PERKIN 2

Novel intermolecular C–H ··· π interactions: an *ab initio* and density functional theory study

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The recent characterisation of short contacts between chloroform solvate molecules and the C–C triple bond of gold ethynides has prompted a theoretical investigation of the strength of C–H ··· π interactions. Extensive *ab initio* and density functional theory calculations have been performed on a variety of model systems displaying a T-shaped C–H ··· π motif. The interaction of ethyne, C_2H_2, with a variety of small proton donor molecules (HCN, $CH_{4-n}Cl_n$, n = 0–3) is invariably found to be weak ($\Delta E_{int} < 10$ kJ mol^{-1}). Replacement of the two acetylenic protons with more electron-donating sodium atoms increases the electron density in the C–C π bond and results in a substantial increase in the interaction with the proton donor. The calculated interaction energies rise to as much as 60 kJ mol^{-1} in the case of C_2Na_2 ··· $CHCl_3$. The interaction of $CHCl_3$ with a model gold ethynide, $H_3PAuCCAuPH_3$, is intermediate between these two extremes, *ab initio* and density functional calculations both giving estimates of *ca.* 25 kJ mol^{-1} comparable to a reasonably strong hydrogen bond. The unusually strong C–H ··· π interactions in the gold ethynide arise directly as a consequence of the electron-donating properties of the $AuPR_3$ fragment and are fundamentally different to the much weaker C–H ··· π interactions in purely organic systems.

Introduction

The nature of weak intermolecular interactions is a topic of enduring interest in chemistry[1] and with recent advances in the field of supramolecular chemistry, there has been a renewed interest in providing an adequate description of these forces within a theoretical framework.[2] Intermolecular forces are generally placed into one of two categories, either very weak van der Waals-type interactions, mediated primarily by dispersion forces, or stronger hydrogen bonds, which are classically described as an interaction between an acidic hydrogen and an electronegative atom bearing one or more lone pairs of electrons. More recently a novel type of intermolecular interaction has been described where π electrons act as the electron donor, notable examples being the water–benzene[3] and ammonia–benzene complexes.[4]

The C–H bond is clearly less polar than either an O–H or N–H bond and consequently C–H ··· π interactions will be considerably weaker than those in either the water–benzene or ammonia complexes. However, the prevalence of C–H and π bonds in organic systems suggests that the cumulative effect of many such interactions may be more significant than previously suspected in determining the conformational preferences and three-dimensional structure of a wide variety of molecules.[5] Structural evidence for the existence of significant C–H ··· π interactions has recently been provided with the X-ray crystallographic characterisation of the complexes $NpPh_2Au$-CC-$AuPh_2Np$·$(CHCl_3)_2$ and Np_2Ph-Au-CC-$AuPhNp_2$·$(CHCl_3)_6$ (Np = naphthyl).[6] In both cases the C–H bonds of the chloroform molecules lie approximately perpendicular to the CC axis in a T-shaped arrangement, with the proton lying between 2.42 and 2.58 Å from the centre of the C–C triple bond (henceforth referred to as the C–H ··· π distance).

Ab initio calculations with extended basis sets and incorporating electron correlation have been widely applied to hydrogen bonded systems, resulting in estimates of interaction energies and distances comparable to experiment.[7] Theoretical investigations of the interaction between proton donors and the π system of C–C triple bonds are much less common and are limited to relatively low level calculations on model systems such as C_2H_2 ··· C_2H_2,[8] CH_4 ··· C_2H_2[9] and HCN ··· C_2H_2.[10] These systems are all very weakly bonded with interaction energies lying in the region of 5 kJ mol^{-1} and are best described as van der Waals complexes. The most stable conformation is found to be the same T-shaped arrangement observed in the gold complexes, but the calculated C–H ··· π separation in CH_4 ··· C_2H_2 is *ca.* 3.3 Å, some 0.8 Å longer than the crystallographically determined values. Thus it would appear that the C–H ··· π interactions in the gold complexes are substantially stronger than those described previously in the literature and it is unclear whether these interactions also fall into the weak van der Waals category or are in fact more akin to the stronger interactions characteristic of a conventional hydrogen bond.

