On the Validity of the Mulliken-Type Model in Describing the Benzene-Tetracyanoethylene Complex

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The validity of the classical Mulliken model of electron donor-acceptor complexes is examined for the benzene-tetracyanoethylene (TCNE) complex. Some theoretical predictions based on this model are verified by means of the CNDO/S CI-1 method. The observed discrepancies are analysed with the aid of configuration analysis. The Mulliken model is shown to be too crude for a quantitative description of the benzene-TCNE supermolecule. A comparison between the experimental and theoretical data is made.

1. Introduction

Electron donor-acceptor (EDA) complexes belong to a class of compounds, which is of a great interest for experimental and theoretical research. Since the classical works of Mulliken [1] many calculations concerning these complexes have been performed, based on semiempirical quantum methods such as: CNDO/2 [2, 3], PCILO [4], PPP [5, 6] and INDO [7, 8]. Recently, some ab initio calculations have been also carried out for tetrathiofulvalene-7,7,8,8-tetracyanoquinodimethane [9] and benzene-tetracyanoethylene (TCNE) [10] systems. However, results of these calculations are rather dubious when compared with experimental data.

The relative conformation of the donor and acceptor moieties and the influence of this on the energy of the charge transfer (CT) excited state of the complex is one of the problems that we expect to be solved by quantum mechanical considerations. On the other hand, a comparison between the predictions of a simple Mulliken theory and the results of more sophisticated calculations seems to be interesting. For this purpose we have chosen the benzene-TCNE complex because of its high symmetry, accurate UV data available and possibility of comparison with other reported calculations [2–6, 10].

The recently developed configuration analysis (CA) was found to be useful in the evaluation of the reliability of "molecules-in-molecule" (MIM) models applied to π-electron systems [11]. In this paper we try to determine the degree of appropriateness of the Mulliken-type model in describing the electronic structure of the benzene-TCNE complex. In order to elucidate this problem, the all-valence configuration analysis is applied to the results provided by the CNDO/S method.

2. Computational Method

The calculations were carried out with Ellis et al. parametrization [12] and CI procedure taking into consideration 140 singly excited configurations. The geometry of the considered complex was obtained from MNDO [13] optimized bond lengths and angles of the benzene and TCNE molecules. Two possible conformations were taken into account (Fig. 1); in both of them the planes of the benzene

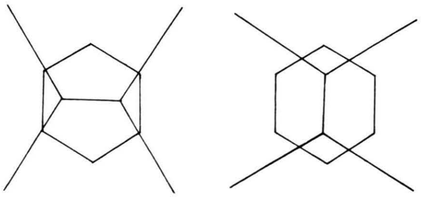

Fig. 1. Two possible conformers of the benzene-TCNE complex.

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and TCNE moieties were maintained parallel to each other.

The wavefunction of the ground state of the complex was projected onto the wavefunctions corresponding to the non-bonded (NB), charge transfer (CT) and localized excitation (LE) configurations.

3. The Mulliken-Type Model

The Mulliken model is one of the traditional approaches to describe the electronic structure of EDA complexes. It is based essentially on the MIM method. In the Mulliken model the ground state wavefunction arises from a combination of the non-bonded $|\mathrm{NB}\rangle$ configuration and the charge transfer $|\mathrm{CT}\rangle$ configuration:

$$|\mathrm{G}\rangle = |\mathrm{NB}\rangle \cos \varphi + |\mathrm{CT}\rangle \sin \varphi . \tag{1}$$

By the same token the excited state wavefunction can be written as an appropriate orthogonal complement:

$$|\mathrm{E}\rangle = - |\mathrm{NB}\rangle \sin \varphi + |\mathrm{CT}\rangle \cos \varphi . \tag{2}$$

Oftentimes the assumption is made that it is enough to take into consideration only one CT configuration arising from electron transfer from an occupied orbital of the donor to a virtual orbital of the acceptor. Other CT states as well as LE states are usually neglected.

In the case of the investigated complex the $|\mathrm{CT}\rangle$ configuration corresponds to a HOMO (π benzene) → LUMO (π TCNE) electronic transition (Fig. 2).

