

**THEORETICAL STUDY OF SOLVENT EFFECT ON  $\pi$ -EDA COMPLEXATION I. SCF AND DFT CALCULATIONS WITHIN POLARIZED CONTINUUM MODEL ON TCNE-BENZENE COMPLEX**Ondrej KYSEĽ<sup>a1,\*</sup>, György JUHÁSZ<sup>a2</sup> and Pavel MACH<sup>b</sup><sup>a</sup> Department of Chemistry, Faculty of Natural Sciences, Constantine the Philosopher University, A. Hlinku Av. 1, 949 74 Nitra, Slovakia; e-mail: <sup>1</sup> okysel@ukf.sk, <sup>2</sup> jjuhasz@ukf.sk<sup>b</sup> Department of Biophysics and Chemical Physics, Faculty of Mathematics, Physics and Informatics, Comenius University, Mlynská dolina, F1, 842 48 Bratislava, Slovakia; e-mail: mach@fmph.uniba.sk

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SCF, MP2, DFT(B3LYP) and the polarizable continuum model (PCM) were used to study geometry, charge distribution and energetics of the  $\pi$ -EDA complex formation between tetracyanoethene (TCNE) and benzene both in gas phase and in various polar solvents (cyclohexane, dichloromethane and water). MP2/6-31G\*, MP2/6-31+G\*, MP2/6-31G\*(0.25) calculations have shown that geometry of the complex is planparallel with interplane distance of  $3.05 \times 10^{-10}$  m on the MP2/6-31G\* level and the complexation energy is equal to  $-6.8$  to  $-8.95$  kcal/mol, while dominant contributions to the complexation energy come from intermolecular correlation and energy. The PCM continuum model of polar solvents describes well both the Gibbs energy of solvation of individual solutes and the difference between the complex and its constituents and also agrees with the experimental finding that the polar solvent effect decreases the complexation constant of the  $\pi$ -EDA complex formation by a factor of 2–4 when chloroform is replaced by more polar dichloromethane, and by a factor of 9, when tetrachlormethane is replaced by dichloromethane. It seems that the solvation Gibbs energy of the  $\pi$ -EDA complex formation always prefers stability of solvated constituents to that of the solvated complex. The electrostatic polarization Gibbs energy of solvation is responsible for the tendency of complexation constants to decrease with increasing solvent polarity; however, non-electrostatic terms contribute as well. While the enthalpy of complexation between benzene and TCNE in gas phase is about  $-10.0$  kcal/mol due to the negative complexation entropy  $\Delta(\Delta S) = -22.56$  cal/mol K, the  $\Delta G$  of complexation is  $-3.8$  kcal/mol. The solvation part of the complexation Gibbs energy in dichloromethane is  $+5.14$  kcal/mol (PCM-SCF/6-31G\* calculation) so that complexation constant  $K = 0.1$  dm<sup>3</sup>/mol in this solvent was found.

**Keywords:** EDA complexes; Charge-transfer complexes; Polarized continuum model (PCM); Solvent effects; *Ab initio* calculations; DFT; Weak molecular interactions.

Weak intermolecular interactions are of crucial importance for numerous structures of condensed liquid and solid matter and their behaviour. They are a key for understanding structures and functions of matter in nonliving and living nature and of synthetic materials as well. The monograph by Hobza and Zahradník<sup>1</sup> is very useful, comprising valuable references on theoretical and particularly experimental studies of intermolecular complexes until year 1988.

Electron donor–acceptor (EDA) complexes are currently of great importance since they can occur in materials and influence their semi-conductivity<sup>2</sup>, photocatalysis<sup>3</sup>, *etc.* The formation of such complexes plays a role in the self-assembling of supramolecular structures such as host–guest complexes, catenanes, rotaxanes webs and mosaics<sup>4</sup>. The spectrophotometric determinations of some antibacterial<sup>5</sup> and antibilharzial<sup>6</sup> drugs are based on the formation of EDA complexes. Complexes of 1,2,4,5-tetracyanobenzene (TCNB) with arenes were found to be promising candidates for probing the basicity of various alkali metal-exchanged faujasite zeolites<sup>7</sup>. A characteristic feature of  $\pi$ -EDA complexes formation is the appearance of a new longest-wavelength UV-VIS absorption band. Mulliken and Person<sup>8</sup> reported the pioneering work based on quantum chemical arguments to explain the mechanism of new complex formation in solution as well as the appearance of new CT electron absorption band. Semiempirical CNDO and INDO calculations usually strongly overestimate binding energies and give too short interplanar distances<sup>9</sup>. Full optimization of the benzene–TCNE complex was provided on HF/6-311G\*\* level of theory by Cioslowski *et al.*<sup>10</sup> They found a significant contribution of TCNE to total dipole moment of the complex. *Ab initio* calculations of the TCNE–hexamethylbenzene (HMB) complex by Hayashi *et al.*<sup>11</sup> give the optimized geometry and the vibration modes of ground state. They found that the  $C_{2v}$  symmetry is broken due to the formation of hydrogen bond between one of the hydrogens of the methyl groups of HMB and one of the nitrogen atom of TCNE.

Rauwolf *et al.*<sup>4</sup> studied complexes consisting of tetrathiafulvalene (TTF) or related compounds and TCNE by second-order many-body perturbation theory and by gradient-corrected hybrid Hartree–Fock/density functional theory (B3LYP exchange-correlation functional). They concluded that the relatively large MP2 binding energies suggest that the dispersion energy is underestimated or not considered by the B3LYP functional at all. These results agree with the results of Michinori *et al.*<sup>12</sup> who studied benzene–ethene interactions by *ab initio* calculations at HF/6-31G\*\*, MP2/6-31G\*\* and B3LYP/6-31G\*\* levels of theory. The obtained dipole moments suggest the existence of charge transfer interactions between benzene and ethene. The

binding energy calculated by the MP2 method increases as the dispersion energy increases, and the distance between the two molecules decreases. Thus the dispersion forces for the stabilization of the EDA complexes are important.

