

Commentationes

Structure and Packing Arrangement of Molecular Compounds

VI. Molecular Orbitals and Charge-Transfer Interactions in TCNQ-Containing π - π^* Complexes

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The calculation of electronic structures of TCNQ and several electron-donor molecules has been performed by the Iterative Extended Hückel Method, taking into account all valence electrons of various atoms and retaining the overlap integrals. Calculations of intermolecular overlaps involving the lowest vacant molecular orbital of TCNQ and one or more highest occupied orbitals of each of the donors have been correlated with the observed donor-TCNQ geometrical configurations. The results of this simple approach, which is based on Mulliken's "Overlap and Orientation Principle", suggest that the charge-transfer interaction plays an important role in the particular observed packing arrangement in the solid state.

Key words: Charge-transfer interactions in molecular compounds – Packing arrangement in TCNQ-containing π - π^* complexes

1. Introduction

Several attempts at correlating known crystal structures of electron donor-acceptor π - π^* complexes with the estimated energy of intermolecular interaction are described in the literature (e.g., [1–3]). The most extensive investigation was carried out by Mayoh and Prout [3] on a large number of charge-transfer (CT) compounds. They concluded that in the absence of large packing forces in a crystal the CT-stabilization energy is maximized in the observed donor-acceptor orientation, indicating also that consideration of only the lowest energy CT state may lead to an inadequate description of the correct geometry.

During investigation of molecular complexes in this laboratory [4, 5], similar attempts at rationalizing the observed donor-acceptor overlap modes in a complex were made. The results indicated clearly, however, that interpretations of the expensive energy calculations should be at most semi-quantitative; the variation in the calculated energy, when the geometry of a complex is systematically altered, is of the order of 10^{-2} eV (0.2 kcal/mole) while the corresponding total energy of intermolecular interaction is of the order of 10^3 eV.

The purpose of the present paper is to describe different simple theoretical considerations on the CT interactions in these complexes, correlating the geometrical configuration of a complex with the intermolecular overlap of interacting

orbitals; this approach is based on Mulliken's "Overlap and Orientation Principle" [6]. Thus, it was assumed in this study that the intermolecular charge-transfer orbital interaction energy is directly related to the corresponding overlap integral [6, 7], and such integrals rather than extensive energy calculations were evaluated for systematically varied relative orientations and locations of the donor and the acceptor. Ground state electronic structures of the isolated molecular species were defined for this purpose using the Iterative Extended Hückel Theory (IEHT) [8]. A dependence of the observed perpendicular interplanar separation in the mixed-stacked structures on the ionization potentials of the donors, which might be associated with the relative contribution of CT interactions to the intermolecular bonding, is also discussed.

The results reported below are limited to selected systems which apparently are characterized by a similar array of repulsion and dispersion interactions; i.e., nearly isosteric 1 : 1 π complexes of various organic donors with a common acceptor, 7,7,8,8-tetracyanoquinodimethane (TCNQ). Complexes of TCNQ with the following donors were included in our investigation: anthracene [9], phenazine, dibenzo-*p*-dioxine (DPDO) [4], 1,10-phenanthroline (PHT) [5] and N,N,N',N'-tetramethyl-*p*-phenylenediamine (TMPD) [10]. Some results on a TCNQ complex with a larger donor, pyrene [11], are discussed in the last sections of this communication.

2. Method of Calculation

Molecular wave functions were calculated by the charge-self-consistent IEHT method [8, 12] which accounts for all valence states of the involved atoms. Interatomic overlap integrals S_{ij} for the Slater basis orbitals were calculated directly, diagonal Hamiltonian matrix elements H_{ii} were initially set equal to the negative of the corresponding valence state ionization potential (being varied in subsequent steps), and off-diagonal elements H_{ij} were approximated by the Cusachs [13] equation: $H_{ij} = S_{ij}(1.0 - 0.5|S_{ij}|) \cdot (H_{ii} + H_{jj})$.

In view of the fact that the contribution of π -binding energy to the stability of the molecular ground state is relatively small (e.g., [14]), it has been suggested to adjust the diagonal elements of the effective Hamiltonian in such a way as to split accordingly the input degeneracy of $2p$ atomic orbitals in conjugated systems [15]. As shown in [15] and below an improved description of some molecular quantities (e.g., ionization potentials and order of molecular levels) is achieved with appropriately modified calculation scheme. We shall refer hereafter to the modified iterative extended Hückel method as IEHT₁.

