BINDING ENERGIES OF ORGANIC CHARGE-TRANSFER COMPLEXES CALCULATED BY FIRST-PRINCIPLES METHODS

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Weak interactions between organic donor and acceptor molecules resulting in cofacially-stacked aggregates ("CT complexes") were studied by second-order many-body perturbation theory (MP2) and by gradient-corrected hybrid Hartree–Fock/density functional theory (B3LYP exchange-correlation functional). The complexes consist of tetrathiafulvalene (TTF) and related compounds and tetracyanoethylene (TCNE). Density functional theory (DFT) and MP2 molecular equilibrium geometries of the component structures are calculated by means of 6-31G*, 6-31G*(0.25), 6-31++G**, 6-31++G(3df,2p) and 6-311G** basis sets. Reliable molecular geometries are obtained for the donor and acceptor compounds considered. The geometries of the compounds were kept frozen in optimizing aggregate structures with respect to the intermolecular distance. The basis set superposition error (BSSE) was considered (counterpoise correction). According to the DFT and MP2 calculations laterally-displaced stacks are more stable than vertical stacks. The charge transfer from the donor to the acceptor is small in the ground state of the isolated complexes. The cp-corrected binding energies of TTF/TCNE amount to –1.7 and –6.3 kcal/mol at the DFT(B3LYP) and MP2(frozen) level of theory, respectively (6-31G* basis set). Larger binding energies were obtained by Hobza's 6-31G*(0.25) basis set. The larger MP2 binding energies suggest that the dispersion energy is underestimated or not considered by the B3LYP functional. The energy increases when S in TTF/TCNE is replaced by O or NH but decreases with substitution by Se. The charge-transferred complexes in the triplet state are favored in the vertical arrangement. Self-consistent-reaction-field (SCRF) calculations predicted a gain in binding energy with solvation for the ground-state complex. The ground-state charge transfer between the components is increased up to 0.8 e in polar solvents.

Key words: Charge-transfer complexes; Donor compounds; Acceptor compounds; Donor–acceptor interaction; Face-to-face stacking; *Ab initio* calculations; Quantum chemistry; Density functional theory; Solvent effect; Self-consistent reaction field.

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One of the great merits of Rudolf Zahradnik was the development and dissemination of basic concepts in applied quantum chemistry. The study of the weak noncovalent interaction was one of the fields of his long-standing interest and engagement. Excellent reviews written by Hobza and Zahradnik[1] have received wide attention and had a large stimulating effect. Weak intermolecular interaction is of utmost importance in molecular aggregation and in formation of supramolecular structures. Knowledge about weak intermolecular forces is the *sine qua non* for molecular modeling of complex structures, such as nowadays practised by methods of molecular mechanics[2].

Semiempirical quantum chemical calculations of weakly-interacting conjugated compounds aligned in the face-to-face fashion more or less failed. CNDO and INDO calculations strongly overestimate binding energies concomitant with very short interplanar distances[3]. By contrast, MNDO and AM1 binding energies are small or absent[4]. Thus, the additional estimation of the van der Waals energy was recommended (*e.g.* MNDO/D-method[4b]). At levels of *ab initio* theory, van der Waals interaction (dispersion energy) is only considered at the beyond-Hartree–Fock level. In basic investigations various dimers of benzene were studied at high levels of *ab initio* theory[5,6] and compared with experimental binding energies available from gas-phase experiments. The theoretical studies resulted in definite weakly-interacting π-stacked pairs. After consideration of the basis set superposition error (BSSE) the parallely-displaced dimer of benzene was found to be slightly favored over the parallel and T-shaped dimers[6]. Face-to-face stacking plays an important role in aggregation of nucleic bases of DNA (ref.[7]). Another basic type of π-stacks consists of donor and acceptor molecules (EDA complexes). The formation of such complexes plays an essential role in the recently studied self-assembling of supramolecular structures such as of host–guest complexes, catenanes, rotaxanes, webs and mosaics[8].

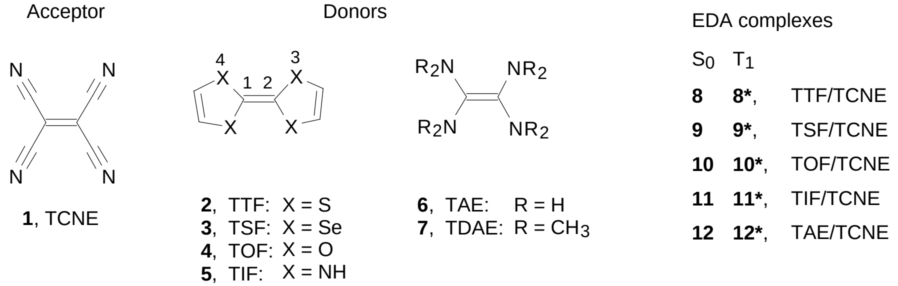
EDA complexes of π-stacked molecules are mostly colored[9]. The long wavelength absorption is due to a low-energy donor-to-acceptor charge-transfer (CT) transition. While the charge transfer is generally low in the ground state, the charge transfer is large in the excited state of the complex[10]. Weak ground state and large excited state charge transfer favor deep colors. Former semiempirical calculations of EDA complexes were mostly directed to spectral absorption[9]. Charge transfer in the ground state between the two interacting molecules stabilizes the ground state relative to the lowest-energy excited state. "Charge-transfer forces" therefore have been invoked to explain the donor–acceptor complex in the molecular ground state. This type of intermolecular interaction may be understood in terms of orbital overlap estimated by second-order perturbation theory or, more qualitatively, by frontier orbital considerations. According to this approach, the orientation of the components is favored where the overlap of occupied donor orbital and the vacant acceptor orbital is maximal[11]. Electron delocalization because of orbital overlap in the dimer will be associated with migration of electron charge from the donor to the acceptor component in the molecular ground state.

The amount of electrons transferred should be an indicator of the extent of electron delocalization in the complex. This model corresponds to an overlap-controlled stabilization. Another model rather refers to the intermolecular interaction of charges of the components (charge-controlled intermolecular interaction). Hunter *et al.*[12] developed an electrostatic model in terms of σπ-attractive and ππ-repulsive interactions. Detailed charge distribution analyses were carried out for donor and acceptor molecules[13]. In addition, electrostatic potentials were calculated. A more complete analysis of energy contributions has to consider the polarization (induction) term in addition to the above mentioned dispersion, charge transfer and electrostatic terms[1].

