Direct relationship between intermolecular charge-transfer and charge-resonance complexes *via* structural changes in the arene donor with various π-acceptors

Pierre Le Maguères, Sergey V. Lindeman and Jay K. Kochi

Department of Chemistry, University of Houston, Houston, Texas, 77204-5003, USA

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Aromatic donors (D) spontaneously form a series of colored intermolecular charge-resonance (CR) complexes with their cation radicals ($D^{+\bullet}$) as well as charge-transfer (CT) complexes with various π-acceptors (A). Spectroscopic changes during the formation of these CR and CT complexes are both included in a single Mulliken plot of $E_{CR,CT}$ *versus* $E°_{ox} - E°_{red}$. Precise X-ray crystallographic studies now reveal almost identical structural features of the CR and CT complexes, especially with a prototypical strong electron donor such as octamethylbiphenylene (**OMB**). Whereas most weaker donors do not show perceptible alterations of their molecular geometry during complex formation, **OMB** exhibits pronounced bond elongation/contraction of almost 2 pm both in its CT complexes with strong acceptors (**TCNE** and **TCNQ**) and in its CR complex ($\mathbf{OMB}_2$)$^{+\bullet}$. In both cases, the structural changes lie midway between geometries of the neutral **OMB** donor and its fully oxidized cation radical $\mathbf{OMB}^{+\bullet}$. The CT and CR complexes of **OMB** in the solid state also show similar crystal packing features that maintain interplanar separations as short as 3.1–3.2 Å with significant distortion (~6°) from planar molecular geometry. Together with the similar values of $K_{CR} = 350\ M^{-1}$ and $K_{EDA} = 440–490\ M^{-1}$, we acknowledge the common nature of the CT and CR complexes through an orbital consideration (Chart 1) that recognizes the antibonding component in CR complex formation.

Introduction

Aromatic hydrocarbons are electron donors (D) by virtue of their ready conversion to the corresponding cation radicals ($D^{+\bullet}$), and the ease with which they react with a wide variety of electron-poor electrophiles or acceptors (A) to form intermolecular electron donor–acceptor (EDA) complexes [eqn. (1)].[1,2] Importantly, there is increasing experimental

$$D + A \overset{K_{EDA}}{\rightleftharpoons} [D,A] \qquad (1)$$

evidence that such a prior donor–acceptor complexation facilitates the oxidation of the aromatic nucleus as well as its susceptibility to nucleophilic attack.[3,4]

A characteristic feature of the EDA interaction of an aromatic donor and a π-acceptor is the appearance of a new absorption band in the electronic (UV–vis) spectrum that is absent in the individual spectrum of each D and A component separately.[1,5] The new absorption bands are associated with the charge-transfer transition from the ground-state ($\Psi_{D,A}$) of the EDA complex to the first excited state. According to Mulliken theory,[7,8] the ground state of the EDA complex (in first approximation for weak donor–acceptor complexes) is given by eqn. (2), where ψ_{DA} corresponds to the no bond (van

$$\Psi_{D,A} \cong a\psi_{DA} + b\psi_{D^+A^-} + \ldots \qquad (2)$$

der Waals) association of D and A, and $\psi_{D^+A^-}$ corresponds to the dative or charge-transfer contribution. As such, the ratio $b^2/(a + b)^2$ is a viable indication of the degree of charge-transfer in the ground-state complex.[9,10]

It is also known that the aromatic donors readily self-associate with their corresponding cation radicals in solution to afford stabilized dimeric cation radicals [eqn. (3)].[11,12] The dimeric cation-radical possesses a completely electron-delocalized structure[13] and also exhibits a new broad (charge-resonance) absorption band in the near-IR region which is absent in the spectrum of either the neutral donor (D) or its cation radical component ($D^{+\bullet}$).[14,15] When an electron-deficient cation radical of the aromatic donor is considered as a strong cationic acceptor, we re-formulate Mulliken theory as eqn. (4), where the degree of charge transfer is exactly one half.

$$D^{+\bullet} + D \rightleftharpoons (D,D)^{+\bullet} \qquad (3)$$

$$\Psi_{(D,D)^+} \cong a\psi_{DD^+} + b\psi_{D^+D} + \ldots \qquad (4)$$

We have addressed the question of whether the analogy between the charge-transfer and the charge-resonance complexes is merely a formalism or whether the nature of the intermolecular forces in these complexes is indeed the same.[16] We recently showed that the charge-resonance absorption bands ($h\nu_{CR}$) of the cation-radical dimeric species of various aromatic donors are precisely included into the Mulliken plots of the charge-transfer energies ($h\nu_{CT}$) of EDA complexes of the same arenes with common electron acceptors.[17] We now turn our attention toward the *structural* features of these two kinds of complexes. When we take the magnitude of the structural change of the arene donor during complex formation as the most direct experimental measure of its degree of oxidation, we can directly compare the degree of charge transfer in charge-transfer and charge-resonance complexes, as described by eqns. (2) and (4).[18,20] To make a quantitative comparison of the structural geometry of arene donors in the EDA complexes relative to that extant in the neutral (non-complexed) donor and their corresponding cation radicals, we carefully prepared high-quality single crystals of the EDA complexes for X-ray crystallography at 120 K. Such precise low-temperature crystallographic measurements allowed us to routinely evaluate changes in C–C bond lengths in the donor and acceptor

