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A CNDO/S STUDY ON THE ALKYLBENZENE–TCNE COMPLEXES

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Abstract—The calculations based on the semiempirical CNDO/S Hamiltonian appeared useful in predicting the electronic structures of electron donor–acceptor (EDA) complexes of tetracyanoethylene (TCNE) and various alkylbenzenes. The results are in satisfactory agreement with the experimental data. The calculated complex stabilization energies are related to the experimental gas phase enthalpies of formation by linear regression ($r = 0.941$). A fairly good correlation ($r = 0.985$) between the measured and calculated energies of the charge transfer (CT) electronic transitions is established. The problem of double CT absorption bands is discussed by referring to the theoretical results. The ionization potentials of alkylbenzenes calculated by CNDO/S and MNDO methods are considered as well.

EDA complexes form a class of compounds with intriguing properties, that is under both experimental and theoretical intensive study. In general, two problems concerning the EDA complexes are of a great interest: the conformation in the ground electronic state and the electronic structure of the excited states. The first attempt ever made to elucidate the nature of these compounds was due to Mulliken and Person.[1] Their approach has been used many times to calculate the excited energy states of a number of EDA systems.[2] However, more advanced calculations point out that Mulliken-type models have an intrinsic inability to estimate the properties of the complex to an acceptable accuracy.[3] Therefore, the calculations making use of the semiempirical ZDO methods, especially the all-valence ones, should be preferred.

In this paper the CNDO/S calculations for the complexes formed by TCNE with divers alkylbenzenes are presented. For each complex two conformations X and Y (Fig. 1) are considered. The calculations yield the stabilization energies, the dipole moments of the ground state and the energies of the electronic transitions. Values of the ionization potentials for alkylbenzenes are available, as well.

COMPUTATIONAL PROCEDURE

The geometry of single TCNE and alkylbenzene molecules was evaluated in calculations employing the MNDO method.[4] For each molecule a C_s symmetry was assumed during the MNDO geometry optimization. Different EDA complexes of TCNE with benzene, toluene, *o*-xylene, *p*-xylene, mesitylene, durene and hexamethylbenzene were taken into consideration and in each case the TCNE and alkylbenzene moieties were maintained parallel to one another. The intermolecular distance of 3.4 Å was assumed to be in line with X-ray data.

After CNDO/S SCF iterations, making use of Ellis *et al.*'s parametrization,[5] the CI-1 procedure involving 140 configurations was performed. The total energy of the ground state was calculated within "the hole approximation", e.g. assuming the core–core repulsion is equal to a product of the core charges and the two-centre electron repulsion integral.

All the computations were carried out on CDC 6600 and CDC 175 machines located at Regional Computer Center "Cyfronet" (Cracow) and Rechenzentrum, Bochum University.

RESULTS AND DISCUSSION

The gas phase measurements of the enthalpy of formation[6,7] yield results indicating that there is an increasing stability of the EDA complexes in the series from benzene to hexamethylbenzene. The values of ΔH are within the range 6–11 kcal mol^{-1}. The considered CNDO/S calculations strongly support these results. The calculated energies of stabilization should be derived from the ground state energies of the complex

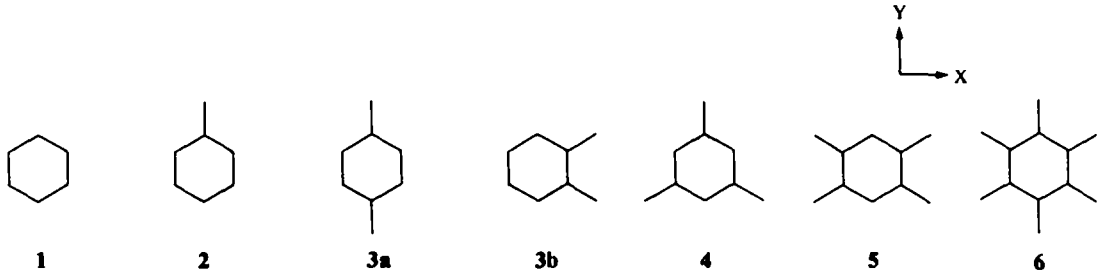

Fig. 1. The investigated alkylbenzene molecules. For each molecule two conformers, denoted as X and Y, are considered. In these conformers the long axis of the TCNE molecule is parallel to the *X*- or *Y*-axis, respectively.