Face-to-face π-stacking of proper donor and acceptor molecules has became of particular interest in search of organic conductors and superconductors[16]. Interesting cases for application are separate columnar stacks of donor and acceptor molecules (segregated stacks) with a half-electron charge transfer on the average. As known from numerous X-ray analyses, the molecules in EDA complexes are stacked face-to-face and spaced by about 3.5 Å. An alternative stacking pattern is the formation of mixed stacks that consist of an alternate arrangement of donor and acceptor molecules in columnar arrays.

Whereas numerous studies[15] on donors and acceptors by first-principles methods are known, calculations of face-to-face stacked EDA complexes are rare at this level of theory. An early study was done by Clementi *et al.*[16] who calculated the tetrathiafulvalene/tetracyanoquinodimethane (TTF/TCNQ) complex at the restricted-Hartree–Fock (RHF) *ab initio* level using a minimal basis set. The calculation of the complex resulted in a net stabilization with an intermolecular distance of 3.7 Å. The binding energy, however, was not corrected for BSSE. Equilibrium intermolecular distances of EDA complexes of tetracyanoethylene (TCNE) with various aromatic donors, such as benzene[17,18] and hexamethylbenzene[19], were optimized at the RHF/3-21G or 6-31G* level of theory. Because of the neglect of electron correlation, RHF binding energies are in error. On the other hand, post-RHF calculations of larger molecules such as stacks of conjugated compounds are expensive or cannot be performed at present. In view of these limitations, the density functional theory[20] (DFT) appeared as a promising alternative, for electron correlation is included inherently in this approach. According to recent DFT calculations, however, the dispersion energy contribution is not considered in the functionals available at present[5,21]. Thus binding energies are expected to be too low. Unexpectedly, the calculated DFT binding energy is larger than expected in ethylene/halogen CT complexes[22]. These CT complexes, however, differ completely in structure from CT complexes considered in this study. The components are perpendicularly-aligned rather than coplanarly-stacked. A comparative three-dimensional Hartree–Fock crystal orbital study of coplanar double stack EDA complexes have been recently performed to estimate the degree of charge transfer in the crystal[23].

This study aims at the calculation of structure and binding energies of some representative face-to-face stacked EDA complexes at the MP2 and DFT(B3LYP) level of theory. Tetracyanoethylene (TCNE, **1**) as an acceptor component and tetrathiafulvalene (TTF, **2**) as a donor component are calculated in more detail. The donors and the acceptor are assembled in Scheme 1. To reveal structure–property relationships, a series of heteroanalogous donor compounds are considered with the sulfur atoms in **2** replaced by selenium ("tetraselenafulvalene", TSF, **3**), by oxygen ("tetraoxafulvalene", TOF, **4**), or by the NH group ("tetraiminofulvalene", TIF, **5**). The X-ray structure of the donors of **2** and **3** is known experimentally. They encounter in various EDA complexes[24] with acceptors such as TCNE (ref.[25]) and tetracyanoquinodimethane[26,27] (TCNQ). The study also includes the ring-open donor compound tetraaminoethylene (TAE, **6**), which may be considered as the parent structure of the experimentally known tetrakis(dimethylamino)ethylene (TDAE, **7**) (*cf.* Scheme 1). The latter compound also forms EDA complexes, *e.g.* with buckminsterfullerene[28].



SCHEME 1

Since the potential energy surfaces of EDA complexes are flat, the search for minima is a nontrivial and very expensive task. Therefore, the calculated equilibrium geometries of the components are fixed and intermolecular distances were only optimized for selected orientations. The complexes considered are coplanar with the molecular principal rotation axes of the components either coincident or displaced parallel. The resulting vertically-stacked or laterally-displaced stacks considered are shown in Fig. 1.

In contrast to the EDA complexes in the composite molecule ground state, dipolar (charge-transferred) EDA complexes may be generated in the lowest-energy excited state with a predominantly cationic donor and an anionic acceptor component. In order to confirm this expectation, some triplet complexes were calculated as well. Triplet complexes are distinguished from singlet complexes by "*" in this paper. The calculations of the complexes **8*** to **12*** are performed with radical anion **1**$^-$ and radical cation **2**$^+$–**6**$^+$ component structures.

COMPUTATIONAL

The compounds were investigated by density functional theory (DFT) and by conventional *ab initio* quantum theory using the GAUSSIAN-94 set of codes[29]. The *ab initio* calculations were performed at the beyond-Hartree–Fock level[30] using the second-order perturbation method MP2. The DFT calculations were performed with the gradient-corrected (non-local) HF-hybrid functional B3LYP (Becke's three-parameter Lee–Yang–Parr functional)[31]. The superposition error of the calculated binding energy was estimated by using the Boys–Bernardi counterpoise method[32].

Geometries of the components of the complexes were fully optimized while distances between the components were optimized only in the complex. Structures of components and complexes, intermolecular distances and binding energies were investigated with different basis sets. The split-valence basis set 6-31G was augmented by a set of d-polarization functions at the non-hydrogen atoms (6-31G(d) = 6-31G*). This basis set is well-approved in calculating ground-state geometries of the component molecules. In order to improve intermolecular interaction by DFT, up to two sets of diffuse functions were added as well as basis functions with higher angular momentum. As shown by Hobza *et al.*[33] in studies of the H-bonded DNA base pairs, the estimation of binding energies is improved when d-exponents of first-row elements are reduced from 0.8 (GAUSSIAN-94 default value) to 0.25. Therefore, MP2 and DFT calculations were also performed with 6-31G*(0.25) basis sets where the exponent 0.25 was taken for all non-hydrogen atoms. In all calculations, the calculated B3LYP/6-31G* and MP2/6-31G* geometries were kept frozen and the intermolecular distances in the complexes were only optimized by DFT/6-31G*(0.25) and MP2/6-31G*(0.25).

EDA complexes in the triplet excited state were calculated using the unrestricted Kohn–Sham (UKS) DFT and the unrestricted second-order perturbation theory (UMP2). Singlet/triplet (S_0/T_1) splitting energies are calculated from the total energies of singlet and triplet molecules at optimized intermolecular distances.

