

INTRAMOLECULAR DONOR-ACCEPTOR INTERACTIONS
IN N-ARALKYL-3,5-DINITROBENZAMIDES AS REVEALED
BY CHARGE-TRANSFER ABSORPTIONS AND PMR SPECTRA

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The electronic absorption and ¹H-NMR spectra of compounds containing aryl groups as donors, and 3,5-dinitrobenzamido group as acceptor, linked by chains of one to three methylene groups, have been examined. Charge transfer absorptions are observed where the aryl group is *p*-dimethylaminophenyl, and are interpreted in terms of folded conformations of two distinct types.

The electronic charge-transfer (CT) spectra shown by aromatic donor-acceptor complexes formed by two independent molecules have been examined¹, and attention also been paid to CT absorptions where donor and acceptor components occur within one molecule, separated by an insulating chain²⁻⁴. In species of the type D-(CH₂)_n-A *n* = 1, 2, 3, 4 ..., the dependences of the frequencies and intensities of the CT absorptions with increasing *n* have been explored²: strong absorptions observed with *n* = 1 have been rationalized in terms of localized overlap, "homoconjugation", between orbitals of ring atoms of the donor and acceptor moieties directly bonded to the methylene carbon⁵. For *n* = 3 and 4, only weak absorptions are often observed⁵, although "sandwich" structures involving π - π complexing by quasiparallel stacking of the donor and acceptor rings in the folded conformations would be acceptable. The weakness of the CT absorptions is cited⁵ as evidence against the "sandwich" structures.

This paper reports the results of electronic and ¹H-NMR spectroscopic of molecules of the general type *I*:



A = 3,5-dinitrophenyl D = 4-dimethylaminophenyl

Ia; *n* = 1 *Ib*; *n* = 2 *Ic*; *n* = 3,

where we have evidence consistent with significantly populated conformations showing intramolecular donor-acceptor stacking in solution.

EXPERIMENTAL

Electronic absorption spectra were recorded for solutions in chloroform at 20°C using a Specord UV VIS (Zeiss, Jena) instrument. The differential absorbance for a molecule of species *I* and identical concentrations of separated donor and acceptor species (N,N-dimethyl-*p*-toluidine and N-methyl-3,5-dinitrobenzamide) was recorded and considered as the CT absorbance. The equilibrium constant for the formation of the intermolecular complex *II* between N,N-dimethyl-*p*-toluidine and N-methyl-3,5-dinitrobenzamide was established as $0.3 \pm 0.1 \text{ mol}^{-1}$ by measuring the absorbance *E* at 22000 cm^{-1} at varying concentrations of donor (c_D from 10^{-1} to $10^{-3} \text{ mol} \cdot \text{l}^{-1}$) and a constant acceptor concentration ($c_A = 10^{-3} \text{ mol l}^{-1}$). The equilibrium constant *K* for the association



and the molecular extinction coefficient ϵ were determined from the intercept and slope of the modified Benesi-Hildebrand equation (*I*):

$$c_D = -1/K + \epsilon c_A \cdot c_D/E. \quad (I)$$

¹H-NMR *Spectra* were recorded for 0.1% solutions in deuteriochloroform using a Varian A-60D spectrometer and a C-1024 time-averaging accessory.

Syntheses of Compounds

To a solution of the appropriate amine (0.01 mol) in pyridine 3,5-dinitrobenzoyl chloride (0.01 mol) was added and the mixture was stirred for 10 min and heated under reflux for 15 min, cooled to room temperature and diluted with ligroin (100 ml). The solvents were decanted, water (100 ml) was added, and the precipitate was collected and crystallized from an appropriate solvent. This method provided N-benzyl-3,5-dinitrobenzamide (*III*), m.p. 203°C (from aqueous methanol); N-(*p*-N,N-dimethylaminobenzyl)-3,5-dinitrobenzamide (*Ia*), m.p. 220°C, red needles from aqueous acetone; N-(2-*p*-N,N-dimethylaminophenylethyl)-3,5-dinitrobenzamide (*Ib*), m.p. 212°C, red needles from aqueous acetone; and N-(3-*p*-N,N-dimethylaminophenylpropyl)-3,5-dinitrobenzamide (*Ic*), m.p. 137–138°C, red needles from methanol.

