Through-bond Charge-transfer Interaction in *N*-(*p*-Methoxyphenylalkyl)-pyridinium Ions

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Intramolecular charge-transfer absorption is observed for a series of molecules containing the *p*-methoxyphenyl group as an electron donor and the 4-methoxycarbonylpyridinium group as an electron acceptor separated by a saturated carbon–carbon bond. The appearance of this absorption even in rigid model systems, where donor and acceptor are spatially far apart, is used as evidence for the through-bond character of the charge-transfer interaction. A simple theoretical model is shown to predict qualitatively the dependence of the charge-transfer absorption intensity on the dihedral angle defined by donor, acceptor, and the interconnecting carbon–carbon bond.

PHOTOELECTRON spectroscopy has recently revealed[1,2] interactions between π- or n-electron systems which are interconnected by σ-bonds in such a way that direct ('through-space') overlap is excluded. Calculations[3] and experimental evidence[4] indicate these interactions to be of the 'through-bond' type, in which the interconnecting σ-bonds are involved. The interaction between two identical n-electron systems is especially well documented. Optimal through-bond interaction of two such systems separated by a saturated carbon–carbon bond (*i.e.* $\dot{\mathrm{N}}\text{–}\mathrm{C}^1\text{–}\mathrm{C}^2\text{–}\dot{\mathrm{N}}$) is attained when the lone pair orbitals are parallel to each other and to the $\mathrm{C}^1\text{–}\mathrm{C}^2$ bond (thus resulting in the conformation depicted in Figure 1 and those obtained from it by rotation round the $\mathrm{C}^1\text{–}\mathrm{C}^2$ bond).

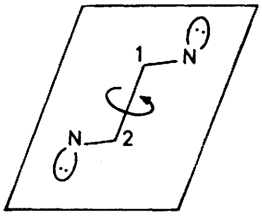
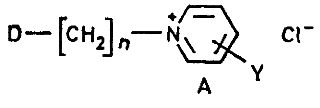


FIGURE 1 Conformations for maximum through-bond interaction between lone pair orbitals

Recently it has been shown[5] that through-bond interactions can lead to the appearance of a 'new' absorption band in the near u.v. region, when one of the n-electron systems is replaced by a π-electron system of sufficiently strong electron-accepting properties (*e.g.* carbonyl or 1,1-dicyanovinylidene). This absorption band was attributed to an intramolecular charge-transfer (CT) transition, involving excitation of an electron from the n-electron system to the lowest unoccupied molecular orbital (LUMO) of the π-electron system.

There have been several reports by us[6a,b] and by others[7,8] on the intramolecular CT absorption observed for systems of type (1), involving an aromatic system of low ionization potential as an electron donor (D) and an electronegatively substituted pyridinium ion as an electron acceptor (A). We have suggested[9] that



(1)

through-bond interaction between D and A plays an important role in the intramolecular CT absorption observed for (1; $n = 2$). Our early conclusions were rather tentative due to the lack of suitable rigid model systems and have therefore been questioned.[8]

We now report on the intramolecular CT absorption in a series of model systems containing a *p*-methoxyphenyl group and an *N*-(4-methoxycarbonyl)pyridinium ion separated by a saturated carbon–carbon bond and in a known mutual orientation as shown by their ^{1}H n.m.r. spectra.

RESULTS AND DISCUSSION

Model Compounds.—The compounds compiled in Tables 1 and 2 were used as model systems for the study of intramolecular CT interaction between a *p*-methoxyphenyl group as an electron donor (D) and an *N*-(4-methoxycarbonyl)pyridinium ion as an electron acceptor (A). In all systems D and A are linked by a saturated C–C bond. Thus the relative orientation of D and A is determined by the dihedral angles θ_1, ϕ, and θ_2 defined in Figure 2. Information about the dihedral angle ϕ can in principle be gained from the vicinal coupling constants between protons attached to the $\mathrm{C}^1\text{–}\mathrm{C}^2$ fragment. These coupling constants are related to the dihedral angle defined by $\mathrm{H}\text{–}\mathrm{C}^1\text{–}\mathrm{C}^2\text{–}\mathrm{H}$ *via* the well known Karplus relation.[10] The main problem in application of the Karplus relation lies in the optimal choice of the characteristic parameters. These parameters are

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[1] P. Bishof, J. A. Hashmall, E. Heilbronner, and V. Hornung, (*a*) *Helv. Chim. Acta*, 1969, **52**, 1745; (*b*) *Tetrahedron Letters*, 1969, 4025.