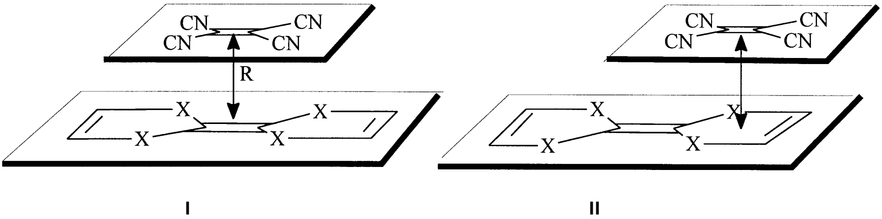


FIG. 1
Vertically-stacked (**I**) and laterally-displaced (**II**) arrangements of the aggregates **8** to **11**

Understanding of the electron structure of the molecules may benefit from such quantities as atomic charges and bond orders. Because of the extended basis sets used, atomic charges were calculated by the Weinhold's natural population analysis[34] (NPA) in addition to the Mulliken population analysis. Natural populations correspond to occupancies of the orthogonal atomic natural orbitals. Natural bond orbitals, *i.e.* localized orbitals or two-center orbitals, are than computed therefrom. The natural bond orbital (NBO) theory provides natural atomic charges. The NBO analysis also provides stabilization energies by second-order perturbative interaction between the occupied natural orbitals Y of the donor component of the complex and the acceptor natural antibonding bond orbital of the acceptor component. This interaction corresponds to a correction of the zero-order natural reference Lewis structure by additional structures where an electron pair is transferred from the donor to the acceptor. The second-order stabilization energy $E(2)$ associated with the electron delocalization is given by Eq. (*1*):

$$E(2) = 2(\langle n_\mathrm{Y} |\hat{F}| \sigma^*_{\mathrm{X-H}}\rangle)^2/(\varepsilon_j - \varepsilon_i)\,, \qquad (1)$$

where the nominator is the interaction term of the corresponding Fock operator $\hat{F}$ and the denominator the difference of the orbital energies ε_i and ε_j of the natural orbitals involved in the orbital overlap. The computations were carried out by the NBO 4.0 program[35] which was implemented into GAUSSIAN-94.

In the case of the DFT calculations the analysis was directly performed by the density matrix of SCF converged Kohn–Sham orbitals. The relaxed density matrix was taken to calculate MP2 atomic charges. The bulk solvent effect is modeled by means of the dielectric continuum. The solute is placed in a cavity which is surrounded by a solvent continuum characterized by the dielectric constant ε. The electronic distribution of the solute polarizes the continuum and generates an electrical field inside the cavity which in turn affects the electronic structure of the solute. Tomasi's self-consistent-reaction-field (SCRF) method was employed as described in ref.[36].

RESULTS AND DISCUSSION

The Components of the Complexes

The neutral acceptor, donor compounds, and the charged radical derivatives were optimized by DFT and *ab initio* calculations. TCNE (**1**) is a planar molecule of D_{2h}-symmetry[37,38]. The lower total energy of radical anion $\mathbf{1}^-$ relative to the neutral compound indicates the large electron affinity (A) of **1**. TCNE has the experimental adiabatic electron affinity of 3.17 eV (ref.[39]) and belongs to the strong electron acceptors known. As shown in the Table I, the theoretical adiabatic electron affinity calculated by DFT ranges from 3.10 to 3.51 eV and increases with extension of the basis set. Thus, the calculated values are in good agreement with the experimental one. The electron affinity values calculated by MP2 are too low.

The tetrachalcogenofulvalenes **2** to **4** were hold planar and the calculations resulted in D_{2h}-symmetry. The structural parameters are in good agreement with those of X-ray structures[26,40,41]. As shown recently[15a], TTF (**2**) and TSF (**3**), however, are slightly bent out of the plane with a very low barrier to inversion (0.5 kcal/mol). This peculiarity was disregarded in this study. Compound **4** is not yet known[24]. TIF (**5**) is a slightly puckered molecule. The NH group is pyramidal rather than planar (angle of pyramidalization of about 134 degrees). There is also a slight distortion around the central C=C bond (2.9 degrees). The corresponding angles of pyramidalization and torsion of the radical cations $\mathbf{5}^+$ are 162 and 13.7 degrees, respectively (DFT/6-31G*). The DFT geometry is close to that of MP2. A strong lengthening of the double bond between the carbon atoms and a strong shortening of carbon–nitrogen bonds is calculated upon ionization of **5**.

Compound **7** is a stronger donor than the tetrachalcogenofulvalenes. This compound has been investigated experimentally and theoretically by several research groups[28a,42]. To reduce the computational expenditure in calculating the complexes, the methyl groups of **7** were replaced by hydrogen atoms (Scheme 1). Geometry optimization of **6** resulted in a molecule of C_2-symmetry. The calculated geometric parameters of **6** obtained by DFT and MP2 agree satisfactorily well with the experimental structure of **7**

TABLE I
Electron affinities (*A*) of TCNE (**1**) and vertical and adiabatic ionization energies (*I*) of TTF (**2**) and the heteroanalogues **3** to **5** and TAE (**6**)[a]

Method	Basis set	*A*, eV	I_{vert} (I_{ad}), eV				
		1	**2**	**3**	**4**	**5**	**6**
DFT	6-31G*	3.10	6.29 (6.18)	6.31 (6.14)	6.27 (6.05)	5.14 (4.50)	6.97 (5.53)
	6-31++G**	3.51	6.44 (6.33)	6.39 (6.31)	6.55 (6.35)	5.38 (4.80)	7.23 (5.83)
	6-311G**	3.32	6.43 (6.32)	6.55 (6.38)	6.48 (6.25)	5.32 (4.86)	7.13 (5.69)
MP2	6-31G*	1.35	5.87	6.02	5.98	4.89	6.98
Experiment		3.17[b] 2.3[c]	6.83[b] 6.92[e] (6.4)[e]	7.21[d] 6.90[e] (6.68)[e]	–	6.14[f] (5.41)[f]	6.13[g]

[a] Extended version of the table with total energies, zero-point energies, and selected geometrical parameters for neutral compounds and radical ions is available from the authors on request. [b] Ref.[39a,b]. [c] Ref.[39c]. [d] Ref.[45]. [e] Ref.[46]. [f] Ref.[44]. [g] Ref.[42a,b].

(*cf.* ref.[42]). The compound **6** exhibits, in turn, some torsion around the central C=C bond. It has a dipole moment of about 1.7 D (DFT/6-31G*). In the radical cation $\mathbf{6}^+$ the central carbon–carbon bond is a single rather than a double bond whereas the carbon–nitrogen bonds are shortened.

In the CT complexes considered in this study strong electron acceptor compounds are combined with strong electron donor compounds. The donor strengths is reflected in the first ionization energy (I) of the donor. Based on the DFT total energies of the neutral molecules and the corresponding cations, the first adiabatic ionization energies of the series **2** to **6** were calculated by the energy difference method. Vertical I_{vert} were also calculated by DFT and MP2 with frozen geometries, *i.e.* the cations were unrelaxed. Since electron ejection corresponds to Frank–Condon transitions[43] the vertical rather than adiabatic ionization energies should be compared with experimental values measured by mass spectrometry or photoelectron spectroscopy. In agreement with the experiment[42,44–46], the calculated ionizaton energies of the heterofulvalenes increase in the order N < S ≈ Se (*cf.* Table I). As shown in Table I, ionization energy increases with the extension of the basis set. The ionization energies of ring-closed donors **2** to **5** are underestimated. Compound **5** should most easily form the radical cation. Its ionization energy is nearly that of alkali metals. The first ionization energy of the unknown compound **4** is predicted in the magnitude of the ionization energies of **2** and **3**. The calculated DFT ionization energy of **6** is overestimated by about 1.0 eV relative to the experiment.

