# C–H···C Hydrogen bonding involving ylides

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***Ab initio* calculations on nitrogen and phosphorous ylides, and their complexes with methane and acetylene, are reported. A hydrogen bond strength of 35 kJ mol$^{-1}$ is found between $H_3N$–$CH_2$ and acetylene at the MP2/6-311++G(3d,3p) level; even with methane as the proton donor some stabilisation (*ca.* 5 kJ mol$^{-1}$) is predicted. Complexes of $H_3P$–$CH_2$ are found to be rather less stable (19 kJ mol$^{-1}$ with acetylene). Topological analysis of the charge density indicates a fundamental difference in the bonding between $H_3N$–$CH_2$ and $H_3P$–$CH_2$, with significant double bond character only in the latter. Atoms in molecules decomposition identifies the source of the hydrogen bond strength to be stabilisation of C in the N ylides and stabilisation of P in the P ylides. The effects of methyl and phenyl substituents on the ylidic carbon are investigated: methyl substitution enhances basicity slightly, but phenyl substitution decreases it dramatically. There is some suggestion that this may be a steric as well as an electronic effect.**

## Introduction

In an initial communication[1] (hereafter Paper 1), we reported the remarkable stability of C–H···C hydrogen bonds found when the basic atom is incorporated into an ylide. The complex of $H_3N$–$CH_2$ with acetylene was found to be stabilised by upwards of 30 kJ mol$^{-1}$, and even complexes with methane were shown to have significant stabilisation. While we believe this property of ylides to be of inherent interest, it may also be of great practical importance. Hydrogen bonding is probably the single most important tool in the kit of the 'crystal engineer'[2], its directional nature being a particularly useful feature. Indeed, since the publication of Paper 1 an intriguing study of crystalline ylides has appeared,[3] in which C–H···C H-bonds appear to be the dominant intermolecular interactions.

The importance of H-bonding is reflected in the large and ever-growing number of theoretical studies on the subject.[4] Such studies typically involve polar molecules containing first-row atoms such as HF or $H_2O$, resulting in strong, primarily electrostatic H-bonds. Weaker H-bonds involving second- and third-row atoms have been somewhat less studied.[5] Similarly, H-bonds involving less polar groups, such as C–H···O interactions, have been only sparsely studied.[6] A study of the complex of methane with water[6a] found an interaction energy of just 2.4 kJ mol$^{-}$ as the MP2 level, approximately ten times weaker than the water dimer.[4d] The weakness of the interactions of such non-polar molecules makes them difficult to study theoretically, since large basis sets and correlated methods must be used.

The ability of the basic carbon in ylides to act as hydrogen bond acceptors is the main interest of this study. We also report results of topological charge density analysis and atoms in molecules (AIM) decomposition of the ylides themselves, since there is some debate over the nature of bonding in these systems.[7] Of interest here is the double bond character of the Y–C bond, the lone pair (LP) properties of the ylidic carbon and the way such properties are modified by substitution and by hydrogen bonding.

## Computational

Full geometry optimisations were carried out on the $C_s$ species $H_3N$–$CH_2$ and $H_3P$–$CH_2$ and their complexes with methane and acetylene, along with $CH_4$ and HCCH at the MP2(FC)/6-311++G(d,p) level[8,9] using GAUSSIAN94.[10] Subsequent energy calculations at these optimised geometries used the 6-311++G(2d,2p) and (3d,3p) basis sets. Counterpoise corrections[11] were used to estimate the basis set superposition error (BSSE) involved in the resulting binding energies. In order to probe the effects of electron correlation, HF/6-311++G(d,p) optimisations on all the above species were performed for comparison with the MP2 results.

The effects of substituents on the proton acceptor properties of the N- and P-ylides were examined using the compounds $H_3Y$–$CMe_2$ and $H_3Y$–$CPh_2$ (Y = N or P). These ylides, and their acetylene complexes, were optimised at the HF level. Problems with SCF convergence forced us to use a modified basis set, consisting of 6-31G(d,p)[12] on the methyl and phenyl substituents and 6-311++G(d,p) on the remainder of the molecule.

Analysis of the ylides $H_3Y$–$CH_2$ (Y = N or P) and their complexes followed the techniques developed by Bader.[13] According to Bader and Essen[14] the presence of a minimum on the line of maximal charge density joining the nuclei—termed a (3,−1) critical point (CP)—is a necessary condition for two atoms to be bonded. The same authors also demonstrated that the properties of the charge density at such a point characterise atomic interactions. In particular, the values of $\rho$ and $\nabla^2\rho$ are often diagnostic of ionic/covalent character, while the ellipticity, $\varepsilon$, defined as $\lambda_1/\lambda_2$-1 (where $\lambda_1$ and $\lambda_2$ are the negative curvatures of the density) usually quantifies π-character. In a similar fashion, maxima in $-\nabla^2\rho$ have been demonstrated[15] to recover the expected behaviour of Lewis electron pairs, and the values of $\nabla^2\rho$ at such points are widely used as a predictor of reactivity.[16] Topological analyses of $\rho$ and $-\nabla^2\rho$ used the programs EXTREME and BUFFALO, part of the AIMPAC suite of programs.[17]

Integrated atomic properties were calculated using the AIMPAC program PROAIMV. The boundaries of an atomic sub-system (Ω) are defined such that the sub-system obeys the 'zero-flux' condition, eqn. (1), for all points $r$ on the surface ($\boldsymbol{n}$ is

$$\nabla\rho(r)\cdot\boldsymbol{n}(r) = 0 \qquad (1)$$

a vector normal to this surface). Sub-systems so defined obey the Virial theorem.[18] A property density, $\rho_A(r)$, corresponding to an observable $\hat{A}$ can be integrated over the basin defined by the zero-flux surface to yield the atomic expectation value of $\hat{A}$, eqn. (2).

$$A(\Omega) = \int_\Omega d\tau\rho A(r) \qquad (2)$$

In this fashion, it is possible to evaluate atomic properties such as populations and charges,[19] total energies,[20,21] volumes[22]

