A THEORETICAL STUDY ON ACETYLENE DIMER, ACETYLENE–
–s-TETRAZINE AND ACETYLENE–BENZENE ASSOCIATES

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Dedicated to the memory of Dr Karel Bláha.

Stabilization energies for the title van der Waals molecules were calculated for various mutual orientations of the subsystems. The interaction energy was expressed as a sum of three contributions: the Hartree Fock interaction energy, the basis set superposition error and the dispersion energy. The potential energy minima represent reasonably good estimates of the structures of the van der Waals molecules.

The huge realm of van der Waals species includes systems ranging from very weak complexes, such as $(He)_2$ and $(H_2)_2$ to relatively strong hydrogen-bonded complexes, e.g. $(HF)_2$ and $(H_2O)_2$. The associates studied here are more stable than the majority of van der Waals (vdW) associates between organic molecules but do not attain the relatively high stabilization energies of strong hydrogen-bonded complexes. The title van der Waals species consist of Brönsted (or Lewis) acids and bases. Although chemically attractive and tempting candidates for reactivity studies in molecular beams, they have been studied rather rarely.
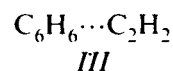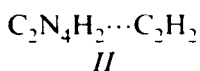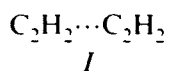
Some attention was recently paid to the acetylene dimer, the acetylene s-tetrazine complex and related systems[1,9]. The electrostatic energy was calculated using the Buckingham–Fowler model and the minima were located for complexes of s-tetrazine with HCl, H_2O, C_2H_2, benzene and s-tetrazine and for benzene with C_2H_2, benzene, anthracene and perylene[1]. The electronic spectra of complexes of s-tetrazine with H_2O and HCl were observed in a supersonic free jet. The geometries of these complexes have been determined from the rotational structures of the spectra[2,3].

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A simple model for computation of intermolecular interactions has been employed for hydrogen-bonded dimers[4] of such molecules as C_2H_2, HF, HCl, HCN. Geometries have been estimated from microwave spectra for complexes of acetylene with HF, HCl, and HCN using a pulsed Fourier transform microwave spectrometer, employing a Fabry–Perot cavity[5-7]. The infrared spectra of the acetylene dimer have been measured using a supersonic free jet[8].

The benzene–acetylene complex was formed in a supersonic molecular beam and its spectrum was recorded using multiphoton ionization spectroscopy[9].

The purpose of this work is to localize the stationary points on the potential energy surfaces of the acetylene dimer (*I*) and the *s*-tetrazine–acetylene (*II*) and benzene–acetylene (*III*) complexes. The localization is performed with geometrical constraints resulting from the symmetry of selected shapes of the vdW associates. Estimates of the structure and stabilization energy of van der Waals species *I – III* are obtained.

$$C_2H_2 \cdots C_2H_2 \qquad\qquad C_2N_4H_2 \cdots C_2H_2 \qquad\qquad C_6H_6 \cdots C_2H_2$$
$$\textit{I} \qquad\qquad\qquad\qquad \textit{II} \qquad\qquad\qquad\qquad \textit{III}$$

CALCULATION

It has been convincingly demonstrated that the interaction energies of small and medium-size vdW molecules can be evaluated using the expression

$$\Delta E = \Delta E^{SCF} + \Delta E^{COR},\qquad\qquad (1)$$

where ΔE describes the energy of formation of the vdW molecule $R \cdots T$ (Eq.(2))

$$R + T \rightarrow R \cdots T, \quad \Delta E.\qquad\qquad (2)$$

Energy changes ΔE^{SCF} and ΔE^{COR} are the Hartree–Fock interaction energy and the correlation interaction energy, respectively. For reliable estimates of the equilibrium geometry and interaction energy of the systems under study, the following simplifications of the terms of Eq. (1) were used: ΔE^{SCF} was calculated at the SCF level with a minimal basis set MINI-1 by Huzinaga[10] and the basis set superposition error (BSSE) was estimated by the function counterpoise method[11]. The other energy term, ΔE^{COR}, was approximated by the London dispersion energy (E^D) evaluated according to two different empirical expressions. Finally, Eq. (1) assumes the form

$$\Delta E = \Delta E^{SCF} \text{(MINI-1)} + \Delta E\text{(BSSE)} + E^D.\qquad\qquad (3)$$