In this paper, we describe calculations on a variety of systems containing a single C–H ··· π unit, using both *ab initio* methods and density functional theory (DFT). DFT has only recently been applied to the problem of weakly interacting systems, but several groups have shown that the method is capable of providing results of similar quality to correlated *ab initio* treatments, but at a significantly reduced computational cost.[11] Our aim in this paper is first to re-examine the intermolecular forces present in the CH_4 ··· C_2H_2 system, paying particular attention to the influence of different levels of approximation available within both *ab initio* and DFT methodologies. We then explore the effects of increasing the acidity of the proton donor by studying the systems HCN ··· C_2H_2 and $CH_{4-n}Cl_n$ ··· C_2H_2 (n = 0–3). The influence of the electron density of the ethynide group is also examined, using the series $CH_{4-n}Cl_n$ ··· C_2Na_2 (n = 0–3). Finally, we calculate the interaction energy of chloroform with a model gold substituted ethynide, $H_3PAuCCAuPH_3$.

Computational details

The model systems studied all have the T-shaped conformation shown in Fig. 1, with the line of the C–H bond bisecting the CC

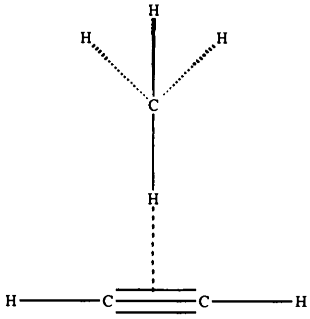


Fig. 1 T-Shaped configuration typical of C–H ··· π interactions

bond. In all cases geometry optimisations were performed in C_s symmetry, with the symmetry plane lying perpendicular to the C–C triple bond. For $CHCl_3$ and CH_4 ligands, local C_{3v} symmetry was also imposed. The bonds adjacent to the ethynide unit (H–C, Na–C or Au–C) were allowed to bend in a plane defined by the C–H ··· C–C core.

Ab initio calculations on the $CH_4 \cdots C_2H_2$ and $HCN \cdots C_2H_2$ systems were performed at Hartree–Fock (HF) and Møller-Plesset (MP*n*) [n = 2,3,4 (with all single-through-quadruple excitations)] levels with the Gaussian basis sets 6-31g*, 6-311g*, 6-311g** and 6-311++g(df,pd) without contraction (*i.e.* the full analytical 6 d and 10 f basis functions). For the systems incorporating heavier main group atoms (Na, Cl), optimisations were performed only at the MP2/6-31g* level. On the $H_3PAuCCAuPH_3 \cdots CHCl_3$ system, calculations were performed at the MP2 level with 6-311g** on the C–H ··· CC core, while the other atoms were described using an effective core potential (ECP) and double zeta valence functions[12] with contracted d basis sets (uncontracted d basis sets fail to give convergence of the total energy for this system). At the HF and MP2 levels, geometries were optimised using analytic gradients, while at the MP3 and MP4 levels the Fletcher–Powell optimisation algorithm was employed. Interaction energies were calculated using the supermolecular approach, corrected for basis set superposition error using the counterpoise method of Boys and Bernardi.[13]

For the $CH_4 \cdots C_2H_2$ and $HCN \cdots C_2H_2$ systems, DFT calculations were performed using either the local density approximation (LDA) in isolation[14] or in conjunction with the gradient corrections to exchange (Becke)[15] and correlation (Perdew)[16] functionals (henceforth abbreviated as BP). Two types of basis sets of Slater-type functions were used, one of double zeta quality augmented with a single polarisation function (DZP), the other of triple zeta quality with two polarisation functions (TZ2P). Calculations on $CH_{n-4}Cl_n \cdots C_2H_2$ and $CH_{n-4}Cl_n \cdots C_2Na_2$ were performed only at the BP/DZP level. Finally, calculations on $H_3PAuCCAuPH_3 \cdots CHCl_3$ were performed with the BP functional and a DZP basis set on the C–H ··· C–C core, but only a DZ basis on the $AuPH_3$ groups. Interaction energies were again calculated using the supermolecular approach, but without counterpoise correction.