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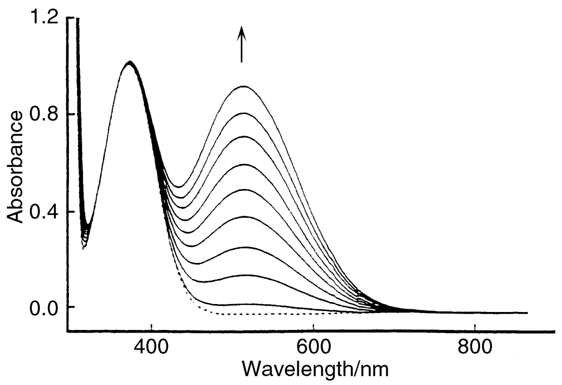
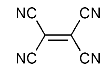
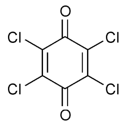
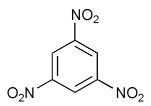
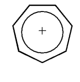


Fig. 1 Progressive growth of the charge-transfer absorption band at λ_{max} = 520 nm upon the incremental addition of hexamethylbenzene (**HMB**) to a 0.1 M solution of chloranil (**CA**) in dichloromethane.

Table 1 Donor–acceptor association of hexamethylbenzene with various π-acceptors [a]

Acceptor		λ_{max}/nm	K_{EDA}/M^{-1}	ε_{CT}/M^{-1} cm^{-1}
TCNE		544	15.3	5200
CA		520	2.80	2800
TNB		392	0.84	3300
Tr$^+$		414	0.54	6300

[a] In dichloromethane containing 4–6 mM acceptor and 50–500 mM hexamethylbenzene at 20 °C.

components upon complexation with a typical precision of ≤ 0.3 pm.[20]

Results

Spectroscopic and structural changes in weak EDA complexes

The UV–vis spectral changes occurring upon the incremental addition of hexamethylbenzene (**HMB**) to a solution of chloranil (**CA**) as a typical π-acceptor (Fig. 1) showed the monotonic growth of an additional absorption band (λ_{CT} = 520 nm), symptomatic of the Mulliken intermolecular EDA interaction. The treatment of these spectral changes according to Benesi–Hildebrand's procedure[21] yielded the formation constants (K_{EDA}) for the EDA complexes, the magnitudes in Table 1 of which are low—indicative of weak complexation between this aromatic donor and acceptor moieties.[22]

In 1:1 EDA crystals, the **HMB** donor and **CA** acceptor form regular alternate stacks with an interplanar separation (σ = 3.51 Å) sufficient to give rise to measurable intermolecular interactions (Fig. 2a). This is confirmed by the solid-state (UV–vis) reflectance spectrum of [**HMB**, **CA**] that showed the same additional absorption band (λ = 520 nm) as observed in solution, to confirm the existence of the same CT interactions in the crystal. However, all the aromatic C–C bond lengths [av. 1.410(2) Å] of the **HMB** donor in the weak complex do not show any significant change (within the precision of the measurement) relative to those in the free donor [1.411(2) Å].[20b] Such an apparent lack of structural deformation in **HMB** suggests that its complexation with planar π-acceptors induces only a low degree of charge transfer, which is also in accord with the limited values of the formation constants reported in Table 1.

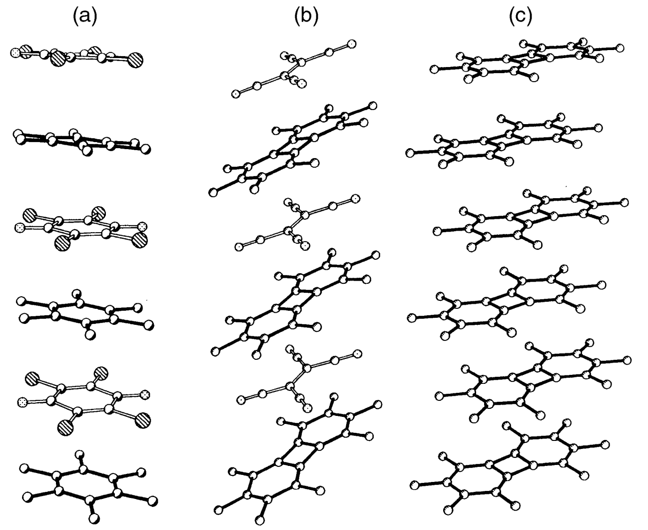
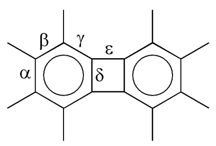


Fig. 2 Formation of regular stacks in the crystals of (a) the weak [**HMB**, **CA**] charge-transfer complex, (b) the strong [**OMB**, **TCNE**] charge-transfer complex, and (c) the α-modification of the [**OMB**$_2$]$^{+\bullet}$ charge-resonance complex.