The dispersion energy was calculated by means of the London expression employing either the experimental atomic polarizabilities and ionization potentials in the respective valence state[12] or the experimental bond polarizabilities and molecular ionization potentials[13-15]. The first expression using the atomic polarizabilities gives surprisingly good estimates of the dispersion energy[12]. However, the method cannot yield a proper estimate of the anisotropy of the dispersion energy

because of the isotropy of the atomic polarizabilities. The anisotropy is especially important for complexes *II* and *III*. We have therefore used a second expression for the London dispersion energy including the bond polarizabilities[13]. The expression was extended[14] by taking the vertical component of the bond polarizability into consideration. The following values of the longitudinal, transversal, and vertical bond polarizabilities (in 10^{-23} cm^3) were taken from ref.[15]: C—H ($0 \cdot 064$, $0 \cdot 064$, $0 \cdot 064$), (C—C)$_{ar}$ ($0 \cdot 224$, $0 \cdot 021$, $0 \cdot 059$). C≡C ($0 \cdot 350$, $0 \cdot 130$, $0 \cdot 130$), (N—C)$_{ar}$ ($0 \cdot 224$, $0 \cdot 021$, $0 \cdot 059$), N=N ($0 \cdot 280$, $0 \cdot 100$, $0 \cdot 080$). The subsystem geometry, determined experimentally[16], was kept rigid during supersystem geometry variation. The subsystem SCF (MINI-1) energies are as follows: C$_2$H$_2$ ($-76 \cdot 234482$ a.u.); C$_6$H$_6$ ($-228 \cdot 954743$ a.u.); *s*-C$_2$N$_4$H$_2$ ($-292 \cdot 370362$ a.u.). The geometries of all the supersystems were varied step by step (with step size of 10 pm) along a selected path keeping the shape of the associate fixed.

RESULTS AND DISCUSSION

We have studied four, seven, and two mutual orientations of the subsystems in complexes *I*, *II* and *III* respectively (Scheme 1). The total interaction energies (Eq. (*3*)) were calculated for several points per structure (Figs 1 and 2). Table I gives the characteristics of the individual systems, possessing energy minima with the largest stabilization energies.
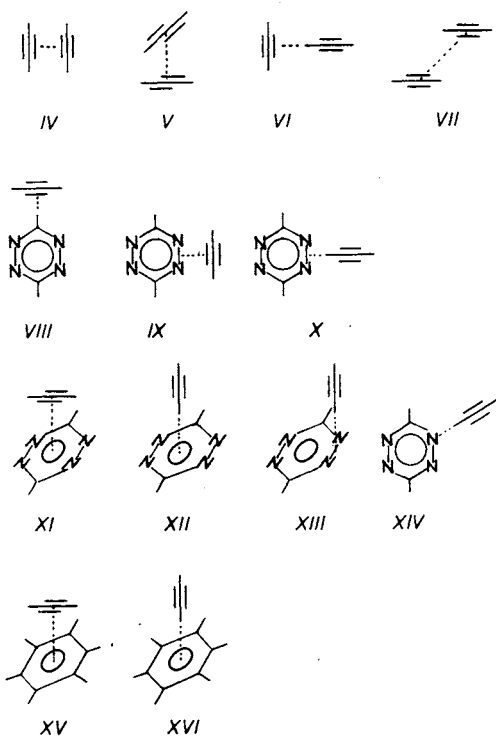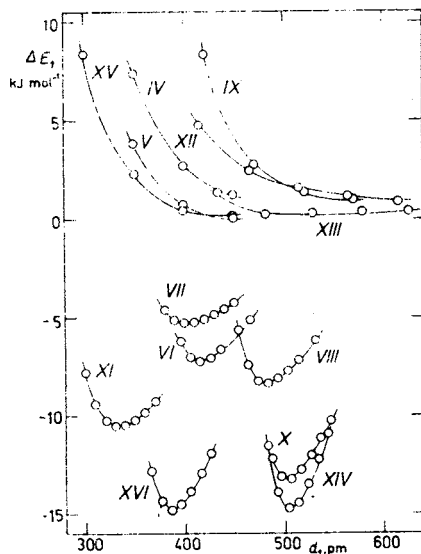