The other types of EDA interaction are  $\pi$ - $\pi$  interactions such as in the benzene dimer. Many *ab initio* calculations on benzene dimer have been reported in the literature<sup>13,14</sup>, which were mainly focused on the geometry and binding energy of the complex. The calculations of Hobza *et al.*<sup>13e</sup> and Tsuzuki *et al.*<sup>14c</sup> showed that the dimer has two nearly isoenergetic structures (T-shaped and slipped parallel) with the binding energy of about 2 kcal/mol. The *ab initio* calculations<sup>13,14</sup> of benzene dimers show a strong basis set dependence of the calculated interaction energy. Small basis sets considerably underestimate the molecular polarizability and thereby the dispersion interaction. Tsuzuki *et al.*<sup>15</sup> develop a new precise model for the evaluation of intermolecular interaction between aromatic molecules (AIMI model). In this model the CCSD(T) interaction energy at the basis set limit has been estimated from the MP2 interaction energy near the basis set limit and the CCSD(T) correction term obtained using a medium basis set. They obtained interaction energy in the range 1.5–2.48 kcal/mol for benzene dimer. Li *et al.*<sup>16</sup> reported *ab initio* calculations performed to investigate the transition state in photoinduced electron transfer reaction between TCNE and biphenyl (Bip) as well as naphthalene (Nap). Planparallel conformation of EDA complexes and the complete active space SCF (CASSCF) model were selected for this purpose. The potential-energy calculations were performed at the HF/6-31G level. Stabilization energy of the EDA complex defined as

$$E_S = E(D) + E(A) - E(D \cdots A) \quad (1)$$

reaches its maximum value 2.35 kcal/mol for the [TCNE–Bip] complex at equilibrium distance  $R = 4.4 \times 10^{-10}$  m and 2.05 kcal/mol for the [TCNE–Nap] complex at equilibrium distance  $R = 4.2 \times 10^{-10}$  m.

Whereas a few studies of EDA complexes by first-principle methods are known, the solvent effect calculations of EDA complexes are rare.

Rauwolf *et al.*<sup>4</sup> determined the binding energy of EDA complexes of TTF and related compounds with TCNE in solution by the polarized continuum model (PCM)<sup>17</sup>. Hexane was chosen as nonpolar solvent, acetonitrile and water as polar media. The conclusions were that the slightly polar character of the EDA complexes in the ground state is sufficient to result in a noticeable stabilization of the complexes in polar solvent. Self-consistent-

reaction-field (SCRF) calculations predicted a gain in binding energy with solvation for the ground-state complex. DFT calculations of the ground-state charge transfer between the components supply values up to  $0.8|e|$  in polar solvents<sup>4</sup>, which is really very large value of CT.

On the basis of the Onsager model<sup>18</sup>, CT absorption in dichloromethane was investigated by considering the solvent reorganization energy by Li *et al.*<sup>16</sup> In general, polar solvents can influence the dipole moment of the solute; however, in the case of the [TCNE–Bip] and [TCNE–Nap] EDA complex<sup>16</sup>, the planparallel arrangement of the donor and acceptor was found and the distribution of the electron density and thus the dipole moment in solution was predicted not to change too much compared with the gas phase<sup>16</sup>.

## CALCULATIONS

Binding energy, intermolecular interaction energy or complexation energy of EDA complex  $[A \cdot B]$  was calculated by supermolecular approach<sup>19</sup> as difference

$$\Delta E^{AB} = E^{AB} - (E^A + E^B) , \quad (2)$$

where  $E^{AB}$ ,  $E^A$  and  $E^B$  are total electronic energy of the EDA complex and its constituents A and B. The complexation or binding energy may be generally decomposed into the following interaction energies components<sup>12</sup>

$$\Delta E^{AB} = E_{\text{disp}} + E_{\text{CT}} + E_{\text{ex}} + E_{\text{es}} + C , \quad (3)$$

where  $E_{\text{disp}}$ ,  $E_{\text{CT}}$ ,  $E_{\text{ex}}$ ,  $E_{\text{es}}$  and  $C$  mean dispersion, charge transfer, exchange repulsion and electrostatic energies, and a correction term, respectively. For the interaction between nonpolar molecules, the electrostatic energy can be neglected. Therefore,  $E_{\text{disp}}$  and  $E_{\text{CT}}$  comprise the main portion of the binding energy.

Since in the case of weak intermolecular interaction the binding energies are usually very small, it is necessary to consider the effects of the basis set superposition error (BSSE) in the calculation. We used the counterpoise correction method of Boys and Bernardi<sup>20</sup>. The counterpoise-corrected binding energy  $\Delta E_{\text{cor}}^{\text{AB}}$  can be written as

$$\Delta E_{\text{cor}}^{\text{AB}} = E^{\text{AB}} - (E^{\text{A(B)}} + E^{\text{B(A)}}) , \quad (4)$$

where  $\Delta E_{\text{cor}}^{\text{AB}}$  is the binding energy corrected by the counterpoise method,  $E^{\text{AB}}$  is the total energy of the complex,  $E^{\text{A(B)}}$  and  $E^{\text{B(A)}}$  are the donor and acceptor energies calculated including “phantom” basis set on the acceptor and donor molecules, respectively.

The difference

$$\Delta E_{\text{cp}} = (E^{\text{A}} + E^{\text{B}}) - (E^{\text{A(B)}} + E^{\text{B(A)}}) \quad (5)$$

represents the basis superposition error.

The compounds were calculated by conventional *ab initio* quantum-chemical method using the Gaussian 98 set of codes<sup>21</sup> both for SCF and DFT<sup>22,23</sup>. The *ab initio* calculations were performed using a Møller–Plesset second-order theory (MP2). The DFT calculations were performed with gradient-corrected hybrid B3LYP (Becke’s three parameters exchange functional with the Lee–Yang–Parr fit for the correlation functional<sup>24</sup>). The superposition error of the calculated binding energy was estimated using the Boys–Bernardi counterpoise method<sup>20</sup>.

Geometries of the components of the complex and the complex were fully optimized by each method (HF, MP2, DFT) in the split valence basis set 6-31G augmented by a set of *d*-polarization functions at the non-hydrogen atoms (6-31G\*). For calculating the interaction energies, we have used the basis set 6-31G\*(0.25), which is a variant of Pople’s 6-31G\* basis set. However, the exponents of *d*-atomic orbitals are modified to a value of 0.25 (ref.<sup>25</sup>) instead of the standard value of 0.8. From the study by Šponer *et al.*<sup>26</sup> appears that the use of the above-mentioned diffuse 6-31G\*(0.25) basis set at the MP2 level provides better estimates of stacking interaction than assumed originally. We used the 6-31+G\* basis where one set of diffuse *s* and *p* function is added. In these two basis sets we fully optimized the geometry of two constituents of the complex, and then their geometry was kept frozen and the intermolecular distances in the complex were only optimized by the MP2 method.