**Table 1** Hydrogen bond energies/kJ mol$^{-1}$ [a]

| | $H_3Y–CH_2\cdots HCH_3$ | | $H_3Y–CH_2\cdots HCCH$ | | $H_3Y–CMe_2\cdots HCCH$ |
|---|---|---|---|---|---|
| Method/basis set | I | II | I | II | I |
| Y = N | | | | | |
| HF/6-311+ +G(d,p) | 2.36 | — | 22.80 | 21.91 | 20.90 |
| MP2/6-311+ +G(d,p) | 6.21 | 2.74 | 35.64 | 30.43 | — |
| MP2/6-311+ +G(2d,2p) | 5.23 | 3.57 | 34.95 | 33.89 | — |
| MP2/6-311+ +G(3d,3p) | 4.90 | 3.95 | 35.64 | 34.14 | — |
| Y = P | | | | | |
| HF/6-311+ +G(d,p) | 2.09 | — | 13.03 | 12.77 | 12.10 |
| MP2/6-311+ +G(d,p) | 5.83 | 1.91 | 20.95 | 14.64 | — |
| MP2/6-311+ +G(2d,2p) | 3.68 | 2.75 | 17.23 | 15.53 | — |
| MP2/6-311+ +G(3d,3p) | 4.89 | 3.03 | 18.76 | 15.92 | — |

[a] All energies, except the HF values, correspond to the MP2/6-311+ +G(d,p) optimised geometry; I indicates no counterpoise correction, II indicates counterpoise correction included.

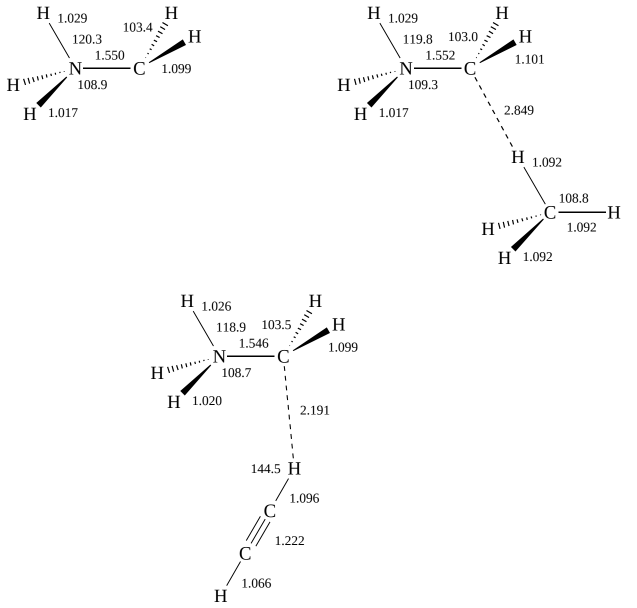

**Fig. 1** MP2/6-311++G(d,p) optimised geometries of $H_3N–CH_2$ and its complexes with methane and acetylene

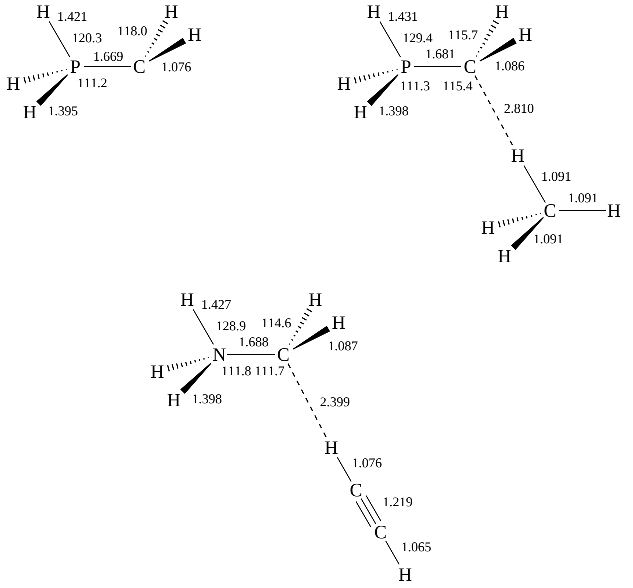

**Fig. 2** MP2/6-311++G(d,p) optimised geometries of $H_3P–CH_2$ and its complexes with methane and acetylene

and multipole moments.[23] While many schemes exist for the computation of atomic charges,[24] and Stone's DMA technique[25] is able to deliver atom-centred multipoles, it is a unique feature of Bader's zero-flux partioning scheme that atomic energies may be computed.

## Results and discussion

### I. Geometries and energies

Results of geometry optimisation at the MP2/6-311++G(d,p) level for the ylides $H_3N–CH_2$ and $H_3P–CH_2$, and their complexes with $CH_4$ and HCCH, are shown in Figs. 1 and 2. The rotational isomers shown were found to be the global minima for the free ylides; this conformation was assumed in all optimisations of complexes. The N–C bond length in the free ylide is very long—much longer than an N=C double bond and even longer than a typical N–C single bond,[26] in agreement with a previous MP2 result.[27] Thus, it seems that there is no possibility of any π-character existing in this bond. The P ylide $H_3P–CH_2$ has also been investigated before,[28] and substantial double bond character was found. Close agreement between our MP2 geometry and the reported CCD and QCISD geometry is observed, indicating that the MP2 level is sufficiently accurate for these system.

