The Acetylene−Ammonia Dimer as a Prototypical C−H···N Hydrogen-Bonded System: An Assessment of Theoretical Procedures

Michael Hartmann and Leo Radom*

Research School of Chemistry, Australian National University, Canberra, ACT 0200, Australia

Received: June 30, 1999; In Final Form: November 5, 1999

The effect of a variety of theoretical methods (HF, B3-LYP, MP2, QCISD, and CCSD(T)) and basis sets (from 6-31G(d) to 6-311+G(3df,2p)) on the calculated geometry and dimerization energy of the acetylene−ammonia dimer HCCH···NH_3 is examined. The dimer has C_{3v} symmetry with acetylene acting as the hydrogen bond donor. Our highest level calculations (viz. CCSD(T)/6-311+G(3df,2p) including BSSE correction) predict an equilibrium contact distance r(H···N) of 2.280 Å and an equilibrium binding energy ΔE_e of 14.1 kJ mol^{-1}. Incorporation of a scaled B3-LYP/6-311+G(3df,2p) zero-point vibrational correction leads to $\Delta E_0 = 9.3$ kJ mol^{-1}. The less expensive CCSD(T)/6-311+G(3df,2p)//B3-LYP/6-311+G(3df,2p) procedure reproduces these benchmark energies and is therefore recommended for general application on small hydrogen-bonded systems. For larger hydrogen-bonded systems, the still less expensive B3-LYP/6-311+G(3df,2p)//B3-LYP/6-311+G(d,p) procedure is recommended, and this yields $\Delta E_0 = 7.8$ kJ mol^{-1} for the acetylene−ammonia dimer.

1. Introduction

The study of hydrogen-bonded systems Y−H···X has traditionally focused on species in which the hydrogen of the proton donor is bonded to an electronegative element Y. Although the ability of C−H groups to act as proton donors in hydrogen bonding has been known since the early 1960s,[1] it was not until 1982 before the first survey of C−H···X hydrogen bonds based on crystallographic data appeared.[2] Since that time, supported by crystal correlation studies and spectroscopic examinations, increasing attention has been directed toward these attractive, directional interactions.[3] In particular, C−H···O,[4] C−H···N,[5] and C−H···π[6] hydrogen bonds have been the focus of such investigations, and are well established and accepted. There is less information concerning C−H···S,[7] C−H···Se,[8] and C−H···Hal/Hal$^-$ (Hal = Cl, Br, I)[9] interactions, while the questions as to whether C−H···C hydrogen bonds[10] or the soft-donor/hard-acceptor combination C−H···F[9d,11] exist are still subjects of some controversy.

As a preliminary to a comprehensive study of C−H···X hydrogen-bonded systems in which the proton donor and acceptor molecules are systematically varied, we have carried out a detailed examination of the acetylene−ammonia dimer HCCH···NH_3 as a prototypical example. In the present work, we focus on two main aspects. In the first place, by carrying out calculations with a large variety of theoretical procedures and basis sets, and including an assessment of the importance of basis set superposition errors (BSSEs) and zero-point vibrational energies (ZPVEs), we wish to identify levels of theory suitable for general application. In the second place, the acetylene−ammonia dimer is of interest in its own right,[12−16] and we present here the highest level predictions to date for this system.

2. Theoretical Procedures

Standard ab initio molecular orbital theory[17] and density functional theory (DFT)[18] calculations were carried out using the program packages GAUSSIAN 94,[19] GAUSSIAN 98,[20] ACES II,[21] and MOLPRO 97,[22] using default criteria for convergence in all cases. The default numerical integration grid of GAUSSIAN 94[19] and 98[20] was used for the evaluation of the DFT Kohn−Sham orbitals. The effect of level of theory on the preferred gas-phase structures, dimerization energies, BSSEs, and ZPVEs was examined. Geometry optimization procedures included the HF, B3-LYP, MP2, QCISD, and CCSD(T) methods combined with the 6-31G(d), 6-31+G(d), 6-311+G(d,p), 6-311+G(2df,p), and 6-311+G(3df,2p) basis sets. Frequency analyses were performed using HF, B3-LYP, and MP2 including all of the aforementioned basis sets. Additional single-point energy calculations on selected geometries used the B3-LYP, QCISD, and CCSD(T) methods combined with the 6-311+G(3df,2p) basis set. All electrons were correlated in the MP2, QCISD, and CCSD(T) calculations.

To account for the inherent basis set superposition error, the binding energy (ΔE_e or ΔE_0) was corrected by subtracting the BSSE, calculated according to the Boys and Bernardi counterpoise method:[23]

$$\mathrm{BSSE} = (E_{\mathrm{HCCH}}^{\mathrm{full}} - E_{\mathrm{HCCH}}^{\mathrm{monomer}}) + (E_{\mathrm{NH_3}}^{\mathrm{full}} - E_{\mathrm{NH_3}}^{\mathrm{monomer}}) \quad (1)$$

In this expression, $E_{\mathrm{HCCH}}^{\mathrm{full}}$ and $E_{\mathrm{NH_3}}^{\mathrm{full}}$ are the total energies of the monomers (acetylene and ammonia) in their respective dimer geometries using the full basis set of the dimer, while $E_{\mathrm{HCCH}}^{\mathrm{monomer}}$ and $E_{\mathrm{NH_3}}^{\mathrm{monomer}}$ are the total energies of the monomers calculated at their respective dimer geometries but using only the monomer basis sets. A summary of the total energies used to calculate binding energies and BSSE corrections is given in the Supporting Information (Tables S1 and S2). The ZPVE contribution to the dimerization energy for the process HCCH + NH_3 → HCCH···NH_3 is significant and depends strongly on the basis set. It therefore warrants careful consideration. Although optimum ZPVE scale factors for a wide variety of levels of theory have been reported,[24] such factors are not available for the higher level procedures used in the present study. We have therefore derived scale factors (sf) for the ZPVE of the

10.1021/jp992234e CCC: $19.00

TABLE 1: Structural Parameters for the Monomers HCCH and NH_3[a]