The following expectations can be verified while examining the validity of the Mulliken model:

1. From (1) and (2), by application of the ZDO approximation and symmetry conditions we can get

$$\left(\frac{\mu_{\mathrm{GE}}}{\mu_0}\right)^2 + \left(\frac{\mu_{\mathrm{G}}}{\mu_0} - \frac{1}{2}\right)^2 = \left(\frac{1}{2}\right)^2 , \tag{3}$$

where μ_{GE} is the transition dipole moment between $|\mathrm{G}\rangle$ and $|\mathrm{E}\rangle$ states, μ_{G} is the dipole moment of the ground state $|\mathrm{G}\rangle$ and $\mu_0 = e \cdot R$, where R is the interplanar separation between the benzene and TCNE moieties. Thus a plot of the μ_{GE}/μ_0 vs. μ_{G}/μ_0 should be a hemicircle.

2. The energy of the $|\mathrm{G}\rangle \rightarrow |\mathrm{E}\rangle$ electronic transition can easily be derived from (1) and (2) and written as

$$E_{\mathrm{GE}} = (E_0^2 + 4 V^2)^{1/2} , \tag{4}$$

where E_0 is the energy difference between the $|\mathrm{NB}\rangle$ and $|\mathrm{CT}\rangle$ configurations, and $V = \langle \mathrm{NB} | \hat{\mathrm{H}} | \mathrm{CT} \rangle$. Both E_0 and V can be evaluated by means of the CNDO/S Hamiltonian, and the related E_{GE} value can be compared either with that calculated directly by the CNDO/S method or the experimental one.

3. We cannot leave out of consideration the fact that the $\pi - \sigma$ electron separation is not strictly preserved in such EDA complexes as the benzene-TCNE supermolecule. Regardless of this it is still possible to distinguish between π and σ orbitals by taking into account the local symmetry of the donor and acceptor molecules. Since the $|\mathrm{CT}\rangle$ state follows from a $\pi \rightarrow \pi^*$ type transition we should expect that formation of the complex from isolated molecules will not involve any change in the σ electron densities. Moreover, we can expect that due to the symmetry of the benzene HOMO orbitals the change in the π electron densities on the benzene carbon atoms which are positioned perpendicular to the long axis of the TCNE molecule will not be considerable.

Verification of the above predictions sets forth three clearly defined objectives of our CNDO/S calculations on the benzene-TNCE complex.

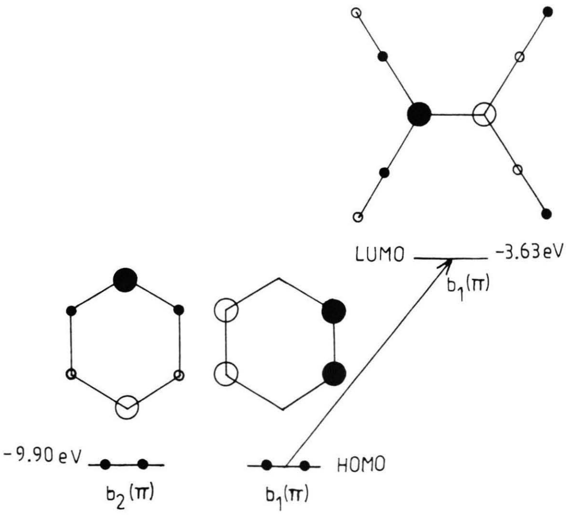

Fig. 2. HOMO and LUMO orbitals of the benzene-TCNE EDA complex. (Electric transition responsible for the $|\mathrm{CT}\rangle$ state is marked with an arrow.)

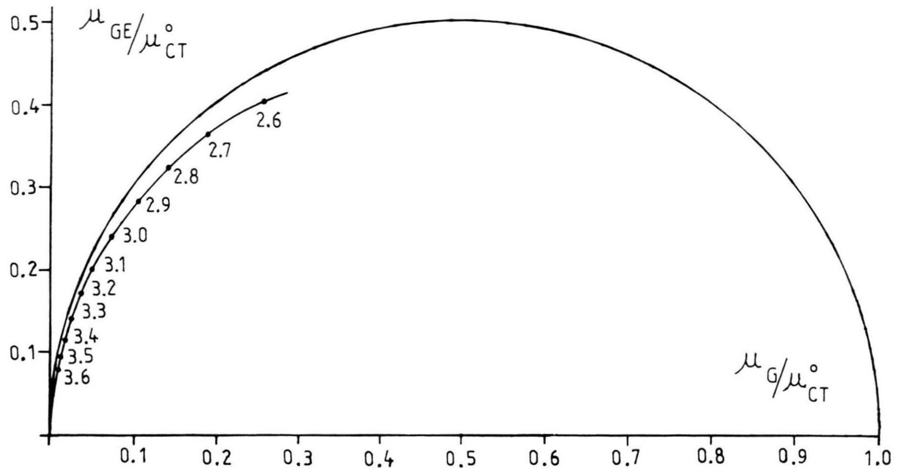

Fig. 3. Plot of μ_{GE}/μ_0 vs. μ_G/μ_0. (μ_{GE} and μ_G are taken from the CNDO/S calculations performed in the range of $R = 2.6-4.0$ Å, every 0.1 Å.)