Complexes and Dimers of Tetrathiafulvalene and Tetracyanoethylene

The fully optimized structures of the closed-shell acceptor molecule TCNE (**1**) and donor molecule TTF (**2**) as well as the fully optimized radical ions $\mathbf{1}^-$ and $\mathbf{2}^+$ were assembled in face-to-face oriented complexes. The singlet multiplicity is retained in the composed compound **8** while the triplet multiplicity is presumed in the complex **8***. In each case the vertically-stacked (**I**) and the laterally-displaced (**II**) arrangement was considered, such as shown in Fig. 1. Because of the size of the systems, the number of geometric variables was limited to the intermolecular distance. The binding energy ΔE_{bind} is the difference of the total energy of the complex and the sum of energies of the components with consideration of the counterpoise correction energy (ΔE_{cp}). Binding energies without and with cp-correction, intermolecular distances and the amount of charge transfer from the donor to the acceptor molecule of the EDA complexes **8** and **8*** are summarized in Table II. The energies and intermolecular distances are markedly dependent on the theoretical model and the level of theory. In general, the calculated binding energies are relatively small, and the laterally-displaced arrangement (**II**) is energetically favored. At the B3LYP/6-31G* level of theory the binding energies amount to –2.5 kcal/mol (vertically-stacked form) and –3.5 kcal/mol (displaced form), respectively. Cp-correction reduces the value to –1.6 and –1.7 kcal/mol, respectively. If the basis set 6-31G* is replaced by 6-31++G(3df,2p) the gain in binding energy amounts to 0.2 kcal/mol for arrangement **II** (without cp-correction). The addition of diffuse and polarization functions did not improve the binding energy but rather resulted in a slight decrease. In addition, the diffuse orbitals and polarization functions increase the intermolecular distance between the donor and the acceptor molecule. Thus, the increase in the intermolecular distance with two sets of d-orbitals amounts to 0.26 Å for the stacked arrangement **I** and 0.13 Å for the laterally-displaced arrangement **II**. Hobza's basis set 6-31G*(0.25) improves the description of dispersion energy. The DFT binding

TABLE II

Binding energies of complexes of TTF/TCNE (**8**) in the cofacially-stacked (**I**) and laterally-displaced (**II**) arrangements without and with counterpoise correction (ΔE_{bind} and ΔE_{cp}, respectively), optimized intermolecular distances R, and charge transfer between the donor and the acceptor according to the Mulliken population analysis (Δq_M) and the natural population analysis (Δq_N) and S_0/T_1-splitting energies calculated by DFT(B3LYP) and MP2 using different basis sets[a]

Method	Basis set	**8**					**8***		**8**/**8***
		ΔE_{bind} kcal/mol	ΔE_{ep} kcal/mol	R, Å	Δq_M	Δq_N	R, Å	Δq_M	S_0/T_1 kcal/mol
				Arrangement **I**					
DFT	6-31G*	–2.54	–1.59	4.18	0.12	0.12	3.48	0.82	11.95
	6-31G*(0.25)	–3.11	–1.33	4.00	0.09	–	–	–	–
	6-31++G**	–2.77	–1.96	4.44	0.15	0.15	3.56	0.87	9.54
	6-31++G(3df,2p)	–2.62	–2.16	4.54	0.18	–	–	–	–
	6-311G**	–2.48	–1.63	4.17	0.12	0.13	3.48	0.84	10.35
MP2	6-31G*	–8.53	–5.17	3.60	0	0.01	–	–	–
	6-31G*(0.25)	–15.09	–7.81	3.39	0.01	–	–	–	–
				Arrangement **II**					
DFT	6-31G*	–3.52	–1.74	3.63	0.14	0.15	3.36	0.91	14.81
	6-31G*(0.25)	–4.53	–1.67	3.52	0.13	–	–	–	–
	6-31++G**	–3.48	–2.42	3.76	0.23	0.18	3.44	1.00	11.42
	6-31++G(3df,2p)	–3.35	–2.69	3.82	0.17	–	–	–	–
	6-311G**	–3.59	–1.93	3.63	0.15	0.16	3.37	0.91	12.93
MP2	6-31G*	–12.26	–6.31	3.13	0.03	0.05	–	–	–
	6-31G*(0.25)	–22.40	–10.04	2.94	0.04	–	–	–	–

[a] Extended version of the table with total energies, and selected geometrical parameters for complexes is available from the authors on request.

energies are increased to –3.1 and –4.5 kcal/mol and the intermolecular distances are diminished to 4.00 and 3.52 Å in the arrangements **I** and **II**, respectively. However, the BSSE reduces the binding energies to rather small values.

The MP2/6-31G* binding energy is –5.2 and –6.3 kcal/mol in the arrangements **I** and **II** after counterpoise correction. As found by DFT calculations, MP2 predicts the laterally-slipped arrangement more stable than the vertically-stacked one. The intermolecular distance is shorter than found by DFT. In excellent agreement with the X-ray structure[25], the intermolecular distance between donor and acceptor of **8** amounts to 3.13 Å (experiment: 3.15 Å). The basis set 6-31G*(0.25) gives the largest corrected binding energies of –7.8 and –10.0 kcal/mol in the vertically-stacked and laterally-displaced form, respectively. However, the intermolecular distances decrease to 3.39 and 2.94 Å in the arrangements **I** and **II**.

The triplet complex **8*** was also calculated using the frozen radical ion geometries of $\mathbf{1}^-$ and $\mathbf{2}^+$ in stacks arranged vertically or displaced parallelly as depicted in Fig. 1. As to be expected, the total energy of the open-shell complex **8*** is higher than that of the singlet complex **8**. The S_0/T_1-gap is relatively small and is in the range 11.9 to 14.8 kcal/mol (6-31G*). The S_0/T_1-splitting energies are summarized in Table II. In contrast to singlet EDA complexes, triplet complexes are favored in the vertically-stacked arrangement. This arrangement is favored over the displaced arrangement by –1.7, –1.2 and –1.5 kcal/mol for the basis sets 6-31G*, 6-31++G** and 6-311G**, respectively. The intermolecular distances in the triplet complexes are shorter than in the singlet complexes. In the favored arrangement **I** the equilibrium distances are between 3.48 and 3.56 Å. Surprisingly, they are larger in the favored arrangement **I** than in the less favored arrangement **II**. The contraction of the interplanar spacing between the predominantly ionic pairs in the triplet complex may be essentially electrostatic in origin.