	HCCH		NH_3	
method	r(C−H)	r(C≡C)	r(N−H)	∠(HNH)
experiment[b]	1.061	1.203	1.012	106.7
B3-LYP/6-31G(d)	1.067	1.205	1.019	105.8
B3-LYP/6-31+G(d)	1.067	1.208	1.018	107.6
B3-LYP/6-311+G(d,p)	1.063	1.199	1.014	107.9
B3-LYP/6-311+G(2df,p)	1.064	1.196	1.014	107.7
B3-LYP/6-311+G(3df,2p)	1.062	1.196	1.013	107.3
MP2/6-31G(d)	1.066	1.216	1.017	106.4
MP2/6-31+G(d)	1.068	1.220	1.017	108.0
MP2/6-311+G(d,p)	1.065	1.215	1.013	107.5
MP2/6-311+G(2df,p)	1.064	1.208	1.012	107.7
MP2/6-311+G(3df,2p)	1.061	1.209	1.009	107.3
QCISD/6-31G(d)	1.068	1.211	1.020	106.0
QCISD/6-31+G(d)	1.070	1.215	1.020	107.5
QCISD/6-311+G(d,p)	1.066	1.210	1.014	107.1
QCISD/6-311+G(2df,p)	1.065	1.202	1.014	107.3
QCISD/6-311+G(3df,2p)	1.062	1.202	1.010	107.0
CCSD(T)/6-31G(d)	1.070	1.216	1.021	105.8
CCSD(T)/6-31+G(d)	1.071	1.220	1.021	107.4
CCSD(T)/6-311+G(d,p)	1.067	1.215	1.016	107.0
CCSD(T)/6-311+G(2df,p)	1.066	1.207	1.015	107.2
CCSD(T)/6-311+G(3df,2p)	1.063	1.207	1.012	106.9

[a] Bond lengths are given in angstroms, bond angles in degrees. [b] Reference 26.

monomers and dimer according to

$$\mathrm{sf}_{\mathrm{HCCH}} = \frac{\mathrm{ZPVE}^{\mathrm{exp}}_{\mathrm{HCCH}}}{\mathrm{ZPVE}^{\mathrm{calc}}_{\mathrm{HCCH}}} \quad \mathrm{sf}_{\mathrm{NH_3}} = \frac{\mathrm{ZPVE}^{\mathrm{exp}}_{\mathrm{NH_3}}}{\mathrm{ZPVE}^{\mathrm{calc}}_{\mathrm{NH_3}}} \tag{2}$$

$$\mathrm{sf}_{\mathrm{HCCH\cdots NH_3}} = \frac{\mathrm{ZPVE}^{\mathrm{exp}}_{\mathrm{HCCH}} + \mathrm{ZPVE}^{\mathrm{exp}}_{\mathrm{NH_3}}}{\mathrm{ZPVE}^{\mathrm{calc}}_{\mathrm{HCCH}} + \mathrm{ZPVE}^{\mathrm{calc}}_{\mathrm{NH_3}}} \tag{3}$$

where $\mathrm{sf}_{\mathrm{HCCH}}$, $\mathrm{sf}_{\mathrm{NH_3}}$, and $\mathrm{sf}_{\mathrm{HCCH\cdots NH_3}}$ are the scale factors to be applied to the calculated ZPVE of acetylene, ammonia, and the acetylene−ammonia dimer. $\mathrm{ZPVE}^{\mathrm{exp}}_{\mathrm{HCCH}}$, $\mathrm{ZPVE}^{\mathrm{exp}}_{\mathrm{NH_3}}$, $\mathrm{ZPVE}^{\mathrm{calc}}_{\mathrm{HCCH}}$, and $\mathrm{ZPVE}^{\mathrm{calc}}_{\mathrm{NH_3}}$ are the experimental and calculated ZPVEs of the monomers acetylene and ammonia, respectively.[25] The scale factor given by eq 3 is exact in the case of infinitely separated monomers and should therefore hold reasonably well for weakly interacting species, such as C−H···X hydrogen-bonded systems. Scale factors and ZPVEs for the monomers and the dimer at the various levels of theory are listed in the Supporting Information (Table S3).

Full geometry optimizations were performed within the respective experimentally observed symmetries, i.e., $D_{\infty h}$ for HCCH,[26] C_{3v} for NH_3,[26] and C_{3v} for HCCH···NH_3,[12,14,15] and the resultant geometries were confirmed through the frequency calculations to represent minima on the respective potential energy surface. Structural parameters and dimerization energies obtained at the HF level of theory are summarized in the Supporting Information (Tables S4−S6).

3. Results and Discussion

3.1. Geometries of the Monomers HCCH and NH_3. Structural parameters obtained for the acetylene and ammonia monomers at the selected levels of theory are compared with corresponding experimental geometries[26] in Table 1. At our highest level of theory (viz. CCSD(T)/6-311+G(3df,2p)), close agreement with the experimental data is achieved. Simpler levels of theory like QCISD, MP2, and B3-LYP also give very reasonable results once a sufficiently large basis set is used (i.e., at least 6-311+G(d,p)) and therefore may offer an economical alternative in the calculation of monomer and dimer geometries. The HF method underestimates the bond lengths by up to 0.02 Å (Table S4 of the Supporting Information).

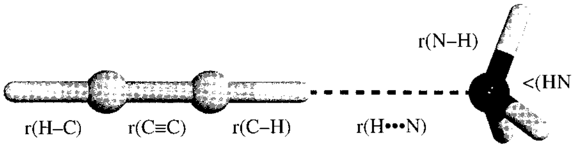

Figure 1. Geometry of the acetylene−ammonia dimer HCCH···NH_3 and notation used to describe structural parameters.

3.2. Geometry of the Dimer HCCH···NH_3. Structural parameters obtained at each level of theory are summarized in Table 2. The most stable equilibrium geometry of the acetylene−ammonia dimer has C_{3v} symmetry, with acetylene acting as proton donor (Figure 1).[27] The good performance of CCSD(T)/6-311+G(3df,2p) in the prediction of the monomer geometries lends confidence to the geometry predicted at this level for the HCCH···NH_3 dimer. It predicts the intermolecular contact distance r(H···N) between the acetylenic hydrogen and the ammonia nitrogen involved in the hydrogen bond to be 2.280 Å. The corresponding vibrationally averaged value derived experimentally by Klemperer et al.[12] is 2.333 Å. This difference is in the direction expected from the vibrational averaging of this quite anharmonic mode in the experimental structure. A previous lower-level theoretical estimate yielded an r(H···N) length of 2.329 Å.[13]

We find that the HF method generally overestimates the intermolecular r(H···N) bond distance, while intramolecular parameters of the monomers within the dimer are predicted to be too short compared with the reference values (Table S5 of the Supporting Information). On the other hand, the B3-LYP and MP2 methods in conjunction with a 6-311+G(d,p) or larger basis set closely reproduce the corresponding CCSD(T)/6-311+G(3df,2p) intermolecular contact distance of the acetylene−ammonia dimer at a significantly reduced computational cost. QCISD also performs quite well.[28] We note that small changes (e.g., ±0.1 Å) in the equilibrium H···N contact distance have an almost negligible effect on the calculated total energy.[29]