After calculation of component-molecule MO's, some donor-acceptor intermolecular overlap integrals were computed with standard expressions [16]. The varying donor-acceptor orientation for which overlap calculations were carried out were generated by coordinate shift of $5i^\circ$, $0.5j$ and $0.5k$ Å for rotation of the donor above TCNQ, and for its displacement in the directions of the long (**l**) and the (in-plane) short (**m**) molecular axes of TCNQ, respectively. Any orientation is then defined by the numbers i , j and k necessary to generate it from a starting orientation of a complete center-to-center superposition.

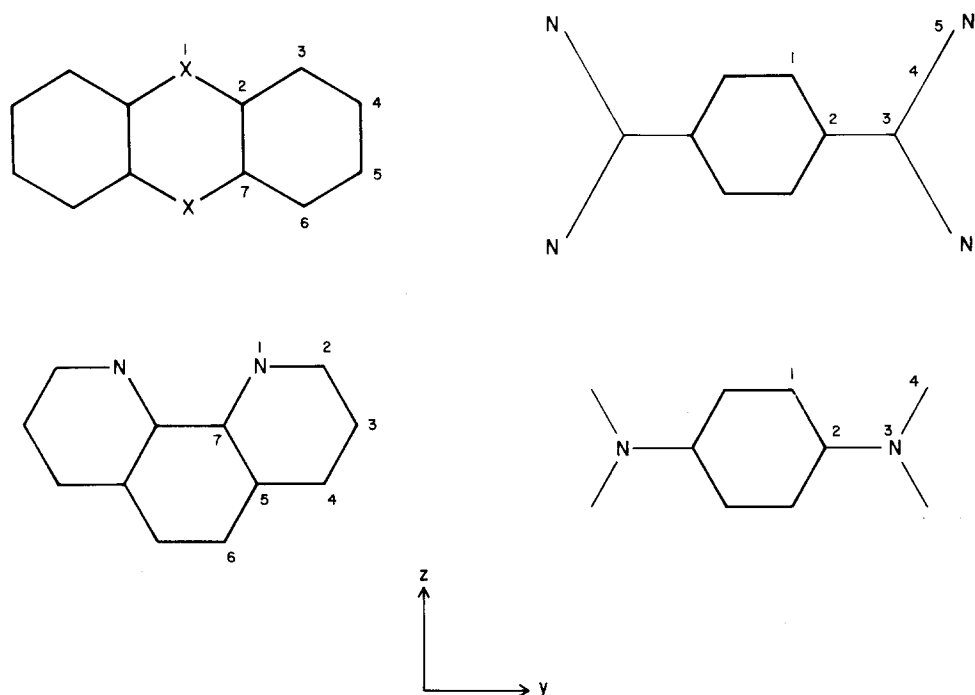


Fig. 1. The axial system and atom numbering in MO calculations

In the crystal structures involved in the present study the constituent molecules either occupy sites of centers of inversion, each of them thus maintaining identical interactions with adjacent neighbours in the continuous mixed stacks, or the molecular units are arranged as separate entities rather than in the form of stacks. Hence, our calculations are approximated to isolated pairs of overlapping donor and acceptor molecules. In fact, recent studies of Suzuki and I'Haya [17] indicate that results obtained in such cases for the pair model do not differ significantly from those for a three-molecule system.

Most of the calculations were performed on the CDC 6600 computer at the Tel-Aviv University Computation Center.

3. Molecular Orbitals

Molecular orbitals and the corresponding energy levels of ground closed shell configurations of TCNQ and the donor molecules were defined with the aid of both the IEHT method and its modified version IEHT₁. All the calculations were performed on planar molecular models of idealized geometry: symmetry D_{2h} for anthracene, phenazine, DPDO, TCNQ and TMPD (when hydrogen atoms of the methyl groups are ignored), and C_{2v} for PHT. The dimensions of the molecular models were based on the averaged bond distances and angles observed in relevant crystal structures. The computation was referred to the axial system and atom numbering shown in Fig. 1.