Complexes of Heteroanalogous Tetrathiafulvalenes and the Nitrogen-Containing Analogues

The complexes **9**, **10** and **11** as well as the corresponding triplet complexes **9***, **10*** and **11*** are formed by replacing S in **8** by Se, O and NH, respectively. In analogy to **8** and **8*** the fully optimized substructures in their singlet and doublet states are calculated in the stacks **I** and **II** with the TCNE acceptor molecule in the singlet and triplet state, respectively. The results are collected in the Tables III–V.

The main features of this series are closely similar to those of the $TTF^+/TCNE^-$ couple. In case of singlet complexes laterally-displaced arrangements are again favored. Weak intermolecular interactions were calculated by DFT. The corrected DFT binding energy for complex **9**/**II** amounts to –3.3 kcal/mol (6-31G*(0.25)) and –1.7 kcal/mol (6-311G**). DFT binding energies calculated using 6-31G* and 6-31++G** basis sets are overcompensated by the BSSE. The energies of the complex **10**/**II** are in the range –2.2 to –2.9 kcal/mol, depending on the level of theory, and the distances are between

3.28 and 3.65 Å. The optimized intermolecular distances for complex **11**/**II** are between 3.21 and 3.35 Å. Interestingly, with exception of complex **10** cp-corrected MP2 binding energies of complexes are smaller than those obtained by DFT and the intermolecular spacing is reduced with respect to DFT intermolecular distances.

As with the triplet $TTF^+/TCNE^-$ (arrangement **I**), triplet complexes of heteroanalogous tetrathiafulvalene are favored if vertically-stacked. However, the intermolecular distances between the subsystems are larger than in arrangement **II**. The singlet–triplet splitting energies of the complexes are assembled in the Tables III–V. In the case of **9** the singlet–triplet splitting energy amounts to 15.5 kcal/mol (6-311G**), and in the case of complex **10** to 10.3 kcal/mol (6-31G*). Interestingly, in the case of **11** the triplet excited complex is energetically favored over the singlet state at the level of

TABLE III

Binding energies of complexes of TSF/TCNE (**9**) in the cofacially-stacked (**I**) and laterally-displaced (**II**) arrangements without and with counterpoise correction (ΔE_{bind} and ΔE_{cp}, respectively), optimized intermolecular distances R, and charge transfer between the donor and the acceptor according to the Mulliken population analysis (Δq_M) and the natural population analysis (Δq_N) and S_0/T_1-splitting energies calculated by DFT(B3LYP) and MP2 using different basis sets[a]

Method	Basis set	**9**					**9***		**9**/**9***
		ΔE_{bind} kcal/mol	ΔE_{cp} kcal/mol	R, Å	Δq_M	Δq_N	R, Å	Δq_M	S_0/T_1 kcal/mol
			Arrangement **I**						
DFT	6-31G*	–11.23	+2.63	3.54	0.12	0.04	–	–	–
	6-31G*(0.25)	–5.29	–2.51	4.00	0.01	–	–	–	–
	6-31++G**	–21.19	+0.10	3.83	0.16	0.15	3.48	0.86	6.53
	6-311G**	–1.96	–0.18	4.49	0.09	0	3.58	0.84	13.43
MP2	6-31G*	–23.88	–0.58	3.35	0	0.02	–	–	–
			Arrangement **II**						
DFT	6-31G*	–14.88	+0.26	3.18	0.17	0.18	–	–	–
	6-31G*(0.25)	–7.40	–3.27	3.52	0.13	–	–	–	–
	6-31++G**	–19.90	–1.15	3.42	0.28	0.20	3.32	0.99	10.54
	6-311G**	–3.03	–1.73	3.79	0.13	0.13	3.41	0.91	15.50
MP2	6-31G*	–29.71	–3.15	2.95	0.07	0.09	–	–	–

[a] Extended version of the table with total energies, and selected geometrical parameters for complexes is available from the authors on request.

theory used. The complex **11** actually contains the strongest donor in the series considered.

Tetraaminoethylene/Tetracyanoethylene Complexes

In the complex **12** the ring-open donor compound TAE (**6**) forms the EDA complex with TCNE. In the arrangements **III** to **VI** the acceptor molecule is shifted parallel to the long donor molecule axis as shown in Fig. 2. If the length of the ethylene bond of **6** is given by x in Å, the extent of shift x_i in Å is defined by $x_i = nx$ with n = 0, 0.25, 0.5 and 1. The results for complex **12** are presented in Table VI.

TABLE IV
Binding energies of complexes of TOF/TCNE (**10**) in the cofacially-stacked (**I**) and laterally-displaced (**II**) arrangements without and with counterpoise correction (ΔE_{bind} and ΔE_{cp}, respectively), optimized intermolecular distances R, and charge transfer between the donor and the acceptor according to the Mulliken population analysis (Δq_M) and the natural population analysis (Δq_N) and S_0/T_1-splitting energies calculated by DFT(B3LYP) and MP2 using different basis sets[a]