3.3. Changes Upon Complex Formation. The effect on the structures of the monomers upon complex formation is found to be relatively small (Tables 1 and 2). At the CCSD(T)/6-311+G(3df,2p) level, the more significant changes occur for the inner C−H bond length r(C−H) of the acetylene moiety which is longer than that in free acetylene by 0.009 Å and for the triple-bond r(C≡C) which is elongated by 0.002 Å. Changes in other parameters are smaller; the N−H bond of ammonia is elongated by only 0.001 Å, and the ∠HNH angle diminished by just 0.2°, while the outer C−H bond length r(H−C) of acetylene is not changed at all. These findings are consistent with the work of Schulz and Botschwina, who reported corresponding CEPA-1 increments for r(C−H) and r(C≡C) in the acetylene−ammonia dimer of 0.008 and 0.002 Å, respectively.[16] They are also well reproduced by all of the lower level calculations examined in the present work; the changes in the most variable intramolecular parameters lie between 0.005 and 0.014 Å for r(C−H) and between 0.001 and 0.003 Å for r(C≡C) (see also Tables S4 and S5 of the Supporting Information).

Although the CCSD(T)/6-311+G(3df,2p) geometry represents our best estimate for the structure of the acetylene−ammonia dimer, this level of geometry optimization is not practical for

TABLE 2: Structural Parameters of the Dimer HCCH···NH_3[a]

	HCCH···NH_3					
method	r(H−C)	r(C≡C)	r(C−H)	r(H···N)	r(N−H)	∠(HNH)
experiment [b]				2.333		
B3-LYP/6-31G(d)	1.066	1.207	1.081	2.149	1.019	106.3
B3-LYP/6-31+G(d)	1.067	1.210	1.079	2.202	1.019	107.1
B3-LYP/6-311+G(d,p)	1.063	1.202	1.074	2.260	1.016	107.2
B3-LYP/6-311+G(2df,p)	1.063	1.198	1.073	2.296	1.015	107.3
B3-LYP/6-311+G(3df,2p)	1.062	1.198	1.072	2.308	1.014	107.2
MP2/6-31G(d)	1.066	1.218	1.077	2.202	1.017	106.5
MP2/6-31+G(d)	1.067	1.222	1.076	2.235	1.018	107.1
MP2/6-311+G(d,p)	1.064	1.217	1.074	2.282	1.015	106.5
MP2/6-311+G(2df,p)	1.064	1.210	1.073	2.291	1.014	107.1
MP2/6-311+G(3df,2p)	1.061	1.211	1.070	2.275	1.010	107.1
QCISD/6-31G(d)	1.068	1.213	1.078	2.243	1.020	106.2
QCISD/6-31+G(d)	1.070	1.217	1.077	2.268	1.021	106.7
QCISD/6-311+G(d,p)	1.066	1.211	1.073	2.321	1.016	106.3
QCISD/6-311+G(2df,p)	1.064	1.203	1.072	2.332	1.015	106.9
QCISD/6-311+G(3df,2p)	1.062	1.203	1.069	2.314	1.011	106.8
CCSD(T)/6-31G(d)	1.070	1.217	1.079	2.224	1.021	106.0
CCSD(T)/6-31+G(d)	1.071	1.221	1.079	2.249	1.023	106.6
CCSD(T)/6-311+G(d,p)	1.067	1.217	1.076	2.296	1.017	106.1
CCSD(T)/6-311+G(2df,p)	1.066	1.209	1.075	2.280	1.016	106.7
CCSD(T)/6-311+G(3df,2p)	1.063	1.209	1.072	2.280	1.013	106.7

[a] Bond lengths are given in anstroms, bond angles in degrees. See Figure 1 for the notation used. [b] Reference 12.

TABLE 3: Equilibrium Binding Energies, BSSE Contributions, and BSSE-Corrected Equilibrium Binding Energies for the Acetylene−Ammonia Dimer[a]

method	ΔE_e[b]	BSSE	ΔE_e
B3-LYP/6-31G(d)	22.0	4.1	17.9
B3-LYP/6-31+G(d)	19.1	5.1	14.0
B3-LYP/6-311+G(d,p)	16.7	2.7	14.0
B3-LYP/6-311+G(2df,p)	14.8	1.9	12.9
B3-LYP/6-311+G(3df,2p)	13.0	0.4	12.6
MP2/6-31G(d)	23.2	7.1	16.1
MP2/6-31+G(d)	21.6	8.5	13.1
MP2/6-311+G(d,p)	18.7	5.5	13.2
MP2/6-311+G(2df,p)	17.5	3.7	13.8
MP2/6-311+G(3df,2p)	16.0	2.0	14.0
QCISD/6-31G(d)	21.6	6.7	14.9
QCISD/6-31+G(d)	20.2	8.0	12.2
QCISD/6-311+G(d,p)	17.5	5.1	12.4
QCISD/6-311+G(2df,p)	16.2	3.3	12.9
QCISD/6-311+G(3df,2p)	14.9	1.8	13.1
CCSD(T)/6-31G(d)	22.5	7.3	15.2
CCSD(T)/6-31+G(d)	21.3	8.7	12.6
CCSD(T)/6-311+G(d,p)	18.5	5.7	12.8
CCSD(T)/6-311+G(2df,p)	17.3	3.8	13.5
CCSD(T)/6-311+G(3df,2p)	16.1	2.0	14.1

[a] All values are given in kJ mol^{-1}. [b] Binding energy without BSSE contribution.

general application and thus should rather be used to produce benchmark results. The good performance of computationally less expensive methods, particularly B3-LYP and MP2 in conjunction with basis sets incorporating at least diffuse and polarization functions on carbon and nitrogen, however, offers a reliable alternative for geometry predictions of such hydrogen-bonded dimers.

3.4. Equilibrium Binding Energy ΔE_e Including BSSE Correction. Table 3 summarizes our calculated equilibrium binding energies, defined as the negative of the energy changes for the process HCCH + NH_3 → HCCH···NH_3. These have been obtained both with and without the incorporation of BSSEs, the BSSEs being estimated according to eq 1. The CCSD(T)/6-311+G(3df,2p) calculations are again used as benchmark results, giving values for the binding energy of 16.1 kJ mol^{-1} before the BSSE correction and 14.1 kJ mol^{-1} after the BSSE correction.

