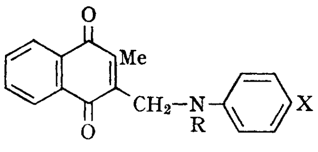
Intramolecular Donor–Acceptor Interaction between Aromatic Amines and Quinones

By R. CARRUTHERS, F. M. DEAN, L. E. HOUGHTON, and A. LEDWITH*
(*Donnan Laboratories, University of Liverpool, Liverpool* 7)

INTERMOLECULAR adducts of aromatic amines and quinones form one of the best known classes of donor–acceptor complexes.[1] Crystalline adducts have been isolated[2,3] and, depending on the electron affinity of the quinone, the complexes are either completely covalent, or completely ionic as a result of electron transfer from amine to quinone.

The compounds (I a—e) were available from studies on the reactivity of quinone methides[4] and all possess intense magenta-black colours in the crystalline state.



	R	X
a:	Me	H
b:	Me	Cl
c:	H	H
d:	H	Me
e:	H	CO$_2$Me

(I)

The complexes (I a—e) dissolve readily in a wide range of organic solvents giving solutions exhibiting very broad absorption bands in the visible part of the spectrum. From the shape of the absorption band, the lack of any correlation between λ_{max} and solvent dielectric, and the effect of substituents on λ_{max}, it is evident that the solution colours result from typical charge-transfer spectra. The donor properties of the amine residues are destroyed by protonation, as shown by the reversible bleaching of the solutions upon acidification. Representative data are given in the Table.

TABLE

Charge transfer spectra of compounds (Ia—e)

Compound	CH$_3$OH solvent λ_{max} (nm)	CH$_3$OH solvent ϵ_{max}	CH$_2$Cl$_2$ solvent λ_{max} (nm)	CH$_2$Cl$_2$ solvent ϵ_{max}
(Ia)*	506	220	514	306
(Ib)	501	294	513	363
(Ic)	475	214	480	232
(Id)	485	194	495	232
(Ie)	466	348	470	303

* In other solvents values of λ_{max} (nm) [and ϵ_{max}] were: cyclohexane 506, [226]; benzene 518, [338]; nitromethane 510, [206]; tetrahydrofuran 505, [162].

The absorbance of (Ia) was found to obey Beer's Law in CH$_2$Cl$_2$ and CH$_3$OH for the concentration range employed (40—8 × 10^{-4}M) suggesting that these charge transfer spectra result from non-conjugative, *intramolecular*, donor–acceptor interaction.

Parallel studies on the related intermolecular complexes (*e.g.*, between 2-methyl-, and 2,3-dimethyl-naphthaquinone, and *N*-methyl- and *NN*-dimethyl-anilines, respectively) have established that the intermolecular charge-transfer spectra have maxima 1200—2000 cm.$^{-1}$ higher in energy than the corresponding intramolecular values. Benesi–Hildebrand[5] or Rose–Drago[6] evaluation of the data for the intermolecular complexes gives values of $\epsilon_{\text{max}} = 200$—$300$, and $K_c \sim 0{\cdot}5$ l./mole. It is interesting that the values of ϵ_{max} are almost identical for the corresponding inter- and intra-molecular complexes.

Examination of the crystalline form of (Ie) by diffuse reflectance spectroscopy shows that the charge-transfer spectra has been subjected to a substantial red shift due to the expected crystal interaction effects.[2] The very broad reflectance spectrum of (Ie) (Figure) can be resolved, by band analysis,† into two peaks centred around 515 nm. and 655 nm. From similar analyses of the reflectance spectra of the other compounds we find that whereas the longer wavelength band shifts with changing substituents (as for the solution spectra), the shorter wavelength charge-transfer band remains centred around 510 nm. 1,4-Disubstituted benzenes are known to give rise to two charge transfer bands, one of which is fixed and one varying in energy according to the nature of the substituents.[7] Consequently it appears that the compounds (I a—e) are neutral donor–acceptor complexes in solution and in the crystalline state. Further evidence for the non-ionic nature of (I) was obtained by i.r. analysis. The carbonyl stretching frequencies of (I a—e) are all similar to those of 2-methyl-, and 2,3-dimethyl-naphthaquinone, whereas quinone–amine adducts in which electron transfer has occurred, show marked shifts in carbonyl stretching frequencies, as expected from the decrease in bond orders.[8]

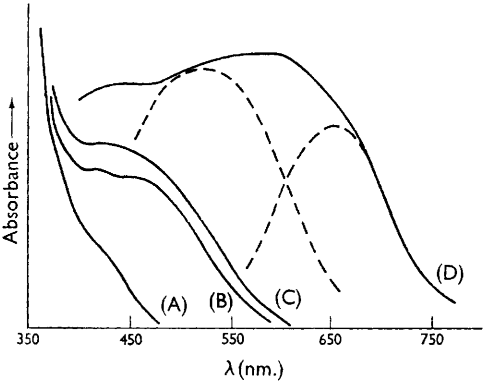


FIGURE. *Absorption spectra:* (A) *2,3-dimethylnaphthaquinone in* MeOH; (B) (Ie) *in* MeOH; (C) *thin film of glass from* (Ie); *and* (D) *diffuse reflectance spectrum of crystaline sample of* (Ie), *"diluted" with magnesium carbonate, showing band analysis.*

Observation of a crystal of (Ie) under a polarising microscope revealed distinct dichroism, the light polarised *perpendicular* to the needle axis being more strongly absorbed. This result contrasts sharply with the general observation[9] that intermolecular complexes crystallise with the donor and acceptor molecules stacking alternately along the needle axis, and give rise to a charge-transfer band polarised parallel with the needle axis, *i.e.*, perpendicular to the molecular planes.

On melting, (Ie) readily cools to a glass which shows only the less intense charge-transfer band characteristic of the solution spectra (Figure). It is probable, therefore, that the regular crystal lattice enforces a molecular conformation favouring the donor–acceptor orbital overlap, in addition to causing a "crystal shift" of the charge transfer bands.

Intramolecular complexes such as (I) have not been extensively reported in the literature,[10] but clearly provide convenient substrates for the study of absorption and emission characteristics of donor–acceptor complexes and for a better understanding of the conformational requirements of charge-transfer spectra.

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† The "crystal shift" of the long wavelength peak, derived from the band analysis, is very similar to that reported for related crystalline, intermolecular quinone–amine adducts (ref. 2). In solution the first-charge transfer band would be masked by the quinone absorption bands.

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