

حسابات نظرية الدالة الوظيفية للكثافة (DFT) والطيف لمتراكب الشحنة  
بين مادتي ٣ - ميثيل - أندول (SKATOL) وتتراسيانو اثيلين (TCNE)

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تم قياس الطيف لمتراكب الشحنة لمادتي ٣ ميثيل أندول (سكاتول) ورباعي سيانو اثيلين وحساب الشكل الهندسي المحتمل لهذا المركب المسئول عن حزمة الامتصاص باستخدام نظرية الكثافة الوظيفية.

تمت دراسة ثلاثة عناصر مرتبطة بالمركب: المسافة الفاصلة بينهما واتجاه المستقبل والمُعطى وطاقة الربط لهما وحساب طاقة الانتقالات من أعلى مدار للطاقة ممتلئ وأقل مدار للطاقة خالي.

وقد أظهرت نتائج الحسابات التطابق مع النتائج العملية.

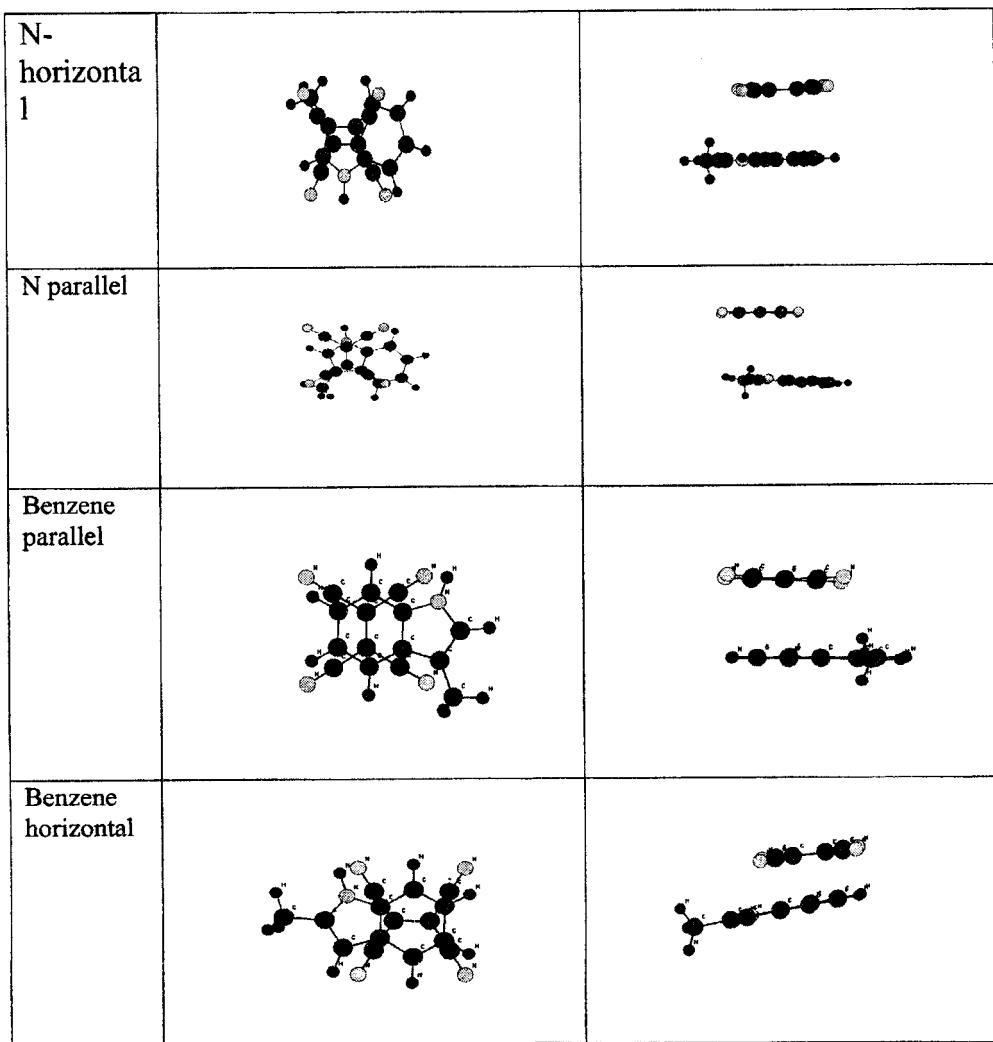
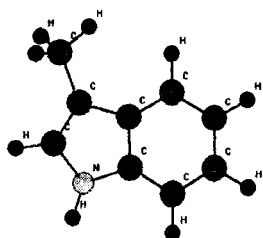