Formation of complexes between these ylides and methane results in weak H-bonds (see Table 1 for H-bond energies) with long $C–H\cdots C$ distances, which are nevertheless considerably shorter than the sum of the van der Waals radii for C and H of 3.05 Å.[29] The weakness of such $C–H\cdots C$ interactions is apparent in the very small differences in geometry between the monomers and the complexes, where changes of less than 1% are observed. The stabilisation due to H-bond formation of the methane complexes is low, between 5 and 6 kJ mol$^{-1}$ at the MP2/6311++G(d,p) level. This stabilisation is further reduced by a counterpoise correction to less than 3 kJ mol$^{-1}$. Increasing the size of the basis set by adding further d- and p-type polarisation functions to give (2d,2p) and (3d,3p) reduces the size of the counterpoise correction to around 1 kJ mol$^{-1}$. Our best estimates for the strengths of the H-bonds in the methane complexes are between 3 and 5 kJ mol$^{-1}$ for both the N and P ylides (exclusive of any zero-point energy corrections). A study of the methane–water complex[6a] indicates that further expansion of the MP*x* series makes little difference to such H-bond strengths.

In contrast to the methane complexes, acetylene forms strong H-bonds to the N and P ylides. Optimisations at the MP2/6-311++G(d,p) level results in short $C–H\cdots C$ contact distances of 2.2–2.4 Å (Figs. 1 and 2). This is reflected in the rather larger changes in geometry on complexation, and in the calculated interaction energy (Table 1). At the MP2/6-311++G(d,p) level stabilisations of 35.64 and 20.97 kJ mol$^{-1}$ are found for the N and P ylides, respectively. Counterpoise corrections reduce these stabilisations by 5–6 kJ mol$^{-1}$. Again, increasing the basis set size lowers the counterpoise correction, giving corrected

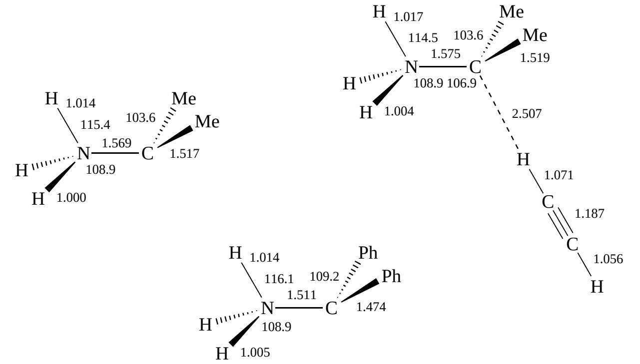

**Fig. 3** HF optimised geometries of the methyl and phenyl substituted nitrogen ylide and its acetylene complex

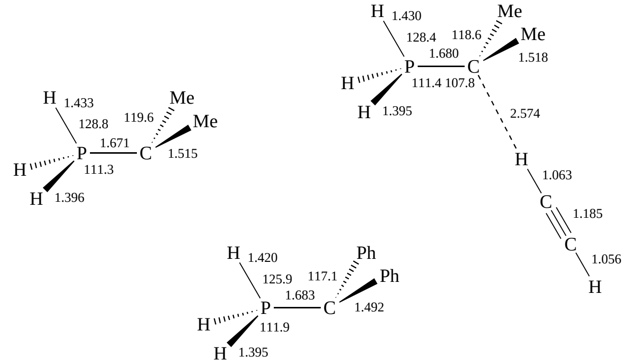

**Fig. 4** HF optimised geometries of the methyl and phenyl substituted phosphorous ylide and its acetylene complex

H-bond strengths of 34.1 and 15.9 kJ mol$^{-1}$ for $H_3Y{-}CH_2\cdots HCCH$, Y = N and P, respectively. These results represent surprisingly large H-bond energies for the nominally weak C–H···C interaction [*cf.* $(H_2O)_2$ which has an H-bond energy of 22.6 kJ mol$^{-1}$].

The geometry of the $H_3N{-}CH_2\cdots HCCH$ complex is unusual, with an N–C···H angle of just 84.1° and a C–H···C angle of 144.5°. This bent hydrogen bond may be a product of a secondary interaction between the C≡C bond of acetylene and the acidic hydrogens on N; these hydrogens are 3.07 Å from the midpoint of the triple bond. Such secondary interactions have been invoked to explain bent H-bonds found *via* microwave spectroscopy[30]—their presence or otherwise is discussed below in terms of the topology of the charge distribution.

The surprising strength of the interaction between ylides and acetylene prompted us to investigate the likely effects of C-substituents on the above results. As models of substituents common throughout organic chemistry, we have studied the ylides $H_3Y{-}Me_2$ and $H_3Y{-}CPh_2$ (Y = N or P) and their acetylene complexes. These systems are too large for MP2 optimisations to be performed with large basis sets, so it was necessary to use Hartree–Fock methods. As a first step in these investigations, we tested the performance of HF/6-311++G(d,p) optimisations against the MP2 results. In general, the HF description of the monomers is reasonable, though the N–C and P–C bond lengths differ somewhat; the former is 0.031 Å too long while the latter is 0.009 Å too short at the HF level. A more serious failing is observed in the H···C contact distance, which is overestimated by 0.298 and 0.223 Å, respectively. Table 1 shows that the HF level consequently underestimates binding energies by between 5 and 15 kJ mol$^{-1}$ relative to the MP2 values. These results, whilst indicating electron correlation to be necessary for an accurate description of the C–H···C interaction, provide detailed information on the shortcomings of HF methods here.

The results of HF geometry optimisations of the ylides $H_3Y{-}CMe_2$ and $H_3Y{=}CPh_2$ (Y = N or P) are depicted in Figs. 3 and 4. In general, the changes in geometry induced by these substitutions are small, almost negligible. One interesting feature is the planarity of the ylidic C atom, measured by summing its valence angles (a truly planar atom would result in 360.0°). These values are summarised in Table 2. Firstly, the P ylides have very much more planar carbons than the N ylides, and secondly phenyl substitution markedly increases the planarity of carbon in both types of ylide.

