CHARGE TRANSFER COMPLEX FORMED BY MELATONIN WITH TETRACYANOETHYLENE. DENISTY FUNCTIONAL THEORY CALCULATIONS AND SPECTRAL MEASUREMENTS.

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Charge transfer spectra of melatonin [acting as donor (D)] with acceptor A [A = tetracyanoethylene (TCNE)] was measured in 1,2-dichloroethane. Denisty functional theory (DFT) calculations were carried out in 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 D and A, the D-A binding energy, and the excitation energy of transition from the HOMO (highest occupied molecular orbital) of D to the LUMO (lowest unoccupied molecular orbital) of A. The calculated results are in a good agreement with the experimental results.

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1. Introduction

Intermolecular charge-transfer (CT) complexes are formed when electron donor (D) and electron acceptor (A) interact, a general phenomenon in organic chemistry [1]. Mulliken [2] considered such complexes to arise from a Lewis acid-Lewis base type of interaction, the bond between the components of the complex being postulated to arise from the partial transfer of a π electron from the base (D) to π^* orbitals of the acid (A). In solution, the composition of the complexed species could be represented by a 1:1 molar ratio [3], and the association equilibrium may be written as

$$D + A \underset{}{\overset{K_{DA}}{\rightleftharpoons}} D - A$$

One characteristic feature of a D – A complex is the appearance of a new absorption band in the spectrum of the complex other than that of both D and A separately, This band commonly attributed to an intermolecular CT transition, involving electron transfer from the donor to the acceptor.

The nature of intermolecular CT complexes has been the subject of many investigations. Early work in this field was based mainly on Mulliken's valence bond theory [4] in which the D – A complex is described as a resonance hybrid of an uncharged aggregate (D, A) and an ionic structure (D^+- A^-) formed by charge transfer from D to A.

Accurate descriptions of the bonding properties of weakly bound systems have proven to be a challenge to theoretical researchers[5]. The Hartree-Fock (HF) method is clearly inadequate because of its failure to account for electron correlation and dispersion. Ab initio studies require the use of high-quality correlated methods [6]; such calculations remain very time-consuming and impractical for large molecular systems.

Density functional theory (DFT) is an alternative to conventional ab initio method because it provides an estimate of the correlation energy at a relatively modest cost. There have been several papers[7] assessing DFT for some simple CT complexes, showing that the hybrid DFT methods can provide remarkably accurate results for the properties considered.

Because of their wide application and use (ranging from chemistry, materials science, and medicine to biology), CT complexes have attracted considerable research interest, and over the years, a very large number of CT complexes have been prepared and experimentally studied [8].

Indole and its derivatives are regarded as one of the most important electron donor moieties in biomolecules, it forms a wide variety of stacking or molecular complexes through CT [9]. Melatonin (N-acetyl-5-methoxytryptamine), which is indole derivative, occurs naturally in mammals and its biological activity is believed to involve changes in certain neurons in the central nervous system [10]. Tetracyanoethylene (TCNE) Figure 1 is strong electron acceptor that forms complexes with a variety of donors. This work concerns the formation of CT complex of melatonin with TCNE. DFT calculations have been carried out in solvent in order to understand the energetics and origin of the CT spectra. By calculating electron excitation energies (E^{exc}) and D – A binding energies (E_{bind}), the most probable geometric structure of the complexes that are responsible for the absorption band is determind.

2. Experimental and Computational Details

The structure of the electron donor melatonin is illustrated in Figure 1. It was obtained from Sigma Chemical Company, St. Lowis, MO, USA. TCNE (Fluka AG. Purum grade reagent) was purified by repetitive crystallization from chlorobenzene. The solvent 1,2-

Dichloroethane , BDH reagent grade was bidistilled before use. The spectrum was scanned on Pye – Unicam SP 8-200 spectrophotometer and was recorded soon after the two substance solutions were mixed.