Solvent effect on complexation of TCNE with benzene was theoretically studied by PCM<sup>17</sup> included in Gaussian 98 (ref.<sup>21</sup>) program. Here solvent is treated as continuum characterized by relative permittivity ( $\epsilon_r$ ). The cavity surface-induced charge density is calculated using the equation

$$\sigma(\text{s}) = -\frac{\epsilon_r - 1}{4\pi\epsilon_0\epsilon_r} E(\text{s})_{n^-}, \quad (6)$$

where  $E(\mathbf{s})_{n^-}$  is an intensity of electric field (due to potential  $V$  coming from electron distribution of solute  $\rho$  and of induced charge densities  $\sigma(\mathbf{s})$ ) perpendicular to the cavity surface element ( $\mathbf{s}$ ).  $E(\mathbf{s})_{n^-}$  is calculated as follows:

$$E(\mathbf{s})_{n^-} = - \left( \frac{\partial V(\mathbf{r})}{\partial \mathbf{n}} \right)_{\mathbf{s}^-}, \quad (7)$$

where  $\mathbf{s}^-$  means that potential gradient is calculated from outside of the cavity surface. Schrödinger equation for solute is then solved including the perturbation potential  $\hat{V}(\varepsilon, \sigma)$  due to induced charges on the surface cavity. The electrostatic polarization Gibbs energy is then given by relation

$$(\Delta G_{\text{S}})_{\text{els}} = \left\langle \Psi(\varepsilon) \left| \hat{H}^0 + \frac{\hat{V}(\varepsilon, \sigma)}{2} \right| \Psi(\varepsilon) \right\rangle - \left\langle \Psi^0 \left| \hat{H}^0 \right| \Psi^0 \right\rangle, \quad (8)$$

where  $\hat{H}^0$  is unperturbed Hamiltonian of solute in gas phase and  $\Psi(\varepsilon)$  is wave function yet reflecting electron redistribution (response) due to perturbation  $\hat{V}(\varepsilon, \sigma)$ . To this electrostatic term the empirical corrections for non-electrostatic terms (cavitation energy<sup>30</sup> and dispersion-repulsion energy<sup>31</sup>) are added to obtain total Gibbs energy of solvation.

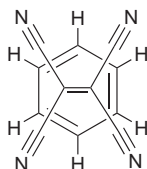
Wave function was calculated by SCF/6-31G\* and B3LYP/6-31G\* approaches both supplying similar numerical results. The distance ( $3.05 \times 10^{-10}$  m) between benzene and TCNE in their planparallel geometric arrangement was taken from the MP2/6-31G\*-optimized geometry of the complex. The solvents used for these calculations were cyclohexane ( $\varepsilon_r = 2.02$ ), dichloromethane ( $\varepsilon_r = 8.93$ ) and water ( $\varepsilon_r = 78.39$ ).

## RESULTS AND DISCUSSION

The results on full geometry optimization on the SCF/6-31G\*, MP2/6-31G\* and B3LYP/6-31G\* levels and the energy of complexation (binding energy) in 6-31+G\* and 6-31G\*(0.25) basis of TCNE and benzene are given in Table I.  $\Delta E_{\text{cor}}$  is complexation energy including counterpoise correction,  $\Delta E_{\text{cp}}$  is basis superposition error,  $\Delta Q_{\text{CT}}$  is charge transfer from benzene to TCNE,  $\mu$  is dipole moment and  $R$  is distance between constituents in the complex.

The above results indicate that energies of complexation corrected for the superposition error by Boys and Bernardi<sup>20</sup> at MP2 level are range from  $-6.8$  to  $-8.95$  kcal/mol and the respective geometry, *i.e.* the distance between constituents at their planparallel equilibrium geometry from  $2.91$  to  $3.12 \times 10^{-10}$  m. For all subsequent calculations by the PCM<sup>17</sup> solvation

model, the optimized geometry on MP2/6-31G\* level of theory with the distance  $3.05 \times 10^{-10}$  m was used. The calculated projected geometrical planparallel orientation of TCNE molecule to benzene molecule is indicated here.



### *Influence of Polar Medium on Charge-Transfer Distribution in TCNE–Benzene Complex*

SCF/6-31G\* and B3LYP/6-31G\* calculations on charge distribution in complex TCNE–benzene depending on polarity of the three used solvents are given in Tables I and II together with dipole moments of the complex and respective plots are in Figs 1 and 2.

From the data we can conclude that in the gas phase of the complex the charge redistribution on the respective atoms both in TCNE and in benzene constituents takes place so that the electron charges on N atoms of TCNE are significantly increased and a decrease in electron charges on C, especially of the ethene group, is observed. As to the donor molecule, here electron charges on H atoms decrease while C atoms gain electron charges. At the same time, transfer of electron charge (CT) from benzene to TCNE amounting to  $0.061|e|$  takes place and this is a main reason for the observed

TABLE I

Geometry optimization of EDA complex TCNE–benzene by SCF, MP2 and B3LYP methods in different basis sets

Method	Basis set	$\Delta E_{\text{bin}}$ kcal/mol	$\Delta E_{\text{cor}}$ kcal/mol	$\Delta E_{\text{cp}}$ kcal/mol	$\Delta Q_{\text{CT}}$  e	$\mu$ $10^{-30}$ C m	$R$ $10^{-10}$ m
SCF	6-31G*	-3.97	-2.41	1.56	0.0167	2.80	3.67
MP2	6-31G*	-11.83	-6.80	5.03	0.0682	5.690	3.05
	6-31+G*	-15.61	-8.19	7.42	0.1421	4.352	3.12
	6-31G*(0.25)	-20.70	-8.95	11.75	0.0711	6.270	2.91
B3LYP	6-31G*	-3.59	-1.62	1.98	0.0420	4.111	3.49

dipole moment ( $5.91 \times 10^{-30}$  C m). The charge transfer calculated by the MP2/6-31G\* method is a little greater being (in gas phase) of  $0.068|e|$  with the calculated dipole moment equal to  $5.69 \times 10^{-30}$  C m.

