QUANTUM-CHEMICAL CALCULATIONS OF DONOR–ACCEPTOR COMPLEXES BETWEEN TETRACYANOETHYLENE AND FIVE-MEMBERED AROMATIC HETEROCYCLES

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In recent years many investigators have become increasingly interested in the theoretical investigation of donor–acceptor complexes or charge-transfer complexes (CTC). A considerable number of papers has been devoted to investigation of such complexes in the benzene series with such acceptors as tetracyanoethylene (TCE), p-benzoquinone, nitro and cyano derivatives of benzene, and many other acceptors [1-7] both by semiempirical methods of calculation and experimentally.

Experimental papers are also known on the charge-transfer complexes of heteroaromatic systems, including thiophene and its derivatives [8] and furan, selenophene, and tellurophene and their derivatives [9] in particular, as donors with TCE and a series of other acceptors. However, there have been very few quantum-chemical calculations in this region. For example, in [10, 11] calculations were made for the charge-transfer complexes of pyridine + TCE and thiazole + TCE, respectively.

As known, one of the important and difficultly resolved experimental tasks is the problem of establishing the geometry of charge-transfer complexes, which is of some importance for understanding their nature.

This problem can, however, be solved by quantum-chemical methods of calculation. At the same time, the question of the adequacy of these approaches is the subject of debate. Let us consider, for example, the benzene + TCE system, which has been well studied both experimentally and by quantum-chemical methods such as the CNDO/2 method, the MINDO/2 method, the extended Hückel method (EHM), the Pople π-electron method with allowance for doubly excited configurations (CE2), and the PCILO method. The data from these calculations with reference to the stabilization energy ΔE and R_{eq} are given in Table 1. These data relate to the most stable geometry of the benzene + TCE charge-transfer complex (IB).

Scheme 1

IA   IB

As seen from comparison of the calculated data for the energy of stabilization with the experimental values, none of the presented methods of calculation gives satisfactory results. The R_{eq} value for this system was not determined experimentally on account of the difficulty of such a task, although it is known that in crystals the molecular separations in the charge-transfer complex vary between 3.0 and 3.5 Å [18].

In the present work by the semiempirical LCAO-MO SCF method in the CNDO/2 approximation with separation of the full energy into one-center and bond components we undertook calculations of ΔE and R_{eq} for the charge-transfer complexes (IA) and (IB) and also for the complexes of TCE with the five-membered heteroaromatic molecules of furan and thiophene as donors. In the calculations it was assumed that the geometry of the donor and the acceptor does not change during complex formation, and only the distance between the planes of the donor and the acceptor was varied. The standard parametrization of the CNDO/2 method [20, 21] was used in the calculations. The investigated isomeric structures, which differ in the mutual arrangement of the heteroaromatic donor and acceptor, are given in Scheme 2. The

TABLE 1. Energies of Stabilization ΔE and R_{eq} for the Charge-Transfer Complex of Benzene + TCE, Calculated by Various Methods

Method of calculation	ΔE_{stab}, kcal/mole	R_{eq}, Å	Reference
CNDO/2	−125	1.75	[12]
MINDO/2	Complex not		[13]
EHM	stabilized		[14]
Pople π-electron method (CE2)	−1.8	3.5	[6]
PCILO	−22.5	2.20	[15]
Experimental value	−2.30; −3.34; −6.6±3		[7, 16, 17]

results from the calculations, obtained by the direct CNDO/2 method and by a modified CNDO/2 method for the charge-transfer complexes of benzene, thiophene, and furan with TCE, are given in Table 2.