[2] R. Gleiter, *Angew. Chem.*, 1974, **86**, 770.

[3] R. Hoffmann, *Accounts Chem. Res.*, 1971, **4**, 1.

[4] E. Heilbronner and K. A. Muszkat, *J. Amer. Chem. Soc.*, 1970, **92**, 3818.

[5] A. W. J. D. Dekkers, J. W. Verhoeven, and W. N. Speckamp, *Tetrahedron*, 1973, **29**, 1691.

[6] (*a*) J. W. Verhoeven, I. P. Dirkx, and Th. J. de Boer, *Tetrahedron*, 1969, **25**, 4037; (*b*) J. W. Verhoeven, Dissertation, University of Amsterdam, Amsterdam, 1969.

[7] S. Shifrin, *Biochim. Biophys. Acta*, 1965, **96**, 173.

[8] H. E. Bosshard, Dissertation, Eidgenössische Technische Hochschule Zürich, Zürich, 1970.

[9] J. W. Verhoeven, I. P. Dirkx, and Th. J. de Boer, *J. Mol. Spectroscopy*, 1972, **42**, 149.

[10] M. Karplus, *J. Chem. Phys.*, 1959, **30**, 11.

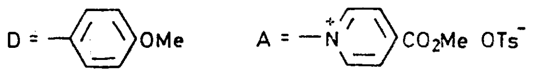
known [11,12] to depend strongly on the particular system studied.

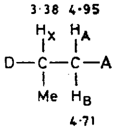
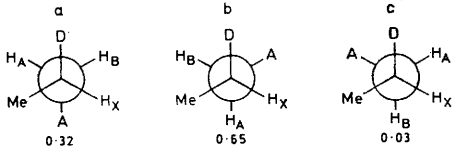
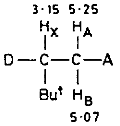
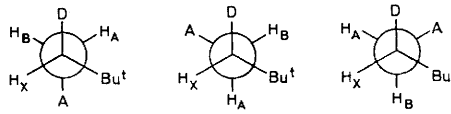
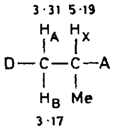
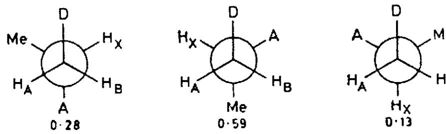
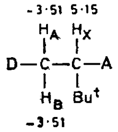
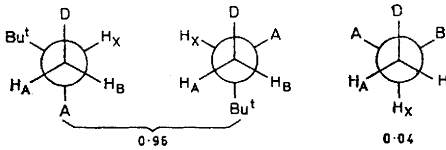
For the salts (2)—(4) (*cf.* Table 1) the coupling constants J_{AX} and J_{BX} of H_X (attached to the chiral centre) with the two methylene protons (at the carbon atom to the chiral centre) were determined by first-order analyses of the AB part of the ABX spectrum.

The AB part of the ABX spectrum of (5) showed a broadened triplet ($W_{1/2}$ *ca.* 16 Hz) from which J_{AX} and J_{BX} could not be determined. From the double doublet of the X part, $J_{AX} + J_{BX}$ was measured as 16·1 Hz.

Table 1

Rotamer population estimated from ^1H n.m.r. data for the aralkylpyridinium ions (2)—(5) in CD_3OD. Coupling constants (±0·3 Hz) were determined by first-order analyses



	Structure and chemical shifts (δ)	Coupling constant (Hz)			Estimated rotamer population (mol fraction)
		J_{AX}	J_{BX}	J_{AB}	a b c
(2)		6·2	10·0	−12·8	 0·32 0·65 0·03
(3)		4·7	12·1	−13·4	 ~0·18 ~0·82 ~0
(4)		5·7	9·3	−14·1	 0·28 0·59 0·13
(5)		*	*		 0·96 0·04

* $J_{AX} + J_{BX}$ = 16·1 Hz, determined from the X part of the ABX spectrum.

Assuming that the vicinal coupling constants measured represent a weighted average over the rotamers *a*—*c*, the rotameric distribution (mole fraction) for (2)—(5), can be estimated by the use of equations (1)—(3) where

$$a = (J_{AX} - J_g)/(J_t - J_g) \qquad (1)$$

$$b = (J_{BX} - J_g)/(J_t - J_g) \qquad (2)$$

$$c = [J_t + J_g - (J_{AX} + J_{BX})]/(J_t - J_g) \qquad (3)$$

J_t and J_g represent *trans* and *gauche* vicinal coupling constants for dihedral angles of 180 and 60° respectively. For an approximate calculation of the rotamer populations *a*—*c*, the values J_t 14 and J_g 2·5 Hz are used, according to Neville,[13] who applied these values to amphetamine hydrochlorides in D_2O. The results are compiled in Table 1 and must be considered as qualitative only since exact J_t and J_g values are not available. In all cases, however, it seems fairly certain that the relative abundance of the various rotamers is correctly predicted.