The effect of polar solvent on isolated components of the complex is as follows: the electron charge on N atoms of TCNE increased from  $-0.38|e|$  (in gas phase) to  $-0.445|e|$  (in water), *i.e.* by about  $0.011|e|$ , while electron charges on H atoms of the isolated benzene decreased from  $0.199|e|$  to

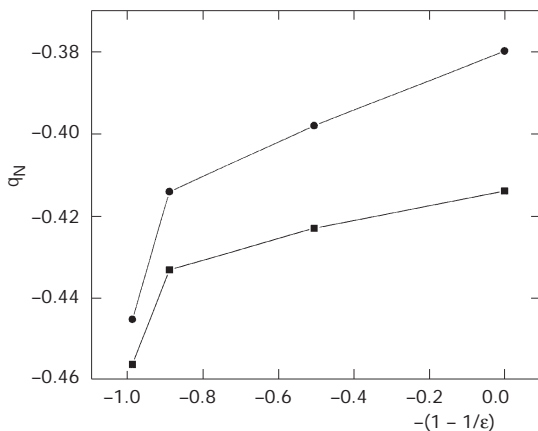


FIG. 1

SCF/6-31G\* charges of N atoms in the CN groups of TCNE and of the TCNE-benzene complex depending on polarity of the solvents. ■  $q_N$  benzene + TCNE, ●  $q_N$  TCNE

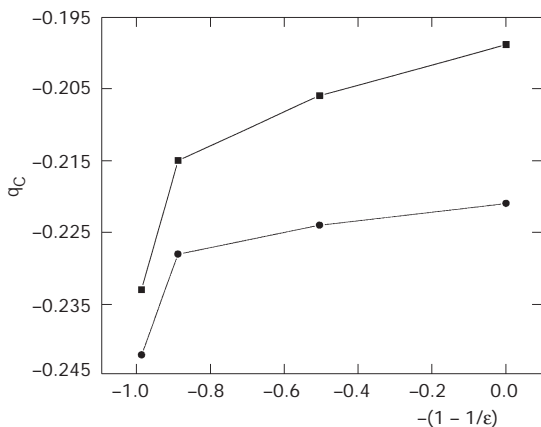


FIG. 2

SCF/6-31G\* charges on C atom of benzene and of the TCNE-benzene complex depending on polarity of the solvents. ■  $q_C$  benzene, ●  $q_C$  TCNE + benzene



TABLE II  
Mulliken atomic charges ( $q$ ) in benzene, TCNE and their EDA complex depending on solvent, calculated by SCF/6-31G\* with equilibrium distance between benzene and TCNE in the complex at  $R = 3.05 \times 10^{-10}$  m

Solute	Charge	Solvent			
		Gas phase $\epsilon_r = 1$	Cyclohexane $\epsilon_r = 2.02$	Dichloro- methane $\epsilon_r = 8.93$	Water $\epsilon_r = 78.39$
Benzene	$q_{C1}$	-0.199	-0.206	-0.215	-0.233
	$q_H$	0.199	0.206	0.215	0.233
TCNE <sup>a</sup>	$q_N$	-0.380	-0.398	-0.414	-0.445
	$q_{C2}$	0.114	0.139	0.154	0.179
	$q_{C3}$	0.322	0.329	0.337	0.356
TCNE <sup>b</sup> -benzene complex	$q_{C1}$	-0.221	-0.224	-0.228	-0.242
	$q_H$	0.228	0.232	0.238	0.253
	$q_N$	-0.414	-0.423	-0.433	-0.456
	$q_{C2}$	0.120	0.124	0.128	0.140
	$q_{C3}$	0.338	0.345	0.352	0.368
SCF dipole moment, $10^{-30}$ C m	$\mu$	5.91	6.16	6.25	6.33
Approximate dipole moment, $10^{-30}$ C m	$\mu = \Delta QR$	3.02	3.21	3.35	3.67
Charge transfer,  e	$\Delta Q$	-0.061	-0.066	-0.069	-0.075
Difference of charges <sup>c</sup>	$\Delta q_{C1}$	-0.021	-0.018	-0.013	-0.009
	$\Delta q_H$	0.028	0.026	0.023	0.020
	$\Delta q_N$	-0.034	-0.025	-0.019	-0.011
	$\Delta q_{C2}$	0.006	-0.015	-0.026	-0.039
	$\Delta q_{C3}$	0.016	0.016	0.015	0.012

<sup>a</sup> C3 is the carbon atom of CN group. <sup>b</sup> Small differences in  $q$  values for N, C2, C3 atoms in TCNE and for C1 and H atoms in benzene, due to formation of the complex and thus loss of geometrical equivalence are neglected. <sup>c</sup> A difference of electron charges on appropriate atoms in the solvated complex and in isolated solvated constituents respective:  $\Delta q_x = q_{x(\text{complex})} - q_{x(A,D)}$ .

0.228|e|, *i.e.* by ca 0.020|e|. The variations of charges on individual atoms of the isolated donor and acceptor when the gas phase is replaced by the polar water solvent are of the same magnitude as those taking place when complex is formed in gas phase both at the SCF/6-31G\* and B3LYP/6-31G\* levels. Thus, the charge redistribution in isolated constituents of the complex due to polar solvent (water) is approximately of the same magnitude and direction as in the complex in gas phase itself.

However, further polarization of charge redistribution within the complex immersed in polar medium proceeds as well. The mentioned changes of charges in dependence on the solvent polarity function  $-(1 - 1/\epsilon_r)$  are plotted in Figs 1 and 2. Besides, one can see, that the difference of the charges on individual atoms in the solvated complex and in particular components decreases when the polarity of solvents increases. That is to say that the complex itself plays a role of a "buffer" which does not allow such an extent of polarization of charges as one found in isolated components since, as mentioned before, significant polarization of charges takes place in the complex itself in gas phase. The changes in charges are consistent with the value of the solvation electrostatic part of the Gibbs energy of complexation, which is positive, and increases with increasing solvent polarity (Figs 3 and 4).

One can also mention that the value of the charge transfer from donor (benzene) to acceptor increases with increasing solvent polarity (and in a non-linear manner with increasing value of  $-(1 - 1/\epsilon_r)$  for large  $\epsilon_r$ ). However

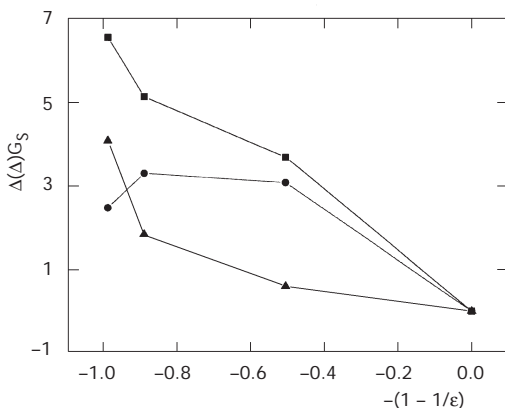


FIG. 3

PCM SCF/6-31G\* values of electrostatic, non-electrostatic and total solvation Gibbs energies of complexation (in kcal/mol) plotted against solvent polarity function  $-(1 - 1/\epsilon_r)$ . ■  $\Delta(\Delta G_S)_{\text{tot}}$ , ●  $\Delta(\Delta G_S)_{\text{nels}}$ , ▲  $\Delta(\Delta G_S)_{\text{els}}$

this effect is relatively very small and of opposite direction as the change of charges due to the presence of polar solvent. By another words, the charge transfer causing dipole moment of the complex is responsible for stabilization of it over the components in the presence of polar medium. However as we have yet mentioned the total solvation Gibbs energy of complexation ( $\Delta(\Delta G_S)_{\text{tot}}$ ), it is always positive and relatively large thus preferring stabilization of components over the complex.