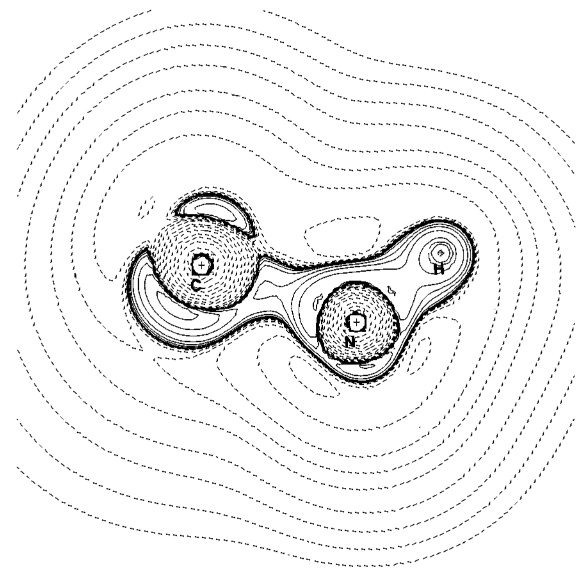

**Fig. 5** MP2/6-311++G(d,p)–$\nabla^2\rho$ distribution of $H_3N{-}CH_2$, in the $C_s$ plane (contour values displayed are ± 2.0 × 10$^n$, ± 4.0 × 10$^n$, ± 8.0 × 10$^n$ e bohr$^{-5}$, with $n$ increasing in steps of 1 from −3)

**Table 2** Planarity of ylidic carbon[a]

| $H_3Y{-}CH_2$ | $H_3Y{-}CMe_2$ | $H_3Y{-}CPh_2$ |
|---|---|---|
| Y = N | | |
| 314.0 | 317.5 | 340.8 |
| Y = P | | |
| 345.6 | 347.6 | 358.8 |

[a] At the HF/6-311++G(d,p) level. Planarity given as sum of bond angles about C.

The complexes of these substituted ylides with acetylene were optimised, taking the optimised geometry of the unsubstituted ylides as a starting geometry. In the methyl-substituted case, very similar geometries to the unsubstituted complexes resulted (remembering that the HF methodology overestimates the C···H distance by around 0.2 Å). Table 1 shows that the strengths of these interactions are very similar to the unsubstituted ylides, and suggests that a correlated treatment would substantially increase the H-bond strength. Phenyl substituents, on the other hand, remove the basicity of the ylide completely. In fact, it proved impossible to obtain an optimised geometry for $H_3Y{-}CPh_2\cdots HCCH$ at the HF level: the two molecules simply drifted apart until the C···H distance was > 5.0 Å, while the nuclear forces were still non-zero. Possible reasons for this will be investigated in the next section.

## II. Topological charge density analysis

Properties of the charge density at the (3,−1) CPs in $\rho$ in the monomers and complexes are reported in Table 3. Of interest is the nature of the Y–C bond, *i.e.* the extent of double bond character here. Comparison with true single and double bonds[32] shows the N–C bond in $H_3N{-}CH_2$ to be very weak (in line with the work of Naito *et al.* who reported a bond order of just 0.77[27] with lower $\rho$ and less negative $\nabla^2\rho$ than in methylamine. A large ellipticity of this bond is observed, which is

**Table 3** MP2/6-311+ +G(d,p) bond critical point properties (au)[a]

| | $\rho$ | $\nabla^2\rho$ | $\varepsilon$ | $r_1$ | $r_2$ |
|---|---|---|---|---|---|
| $H_3N–CH_2\cdots HCH_3$ | | | | | |
| N–C | 0.183 (0.184) | −0.169 (−0.171) | 0.297 (0.292) | 1.911 (1.904) | 1.028 (1.027) |
| C···H′ | 0.008 | +0.017 | 0.026 | 3.426 | 1.960 |
| C′···H′ | 0.275 (0.272) | −0.933 (−0.912) | 0.0 (0.0) | 0.720 (0.750) | 1.344 (1.311) |
| $H_3N–CH_2\cdots HCCH$ | | | | | |
| N–C | 0.186 (0.184) | −0.170 (−0.171) | 0.360 (0.292) | 1.911 (1.904) | 1.018 (1.027) |
| C···H′ | 0.025 | +0.054 | 0.050 | 2.712 | 1.428 |
| C′–H′ | 0.267 (0.284) | −0.959 (−1.025) | 0.0 (0.0) | 0.637 (0.683) | 1.433 (1.329) |
| $H_3P–CH_2\cdots HCH_3$ | | | | | |
| P–C | 0.192 (0.195) | +0.091 (+0.139) | 0.420 (0.441) | 1.244 (1.235) | 1.936 (1.922) |
| C···H′ | 0.007 | +0.016 | 0.007 | 3.307 | 2.010 |
| C′–H′ | 0.274 (0.272) | −0.925 (−0.912) | 0.0 (0.0) | 0.731 (0.750) | 1.331 (1.311) |
| $H_3P–CH_2\cdots HCCH$ | | | | | |
| P–C | 0.191 (0.195) | +0.060 (+0.139) | 0.379 (0.441) | 1.248 (1.235) | 1.944 (1.922) |
| C···H′ | 0.014 | +0.035 | 0.005 | 2.933 | 1.604 |
| C′–H′ | 0.279 (0.284) | −1.102 (−1.025) | 0.0 (0.0) | 0.657 (0.750) | 1.377 (1.311) |

[a] Isolated monomer values are in parentheses.