Ab initio calculations were performed with the GAUSSIAN92 program[17] on Silicon Graphics Onyx, Silicon Graphics Indigo,[2] Extreme and Hewlett-Packard 750/100 workstations. DFT calculations were performed using the Amsterdam Density Functional (ADF) package[18] on a Silicon Graphics Indigo[2] workstation.

Results and discussion

$CH_4 \cdots C_2H_2$

Previous studies at the HF/4-31g level[9] gave an interaction distance of 3.3 Å and interaction energy of 2.75 kJ mol^{-1}. The *ab initio* calculations reported in Table 1 with progressively larger basis sets give much longer distances of *ca.* 3.8 Å at the HF level with virtually zero interaction energy. At the MP*n* levels (n = 2,3,4) the C–H ··· π distance is considerably smaller, lying in the range 3.08–3.19 Å and the interaction energy rises to *ca.* 0.84 kJ mol^{-1}. These results are in accord with the well established tendency of HF calculations to overestimate hydrogen bond lengths.[19] Adding diffuse and higher polarisation functions [6-311g(df,pd)] further shortens the interaction distance to 2.99 Å at the MP2 level, but does not significantly increase the interaction energy. Thus the bulk of the interaction energy in the $CH_4 \cdots C_2H_2$ complex clearly arises from electron correlation, rather than from electrostatic interactions, which are generally well described at the HF level.[7b]

DFT calculations performed within the local density approximation (LDA/DZP, LDA/TZ2P) substantially overestimate the interaction energy, regardless of the basis set used. The interaction distances are also significantly shorter (2.6 Å) than the lowest estimates obtained from *ab initio* calculations at the MP2 level. Gradient corrections (BP/DZP, BP/TZ2P) reduce the interaction energy and result in a non-bonded potential surface at all interaction distances. A recent DFT study of inert gas dimers[20] revealed identical trends (*viz.* overbinding with the LDA, repulsion with gradient corrections). Thus results of both *ab initio* and DFT calculations are consistent with very weak van der Waals-type interactions in the $CH_4 \cdots C_2H_2$ system.

$HCN \cdots C_2H_2$

The structure of the gas-phase $HCN \cdots C_2H_2$ complex has been determined by Fourier transform rotational spectroscopy[21] and is found to exhibit the T-shaped orientation characteristic of C–H ··· π systems with a separation between the carbon of HCN and the midpoint of the C–C bond, *r*CC of 3.656(5) Å. Block *et. al.* have previously reported *ab initio* calculations of the structure of $HCN \cdots C_2H_2$ at the 6-31g*/MP2 level,[10] estimating *r*CC to be 3.586 Å, in reasonable accord with the experimental data. In Table 2, calculated structural parameters and interaction energies are listed for a variety of levels of approximation, including that used by Block, for which we obtain very similar results. The *ab initio* results confirm that at the HF level, interaction distances are substantially overestimated, whereas at the MP*n* levels, the values are in good agreement with experiment. At the MP2 level with 6-311g* (or larger) basis sets, agreement is particularly good. The interaction energy of *ca.* 7.5 kJ mol^{-1} is substantially greater than that in the $CH_4 \cdots C_2H_2$ system. In addition, the HF interaction energy is *ca.* 90% of the MP2 value, in contrast to only 25% in $CH_4 \cdots C_2H_2$, suggesting that dispersion forces do not constitute the major contribution to the interaction energy in this case.