For (5) only the value $J_{AX} + J_{BX}$ was available and thus the contributions of *a* and *b* could not be calculated separately. But from models it can be seen that *b* must be responsible for a very large part of the calculated sum $(a + b) = 0·96$ and is expected to be in the order of 0·80—0·85 as found for (3).

From the rotameric populations it is concluded that in (2)—(5) D and A are mutually *gauche* for most of the time, as expected from consideration of the steric repulsions involved in the various rotamers. It should be noted that reversal of the chemical shift assignments for H_A and H_B would lead to a calculated rotameric population which seems highly unrealistic.

For the more rigid (bi)cyclic compounds (6)—(14), the relevant ^1H n.m.r. data and the estimated dihedral

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[11] K. L. Williamson and W. S. Johnson, *J. Amer. Chem. Soc.*, 1961, **83**, 4623.

[12] H. Booth and G. C. Gidley, *Tetrahedron Letters*, 1964, 1449.

[13] G. A. Neville, R. Deslauriers, B. J. Blackburn, and J. C. P. Smith, *J. Medicin. Chem.*, 1971, **14**, 717.

angles (Φ) are compiled in Table 2. For the *trans*-substituted four-, five-, and six-membered ring systems a conformation is assumed with both D and A (pseudo) equatorial as supported by the large values observed for $J_{1,2}$.

From steric consideration *cis*-(9) is expected to exist as a mixture of two chair conformations. From $W_{1/2}$ for the signals from H-1 and -2 (*ca.* 19·9 and 15·4 Hz respectively), it follows that the H-1 pattern contains one large and two small coupling constants, while that of H-2 has three small coupling constants. This suggests that H-1 is more often axial than H-2, *i.e.* A is more often equatorial than D.

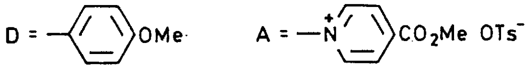
An estimate of the conformational equilibrium can be obtained from the sum of the coupling constants $J_{1,6} + J_{1,6'} \approx 19{\cdot}9 - J_{1,2} \approx 14{\cdot}7$ by using equation (4).[14,15] If we take J_{aa} 11·0 and $J_{ae} \sim J_{ee} \sim J_{ea} \sim 4{\cdot}6$ Hz [values from *trans*-(9)], a contribution of n 0·84 (mole fraction) is calculated for the conformation in which A and D are equatorial and axial respectively. The value of 0·84, found in this way must again be considered as a rough approximation, because J_{ea} and J_{ae} need not always be equal.[16,17]

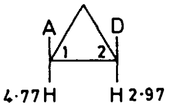
$$J_{1,6} + J_{1,6'} = n(J_{aa} + J_{ae}) + (1 - n)/(J_{ee} + J_{ea}) \quad (4)$$

For *cis*-(10) a smaller energy difference between the two possible half-chair conformations[18] is expected than for *cis*-(9). From $W_{1/2}$ for H-1 and -2 (*ca.* 15 and 16 Hz) indeed no large preference for one of the two half-chair conformations is apparent.

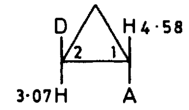
Table 2

^{1}H N.m.r. data (δ; J/Hz) and estimated dihedral angles ϕ for the arylcycloalkylpyridinium ions (6)—(14). Coupling constants (±0·3 Hz) were determined by double resonance experiments

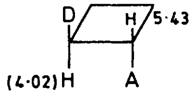




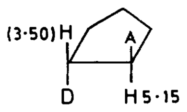
$J_{1,2}$ (10); ϕ 0°
cis-(6)



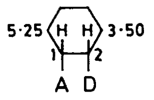
$J_{1,2}$ 4·8; ϕ 144°
trans-(6)



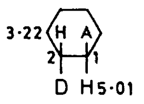
$J_{1,2}$ 9·1; ϕ <120°
trans-(7)



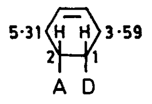
$J_{1,2}$ 9·7; ϕ <120°
trans-(8)