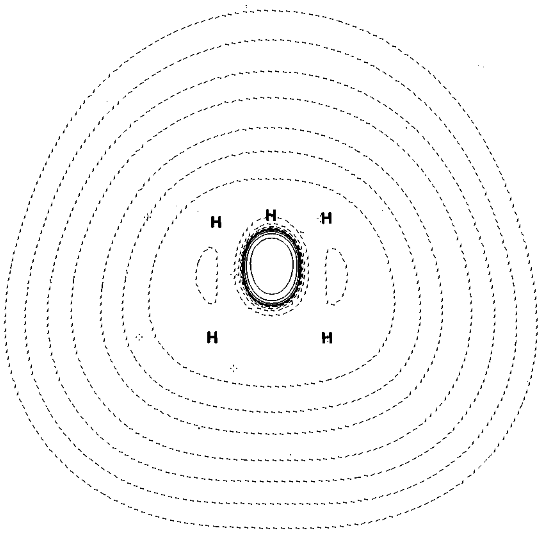

**Fig. 6** MP2/6-311++G(d,p)–$\nabla^2\rho$ distribution of $H_3N–CH_2$, through the bond CP (contours as in Fig. 5)

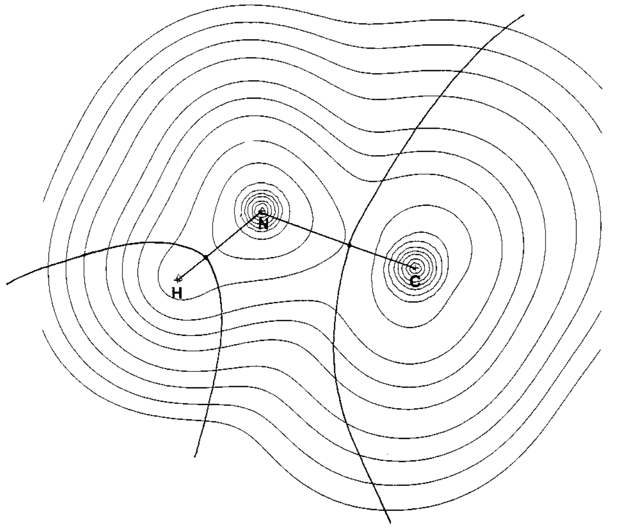

**Fig. 7** MP2/6-311++G(d,p) $\rho$ distribution of $H_3N–CH_2$ in the $C_s$ plane (contours as in Fig. 5)

normally indicative of π-bonding. However, examination of the curvatures of $\rho$ at the bond CP revealed density to be preferentially accumulated *in* the symmetry plane, not perpendicular to it as in π-systems. This is easily seen in a $\nabla^2\rho$ cross-section through the N–C bond (Fig. 6): the bond is clearly elliptical, but the major axis lies in the symmetry plane. Thus there is no evidence of π-character in the N–C bond of $H_3N–H_2$.

There appear to be no pre-existing attempts in the literature to discuss such ylidic N–C bonds in terms of the charge density topology (previous studies have employed various types of population analysis and/or bond orders). So this is a new and somewhat peculiar observation concerning the nature of such bonds. Our tentative explanation for the unusual in-plane distortion of the N–C σ-bond is that it interacts with the large and diffuse lone pair on C. This is suggested by Fig. 6, and also in the position of the bond CP— the N–CP–C angle is found to be 170.6°. Why such an unusual bond should be induced in compounds showing $N^+–C^-$ charge separation is, however, unclear.

An interesting feature of the N ylide is its electron distribution, as shown in Fig. 7. $\rho$ must show a maximum at the nuclear positions, and this is indeed observed. However, distortion of density into the LP on C is even suggested by $\rho$ (although there is no CP in $\rho$ associated with the LP).

In contrast, the P ylide apparently has a strong P–C bond, with charge density properties slightly enhanced relative to the phosphimine $HP{=}CH_2$. This supports the findings of Nyulászi *et al.* who found substantial 'double-bond strength' through consideration of isodesmic reaction schemes and rotation barriers. Again we find a large value of $\varepsilon$ for the P–C bond, and as in the N ylide the smaller curvature of $\rho$ lies in the $C_s$ plane (see Fig. 9 also). The bond CP is displaced from the P–C internuclear vector, though by less than in the N ylide (P–CP–C = 176.5°).

Hydrogen bonding generally causes only small changes in bond CP properties within the monomer fragments; unsurprisingly, the changes in the acetylene complexes are larger than in the methane complexes. In the former, a substantial weakening of the proton donor C–H bond is observed, in common with many other studies of H-bonding.[20] This weakening is assigned to transfer of density from the C–H bond into the H-bonding region, an effect which can be seen in the H-bond CP properties. These CPs show typical properties of 'closed-shell' interactions, with low $\rho$ and small, positive $\nabla^2\rho$. In the methane complexes, a very unusual effect is observed: the C–H bond involved in hydrogen bonding is actually enhanced relative to free methane. These changes are small when compared to the depletion of the acetylene C–H bond, but are seen in both $\rho$ and $\nabla^2\rho$. This suggests that the nature of H-bonds to methane is