4. The CNDO/S Calculations

1. In Fig. 3 a plot of μ_{GE}/μ_0 vs. μ_G/μ_0 is presented. At distances encountered usually in EDA complexes, i.e. 3.0–3.4 Å, the deviation of the calculated relationship from hemicircularity is small. This means that the effects from configurations other than $|CT\rangle$ on the calculated CNDO/S dipole moment of the ground state as well as the transition dipole moment between the ground and excited states are negligible. This, however, is not valid at smaller distances.

2. The transition energy between the $|G\rangle$ and $|E\rangle$ states was calculated both by the CNDO/S method and by means of (4). The results are shown in Figure 4. It is evident that the Mulliken-type model overestimates the energy, the deviation from the CNDO/S results reaching 3000 cm^{-1} (0.4 eV) at distances 3.0–3.4 Å. This effect stems from admixture of other configurations, which stabilizes the $|E\rangle$ state more than the $|G\rangle$ state. For this we must be careful in the interpretation of all the calculations based on Mulliken-type models. They yield a rather poor quantitative description of the observed UV spectra of EDA complexes.

3. The occurrence of the aforementioned mixing becomes apparent also in the analysis of the CNDO/S electron density distribution (Figure 5). The changes of the σ electron densities are as large as the changes of the π electron densities, which is doubtless contrary to the expectations based on the

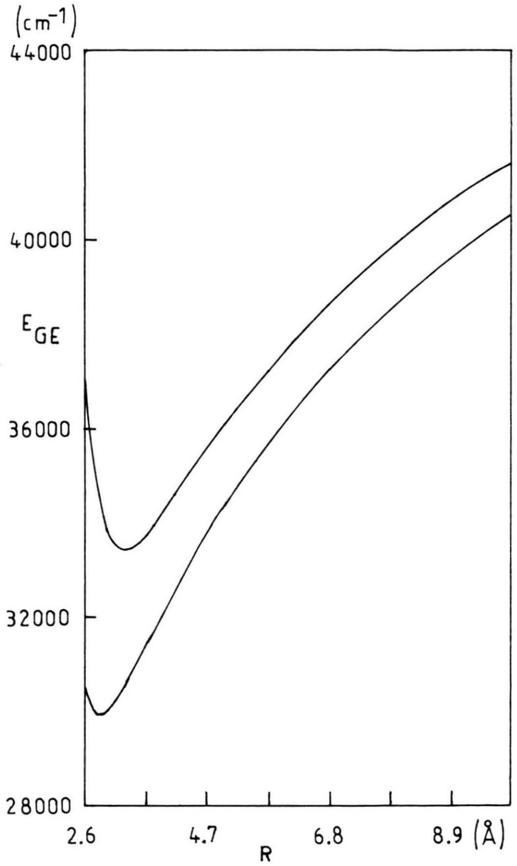

Fig. 4. The transition energy between the $|G\rangle$ and $|E\rangle$ states. The upper curve reflects the CNDO/S results, the lower curve illustrates the results obtained from (4). (The spanned range of the distance R is 2.6–10.0 Å.)

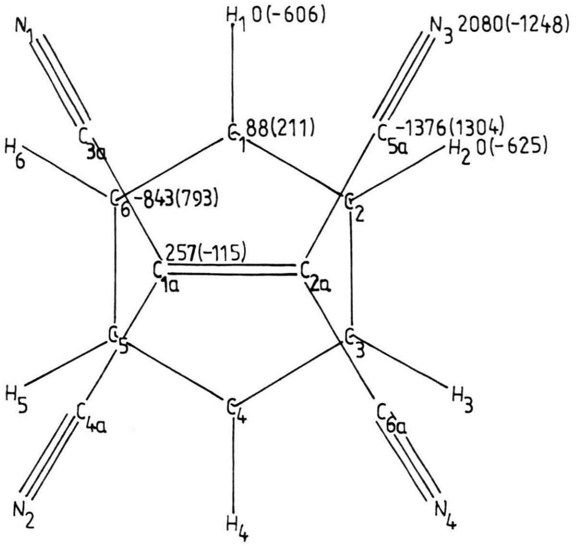

Fig. 5. Electron density changes on individual atoms accompanying the formation of the EDA complex from isolated molecules ($R = 3.2$ Å). The values without parentheses correspond to π-electron densities, those in parentheses to σ-electron densities. The given numbers should be multiplied by 10^{-6}.

