Intramolecular Electron Donor–Acceptor Complexes as a Model for Excited Termolecular Complexes

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Summary The fluorescence spectra of three triple-layered and one double-layered compounds (**1**)—(**4**) were investigated; it is concluded from the solvent effects on the spectra that the stacking arrangement donor–donor–acceptor (DDA) is relevant to the structure of intermolecular 2:1 complexes in the excited state.

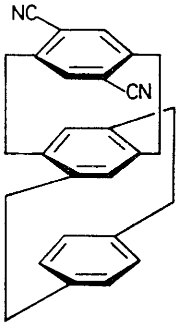
In a study of electron donor–acceptor systems, where the donor (D) is a methyl-substituted benzene or 1-methylnaphthalene and the acceptor (A) is 1,2,4,5-tetracyanobenzene (TCNB) or *p*-dicyanobenzene, it has been found that 2:1 donor–acceptor complexes are formed in the singlet excited state.[1,2] Two possible structures have been postulated for such termolecular complexes, namely $D^+A^-D \longleftrightarrow DA^-D^+$ and $(DD)^+A^-$. On the basis of solvent effects[1] on both fluorescence and $S_n \leftarrow S_1$ absorption spectra,[2] one plausible structure for the complexes is assumed to be $(DD)^+A^-$.

Table. Fluorescence band maxima, in 10^3 cm^{-1}, of (**1**)—(**4**) in several solvents at room temperature

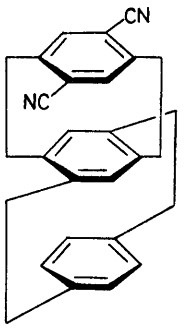
Solvent (dielectric constant)	(1)	(2)	(3)	(4)
Cyclohexane (ε 2·02)	21·7	22·0	23·1	24·6
Ether (ε 4·34)	20·6	21·2	23·0	24·1
Tetrahydrofuran (ε 7·58)	19·6	20·2	22·9	23·5
Acetonitrile (ε 37·5)	18·2	18·9	22·7	22·6

In order to obtain further information about the geometrical structure of the excited termolecular complexes, we have prepared three triple-layered compounds (**1**)—(**3**) in which one A and two D units are fixed face-to-face in the orientations DDA (**1** and **2**) and DAD (**3**), as well as a double-layered compound (**4**). The structures of all new compounds were determined by mass, i.r., n.m.r., and u.v. spectra and elemental analysis. The synthesis of (**1**)—(**4**) will be reported elsewhere.

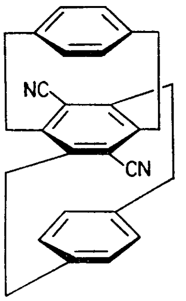
The electronic absorption spectra of (**1**)—(**4**) are almost independent of the polarity of the solvent, indicating that the ground state is non-polar. The layered compounds (**1**)—(**4**) show broad and structureless fluorescence bands in various solvents. Marked red shifts of the bands for (**1**), (**2**), and (**4**) are observed as the solvent polarity increases, but with a decrease in intensity (see Table). The red shifts (cm^{-1}) in changing from cyclohexane to MeCN are 3500 for (**1**), 3100 for (**2**), 2000 for (**4**), but only 400 for (**3**), which indicates that the S_1 states of (**1**), (**2**), and (**4**) are quite



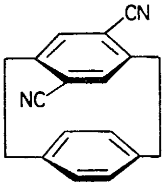
(1)



(2)



(3)



(4)

polar, but that of (**3**) is not, although a plot of ν_{max} (fluorescence) against the solvent polarity parameter $f(\epsilon,n)$[3] showed some deviation from linearity.

The fluorescence band of the termolecular complex formed from TCNB and toluene shows a shift[4] of 3500 cm^{-1} with the increase in solvent polarity in changing from cyclohexane to *o*-dichlorobenzene (ϵ 9·9). Thus, the solvent effect on this intermoleular complex is very similar to that on (**1**) and (**2**), but not (**3**). Consequently, the present work provides strong evidence that the intermolecular 2 : 1 complex between toluene and TCNB has the structure $(DD)^{+}A^{-}$ in the excited states.

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[1] H. Beens and A. Weller, *Chem. Phys. Letters*, 1968, **2**, 82.

[2] N. Tsujino, H. Masuhara, and N. Mataga, *Chem. Phys. Letters*, 1973, **21**, 301.

[3] N. Mataga, Y. Kaifu, and M. Koizumi, *Bull. Chem. Soc. Japan*, 1956, **29**, 465; E. Lippert, *Ber. Bunsenges. Phys. Chem.*, 1957, **61**, 962.

[4] K. Egawa, N. Nakashima, N. Mataga, and C. Yamanaka, *Bull. Chem. Soc. Japan*, 1971, **44**, 3291.