Scheme 2

| A | B | C | D | E | F |

II x-S, III x=O
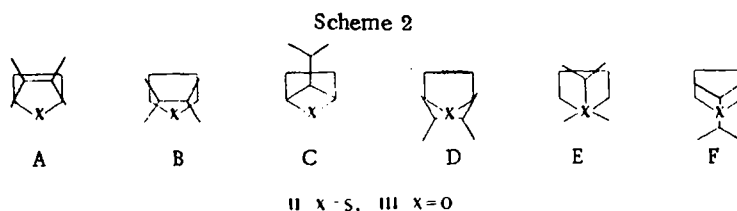
As expected, the ΔE values obtained in the calculation were very high. The equilibrium separations were too low. The reason for this was pointed out in [23] and lies in the too high values for the bond parameters in the CNDO/2 method. In order to correct this discrepancy, at least in the intermolecular region, a modification of the CNDO/2 method was proposed in [24] for calculation of the energetics of donor—acceptor complexes. In this method, with retention of the standard parametrization, the matrix elements $H_{\mu\nu}$ between the AOs, μ and ν, belonging to various molecules were calculated as follows:

$$H_{\mu\nu} = \frac{1}{2} C(\beta_A^0 + \beta_A^0) S_{\mu\nu}, \tag{1}$$

and a perfectly reasonable value for the energy of complex formation ΔE was obtained for C = 0.6.

A disadvantage of such an approach is the need to undertake many series of calculations in order to select the value of C.

In the present work, therefore, a different modification of such an approach is proposed on the basis of the concept of dividing the full energy of the system into one- and two-center components [21]:

$$E_{gen} = \sum_a E_a + \sum_a \sum_b E_{ab}. \tag{2}$$

In this case the energy of complex formation ΔE can be represented in the following form:

$$\Delta E = \left(E'_D + E'_A + \sum_{a \in D} \sum_{b \in A} E_{ab} \right) - (E_D + E_A), \tag{3}$$

where E_D and E_A are the energies of the free donor and acceptor; E_D' and E_A', their energies but in the complex; and E_{ab}, the two-center components of the full energy due to interaction between the atoms of the donor and the acceptor. In turn E_{ab} can be expressed in terms of the sum of the individual components due to specific forms of interaction between the donor and the acceptor:

$$E_{ab} = E_{ab}^{RR} + E_{ab}^{VV} + E_{ab}^{JJ} + E_{ab}^{KK} + E_{ab}^{NN}, \tag{4}$$

where RR, VV, JJ, KK, and NN relate to the resonance, electron—nucleus, electron—electron, exchange, and core components of the interaction energy, respectively.

In such an approach the formal modification of the scheme presented in [23] involves the introduction of some empirical coefficient $K_R < 1$, i.e.,

TABLE 2. Energies of Stabilization ΔE and R_{eq} Values Obtained by the Direct CNDO/2 Method and by the Modified CNDO/2 Method for K_R = 0.78 for the Charge-Transfer Complexes of Benzene, Thiophene, and Furan with TCE

	Direct CNDO/2 method			Modified CNDO/2 method	
geometry	ΔE, kcal/mole	R_{eq}, Å	geometry	ΔE, kcal/mole	R_{eq}, Å
I A	−156.8	1.7	I A	−7.1	2.4
I B	−136.4	1.7	I B	−7.5	2.4
II A	−213.5	1.6	II A	−9.6	2.4
II B	−284.9	1.6	II B*	−19.0	2.2
II C	−180.9	1.6	II C	−9.0	2.4
II C	−125.9	1.8	II D	< −8.2	>2.6
II E	−154.0	1.7	II E	−14.8	2.4
II F	−115.2	1.7	II F	−8.9	2.6
III A	−86.4	1.8	III A	−5.4	2.4
III B	−153.4	1.6	III B	−10.3	2.2−2.4
III C	−11.1	1.8	III C*	< −2.9	>2.6
III D	−88.9	1.6	III D*	< −3.9	>2.6
III E	< −48.7	<2.0	III E	−4.3	2.4
III F	−51.9	1.7	III F*	< −1.9	>2.4

*Divergence of the iteration process at large separations.

$$E_{ab}{}^{RR} = \frac{1}{2} K_R H_{\mu\nu} P_{\mu\nu} \ (\mu \in a, \ \nu \in b) \tag{5}$$

(where $P_{\mu\nu}$ is an element of the bond order matrix) in front of the term E_{ab}^{RR} ($a \in D$, $b \in A$) with retention of the numerical values for the remaining components of the interaction energy.