Spectroscopic and structural changes in strong EDA complexes

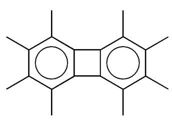
In order to study structural deformations of aromatic donors that show stronger donor–acceptor interactions than those in [**HMB**, **CA**], we next turned to the EDA complexes of the powerful electron donor, octamethylbiphenylene **OMB**,[23] with a pair of strong planar π-acceptors, tetracyanoquinodimethane (**TCNQ**) and tetracyanoethylene (**TCNE**).[25,26] The UV–vis spectra of both complexes show the additional absorption bands (λ_{max} = 870 and 880 nm for complexes with **TCNQ** and **TCNE**, respectively) symptomatic of intermolecular charge-transfer. The Benesi–Hildebrand treatment of the spectral changes upon the incremental addition of neutral **OMB** to a solution of the acceptor afforded formation constants of K_{EDA} = 440 M^{-1} for [**OMB**, **TCNQ**] and 490 M^{-1} for [**OMB**, **TCNE**], respectively.[22] Thus **OMB** indeed showed a significantly stronger tendency for EDA complexation than is apparent with **HMB**.



OMB

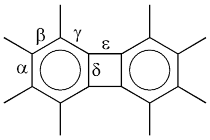
Formation of (alternate) donor–acceptor stacks was also observed in the crystal structures of both these 1:1 complexes—with the donor and acceptor molecules being separated by rather close interplanar distances of σ = 3.09 Å in [**OMB**, **TCNQ**] and 3.14 Å in [**OMB**, **TCNE**] (see Figs. 3a and 2b, respectively). This structural feature also accounts for the stronger CT interactions than that in [**HMB**, **CA**,] (compare the interplanar separation between **HMB** and **CA** of σ = 3.51 Å). Moreover, unlike the weak [**HMB**, **CA**] complex, a moderate but noticeable elongation of the average C–C bond length of Δ = 0.3 pm was observed in the benzenoid rings of **OMB** upon complexation with **TCNE** and **TCNQ** (see Table 2). Furthermore, the structural changes are much more significant for specific bonds in the **OMB** moiety: *e.g.* the α-bonds are elongated by $\Delta = +1.8(1)$ and $+1.9(1)$ pm and ε-bonds are shortened by $\Delta = -0.8(1)$ and $-1.7(1)$ pm in the complexes with **TCNE** and **TCNQ**, respectively (see Table 3). It is

Table 2 Average C–C bond lengths (Å) within the aromatic rings of the **OMB** donor and its relative ring expansion [a] during complex formation

Arene	Neutral (uncomplexed)	**[OMB, TCNE]**	**[OMB, TCNQ]**	**[OMB$_2$]$^{+\bullet}$**	**OMB$^{+\bullet}$**
 **OMB**	1.405	1.408 **+0.3 pm**	1.408 **+0.3 pm**	1.410 [b] **+0.5 pm**	1.415 [b] **+1.0 pm**

[a] The numbers in boldtype are measured, relative to the neutral donor.[b] Average from the two crystal structures.

Table 3 Average lengths (Å) of the chemically equivalent bonds in **OMB** donor and their changes [a] during its complexation



C–C bond	**OMB**	**[OMB, TCNE]**	**[OMB, TCNQ]**	**(OMB)$_2^{+\bullet}$** [b]	**OMB$^{+\bullet}$** [b]
α	1.393(3)	1.411(1)	1.412(1)	1.416(5)	1.438(3)
	1.392(1)	**+1.8 pm**	**+1.9 pm**	**+2.3 pm**	**+4.5 pm**
β	1.435(3)	1.433(1)	1.429(1)	1.427(5)	1.417(3)
	[1.425(1)]	**−0.2 pm**	**−0.6 pm**	**−0.8 pm**	**−1.8 pm**
γ	1.370(3)	1.375(1)	1.377(1)	1.380(5)	1.383(3)
	[1.375(1)]	**+0.5 pm**	**+0.7 pm**	**+1.0 pm**	**+1.3 pm**
δ	1.430(3)	1.422(1)	1.423(1)	1.431(5)	1.447(3)
	[1.428(1)]	**−0.8 pm**	**−0.7 pm**	**+0.1 pm**	**+1.7 pm**
ε	1.520(3)	1.512(1)	1.503(1)	1.497(5)	1.478(3)
	[1.517(1)]	**−0.8 pm**	**−1.7 pm**	**−2.3 pm**	**−4.2 pm**

[a] The numbers in boldtype are measured relative to the neutral molecule.[b] Average from the two structures.