In general, the uncorrected equilibrium binding energies vary considerably with the level of theory used and are calculated to be in the range of 11.2 kJ mol^{-1} (HF/6-311+G(3df,2p)) to 23.2 kJ mol^{-1} (MP2/6-31G(d)) (Tables S6 of the Supporting Information and Table 3). The general trend observed within a series of calculations at a specific level of theory is that increasing the basis set results in reduced binding energies. This is caused in part by the larger BSSEs for calculations with the smaller basis sets.

The BSSE is found to contribute significantly to the equilibrium dimerization energy, particularly when using smaller basis sets such as 6-31G(d) and 6-31+G(d). On going from the 6-31G(d) to 6-31+G(d) basis set within each level of calculations, the expectation of lower corrections with increasing size of basis set is not satisfied and BSSE corrections increase by up to 1.4 kJ mol^{-1}. However, the BSSE corrections become less pronounced with basis sets more complete than 6-31+G(d) and generally show their lowest contribution with 6-311+G(3df,2p). Even with that basis set, however, the BSSE is not negligible and still affects ΔE_e by up to 2 kJ mol^{-1}. The BSSE correction not only depends on the basis set but also on the method used. It is relatively small for the HF and B3-LYP methods but surprisingly large with MP2, QCISD, and CCSD(T), particularly when using only split-valence basis sets. For example, for the MP2, QCISD, and CCSD(T) methods in combination with the 6-31G(d) basis set, the BSSE cancels out approximately 30% of the uncorrected binding energy. This implies that if high-level methods are to be employed without incorporating a BSSE correction, reasonably large basis sets, preferably with multiple polarization functions per atom, must be used for predicting satisfactory binding energies. Within this context, the very small BSSE contribution of 0.4 kJ mol^{-1} found for the B3-LYP/6-311+G(3df,2p) level is noteworthy.

After incorporation of the BSSE correction, the equilibrium binding energies show a much less pronounced dependence on method and basis set compared with the uncorrected equilibrium

TABLE 4: Equilibrium Binding Energies, BSSE Contributions, and BSSE-Corrected Equilibrium Binding Energies for the Acetylene−Ammonia Dimer[a]

method	ΔE_e[b]	BSSE	ΔE_e
CCSD(T)/6-311+G(3df,2p)//B3-LYP/6-31G(d)	15.6	2.5	13.1
CCSD(T)/6-311+G(3df,2p)//B3-LYP/6-31+G(d)	16.0	2.3	13.7
CCSD(T)/6-311+G(3df,2p)//B3-LYP/6-311+G(d,p)	16.2	2.1	14.1
CCSD(T)/6-311+G(3df,2p)//B3-LYP/6-311+G(2df,p)	16.1	2.0	14.1
CCSD(T)/6-311+G(3df,2p)//B3-LYP/6-311+G(3df,2p)	16.1	2.0	14.1
CCSD(T)/6-311+G(3df,2p)//MP2/6-311+G(2df,p)	16.1	2.0	14.1
CCSD(T)/6-311+G(3df,2p)//MP2/6-311+G(3df,2p)	16.1	2.1	14.0
CCSD(T)/6-311+G(3df,2p)//CCSD(T)/6-31+G(d)	16.2	2.1	14.1
CCSD(T)/6-311+G(3df,2p)//CCSD(T)/6-311+G(d,p)	16.0	2.0	14.0
CCSD(T)/6-311+G(3df,2p)//CCSD(T)/6-311+G(2df,p)	16.1	2.0	14.1
CCSD(T)/6-311+G(3df,2p)//QCISD/6-311+G(d,p)	16.0	1.9	14.1
CCSD(T)/6-311+G(3df,2p)//QCISD/6-311+G(2df,p)	16.0	1.9	14.1
QCISD/6-311+G(3df,2p)//B3-LYP/6-31G(d)	14.1	2.3	11.8
QCISD/6-311+G(3df,2p)//B3-LYP/6-31+G(d)	14.6	2.1	12.5
QCISD/6-311+G(3df,2p)//B3-LYP/6-311+G(d,p)	14.9	1.9	13.0
QCISD/6-311+G(3df,2p)//B3-LYP/6-311+G(2df,p)	15.0	1.8	13.2
QCISD/6-311+G(3df,2p)//B3-LYP/6-311+G(3df,2p)	14.9	1.8	13.1
B3-LYP/6-311+G(3df,2p)//B3-LYP/6-31+G(d)	12.8	0.5	12.3
B3-LYP/6-311+G(3df,2p)//B3-LYP/6-311+G(d,p)	13.0	0.4	12.6

[a] All values are given in kJ mol^{-1}. [b] Binding energy without BSSE contribution.

TABLE 5: Scaled ZPVEs (kJ mol^{-1}) for the Reaction $HCCH + NH_3 \rightarrow HCCH\cdots NH_3$

method	ZPVE
HF/6-31G(d)	4.9
HF/6-31+G(d)	5.5
HF/6-311+G(d,p)	4.9
HF/6-311+G(2df,p)	4.6
HF/6-311+G(3df,2p)	4.1
B3-LYP/6-31G(d)	6.0
B3-LYP/6-31+G(d)	6.9
B3-LYP/6-311+G(d,p)	6.0
B3-LYP/6-311+G(2df,p)	5.4
B3-LYP/6-311+G(3df,2p)	4.8
MP2/6-31G(d)	7.0
MP2/6-31+G(d)	7.6
MP2/6-311+G(d,p)	6.2
MP2/6-311+G(2df,p)	5.3
MP2/6-311+G(3df,2p)	4.8

binding energies discussed before. Moreover, taking into account only correlated methods and using basis sets involving at least diffuse functions, the range of ΔE_e is narrowed to 13.2 ± 1.0 kJ mol^{-1}. Our best calculations (CCSD(T)/6-311+G(3df,2p)) predict a BSSE-corrected equilibrium binding energy of 14.1 kJ mol^{-1}. This value is in line with a binding energy of 15.0 kJ mol^{-1} previously reported at a slightly lower level of theory.[16] The MP2/6-311+G(3df,2p) binding energy differs by only 0.1 kJ mol^{-1} from the CCSD(T)/6-311+G(3df,2p) value, whereas the QCISD/6-311+G(3df,2p) and B3LYP/6-311+G(3df,2p) energies of 13.1 and 12.6 kJ mol^{-1}, respectively, slightly underestimate the strength of the $C-H\cdots N$ hydrogen bond.