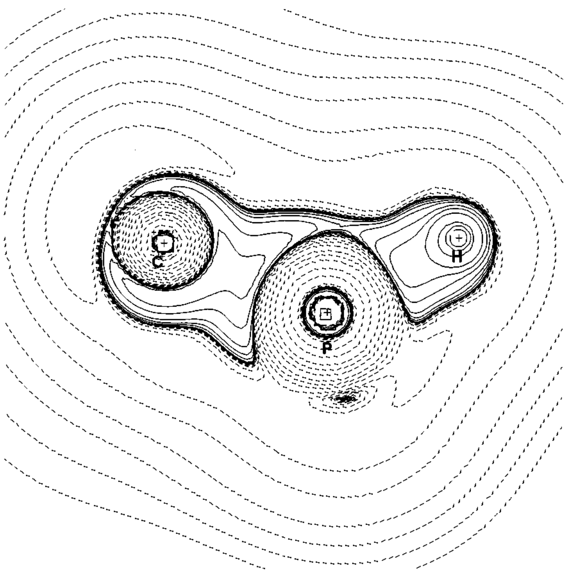

**Fig. 8** MP2/6-311++G(d,p)–$\nabla^2\rho$ distribution of $H_3P–CH_2$ in the $C_s$ plane (contours as in Fig. 5)

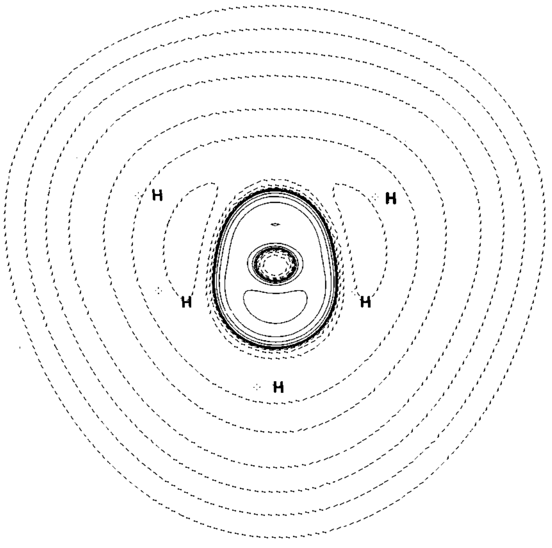

**Fig. 9** MP2/6-311++G(d,p)–$\nabla^2\rho$ distribution of $H_3P–CH_2$, through the bond CP (contours as in Fig. 5)

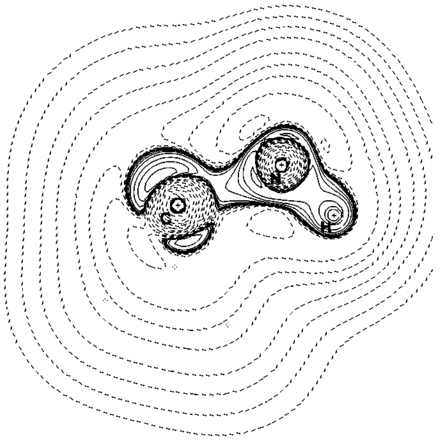

**Fig. 10** HF/6-311++G(d,p)–$\nabla^2\rho$ distribution of $H_3N–CMe_2$, in the $C_s$ plane (contours as in Fig. 5)

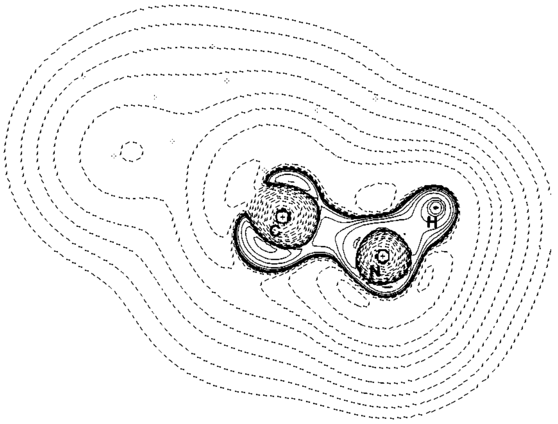

**Fig. 11** HF/6-311++G(d,p)–$\nabla^2\rho$ distribution of $H_3N–CPh_2$, in the $C_s$ plane (contours as in Fig. 5)

fundamentally different from that of 'conventional' H-bonds. In many ways this is understandable since unlike nearly all proton donors methane is almost completely non-polar, so the ultimate source of stabilisation cannot be electrostatic in origin.

Though $\rho$ and $\nabla^2\rho$ in the Y–C bond change little on complex formation, the ellipticity of this bond is affected by H-bonding to acetylene. In the N ylide, the N–C bond becomes 23% more elliptical; in the P ylide the opposite effect is observed, the P–C bond $\varepsilon$ value decreasing by 15%. These changes may be due to an attractive interaction between the density of the Y–C bond and the H-bonding proton. However, there is no evidence for this in the position of the bond CP, as the Y–CP–C angles barely change from the monomer values. Finally, we note that despite the non-linearity of the H-bond, no $(3,-1)$ CP is found between the C≡C bond and the hydrogens on N. Strictly speaking, therefore, we cannot say that these atoms are interacting since they do not share an interatomic surface.

The Laplacian of the charge density, $\nabla^2\rho$, and its topology provide us with further information on the nature of the C–H···C interactions. Figs. 5 and 8 show the distribution of $-\nabla^2\rho$ in the ylides $H_3Y–CH_2$. Comparison of Figs. 5 and 8 shows a fundamental difference between the N and P ylides: the N ylide has a distinct $(3,-3)$ CP in $-\nabla^2\rho$ in the position expected of a lone pair (N–C–LP = 101.2°) and the P ylide has no such maximum (a small peak is observed with an angle of *ca.* 65° to the P–C bond). This supports the general finding that $H_3P–CH_2$ has a predominantly double P=C bond, with the formal LP on C located more in the bonding region. $H_3N–CH_2$, on the other hand, has the single N–C bond anticipated of an ylide. At the LP in $H_3N–CH_2$, $\rho = 0.293$ and $\nabla^2\rho = -1.069$ au, values which hardly change on H-bonding to either $CH_4$ or HCCH. That the P ylide forms complexes with similar geometries to the N ylide is remarkable, given that there is no maximum in $-\nabla^2\rho$ to align with the proton donor in the fashion suggested by Carroll *et al.*[33]

Laplacian maps for the substituted ylides are presented in Figs. 10–13, and shed some light on their ability (or otherwise) to form hydrogen-bonded complexes. Comparison of the three N ylides (Figs. 5, 10 and 11) shows that substitution does not remove the large lone pair on carbon. Similarly, the substituted P ylides (Figs. 12 and 13) do not appear substantially different from $H_3P–CH_2$. These similarities are quantified by the 'lone pair' properties reported in Table 4. It is apparent that methyl substitution enhances the non-bonded charge concentration somewhat, resulting in a larger, more concentrated lone pair on C, in both N and P ylides. Conversely, phenyl substitution depletes the lone pair a little, removing density from the non-bonded region. However, these changes are all relatively small, and are probably insufficient in themselves to explain the total lack of H-bond basicity in the phenyl substituted ylides. It therefore seems that steric repulsion between the incoming acid and the phenyl groups is also important here.