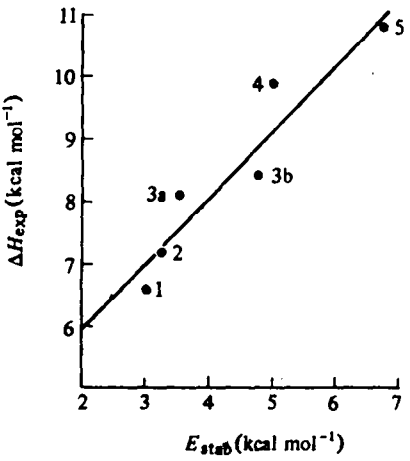

Fig. 2. The correlation between experimental and calculated stabilities of the complexes.

and the separated molecules, covering the range 3–7 kcal mol^{-1}, rise with increasing degree of methylation. It should be noted that the calculated values do not include the van der Waals dispersion interactions, which give an additional contribution of 2–4 kcal mol^{-1} to the stabilization energy of the complex.[8,9] Moreover, the theoretical values refer to the potential energy at 0 K, whereas the experimental data provide the value of the enthalpy at ambient temperature. Despite this, the correlation between the calculated and the experimental energies is satisfactory ($\Delta H = 1.051 E_{stab} + 3.857$, $r = 0.941$, Fig. 2) and makes possible the estimation of the EDA complex stability within the CNDO/S method.

The calculated dipole moments of the ground state appear to be within the range 0.25–0.80 D and are mostly underestimated. This discrepancy is likely to be caused by an inaccurate choice of the assumed intermolecular distance (reduction of R from 3.4 Å to 3.2 Å almost doubles the calculated dipole moment) of the TCNE–benzene complex and by the fact that the experimental determinations are carried out for solutions. For instance, for the TCNE–hexamethylbenzene complex the values are as follows: measured, $\mu = 2.1$ D;[10] calculated, $\mu = 0.39$ D.

The calculations that have been performed for both X and Y rotational conformers take into account the problem of their relative stability. The energy difference values obtained in the CNDO/S method for such conformers are less than 0.2 kcal mol^{-1}. This is explicit evidence that in the considered complexes we deal with almost free rotation of the counterparts. Moreover, it is also confirmed by the experimental[11] and other theoretical results.[8]

The question of the rotational conformers in the EDA complexes is connected with the problem of double CT bands observed in their UV absorption spectra. The occurrence of these bands in the spectrum has been associated with transitions from the first and second highest occupied donor orbitals to the lowest empty orbital of TCNE[12] and/or with the existence of rotational isomers.[13] Recently, direct experimental evidence has been provided for the existence of two different geometries responsible for the observed different bands.[14] The CNDO/S calculation predicts two low energy CT transitions for each X and Y conformation. The energy splitting between them is about 200 cm^{-1} for benzene and rises to 5000 cm^{-1} for the *p*-xylene complex. It results from lifting of the degeneracy of the HOMO and HOMO-1 orbitals of methylbenzenes caused by the influence of their Me groups and by the difference in magnitude of the interaction between these orbitals and the LUMO orbital of TCNE. This is the reason for the calculated small splitting for benzene, mesitylene and hexamethylbenzene complexes in which the donor has degenerate orbitals. Thus, for each complex we have four CT transitions in the region 24,000–31,000 cm^{-1}: two for the X and two for the Y conformation. Two of the bands are calculated as weak and two as strong. If the transition of higher energy is predicted as strong for the X isomer, the transition of lower energy is strong for the Y isomer, and vice versa (Fig. 3). In effect the observed double bands correspond to different rotational conformers, this is fully supported by experiment. For benzene–, mesitylene– and hexamethylbenzene–TCNE complexes the separation between the bands is very small and only one band is observed in the UV spectrum.[6,7]

The calculated energies of the CT transitions can be compared with the experimental values, which are available from deconvolution of the gas phase UV

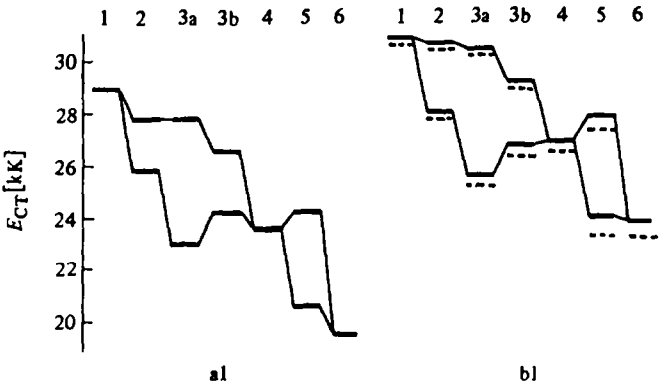

Fig. 3. The energies of the CT transitions: (a) experimental; (b) calculated, the broken lines denote the transitions of weak intensity.