RESULTS AND DISCUSSION

Fig. 1 illustrates the differential electronic absorption spectra of the molecules *Ia–Ic* in chloroform as compared with matched concentrations of separated solutions of donor (N,N-dimethyl-*p*-toluidine) and acceptor (N-methyl-3,5-dinitrobenzamide), and also a differential spectrum for the mixture of donor and acceptor molecules. The main features may be summarized as follows: *Ia* and *Ib* show CT absorption maxima at $\approx 28600 \text{ cm}^{-1}$ with $\epsilon_{\text{max}} \approx 750$ and $550 \text{ l mol}^{-1} \text{ cm}^{-1}$; *Ib* also exhibits a shoulder at $\approx 24000 \text{ cm}^{-1}$ with $\epsilon \approx 250 \text{ l mol}^{-1} \text{ cm}^{-1}$. Compound *Ic* shows a broad maximum centred at 22000 cm^{-1} , $\epsilon_{\text{max}} \approx 150 \text{ l mol}^{-1} \text{ cm}^{-1}$, while the intermolecular donor-acceptor mixture of N,N-dimethyl-*p*-toluidine and N-methyl-3,5-dinitrobenzamide (identified as *II* in the Figure) shows a maximum at 22500 cm^{-1} , $\epsilon_{\text{max}} \approx 900 \text{ l mol}^{-1} \text{ cm}^{-1}$.

Since the CT absorption maxima in *Ia* and *Ib* are over 6000 cm^{-1} to high frequency of the maximum for the mixture *II*, and it seems highly probable that a "sandwich" type of stacked structure is an appropriate description of the intermolecular complex⁶, it seems unlikely that the conformation(s) leading to intramolecular CT interactions in *Ia* and *Ib* are similar to those in the mixture *II*. Conversely, the similarities in absorption maxima for *Ic* and for *II* are consistent with a postulated similarity in structure for these complexes, and the intermediate frequency shoulder found with *Ib* could arise from discrete absorption involving a conformation similar to that generating the CT absorption in *Ic*.

Differing geometries of the entities *I* may be generated, depending upon the constraints to rotation of the —CO—NH—moiety of the acceptor. If rotation occurs to a configuration where the amide moiety is orthogonal to the 3,5-dinitrophenyl residue while the amide moiety maintains its planar character then the donor and acceptor portions of *Ia* and of *Ib* may readily adopt folded conformations with close donor-acceptor proximity. If the amide carbonyl is assumed to maintain a coplanar relationship with the 3,5-dinitrophenyl residue, then *Ia* cannot attain a folded conformation with donor-acceptor proximity, *Ib* may attain a conformation with the donor ring centred over the 4-position of the acceptor, and *Ic* may attain a conformation with the donor ring centred over the 2- and 6-positions of the acceptor. If we identify these two types as orthogonal amide and fully conjugated amide conformations, then in the orthogonal type, much of the conjugative electron-attracting character of the carbonyl function is lost, so that the 3,5-dinitrobenzoyl group will be a less effective acceptor than in the fully conjugated type, and it would be

TABLE I

¹H-NMR Chemical Shifts of Species *I* and Related Compounds

Shifts (in p.p.m., δ scale) were recorded for 0.1% solutions in CDCl₃; internal standard tetramethylsilane.

Compound	3,5-Dinitrobenzoyl		<i>p</i> -Dimethylaminophenyl		
	2, 6	4	N(CH ₃) ₂	A ^a	B ^a
N-Methyl-3,5-dinitrobenzamide	8.96	9.16	—	—	—
N-Benzyl-3,5-dinitrobenzamide (<i>III</i>)	9.02	9.22	—	—	—
<i>Ia</i>	9.05	9.05	2.97	7.11	6.63
<i>Ib</i>	9.00	9.00	2.90	7.10	6.67
<i>Ic</i>	8.68	9.07	2.78	7.07	6.58
N,N-Dimethyl- <i>p</i> -toluidine	—	—	2.88	7.09	6.70

^a A refers to the protons *meta* to the dimethylamino group B to the protons *ortho* to this group.

predicted (as is observed) that the CT transitions occurring in the orthogonal type (*Ia*, major transition in *Ib*) would fall at higher frequencies than in the fully conjugated type (*Ic*, minor transition in *Ib*).