Table 1. Ionization potentials of the donor molecules

Molecule	Negative orbital energies (eV)				Experimental ionization potentials (eV)		Reference
	IEHT		IEHT ₁				
anthracene	10.1(π)		8.0(π)		7.5(π)		[25]
phenazine	10.2(π)	9.1(n)	8.1(π)	9.2(n)	8.4(π)	9.9(n)	[27]
DPDO	9.7(π)	10.2(n)	8.5(π)	9.8(n)	8.1(π)		[28]
TMPD	8.7(π, n)		6.9(π, n)		6.7(π, n) ^a		[26]
PHT	9.5(π)	10.5(n)	8.4(π)	9.6(n)	—		
pyrene	10.0(π)		8.1(π)		7.5(π)		[25]

^a Ionization potential of unsubstituted *p*-phenylenediamine is 7.3 eV (from photoelectron spectra, [29]).

Table 2. Molecular ground configuration; energies and symmetries of molecular orbitals (by the IEHT₁ method)

(a) π molecular orbitals

	anthracene		phenazine		DPDO		TMPD		PHT		TCNQ	
	E(eV)	Sym.	E	Sym.	E	Sym.	E	Sym.	E	Sym.	E	Sym.
1	-2.38	B_{2g}	-2.71	B_{2g}	-3.07	B_{2g}	-2.97	B_{1g}	-2.39	A_2	-2.64	B_{1g}
2	-3.45	A_u	-3.43	A_u	-3.33	A_u	-4.90	B_{3u}	-3.62	B_1	-3.37	B_{3u}
3	-4.76	B_{2g}	-4.96	B_{2g}	-5.43	B_{2g}	-5.40	A_u	-4.73	A_2	-4.59	B_{1g}
4	-4.91	B_{3u}	-5.25	B_{3u}	-5.80	B_{3u}	-6.90 ^a	B_{1g}	-5.22	A_2	-5.73	A_u
5	-5.69	B_{1g}	-5.69	B_{1g}	-5.82	B_{1g}	-7.66	B_{3u}	-5.65	B_1	-5.84	B_{2g}
6	-5.77	A_u	-5.91	A_u	-5.88	A_u	-8.44	B_{2g}	-6.29	B_1	-5.95	A_u
7	-6.68	B_{3u}	-6.82	B_{3u}	-8.51 ^a	B_{3u}	-9.07	B_{1g}	-6.49	A_2	-6.17	B_{3u}
8	-8.05 ^a	B_{2g}	-8.10 ^a	B_{2g}	-8.86	B_{2g}	-9.98	B_{3u}	-8.39 ^a	B_1	-7.88	B_{1g}
9	-8.78	B_{1g}	-8.97	B_{1g}	-9.19	A_u			-8.60	A_2	-8.65 ^a	B_{3u}
10	-8.86	A_u	-9.03	A_u	-9.22	B_{1g}			-9.11	A_2	-9.32	B_{2g}
11	-9.37	B_{2g}	-9.52	B_{2g}	-9.97	B_{3u}			-9.47	B_1	-9.72	B_{1g}
12	-9.47	B_{3u}	-9.52	B_{3u}	-10.81	B_{1g}			-9.69	B_1	-10.13	A_u
13	-10.19	B_{1g}	-10.44	B_{1g}	-10.95	B_{2g}			-10.32	A_2	-10.14	B_{2g}
14	-10.66	B_{3u}	-10.98	B_{3u}	-11.89	B_{3u}			-10.98	B_1	-10.54	B_{3u}
15											-11.36	B_{1g}
16											-11.52	B_{3u}

(b) highest occupied σ molecular orbitals

	anthracene	phenazine	DPDO	TMPD	PHT	TCNQ
1	-10.13 eV	-9.21(n)	-9.84(n)	-10.05	-9.61(n)	-10.48
2	-10.33	-10.33	-10.57	-10.67	-9.74(n)	-10.73
3	-10.65	-10.77	-10.96	-11.07	-10.36	-10.86
4	-10.99	-10.81(n)	-11.05(n)	-11.22	-10.78	-10.94

^a HOMO.