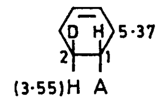
$J_{1,2}$ 5·3; ϕ <60°
cis-(9*)



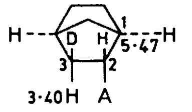
$J_{1,2}$ 11·0 ($J_{1,6}$ 4·6); ϕ 60°
trans-(9)



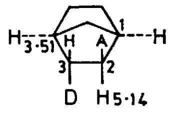
$J_{1,2}$ 3·3; ϕ <60°
cis-(10)



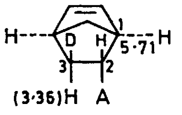
$J_{1,2}$ 11·2; ϕ 60°
trans-(10)



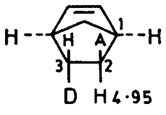
$J_{2,3}$ 5·6; ϕ 120°
(11)



$J_{2,3}$ 5·7; ϕ 120°
(12)



$J_{2,3}$ 4·6; ϕ 120°
(13)



$J_{2,3}$ 4·7; ϕ 120°
(14)†

* The half-chair conformation with D and A axial and equatorial respectively was calculated to be present for *ca.* 80%. † ^{1}H N.m.r. data were obtained from a mixture of (13) and (14) in the ratio 3 : 1.

Theoretical Treatment of Through-bond Charge-transfer Interactions.—Through-bond interaction between D and A in A–C^1–C^2–D requires[3] that the π-orbitals on D and A overlap with the σ-orbitals of the interconnecting C^1–C^2 bond ('π–σ–π conjugation'). This overlap is governed by the values of θ_1 and θ_2 (*cf.* Figure 2), but is independent of ϕ, since the σ-orbitals of the C^1–C^2 bond are symmetric with respect to rotation around this bond.

Through-bond interactions can mix the state in which no charge is transferred (wave function ψ_0, energy W_0) with the state in which one electron is transferred from D to A (wave function ψ_1, energy W_1).

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[14] E. Garbish, *J. Amer. Chem. Soc.*, 1964, **86**, 1780.

[15] H. Booth, *Tetrahedron*, 1964, **20**, 2211.

[16] H. Booth, *Tetrahedron Letters*, 1965, 411.

[17] D. H. Williams and N. S. Bhacca, *J. Amer. Chem. Soc.*, 1964, **86**, 2742.

[18] F. Anet and M. Hag, *J. Amer. Chem. Soc.*, 1965, **87**, 3147.

From this mixing, ground and excited state wave functions ψ_N and ψ_E arise [equations (5) and (6)].

$$\psi_N = a\psi_0 + b\psi_1 \qquad (5)$$

$$\psi_E = a^*\psi_1 - b^*\psi_0 \qquad (6)$$

When the overlap region of ψ_0 with ψ_1 is situated midway between D and A, the electric transition dipole moment for the CT transition $\psi_N \longrightarrow \psi_E$ can be approximated by equation (7) [19-21] (μ_t being the electric moment operator) in which $S_{01} = \langle\psi_0/\psi_1,\rangle$, $\vec{\mu}_0 = \langle\psi_0/\mu_t/\psi_0\rangle$, and $\vec{\mu}_1 = \langle\psi_1/\mu_t/\psi_1\rangle$. For strong CT interaction L will be larger than M, while for weak CT interaction $L \approx M$.[21] Since however in general $\mu_1 \gg \mu_0$ the first term of (7) will be predominant at all levels of CT interaction. The vector sum $\vec{\mu}_1 - \vec{\mu}_0$ can be approximated by equation (8).[21] Here $\vec{r}_D$ and $\vec{r}_A$ are the average position vectors of the donated electron in D before and in A after transfer respectively. Assuming uniform distribution of the donated electron in both D and A, $\vec{r}_D$ and $\vec{r}_A$ reduce to the position vectors of the centres of D and A. When the centre of A is chosen as the origin, equations (7) and (8) lead to (9) in which $\vec{r}_{DA}$ is the vector connecting the centres of D and A.