A key point that we wish to emphasize in this section is that incorporation of a BSSE correction is very important in attempting to obtain reliable binding energies for weakly bound dimers such as $HCCH\cdots NH_3$, even with basis sets as large as 6-311+G(3df,2p).

3.5. Evaluation of ΔE_e Using Alternative Geometries. As mentioned before, CCSD(T)/6-311+G(3df,2p) geometry optimizations are not practical for general application. We have therefore obtained binding energies at the CCSD(T)/6-311+G(3df,2p) level using geometries obtained by less expensive methods. The resulting equilibrium binding energies, again calculated with and without BSSE corrections, are summarized in Table 4.

In essence, although the acetylene−ammonia geometries obtained from the various methods differ slightly from one another (Table 2), CCSD(T)/6-311+G(3df,2p) binding energy calculations based on the various geometries show negligible deviations from the BSSE-corrected reference ΔE_e of 14.1 kJ mol^{-1} (Table 3) in almost all cases. From the point of view of a balance between reliability and computational expense, CCSD(T)/6-311+G(3df,2p) energy calculations on B3-LYP/6-311+G(d,p), B3-LYP/6-311+G(2df,p), B3-LYP/6-311+G(3df,2p), MP2/6-311+G(2df,p), or MP2/6-311+G(3df,2p) geometries can all be recommended for general application to small $C-H\cdots X$ hydrogen-bonded dimers.

The use of less expensive geometry optimization procedures reduces the overall amount of CPU time considerably, which is very apparent in going from geometry optimizations based on the CCSD(T)/6-311+G(3df,2p) level of theory to B3-LYP/6-311+G(3df,2p) calculations. However, the evaluation of energies at the CCSD(T)/6-311+G(3df,2p) level is still fairly expensive, particularly when larger dimers are to be considered. To this end, QCISD/6-311+G(3df,2p) and B3-LYP/6-311+(3df,2p) energy calculations based on B3-LYP geometries were examined.

As with CCSD(T) calculations, we find that the QCISD/6-311+G(3df,2p) and B3-LYP/6-311+G(3df,2p) BSSE-corrected binding energies are not sensitive to the choice of B3-LYP geometry for 6-311+G(d,p) and larger basis sets. The resulting binding energies are close to those obtained with the optimized geometries of Table 3. They are thus 1−2 kJ mol^{-1} smaller than the benchmark CCSD(T)/6-311+G(3df,2p) value of 14.1 kJ mol^{-1}. The B3-LYP/6-311+G(3df,2p)//B3-LYP/6-311+G(d,p) procedure appears suitable for larger $C-H\cdots X$ hydrogen-bonded systems.

3.6. Contribution of the ZPVE to the Binding Energy and Evaluation of ΔE_0. The contribution of the ZPVE to the energy of the dimerization reaction $HCCH + NH_3 \rightarrow HCCH\cdots NH_3$ has been calculated at a number of levels of theory, and the results are summarized in Table 5. Scale factors for the ZPVEs of monomers and the dimer were obtained as described in the theoretical procedures section and are listed in detail in the Supporting Information (Table S3). The results show that the ZPVE contribution to the binding energy ΔE_0 is significant, with calculated values lying between 4.1 and 7.6 kJ mol^{-1} depending on the level of theory used. Within each theoretical method, the scaled ZPVE generally decreases with increasing size of basis set, leading to values of 4.1, 4.8, and 4.8 kJ mol^{-1} at the HF, B3-LYP, and MP2 levels, respectively, with the (largest) 6-311+G(3df,2p) basis set. We have chosen 4.8 kJ mol^{-1} as our best estimate of the ZPVE contribution to the binding energy.

Combination of the ZPVE of 4.8 kJ mol^{-1} with the best BSSE-corrected estimates of ΔE_e from Tables 3 and 4 leads to the values of the binding energy at 0 K (ΔE_0) listed in Table 6. Our best estimate (viz. CCSD(T)/6-311+G(3df,2p)//CCSD)(T)/6-311+G(3df,2p)) is 9.3 kJ mol^{-1}, which is exactly reproduced by the more economical CCSD(T)/6-311+G(3df,2p)//B3-LYP/6-311+G(3df,2p) procedure. Still less expensive theoretical procedures give values ranging from 7.8 (B3-LYP/6-311+G(3df,2p)//B3-LYP/6-311+G(d,p)) to 8.3 kJ mol^{-1} (QCISD/6-311+G(3df,2p)//B3-LYP/6-311+G(3df,2p)).

On the basis of the observed infrared photodissociation of the acetylene−ammonia dimer, Klemperer et al. suggested a binding energy for the acetylene−ammonia dimer of *less* than

TABLE 6: Binding Energies ΔE_0 (kJ mol^{-1}) for the Acetylene−Ammonia Dimer

method	ΔE_0
CCSD(T)/6-311+G(3df,2p)//CCSD(T)/6-311+G(3df,2p)	9.3
CCSD(T)/6-311+G(3df,2p)//B3-LYP/6-311+G(3df,2p)	9.3
CCSD(T)/6-311+G(3df,2p)//MP2/6-311+G(3df,2p)	9.2
QCISD/6-311+G(3df,2p)//QCISD/6-311+G(3df,2p)	8.3
QCISD/6-311+G(3df,2p)//B3-LYP/6-311+G(3df,2p)	8.3
B3-LYP/6-311+G(3df,2p)//B3-LYP/6-311+G(3df,2p)	7.8
B3-LYP/6-311+G(3df,2p)//B3-LYP/6-311+G(d,p)	7.8

11.7 kJ mol^{-1} (2.8 kcal/mol^{-1}).[14] Our best estimate for ΔE_0 of 9.3 kJ mol^{-1} is consistent with this upper limit. Pople, Del Bene, and Frisch reported a series of ab initio calculations for the acetylene−ammonia dimer, and based on the MP4SDQ/6-31G(d,p)//HF/6-31G(d) results suggested a binding energy of 15.1 kJ mol^{-1}.[13] They predicted that larger basis set calculations will result in a lower binding energy of approximately 12.6 kJ mol^{-1},[13] still somewhat higher than our present best results.

4. Conclusions

The highest level of theory used for calculating geometries in the present study is CCSD(T)/6-311+G(3df,2p). It predicts an intermolecular contact distance r(H···N) in the acetylene−ammonia dimer of 2.280 Å. The main changes in the intramolecular parameters of ammonia and acetylene upon dimerization occur for the internal C−H bond and the acetylenic triple bond, which are lengthened by 0.009 and 0.002 Å, respectively.