The results are summarized in Tables 1–3. The most significant discrepancy between the IEHT and IEHT₁ calculations is reflected in different ordering of the molecular levels. While the unmodified IEHT predicts an interspersing of the populated σ levels among the π levels, the results of the IEHT₁ calculations show that the weak binding energy of π MO's is reflected in their partial gathering above the σ levels of lower energy. Consequently, a comparison of the nature and the

Table 3. Molecular wave functions (eigenvectors and eigenvalues) relevant to present discussion of CT interactions (by the IEHT₁ method)

	anthracene (X=C)		phenazine (X=N)	DPDO (X=O)	TMPD	
MO	$\pi(B_{1g})$	$\pi(B_{2g})$	$\pi(B_{1g})$	$\pi(B_{3u})$		$\pi(B_{2g})$
Energy (eV)	-8.05	-8.78	-8.10	-8.51		-6.90
atom					atom	
X	0.421	0.000	0.430	-0.494	C(1)	-0.237
C(2)	0.102	0.341	0.116	0.268	C(2)	-0.180
C(3)	-0.297	0.010	-0.289	0.077	N	0.624
C(4)	-0.228	-0.315	-0.222	-0.253	C(4)	-0.016
	PHT		TCNQ			
MO	$\pi(B_1)$		$\pi(B_{3u})$	$\pi^*(B_{2g})$		
Energy (eV)	-8.39		-8.65	-7.88		
N	-0.235	C(1)	0.204	-0.215		
C(2)	-0.331	C(2)	-0.116	-0.274		
C(3)	0.053	C(3)	-0.403	0.388		
C(4)	0.327	C(4)	0.046	0.081		
C(5)	0.149	N	0.337	-0.337		
C(6)	-0.383					
C(7)	0.141					

eigenvalues of highest populated MO's (obtained with the IEHT₁ scheme) with experimental values of vertical ionization potentials is more encouraging (Table 1). In fact, discrepancies similar to those resulting from the IEHT computations have been also reported in some nonempirical studies in which the degeneracy of the radial components of p AO's is retained [18, 19]. It is interesting to note, that characterization of the HOMO in heterocyclic compounds is reportedly a controversial issue [20, 21], probably because calculations based on different methods lead to different results. Further discussion is based on the IEHT₁ results.

Eigenvalues of all π MO's and of the highest occupied σ orbitals are listed in Table 2. Table 3 shows the eigenvectors of several bonding orbitals in the various donors and of the lowest unoccupied MO (LUMO) in TCNQ, interaction of which will be considered below.

The energy values given in Tables 1 and 2 indicate that TMPD is the best π -electron donor. The spread in π energy levels is 7–9 eV in all molecules. The arrangement and the symmetry of the corresponding levels in isoelectronic anthracene and phenazine are similar. The highest occupied σ orbital in the heterocyclic molecules is partially localized on the heteroatoms, and can be characterized as a lone-pair orbital. Examination of orbital atomic populations indicates that both oxygen and nitrogen heteroatoms act as a π donor and σ acceptor, while the aromatic carbons play the opposite role. Considering the resulting total net charges, an almost uniform charge distribution is observed in anthracene; in other molecules the heteroatoms carry negative charge, leaving the carbon atoms somewhat positive.

These conclusions are consistent with other reported results on phenazine [22]

