# Extended Hückel Calculation on the Charge Transfer Complex Tetracyanoethylene-Benzene

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Extended Hückel calculations have been performed for 14 different conformations of the charge transfer complex tetracyanoethylene-benzene. The calculations predict all 14 conformations to be unstable. Thus the theory cannot explain the stability of the complex, found by experiment.

The theory of CT (charge transfer) complexes is quite well understood,[1,2] but no simple quantum mechanical calculations have been made on these systems. Hoffmann's success in predicting various properties of organic molecules [3-6] by his extended Hückel method, and a recent extended Hückel calculation on the benzene excimer [7] made it tempting to perform a similar investigation of a CT complex. The complex TCNE-benzene was chosen because of its relatively small size, the matrices involved are of the order 70 × 70. Each calculation takes about 7 minutes on a CDC 3600 computer.

The extended Hückel method is a LCAO—MO method in which the basis set consists of 2s and 2p Slater orbitals on the main atoms (carbon and nitrogen) and 1s Slater orbitals on the hydrogen atoms. The secular equations $\sum_i(H_{ij}-ES_{ij})c_{ij} = 0 \ j = 1, 2, \ldots\ldots$ are solved without further simplifications. The values used for $H_{ii}$ are [6]

|   | $H_{ii}(2s)$ | $H_{ii}(2p)$ |
|---|---|---|
| C | −21.4 eV | −11.4 eV |
| N | −26.0 eV | −13.4 eV |

while $H_{ii}$ (hydrogen 1s) = −13.6. The off diagonal matrix elements are given by $H_{ij} = 0.875 \ (H_{ii} + H_{jj}) \ S_{ij}$. The bond distances used were, in benzene C—C = 1.395 Å and C—H = 1.084 Å, and in TCNE C—C (central) = 1.317 Å, C—CN = 1.448 Å and C—N = 1.150 Å (the TCNE values are mean values of those given in Ref. 8). All bond angles were 120° or 180°.

The different conformations for which the calculations were made are shown in Fig. 1, and Fig. 2 shows the total electronic energy of II as a function
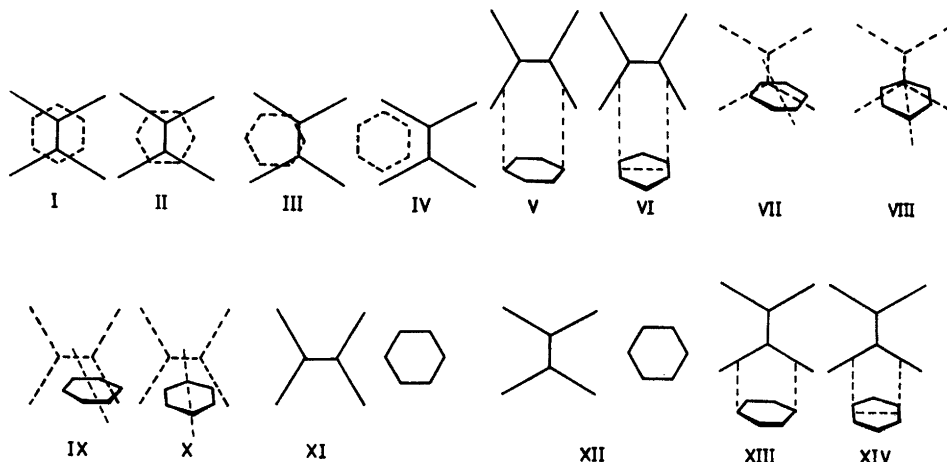
*Fig. 1.* The investigated complex conformations. (Dotted parts lie behind parts drawn with solid lines).
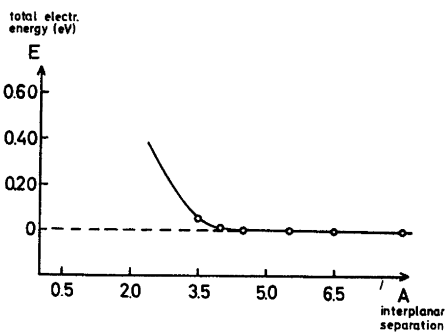


*Fig. 2.* Total electronic energy of II as a function of interplanar separation. (The energy of free components is set to zero).