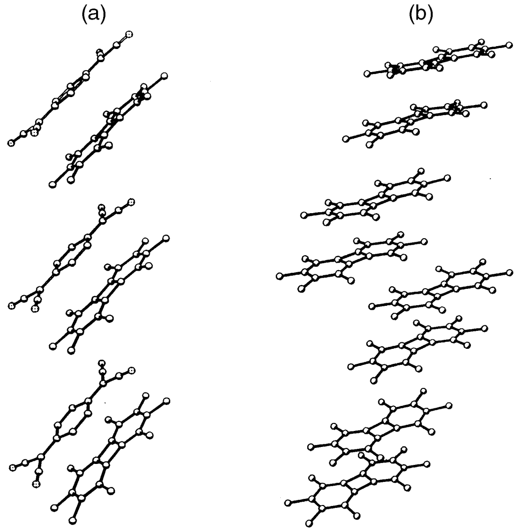


Fig. 3 Formation of degenerate (irregular) stacks consisting of (more or less) isolated molecular dyads in crystals consisting of (a) the strong [**OMB**, **TCNQ**] charge-transfer complex, and (b) the β-modification of the [**OMB**$_2$]$^{+\bullet}$ charge-resonance complex.

singularly remarkable that in the crystalline [**OMB**, **TCNQ**] complex in which the regular stacks vanish (see Fig. 3a), both the donor and acceptor components are significantly bent toward each other—the (average) dihedral angles between terminal groups in the paired **OMB** and **TCNQ** molecules (that appear almost planar in the regularly stacked structures) being $\theta = 5.5$ and 5.3°, respectively (see Fig. 4a).

Complexation of OMB in the charge-resonance complex with its cation radical. Spectroscopic and structural properties of the resulting mixed-valence dimeric cation radical

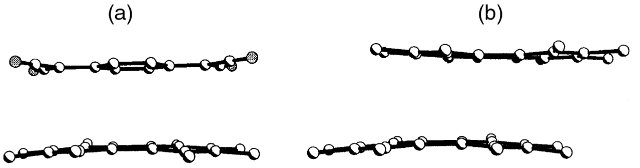


Fig. 4 Bending of planar π-moieties during EDA complex formation in (a) the strong [**OMB**, **TCNQ**] charge-transfer complex, and (b) the β-modification of the [**OMB**$_2$]$^{+\bullet}$ charge-resonance complex.

The one-electron oxidation of a variety of planar aromatic donors (D) generates cation radicals which spontaneously associate in solution with their neutral precursor to afford stabilized dimeric cation radicals [see eqn. (3)], and allowed us to isolate single crystals of the dimeric cation-radical complex (**OMB**)$_2^{+\bullet}$SbCl$_6^-$ as well as the corresponding cation-radical salt **OMB**$^{+\bullet}$SbCl$_6^-$.

The charge-resonance absorption in the dimeric salt (**OMB**)$_2^{+\bullet}$SbCl$_6^-$ was established by UV–vis spectroscopy. Thus when neutral **OMB** was added incrementally to a blue solution of the pure monomeric **OMB**$^{+\bullet}$SbCl$_6^-$ at room temperature, UV–vis spectral analysis (Fig. 5) indicated the growth of a new broad NIR absorption band at $\lambda_{max} = 1850$ nm. The solid-state UV–vis spectrum of the dimeric salt (diffuse reflectance in a K$^+$PF$_6^-$ matrix) also revealed the same NIR absorption band at 1850 nm as that observed in solution. This characteristic NIR absorption band, ascribed to electron delocalization within the dimeric (**OMB**)$_2^{+\bullet}$ units, is highly reminiscent of new charge-transfer absorptions (compare Fig. 1) appearing upon EDA complexation between an electron donor and an electron acceptor (as described for [**OMB**, **TCNQ**] above). Moreover, the incremental growth of the charge-resonance band at 1850 nm could be treated according to the Benesi–Hildebrand procedure,[27] and a formation constant for the dimeric (**OMB**)$_2^{+\bullet}$ units was established as $K_{CR} = 350$ M^{-1}. Note that this value is of the same order as the formation constant of $K_{EDA} = 440$ M^{-1} calculated for the