All calculations were carried out using the Gaussian 03 program[11]. To estimate the effects of the polar solvent, self-consistent reaction field (SCRF) calculations were carried out using a polarized continuum model (PCM) [12]. The density functional that was used was based on the combination of Becke's half (-HF) and half (-DFT) exchange[13] with the correlation functional of Lee, Yang, and Parr (LYP) [14]. A systematic test of various density functionals was performed previously on some $\pi-\pi$ CT complexes[15], and it was shown that this hybrid BH&HLYP functional provides satisfactory excitation energies and also in other ways furnishes the best performance for describing the properties of $\pi-\pi^*$ CT complexes in general. The basis set employed was the standard 6-31G*, which has been shown to be adequate for calculations on weakly bound CT complexes[16]. Larger basis sets have also been tested for the CT system 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) as implemented in the Gaussian program. TDDFT provides a first-principles method for the calculation of excitation energies and represents an excellent alternative to conventional highly correlated CI method[17].

3. Results and Discussion

Selected bond lengths and angles, optimized for the isolated donor and acceptor molecules, are reported in Figure 1. Upon pairing to form a CT complex, the principle of maximum overlap would lead one to expect a conformation wherein the planes of the donor and acceptor

molecules lie parallel to one another in a stacked arrangement. This structure has been observed in the solid state[18]. A similar structural arrangement is believed to occur in solution as well. The geometric parameters of interest in the stacked structure is the intermolecular distance R_{D-A} (separating the parallel D and A planes). There are a number of geometric possibilities for the D-A complexes (The internal geometries of the subunits remain nearly unaffected in the complex[19]). These structures are illustrated in Figure 2.

The calculated properties of the D-A complex, with A=TCNE and D=melatonin, are collected in Table 2. Excitation energies (E^{exc}) refer to the lowest transitions, along with their oscillator strengths, *f*. The D-A binding energy, E_{bind} is defined as the difference between the total energy of the complex (in solvent) and the sum of the individual components (in solvent).

3.1. Basis Set Effects.

An accurate calculation of a molecular system requires the use of basis sets of sufficient size and flexibility, but an overly large set can create computational problems. It therefore becomes important to identify an optimal basis set, one of manageable size but also one that provides reliable calculated properties. The effects of adding diffuse functions to the basis set (6-31+G*) and using the larger basis sets (6-311G*, 6-311+G*) were carefully assessed.

A comparison of results obtained with these different basis sets is reported in Table 1. 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 0.09. The enlargement of the valence segment from 6-31G* to 6-311G* remaines R_{D-A} unchanged. After the valence has been enlarged to 6-311G*, the addition of diffuse function continues to elongate R_{D-A}, but by a smaller amount.

For our system, the 6-31G* 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 variations of E^{exc} are 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 for the CT complexes, and the larger basis sets do not significantly affect the molecular properties in a qualitative way.

3.2 Solvent Effects.

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 (ΔX) between solvated and free D-A complexes are presented in Table 3. Upon solvation the binding energy of the complex decreased by 4 kcal/mol and the equilibrium D-A distance is diminished by 0.16 A^0. Most importantly for our purposes, the excitation energy is scarcely affected by solvation; the deviation from the gas phase is less than 0.1 eV.

In summary, the D-A complex is stabilized by the polar solvent, which gives rise to a shortening of D-A in the solvent is decreased owing to the greater stabilization of the isolated components. Concerning the excitation energy, the solvent effect on E^{exc} is quite small.

3.3 Melatonin-TCNE

Calculations were carried out on four possible conformations (a, b, c and d), illustrated in Figure 3. Conformations a and b place TCNE above the five membered ring of melatonin, 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 Melatonin and TCNE (Figure 3) shows a single broad, intense band with a peak at 1.91 eV that we attribute to HOMO→ LUMO transition. The Gaussian analysis for the broad band gives two transitions at 1.91 eV and 1.59 eV. The calculated excitation energies of 1.95 eV and 1.63 are close to the observed value.

Previous studies[20]. for some CT complexes reveal that the single broad band is composed of two strongly overlapping bands (CT1, CT2), which arise from transitions between the HOMO and HOMO-1 of donor and the LUMO of TCNE. Thus, the obtained band is likely a composite of two overlapping bands.