As in the case of $CH_4 \cdots C_2H_2$, the LDA overestimates interaction energies relative to either HF or MP2, regardless of basis set and also underestimates the interaction distance. Gradient corrections again reduce the interaction energy significantly, but in contrast to the $CH_4 \cdots C_2H_2$ system, a shallow minimum in the potential energy surface remains at the BP level, located at *r*CC = 3.726 Å (BP/DZP) and at 3.730 Å (BP/TZ2P). These distances are comparable to MP3 and MP4 values and only 0.06 Å greater than the experimentally observed value. The interaction energies at the BP level are, however, substantially lower than either the MP2 or HF estimates. The relative accuracy of *ab initio* and DFT calculated interaction energies cannot be assessed in the absence of experimental data, but the larger values from *ab initio* calculations are more consistent with the fact that the molecule is sufficiently stable to be observed in the gas phase.

$CH_{4-n}Cl_n \cdots C_2H_2$ (n = 0–3)

The effect of increasing the positive charge on the coordinated proton has been investigated by replacing CH_4 with $CH_{4-n}Cl_n$ (n = 0–3). Owing to limitations in computer resources and the

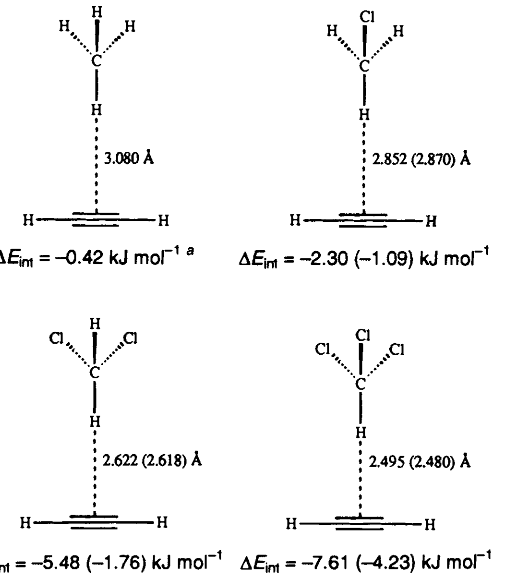
Table 1 Structural parameters and interaction energies for the $CH_4 \cdots C_2H_2$ complex

		ab initio				DFT		
	Basis	HF	MP2	MP3	MP4 (SDTQ)	Basis	LDA	BP
C–H···π/Å	6-31g*	3.423	3.080	3.089	3.090	DZP	2.591	nb[a]
	6-311g*	3.817	3.163	3.192	3.192	TZ2P	2.601	nb[a]
	6-311g**	3.798	3.113	3.158	3.151			
	6-311++g(df,pd)		2.992					
C_2H_2								
C–C/Å	6-31g*	1.186	1.218	1.207	1.220	DZP	1.202	
	6-311g*	1.182	1.215	1.204	1.218	TZ2P	1.204	
	6-311g**	1.182	1.215	1.204	1.218			
	6-311++g(df,pd)		1.214					
C–H/Å	6-31g*	1.057	1.066	1.066	1.070	DZP	1.075	
	6-311g*	1.057	1.066	1.066	1.070	TZ2P	1.073	
	6-311g**	1.056	1.065	1.064	1.068			
	6-311++g(df,pd)		1.064					
CH_4								
C–H/Å	6-31g*	1.083	1.090	1.091	1.094	DZP	1.099	
(π bond)	6-311g*	1.083	1.089	1.090	1.093	TZ2P	1.101	
	6-311g**	1.084	1.090	1.091	1.093			
	6-311++g(df,pd)		1.087					
C–H/Å	6-31g*	1.084	1.090	1.092	1.095	DZP	1.100	
(non π)	6-311g*	1.084	1.089	1.091	1.094	TZ2P	1.101	
	6-311g**	1.084	1.090	1.091	1.094			
	6-311++g(df,pd)		1.088					
ΔE_{int}/kJ mol^{-1}	6-31g*	0.04	−0.42	−0.33	−0.33	DZP	−5.56	>0
	6-311g*	−0.17	−0.79	−0.75	−0.67	TZ2P	−5.23	>0
	6-311g**	−0.17	−0.88	−0.75	−0.79			
	6-311++g(df,pd)		−0.79					

[a] nb = non-bonded.