Figure 2. Four distinct conformations of Skatole-TCNE

Skatol



Tcne

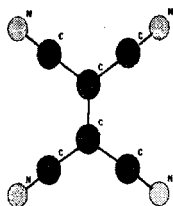


Table 2  
Calculated Properties of the CT Complex in 1,2-dichloroethane Solvent

D-A <i>b</i> complex	$R_{D-A}$	Transitions Singlet → Singlet	$E^{exc}$ eV  Calc exptl <sup>c</sup>	f	$E_{bind}$ (kcal/mol)
Skatole- TCNE (a)	3.33	HOMO → LUMO HOMO- 1 → LUMO	1.68 2.31	.0012 .0775	8.91
Skatole- TCNE (b)	3.37	HOMO → LUMO HOMO- 1 → LUMO	1.95 2.38	.1149 .0084	8.77
Skatole- TCNE (c)	3.3	HOMO → LUMO HOMO- 1 → LUMO	1.86 1.85 2.25 2.25	.074 .0174	8.85
Skatole- TCNE (d)	3.4	HOMO → LUMO HOMO- 1 → LUMO	1.6 2.24	.0016 .0831	13.45

Table 3:  
Solvent Effects on Calculated Properties [  $\Delta X = X(solvent) - X(gasphase)$  ]

	Skatole TCNE Complex	
$\Delta E_{bind}$	-.012	kcal/mol
$\Delta R_{D-A}$	-.13	eV
$\Delta E^{exc}$	-.079	eV

Table 1  
Calculated Properties of Sktole-TCNE complex with Different Basis Sets

Basis Set	R	Lu-Ho	E ex eV	f	Binding energy (kcal/mol)
6-31G*	3.329	3.52	2.257	0.0174	8.85
6-31+G*	3.368	3.44	2.204	0.0117	6.78
6-311G*	3.297	3.55	2.2914	0.0175	9.08
6-311+G*	3.354	3.51	2.2471	0.0137	8.22

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Conformations c and d are energetically preferred to a and b. Both c and d give rise to two allowed CT transitions, arising from HOMO  $\rightarrow$  LUMO and HOMO-1  $\rightarrow$  LUMO.

Structure c is computed to be energetically preferable than d, it is more stable by some 1.5 Kcal/mol, and it also has a shorter  $R_{D-A}$  value, the calculated D-A distance is 3.3 Å for c and is longer, 3.4 Å, in d. The two isomers c and d could exist in solution.

### Conclusions

The lowest-energy conformations of skatole-TCNE complex has the TCNE, double bond parallel with the 1,4-carbon atom line in the six membered ring of skatole. The appearance of a second CT band would indicate the simultaneous presence of a second conformation. The broad visible CT band is attributed to overlapping CT transitions arising from the HOMO and HOMO-1 of skatole. Various orientation isomers may coexist in solution because of the ease of rotation interconversion among them (25), they may contribute to the broadness and intensities of the CT absorption.

of  $E_{exc}$  is less than 0.1 eV. The calculated oscillator strengths,  $f$ , are lowered by the inclusion of diffuse functions. The same is true for the binding energies, where the addition of diffuse functions leads to a decrease in this quantity.

In summary, the 6-31G\* basis set appears to be sufficiently reliable to provide reasonable results when used for the CT complexes, and the larger basis sets do not significantly affect the molecular properties in a qualitative way.

To assess the effects of solvent on the calculated properties, calculations were also performed on free D-A complex (i.e., D-A in the gas phase). The differences in the results ( $\Delta X$ ) between solvated and free D-A complexes are presented in Table 3.

Calculations were carried out on four possible conformations (a, b, c, d), illustrated in Figure 2. Conformations a and b place TCNE above the five membered ring of skatole, where the TCNE double bond is parallel and perpendicular to nitrogen respectively, Both c and d center the TCNE above the six membered ring, in conformation c, the TCNE double bond is parallel to the line connecting the 1,4 carbon atoms in the ring, whereas the two are perpendicular in conformation d. Geometry optimizations indicate that the center of TCNE lies over the center of the ring in either case. The calculated binding energies indicate that this latter location, above a phenyl ring, provides better  $\pi-\pi$  electron interaction and is thus energetically favorable to a and b. It might be observed that the calculated values of  $R_{D-A}$  are directly related to the D-A binding strength. That is the most strongly bound complexes are associated with shorter intermolecular separations.

Our experimental charge transfer spectrum of Skatole and TCNE (Figure 2,c) shows two transitions at 1.85 eV and 2.25 eV. The calculated excitation energies 1.86 eV and 2.25 eV, are close to the observed values.

bound CT complexes. (20). Larger basis sets have also been tested for two of the CT systems so as to gauge the influence of basis-set size.