Conformations b and d are energetically preferred to a and c. Both b and d give rise to two allowed CT transitions, arising from HOMO→ LUMO and HOMO-1→LUMO, which are all similar.

According to the calculation, the HOMO→ LUMO transition is weaker than the HOMO-1→ LUMO, for both b and d. The energy splitting between the CT1 and CT2 excitations is ≈0.3 eV and the lower energy transition (CT1) has smaller oscillator strength (f) than does CT2.

Castellano *et al.*[21] reported that skatol-TCNE complex is planar with superposition of the donor with two neighboring TCNE molecules, one is stacked on top of the six membered ring and the other on top of the five membered ring of the donor. The band observed for skatol-TCNE was corresponding to the electron transfer from the second highest orbital of the donor to the lowest vacant of TCNE. A similar feature has been observed in perylene-TCNE complex[22].

Structure d is computed to be energetically preferable than b, it is more stable by some 1.0 kcal/mol, and it also has a shorter R_{D-A} value, the calculated D-A distance is 3.35 A^o for d and is longer, 3.53 A^o, in b. The two isomers d and b could exist in solution.

4- Conclusions

For the complex melatonin-TCNE, the lowest-energy conformation has the acceptor's double bond perpendicular with the 1,4-carbon atom line in the six membered ring of melatonin. 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 melatonin. For some complexes, various orientation isomers may coexist in solution because of the ease of rotation interconversion among them[23].they may contribute to the broadness and intensities of the CT absorption.

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Table 1: Calculated Properties of Melatonin-TCNE Complex with Different Basis Sets

Basis set	R_{D-A} (A°)	Δ_{LU-HO} (eV)	E^{exc} (eV)	f	E_{bind} (kcal/mol)
6-31G*	3.35	3.40	1.955	0.0913	4.220
6-31+G*	3.44	3.39	1.867	0.0753	1.508
6-311G*	3.35	3.44	1.970	0.0862	3.247
6-311+G*	3.37	3.33	1.907	0.0770	2.260

Table 2: Calculated Properties of the CT Complex in 1,2-dichloroethane[a] Solvent

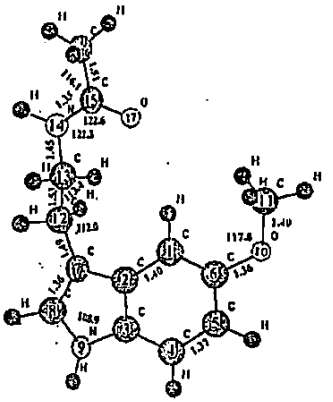
D-A complex[b]	R_{D-A}	Transitions Singlet → singlet	E^{exc} eV Calcd	exptl[c]	f	E_{bind} (kcal/mol)
Melatonin-TCNE (a)	3.43	HOMO → LUMO HOMO-1 → LUMO	1.88 1.77		0.0992 0.0172	3.1129
Melatonin-TCNE (b)	3.53	HOMO → LUMO HOMO-1 → LUMO	1.63 1.95		0.0109 0.0913	3.3241
Melatonin-TCNE (c)	3.40	HOMO → LUMO HOMO-1 → LUMO	1.84 1.76		0.0833 0.0226	3.1284
Melatonin-TCNE (d)	3.35	HOMO → LUMO HOMO-1 → LUMO	1.63 1.95	1.59[g] 1.91	0.0109 0.0913	4.220

a Dielectric constant $\varepsilon = 1.8$. b For the various D-A structures considered, see Figure 3: the most probable structure is indicated in bold. c The experimental data refer to the absorption maxima in the absorption spectra, g from Gaussian analysis.

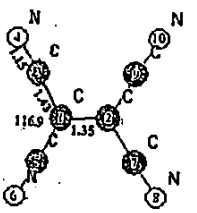
TABLE 3: Solvent Effects on Calculated Properties[a] [$\Delta X = X$ (in solvent) – X (in gas phase)]

	Melatonin TCNE Complex
ΔE_{bind}	-4.322
ΔR_{D-A}	-0.16
ΔE^{exc}	-0.095

a D-A binding energy E_{bind} in kcal/mol, D-A distance R_{D-A} in A^0, and excitation energy E^{exc} in eV. Values refer to the lowest-energy geometry of the complex



D



A

Figure1.Molecular Structures of the Electron Donor (D) Melatonin and Electron Acceptor (A) TCNE, along with the Optimized Values of Selected Bond Lengths (in A°) and Bond Angles.

