Relative Intensities and Temperature Effects on Charge Transfer Transitions of Carbazoles with *p*-Chloranil

By ROBERTO SOLARO and EMO CHIELLINI
(*Centro di Studio del CNR per le Macromolecole Stereordinate ed Otticamente Attive, Istituto di Chimica Organica Industriale, Università di Pisa,* 56100 *Pisa, Italy*)

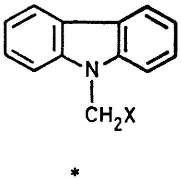
and ANTHONY LEDWITH*
(*Donnan Laboratories, University of Liverpool, Liverpool* L69 3BX)

Summary Multicomponent charge transfer (CT) spectra of carbazoles with *p*-chloranil are shown to arise *via* two different conformational arrangements of donor and acceptor units; surprisingly the most intense CT transition arises from the second-highest energy, rather than from the highest-energy filled orbital of the carbazole.

INTEREST in the formation and properties of charge transfer (CT) complexes of carbazole derivatives is due to their carrier generation and electron transport properties,[1,2] which have led to commercial applications in electrophotography.[3] A common feature of all published CT spectra of poly-(9-vinylcarbazole) complexes is the highly asymmetric nature of the absorption envelope caused by two distinct CT transitions arising from the HOMO(1) and HOMO(2) orbitals of the carbazole unit.[1] However, it is not yet clear whether the two CT transitions arise from a single orientation of donor with respect to acceptor or from two distinct donor–acceptor conformations. This problem occurs wherever multiple CT transitions are observed[4] and is aggravated by uncertainty over the exact shapes and positions of the individual CT absorption peaks. Very recent work suggests[5] that multiple CT transitions in complexes of tetracyanoethylene with a range of aromatic molecules arise from different conformational arrangements of donor and acceptor units.

Many examples of CT spectra of carbazoles with *p*-chloranil, and other acceptor molecules, are given in the papers by Okamoto *et al.*,[6] Landman *et al.*,[7] and the preceding paper[8] where it is shown that the circular dichroism (c.d.) of CT complexes of optically active carbazoles permits unambiguous assignments of the two CT transitions.

In the band resolution made by Landman *et al.*,[7] it was assumed that the most intense CT transition would arise from the HOMO(1) of the carbazole molecule, and hence would be of lower energy. Okamoto *et al*,[6] in contrast, used a band analysis which suggested that the most intense CT band arises from HOMO(2) and has the higher energy. The present data support the conclusions of Okamoto *et al.*,[6] and illustrate the difficulties of assigning ionisation potentials on the basis of CT peak positions.



(1) X = $\overset{*}{C}H(Et)Me$
(2) X = $SiMe_3$

Charge transfer spectra of carbazoles (**1**) and (**2**) (0·20—0·03 M) with *p*-chloranil (0·14 M) were determined in CH_2Cl_2. The CT spectra of (**2**) were measured at room temperature only, whereas the CT and c.d. spectra of complexes of the optically active carbazole (**1**) were measured over the temperature range −30 to +30 °C in sealed cells.

9-(Trimethylsilylmethyl)carbazole (**2**) with *p*-chloranil gives CT spectra in which not only are the two transitions sufficiently well separated to permit unambiguous band resolution (Figure 1), but also the higher energy transition is clearly the more intense. Separation of the two CT peak positions is determined by the ionisation potentials of HOMO(1) and HOMO(2) of the carbazole derivative[9] and it is well established that a trimethylsilylmethyl group lowers ionisation potential.[10] For carbazoles, substituents on the nitrogen atom have an important effect on the ionisation potential of HOMO(1) but relatively little effect on HOMO(2).[7,9] Thus, for compound (**2**), the net result is a widening of the separation in peak positions of the two CT bands. In contrast, an electron withdrawing substituent (*e.g.* 9-acetylcarbazole) lowers the energy of HOMO(1) and causes the peak positions to become unresolvable.[7] The usual range of 9-alkylcarbazoles [*e.g.* (**1**)] falls somewhere between these two extremes.[6,7]

