Identification of Multiple Charge Transfer Transitions by Circular Dichroism Studies

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Summary Charge transfer (CT) transitions of optically active carbazoles with chloranil, tetracyanoethylene, and tetracyanoquinodimethane exhibit induced circular dichroism, for five of the six compounds studied the CT complex exhibited two dichroic absorption bands, having positive and negative signs respectively, providing unambiguous evidence of two CT transitions arising from the two highest-energy filled orbitals of the carbazole derivatives

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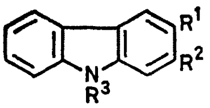
MULTIPLE charge transfer (CT) transitions are known to occur for several donor-acceptor combinations and are thought to arise *via* either HOMO(1) and HOMO(2) orbitals of the donor with LUMO(1) of the acceptor, or HOMO(1) of the donor with LUMO(1) and LUMO(2) of the acceptor.[1] CT complexes of carbazoles, including polymeric derivatives, are of interest as organic photoconductors[2,3] and are characterised by their highly asymmetric absorption spectra. The existence of two distinct CT transitions is the most obvious explanation, as was first recognised by Klöpffer.[4] More recently Landman *et al.*[5] and Okamoto *et al.*[6] have independently studied, in detail, the nature and origins of CT spectra for a wide series of carbazole derivatives with chloranil as the acceptor.

The availability[7] of a number of optically active carbazole compounds (**1**—**4**) has facilitated studies of the circular dichroism (c.d.) of CT complexes with the symmetrical acceptor molecules chloranil, tetracyanoethylene (TCNE), and tetracyanoquinodimethane (TCNQ).



(**1**) $R^1 = R^2 = H$, $R^3 = CH_2\overset{*}{C}H(Et)Me$

(**2**) $R^1 = Et$, $R^2 = H$, $R^3 = CH_2\overset{*}{C}H(Et)Me$

(**3**) $R^1 = H$, $R^2 = Et$, $R^3 = CH_2\overset{*}{C}H(Et)Me$

(**4**) $R^1 = \overset{*}{C}H(Et)Me$, $R^2 = H$, $R^3 = Pr^i$

Applications of c.d. to the study of CT complexes have been very limited[8] and, to the best of our knowledge, have not been used in cases where multiple CT transitions are involved.

Charge transfer spectra for the carbazoles (**1**—**4**) (0·20—0·03 M) with the three acceptor molecules (0·014 M) have been measured in CH_2Cl_2 at approximately 37 °C in sealed cells. For complexes with chloranil, broad CT spectra with an apparent λ_{max} in the region 530—580 nm and a distinct shoulder around 700 nm were observed (Figure 1). Asymmetric CT spectra were also observed for related complexes of the simple *N*-alkylcarbazole (**1**) with the acceptors TCNE and TCNQ (Figure 2).

Spectroscopic properties of the CT complexes are given in the Table. The data for association constants (K) and molar extinction coefficients (ϵ_{max}) were derived by the usual Benesi–Hildebrand technique and so are potentially subject to large errors, especially as multiple transitions are involved. Nevertheless use of these data to estimate values of the molar rotation $[\phi]^{25}_D$ indicates substantial rotatory strength for the CT transitions. The use of K and ϵ_{max} values for this purpose, without resolution of the CT transitions into their individual components, is partially justified by the constancy of K values determined at different wavelengths.

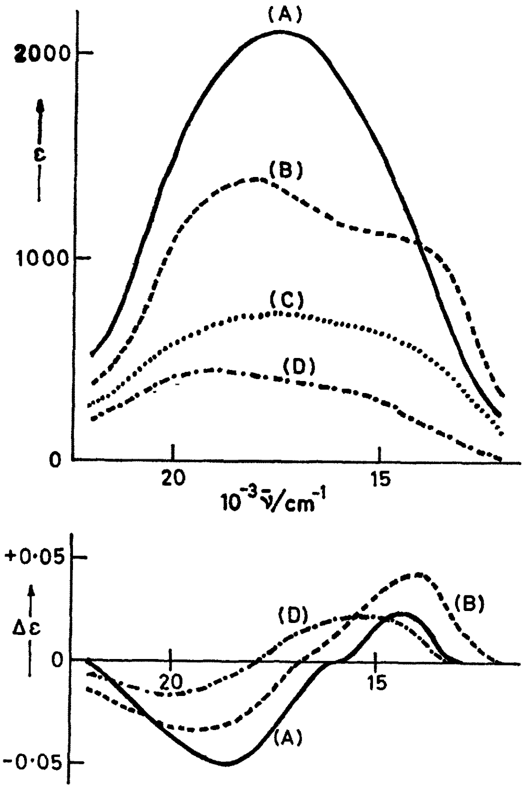


FIGURE 1. U.v. and c.d. spectra of CT complexes of optically active carbazole derivatives with chloranil, in CH_2Cl_2 at 37 °C: (A) (*S*)-2-ethyl-9-(2-methylbutyl)carbazole (**3**); (B) (*S*)-3-ethyl-9-(2-methylbutyl)carbazole (**2**); (C) (*S*)-3-s-butyl-9-isopropylcarbazole (**4**); (D) (*S*)-9-(2-methylbutyl)carbazole (**1**).

