Quantum chemical evidence for C–H···C hydrogen bonding

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***Ab initio* MP2/6-311++G(3d,3p) calculations indicate that C–H···C hydrogen bonds with strengths of up to 35 kJ mol^{-1} may exist in complexes of ylides with molecules containing acidic hydrogens**

Weak interactions, both inter- and intra-molecular, play a crucial role in a wide range of chemical and biological systems. Their weakness is a distinct advantage in that they may be formed and broken relatively easily. Of these weak interactions, the hydrogen bond is surely the most important;[1] it is almost ubiquitous in molecular crystals and biological molecules, and its directionality makes it particularly useful in crystal engineering[2] and molecular recognition.[3] This importance is reflected in the ever growing number of theoretical studies of hydrogen bonding.[4]

Most published studies of hydrogen bonding considered either very strong hydrogen bonds, such as [O–H···O]$^-$ or [N–H···N]$^+$,[5] or moderately strong ones, such as O–H···O, N–H···O, O–H···N or N–H···N. Much less attention has been paid to weaker interactions, for example involving second-row elements[6] or less electronegative elements such as carbon.[2b,7] This is primarily due to practical considerations; weaker interactions are harder to observe and measure experimentally and require more sophisticated theoretical techniques to obtain realistic results. However, the practical advantages of this weakness make the study of such interactions very desirable.

We have therefore undertaken an investigation of one of the least studied types of hydrogen bond—the C–H···C bond. These are typically weak because of the low acidity and basicity of the C–H and C moieties, respectively. It follows that the interaction may be enhanced by the use of more acidic proton donor fragments such as acetylenes,[8] or by increasing the basicity of the acceptor. Both approaches are employed here. The basicity of carbon may be maximised by placing it in an ylide, wherein it bears a formal negative charge, and is certainly more basic than a 'normal' carbon. The acidity of C–H is similarly enhanced in an acetylenic fragment. In this preliminary study, we have studied two simple models, the complexes of $H_3\overset{+}{N}–\overset{-}{C}H_2$ with methane and acetylene, and have found a remarkably strong hydrogen bond in the latter case.

Initially, the geometries of the monomer fragments and the hydrogen-bonded complexes were optimized at the Hartree-Fock (HF) level using the 6-311++G(d,p) basis set[10] (all calculations reported were performed using the Gaussian2 package[9] running on the University of London and Manchester Computing Centres' supercomputing facilities). At this level, $H_3\overset{+}{N}–\overset{-}{C}H_2$ was found to have a plane of symmetry with the hydrogens on carbon either side of the C_s plane; this orientation was assumed for all further optimizations, both in the ylide itself and in its complexes. CH_4 and HCCH were assumed to have T_d and $D_{\infty h}$ symmetries. At this level, the binding energy of the methane complex is around 2 kJ mol^{-1} (see Table 1), which is barely significant, given the known errors of such supermolecule calculations (Basis Set Superposition Error, BSSE, in particular). In contrast, the acetylene complex is bound by 22.80 kJ mol^{-1} at an r(C···H) separation of 2.226 Å, some 0.5 Å shorter than the sum of the van der Waals radii. This binding energy is hardly diminished by a counterpoise correction.[11] However, correcting for the change in zero-point energy (ZPE) on formation of the hydrogen bond reduces this binding energy by 4.81 kJ mol^{-1}.

These results, and in particular the very low binding energy of the methane complex, prompted us to carry out further geometry optimization using the same basis sets and second-order Moller–Plesset perturbation theory (MP2). This resulted in a substantially shorter hydrogen-bond length and greater interaction energy (see Fig. 1 and Table 1) for the methane complex, with methane approaching the ylide in a direction close to the lone pair (LP) position [as seen in the $-\nabla^2\rho$ distribution, Fig. 2(*a*)].[1] The binding energy of 6.21 kJ mol^{-1} found at this level is, however, greatly diminished when a counterpoise is applied. While such a correction is only a crude estimate of the actual BSSE,[14] this suggests the 6-311++G(d,p) basis set is inadequate for a correct description of this system at a correlated level. We therefore used the MP2/6-311++G(d,p) optimized geometry in calculations employing larger basis sets.

For expansion of the basis set, we chose to add further polarization functions to give the 6-311++G(2d,2p) and 6-311++G(3d,3p) basis sets. Table 1 clearly shows that the use of these larger basis sets reduces the counterpoise correction to *ca.* 1.0–1.5 kJ mol^{-1}, giving a hydrogen-bond strength which appears to be converging toward 4.5 kJ mol^{-1}, or approximately 1 kcal mol^{-1}. Previous studies of hydrogen bonding[15] indicate that extending the treatment of correlation to higher order in the MPx series is relatively unimportant. We estimate the error on this hydrogen-bond energy at *ca.* ±2 kJ mol^{-1}, based on ref. 15.

Table 1 Hydrogen bond energies (kJ mol^{-1})[a]

	$H_3\overset{+}{N}–\overset{-}{C}H_2$···H–$CH_3$		$H_3\overset{+}{N}–\overset{-}{C}H_2$···H–CCH	
Method/Basis set	I	II	I	II
HF/6-311++G(d,p)	2.36	—	22.80	21.91
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

[a] All energies, except at the HF/6-311++G(d,p) level, correspond to the MP2/6-311++G(d,p) optimized geometry; **I** no counterpoise correction, **II** counterpoise correction made.