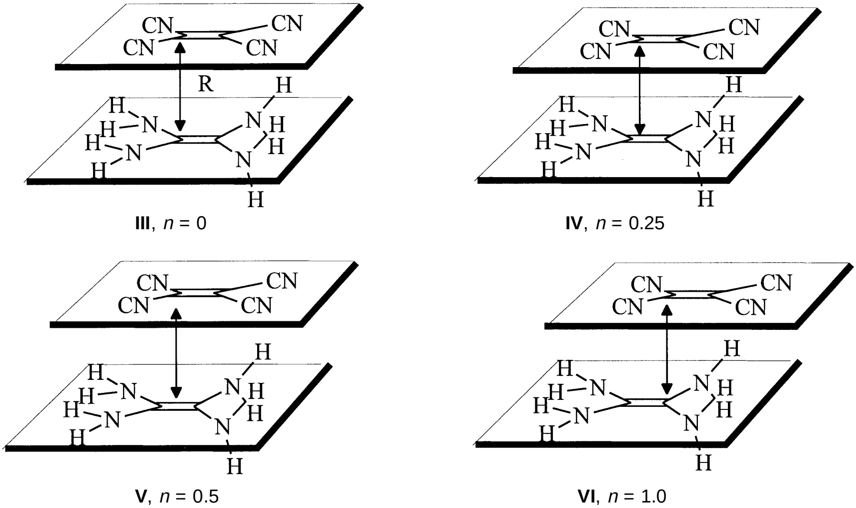
Method	Basis set	**10**					**10***		**10**/**10***
		ΔE_{bind} kcal/mol	ΔE_{cp} kcal/mol	R, Å	Δq_M	Δq_N	R, Å	Δq_M	S_0/T_1 kcal/mol
Arrangement **I**									
DFT	6-31G*	–4.34	–2.64	3.66	0.19	0.19	3.19	0.89	6.78
	6-31G*(0.25)	–5.62	–1.98	3.48	0.15	–	–	–	–
	6-31++G**	–3.64	–2.67	4.11	0.20	[b]	3.27	0.89	6.40
	6-311G**	–3.72	–2.49	3.72	0.18	0.01	3.21	0.90	6.46
MP2	6-31G*	–10.30	–5.36	3.17	0.01	0	–	–	–
	6-31G*(0.25)	–19.58	–6.65	2.98	0.04	–	–	–	–
Arrangement **II**									
DFT	6-31G*	–4.93	–2.83	3.40	0.20	0.20	3.21	0.93	10.35
	6-31G*(0.25)	–6.33	–2.24	3.28	0.17	–	–	–	–
	6-31++G**	–3.96	–2.89	3.65	0.22	0.19	3.30	0.91	9.10
	6-311G**	–4.44	–2.71	3.41	0.20	0.18	3.23	0.98	9.79
MP2	6-31G*	–11.02	–5.11	2.99	0.06	0.03	–	–	–
	6-31G*(0.25)	–22.25	–6.55	2.78	0.08	–	–	–	–

[a] Extended version of the table with total energies, and selected geometrical parameters for complexes is available from the authors on request. [b] No convergence.

The data in Table VI may suggest that the intermolecular interaction in **12** is best described by DFT/3-21G calculations. Both relatively strong binding energies and reasonable intermolecular distance (2.98 and 3.45 Å) were obtained. Due to considerable BSSE, however, the stabilization energy actually amounts to –3.1 kcal/mol in the most favored arrangement **VI**. Additional polarization and diffuse functions are expected to strengthen the intermolecular interaction but they rather resulted in opposite effects with smaller binding energies and larger intermolecular distances. The stacked arrangement **III** (*n* = 0) and the mostly displaced arrangement **VI** (*n* = 1) are mostly favored. With longitudinal shifting the maximum energy appeared at *n* = 0.25 with the intermolecular distance between donor and acceptor at maximum.

MP2 binding energies are again relatively large for all arrangements. After cp-correction, however, the binding energies are either repulsive, when using the small split valence basis set 3-21G, or comparable with DFT binding energies with more extended basis sets. The energetic characteristics are now clearly changed. The vertically-stacked form **III** is energetically preferred, arrangement **IV** (*n* = 0.25) comes next, and the potential curve of the displaced arrangement with *n* = 1 is disfavored. The optimum intermolecular distances are between 2.92 and 3.41 Å.

Triplet complexes were also studied. The results are summarized in Table VI. Using the UDFT/3-21G and UDFT/6-31++G** levels only the displaced arrangement **VI** is more stable whereas the vertically-stacked form **III** is favored in the cases of UDFT/6-31G*. The total energies of the other arrangements are nearly the same. The S_0/T_1-splitting



III, *n* = 0

IV, *n* = 0.25

V, *n* = 0.5

VI, *n* = 1.0

FIG. 2

Vertically-stacked arrangement **III** and the laterally-displaced arrangements **IV** to **VI** of TAE/TCNE complexes (for the definition of *n* see text) energies are listed in Table VI. They suggest triplet complexes are lower in energy than singlet complexes.

Electron Distribution and Nature of the Intermolecular Bonding

The question has been raised as to whether charge or overlap control plays the more important role in intermolecular bonding of stacked EDA complexes. In general, the donor strength of the heteroatoms considered decreases in the sequence NH, O, S, Se. The stronger electron delocalization in the tetrachalcogenafulvalenes substructures is therefore expected for compounds with first-row elements. On the other hand, the second and third-row elements sulfur and selenium, respectively, are distinguished from

TABLE V

Binding energies of the complex of TIF/TCNE in the cofacial-stacked (**I**) and laterally-displaced (**II**) arrangements without and with counterpoise correction (ΔE_{bind} and ΔE_{cp}, respectively), optimized intermolecular distances *R*, and charge transfer between the donor and the acceptor according to the Mulliken population analysis (q_{M}) and the natural population analysis (q_{N}) and S_0/T_1-splitting energies calculated by DFT(B3LYP) and MP2 using different basis sets[a]

Method	Basis set	**11**					**11***		**11/11***
		ΔE_{bind} kcal/mol	ΔE_{cp} kcal/mol	*R*, Å	Δq_M	Δq_N	*R*, Å	Δq_M	S_0/T_1 kcal/mol
				Arrangement **I**					
DFT	6-31G*	–13.42	–10.97	3.53	0.43	0.46	3.32	0.95	–18.20
	6-31G*(0.25)	–15.00	–10.75	3.43	0.44	–	–	–	–
	6-31++G**	–12.03	–11.00	3.80	0.42	0.47	3.38	0.82	–19.70
	6-311G**	–12.36	–10.74	3.63	0.44	0.46	3.31	0.96	–17.69
MP2	6-31G*	–11.51	–6.05	3.28	0.02	0	–	–	–
	6-31G*(0.25)	–20.29	–8.39	3.11	0.04	–	–	–	–
				Arrangement **II**					
DFT	6-31G*	–15.81	–12.84	3.28	0.44	0.45	3.21	0.95	–15.75
	6-31G*(0.25)	–17.56	–12.62	3.21	0.43	–	–	–	–
	6-31++G**	–14.44	–13.29	3.35	0.44	0.48	3.28	0.87	–17.13
	6-311G**	–15.28	–13.17	3.28	0.44	0.47	3.21	0.95	–14.62
MP2	6-31G*	–16.93	–8.97	2.92	0.15	0.07	–	–	–
	6-31G*(0.25)	–29.29	–12.29	2.77	0.17	–	–	–	–

[a] Extended version of the table with total energies, and selected geometrical parameters for complexes is available from the authors on request.