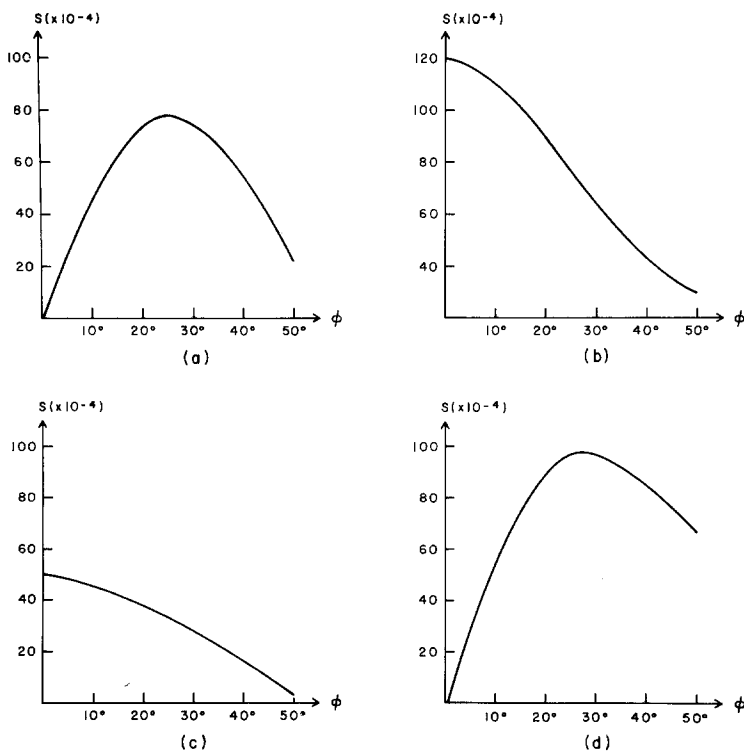


Fig. 2. Intermolecular overlap integral S as a function of rotation of the donor above a fixed acceptor by an angle of ϕ . The results correspond to overlap between the HOMO of the donor and the LUMO of the acceptor in the TCNQ complexes with (a) PHT (HOMO symmetry B_1), (b) TMPD (B_{1g}), (c) DPDO (B_{3u}), (d) phenazine (B_{2g}). In (a), (b) and (d) molecular centers of unlike molecules are superimposed, while in (c) the center of DPDO is displaced by 1.0 Å along the axis of lowest inertia of TCNQ. $\phi = 0^\circ$ corresponds to parallel axial systems of the constituents

and on TCNQ [23]. In comparison to previous EHT and IEHT calculations on anthracene [8] and on DPDO [24], they suggest also an improved representation of molecular properties for both molecules.

4. Intermolecular Overlap Integrals

Donor-acceptor intermolecular overlap integrals were calculated separately for interactions of each of the three highest occupied MO's of the donor molecules with the LUMO of TCNQ. Other vacant orbitals of TCNQ were not considered since their energies are higher by at least 1.7 eV than that of the LUMO. The observed interplanar donor-acceptor distances were kept fixed during the calculations.

In molecules characterized by point group symmetry D_{2h} , the symmetry species of populated MO's (in the chosen axial system) are B_{1g} , B_{2g} , A_u and B_{3u} . In PHT (point group C_{2v}) the characteristic elements are B_1 and A_2 . Fig. 2 describes the variation in value of the overlap integral S_{ij} , where i symbolizes a high occupied MO of the donor and j the LUMO of TCNQ, with rotation of the donor above the

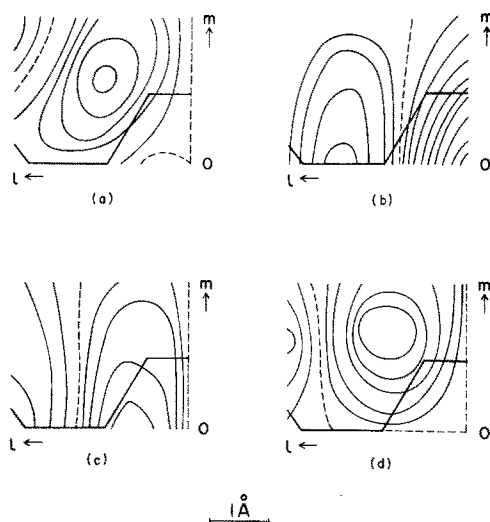


Fig. 3. Contour maps representing the variation in value of the intermolecular overlap integral with displacement of the donor in directions of the long (**l**) and short (**m**) axes of TCNQ (heavy line) localized on the origin. Principal axes of unlike molecules, which are fully superimposed at 0, remain parallel. The dotted line represents zero overlap, contour intervals are arbitrary, and the peak values of the overlap are of the order of 10^{-2} . The results correspond to overlap between the HOMO of the donor and the LUMO of the acceptor in the TCNQ complexes with (a) PHT (B_1), (b) TMPD (B_{1g}), (c) DPDO (B_{3u}), (d) phenazine (B_{2g})

acceptor for four complexes. Except for part (c) in the figure the molecular centers are overlapped. The contours on Fig. 3 illustrate the correlation between the calculated values of S_{ij} and the relative displacement of the donor with respect to the fixed acceptor, while the axial systems of inertia of both constituents remain parallel. Only representative examples are shown on both figures since the description of the overlap and of its variation for MO's of the same order and symmetry in the different donors is very similar.

The overlap integral for the interacting LUMO (B_{1g}) of TCNQ and highest occupied B_{2g} MO of the donor (e.g., Figs. 2(d) and 3(d)) receives maximal values for an angular offset of the donor by 25° , as well as for a configuration in which the donor is shifted 1.5 \AA along **l** and by 1.5 \AA along the **m** axis of TCNQ. A complete superposition of both molecules results in zero value for S_{ij} . Consideration of the B_{1g} highest occupied level of the donors in similar overlap calculations leads to two different configurations of the CT complex that correspond to calculated extreme values for S_{ij} . The overlap integral for the MO's of the same symmetry (e.g., Figs. 2(b) and 3(b)) has a maximal value when the molecules are directly superimposed. A second maximum is calculated for a displacement of the donor by 2.1 \AA along the **l** axis of TCNQ.