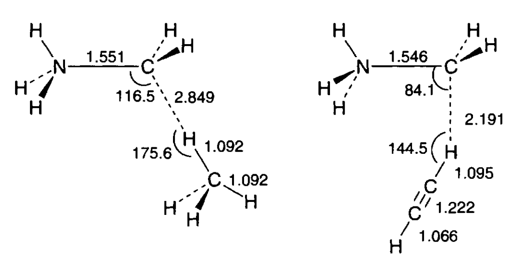

Fig. 1 MP2/6-311++G(d,p) optimized geometries (bond lengths in Å, angles in °) of the complexes of $H_3\overset{+}{N}–\overset{-}{C}H_2$ with methane and acetylene

At this higher level, the acetylene complex also has a substantially higher stabilization; the hydrogen-bond length shortens slightly to 2.191 Å but the bond energy increases markedly to 35.64 kJ mol^{-1}. The optimized geometry (Fig. 1), however, indicates a secondary interaction between the hydrogens on nitrogen and the triple bond of acetylene. The N–C···H angle of 84.1° differs considerably from the N–C···LP angle, either in the free ylide (101.1°) or the complex (101.9°) [see Fig. 2(*b*)]. Further evidence for a secondary interaction comes from the non-linearity (144.5°) of the C–H···C linkage. The hydrogens are 3.07 Å from the midpoint of the C–C triple bond. The mismatch between the angular position of the LP and the hydrogen-bond angle is not, itself, conclusive proof of a secondary interaction since this is also observed in the complexes of HF with H_2O and H_2CS,[4a] neither having secondary interactions. However, the *r*(H···triple bond) contact distance and deviation from linearity reported here are close to analogous gas-phase experimental values measured by Legon and co-workers[16] for complexes where secondary interactions certainly are present.

It seems unlikely that any secondary interaction is responsible for the large binding energy of the complex, given that the C–H···π interaction in the acetylene dimer is known[17] to be *ca.* 6 kJ mol^{-1} at a very similar contact distance. The binding energy calculated using the three basis sets described above is consistently around 35 kJ mol^{-1}. The MP2/6-311++G(d,p) strength is diminished somewhat by the counterpoise correction, but this effect falls as the basis set is expanded. The topology of the charge density, and in particular the 'bond critical points' found between interacting atoms, ought to provide further insight into the origins of these hydrogen bonds.[18] We find properties typical of covalent bonds within each monomer fragment, even in the ylidic $N^+–C^-$ bond, with a 'closed-shell' hydrogen-bond critical point in both complexes. Intriguingly, we find no such critical point for the postulated secondary interaction.

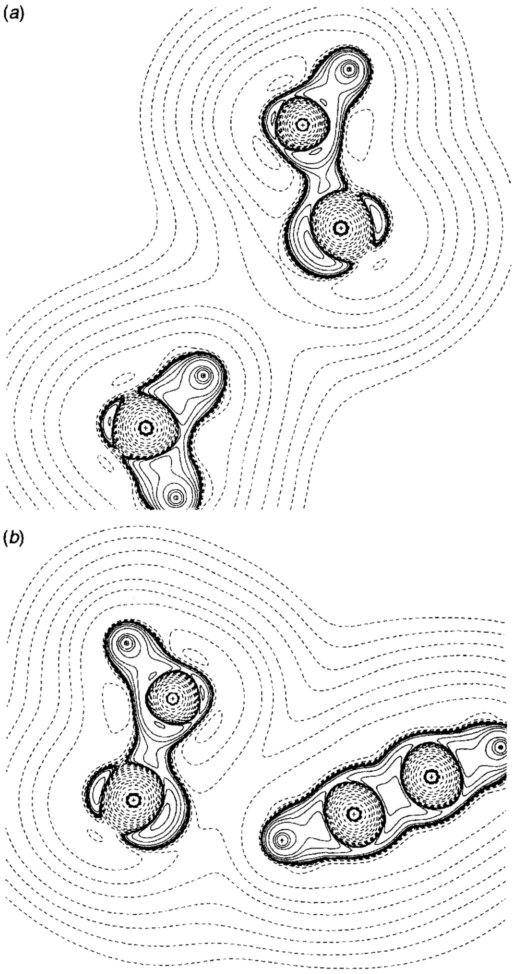

Fig. 2 Plot of $-\nabla^2\rho$ in (*a*) $H_3\overset{+}{N}–\overset{-}{C}H_2\cdots H–CH_3$ and (*b*) $H_3\overset{+}{N}–\overset{-}{C}H_2\cdots H–CCH$

In conclusion, we have demonstrated that C–H···C hydrogen bonds are possible, and may even be as strong as O–H···O interactions if a sufficiently basic carbon centre is used. In such a situation, even a very weak acid such as methane is capable of undergoing hydrogen bonding. Stronger acids, such as acetylene, give rise to remarkably high stabilization. Such interactions are likely to find use in the fields of crystal engineering and materials science. Further theoretical work is underway in order to conclusively identify these binding energies with the C–H···C hydrogen bond, using an Atoms-in-Molecules decomposition of the charge distribution and energy (in a similar fashion to the authors previous studies[4a,5a,19]); synthetic experimental work on such complexes is also in progress.

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Footnote

† A negative value of $\nabla^2\rho$ indicates that charge is concentrated relative to its surroundings, while positive $\nabla^2\rho$ is characteristic of charge depletion. Local maxima in $-\nabla^2\rho$ are found to closely reflect the lone pairs and bound pairs of Lewis theory[12] and the VSEPR rule.[13]

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