Table 2 Structural parameters and interaction energies for the $HCN \cdots C_2H_2$ complex

		ab initio				DFT		
	Basis	HF	MP2	MP3	MP4 (SDTQ)	Basis	LDA	BP
C–H···π/Å	6-31g*	2.746	2.535	2.561	2.559	DZP	2.319	2.648
	6-311g*	2.821	2.631	2.661	2.661	TZ2P	2.318	2.650
	6-311g**	2.826	2.619	2.657	2.652			
	6-311++g(df,pd)		2.568					
rC–C/Å	6-31g*	3.808	3.608	3.633	3.635	DZP	3.406	3.726
	6-311g*	3.883	3.704	3.733	3.738	TZ2P	3.409	3.730
	6-311g**	3.887	3.691	3.727	3.727			
	6-311++g(df,pd)		3.638					
Expt/Å		3.656 ± 0.005						
C_2H_2								
C–C/Å	6-31g*	1.187	1.219	1.208	1.221	DZP	1.203	1.208
	6-311g*	1.183	1.215	1.204	1.218	TZ2P	1.202	1.206
	6-311g**	1.183	1.216	1.205	1.219			
	6-311++g(df,pd)		1.215					
C–H/Å	6-31g*	1.058	1.067	1.067	1.070	DZP	1.077	1.074
	6-311g*	1.058	1.067	1.067	1.071	TZ2P	1.076	1.073
	6-311g**	1.056	1.066	1.065	1.069			
	6-311++g(df,pd)		1.064					
HCN								
C–H/Å	6-31g*	1.062	1.073	1.072	1.076	DZP	1.087	1.078
	6-311g*	1.062	1.073	1.072	1.077	TZ2P	1.091	1.083
	6-311g**	1.061	1.072	1.070	1.075			
	6-311++g(df,pd)		1.070					
C–N/Å	6-31g*	1.133	1.177	1.158	1.177	DZP	1.154	1.158
	6-311g*	1.126	1.170	1.149	1.171	TZ2P	1.151	1.156
	6-311g**	1.127	1.170	1.150	1.171			
	6-311++g(df,pd)		1.169					
ΔE_{int}/kJ mol^{-1}	6-31g*	−7.82	−8.70	−8.41	−8.24	DZP	−13.72	−2.68
	6-311g*	−7.11	−8.28	−7.57	−7.82	TZ2P	−12.89	−2.38
	6-311g**	−6.86	−7.82	−7.45	−7.36			
	6-311++g(df,pd)		−7.82					



[a] No minimum found using DFT.

Fig. 2 Optimised structures and interaction energies for $CH_{4-n}Cl_n \cdots C_2H_2$ (n = 0–3). Values from DFT calculations are shown in parentheses.

unavailability of standard split valence triple zeta basis sets for Cl, *ab initio* calculations were performed only at the MP2/6-31g* level, while DFT calculations were restricted to optimisations at the BP/DZP level. From the work described in the previous two sections, we anticipate that these levels of approximation can provide a qualitatively correct description of the C–H ··· π interaction.