*Table 1.* Bond populations and net charges in TCNE and benzene.

|  |  | This investigation | | Ordinary Hückel values |
|  |  | $\pi$ | $\pi + \sigma$ | |
|---|---|---|---|---|
| TCNE net charges | central C | $+0.136$ | $+0.339$ | $+0.11$ |
|  | nitrile C | $+0.311$ | $+0.816$ | $+0.32$ |
|  | nitrile N | $-0.379$ | $-0.985$ | $-0.37$ |
| bond popul. | central C—C | 0.322 | 1.112 | 0.76 |
|  | C—CN | 0.081 | 0.897 | 0.35 |
|  | C—N | 0.393 | 1.654 | 0.87 |
| Benzene net charges | C | 0.0 | $-0.101$ | 0.0 |
|  | H | 0.0 | $+0.101$ | 0.0 |
| bond popul. | C—C | 0.241 | 1.074 | 0.67 |
|  | C—H | 0.0 | 0.831 | 0.0 |

*Table 2.*

| Energy (eV) | | Type | |
|---|---|---|---|
| −31.097 | | TCNE $\sigma$ | |
| −30.077 | | TCNE $\sigma$ | |
| −29.737 | | TCNE $\sigma$ | |
| | −29.567 | Benzene $\sigma$ | |
| −29.528 | | TCNE $\sigma$ | |
| −26.143 | | TCNE $\sigma$ | |
| | −25.785 | Benzene $\sigma$ | |
| | −25.785 | Benzene $\sigma$ | |
| −21.881 | | TCNE $\sigma$ | |
| | −19.933 | Benzene $\sigma$ | |
| | −19.933 | Benzene $\sigma$ | |
| −18.777 | | TCNE $\sigma$ | |
| −17.602 | | TCNE $\sigma$ | |
| | −16.601 | Benzene $\sigma$ | |
| | −16.576 | Benzene $\sigma$ | |
| −16.404 | | TCNE $\sigma$ | |
| −15.219 | | TCNE $\pi$ | |
| −14.911 | | TCNE $\sigma$ | |
| −14.856 | | TCNE $\pi$ | |
| −14.775 | | TCNE $\sigma$ | |
| −14.729 | | TCNE $\sigma$ | |
| −14.716 | | TCNE $\pi$ | |
| −14.667 | | TCNE $\pi$ | |
| | −14.637 | Benzene $\sigma$ | |
| | −14.637 | Benzene $\sigma$ | |
| −14.542 | | TCNE $\sigma$ | |
| | −14.510 | Benzene $\pi$ | |
| −14.462 | | TCNE $\sigma$ | |
| | −14.297 | Benzene $\sigma$ | |
| −14.004 | | TCNE $\sigma$ | |
| −13.547 | | TCNE $\sigma$ | |
| −13.209 | | TCNE $\sigma$ | |
| −13.166 | | TCNE $\pi$ | |
| | −12.839 | Benzene $\sigma$ | Ground state |
| | −12.839 | Benzene $\sigma$ | occ. levels |
| | −12.797 | Benzene $\pi$ | |
| | −12.797 | Benzene $\pi$ | |
| −10.520 | | TCNE $\pi$ | |

of interplanar separation. The shape of this curve is very similar to corresponding curves of the other conformations, and in no case binding occurs.

Table 1 shows the net charges and the bond populations obtained by a Mulliken population analysis.[9] Only the values of TCNE and benzene are tabulated, since the electron distributions in all the complexes and the free components are very much alike. The ordinary Hückel values [10] are shown for comparison. The values are to three decimals exactly the same in the free components and in all 14 complex conformations provided that the components of the complex not are brought closer than 3.5 Å to each other. The same reason makes it unnecessary to tabulate more than the free component energies which are shown in Table 2 (values of benzene are taken from Ref. 3).

The Mulliken CT theory [1,2] assumes the ground state of a CT complex to be of the form $a\ \varphi_A\varphi_D + b\ \varphi_A{}^-\varphi_D{}^+$ and the excited state of the form $a'\varphi_A{}^-\varphi_D{}^+ + b'\varphi_A\varphi_D$, where $a$ and $a'$ are large compared to $b$ and $b'$.

$\varphi_A$ and $\varphi_D$ are the ground state wave functions of the acceptor and donor, respectively, while $\varphi_A{}^-$ and $\varphi_D{}^+$ represent the acceptor and the donor when the former has gained one electron and the latter has lost one.

From Table 2 it is seen that the first excitation in the complex corresponds to an excitation of an electron from an almost pure benzene $\pi$-orbital to an almost pure TCNE $\pi$-orbital. This corresponds to a ground state and an excited state of the type given by the Mulliken CT theory with $b$ and $b'$ being almost zero. The excitation energy is seen to be 2.28 eV compared to the experimental value 3.22 eV.[11]

The present investigation cannot make any suggestion which conformation is the true one, but crystallographic investigations on other TCNE CT complexes [12] and the generally parallel plane structure of CT complexes [1,2] make the configurations I—IV the most probable.

The apparent failure of the extended Hückel method in this investigation is not easy to explain, the overemphasis of steric repulsions found by Hoffmann [3] might be important.

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