Using the Onsager model<sup>18</sup> for calculation of the Gibbs electrostatic solvation energy for a molecular system with dipole moment  $\mu$  immersed into solvent with relative permittivity constant  $\epsilon_r$  and cavity radius  $r$ , *i.e.*

$$\Delta G_{\text{elstat}} = -\frac{1}{4\pi\epsilon_0} \frac{(\epsilon_r - 1)\mu^2}{(2\epsilon_r + 1)r^3} \cong -\frac{1}{8\pi\epsilon_0} \left(1 - \frac{1}{\epsilon_r}\right) \frac{\mu^2}{r^3} \quad (9)$$

we obtained a value of  $-0.2$  kcal/mol for  $\mu = 5.91 \times 10^{-30}$  C m (see Table III),  $\epsilon_r = 78.2$  and the roughly estimated radius of *ca*  $5.0 \times 10^{-10}$  m (MP2/6-31G\* distance between TCNE and benzene is  $3.05 \times 10^{-10}$  m, see above). This model reflects the solvation energy due to the solute dipole moment only. From the negligible value of this contribution it is obvious, that also small changes in the solute dipole moment, depending on solvent polarity changes bring insignificant contribution.

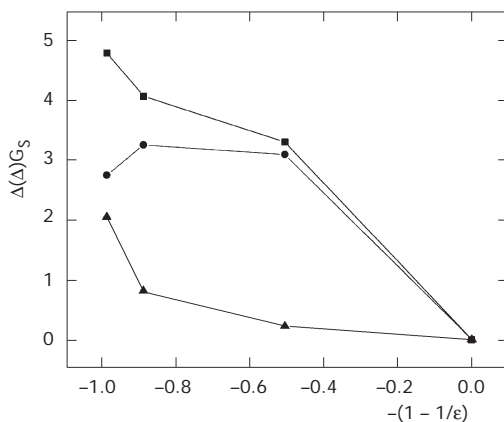


FIG. 4

PCM B3LYP/6-31G\* values of electrostatic, non-electrostatic and total solvation Gibbs energies of complexation (in kcal/mol) plotted against solvent polarity function  $-(1 - 1/\epsilon_r)$ .

■  $\Delta(\Delta G_S)_{\text{tot}}$ , ●  $\Delta(\Delta G_S)_{\text{nel}}$ , ▲  $\Delta(\Delta G_S)_{\text{els}}$

TABLE III  
Mulliken atomic charges ( $q$ ) in benzene, TCNE and their EDA complex depending on solvent, calculated by B3LYP/6-31G\* with equilibrium distance between benzene and TCNE in the complex at  $R = 3.05 \times 10^{-10}$  m

Solute	Solvent				
	Charge	Gas phase $\epsilon_r = 1$	Cyclohexane $\epsilon_r = 2.02$	Dichloro- methane $\epsilon_r = 8.93$	Water $\epsilon_r = 78.39$
Benzene	$q_{C1}$	-0.128	-0.134	-0.141	-0.158
	$q_H$	0.128	0.134	0.141	0.158
TCNE <sup>a</sup>	$q_N$	-0.422	-0.436	-0.448	-0.475
	$q_{C2}$	0.206	0.216	0.227	0.252
	$q_{C3}$	0.318	0.328	0.334	0.348
TCNE <sup>b</sup> -benzene complex	$q_{C1}$	-0.134	-0.138	-0.143	-0.159
	$q_H$	0.157	0.162	0.167	0.183
	$q_N$	-0.449	-0.458	-0.467	-0.486
	$q_{C2}$	0.197	0.201	0.205	0.215
	$q_{C3}$	0.327	0.331	0.337	0.347
SCF dipole moment, $10^{-30}$ C m	$\mu$	6.99	7.53	7.89	8.66
Approximate dipole moment, $10^{-30}$ C m	$\mu = \Delta QR$	4.80	5.21	5.59	6.46
Charge transfer, $ e $	$\Delta Q$	0.098	0.107	0.114	0.132
Difference of charges <sup>c</sup>	$\Delta q_{C1}$	-0.006	-0.004	-0.002	-0.001
	$\Delta q_H$	0.029	0.028	0.026	0.025
	$\Delta q_N$	-0.027	-0.022	-0.019	-0.011
	$\Delta q_{C2}$	-0.009	-0.015	-0.022	-0.037
	$\Delta q_{C3}$	0.009	0.003	0.003	-0.001

<sup>a</sup> C3 is the carbon atom of CN group. <sup>b</sup> Small differences in  $q$  values for N, C2, C3 atoms in TCNE and for C1 and H atoms in benzene, due to formation of the complex and thus loss of geometrical equivalence are neglected. <sup>c</sup> A difference of electron charges on appropriate atoms in the solvated complex and in isolated solvated constituents respective:  $\Delta q_x = q_{x(\text{complex})} - q_{x(A,D)}$ .

*Dependence of  $\Delta G$  Solvation Energy for Complexation of TCNE with Benzene on Solvent Polarity*

Tables IV and V contain solvation Gibbs energies of isolated TCNE and benzene molecules and the complex and the difference between them, *i.e.* the solvation Gibbs energies of complexation calculated by B3LYP/6-31G\* (Table IV) and SCF/6-31G\* (Table V) methods in PCM<sup>17</sup> solvent model. From the results we can conclude that both approaches give similar values of calculated quantities; however, electrostatic part of  $\Delta G$  and thus  $\Delta G_{\text{tot}}$  are

TABLE IV  
B3LYP/6-31G\* values of solvation Gibbs energies (in kcal/mol) of benzene, TCNE and the complex in dependence on polarity of selected solvents