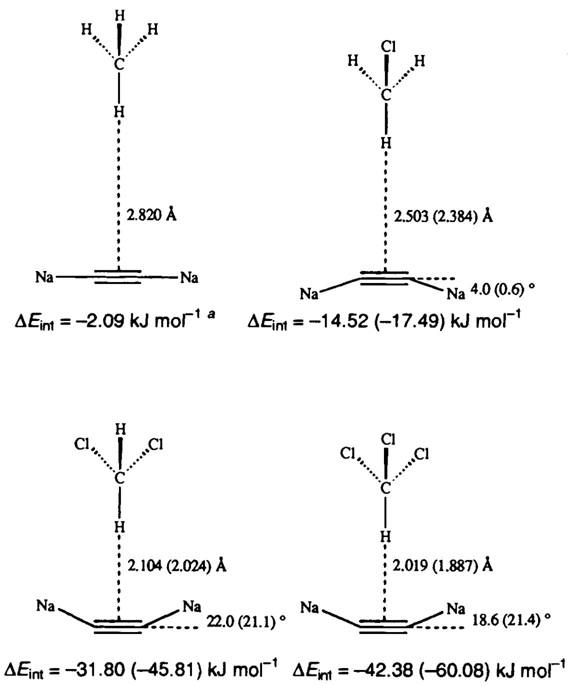
In Fig. 2, the structures of complexes in the series $CH_{4-n}Cl_n \cdots C_2H_2$ (n = 0–3) are summarised. Optimised C–H ··· π distances and interaction energies (ΔE_{int}) are shown in the Figure (values obtained from DFT are given in parentheses). Both *ab initio* and DFT calculations predict an approximately linear increase in interaction energy with increasing n with a concomitant decrease in C–H ··· π distance. The result is consistent with the classical expectation that the interaction will strengthen as the positive charge on the proton increases. In all cases the structural predictions of the two methods are remarkably similar, *ab initio* and DFT calculated distances lying within 0.02 Å of each other. The DFT calculated interaction energies are, however, considerably lower than the *ab initio* estimates in each case. As in the $HCN \cdots C_2H_2$ system, it is impossible to evaluate the accuracy of the different interaction energies derived from *ab initio* and DFT calculations in the absence of experimental data for the $CH_{4-n}Cl_n \cdots C_2H_2$ complexes.

$CH_{4-n}Cl_n \cdots C_2Na_2$ (n = 0–3)

The effect of increasing the electron density of the C–C triple bond has been modelled using the C_2Na_2 system which contains a highly ionic Na–C bond. Optimised C–H ··· π distances and Na-C–C angles for $CH_{4-n}Cl_n \cdots C_2Na_2$ (n = 0–3) are summarised in Fig. 3, along with interaction energies. Once again an approximately linear increase in interaction energy with increasing chloride substitution is predicted, along with a corresponding decrease in C–H ··· π distance. The changes are however rather more dramatic than for unsubstituted ethyne and the interaction energy of chloroform with the C_2Na_2 electron-donor is greater than 40 (60) kJ mol⁻¹, an increase of almost an order of magnitude over the corresponding complex with C_2H_2. Thus increasing the π electron density of the triple bond exerts a greater influence on the strength of the C–H ··· π interaction than does the acidity of the proton.

In addition to short C–H ··· π distances, both methods predict a significant (*ca.* 20°) bending of the Na atoms towards the coordinated $CH_{4-n}Cl_n$ group for n = 2 and 3. In all other cases, this angle is less than 5° in the outward direction, within the current theoretical error of bond angle determination. We can propose a simple molecular orbital argument for this observation. The inward bending allows the pπ orbitals on each carbon to point towards the proton, concentrating electron density in the C–H ··· π region and enhancing the interaction with the proton (Fig. 4). Block *et al.* noted a similar but very much reduced (< 1°) distortion in their study of the $HCN \cdots C_2H_2$ system[10] and suggested that the effect indicated a small transfer of charge to the proton. The much larger distortion noted here is consistent with the greater electron density at the sodium-substituted triple bond. Similar distortions have also been observed many times in transition metal π-complexes and have been interpreted in an analogous fashion.[22]

Finally, note that while the DFT estimate of the interaction energy for very weakly bonded systems such as $CH_4 \cdots C_2H_2$, $HCN \cdots C_2H_2$ and $CH_{4-n}Cl_n \cdots C_2H_2$ is generally lower than that obtained from *ab initio* calculations, the opposite trend is observed when the bonding is stronger. Within a series of related complexes, however, the trends predicted by the



[a] No minimum found using DFT

Fig. 3 Optimised structures and interaction energies for $CH_{4-n}Cl_n \cdots C_2Na_2$ (n = 0–3). Values from DFT calculations are shown in parentheses.