Corrections to the raw equilibrium binding energy due to basis set superposition error and zero-point vibrational contributions are found to be very significant and therefore are essential for the prediction of a reliable binding energy at 0 K (ΔE_0). Our best estimate of the ZPVE contribution to the binding energy is 4.8 kJ mol^{-1} (B3-LYP/6-311+G(3df,2p)), while our best CCSD(T)/6-311+G(3df,2p) estimate of ΔE_0 is 9.3 kJ mol^{-1}.

The use of CCSD(T)/6-311+G(3df,2p) geometries is not practical for general application. However, our finding that CCSD(T)/6-311+G(3df,2p) calculations with geometries optimized at simpler levels such as B3-LYP/6-311+G(d,p) or B3-LYP/6-311+G(3df,2p) give almost identical binding energies allows us to recommend the CCSD(T)/6-311+G(3df,2p)//B3-LYP//6-311+G(3df,2p) procedure for calculations on small C−H···X hydrogen-bonded systems. This method exactly reproduces the benchmark binding energies and also gives an only slightly overestimated H···N contact distance of 2.308 Å for the acetylene−ammonia dimer. For larger systems for which CCSD(T)/6-311+G(3df,2p) energy calculations might be prohibitive, the B3-LYP//6-311+G(3df,2p)//B3-LYP//6-311+G(d,p) procedure is recommended. This gives a binding energy of 7.8 kJ mol^{-1} for the acetylene−ammonia dimer.

Acknowledgment. We gratefully acknowledge the generous allocation of computer time on the Fujitsu VPP-300 supercomputer and SGI Power Challenge of the Australian National University Supercomputer Facility and the award to M. H. of a postdoctoral fellowship from the Deutsche Forschungsgemeinschaft.

Supporting Information Available: Listing of the total energies of the monomers acetylene and ammonia, the acetylene−ammonia dimer, and all energy contributions used to calculate BSSE corrections according to eq 1 (Tables S1 and S2), the calculated ZPVEs together with their corresponding scale factors obtained by eqs 2 and 3 (Table S3), and all results obtained using the HF method (Tables S1−S6). This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) (a) Pimentel, C. G.; McClellan, A. L. *The Hydrogen Bond*; W. H. Freeman and Co.: San Francisco, 1960, Chapter 6.2. (b) Allerhand, A.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1963**, *85*, 1715 and references therein. (c) Sutor, J. D. *J. Chem. Soc.* **1963**, 1105.

(2) Taylor, R.; Kennard, O. *J. Am. Chem. Soc.* **1982**, *104*, 5063.

(3) For review articles, see: (a) Sarma, J. A. R. P.; Desiraju, G. R. *Acc. Chem. Res.* **1986**, *19*, 222. (b) Desiraju, G. R. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2311. (c) Desiraju, G. R. *Acc. Chem. Res.* **1991**, *24*, 290; **1996**, *29*, 441. (d) Steiner, T. *J. Chem. Soc., Chem. Commun.* **1997**, 727.

(4) See, for example: (a) Engdahl, A.; Nelander, B *Chem. Phys. Lett.* **1983**, *100*, 129. (b) Fillery-Travis, A. J.; Legon, A. C.; Willoughby, L. C. *Proc. R. Soc. London A* **1984**, *396*, 405. (c) Peterson, K. I.; Klemperer, W. *J. Chem. Phys.* **1984**, *81*, 3842. (d) DeLaat, A. M.; Ault, B. S. *J. Am. Chem. Soc.* **1987**, *109*, 4232. (e) Goodwin, E. J.; Legon, A. C. *J. Chem. Phys.* **1987**, *87*, 2426. (f) Desiraju, G. R. *J. Chem. Soc., Chem. Commun.* **1989**, 179; **1990**, 454. (g) Mielke, Z.; Andrews, A. *J. Phys. Chem.* **1990**, *94*, 3519. (h) Jeng, M.-L. H.; Ault, B. S. *J. Phys. Chem.* **1990**, *94*, 4851. (i) Gutowsky, H. S.; Germann, T. C.; Augspurger, J. D.; Dykstra, C. E. *J. Chem. Phys.* **1992**, *96*, 5808. (j) Pedireddi, V. R.; Desiraju, G. R. *J. Chem. Soc., Chem. Commun.* **1992**, 988. (k) Steiner, T.; Saenger, W. *J. Am. Chem. Soc.* **1993**, *115*, 4540. (l) Steiner, T. *J. Chem. Soc., Chem. Commun.* **1994**, 2341. (m) Lutz, B.; van der Maas, J.; Kanters, J. A. *J. Mol. Struct.* **1994**, *325*, 203. (n) Sharma, C. V. K.; Desiraju, G. R. *J. Chem. Soc., Perkin Trans. 2* **1994**, 2345. (o) Seiler, P.; Isaacs, L.; Diederich, F. *Helv. Chim. Acta* **1996**, *79*, 1047. (p) Musah, R. A.; Jensen, G. M.; Rosenfeld, R. J.; McRee, D. E.; Goodin, D. B.; Bunte, S. W. *J. Am. Chem. Soc.* **1997**, *119*, 9083. (q) Steiner, T.; Desiraju, G. R. *J. Chem. Soc., Chem. Commun.* **1998**, 891. (r) Steiner, T.; Lutz, B.; van der Maas, J.; Schreurs, A. M. M.; Kroon, J.; Tamm, M. *J. Chem. Soc., Chem. Commun.* **1998**, 171. (s) van de Bovenkamp, J.; Matxain, J. M.; van Duijneveldt, F. B.; Steiner, T. *J. Phys. Chem. A* **1999**, *103*, 2784.

(5) See, for example: (a) Reddy, D. S.; Goud, B. S.; Panneerselvam, K.; Desiraju, G. R. *J. Chem. Soc., Chem. Commun.* **1993**, 663. (b) Reddy, D. S.; Craig, D. C.; Desiraju, G. R. *J. Am. Chem. Soc.* **1996**, *118*, 4090. (c) McCarthy, W.; Plokhotnichenko, A. M.; Radchenko, E. D.; Smets, J.; Smith, D. M. A.; Stephanian, S. G.; Adamowicz, L. *J. Phys. Chem. A* **1997**, *101*, 7208. (d) Cotton, F. A.; Daniels, L. M.; Jordan, G. T., IV; Murillo, C. A. *J. Chem. Soc., Chem. Commun.* **1997**, 1673. (e) Thaimattam, R.; Reddy, D. S.; Xue, F.; Mak, T. C. W.; Nangia, A.; Desiraju, G. R. *J. Chem. Soc., Perkin Trans. 2* **1998**, 1783. (f) Kumar, S.; Subramanian, K.; Srinivasan, R.; Rajagopalan, K.; Steiner, T. *J. Mol. Struct.* **1998**, *471*, 251. (g) Mascal, M. *J. Chem. Soc., Chem. Commun.* **1998**, 303. (h) Sigel, R. K. O.; Freisinger, E.; Metzger, S.; Lippert, B. *J. Am. Chem. Soc.* **1998**, *120*, 12000.