Table 1. Contributions (in %) from individual configurations to the ground state of the benzene-TCNE complex.

Configurations	Intermolecular distance R		
	3.0 Å	3.2 Å	3.4 Å
Non-bonded $\|NB\rangle$	90.9860	95.8044	98.1039
HOMO → LUMO CT $\|CT\rangle$	5.9719	2.9069	1.3382
Other CT (B → TCNE)	1.4005	0.6069	0.2396
CT (TCNE → B)	0.8368	0.3863	0.1708
LE (TCNE)	0.4647	0.1167	0.0271
LE (B)	0.0344	0.0144	0.0074
Sum	99.6942	99.8356	99.9869

Mulliken-type model. Moreover, the π electron density change on the C_1 and C_4 atoms is non-zero. Therefore we can draw the conclusion that a considerable amount of the $\sigma \rightarrow \pi^*$ and $\pi \rightarrow \sigma^*$ configurations is involved in mixing with the $|NB\rangle$ and $|CT\rangle$ states.

5. The Configuration Analysis

The results presented in Sect. 4 are supported by the configuration analysis (CA) of the CNDO/S wavefunction of the ground state of the complex. We performed this analysis for three interplanar distances of R (Table 1). The results indicate crudeness of the Mulliken approach at least as to the interplanar separations typical for the EDA complexes. The contributions from configurations other than $|CT\rangle$ are considerable and become even larger with shortening of the distance R. These configurations include states arising from electron transfer to higher TCNE orbitals, "back-CT states", as well as local excitations (LE) of the TCNE molecule. The completeness of the projection of the ground state of the complex onto the CT and LE type configurations is always greater than 99%, which provides a reasonable argument for performing of the CA. We face here a much better situation than for instance in the PPP/MIM treatment of polycyclic hydrocarbons where the completeness is only of the order of 80–95% [11].

In conclusion we can say that in the case of the benzene-TCNE complex the Mulliken approach appears to be a very crude model and that the results obtained from this model are inconsistent with the results provided by the SCF/CI-1 method.

6. Comparison of the CNDO/S Results with the Experimental Data

The considerations in the previous sections center around the comparison of two computational models. This makes sense only when there is also a possibility to compare both models with the experimental data.

Analysis of the Raman spectra [14] and the temperature dependence of the UV absorption spectra [15] points to an almost free rotation of the TCNE molecule with respect to the molecules of aromatic hydrocarbons in the EDA complexes. Theory leads to the same conclusion. For instance, the CNDO/2 method gives for the energy difference between the two possible conformers 0.134 kcal/mole [3]. In the case of the CNDO/S method the difference is 0.182 kcal/mole ($R = 3.2$ Å), and the calculations predict that among the two conformers the more stable one is that in which the long axes of the donor and acceptor molecules are perpendicular to each other.

The dipole moment resulting from the CNDO/S calculations is 0.52 Debye ($R = 3.2$ Å), a value comparable with that obtained from an ab initio calculation [10]. The experimental data [16] show up a value of μ that is of the order of 1 Debye.

The most important quantity that can be confronted with the experimental data is the CT transition energy. For this distance R in the range of 3.0 – 3.5 Å, typical for this kind of complexes, the calculated energy is 30000 – 31000 cm^{-1}, while the value measured for the gas phase equals 28950 cm^{-1} [17] or 29590 cm^{-1} [18]. This good agreement testifies in favour of the CNDO/S method.

7. Conclusions

The undertaken analysis shows that it is necessary to replace the traditional calculations based on the Mulliken model by more advanced calculations. It seems that the CNDO/S method in its present version provides a good compromise between the required accuracy level and the aspect of time-consumption. It should be mentioned that this method has been found to work well enough also for other EDA complexes [19]. On the other hand, the presented results confirm the usefulness of the configuration analysis in testing the appropriateness of the approximations made in the models that are developed on the basis of the MIM method.

Acknowledgement

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