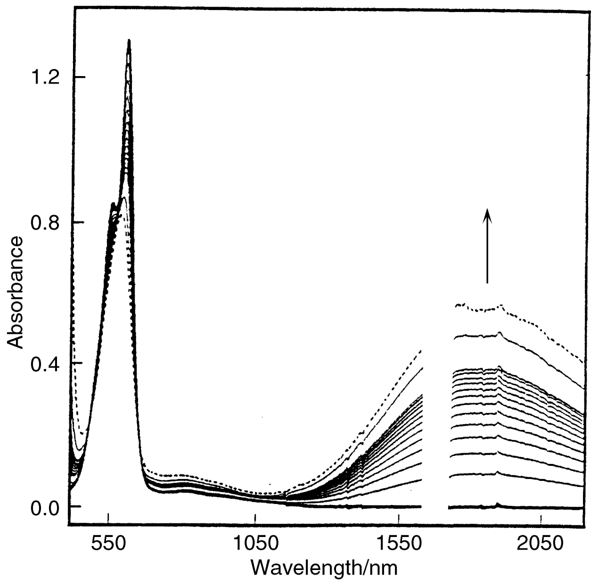


Fig. 5 Progressive growth of the charge-resonance absorption band at λ_{max} = 1850 nm in the NIR spectral region upon the incremental addition of arene donor (**OMB**) to a 0.1 M solution of its cation radical (**OMB**$^{+\bullet}$) in dichloromethane.

charge-transfer complex [**OMB**, **TCNQ**]. We now address the question as to whether the structural changes of the **OMB** moiety in both these complexes are also comparable.

X-ray structural analysis of the dimeric cation-radical salt revealed the formation of alternate stacks of **OMB** moieties in two crystalline forms. These stacks have different degrees of regularity[28] (Figs. 2c and 3b) reminiscent of those in [**OMB**, **TCNE**] and [**OMB**, **TCNQ**] (see Figs. 2b and 3a). In the α-form (mixed salt with $OEt_3^+SbCl_6^-$)[29] the separations between the **OMB** units in the stacks are σ = 3.40 and 3.53 Å (compare with σ = 3.14 Å in [**OMB**, **TCNE**]), and the **OMB** moieties are almost planar. On the other hand, in the β-form (toluene monosolvate) they are as different as σ = 3.22 and 3.57 Å (compare with 3.09 Å in [**OMB**, **TCNQ**]), and the **OMB** moieties within the closely separated dyads exhibit significant bending toward each other by θ = 3.9 and 7.6° (see Fig. 4b). Tables 2 and 3 show that the geometrical parameters of the partially oxidized **OMB** moieties lie precisely in-between the corresponding values found in neutral **OMB** and its cation radical **OMB**$^{+\bullet}$.

Discussion

According to Mulliken theory [eqn. (2)], the donor and acceptor components within a charge-transfer complex can be considered as partially oxidized and reduced species, respectively. As such, the degree of charge transfer can be derived from structural changes of the donor and acceptor components in the complex by comparison with the geometry of the corresponding neutral donor–acceptor and the cation-/anion-radical pair.[18] Such a structural approach has been previously used for π-acceptors such as **TCNQ**,[30,31] and similar correlations have also been employed for π-donors such as tetrathiafulvalene derivatives.[32] Unfortunately, the earlier estimates of degree of charge transfer were based on rather imprecise structural data that left error bars that were too large for the derived values. In this study, we used our own (precise) crystallographic data of a series of donor and acceptors under comparable (low-temperature) conditions with a typical precision better than 0.3 pm. The resulting geometric changes measured for the **OMB** donor at different oxidation degrees are summarized in Table 3 and graphically represented in Fig. 6.

For the progressive series: **OMB** to [**OMB**$_2$]$^{+\bullet}$ and to **OMB**$^{+\bullet}$, we observe monotonic changes in bond lengths (elongation or contraction) proportional to the successive oxidation of the donor from 0 to $+\frac{1}{2}$ to +1. The deviations from linearity lie well within the experimental precision of the measurements, and do not exceed 0.3 pm (except for the δ bond in the [**OMB**$_2$]$^{+\bullet}$ moiety which deviated by −0.7 pm from the average bond lengths in **OMB** and **OMB**$^{+\bullet}$). In order to fit the points corresponding to the experimental geometry of **OMB** within the charge-transfer complexes, and thus to obtain a degree of their effective oxidation states, we used the relationship eqn. (5),

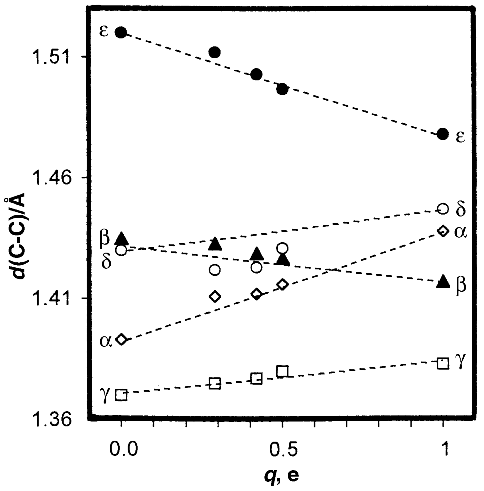


Fig. 6 Changes in chemically equivalent **OMB** bond lengths [d(C–C), Å] with different oxidation degrees [q, e], as presented in Table 3.