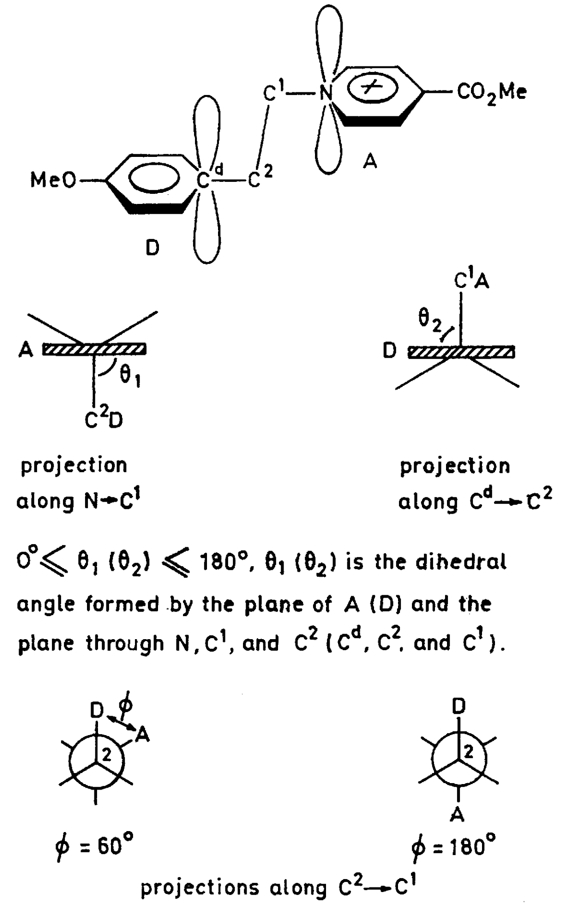

FIGURE 2

$$\vec{\mu}_{EN} = \{a^*b + \tfrac{1}{2}S_{01}(aa^* - bb^*)\}(\vec{\mu}_1 - \vec{\mu}_0) + \tfrac{1}{2}S_{01}(aa^* - bb^*)\vec{\mu}_0 = L(\vec{\mu}_1 - \vec{\mu}_0) + M\vec{\mu}_0 \qquad (7)$$

$$\vec{\mu}_1 - \vec{\mu}_0 = e(\vec{r}_D - \vec{r}_A) \qquad (8)$$

$$\vec{\mu}_{EN} = Le\vec{r}_{DA} \qquad (9)$$

At fixed values θ_1 and θ_2 the through-bond overlap S_{01} remains constant independent of ϕ. Since also (neglecting van der Waals interaction) W_1 and W_0 are independent † of ϕ, the coefficients a, a^*, b, and b^*, and thus L must be independent of ϕ, when only through-bond interaction is involved.

The oscillator strength (f_{CT}) of the CT transition should be proportional to μ_{EN}^2 and therefore (at fixed θ_1 and θ_2) to the square of $\vec{r}_{DA}$. It can be shown [6b] that in the systems studied by us equation (10) applies.

$$r_{DA}^2 = 12{\cdot}2 + 29{\cdot}6 \sin^2\phi/2 \text{ (Å)} \qquad (10)$$

The oscillator strength predicted in this way has been plotted schematically in Figure 3. At ϕ values below 60°, D and A approach each other sufficiently for through-space π–π overlap. Thus S_{01} will increase and thereby b and b^*, leading to an increase of $\vec{\mu}_{EN}$ and f_{CT} as schematically depicted in Figure 3.

Comparison of Experimental Data with Theory.—All the model compounds studied show a distinct long wavelength absorption band in the 320—340 nm region which obeys Beers law (see Table 3). This band

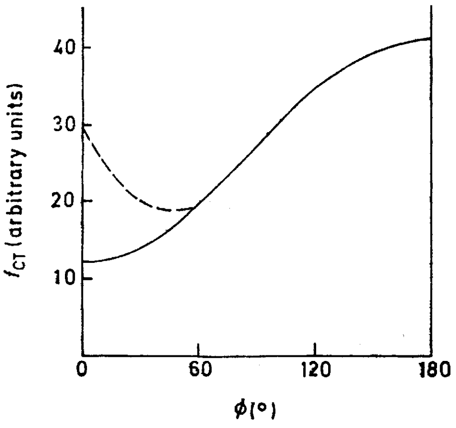

FIGURE 3 Oscillator strength of intramolecular CT transition as a function of ϕ (at fixed θ_1 and θ_2): —— through-bond interaction only; - - - - after inclusion of additional through-space overlap

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† For interaction between D and A species which are neutral in the ground state, this assumption is not allowed, since W_1 then contains a large Coulombic interaction term between D^+A^-, which depends on r_{DA} and thus on ϕ.

[19] R. S. Mulliken, *J. Amer. Chem. Soc.*, 1952, **74**, 811.

[20] B. Mayoh and C. K. Prout, *J.C.S. Faraday II*, 1972, 1072.