SCHEME 1

FIG. 1
Dependence of the total interaction energy (dispersion energy calculated by the atom–atom approach) on the distances between the subsystem centers. The curve numbers correspond to the different structures of complexes *I*, *II* and *III*
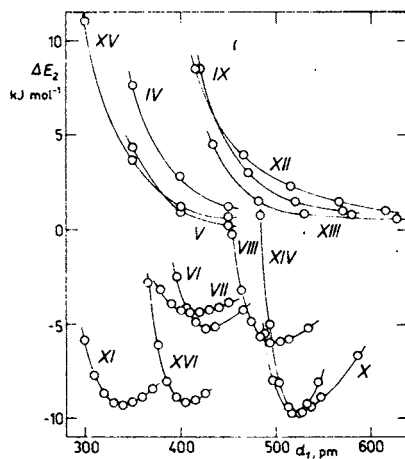

FIG. 2
Dependence of the total interaction energy (dispersion energy calculated by the bond–bond approach) on the distances between the subsystem centers. The curve numbers correspond to the different structures of complexes *I*, *II* and *III*

The Acetylene Dimer

Acetylene is a relatively strong C-acid and moderate π-base. Mutual approach of the π-electronic clouds, centers of π-basicity, is connected with rather strong repulsion (structures *IV* and *V*). On the other hand, approach of the acidic acetylene hydrogen to the triple bond of the partner is connected with a significant energy decrease. Note, however, that the stabilization energy amounts to only about 20 – 25 % of the formation energy of a typical hydrogen-bond.

The SCF interaction energy for structures *IV* and *V* is repulsive, whereas for *VI* and *VII* it is slightly attractive, partially due to the quadrupole–quadrupole interaction. The dispersion energy is largest for the T-shape structure *VI*. A minimum of the total interaction energy was found only for structures *VI* and *VII*.

TABLE I

Interaction energies, components thereof (in kJ/mol), and subsystem distances (in pm)

System	d_1 [a]	d_2 [b]	ΔE^{SCF}	BSSE	E_1^{D} [c]	E_2^{D} [d]	ΔE_1 [e]	ΔE_2 [f]
VI	416	250	−3.76	1.74	−5.17		−7.19	
	426	260	−4.10	1.33		−2.43		−5.20
VII	400	400	−1.87	1.04	−4.44		−5.27	
	410	410	−2.31	0.84		−2.91		−4.38
VIII	484	250	−4.25	1.80	−5.90		−8.35	
	494	260	−4.61	1.40		−2.75		−5.96
X	507	220	−6.81	1.98	−8.39		−13.22	
	517	230	−7.40	1.45		−3.78		−9.73
XI	330	330	−4.14	2.68	−9.07		−10.53	
	340	340	−4.75	2.06		−6.60		−9.29
XIV	504	200	−6.73	3.35	−11.34		−14.72	
	524	220	−8.49	2.20		−3.40		−9.69
XVI	386	220	−4.96	4.39	−14.22		−14.79	
	406	240	−6.09	2.44		−5.49		−9.14

[a] Distance between subsystem centers. [b] Distance between the nearest atoms belonging to different subsystems. [c] Dispersion energy calculated by the atom–atom approach. [d] Dispersion energy calculated by the bond–bond approach. [e] Total interaction energy calculated on the basis of E_1^{D}. [f] Total interaction energy on the basis of E_2^{D}.

Obviously, both acetylene molecules can act as acids as well as bases. Therefore, two equivalent isomers exist, *VIa* and *VIb*:

VIa   *VIb*
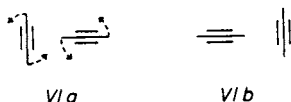
These potential energy minima must be separated by a saddle point. It is possible to pass from *VIa* to *VIb* by rotation of the subsystems as indicated in *VIa*. The structure of the activated complex is, approximately speaking, that ascertained for stationary point *VII* possessing C_{2h} symmetry. There is a remarkable similarity between the structures and relative energies of the acetylene dimer and of the recently studied $(H_2)_2$ dimer[17]. The established stationary points on the $(H_2)_2$ potential energy surface, *XVII — XIX* are structurally similar to *VIa*, *VIb*, and *VII*.