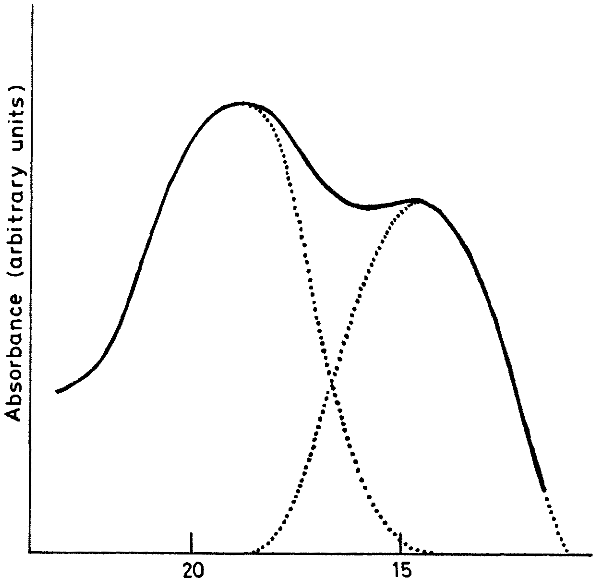


FIGURE 1. U.v. spectrum of CT complex of 9-(trimethylsilylmethyl)carbazole (**2**) with chloranil in CH_2Cl_2 at 37 °C.

More compelling evidence for the general conclusion that carbazoles give CT spectra with greater intensity in bands derived from HOMO(2) is provided by temperature studies of the complexes of (**1**) with *p*-chloranil. Figure 2 shows CT (normalised at 500 nm) and CT spectra (not normalised) over a 60 °C temperature range. The data show that, on lowering the temperature, the intensity of the longer wavelength CT band decreases relative to that of the higher energy transition; the effect is shown even more clearly by the c.d. spectra which are taken over a rather smaller temperature range.

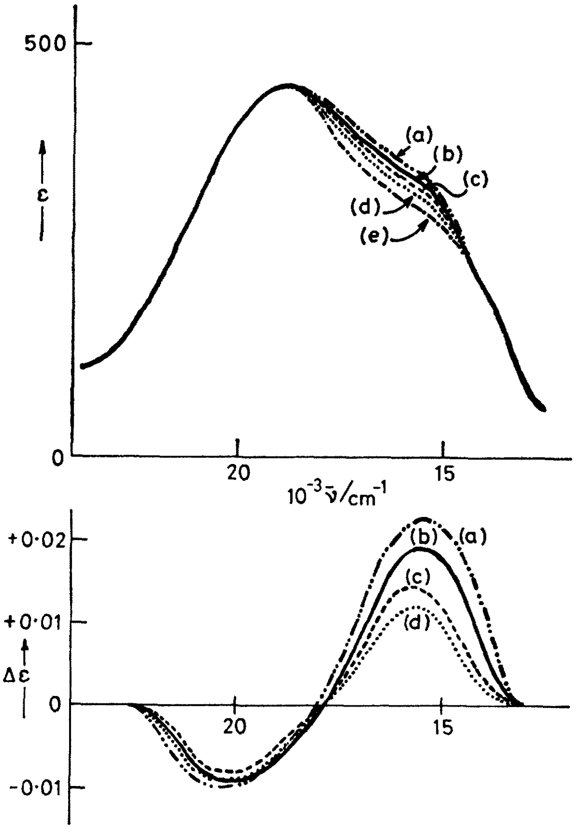
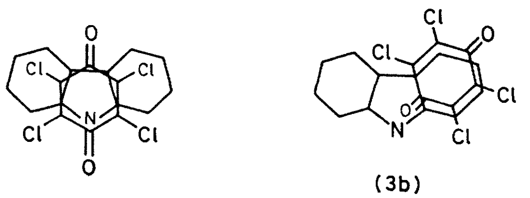


FIGURE 2. U.v. and c.d. spectra of CT complexes of (*S*)-9-(2-methylbutyl)carbazole (**1**) with chloranil, in CH_2Cl_2 at different temperatures: (a) 30 °C; (b) 10 °C; (c) 0 °C; (d) −10 °C; (e) −30 °C.