### III. Atomic properties

Table 5 reports selected atomic charges, energies and higher multipoles for the ylides and their complexes with methane and acetylene. In $H_3N{-}CH_2$, N is found to be negatively charged despite bearing a formal positive charge, while C has only a slight negative charge. Including hydrogen populations (not reported), the two fragments $NH_3$ and $CH_2$ are almost neutral. The P ylide, conversely, has a negative carbon. The atomic populations do not, therefore, agree with those anticipated on the bases of 'formal charges', and the stabilisation due to H-bonding (in the N ylide at least) is not due to simple charge–charge electrostatic attraction. A striking feature of Table 5 is the magnitude of the dipole ($M$) and quadrupole ($Q$) moments of C in both ylides. The positive $M_X$ indicates that the centroid of C density is shifted towards the LP region, while the negative $Q_{XX}$ means density is concentrated in the direction of the LP and depleted in the orthogonal directions. This is particularly evident in the N ylide, where the multipole moments are of a similar size to those found for second row atoms;[20d] the P ylide, which does not appear to have an LP on carbon, also shows this effect, though to a lesser extent.

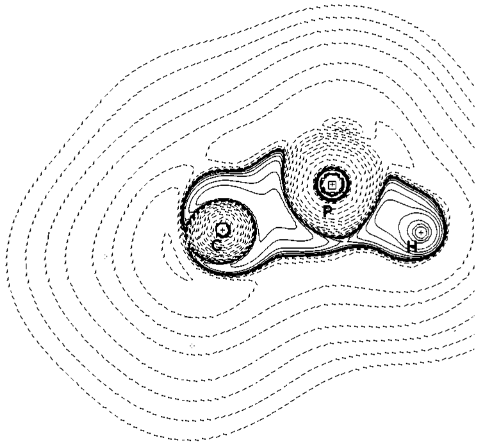

Fig. 12 HF/6-311++G(d,p)–$\nabla^2\rho$ distribution of $H_3P{-}CMe_2$, in the $C_s$ plane (contours as in Fig. 5)

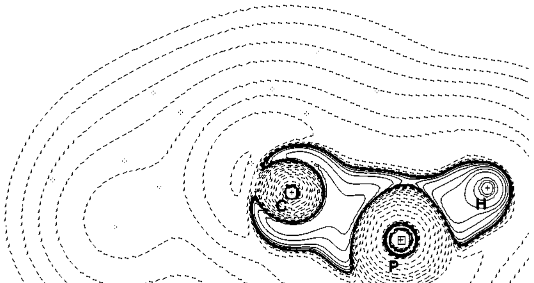

Fig. 13 HF/6-311++G(d,p)–$\nabla^2\rho$ distribution of $H_3P{-}CPh_2$, in the $C_s$ plane (contours as in Fig. 5)

Formation of a complex between $H_3N{-}CH_2$ and $CH_4$ generally causes small changes in the atomic properties, the largest changes occurring in those atoms participating directly in the H-bond. The proton acceptor C loses population, but in doing so is stabilised by its proximity to the proton donor. Carbon multipole moments are diminished on H-bonding, though in the complex these are still very large; the introduction of a new atomic surface, reducing the size of C, is the origin of this apparent depolarisation. The proton donor H′ also loses charge, and the resulting loss of self-stabilisation outweighs the stabilising presence of the ylide, yielding an overall destabilisation. Summing the changes in atomic properties reveals that 0.02 e is transferred from base to acid, considerably less than found in stronger H-bonds.[20] Although changes in individual atomic properties are small, large changes are found in the energies of base and acid fragments. The ylide is stabilised by 0.020 au (52.5 kJ mol$^{-1}$), with $CH_4$ destabilised by 0.018 au. The stabilisation of the complex is therefore due solely to a

**Table 4** HF/6-311+ +G(d, p)[a] lone pair properties (au)

| | $\rho$ | $\nabla^2\rho$ | $r$ | $\psi^b$ |
|---|---|---|---|---|
| $H_3N{-}CH_2$ | 0.301 | −1.182 | 0.885 | 101.6 |
| $H_3N{-}CMe_2$ | 0.310 | −1.253 | 0.881 | 103.8 |
| $H_3N{-}CPh_2$ | 0.286 | −1.018 | 0.898 | 101.3 |
| $H_3P{-}CH_2$ | 0.245 | −0.683 | 0.944 | 69.5 |
| $H_3P{-}CMe_2$ | 0.260 | −0.782 | 0.935 | 68.2 |
| $H_3P{-}CPh_2$ | 0.248 | −0.682 | 0.942 | 72.1 |

[a] 6-31G(d,p) on Me and Ph substituents. [b] $\Psi$ defined as angle Y–C–LP.

**Table 5** MP2/6-311+ +G(d,p) atomic properties (au)[a]

| | Y | C | H′ | C′ |
|---|---|---|---|---|
| $H_3N{-}CH_2 \cdots HCH_3$ | | | | |
| $N$ | 7.944 (7.944) | 6.101 (6.119) | 0.926 (0.996) | 6.045 (6.016) |
| $E$ | −55.100 (−55.092) | −37.734 (−37.719) | −0.583 (−0.615) | −37.915 (−37.919) |
| $M_X$ | −0.034 (+0.025) | +0.749 (+1.181) | +0.051 (+0.129) | +0.029 (0.0) |
| $Q_{XX}$ | +0.305 (+0.314) | −4.098 (−5.715) | −0.278 (−0.246) | +0.031 (0.0) |
| $H_3N{-}CH_2 \cdots HCCH$ | | | | |
| $N$ | 7.958 (7.944) | 6.103 (6.119) | 0.715 (0.844) | 6.201 (6.157) |
| $E$ | −55.100 (−55.092) | −37.743 (−37.719) | −0.478 (−0.548) | −38.027 (−38.008) |
| $M_X$ | −0.039 (+0.025) | +0.856 (+1.181) | −0.117 (−0.138) | −0.440 (−0.113) |
| $Q_{XX}$ | +0.456 (+0.314) | −3.994 (−5.715) | +0.412 (+0.453) | +3.782 (+4.369) |
| $H_3P{-}CH_2 \cdots HCH_3$ | | | | |
| $N$ | 12.066 (12.011) | 7.184 (7.234) | 0.953 (0.996) | 6.045 (6.016) |
| $E$ | −339.676 (−339.574) | −38.346 (−38.367) | −0.596 (−0.615) | −37.882 (−37.919) |
| $M_X$ | −0.274 (−0.194) | +0.377 (+0.353) | −0.125 (−0.067) | +0.029 (0.0) |
| $Q_{XX}$ | −0.133 (−0.150) | −4.414 (−5.652) | −0.162 (−0.123) | +0.084 (0.0) |
| $H_3P{-}CH_2 \cdots HCCH$ | | | | |
| $N$ | 12.067 (12.011) | 7.181 (7.234) | 0.779 (0.844) | 6.180 (6.157) |
| $E$ | −339.678 (−339.574) | −38.346 (−38.367) | −0.513 (−0.548) | −37.996 (−38.008) |
| $M_X$ | −0.273 (−0.194) | +0.403 (+0.353) | −0.045 (−0.084) | −0.207 (−0.104) |
| $Q_{XX}$ | −0.172 (−0.150) | −2.338 (−5.652) | +0.243 (+0.356) | +2.042 (+3.487) |

