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Mendeleev Commun., 1995, **5(5)**, 205–206
Mendeleev Communications

The Bimolecular Model of a Trimolecular Electron Donor–Acceptor Complex

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The spectrum of the charge-transfer complex of 1,3-bis(diphenylamino)propane with CBr_4 is red-shifted by 900 cm^{-1} with respect to that of *N*-methyldiphenylamine, which simulates the shift of the spectrum of the 2:1 complex with respect to that of the 1:1 analogue.

Many donor–acceptor systems have been shown to be capable of forming not only a 1:1 charge transfer (CT) complex but 2:1 and the higher order analogues as well. When employing diphenylamine as a donor and CBr_4 as an acceptor, formation of complexes of different compositions manifests itself in the fact that the observed spectrum of the reaction mixture is red-shifted as component concentrations increase.[1] In that case the spectrum is a sum of the CT bands of different complexes and is described satisfactorily by assuming that the shift of the CT band of the 2:1 complex with respect to that of the 1:1 analogue comprises 1000 cm^{-1}.

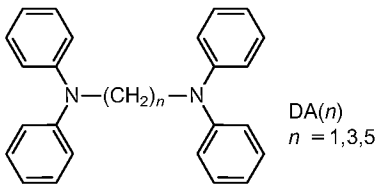
The problem of the relationship between the CT bands of different complexes is discussed in the literature.[2,3] The main difficulty arises in the determination of the individual spectral properties of the 1:1 and 2:1 complexes. The spectrum of mainly the 1:1 complex can be observed experimentally in dilute solution, but the CT band of the 2:1 complex can be separated from the combined spectrum of the concentrated solution only by mathematical processing.

We assumed that the spectrum of mainly the 2:1 complex can be directly observed experimentally by using a 'bidonor' compound. In fact, in the 2:1 complex a molecule of acceptor A binds two molecules of donor D into a common unstable molecular system, the latter being formed in solution in appreciable quantity only on increasing component concentrations, reaction (1).

$$A + D \rightleftharpoons A{\cdot}D \overset{D}{\rightleftharpoons} D{\cdot}A{\cdot}D \quad (1)$$

$$A + D\sim\!\!\sim D \rightleftharpoons A{\cdot}D\sim\!\!\sim D \rightleftharpoons D{\cdot}A{\cdot}D \quad (2)$$

However, once two donor groups are bound to one another by a bridge of covalent bonds in one molecule of 'bidonor', the formation of a complex of 2:1 functional structure but of 1:1 molecular structure is possible at a given length and flexibility of the bridge, reaction (2).



As indicated below, using α,ω-bis(diphenylamino)alkanes DA(*n*) as an example, the polymethylene chain consisting of three links satisfies these requirements.

Fig. 1 shows differential spectra of the complexes of diamines DA(*n*) with CBr_4 as well as the CT band of the complex of a similar monoamine, *N*-methyldiphenylamine (MA). For the purpose of comparison all spectra are measured under identical conditions and at equal concentration of functional groups of donor and acceptor. The alteration of optical density of the CT band on transition from one complex to another (Fig. 1) can reflect the change of both complex concentration (and thereby equilibrium constant) and extinction coefficient.

The maximum of the CT band of the MA·CBr_4 complex lies at 352 nm (Fig. 1, spectrum 1). The position of the bands in the spectra of diamine complexes depends considerably on the length of the polymethylene bridge. Given minimal length (one CH_2 group), steric hindrance appears to be created for optimum interaction of two diphenylamine groups because of their non-planar structure. As a result the band of the complex of the simplest diamine DA(1) (spectrum 2) is blue-shifted to 341 nm with respect to that of the DA complex.

Another hindrance arises in the formation of an intramolecular complex in compounds with a maximum investigated length of bridge (five CH_2 groups). The complexes of DPA derivatives with CBr_4 have a small formation enthalpy,[4] which appears to be insufficient to compensate for entropy losses on coiling up and fixing of one of the conformations. As a result, in diamine DA(5) two amine groups behave practically independently of one another, and the properties of the DA(5)·CBr_4 complex, possessing a maximum of the CT band at 355 nm (Fig. 1, spectrum 4), are practically similar to that of the monoamine complex [reaction (2) is limited by the first stage].

The combination of properties of the polymethylene bridge – flexibility and length – required for formation of an intramolecular 2:1 complex is realized in diamine DA(3). Its complex shows the CT band (Fig. 1, spectrum 3) red-shifted with respect to that of the monoamine model by 11 nm (900 cm^{-1}). This value is close to that of 1000 cm^{-1} calculated earlier for the intermolecular complex.[1] The second stage of reaction (2) with participation of 'bidonor' proceeds intramolecularly, and the 2:1 complex is then formed without increase in component concentrations, *i.e.* under those conditions, when 'monodonor' forms predominantly the 1:1 complex. Thus, the assumption is confirmed about the possibility of direct experimental registration of the CT band of the 2:1 complex and about the red shift of this band with respect to that of the 1:1 analogue.

It is worth noting that the initial pre-conditions in the intermolecular and intramolecular 2:1 complexes are different. In the 2:1 complex of monofunctional donor the acceptor itself is a centre, through which and due to which MOs of

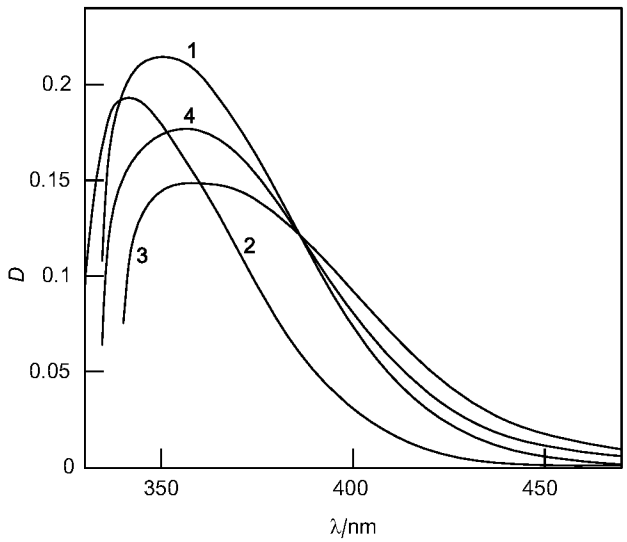


Fig. 1 Differential absorption spectra of amine–CBr_4 complexes in toluene: 1, MA; 2, DA(1); 3, DA(3); 4, DA(5); [CBr_4] = [MA] = 0.07 M, [DA(*n*)] = 0.035 M.

two donors interact giving rise to an increase in the HOMO energy of the molecular system,[5] an interaction which disappears on dissociation of the complex. In other words, the acceptor is a temporary bridge between two donors. In the 2:1 complex of a bifunctional donor the acceptor only displays the MO splitting already present irrespective of acceptor,[6] since two donor groups are bound by a covalent bridge. Nevertheless, despite the difference in the pre-conditions, in both cases the same result is achieved, *i.e.* red shift of the CT band of the 2:1 complex with respect to that of a similar or model 1:1 analogue, the shifts being practically to the same extent in both cases.

The work is financially supported by the Russian Foundation for Basic Research.

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Received: Moscow, 25th January 1995
Cambridge, 6th April 1995; Com. 5/00544B