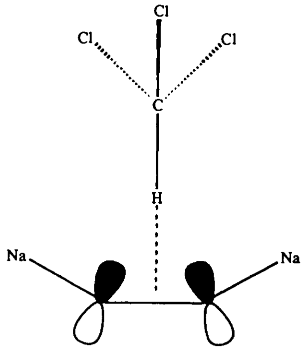


Fig. 4 Enhanced C–H ··· π overlap caused by an inward distortion of the Na–C–C angle

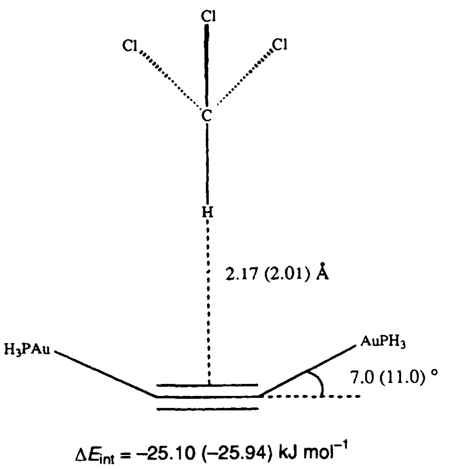


Fig. 5 Optimised structure and interaction energy for $CHCl_3 \cdots H_3PAuCCAuPH_3$. Values from DFT calculations are shown in parentheses.

different methodologies are entirely parallel and fully in accord with chemical intuition. Most importantly, both *ab initio* and DFT calculations indicate that the nature of the $C\text{–}H \cdots \pi$ interaction in systems such as $C_2Na_2 \cdots CHCl_3$ is fundamentally different to that in $C_2H_2 \cdots CH_4$.

$H_3PAuCCAuPPH_3 \cdots CHCl_3$

In *ab initio* calculations on the model gold complex, a relatively low quality basis set (ECP/DZ) was used on the peripheral atoms, but the $C\text{–}C \cdots H$ core retains a full 6-311**g basis and so results should be comparable to those reported in the previous two sections. Likewise, the full DZP basis is used for the $C\text{–}C \cdots H$ core in DFT calculations, but a smaller DZ basis is used on the $AuPH_3$ fragments. Geometries are again optimised at the MP2 (*ab initio*) and BP (DFT) levels of theory.

The optimised structures and interaction energies of $H_3PAuCCAuPPH_3 \cdots CHCl_3$ are summarised in Fig. 5. DFT results are again given in parentheses. The estimates of the interaction energy (ΔE) from *ab initio* and DFT methods are remarkably similar, -25.1 and -25.9 kJ mol^{-1}, respectively. The magnitude of both the energies and the $C\text{–}H \cdots \pi$ distances suggest that the $H_3PAuCCAuPPH_3 \cdots CHCl_3$ complex is somewhat weaker than the corresponding disodium complex. This is consistent with the more covalent nature of the Au–C bond relative to Na–C. Thus, while the ethynide unit in $H_3PAuCCAuPH_3$ may be formally described as C_2^{2-}, the negative charge present on the ethynide unit, and hence the π-electron density, will be somewhat lower than in C_2Na_2.

The calculated interaction distances are significantly lower than the experimentally observed values (2.42–2.58 Å). This probably reflects the presence of only a single coordinated $CHCl_3$ group in the model complexes, as opposed to either two or four in the crystallographically characterised complexes. The coordination of more than one $CHCl_3$ group will remove some electron density from the triple bond and also prevent the distortion of the gold atoms towards the proton.

