–A interaction with a larger BDE.



(a) (b)

Fig. 4 Orbital energy (in eV) of NH_3 and PH_3 and different AH_n calculated at the HF/aug-cc-pVTZ level of theory: (a) A = elements from the first row of the periodic table, (b) A = elements from the second row of the periodic table. Complexes with larger BDEs are underlined when comparing H_3P–AH_n and H_3N–AH_n.

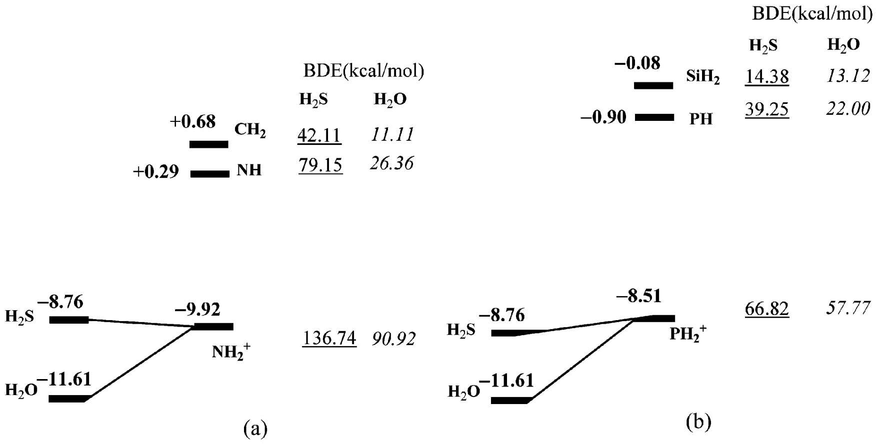


Fig. 5 Orbital energy (in eV) of H_2O and H_2S and different AH_n calculated at the HF/aug-cc-pVTZ level of theory: (a) A = elements from the first row of the periodic table, (b) A = elements from the second row of the periodic table. Complexes with larger BDEs are underlined when comparing H_2S–AH_n and H_2O–AH_n.

Acknowledgements

We are grateful to the National Center for High-performance Computing for computer time and facilities. We also thank the National Science Council of Taiwan for financial support (NSC 96-2113-M-152-001) and Prof. Dr San-Yan Chu for helpful and generous suggestions. Also, we are grateful to the referees for their useful comments.

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