The possibility of using such an approach was based on the introduction of a series of assumptions about the character of the interaction in donor—acceptor complexes and of the fragmentation of the energy in them. The main assumption is the fact that the charge density-bond order matrices in the calculation with C < 1 in (I) and with C = 1 (the standard CNDO/2 method) do not differ very greatly. This can be fulfilled when C or, in our proposed variant, K_R do not differ too greatly from 1. The results of this assumption are: 1) the assumption that the changes of E_D and E_A with small changes in the size of the transferred charge approximately compensate for each other; 2) the sum of the last four terms in Eq. (4) is substantially less than E_{ab}^{RR}. Our analysis showed that these assumptions are fulfilled sufficiently satisfactorily beginning with $R_{DA} \geq 2$ Å, i.e., calculation within the scope of the procedure proposed in the present work will give the greatest deviation from the results of more correct methods in the initial part of the Morse curve, with small distances between the donor and the acceptor, and not in the region of the minimum, which (as will be shown below) lies in the region where $R_{DA} > 2$ Å.

The selection of the K_R value was made for the benzene + TCE system in the conformation (IB) so as to describe known experimental data on their energies of complex formation with the greatest possible accuracy. For K_R = 0.78 we obtained the energy ΔE = −7.5 kcal/mole and R_{DA}^{eq} = 2.4 Å, and this reproduces the existing experimental data on ΔE (from −2.5 to −6.6 kcal/mole [7, 16, 17]) fairly satisfactorily. As far as R_{DA}^{eq} is concerned, it is rather less than the values discussed in the literature (~3−3.5 Å), but (as already mentioned [18]) these data relate to crystals.

By means of the value K_R = 0.78 we calculated the other donor—acceptor complexes examined in the present work. The results of these calculations are given in Table 2.

From comparison of the data in Table 2 for the benzene + TCE charge-transfer complex it can be seen that the proposed modification of the method gives satisfactory results. Thus, the energy of stabilization ΔE for the geometry of (IB) is equal to −7.5 kcal/mole (R_{eq} = 2.4), and this is much closer than the other calculated results to the experimental value of ΔE given in Table 1. The experimental value varies between −2.3 and −6.6 kcal/mole, depending on the method used.

It is not possible to compare ΔE obtained in the present work for the most stable isomers of the thiophene + TCE (IIB) and furan + TCE (IIIB) charge-transfer complexes directly with the experimental value, since the ΔE values of these complexes were not determined experimentally.

TABLE 3. Energies of Stabilization ΔE and the R_{eq} Values of the Complexes in Solvents with ε = 10, 20, and 80 in Their Most Stable Conformations

Geometry	R_{eq}	ΔE for ε=10	ΔE for ε=20	ΔE for ε=80
IP	2,0	−44,8	−47,8	−50,0
IB	2,2	−31,8	−33,0	−34,2
IIA	2,0	−48,1	−50,8	−53,5
IIB	1,8	−78,3	−84,0	−89,6
IIC	2,0	−43,5	−46,1	−48,8
IID	2,2	−30,1	−32,4	−32,9
IIE	2,2	−44,0	−45,5	−46,9
IIF	2,0	−37,4	−40,4	−43,5
IIIA	2,0	−31,4	−33,9	−36,5
IIIB	2,0	−45,8	−48,0	−50,2
IIIC	2,0	−20,5	−22,7	−25,0
IIID	2,0	−19,5	−21,3	−23,0
IIIE	2,4	−14,3	−14,8	−15,2
IIIF	2,2	−13,4	−14,2	−15,0

However, the ΔH values are known for the $CO(CN)_2$ + thiophene and $CO(CN)_2$ + furan charge-transfer complexes [19], on the basis of which we can approximately determine the value in which we are interested. Thus, the electron affinity of an acceptor with two CN groups can be considered approximately equal to 1 eV [23], and since the donors are the same, it can be expected that ΔE in the case of TCE will be approximately twice as large, i.e., close to the values which we obtained.