TABLE VI
Binding energies of complexes of TAE/TCNE (**12**) in the arrangements **III** to **VI** without and with counterpoise correction (ΔE_{bind} and ΔE_{cp}, respectively), optimized intermolecular distances R, and charge transfer between the donor and acceptor according to the Mulliken population analysis (Δq_M) and the natural population analysis (Δq_N) and S_0/T_1-splitting by DFT(B3LYP) and MP2 using different basis sets[a]

Method	Basis set	**12**					**12***			**12**/**12***
		ΔE_{bind} kcal/mol	ΔE_{cp} kcal/mol	R, Å	Δq_M	Δq_N	R, Å	Δq_M	Δq_N	S_0/T_1 kcal/mol
				Arrangement **III**						
DFT	6-21G*	–8.72	–2.75	3.32	0.20	0.21	3.22	0.95	0.96	–7.10
	6-31G*	–4.20	–2.00	3.59	0.12	0.14	3.37	0.94	0.98	–3.93
	6-31G*(0.25)	–5.84	–2.11	3.49	0.12	–	–	–	–	–
	6-31++G**	–2.49	–1.79	3.76	0.10	0.12	3.40	0.86	0.98	–5.64
MP2	6-21G	–7.81	–0.43	3.32	0.01	0.01	–	–	–	–
	6-31G*	–8.08	–3.72	3.38	0.01	0.01	–	–	–	–
				Arrangement **IV**						
DFT	6-21G*	–5.66	–1.17	3.45	0.18	0.19	3.21	0.95	0.96	–10.15
	6-31G*	–2.61	–0.74	3.72	0.08	0.09	3.36	0.95	0.97	–5.27
	6-31G*(0.25)	–4.06	–0.65	3.59	0.06	–	–	–	–	–
	6-31++G**	–1.40	–0.80	4.06	0.08	0.07	3.39	0.86	0.98	–6.71
MP2	6-21G	–6.75	–0.26	3.37	0	0	–	–	–	–
	6-31G*	–7.20	–3.17	3.41	0	0	–	–	–	–
				Arrangement **V**						
DFT	6-21G*	–6.40	–1.21	3.33	0.18	0.19	3.12	0.99	0.97	–9.50
	6-31G*	–3.50	–1.39	3.57	0.13	0.14	3.47	0.95	0.98	–3.40
	6-31G*(0.25)	–5.00	–1.32	3.47	0.12	–	–	–	–	–
	6-31++G**	–1.77	–1.15	3.85	0.13	0.11	3.37	0.86	0.99	–6.35
MP2	6-21G	–6.53	+0.11	3.32	0.01	0.01	–	–	–	–
	6-31G*	–7.12	–2.92	3.35	0.02	0.01	–	–	–	–
				Arrangement **VI**						
DFT	6-21G	–11.28	–3.05	2.98	0.3	0.30	3.07	0.94	0.97	–5.59
	6-31G*	–5.79	–2.97	3.22	0.22	0.23	3.35	0.95	0.99	–1.23
	6-31G*(0.25)	–7.36	–2.81	3.18	0.21	–	–	–	–	–
	6-31++G**	–3.26	–2.37	3.30	0.22	0.22	3.28	0.84	0.99	–5.08
MP2	6-21G	–9.01	+1.76	2.97	0.13	0.11	–	–	–	–
	6-31G*	–9.32	–2.46	2.92	0.16	0.16	–	–	–	–

[a] Extended version of the table with total energies, and selected geometrical parameters for complexes is available from the authors on request.

first-row elements by the lower ionization potential giving rise to lower ionization potentials of the corresponding tetrachalcogenafulvalenes **2** and **3**. In addition, the more heavy elements may more efficiently overlap with the acceptor molecule TCNE. While electron delocalization is indicated in the atomic charges of the subunits, any noticeable overlap will be indicated in the changes of orbital energies of the components on EDA complex formation. In this connection, Hartree–Fock (Kohn–Sham) frontier orbitals deserve particular interest. Overlap is the precondition for electron migration from the donor to the acceptor component.

The charge interaction between the calculated atomic charges of the components proved to be a less appropriate model for the intermolecular interaction. The attractive or repulsive interaction calculated are not clearly related to the calculated binding energies.

There are, however, arguments in favor of orbital overlap. First, the molecular orbital energies are noticeably shifted. In particular, the HOMO of the donor is lowered by about 0.46 and 0.56 eV whereas the LUMO of the acceptor is raised by about 0.57 and 0.66 eV for the complex **8/I** and **8/II** calculated by DFT/6-31G*, respectively. Secondly, energetic effects are clearly indicated by the second-order stabilization of Weinhold's natural bond orbitals according to Eq. (*1*). Stabilization is indicated in the more stable laterally-shifted arrangements **II** of EDA complexes. Interestingly, the NBO $\pi_{C=C}$ of the donors and the NBO $\pi^*_{C=C}$ of acceptor (TCNE) display the largest second-order term $E(2)$. The $E(2)$ energies amount to more than –0.5 kcal/mol for the complexes **8** to **11** (DFT/6-31G*). Thirdly, the charge transfer in the ground state of the complex is small but non-zero. The charge transfer in complexes of tetrachalcogenafulvalene and TCNE amounts to 0.20 e computed by Weinhold's natural population analysis (atomic natural charges). Results of the Mulliken analysis are not detailed in this paper since the results are closely similar. An appreciable dependency of the charge transfer on the intermolecular distance has not been found. Any stronger charge transfer found experimentally is obviously bound to the condensed phase such as in polar solvents or in the crystal.

The complex in the triplet excited state is of quite different nature. According to the calculations the components of the triplet complex is essentially ionic in nature and the charge transfer relative to the neutral components amounts to nearly 1. In other words, charge of the ionic components is overwhelmingly preserved. In that case the electrostatic interaction between the components plays an important role. This feature may be also relevant for the singlet excited state of the complex expected to be slightly higher in energy than the triplet state of the complex. This result deserves interest with regard to the potential formation of radical ion pairs upon irradiation and their subsequent transformation to radical ions in polar solvents.

Solvent Effects

To determine the binding energy of complexes in solution (ΔE_{stab}) Tomasi's polarized continuum model[36] was used. Hexane was chosen as a nonpolar solvent ($\varepsilon = 2.02$), acetonitrile ($\varepsilon = 35.94$) and water ($\varepsilon = 78.32$) as polar media. In all cases DFT or MP2/6-31G* single-point calculations of the optimized gas-phase structure were performed assuming that the solvent effect on the geometry of solute is sufficiently small.