The postulated types of folded conformation receive some support from the $^1\text{H-NMR}$ chemical shift patterns shown by the compounds *Ia*–*Ic* and related models. Donor–acceptor interaction may give rise to mutual upfield shifts of *c.* 1 p.p.m. for pure intermolecular complexes (*cf.*⁷), and the data assembled in Table I show upfield shifts of 0.17–0.22 p.p.m. for the 4-protons in the acceptor components of *Ia* and *Ib* as compared with the model species *N*-benzyl-3,5-dinitrobenzamide (*III*) while for *Ic* the 2,6-protons are shielded by 0.34 p.p.m. and the 4-proton by 0.15 p.p.m. as compared with the model *III* (in which the donor–acceptor interactions would be much weaker). Comparisons of the shifts in the donor components of the species *I* with the donor *N,N*-dimethyl-*p*-toluidine show small upfield shifts for the protons *ortho* to the dimethylamino group, increasing in the order *Ib*, *Ia*, *Ic*, and an upfield shift of 0.10 p.p.m. for the dimethylamino protons of *Ic*. It appears difficult to account for these specific shielding effects on any other basis than the existence of significant proportions of molecules in folded conformations.

Further supporting information is provided by comparisons of the molecular extinction coefficients ϵ for the intermolecular complex *II* (as evaluated using the Benesi–Hildebrand equation to determine the equilibrium constant for complexation) and for the compound *Ic*. If it is assumed that CT absorption for *Ic* is restricted to the suggested folded conformation, and that the transition probabilities for *II* and for the folded *Ic* are identical, than *c.* 150/900, or one-sixth of the *Ic* species are folded

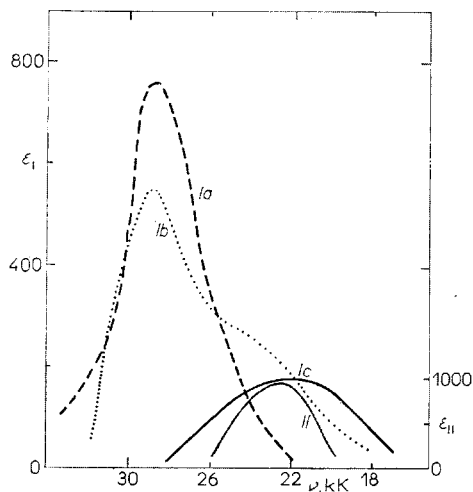


FIG. 1
Charge-Transfer (CT) Spectra for the Molecules *Ia*–*Ic*, (left scale) and for the Intermolecular Complex *II* (right scale)

(since the CT absorption for *Ic* is significantly broader than for *II* (Fig. 1), this estimate is a conservative one).

We conclude that there is reasonably strong evidence for the presence of folded conformations of the species *I* in solution, consistent with the observed CT absorptions. However, the intensely and similarly colored solid compounds *Ia*–*Ic* probably owe their appearance to intermolecular donor-acceptor interactions corresponding to those in a mixture of N-methyl-3,5-dinitrobenzamide and N,N-dimethyl-*p*-toluidine.

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REFERENCES

1. Foster R.: *Organic Charge-Transfer Complexes*. Chapter 3. Academic Press, London 1969.
2. Oki M., Mutai K.: *Tetrahedron Lett.* 1968, 2019.
3. Craenen H. A. H., Verhoeven J. W., DeBoer T. J.: *Tetrahedron Lett.* 1970, 1167.
4. Craenen H. A. H., Verhoeven J. W., DeBoer T. J.: *Tetrahedron* 27, 2561 (1971).
5. Verhoeven J. W., Dirks I. P., DeBoer T. J.: *J. Mol. Spectrosc.* 42, 149 (1972).
6. Ref. 1, Chapter 5.
7. Foster R., Fyfe C. A.: *Trans. Faraday Soc.* 61, 1626 (1965).