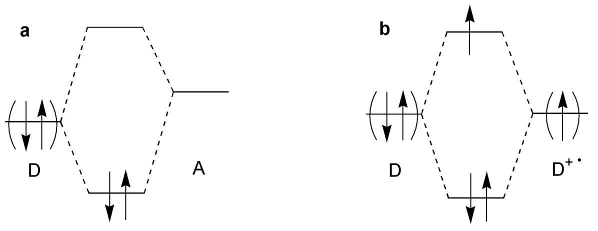
$$\boldsymbol{q} = (\pm)\Sigma|\delta_i|/\Sigma|\Delta_i| \qquad (5)$$

where q is the effective charge (oxidation degree) of the molecule, δ_i is a deviation of a bond length in the CT complex from that in the neutral molecule, Δ_i is a deviation of a bond length in the corresponding cation radical from that in the neutral molecule, and all the summations (i) have been carried out over every C–C π-bond in the donor and cation. It is particularly noteworthy that eqn. (5) yields an exact value of q = +0.50 for the **OMB** moiety in [**OMB**$_2$]$^{+\bullet}$.

The calculated oxidation degrees of the **OMB** moiety in the [**OMB**, **TCNE**] and [**OMB**, **TCNQ**] complexes are q = +0.29 and +0.42, respectively. This indicates that a significant charge redistribution occurs in the **OMB** moiety (approaching $+\frac{1}{2}$) during the formation of the strong charge-transfer complexes. Remarkably, the δ bonds both in [**OMB**, **TCNE**] and [**OMB**, **TCNQ**] complexes also exhibit large negative deviations of Δ = −1.2 and −1.3 pm, respectively, from the extrapolated values (compare with Δ = −0.7 pm deviation in [**OMB**$_2$]$^{+\bullet}$).

Significant similarities between the charge-transfer and the charge-resonance complexes of **OMB** become more obvious from a comparative analysis of their crystal packings. First, we observe a regular stacking both in the charge-transfer and the charge-resonance complexes of **OMB**. Second, this stacking can easily vanish for both kinds of complexes with the formation of (more or less) isolated dimeric associates. Third, the intermolecular separations (σ) in the duplexes are much shorter than those within the stacks. (For example, σ = 3.09 Å in [**OMB**, **TCNQ**] *versus* σ = 3.14 Å in [**OMB**, **TCNE**], and σ = 3.22 Å in β-[**OMB**$_2$]$^{+\bullet}$ *versus* σ = 3.40 Å in α-[**OMB**$_2$]$^{+\bullet}$.) Furthermore, undistorted planar shapes of the donor–acceptor dyads within the stacks change into significantly bent ones in the couples with θ = 5.5° in the charge-transfer couples, and by an average of θ = 5.7° in the charge-resonance couple.

In other words, the (strong) charge-transfer and the charge-resonance complexes both exhibit qualitatively very similar structural features that arise from similar degrees of electron redistribution. The accompanying spectroscopic changes also point to the common electronic nature of these associates, as represented in the qualitative orbital diagrams depicted in



Donor/acceptor (CT) complex

Charge-resonance (CR) complex

Chart 1

Chart 1. These molecular orbital diagrams schematically emphasize the pair of bonding and antibonding *intermolecular* orbitals to arise from the donor–acceptor dyad consisting of either D with A or D with $D^{+\bullet}$.

In the case of EDA complexes in which the HOMO of a donor interacts with the LUMO of an acceptor in **a** (Chart 1), a purely attractive interaction results from the formation of a filled intermolecular bonding orbital and an empty antibonding intermolecular orbital. By contrast, a closed-shell donor interacting with its cation radical will produce in **b** (Chart 1) a filled bonding orbital as well as a *half-filled* antibonding intermolecular orbital with a resultant weakened intermolecular attraction.

Our experimental data are consistent with this representation, since the strength of the intermolecular association derived both from the X-ray data and from the equilibrium constants in solutions does not correspond directly to the degree of charge transfer in these complexes. Thus, the charge-transfer complex [**OMB**, **TCNQ**] with $q \cong 0.4$ exhibits a stronger (separation $\sigma = 3.09$ Å, bend $\theta = 5.5°$, $K_{EDA} = 440$ M^{-1}) intermolecular association than the charge-resonance complex $[\mathbf{OMB}_2]^{+\bullet}$ — despite the larger value of $q = 0.5$ (separation 3.22 Å, bend 5.7°, $K_{CR} = 350$ M^{-1}).