[a] Isolated monomer values are in parentheses; all systems are oriented in the $xy$-plane, with the Y–C bond along $y$.

stabilisation of the base fragment; this is in turn concentrated in the basin of the proton acceptor carbon atom.

As may be expected, the stronger interaction with acetylene results in larger changes in atomic properties. Again, C loses a small amount of electron density but undergoes stabilisation on H-bond formation. This stabilisation is substantially more than in the methane complex, since the H in acetylene is much more positive than that in methane, and can therefore stabilise the carbon density more effectively. The depletion of density and destabilisation of H′ is also more marked than in the methane complex, though this is offset by changes in the attached C′. N increases its population at the expense of its attached hydrogens: despite this, only very small changes occur in the energies of these atoms. Overall, a charge transfer of 0.045 e from base to acid is found, in line with previous studies of H-bonding.[20] Here, base and acid are stabilised relative to the isolated fragments by 21.0 and 15.7 kJ $mol^{-1}$, respectively, unlike the methane complex where only the base was stabilised.

Some similarities are evident in the atomic property changes between the N and P ylides, though some important differences are found. In both complexes the population of C falls, but unlike in the above systems this atom is destabilised by H-bonding. H′ is again depleted and destabilised, though to a lesser degree than in the complexes with N ylides. In $H_3P{-}CH_2 \cdots HCH_3$, just 0.013 e is shifted from base to acid at the expense of the carbon population. As in the methane complex of the N ylide the base has a large stabilisation (130.0 kJ $mol^{-1}$) offset by the destabilisation of the acid fragment (123.9 kJ $mol^{-1}$). Formation of the complex between acetylene and the P ylide causes a charge transfer of 0.029 e, reflecting the weakness of this interaction compared with the N ylide. Here, the base is stabilised by 123.1 kJ $mol^{-1}$ and the acid is destabilised by 101.8 kJ $mol^{-1}$. Thus in both $H_3P{-}CH_2$ complexes, the stability of the complex is due to a stabilisation of the acid, which is driven by the stabilisation of the P atom. This is very different from the behaviour of the $H_3N{-}CH_2$ complexes, where the N atom is barely stabilised and changes in the energy of C seem to dominate.

The dipole polarisation of the C atom in $H_3P{-}CH_2$ increases on formation of both complexes. This contrasts with the behaviour of the N ylide, whose carbon atom is depolarised by H-bonding. P is also polarised on complex formation, and in the same direction as C. This is in line with the increase in $\varepsilon$ for the P–C bond, the atomic dipole moments in the plane of the molecule increasing due to an increase in the concentration of charge in this plane. As in the nitrogen ylide, the introduction of a new inter-atomic surface on H-bonding results in a reduction of the carbon quadrupole moment in this plane.

## Conclusions

The results presented in this study show $C{-}H \cdots C$ hydrogen bonds to exist with remarkable stability where the proton acceptor carbon is situated within an ylide. The simplest example of a nitrogen ylide, $H_3N{-}CH_2$, forms a complex with acetylene with a stabilisation estimated at 35 kJ $mol^{-1}$, greater than that of the water dimer. Even with very poor proton donors, such as methane, hydrogen bonds with energies of up to around 5 kJ $mol^{-1}$ are predicted. The analogous phosphorous ylide, $H_3P{-}CH_2$, forms somewhat more weakly bound complexes with such acids, but even here substantial stabilisation is found. That ylides may form significant hydrogen bonds with alkane C–H bonds (which are otherwise highly unreactive) may be of use in the design of materials.

Substituent effects, estimated by calculations on methyl and phenyl substituted ylides, indicate that diphenyl substitution on the ylidic carbon completely removes the Lewis basicity of the ylide. The properties of these ylides, particularly their lone pair structure, suggests that this is not solely an electronic, delocalisation effect, and that steric repulsion also comes into play. Dimethyl substitution, on the other hand, slightly increases the basicity of the ylidic carbon, as measured by the lone pair properties, though the geometry and energy of the resulting hydrogen bond are barely affected.

Analysis of the charge density properties of the ylide and their complexes highlights a number of interesting features. The N and P ylides differ fundamentally in the nature of the ylidic bond: $H_3N{-}CH_2$ has a weak N–C bond, apparently weaker than that in methylamine. $H_3P{-}CH_2$, on the other hand, has properties typical of a relatively strong double bond. The N ylide therefore has a distinct lone pair on C while the P ylide has no such feature (as seen in the $\nabla^2 \rho$ distribution and in the atomic multipole moments), perhaps explaining the weaker hydrogen bonds formed to the latter. In all cases, between 0.02 and 0.05 e are transferred from base to acid on hydrogen bonding, the actual amount roughly corresponding to the stabilisation. In the N ylide, hydrogen bonding stabilises the C atom, accounting for a great deal of the total stabilisation; in the P ylide this atom is destabilised on complexation, and the stabilisation is concentrated largely in the P atom.

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