Almost identical results are obtained for the overlap between the highest occupied B_1 (Figs. 2 and 3) and A_2 orbitals of PHT and the LUMO of the acceptor.

Overlap interaction between MO of odd symmetry (A_u or B_{3u}) of the donor and the LUMO of TCNQ is zero as long as the molecular centers in the model are not

Table 4. Packing modes in several complexes of TCNQ^a

Compound	anthracene-TCNQ	phenazine-TCNQ	DPDO-TCNQ	TMPD-TCNQ	PHT-TCNQ
Repeating distance	7.00 Å	8.57 Å	7.04 Å	3.86 Å	—
Interplanar spacing	3.50	3.38	3.46	3.27	~3.41 Å
Offset along l	0	1.85	0.51	2.10	0
Offset along m	0	1.89	0.48	0	~0.50
Angular offset ϕ	0	0	0	0	22°
Relevant illustrations		2(d), 3(d)	2(c), 3(c)	2(b), 3(b)	2(a), 3(a)

^a The center of the donor is offset from above the center of TCNQ in the directions of the long (**l**) and short (**m**) axes of the acceptor, and the molecular axial system of the donor is rotated by angle ϕ with respect to axial system of the parallel acceptor.

shifted from their initial position. A single maximum in the corresponding overlap integrals is at $m=0$, $l=1.0$ Å and at $m=1.3$ Å, $l=0$ for the B_{3u} and A_u functions, respectively.

These results correlate surprisingly well with the packing modes observed in crystalline CT complexes of TCNQ (Table 4). With the exception of the anthracene-TCNQ complex, the geometry of all structures can be related to one of the configurations that correspond to maximal overlap between the HOMO of the donor and the LUMO of the acceptor. In the TCNQ compounds with phenazine, DPDO and TMPD the overlapping molecules are displaced relative to each other without rotation, while in the complex with PHT the rotated orientation is preferred, with a small displacement.

The observed structure of anthracene-TCNQ, in which the unlike molecules are fully superimposed, is not stabilized by the lowest energy CT state arising from promotion of an electron from the HOMO of anthracene to the LUMO of TCNQ. The transition moment for such interaction is zero. Mayoh and Prout [3] have suggested recently that interaction between the second highest occupied MO of anthracene and the LUMO of TCNQ is the main contributor to the stabilization energy. As shown above, one of the maximal values for the corresponding overlap integral is related to the same interaction. However, as far as the simple overlap calculations are concerned this is a trivial case, since the interacting MO's are of the same symmetry. The relative contribution of such interaction to the CT stabilization energy will obviously depend on the energy gap between the interacting levels (see below).

It is interesting to note that the observed geometry of the pyrene-TCNQ complex is characterized, in addition to a minor displacement of molecular centers from overlapping, by a rotation of pyrene by about 23° relative to TCNQ. MO calculations on pyrene with respect to a cartesian axial system in which the y - and z -directions are parallel respectively to the long and short molecular axes, show that the symmetries of the two highest occupied MO's are, as for anthracene, B_{2g} (-8.09 eV) and B_{1g} (-8.61 eV). One of the maxima in the calculated overlap integral between the HOMO of pyrene and the LUMO of TCNQ, that corresponds to rotation of pyrene by 25°, correlates, therefore, well with the observed packing mode. Paradoxically, a rather poor agreement has been reported between the

experimental geometry and that predicted by calculations of CT stabilization energy [3, 11].

For purposes of comparison with the above results, separate calculations have been carried out on the complexes of anthracene, phenazine and DPDO, taking into account the lowest energy as well as two higher energy CT configurations associated with electron transfer from the three highest populated MO's of the donor to the LUMO of TCNQ. The energy of each CT configuration was estimated by $\Delta E_k = I_k - A + C_k$, where I_k is the negative energy of the k -th MO of the donor, A the electron affinity of the acceptor, and C_k the relevant Coulomb interaction, and the CT ground state energies were approximated employing a configuration interaction scheme [2].