Solute	Solvent				
	Solvation Gibbs energy	Gas phase $\epsilon_r = 1$	Cyclohexane $\epsilon_r = 2.02$	Dichloro- methane $\epsilon_r = 8.93$	Water $\epsilon_r = 78.39$
Benzene	$\Delta G_{\text{elst}}$	0	-0.52	-1.21	-3.61
	$\Delta G_{\text{nels}}$		-2.18	-3.0	0.09
	$\Delta G_{\text{tot}}$		-2.69	-4.21	-3.52
TCNE	$\Delta G_{\text{elst}}$	0	-1.51	-3.43	-8.18
	$\Delta G_{\text{nels}}$		2.70	2.17	6.42
	$\Delta G_{\text{tot}}$		1.20	-1.26	-1.75
TCNE-benzene complex	$\Delta G_{\text{elst}}$	0	-1.8	-3.82	-9.74
	$\Delta G_{\text{nel}}$		3.61	2.42	9.26
	$\Delta G_{\text{tot}}$		1.81	-1.40	-0.48
Dipole moment, $10^{-30}$ C m	$\mu$	7.0	7.53	7.89	8.66
$\Delta(\Delta G_{\text{S}})^a$ Gibbs solvation energy of complexation	$\Delta(\Delta G_{\text{S}})_{\text{elst}}$	0	0.23	0.82	2.05
	$\Delta(\Delta G_{\text{S}})_{\text{nels}}$	0	3.09	3.25	2.75
	$\Delta(\Delta G_{\text{S}})_{\text{tot}}$	0	3.3	4.07	4.79

<sup>a</sup> Solvation energies of complexation are taken as differences between the energies for the complex and the sum of those for benzene and TCNE:  $\Delta(\Delta G_{\text{S}}) = \Delta G_{\text{complex}} - (\Delta G_{\text{TCNE}} + \Delta G_{\text{benzene}})$ .

noticeably lower for DFT compared with the SCF method. Although DFT charges on individual atoms are approximately the same as those calculated by the SCF method, the changes in charges due to a solvent polarity increase are lower for DFT and thus DFT electrostatic solvation energies are smaller than SCF ones and, consequently, electrostatic solvation energy  $\Delta G$  for complexation in different polar solvents is smaller for DFT. In spite of that, it is peculiar to note that change in dipole moment and, consequently, the amount of electron charge transfer from benzene to TCNE is

TABLE V  
SCF/6-31G\* values of solvation Gibbs energies (in kcal/mol) of benzene, TCNE and the complex in dependence on polarity of selected solvents

Solute	Solvent				
	Solvation Gibbs energy	Gas phase $\epsilon_r = 1$	Cyclohexane $\epsilon_r = 2.02$	Dichloro- methane $\epsilon_r = 8.93$	Water $\epsilon_r = 78.39$
Benzene	$\Delta G_{\text{elst}}$	0	-0.72	-1.67	-4.7
	$\Delta G_{\text{nels}}$		-2.17	-3.01	0.09
	$\Delta G_{\text{tot}}$		-2.89	-4.68	-4.61
TCNE	$\Delta G_{\text{elst}}$	0	-1.95	-4.61	-10.39
	$\Delta G_{\text{nels}}$		2.69	2.13	6.40
	$\Delta G_{\text{tot}}$		0.74	-2.48	-3.99
TCNE–benzene complex	$\Delta G_{\text{elst}}$	0	-2.06	-4.44	-11.3
	$\Delta G_{\text{nels}}$		3.61	2.43	9.26
	$\Delta G_{\text{tot}}$		1.55	-2.01	-2.04
Dipole moment, $10^{-30}$ C m	$\mu$	5.91	6.16	6.25	6.33
$\Delta(\Delta G_S)^a$ Gibbs solvation energy of complexation	$\Delta(\Delta G_S)_{\text{elst}}$	0	0.61	1.84	4.09
	$\Delta(\Delta G_S)_{\text{nels}}$	0	3.08	3.3	2.47
	$\Delta(\Delta G_S)_{\text{tot}}$	0	3.69	5.14	6.56

<sup>a</sup> Solvation energies of complexation are taken as differences between the energies for the complex and the sum of those for benzene and TCNE:  $\Delta(\Delta G_S) = \Delta G_{\text{complex}} - (\Delta G_{\text{TCNE}} + \Delta G_{\text{benzene}})$ .

larger for DFT calculations. It seems that the value of DFT/6-31G\* dipole moment ( $7.027 \times 10^{-30}$  C m) for the complex in gas phase is too large in comparison with both the SCF/6-31G\* value ( $5.91 \times 10^{-30}$  C m) and the MP2/6-31G\* value ( $5.69 \times 10^{-30}$  C m) indicating that the DFT approach is not probably optimal for describing EDA complexes where distances between constituents are too large and, consequently, electron density between them is very small.

### *Non-Electrostatic Contributions to Solvation Gibbs Energies*

Non-electrostatic solvation Gibbs energies consist of three parts and their B3LYP/6-31G\* values are given in Table VI. The cavitation energy contribution is always positive, being associated with reversible work to form cavity, depends mainly on the size of cavity and polarity of medium as well. The dispersion Gibbs energy of solvation being always negative reflects attractive dispersion energy between electrons of solute molecules and electrons of solvents surrounding the solute. Repulsion Gibbs energy is caused by exchange repulsion energy between electrons of solutes and those of solvent reflecting the Pauli exclusion principle. Total  $\Delta G$  of non-electrostatic solvation energies depends on electron nature of solutes (TCNE, complex), and its values are of positive sign for polar solutes. For nonpolar benzene molecule, the values of  $\Delta G_{\text{nels}}$  are negative.

### *Total $\Delta G_{\text{tot}}$ Solvation Energies and Their Dependence on Solvent Polarity*

Total  $\Delta G_{\text{tot}}$  values for solvation of TCNE, benzene and the complex are sum of their electrostatic and non-electrostatic terms (see Tables IV and V) and are usually negative except for polar solutes (TCNE, complex) in nonpolar solvent (cyclohexane).  $\Delta G_{\text{tot}}$  values have tendency to be more negative with increasing solvent polarity due to electrostatic part of  $\Delta G_{\text{tot}}$  (Tables IV and V) which always increases (in absolute values) with more polar solvents due to increased values of density of induced charges on the cavity surface (Eq. (6)).