XVII   *XVIII*   *XIX*

The Acetylene–s-Tetrazine Associate

Once again, both partners possess acidic as well as basic centers. Both are relatively strong C-acids; *s*-tetrazine is, in principle, a π-base as well as an *n*-base. However, the calculations convincingly demonstrate that its π-basicity is weak. No minimum was found for the approach of the subsystems indicated in formula *XII* (cf. the opposite situation with benzene, formula *XVI*, vide infra). There is also no minimum along the path representing the type of approach in formulae *IX* and *XIII*. The in-plane approach, *X*, is, in contrast, bonding. This can be ascribed to the fact that, in the respective area, the basic centers are the nitrogen *n*-pairs, rather than the N=N double bond.

As to the lack of π-basicity of *s*-tetrazine, there is an additional piece of evidence to that one mentioned above, namely the stability of structure *XI*. An analogous structure involving benzene, *XV*, is entirely repulsive. The *n*-basicity of *s*-tetrazine, as measured by its interaction with acetylene, is rather high; the stabilization energy for *XIV* amounts to 14·72 kJ/mol.

It is useful to note that acetylene and *s*-tetrazine are C-acids of comparable strength (structures *VI* and *VIII*): their interaction with the same base, with

acetylene, is connected with a similar interaction energy ($-7 \cdot 19$ kJ/mol for *VI* and $-8 \cdot 35$ kJ/mol for *VIII*).

The Acetylene–Benzene Associate

Several features of this associate are mentioned in the previous paragraph. Benzene behaves as a typical moderately strong π-base. A minimum was found for structure *XVI* but not for *XV*. The dispersion term constitutes the main contribution to the stabilization.

Common Features of the Complexes

The atom–atom approach for the evaluation of the dispersion energy gives, in general, rather reliable energy values[12]. The bond–bond approach is known to underestimate the actual dispersion energy by about 50% (ref.[18]). On the other hand, this approach correctly describes the anisotropy of the dispersion energy. We have tried to find an empirical factor for converting the bond–bond dispersion energy values into the atom–atom ones. For structures *IV*, *V*, *IX*, *XI* and *XV* the dispersion energy evaluated by the two approaches differs by less than 20%. For the remaining structures, this difference is, however, much larger. It is therefore impossible to find a simple relationship between the two approaches.

The anisotropy of the dispersion energy of the *s*-tetrazine–acetylene complex can be studied. The bond–bond approach gives a ratio of $2 \cdot 4$ between the dispersion energy of the most favourable and least favourable structures. The ratio found by the atom–atom approach ($1 \cdot 9$) differs slightly. The bond–bond approach gives the largest dispersion energy for structure *XI*, whereas the atom–atom approach yields the largest values for structures *XIV*. The anisotropy of the SCF interaction energy is, as expected, larger than that of the dispersion energy.

The largest stabilization energy if the atom–atom dispersion energy is considered was found for the benzene–acetylene complex *XVI* and the *s*-tetrazine–acetylene complex *XIV*, followed by the *s*-tetrazine–acetylene complexes *X* and *XI*. The dispersion energy is almost completely responsible for the stabilization of complexes *XVI* and *XI*.

The stabilization energies for the *s*-tetrazine–acetylene complexes *X*, *XI* and *XIV* and benzene–acetylene complex *XVI* are comparable if the bond–bond dispersion energy is considered. The ΔE^{SCF} term is dominant for structure *X*; for structures *XI* and *XVI* the dispersion energy is largest.

It can be concluded that, for the complexes studied, all the contributions to the total interaction energy, ΔE^{SCF}, $\Delta E(BSSE)$, and E^D, are important and

that none of them should be neglected. The dispersion energy is the dominant term when using the more reliable atom–atom formula. This term also includes the part of the anisotropy of the dispersion energy which is due to the anisotropy in the spatial distribution of the atoms.

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