TABLE VII
Binding energies (ΔE_{stab}) of the complexes **8**, **10** and **11** in hexane, acetonitrile and water in kcal/mol and charge transfer between the donor and acceptor according to the Mulliken population analysis (Δq_M) calculated by DFT(B3LYP) at the 6-31G* level of theory[a]

Method	Solvent	**8**		**10**		**11**	
		ΔE_{stab} kcal/mol	Δq_M	ΔE_{stab} kcal/mol	Δq_M	ΔE_{stab} kcal/mol	Δq_M
		Arrangement **I**					
DFT/6-31G*	hexane	–3.82	0.17	–5.60	0.21	–15.30	0.49
	acetonitrile	–16.67	0.50	–17.78	0.30	–28.85	0.76
	water	–15.79	0.50	–13.92	0.30	–28.67	0.78
		Arrangement **II**					
DFT/6-31G*	hexane	–5.03	0.19	–6.23	0.22	–17.83	0.48
	acetonitrile	–17.84	0.49	–19.97	0.30	–33.13	0.73
	water	–18.21	0.51	–20.38	0.31	–33.20	0.75
		8*		**10***		**11***	
		Arrangement **I**					
DFT/6-31G*	hexane	–21.63	0.88	–22.34	0.93	–23.65	0.96
	acetonitrile	–4.86	0.96	–1.16	0.98	–2.81	0.98
	water	–3.85	0.96	–1.20	0.98	–2.73	0.98
		Arrangement **II**					
DFT/6-31G*	hexane	–21.11	0.94	–20.22	0.96	–23.85	0.96
	acetonitrile	–5.85	0.98	+1.17	0.99	–4.97	0.99
	water	–6.30	0.98	+1.23	0.99	–5.12	0.99

[a] Extended version of the table with total energies in solution is available from the authors on request.

TABLE VIII
Binding energies (ΔE_{stab}) of the complex **12** in hexane, acetonitrile and water in kcal/mol and charge transfer between the donor and acceptor according to the Mulliken population analysis (Δq_M) calculated by DFT(B3LYP) and MP2 at the 6-31G* level of theory[a]

Method	Solvent	**12**			
		ΔE_{stab} kcal/mol	Δq_M	ΔE_{stab} kcal/mol	Δq_M
		Arrangement **III**		Arrangement **IV**	
DFT/6-31G*	hexane	–4.60	0.10	–3.00	0.04
	acetonitrile	–12.24	0.09	–8.77	0
	water	–12.22	0.09	–8.55	0
MP2/6-31G*	hexane	–6.29	0.01	–8.56	0
	acetonitrile	–15.08	0	–16.75	0
	water	–15.69	0	–17.50	0
		Arrangement **V**		Arrangement **VI**	
DFT/6-31G*	hexane	–4.18	0.10	–6.09	0.20
	acetonitrile	–14.01	0.07	–15.20	0.20
	water	–13.56	0.07	–16.86	0.20
MP2/6-31G*	hexane	–8.14	0.01	–9.69	0.14
	acetonitrile	–14.19	0	–15.53	0.11
	water	–14.78	0	–16.47	0.11
		12*			
		Arrangement **III**		Arrangement **IV**	
DFT/6-31G*	hexane	–21.53	0.96	–21.15	0.96
	acetonitrile	+6.29	0.98	+5.97	0.98
	water	+6.74	0.98	+6.34	0.98
		Arrangement **V**		Arrangement **VI**	
DFT/6-31G*	hexane	–20.15	0.99	–20.24	0.96
	acetonitrile	+7.56	1.00	+6.95	0.97
	water	+8.00	1.00	+7.20	0.97

[a] Extended version of the table with total energies in solution is available from the authors on request.

The Tables VII and VIII show the binding energies ΔE_{stab} of the complexes in solution. With respect to the gas phase, the DFT binding energies for the solvated complexes **8**, **10** and **11** are larger, in particular in polar media. The laterally-displaced arrangement **II** is again favored over the vertically-stacked form. The complex **11** shows always the largest binding energy in all solvents. The charge transfer from the donor to the acceptor is significantly larger in polar media than in the gas phase. Complex **11** has a nearly ionic structure (0.8 e). In the complexes **8** and **10** the charge transfer amounts to 0.5 and 0.3 e, respectively. The DFT binding energies of complex **12** are also larger in solution than in the gas phase and comparable to those of complexes **8** and **10**. As found in the gas-phase calculations the mostly displaced arrangement **VI** is energetical favored. The maximum energy was calculated with arrangement **IV**. According to MP2 binding energies of complex **12** in solution the slightly displaced arrangement **IV** and the laterally-displaced form **VI** are favored. In contrast to the aforementioned cases the effect of the solvent on the charge transfer of **12** is low. Only 0.2 e at best are transferred from donor to acceptor in this case.

The binding energies of the triplet excited complexes are larger in less polar solvents since the complexes are strongly bipolar (dipole moments amount to more than 12 D) and their solvation is favored over that of the ions. In polar solvents the stabilization of the ions becomes more important and the dissociation may be favored. The complex **10** should dissociate in the components.

CONCLUSIONS

Tetrathiafulvalene (TTF) and a series of closely related donor compounds, and the acceptor compound tetracyanoethylene (TCNE) were studied by DFT(B3LYP) and *ab initio* (MP2) methods on equal footings. The binding energies were calculated at optimized intermolecular distances in selected orientations with the optimized ground-state geometries of the donor and acceptor substructures. With the exception of complexes TSF/TCNE (**9**) and TIF/TCNE (**11**) the cp-corrected MP2 binding energies were larger than the corresponding corrected DFT energies. The binding energy of the TTF/TCNE (**8**) in the energetically favored slightly slipped coplanar arrangement was calculated to be of –6.3 kcal/mol by MP2(frozen)/6-31G(d) and –10.0 kcal/mol by MP2(frozen)/6-31G*(0.25), respectively. Although the ground-state charge transfer from the donor to the acceptor is low, electron delocalization within the complex is clearly indicated for the most stable structures. According to the binding energies the most efficient donor is TIF (**5**). The large binding energy of the TIF/TCNE complex (about –12.8 kcal/mol by DFT/6-31G* and –9.0 kcal/mol by MP2/6-31G*) is obviously associated with the low ionization energy of the donor component. The ground-state charge transfer is largest in that case.

The slight polar character of the EDA complexes in the ground state is sufficient to result in a noticeable stabilization of the complexes in polar solvents. According to self-consistent-reaction-field calculations the binding energies of the complexes in solution relative to the energies of the solvated components is increased by several kcal/mol, depending on the dielectric constant of the solvent. Concomitantly, the charge transfer from the donor to the acceptor is increased. This outcome may rationalize the appreciable charge transfer in EDA complexes observed in the condensed phase and, in particular, in the crystal.

The triplet EDA complex may be considered as a model for the lowest-energy singlet excited state generated by optical excitation. If the triplet complex is constructed from the ionic donor and acceptor species, the calculation of the frozen supermolecular structure results in a complex where the charge separation is essentially retained. In other words, a nearly complete charge transfer occurs on excitation. Since the solvation energy is larger for the constituent ions than for the bipolar complex, the excited state complex may undergo dissociation into the solvated ions in polar solvents.

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