It must be concluded that multiple CT spectra of carbazoles with *p*-chloranil (and presumably with other acceptors) arise from two different conformational arrangements of donor and acceptor. Landman *et al.*,[7] have suggested that the two arrangements (**3a**) and (**3b**) (Figure 3) are the most probable and that symmetry would favour CT transitions from HOMO(1) and HOMO(2) in conformation (**3b**) but only from HOMO(1) in the more symmetrical conformation (**3a**). Thus conformation (**3a**) would give rise to only the lower energy (longer wavelength) transition and, since this is now found to be less intense at lower temperatures, conformation (**3b**) is confirmed as the more thermodynamically stable arrangement.



(3a) (3b)

FIGURE 3. Possible conformations for change transfer complexes of chloranil and carbazoles (ref. 7).

Significantly, even though both CT transitions are expected from conformation (**3b**), the relatively high intensity of the higher energy component is clear from the spectra given in Figure 2. This result is very surprising and contrasts with the usual situation in which electron promotion from HOMO(1) of donor to LUMO(1) of the acceptor accounts for the intensity of most CT transitions. There are very few reported examples of related phenomena[11] and it may be that the relative intensities of CT transitions for carbazoles is determined by different extents of coupling with the locally excited carbazole ($^1L_b \leftarrow {}^1A$, $^1L_a \leftarrow {}^1A$) transitions having perpendicular polarisations.[9] In any case, actual λ_{max} values for unresolved CT spectra of carbazoles (see Figure 2) are, therefore, located nearer the transition from HOMO(2) than that from HOMO(1), and thus provide a most unreliable guide to the lowest ionisation potential.

(*Received*, 10*th March* 1980; *Com.* 265.)

---

[1] J. M. Pearson, S. R. Turner, and A. Ledwith in 'Molecular Association' Vol. 2, ed. R. Foster, Academic Press, London, 1979, p. 80.

[2] 'Photoconductivity in Polymers,' eds. A. V. Patsis and D. A. Seanor, Technomic Publishing Co., Westport, 1976.

[3] R. M. Schaffert, *IBM J. Res. Dev.*, 1971, **15**, 75.

[4] R. Foster, 'Organic Charge Transfer Complexes,' Academic Press, London, 1969.

[5] M. J. Mobley, K. E. Rieckhoff, and E. M. Voight, *J. Phys. Chem.*, 1978, **82**, 2005; C. J. Eckhardt and R. J. Hood, *J. Am. Chem. Soc.*, 1979, **101**, 6170.

[6] K. Okamoto, M. Ozeki, A. Itaya, S. Kusabayashi, and H. Mikawa, *Bull. Chem. Soc. Jpn.*, 1975, **48**, 1362.

[7] U. Landman, A. Ledwith, D. G. Marsh, and D. J. Williams, *Macromolecules*, 1976, **9**, 833.

[8] R. Solaro, E. Chiellini, and A. Ledwith, preceding paper.

[9] H. J. Haink, J. E. Adams, and R. J. Huber, *Ber. Bunsenges. Phys. Chem.*, 1974, **78**, 436; R. W. Bigelow and G. E. Johnson, *J. Chem. Phys.*, 1977, **66**, 4861.

[10] H. Sakurai and M. Kira, *J. Am. Chem. Soc.*, 1975, **97**, 4879; B. E. Cooper and W. J. Owen, *J. Organomet. Chem.*, 1971, **29**, 33.

[11] C. J. Eckhardt and R. R. Pennelly, *J. Am. Chem. Soc.*, 1976, **98**, 2034.