(6) See, for example: (a) Aldrich, P. D.; Kukolich, S. G.; Campbell, E. J. *J. Chem. Phys.* **1983**, *78*, 3521. (b) Ohshima, Y.; Matsumoto, Y.; Takami, M.; Kuchitsu, K. *Chem. Phys. Lett.* **1988**, *147*, 1. (c) Prichard, D. G.; Nandi, R. N.; Muenter, J. S. *J. Chem. Phys.* **1988**, *89*, 115. (d) Fraser, G. T.; Suenram, R. D.; Lovas, F. J.; Pine, A. S.; Hougen, J. T.; Lafferty, W. J.; Muenter, J. S. *J. Chem. Phys.* **1988**, *89*, 6028. (e) Nishio, M.; Hirota, M.; *Tetrahedron* **1989**, *45*, 7201. (f) Kobayashi, K.; Asakawa, Y.; Kikuchi, Y.; Toi, H.; Aoyama, Y. *J. Am. Chem. Soc.* **1993**, *115*, 2648. (g) Müller, T.; Mingos, D. M. P.; Williams, D. J. *J. Chem. Soc., Chem. Commun.* **1994**, 1787. (h) Fujimoto, T.; Yanagihara, R.; Kobayashi, K.; Aoyama, Y. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 2113. (i) Steiner, T. *J. Chem. Soc., Chem. Commun.* **1995**, 95. (j) Steiner, T.; Starikov, E. B.; Amado, A. M.; Teixeira-Dias, J. J. C. *J. Chem. Soc., Perkin Trans. 2* **1995**, 1321 (k) Steiner, T.; Tamm, M.; Lutz, B.; van der Mass, J. *J. Chem. Soc., Chem. Commun.* **1996**, 1127. (l) Steiner, T.; Starikov, E. B.; Tamm, M. *J. Chem. Soc., Perkin Trans. 2* **1996**, 67. (m) Steiner, T.; Tamm, M.; Grzegorzewski, A.; Schulte, N.; Veldman, N.; Schreurs, A. M. M.; Kanters, J. A.; Kroon, J.; van der Maas, J.; Lutz, B. *J. Chem. Soc., Perkin Trans. 2* **1996**, 2441. (n) Malone, J. F.; Murray, C. M.; Charlton, M. H.; Docherty R.; Lavery, A. J. *J. Chem. Soc., Faraday Trans.* **1997**, *93*, 3429. (o) Madhavi, N. N. L.; Katz, A. K.; Carell, H. L.; Nangia, A.; Desiraju, G. R. *J. Chem. Soc., Chem. Commun.* **1997**, 1953. (p) Weiss, H.-C.; Bläser, D.; Boesse, R.; Doughan, B. M.; Haley, M. M. *J. Chem. Soc., Chem. Commun.* **1997**, 1703. (q) Lutz, B.; Kanters, J. A.; van der Maas, J.; Kroon, J.; Steiner, T. *J. Mol. Struct.* **1998**, *440*, 81. (r) Ciunik, Z.; Berski, S.; Latajka, Z.; Leszczynski, J. *J. Mol. Struct.* **1998**, *442*, 125.

(7) (a) Novoa, J. J.; Rovira, M. C.; Rovira, C.; Veciana, J.; Tarres, J. *Adv. Mater.* **1995**, *7*, 233. (b) Surange, S. S.; Kumaran, G.; Rajappa, S.; Pal, D.; Chakrabarti, P. *Helv. Chim. Acta* **1997**, *80*, 2329. (c) Ueno, T.; Inohara, M.; Ueyama, N.; Nakamura, A. *Bull. Chem. Soc. Jpn* **1997**, 1077. (d) Pedireddi, V. R.; Chatterjee, S.; Ranganathan, A.; Rao, C. N. R. *J. Am. Chem. Soc.* **1997**, *119*, 10867. (e) Potrzebowski, M. J.; Michalska, M.; Koziol, A. E.; Kazmierski, S.; Lis, T.; Pluskowski, J.; Ciesielski, W. *J. Org. Chem.* **1998**, *63*, 4209. (f) Narayanan, S. J.; Sridevi, B.; Chandrashekar, T. K.; Vij, A.; Roy, R. *Angew. Chem., Int. Ed. Eng.* **1998**, *37*, 3394.

(8) (a) Iwaoka, M.; Tomoda, S. *J. Am. Chem. Soc.* **1994**, *116*, 4463. (b) Iwaoka, M.; Komatsu, H.; Tomoda, S. *Bull. Chem. Soc. Jpn.* **1996**, *69*, 1825.

(9) (a) Legon, A. G.; Aldrich, P. D.; Flygare, W. H. *J. Chem. Phys.* **1981**, *75*, 625. (b) Aakeröy, C. B.; Seddon, K. R. *Z. Naturforsch.* **1996**, *B48*, 1023. (c) James, S. L.; Verspui, G.; Spek, A. L., van Koten, G. *J. Chem. Soc., Chem. Commun.* **1996**, 1309. (d) Weiss, H. C.; Boesse, R.; Smith, H. L.; Haley, M. M.; *J. Chem. Soc., Chem. Commun.* **1997**, 2403. (e) Steiner, T. *J. Mol. Struct.* **1998**, *443*, 149. (f) Aakeröy, C. B.; Evans, T. A.; Seddon, K. R.; Palinko, I. *New J. Chem.* **1999**, *3*, 145.