The proposed approach makes it possible not only to calculate the "gas-phase" characteristics of the donor—acceptor complexes but also at a semiquantitative level to estimate the effect of the solvent on ΔE and R_{DA}^{eq}. In fact, in Eq. (4) the terms E_{ab}^{VV}, E_{ab}^{JJ}, and E_{ab}^{NN} which determine the coulombic interaction between the atoms of the donor and the acceptor, must depend on the dielectric constant of the solvent. Functionally, such a relationship can be expressed by multiplying the above-mentioned terms by f(ε), which (according to Kirkwood's theory) is defined as follows:

$$f(\varepsilon) = \frac{1+\varepsilon}{2\varepsilon} .$$

The results from the calculations on the investigated complexes in their most stable conformations in solvents with ε = 10, 20, and 80 are given in Table 3.

As expected from a priori considerations, increase in the polarity of the solvent leads to a significant increase in ΔE and to some decrease in R_{DA}^{eq}.

Thus, the procedure proposed in the present work for calculation of the energetics and geometry of donor—acceptor complexes gives quite real estimates of the indicated values both in the gas phase and in a polar solvent. It may prove useful in the calculation of the physicochemical characteristics of the investigated complexes.

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FORMATION OF HETEROCYCLIC ISOSTERES OF INDENONE IN THE REACTION OF THE σ DERIVATIVES OF IRON WITH TOLANE

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In a number of cases the reaction of σ derivatives of transition metals with acetylenes is accompanied by cyclization reactions, in which one or several molecules of the acetylene and various fragments of the organometallic compound participate. Often it is the formation of new C—C bonds which becomes the main direction of these reactions [1]. In the literature there are few data on the reactions of alkyl and aryl σ derivatives of iron leading to the formation of the products from cyclooligomerization in the coordinated and free state [2-4].

In order to study the reactivity of our previously synthesized heterocyclic σ derivatives of π-cyclopentadienyldicarbonyliron [5] we investigated the reaction of these compounds and of the isosteric σ-benzoylcyclopentadienylcarbonyliron [6] with diphenylacetylene (tolane). It was found that the photochemical reaction of the acyl σ derivatives (Ia-d) with tolane gives 2,3-diphenylindenone (IIa) and its hetero analogs (IIb-d) and also the products from photochemical decarbonylation (IIIa-d):
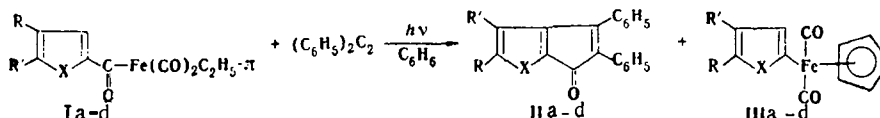
I—III a R=R′=H, X=—CH=CH—; b R=R′=H, X=S; c R=CH₃, R′=H, X=O;
d RR′=—CH=CH—CH=CH—, X=O

Under these conditions the furoyl σ derivative (Ie) (R = R' = H, X = O) does not react with tolane, and the only product is the decarbonylated σ derivative (IIIe).

Until now the heterocyclic analogs of indenone have been unknown. The published data [7-9] concern the isosteres of indanones containing a hydrogenated five-membered ring.

The structure of compounds (IIb-d) is confirmed by elemental analysis and IR, UV, and mass spectra (Table 1). In the IR spectra of compounds (IIa-d) at 1710 cm^{-1} there is a strong absorption band corresponding to the stretching vibrations of the CO group. In the UV spectra the thia- and oxaindenones (IIb-d), like 2,3-diphenylindenone (IIa), have a strong absorption maximum at about 265 nm and a low-intensity absorption maximum in the visible region. Substitution of the benzene ring by the heterocycle gives rise to a bathochromic shift of the long-wave absorption maximum by 30-35 nm for the oxaindenones (IIc, d) and by 60 nm for the thiaindenone (IIb) in comparison with the spectrum of compound (IIa). The