The results of this computation show the following features. The deepest potential minimum for the anthracene-TCNQ complex corresponds to a model with directly superimposed donor and acceptor species (see above and [3]). Two minima of comparable depth at $m=0$, $l=0$ and at $m=1.5$, $l=2.0$ Å are characteristic of the phenazine-TCNQ compound. On the other hand, the preferred geometrical configuration predicted for the DPDO-TCNQ system is in good agreement with the two-orbital results and the experimental data.

5. Discussion

Application of Mulliken's "Overlap and Orientation Principle" in its simplest form to studies of donor-acceptor relative orientation in π - π^* complexes of TCNQ results in a reasonable correlation between the molecular arrangement observed in a crystal and the theoretical principle. In all cases examined, one of the configurations of calculated maximum overlap between a high populated MO of donor and LUMO of TCNQ was found to be close to the observed geometry of the complex. In fact, it has been shown in other studies (e.g., [30]) that the two-orbital model frequently seems to provide *qualitatively* correct results for series of highly symmetric complexes of closely related donors with a given acceptor. The obtained results indicate that low-energy CT interactions, although much weaker than repulsion and dispersion forces, have an effect on the mode of donor-acceptor overlap (the intermolecular overlap, and thus the CT interaction, is directly related to the symmetry properties of MO's in the interacting moieties). Van der Waals and dipole-dipole forces, which determine the overall packing arrangement and the dynamics of such crystals [4, 31], are most probably much less sensitive to the relative orientation of the constituents in the stacked structure. The fact that the phenazine and DPDO molecules have very similar shapes, although different packing arrangements are observed for their TCNQ complexes, may serve as a nice demonstration.

The ionization potentials show a tendency of the donor to participate in CT complexes with TCNQ. It is well known [26, 30] that for a series of complexes having the same acceptor the energy of a CT state is approximately a linear function of the difference between the ionization potential and the electron affinity of the interacting orbitals. Correspondingly, a clear correlation has been observed between the calculated ionization potentials (negative orbital energies) and the

average separation in overlapping donor-acceptor pairs. Complexes with CT band of lower energy appear to have shorter interplanar perpendicular distance, indicating a higher importance of the CT contribution to the intermolecular bonding. A similar regular dependence of interplanar separations on ionization potentials has been found by Wallwork [32] in *s*-trinitrobenzene and chloranil complexes.

It seemed tempting to try to estimate the possible influence of steric interactions on the packing mode. An analysis of the packing arrangement based on minimization of the lattice energy was carried out on anthracene-TCNQ and phenazine-TCNQ complexes, in which the donor molecules have a very similar electronic structure. The lattice energy was approximated by an interaction potential made of a sum of (exp-6-1) nonbonded interatomic potential functions, which account for pairwise intermolecular repulsion, dispersion and monopole-monopole Coulombic forces [33]. From among many possible arrangements, several structural models were considered in these calculations, which aimed at prediction of the most stable crystal packing for the anthracene and the phenazine complexes [34]. It is interesting to note that short contacts between hydrogen atoms substituted on the central rings of neighboring anthracene molecules are the main contributors to the destabilization of a trial model of anthracene-TCNQ that corresponds to maximum overlap between the HOMO of the donor and the LUMO of the acceptor. The destabilization was by more than 2 kcal/mole relative to the experimental structure. In other cases the difference between the observed and the predicted arrangement is less than 0.7 kcal/mole, which is of low significance when dealing with room-temperature structures.

On the basis of the results and the considerations presented above we believe that the relative orientation of donor and TCNQ molecules within the stacks is primarily determined by CT interactions. Other bonding interactions and restrictions on crystal packing modify these effects. This tentative conclusion, which implies that the CT forces are more important at the stage of nucleation than they are in large crystalline aggregates, should be submitted to additional tests by other suitably planned comparative structural studies.

In the present interpretative investigation, many approximations are involved in the calculation of molecular orbitals and intermolecular overlaps, and many factors determining the lattice energy are left out. However, the overall agreement between the overlap results and the experimental data is encouraging. This type of calculation is orders of magnitude cheaper than extensive computations of stabilization energies, and it seems to provide often an acceptable approximate description of possible geometries in π molecular complexes. It appears that the approach, when employed with care (results of calculations based on the HOMO-LUMO model are not always consistent with those based on a configuration interaction scheme), may thus be quite useful to the experimental structure analyst in his routine studies of similar compounds.

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