(10) (a) Mueller-Westerhoff, U. T.; Nazzal, A.; Prössdorf, W. *J. Am. Chem. Soc.* **1981**, *103*, 7678. (b) Mueller-Westerhoff, U. T. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 702. (c) Ahlberg, P.; Davidsson, Ö.; Hilmersson, G.; Löwendahl, M.; Hakansson, M. *J. Chem. Soc., Chem. Commun.* **1994**, 1573. (d) Arduengo, A. J., III; Gamper, S. F.; Tamm, M.; Calabrese, J. C.; Davidson, F.; Craig, H. A. *J. Am. Chem. Soc* **1995**, *117*, 572. (e) Ahlberg, P.; Davidsson, Ö.; Löwendahl, M.; Hilmersson, G.; Karlsson, A.; Hakansson, M. *J. Am. Chem. Soc.* **1997**, *119*, 1745.

(11) (a) Read, W. G.; Flygare, W. H. *J. Chem. Phys.* **1982**, *76*, 2238. (b) Shimoni. L.; Carrell, H. L.; Glusker, J. P.; Coombs, M. M. *J. Am. Chem. Soc.* **1994**, *116*, 8162. (c) Howard, J. A. K.; Hoy, V. J.; O'Hagan, D.; Smith, G. T. *Tetrahedron* **1996**, *52*, 12613. (d) Dunitz, J. D.; Taylor, R. *Chem.−Eur. J.* **1997**, *3*, 89. (e) Grepioni, F.; Cojazzi, G.; Draper, S. M.; Scully, N.; Braga, D. *Organometallics* **1998**, *17*, 296.

(12) Fraser, G. T.; Leopold, K. R.; Klemperer, W. *J. Chem. Phys.* **1984**, *80*, 1423.

(13) Frisch, M. J.; Pople, J. A.; Del Bene, J. E. *J. Chem. Phys.* **1983**. *78*, 4063.

(14) Fraser, G. T.; Nelson, D. D., Jr.; Charo, A.; Klemperer, W. *J. Chem. Phys.* **1985**, *82*, 2535.

(15) Hilpert, G.; Fraser, G. T.; Pine, A. S. *J. Chem. Phys.* **1996**, *105*, 6183.

(16) Schulz, B.; Botschwina, P. *Chem. Phys. Lett*. **1995**, *243*, 378.

(17) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986.

(18) Parr, R. G.; Yang, W. *Density Functional Theory of Atoms and Molecules*; Oxford University Press: New York, 1989.

(19) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *GAUSSIAN 94*, revision E.2; Gaussian, Inc.: Pittsburgh, PA, 1995.

(20) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *GAUSSIAN 98*, revision A.6; Gaussian, Inc.: Pittsburgh, PA, 1998.

(21) (a) Stanton, J. F.; Gauss, J.; Watts, J. D.; Lauderdale, W. J.; Bartlett, R. J. *ACES II. Quantum Theory Project*; Departments of Chemistry and Physics, University of Florida: Gainsville, 1992. (b) Stanton, J. F.; Gauss, J.; Watts, J. D.; Lauderdale, W. J.; Bartlett, R. J. *Int J. Quantum Chem. Symp.* **1992**, *26*, 879.

(22) MOLPRO 97 is a package of ab initio programs written by H.-J. Werner and P. J. Knowles with contributions from J. Almlof, R. D. Amos, A. Berning, D. L. Cooper, M. J. O. Deegan, A. J. Dobbyn, F. Eckert, S. T. Elbert, C. Hampel, R. Lindh, W. A. Lloyd, W. Meyer, A. Nickless, K. Peterson, R. Pitzer, A. J. Stone, P. R. Taylor, M. E. Mura, P. Pulay, M. Schütz, H. Stoll, and T. Thorsteinsson.

(23) Boys, S. F.; Bernardi, F. *Mol. Phys.* **1970**, 553.

(24) See, for example: (a) Grev, R. S.; Janssen, C. L.; Schaefer, H. F., III *J. Chem. Phys.* **1991**, *95*, 5128. (b) Pople, J. A.; Scott, A. P.; Wong, M. W.; Radom, L. *Isr. J. Chem.* **1993**, *33*, 345. (c) Scott, A. P.; Radom, L. *J. Phys. Chem.* **1996**, *100*, 16502.

(25) Experimental ZPVEs were calculated from harmonic vibrational frequencies ω_r and vibrational anharmonic constants χ_{rs} for acetylene and ammonia. The formalism used is described in ref 24a. (a) $\mathrm{ZPVE}^{\mathrm{exp}}_{\mathrm{HCCH}} = 68.86$ kJ mol^{-1} from: Strey, G.; Mills, I. M. *J. Mol. Spectrosc.* **1976**, *59*, 103. (b) $\mathrm{ZPVE}^{\mathrm{exp}}_{\mathrm{NH_3}} = 88.94$ kJ mol^{-1} from: Hoy, A. R.; Molls, I. M.; Strey, G. *Mol. Phys.* **1972**, *24*, 1265.

(26) (a) Harmony, M. D.; Laurie, V. W.; Kuczkowski, R. L.; Schwendeman, R. H.; Ramsay, D. A.; Lovas, F. J.; Lafferty, W. J.; Maki, A. G. *J. Phys. Chem. Ref. Data* **1979**, *8*, 619. (b) Chase, M. W., Jr.; Davies, C. A.; Downey, J. R., Jr.; Frurio, D. J.; McDonald, R. A.; Syverud, A. N. *J. Phys. Chem. Ref. Data* **1985**, *14* (Suppl. 1), 660 and 1293.

(27) A T-shaped dimer (C_{2v} symmetry) with ammonia acting as a proton donor and involving an N−H···π rather than a C−H···N contact was found to be a first-order saddle point at the B3-LYP/6-311+G(3df,2p) level. This dimer is calculated at this level to be less stable than the hydrogen bonded dimer discussed in the text by 11.1 kJ mol^{-1}. The distance between the binding hydrogen of ammonia and the midpoint of the triple bond is 2.938 Å.

(28) For the sake of completeness, we also examined the performance of the CCSD method at a representative level (viz. CCSD/6-311+G(2df,p)). We find that structural parameters obtained at this level are very similar to those of the corresponding QCISD calculations, with differences of up to 0.001 Å for intramolecular parameters and 0.022 Å for the intermolecular contact distance. The calculated equilibrium binding energy (including BSSE) at this level is $\Delta E_e = 12.4$ kJ mol^{-1} compared with the corresponding QCISD/6-311+G(2df,p) value of 12.9 kJ mol^{-1}.

(29) A relaxed potential energy surface scan at the B3-LYP/6-311+G-(3df,2p) level showed that a lengthening/contraction of the equilibrium H···N contact distance by ±0.1 Å results in changes in the total energy of 0.2 kJ mol^{-1} and 0.3 kJ mol^{-1}, respectively.