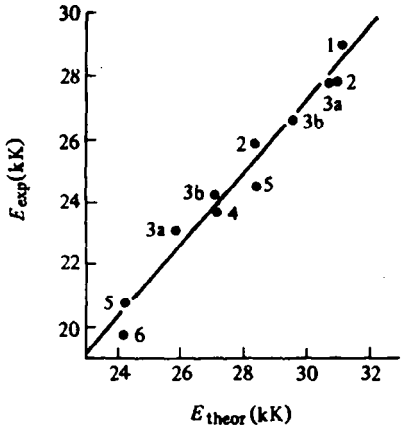

Fig. 4. The calculated vs experimental energies of the CT transitions.

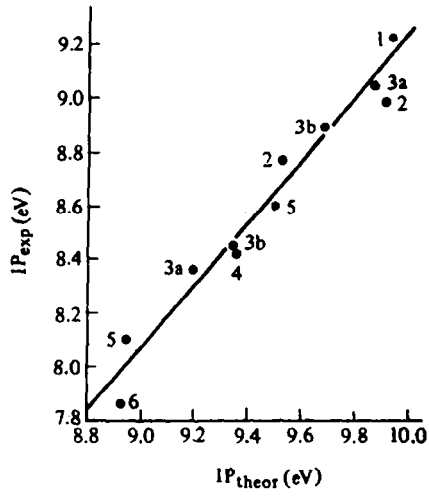

Fig. 6. The correlation between the experimental and the CNDO/S IPs for alkylbenzenes.

spectra.[15] Although all the calculated values are too large, the difference never exceeds 4000 cm^{-1} (0.5 eV). However, a good linear correlation between the calculated and experimental energies exists ($E_{exp} = 1.167E_{calc} - 7670$, $r = 0.985$, Fig. 4). The mean square error between such scaled theoretical and experimental values is 500 cm^{-1}. It should be noted that the experimental error was claimed to be ± 150 cm^{-1}.[6]

It is well known that the energy of the CT transition depends mainly on the difference between the ionization potential (IP) of the donor and the electron affinity (EA) of the acceptor. The CNDO/S method is well established as being a good predictor of the IPs, when an appropriate scaling is applied to the orbital energies.[16] On the other hand, the MNDO method has been especially parametrized to yield good estimations for the ionization potentials of organic molecules.[4] The reliability of the CNDO/S approach in reproducing the energies of the CT transitions of the alkylbenzene–TCNE complexes gives an opportunity to compare these methods as to their accuracy of predicting IPs for alkylbenzenes. Both approaches give satisfactory results. Nevertheless, the correlation for the MNDO results ($IP_{exp} = 3.626IP_{cal} - 24.98$, $r = 0.970$, Fig. 5) seems to have no physical meaning due to a high scaling factor (3.626). It is apparent that the MNDO method in spite of giving quite satisfactory results for benzene ($IP_{calc} = 9.39$ eV,[4] $IP_{exp} = 9.25$ eV)[17] as a whole incorrectly accounts for the influence of the Me groups on the IPs. As opposed to that the CNDO/S approach gives an encouraging correlation ($IP_{exp} = 1.179IP_{calc} - 2.53$, $r = 0.978$, Fig. 6) which is probably a source of a good correlation for E_{CT}.

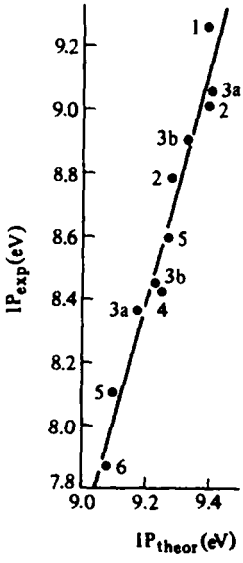

Fig. 5. The correlation between the experimental and the MNDO IPs for alkylbenzenes.

CONCLUSIONS

In our calculations the CNDO/S method appeared to be a convenient tool for predicting the electronic structure of EDA complexes forming between alkylbenzenes and TCNE. The use of this approach allows for a discussion of the relative stability of the complexes and the position of the CT transitions. The theoretical determinations support the experimental observations that the double CT bands occurring in the UV spectra of these compounds correspond to two different rotational isomers. The calculated values testify also to the accuracy of the deconvolution technique applied to analyse the spectra.[18] We think that the reasonable results of the presented effort are on the whole the effect of quite a good estimation of the ionization potentials of alkylbenzenes as well as an adequate enough reflection of the interactions between HOMO and LUMO orbitals of the donor and acceptor molecules within the CNDO/S framework.

The atomic Cartesian coordinates of the molecules used in the computations as well as the singlet transition energies of alkylbenzenes calculated by the CNDO/S method are available from the author upon request.

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