[21] R. S. Mulliken and W. B. Person, 'Molecular Complexes,' Wiley, New York, 1969, pp. 23—32.

should, as we have shown earlier,[6] be attributed to an intramolecular CT transition. Only a slight variation in $\lambda_{\text{max.}}$ is observed, which may be due to variation in $W_1 - W_0$ as the donor and acceptor properties of D and A can vary under the influence of the particular hydrocarbon skeleton connecting them, although alternatively * it might point to small variations in the resonance interaction between ψ_0 and ψ_1 due to variations in θ_1 and θ_2. The $\varepsilon_{\text{max.}}$ values vary from 225 (for ϕ *ca.* 60°) to 1715 (for ϕ *ca.* 144°) (corresponding to $f_{\text{CT}} = 0{\cdot}009$ and $0{\cdot}059$ respectively).

TABLE 3

U.v. spectroscopic data (96% EtOH, 20°) for the intramolecular CT transition

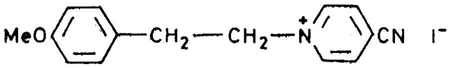
Compound	λ_{max}/nm	ε_{max}	f_{CT}	Estimated ϕ (°)
(2)	328·5	720	0·024	*
(3)	333	360	0·012	60 †
(4)	324	670	0·029	*
(5)	340	200	0·007	60 †
cis-(6)	363	920	0·029	0
trans-(6)	343	1715	0·059	144
trans-(7)	333	1025	0·034	<120
trans-(8)	338	825	0·027	<120
cis-(9)	340	535	0·017	<60
trans-(9)	340	225	0·009	60
cis-(10)	335	775	0·027	<60
trans-(10)	336sh	(240)		60
(11)	328·5	385	0·014	120
(12)	327	745	0·026	120
(13)	325sh	(1000)		120

* Rotameric equilibrium between the rotamers with ϕ 180 and 60°. † Dihedral angle of the preferred rotamer (>80%) has been indicated.

The observation of strong intramolecular CT absorption in systems with large ϕ-values [*e.g. trans*-(6), *trans*-(7), *trans*-(8), and (9)] supports our interpretation, that through-bond interaction occurs. Furthermore the predicted (see Figure 3) ϕ dependence of f_{CT} is found to apply qualitatively, since some of the largest f_{CT} values correspond to large values of ϕ. Minimum intensity is observed at ϕ *ca.* 60°.

At smaller ϕ, f_{CT} increases again, probably because through-space overlap becomes increasingly important. Even for ϕ *ca.* 0° [*cis*-(6)] however, f_{CT} never reaches the values observed at large ϕ. Quantitative comparison of theory and experiment is hampered by our lack of knowledge about θ_1 and θ_2. For compound (15) an *X*-ray analysis[22] revealed the values θ_1 87, θ_2 76, and ϕ 68°. Thus in this case θ_1 and θ_2 are near the value (90°) for optimal through-bond interaction.

Conclusions.—The simple two-state interaction model proposed above predicts reasonably well the conformational dependence of the intramolecular CT transition. It should be remembered however, that this model is an oversimplification, especially since it does not consider the possibility that a CT transition can borrow[23] its intensity from local transitions in D and/or A. Such intensity borrowing has recently been reported[5] for the intramolecular CT transition in 1-aza-4-dicyanomethyleneadamantane. Both in the simple theory and in the more sophisticated approach including locally excited states of D and A, the intensity of the CT transition depends on the degree of through-bond overlap between molecular orbitals on D and A. In the simple theory S_{01} can be shown[19,21] to be proportional to S_{DA} which represents the overlap between the highest occupied MO on D (HOMO) and the lowest unoccupied MO on A (LUMO). It will be clear that efficient through-bond overlap of HOMO and LUMO can only take place when these orbitals have non-zero coefficients (in the LCAO–MO approximation) on the atoms with which D, respectively A, are connected to the C^2–C^1 bond. For our systems, HMO calculations[6] show that this requirement is fulfilled.



(15)

From the present results it seems that, through-bond CT interaction represents a useful tool for probing into the mechanism of σ–π interactions both in the ground and in the electronically excited state.

EXPERIMENTAL

The syntheses of the model compounds have been described previously.[24] ^{1}H N.m.r. spectra were recorded on a Varian HA-100 spectrometer in CD_3OD using tetramethylsilane as an internal reference. U.v. absorption spectra were recorded on a Cary 14 spectrophotometer in Teflon-stoppered silica cells of 1 cm pathlength, using 96% ethanol as solvent.

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* We thank a referee for bringing up this point.

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