Since these charges depend on the value of  $(1 - 1/\epsilon_r)$ , which is greater for more polar solvents, the value of  $\Delta G_{\text{els}}$  will increase (in absolute values) nearly linearly with the solvent polarity function  $f(\epsilon_r)$ . This is really so up to the value of  $\epsilon_r \cong 10$ . However, with more polar solvents, this dependence becomes non-linear (see Figs 3 and 4) since induced charges on the cavity surface depend non-linearly on the solvent polarity factor. Even with unpolarized charge distribution of the solute molecule (where response is

not considered), non-linear dependence with factor  $f(\epsilon_r)$  is still observed. This means that perturbation potential  $\hat{V}(\epsilon, \sigma)$  itself is non-linear in dependence on  $-(1 - 1/\epsilon_r)$ . That is to say that at larger values of potential  $\hat{V}(\epsilon, \sigma)$ , there is a non-linear increase in induced charges  $\sigma(s)$  because of interaction between them which is taken into account in the PCM<sup>17</sup> model to minimize the total energy of solute immersed into a cavity of polarizable continuum. Thus non-linear redistribution of cavity surface charges  $\sigma(s)$  is to great extent caused by electrostatic interaction between charges  $\sigma(s)$  them-

TABLE VI  
B3LYP/6-31G\* values of non-electrostatic contributions to solvation Gibbs energies (in kcal/mol) depending on solvent polarity

Solute	Solvent			
	Solvation Gibbs energy	Cyclohexane $\epsilon_r = 2.02$	Dichloro- methane $\epsilon_r = 8.93$	Water $\epsilon_r = 78.39$
Benzene	$\Delta G_{\text{cav}}$	8.85	8.7	11.66
	$\Delta G_{\text{disp}}$	-15.45	-15.51	-16.86
	$\Delta G_{\text{rep}}$	4.42	3.81	5.29
	$\Delta G_{\text{nels}}$	-2.18	-3.0	0.09
	$\Delta G_{\text{tot}}$	-2.69	-4.21	-3.52
TCNE	$\Delta G_{\text{cav}}$	14.65	14.38	19.22
	$\Delta G_{\text{disp}}$	-13.90	-14.22	-15.08
	$\Delta G_{\text{rep}}$	1.95	2.01	2.28
	$\Delta G_{\text{nels}}$	2.70	2.17	6.42
	$\Delta G_{\text{tot}}$	1.20	-1.26	-1.75
TCNE-benzene complex	$\Delta G_{\text{cav}}$	21.49	21.10	28.24
	$\Delta G_{\text{disp}}$	-22.65	-22.84	-24.69
	$\Delta G_{\text{rep}}$	4.76	4.16	5.71
	$\Delta G_{\text{nels}}$	3.61	2.42	9.20
	$\Delta G_{\text{tot}}$	1.81	-1.40	-0.48
	$\Delta(\Delta G_{\text{S}})_{\text{nels}}$	3.09	3.25	2.75



selves so that the total potential  $\hat{V}(\epsilon, \sigma)$  becomes non-linear with higher values of polarity function  $-(1 - 1/\epsilon_r)$ .

As to values of  $\Delta(\Delta G_S)$ , *i.e.* complexation Gibbs energies due to solvation, their electrostatic, non-electrostatic parts and thus their sums are always positive and their tendency due to change of solvent polarity is dominated by electrostatic contribution. Thus the complex is stabilized by solvent always to a lesser degree than is the sum of stabilization of its constituents. As far as electrostatic contribution to Gibbs energy of solvation  $\Delta(\Delta G_S)_{\text{els}}$  is concerned, its positive value is, due to less intensive electrostatic polarization of the solvent for the complex relatively the sum of electrostatic polarization energies of the solvent due to isolated constituents of the complex. This is understandable since in the complex the part of electrostatic field of constituent molecules that is directed (in planparallel conformation) from one constituent to the other does not polarize directly the solvent. The dependence of positive values of total  $\Delta(\Delta G_S)$  (or its electrostatic solvation part) on  $-(1 - 1/\epsilon_r)$  is also non-linear and this is caused by the above mentioned non-linear dependence of  $\Delta(\Delta G_S)_{\text{els}}$  for individual solutes on the solvent polarity function. Thus the difference of  $\Delta(\Delta G_S)_{\text{els}}$  for the complex and the sum of constituents is also non-linear since the sum of non-linearities of the two constituents prevails over non-linearity of the complex itself.

### *Effect of Solvent Polarity on Equilibrium Complexation Constants*

Complexation constant for TCNE–benzene and other complexes with TCNE in different solvents are given in Table VI.

From the data in Table VII one can conclude that experimental complexation constants decrease by a factor of 1.9–4.3 when less polar chloroform ( $\text{CHCl}_3$ ) ( $\epsilon_r = 4.9$ ) is exchanged for more polar dichloromethane ( $\epsilon_r = 8.93$ ). In the case of the TCNE–hexamethylbenzene complex, the equilibrium constant decreased 9 times when the slightly polar solvent,  $\text{CCl}_4$  ( $\epsilon_r = 2.228$ ), is replaced by polar dichloromethane. We shall try to explain this quite general experimental finding, *i.e.* that  $\pi$ -EDA complexation constants decrease with increasing solvent polarity, by PCM<sup>17</sup> model calculation of the differences in solvation part of the complexation Gibbs energy, *i.e.* in  $\Delta(\Delta G_S)_{\text{tot}}$ . For example, the difference in respective SCF/6-31G\* values (see Table V) for the TCNE–benzene complex in  $\text{CHCl}_3$  and  $\text{CH}_2\text{Cl}_2$  is  $(5.14 - 4.64) = 0.5$  kcal/mol. (The value of 4.64 was interpolated from the SCF/6-31G\*-calculated values assuming linear dependence between  $\Delta(\Delta G_S)_{\text{tot}}$  and  $-(1 - 1/\epsilon_r)$ .)

The corresponding ratio of equilibrium constants for the TCNE–benzene complexation in  $\text{CHCl}_3$  and  $\text{CH}_2\text{Cl}_2$  is

$$\frac{K_1}{K_2} = \frac{K(\text{CHCl}_3)}{K(\text{CH}_2\text{Cl}_2)} = \exp\left(-\frac{(\Delta(\Delta G_S)_{\text{tot1}} - \Delta(\Delta G_S)_{\text{tot2}})}{RT}\right) = \exp\left(\frac{0.5}{RT}\right) \approx 2.3.$$

It is really astonishing that such a rough model for the solvent effect gives results in a good agreement with experiment. If we consider the solvent effect on the experimentally determined equilibrium constant of complexation of TCNE–hexamethylbenzene when nonpolar  $\text{CCl}_4$  solvent is replaced by polar dichloromethane, we obtain that their ratio is 9 (see Table VII). If we take the SCF/6-31G\* calculated values of  $\Delta(\Delta G_S)_{\text{tot}}$  for cyclohexane equal to those for tetrachloromethane, because the solvents have very close  $\epsilon_r$  values ( $\epsilon_r = 2.228$  for  $\text{CCl}_4$  and  $\epsilon_r = 2.023$  for cyclohexane), we obtain the ratio of complexation constants as follows:

$$\frac{K_0}{K_2} = \frac{K(\text{CCl}_4)}{K(\text{CH}_2\text{Cl}_2)} = \exp\left(-\frac{(\Delta(\Delta G_S)_{\text{tot0}} - \Delta(\Delta G_S)_{\text{tot2}})}{RT}\right) = \exp\left(\frac{514 - 369}{298R}\right) \approx 11.6.$$

This value is again in excellent agreement with the experimental ratio. More than that, the dependence of the values of  $K$  on the solvent polarity function is exponential.