TABLE. U.v. and optical rotatory properties of CT complexes of optically active carbazole derivatives with *p*-chloranil in CH_2Cl_2 at 37 °C

		Charge transfer complexes					
		U.v. data			C.d.		
Carbazole	$[\phi]^{25}_D$	ν_{max}/cm^{-1}	ϵ_{max}/ l mol^{-1} cm^{-1}	K/l mol^{-1}	$[\phi]^{25}_D$	ν_{max}/cm^{-1}	$10^2\Delta\epsilon_{max}$/ l mol^{-1} cm^{-1}
(**1**)	−36·7	18,900	450	3·0	−1000	20,400, 15,200	−1, +2
(**1**)	−36·7	16,600[a]	667[a]	6·5[a]	− 300[a]	17,800[a], 12,500[a]	−1[a], +2[a]
(**1**)	−36·7	17,000[b]	2500[b]	2·0[b]	−1300[b]	17,500[b], 13,500[b]	−2[b], +3[b]
(**2**)	−28·9	18,200	1320	1·2	−2400	19,200, 14,100	−3, +4
(**3**)	−34·5	17,500	2100	0·8	−1800	19,500, 14,500	−5, +2
(**4**)	+32·6	17,200	730	0·7	− 900	— —	— —

Circular dichroism measurements provide unequivocal evidence for the existence of two distinct CT transitions in the carbazoles (**1**—**3**) but, significantly, the CT transitions of carbazole (**4**), in which the chiral group is not attached directly to the nitrogen, apparently do not exhibit similar induced optical activity, although there is some rotatory strength in the transitions as measured by $[\alpha]^{25}_{D}$. The two CT transitions in carbazole–chloranil complexes, which are thought to arise *via* the HOMO(1) and HOMO(2) orbitals of carbazole,[5] are characterised by dichroic absorption bands always having positive and negative signs respectively, and this allows for unambiguous resolution of the CT absorption spectra. Usually values of λ_{max} obtained by c.d. measurements differ slightly from the true absorption λ_{max} values,[9] especially in cases where overlapping transitions are involved.[10] However, in this case, the closely related nature of the shapes of the absorption envelopes for each CT transition, and the large separation between the peak heights,[5] suggest that the actual separation between the two c.d. peak positions will be a reliable guide to the separation between the corresponding electronic transitions. Appropriate data for the peak positions in the c.d. spectra are given in the Table and indicate close agreement between the c.d. peak separations and the corresponding energy differences (4000—5000 cm^{-1}) for the lowest energy (${}^1L_a \leftarrow {}^1A$, ${}^1L_b \leftarrow {}^1A$) transitions in the carbazoles.[11]

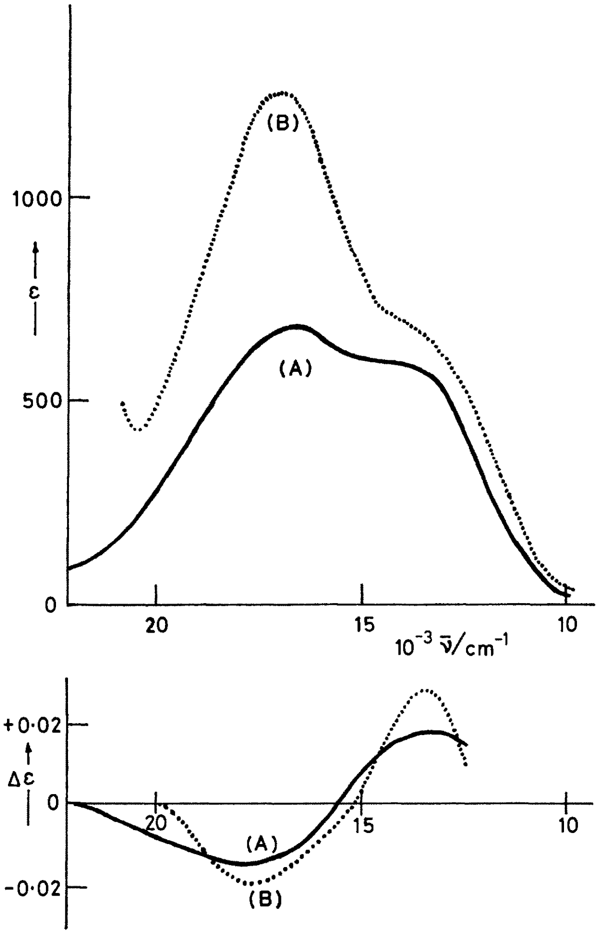


FIGURE 2. U.v. and c.d. spectra of CT complexes of (*S*)-9-(2-methylbutyl)carbazole (**1**) with different acceptors, in CH_2Cl_2 at 37 °C: (A) tetracyanoethylene; (B) tetracyanoquinodimethane.

Although CT spectra for (*S*)-2-ethyl-9-(2-methylbutyl)-carbazole (**3**) do not show the asymmetric nature typical of the other carbazoles, it is important to note that the c.d. spectrum (Figure 1) indicates unambiguously the presence of two CT transitions for complexes with chloranil and illustrates the value of this technique in the study of CT phenomena.

It is not possible to explain fully the apparent absence of c.d. in the CT bands of chloranil complexes with the carbazole (**4**) having a chiral group at the 3-ring position rather than at the nitrogen but, since the c.d. detected is almost at the limit of instrumental sensitivity, the relative remoteness of chiral substituent in the 3-position might be expected to confer a lower degree of local dysymmetry.

The present results indicate that c.d. can be an extremely useful probe into the nature and origins of CT spectra, particularly for cases involving multiple CT transitions.

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