As may be seen in Table 1, there is fairly close agreement between the 6-31G\* and 6-311+G\* calculations. Electron excitation energies related to the absorption spectra were calculated using the time-dependent density functional response theory (TDDFT). (21-23).

### 3- Results and Discussion

The optimized bond length values ( in  $\text{Å}^0$  ) Of the isolated donor and acceptor are reported in Figure 1. Intermolecular distance  $R_{D-A}$  separating D and A planes is of interest, since planes of D and A molecules are parallel in both solid state and also in solution (24).

Table 1 shows the calculated properties of the CT complex, where excitation energies ( $E_{exc}$ ) is the lowest transitions of oscillator strengths  $f$  and binding energy  $E_{bind}$  of the complex which is the difference between the complex total energy (in solvent) and the sum of each components (in solvent).

The use of a sufficient size basis sets is required for the calculation of a molecular system. The effects of adding diffuse functions to the basis set (6-31+G\*) and using larger basis sets (6-311G\*, 6-311+G\*) were assessed.

A comparison of results obtained with different basis sets is reported in Table 2. the calculated intermolecular distance ( $R_{D-A}$ ) varies somewhat with the basis set. Adding diffuse functions to 6-31G\* lengthens the D-A distance by 0.04. The enlargement of the valence from 6-31G\* to 6-311G\* remains  $R_{D-A}$  unchanged. After the valence has been enlarged to 6-311G\*, the addition of diffuse function continues to elongate RA-D, but by a smaller amount. For our system, the 6-316G\* value of  $R_{D-A}$  is close to that obtained by 6-311+G\*.

The calculated LUMO-HOMO energy gap and the associated excitation energy are less sensitive to the choice of basis set, the variation

characterize the donor and acceptor molecule. The activity of biologically active compounds may depend on their capacities to form such molecular complexes with biological receptors.

The formation of charge transfer (CT) complex is identified with a new absorption band in its UV-VIS spectrum. The position and intensity of CT band are useful for identification and analysis of the nature of donors and acceptors qualitatively and quantitatively (14). The qualitative analysis becomes significant if drugs are used as donors in medicinal chemistry (15).

Indole and its derivatives are regarded as one of the most important electron donor moieties in biomolecules. Alkyl derivatives of indole, forms a wide variety of stacking or molecular complexes either through charge transfer or through proton transfer (16a). Skaole (3-methylindole) is one of the indole derivatives, widely used as a therapeutic agent in medicinal chemistry (16b).

The present work aims to study the charge transfer complex of skatole (3-methylindole)-tetracyanoethylene). DFT calculations have been carried out using solvent in order to understand the energies and origin of the CT spectra. By calculating electron excitation energies ( $E_{exc}$ ) and D-A binding energies ( $E_{bind}$ ), the most probable geometric structures of the complexes that are responsible for the absorption bands are determined.

## 2. Computational details

All computational calculations have been done with the Gaussian 03W software (17) implemented on a Pentium computer. Self-consistent reaction field (SCRF) were carried out to estimate the effects of the polar solvent using a polarized continuum model (pcm) (18). The density functional used was based on the combination of Becke's half (-HF) and half (-DFT) exchange<sup>15</sup> with the correlation functional of Lee, Yang, and Parr (LYP). (19). The basis set used in the present work is the standard 6-31G\*, which has been shown to be adequate for calculations on weakly

# DENSITY FUNCTIONAL THEORY CALCULATIONS AND SPECTRAL MEASUREMENTS OF CHARGE TRANSFER COMPLEX FORMED BY SKATOLE ( 3-METHYLINDOLE ) AND TETRACYANOETHYLENE.

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Skatole (3-methylindole) -Tetracyanoethylene charge transfer spectrum was measured in 1,2 dichloroethane. Density functional theory (DFT) calculations were carried out using solvent to determine the probable geometric structure of the complex that is responsible for the absorption band. Three aspects of the intermolecular association were investigated: D-A separation and relative orientation of the Donor (D) and Acceptor (A), the D-A binding energy, and the excitation energy of transition from the highest occupied molecular orbital (HOMO) of D to the lowest unoccupied molecular orbital (LUMO) of A. The results of calculations are in a good agreement with the experimental results.

## 1. Introduction

Since Mulliken presented the well-known theory (1) of the charge transfer (CT) interaction between electron donor (D) and acceptor (A), it has been successfully and widely applied to many interesting research subjects (2-10). The imminence of computer programs for various theoretical calculations like ab initio, density functional theory (DFT), it has become a current trend (11-13) to treat such complexes by these methods.

According to Mulliken's theory (1) chemical hunch is needed to define a 'donor' and 'acceptor' molecule in a CT complex. However, elucidation of electronic charge distribution in an adduct of two different molecules by the help of ab initio and DFT calculations enable us to

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