When we use B3LYP  $\Delta(\Delta G_S)_{\text{tot}}$  values, we get a smaller ratio of the respective equilibrium constants. We can advise SCF/6-31G\* (PCM<sup>17</sup>) calculations perhaps as more appropriate for the solvent effect on equilibrium constants

TABLE VII

Experimental values of complexation equilibrium constants  $K$  (in  $\text{dm}^3/\text{mol}$ ) for various complexes with TCNE in different solvents at 298 K

EDA complex	$\text{CCl}_4$ $K_0$	$\text{CHCl}_3$ $K_1$	$\text{CH}_2\text{Cl}_2$ $K_2$	$K_1/K_2$
TCNE–benzene		0.25 <sup>a</sup>	0.1 <sup>a</sup>	2.5
TCNE–toluene		0.36 <sup>b</sup>	0.19 <sup>a</sup>	1.9
TCNE–biphenyl		0.73 <sup>a</sup>	0.17 <sup>a</sup>	4.3
TCNE–hexamethylbenzene	170 <sup>c</sup>	–	19.25 <sup>a</sup>	9 <sup>d</sup>
TCNE–styrene		0.65 <sup>a</sup>	0.18 <sup>a</sup>	3.6

<sup>a</sup> Ref.<sup>27</sup> <sup>b</sup> Ref.<sup>28</sup> <sup>c</sup> Ref.<sup>29</sup> <sup>d</sup>  $K_0/K_2$ .

of different associates like those studied here of  $\pi$ -EDA complexes, or stacking planparallel associates, *etc.* in comparison with B3LYP calculations.

At the end of the discussion, we roughly evaluate the entropy of complexation between benzene and TCNE taking into account the MP2 calculated value for enthalpy of complexation in gas phase (-6.8 to -8.95 kcal/mol, see Table I), SCF/6-31G\*-calculated  $\Delta(\Delta G_S)_{\text{tot}} = 5.14$  kcal/mol for dichloromethane as solvent and the experimental value of complexation constant in dichloromethane ( $K = 0.1$ )<sup>27</sup>. We use standard thermodynamic equation for  $K$ , *i.e.*

$$K = \exp\left(-\frac{\Delta G}{RT}\right), \quad (10)$$

where  $\Delta G$  of complexation in solvent is equal to

$$\Delta G = \Delta(\Delta G)_{\text{gas}} + \Delta(\Delta G_S)_{\text{tot}}, \quad (11)$$

where

$$\Delta(\Delta G)_{\text{gas}} = \Delta(\Delta H)_{\text{gas}} - T\Delta(\Delta S)_{\text{gas}}$$

and

$$\Delta(\Delta H)_{\text{gas}} = \Delta E_{\text{gas}} - 3RT.$$

The term  $3RT$  reflects the decrease of the complexation enthalpy due to loss of 6 degrees of freedom when the complex is formed from two molecules.

The complexation enthalpy in gas phase is than

$$\Delta(\Delta H)_{\text{gas}} = -8.2 \text{ kcal/mol} - 1.8 \text{ kcal/mol} = -10.0 \text{ kcal/mol},$$

$\Delta E_{\text{gas}}$  is the MP2-calculated complexation energy (in the range from -6.8 to -8.95 kcal/mol with value -8.2 kcal/mol which takes into account ZPE) in gas phase.  $\Delta(\Delta G)_{\text{tot}}$  is the PCM SCF/6-31G\*-calculated solvation Gibbs energy of complexation and is equal to 5.14 kcal/mol (see Table V). Thus the calculated complexation entropy in gas is

$$\Delta(\Delta S)_{\text{gas}} = \frac{\Delta(\Delta H)_{\text{gas}} + \Delta(\Delta G)_{\text{gas}} + RT \ln K}{T} \quad (12)$$

Thus

$$\begin{aligned} \Delta(\Delta S)_{\text{gas}} &= \frac{-10 \times 10^3 \text{ (cal / mol)} + 5.14 \times 10^3 \text{ (cal / mol)} + 298R \ln 0.1}{298} = \\ &= -20.88 \text{ cal / mol K.} \end{aligned}$$

This value ( $-20.88 \text{ cal/mol K} = -87.36 \text{ J/mol K}$ ) reflects the decrease in entropy due to the formation of one molecule of the complex from two molecules of constituents – benzene and TCNE – in gas phase. SCF/6-31G\* and B3LYP/6-31G\* calculations of the entropy of complexation, where the vibration partition function of the complex plays important role, supply values  $-21.67$  and  $-17.74 \text{ cal/mol K}$ , respectively, which are quite close to the above indicated value based particularly on experiment<sup>+</sup>. We conclude that in gas phase,  $\Delta(\Delta G)_{\text{gas}}$  is negative with the value  $\Delta(\Delta H)_{\text{gas}} - T\Delta(\Delta S)_{\text{gas}} = -3.8 \text{ kcal/mol}$ , overwhelmingly preferring the complexation with the calculated value of equilibrium constant  $K = 600$ . This value, however, dramatically decreases in polar medium of dichloromethane to the above-mentioned value  $K = 0.1 \text{ dm}^3/\text{mol}$  (ref.<sup>27</sup>) thus preferring the formation of solvated constituents over the solvated complex. Perhaps this finding is quite general for  $\pi$ -EDA complexes: the large negative enthalpy of complexation in gas phase decreases by more than half of its value due to a positive entropy contribution of the complexation in gas phase. Still, Gibbs energy of complexation is negative and relatively large so that the complex formation is overwhelmingly preferred. In polar solvents, however, the negative value of  $\Delta(\Delta G)_{\text{gas}}$  is almost cancelled out or even predominated by a positive value of the solvation Gibbs energy of complexation, so that the equilibrium constant of the complex formation might be less than 1, thus preferring isolated solvated constituents to the complex. This phenomenon might be important in strengthening/weakening, *e.g.*, the stability of secondary structure of DNA by stacking planparallel interactions between re-

+ We have been notified by one of referee that the vibration partition function which includes interaction between the solute and the solvent may play a role particularly in the presence of solute–solvent hydrogen bonds. We have neglected this in our PCM-calculations which is the most standard procedure to use the PCM<sup>17</sup> model. However, we keep the referee remark in mind.

spective nucleic acid bases depending on the polarity of medium which is changed when A- or B-forms of DNA are formed or in such processes as DNA replication or transcription for example.

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