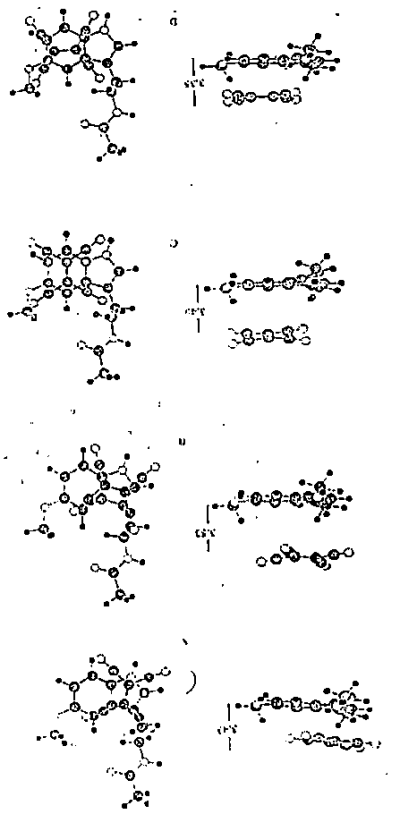


Figure2. Four Distinct Conformations of Melatonin - TCNE

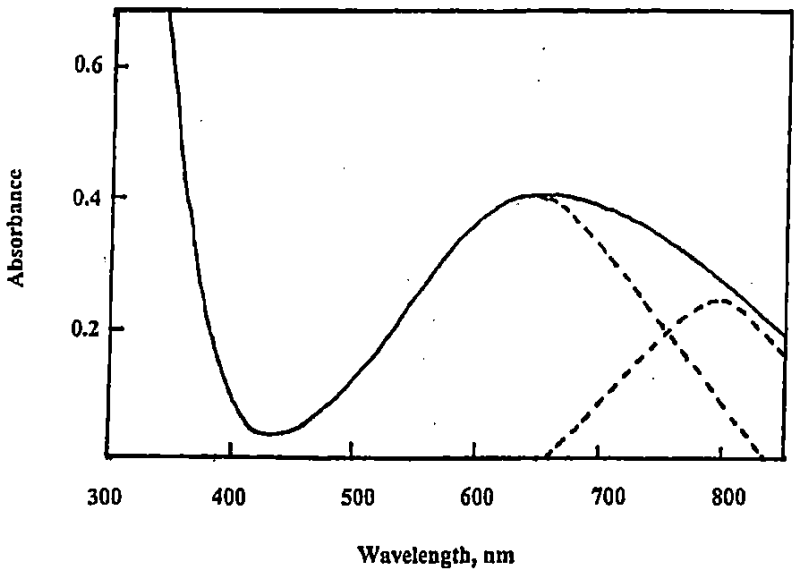


Figure 3. Measured charge-transfer (CT) spectra of Melatonin-TCNA complex in 1,2-dichloroethane. The concentrations of the substances are TCNE, 0.002 M, Melatonin, 0.016 M.

مركب انتقال الشحنة بين الميلاتونين ورباعى سيانوايثيلين
"حسابات نظرية وقياسات طيفية"

محمد عبده

تم قياس انتقال الشحنة لمركب ميلاتونين – رباعى سيانوايثيلين وحساب أفضل شكل مسئول عن الامتصاص الإلكترونى ، وتم حساب ثلاثة عوامل تؤثر فى خواص المركب ، وهى :

- المسافة بين المركبين .
- الشكل الفراغى للمركب .
- طاقة انتقال من أعلى مستوى مملوء وأقل مستوى طاقة فارغ .

وقد أظهرت النتائج النظرية توافقا مع القياسات العملية .