Conclusions

Precise structural studies on the charge-transfer (CT) complexes of the strong π-donor octamethylbiphenylene (**OMB**) with a pair of strong π-acceptors **TCNE** and **TCNQ**, together with the structural data on its charge-resonance (CR) complexes $[\mathbf{OMB}_2]^{+\bullet}$ have shown: (*a*) the **OMB** moiety in both the CT and CR complexes exhibits significant and comparable changes in bond lengths [up to 2.0(3) pm] that indicates partial oxidation (40–50%) upon complexation. (*b*) CT and CR complexes both manifest a tight intermolecular association (with interplanar distances shortened up to $\sigma = 3.1$ Å) that can show up in crystals as (more or less) isolated bimolecular associates. (*c*) In such dyads, the components of both the CT and CR complexes experience a bending ($\theta = 6°$) toward each other that significantly deviates from the original planar molecular shapes. (*d*) The association energies of the CT and CR complexes in dichloromethane solutions are quite similar—based on spectroscopic titration data that afford formation constants of $K_{EDA} = 440$–490 and $K_{CR} = 350$ M^{-1}, respectively.

Along with our recent spectroscopic observations that both the CT and CR complexes fit within the same Mulliken plot, the present structural data offer convincing evidence that *the nature of chemical (electronic) interactions is essentially the same within CT and CR species.* This can be represented in terms of orbital coupling of the interacting species that produce bonding and anti-bonding combinations of *intermolecular* orbitals as depicted in Chart 1 with electron transitions between them. On the other hand, the partial population of the antibonding *intermolecular* orbital in the CR complexes is reflected in a somewhat looser molecular association compared to the corresponding CT complexes.

Experimental

Materials

Hexamethylbenzene (**HMB**) (Aldrich) was purified by repeated crystallization from ethanol and heptane. The synthesis of 1,2,3,4,5,6,7,8-octamethylbiphenylene (**OMB**)[23] was carried out as described previously. Tetrachloro-*p*-benzoquinone (**CA**), tetracyanoquinodimethane (**TCNQ**) and tetracyanoethylene (**TCNE**) (Aldrich) were sublimed *in vacuo* and recrystallized from benzene. Triethyloxonium hexachloroantimonate (Aldrich) and nitrosonium hexachloroantimonate salts were stored in a Vacuum Atmosphere HE-493 dry box kept free of oxygen. Dichloromethane (Mallinckrodt analytical reagent) was repeatedly stirred with fresh aliquots of conc. sulfuric acid (~20% by volume) until the acid layer remained colorless. After separation, it was washed successively with water, aqueous sodium bicarbonate, water, and aqueous sodium chloride and dried over anhydrous calcium chloride. The dichloromethane was distilled twice from P_2O_5 under an argon atmosphere and stored in a Schlenk flask equipped with a Teflon valve fitted with Viton O-rings. The hexane, toluene and tetrahydrofuran were distilled from P_2O_5 under an argon atmosphere and then refluxed over calcium hydride (~12 h). After distillation from CaH_2, the solvents were stored in the Schlenk flasks under an argon atmosphere.

Monomeric octamethylbiphenylene (OMB) cation-radical salt

A 200-mL flask equipped with a Schlenk adapter was charged with triethyloxonium hexachloroantimonate (657 mg, 1.5 mmol) and a solution of **OMB** (266 mg, 1 mmol) in anhydrous dichloromethane (25 mL) was added under an argon atmosphere at −20 °C. The heterogeneous mixture immediately took on a blue coloration which intensified with time. The dark-colored mixture was stirred for 4 hours to yield a blue solution of $\mathbf{OMB}^{+\bullet}$ [λ_{max} (nm) = 600, 550 (sh), see Fig. 5]. The dark-blue solution was cooled to −50 °C in a dry-ice–acetone bath, and anhydrous toluene (100 mL) was added to precipitate the dissolved salt. The dark-blue precipitate was filtered under an argon atmosphere, washed with hexane (3 × 25 mL) and dried *in vacuo*. The highly pure cation-radical salt $\mathbf{OMB}^{+\bullet}SbCl_6^-$ (*vide infra*) was obtained in essentially quantitative yield (530 mg, 0.88 mmol). The preparation of octamethylbiphenylene dimeric cation radical salt $(\mathbf{OMB})_2^{+\bullet}$ $SbCl_6^-$ was described previously.[17]

Preparation of donor–acceptor complexes of arenes with chloranil (CA), tetracyanoquinodimethane (TCNQ), tetracyanoethylene (TCNE)

The donor–acceptor complexes [**HMB**, **CA**], [**OMB**, **TCNQ**] and [**OMB**, **TCNE**] were crystallized from equimolar solutions of the donor and acceptor by slow evaporation of dichloromethane.