Conclusions

In this paper we have described the bonding in $C\text{–}H \cdots \pi$ complexes using both *ab initio* calculations and density functional theory. In accord with previously reported work, complexes between unsubstituted ethyne and a variety of small molecules (CH_4, HCN, $CH_{4-n}Cl_n$) are invariably found to be very weak ($\Delta E_{int} < 10$ kJ mol^{-1}), even in the presence of the relatively acidic HCN proton donor. Enhancement of the π-donor ability of the ethynide unit, however, increases the interaction energies by up to an order of magnitude. Thus the interaction between $CHCl_3$ and C_2Na_2 is far stronger than generally accepted estimates of van der Waals interactions and even stronger than typical estimates of hydrogen bond energies.[11,23] The ethynide unit in $H_3PAuCCAuPH_3$ may be described formally as C_2^{2-}, just as in C_2Na_2, but the higher covalency of the Au–C bond reduces the π-electron density relative to that in C_2Na_2. The interaction of the gold ethynide with $CHCl_3$ is consequently intermediate in strength between that with C_2Na_2 and that with H_2C_2, and both *ab initio* and DFT methods predict an interaction energy in the region of 25 kJ mol^{-1}, a value typical of classical hydrogen bonded systems.

Although we make no attempt to partition the total energy into physical components, it is possible to make some comparisons with hydrogen bonds, whose stabilities depend primarily on electrostatic interactions between a lone pair and the proton.[24] The C–C triple bond is a considerably softer base than a typical lone pair and thus polarisation of the π-electron density may be more significant than in typical hydrogen bonds. In this context it is noteworthy that the interaction of C_2H_2 with HCN is very similar to that with $CHCl_3$, despite the very great difference in acidities of the two proton donors, an observation which is inconsistent with a purely electrostatic attractive force. Both proton donor groups, HCN and $CHCl_3$, contain electronegative substituents and it is possible that delocalisation of the C–C π-electron density *via* an inductive pathway contributes significantly to the stabilisation of the complex. The displacement of the sodium and gold atoms towards the $CHCl_3$ molecule and consequent rehybridisation of the carbon orbitals also suggests that overlap with the hydrogen 1s orbital is significant. Thus it seems likely that both electrostatic and inductive mechanisms contribute to the overall stability of the complex and both are greatly enhanced by the build-up of π-electron density in the metallated ethynes.

In comparison with the well established *ab initio* methodology, gradient corrected DFT calculations consistently underestimate the interaction energies of weakly bonded complexes ($C_2H_2 \cdots HCN$, $C_2H_2 \cdots CH_{4-n}Cl_n$) relative to high level *ab initio* techniques, most noticeably in the $CH_4 \cdots C_2H_2$ complex, where the BP corrected functional fails to find any minimum on the potential energy surface. This observation is consistent with the well established inability of DFT to describe accurately the dispersion forces which dominate the bonding in weakly bound complexes.[19] In more strongly bonded systems such as $C_2Na_2 \cdot CHCl_3$, the trend is reversed, DFT calculated interaction energies generally being larger than those obtained from MP2 calculations. In the absence of experimental estimates of interaction energies, it is not possible to comment on the relative accuracy of the two methods, but both techniques clearly place the interaction of chloroform with electron-rich C_2Na_2 in a very different class to that with free ethyne, C_2H_2.

Thus we conclude that the recently characterised complexes displaying the $R_3PAuCCAuPR_3 \cdots CHCl_3$ interaction represent a new class of $C\text{–}H \cdots \pi$ interaction, fundamentally different in nature to the much weaker interactions in purely organic systems. The unusually large interaction energy arises as a direct consequence of the high π-electron density in the ethynide subunit and similarly strong interactions are likely to be found only in other metallated ethynes. Thus the observation of short $C\text{–}H \cdots \pi$ contacts in metallated ethynes does not necessarily confirm that such interactions exert a significant influence on conformational preferences of purely organic systems.

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Paper 5/06073G
Received 14*th September* 1995
Accepted 31*st October* 1995