X-Ray crystallography

The intensity data for all the compounds were collected with the aid of a Siemens SMART diffractometer equipped with a CCD detector using MoKα radiation ($\lambda = 0.71073$ Å), at −150 °C unless otherwise specified. The structures were solved by direct methods[33] and refined by a full matrix least-squares procedure with IBM Pentium and SGI O_2 computers. [The X-ray structure details of various compounds are on deposit and can be obtained from the Cambridge Crystallographic Data Centre, UK.]†

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† CCDC reference number(s) 162663–162665, 138876, 138877, and 158741. See http://www.rsc.org/suppdata/p2/b0/b009543p/ for crystallographic files in .cif or other electronic format.

Crystal data for [HMB·CA] CT complex. Brutto formula: ($C_{18}H_{18}Cl_4O_2$). MW = 408.12, monoclinic $P2_1/n$, $a = 7.0658(1)$, $b = 8.6430(1)$, $c = 14.8612(3)$ Å, $\beta = 101.874(1)°$, $D_c = 1.526$ g cm^{-3}, $V = 888.15(2)$ Å^3, $Z = 2$. The total number of reflections measured was 10533, of which 3933 reflections were symmetrically non-equivalent. Final residuals were $R1 = 0.0368$ and $wR2 = 0.0883$ for 3116 reflections with $I > 2\sigma(I)$.

Crystal data for [OMB·TCNE] CT complex. Brutto formula: ($C_{26}H_{24}N_4$). MW = 392.49, monoclinic $P2_1/c$, $a = 16.137(2)$, $b = 7.232(1)$, $c = 17.680(2)$ Å, $\beta = 95.526(3)°$, $D_c = 1.269$ g cm^{-3}, $V = 2053.7(5)$ Å^3, $Z = 4$. The total number of reflections measured was 23371, of which 8872 reflections were symmetrically non-equivalent. Final residuals were $R1 = 0.0426$ and $wR2 = 0.1019$ for 5608 reflections with $I > 2\sigma(I)$.

Crystal data for [OMB·TCNQ] CT complex. Brutto formula: ($C_{32}H_{28}N_4$). MW = 468.58, monoclinic $P2_1/c$, $a = 15.1081(8)$, $b = 9.6152(6)$, $c = 17.0229(8)$ Å, $\beta = 95.980(2)$ °, $D_c = 1.266$ g cm^{-3}, $V = 2459.4(2)$ Å^3, $Z = 4$. The total number of reflections measured was 30631, of which 10776 reflections were symmetrically non-equivalent. Final residuals were $R1 = 0.0455$ and $wR2 = 0.1109$ for 6765 reflections with $I > 2\sigma(I)$.

Crystal data for $[OMB_2]^{\bullet+}SbCl_6^-\cdot C_7H_8$ CR complex (β-form, toluene solvate). Brutto formula: ($C_{47}H_{56}Cl_6Sb$). MW = 955.37, triclinic $P\bar{1}$, $a = 12.4774(1)$, $b = 12.6630(1)$, $c = 14.3832(2)$ Å, $\alpha = 74.421(1)$, $\beta = 77.326(1)$, $\gamma = 86.717(1)°$, $D_c = 1.486$ g cm^{-3}, $V = 2135.73(4)$ Å^3, $Z = 2$. The total number of reflections measured was 30219, of which 18187 reflections were symmetrically non-equivalent. Final residuals were $R1 = 0.0724$ and $wR2 = 0.1561$ for 9462 reflections with $I > 2\sigma(I)$.

Crystal data for $OMB^{\bullet+}SbCl_6^-$ Salt. Brutto formula: ($C_{20}H_{24}Cl_6Sb$). MW = 598.84, triclinic $P\bar{1}$, $a = 8.6059(1)$, $b = 11.7390(2)$, $c = 13.2313(1)$ Å, $\alpha = 115.116(1)$, $\beta = 100.611(1)$, $\gamma = 95.783(1)°$, $D_c = 1.707$ g cm^{-3}, $V = 1165.32(3)$ Å^3, $Z = 2$. The total number of reflections measured was 15888, of which 9719 reflections were symmetrically non-equivalent. Final residuals were $R1 = 0.0506$ and $wR2 = 0.0753$ for 6977 reflections with $I > 2\sigma(I)$.

Crystal data for $OMB^{\bullet+}SbCl_6\cdot CH_2Cl_2$ salt (dichloromethane solvate). Brutto formula: ($C_{21}H_{26}Cl_8Sb$). MW = 683.77, triclinic $P\bar{1}$, $a = 9.6343(2)$, $b = 10.6007(2)$, $c = 13.8761(2)$ Å, $\alpha = 81.964(1)$, $\beta = 70.035(1)$, $\gamma = 80.276(1)°$, $D_c = 1.737$ g cm^{-3}, $V = 1307.70(4)$ Å^3, $Z = 2$. The total number of reflections measured was 16484, of which 11276 reflections were symmetrically non-equivalent. Final residuals were $R1 = 0.0369$ and $wR2 = 0.0671$ for 8130 reflections with $I > 2\sigma(I)$.

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