

- (47) S. Tanaka and A. Nakajima, *Macromolecules*, **5**, 714 (1972).
- (48) One can use the present four-state model (h, ϵ , chain reversal, and c state) to predict these conformations, without recourse to the three-state model of papers 1–3, because all of these states are included explicitly in the matrix of eq 17, for example. However, it is more convenient (and requires a smaller-size matrix) to first use the three-state model (h, ϵ , and c) to identify h and ϵ , and then (with the redefinition of c in the four-state model) use the four-state model to identify the chain-reversal and (new) c states.
- (49) Predictions are made in this paper for 23 proteins [the sum of 13 (group 1), 7 (group 2), and 2 (group 3) out of the 26 proteins listed in Table I, and the 1 protein (group 4) not listed in Table I]. As to other proteins, no prediction is made since, for two proteins (lactate dehydrogenase and concanavalin), the amino acid sequences have not been determined completely, and only the known parts of the sequences (and their x-ray structures) were used to compute statistical weights. No prediction is made for sea lamprey hemoglobin simply because there are many other globin homologues as seen in column 1 of Table I, and this protein was omitted to save computer time. As for the α -chymotrypsin C chain, see footnote g of Table IV. Elastase also includes a tosyl residue, and no prediction was made for it. However, a prediction was made for the B chain of α -chymotrypsin.
- (50) These regions of helical and extended sequences predicted in paper 3⁵ should be regarded as tentative assignments, since the statistical weights used in paper 3 are tentative as stated in paper 3.⁵
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Structural Variations and Multiple Charge Transfer Transitions between Chloranil and Carbazole Derivatives

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ABSTRACT: Asymmetric charge transfer (CT) spectra from combinations of carbazole derivatives and chloranil are shown to consist of two bands originating from the highest (HOMO) and second highest (HOMO 2) energy occupied molecular orbitals of carbazole. Symmetry arguments are used to indicate that of two possible (parallel plane) alignments of donor and acceptor, that which is totally symmetric gives rise to only the lower energy CT transition whereas the unsymmetrical alignment which is energetically preferred permits the two observable CT transitions. Low molecular weight model carbazoles all show the asymmetric CT bands which have been resolved into two Gaussian components by means of a computer assisted analysis. Significantly, poly(*N*-vinylcarbazole) (PVCA) gives rise to CT bands much less asymmetric than corresponding model systems and it is concluded that steric interactions in PVCA greatly reduce the possibility for interaction of the carbazole units with chloranil in the 1:1 asymmetric arrangement preferred by the model compounds. As expected from the theoretical argument, poly(*N*-ethyl-3-vinylcarbazole) and poly(*N*-ethyl-2-vinylcarbazole), both of which are derived from unsymmetrically substituted carbazoles, give with chloranil highly asymmetric CT spectra which are very similar to those of the appropriate model compounds.

Carbazole and its ring and *N*-alkylated derivatives like other aromatic amines exhibit long wavelength charge transfer (CT) transitions with acceptors because of relatively high energies for the highest occupied molecular orbitals.¹ This property is manifest in low ionization potentials,¹ low oxidation potentials (~ 1.2 V (SCE)),² and a very high propensity to oxidative coupling.³

Observation of CT transitions when organic electron donors and acceptors are allowed to interact is now a commonplace phenomenon,⁴ it being frequently concluded that these transitions arise from so-called CT complexes without proper regard for the magnitude and nature of the binding forces in such complexes. Carbazoles, no less than other good organic electron donor molecules, readily participate in this type of intermolecular association with electron acceptors, the required close approach of donor and acceptor being favored by the planarity of the carbazole ring system. Particular interest in the formation and properties of CT complexes of carbazole derivatives arise from (mainly two) quite different types of study. Hoegl⁵ was the first to show that poly(*N*-vinylcarbazole) (PVCA) was a useful organic photoconductor and, more importantly, light absorption and photoconductivity were improved when PVCA was mixed with a variety of organic acceptor molecules. Several years later Ellinger⁶ showed that many organic electron acceptors, including chloranil, were useful initiators for the polymerization of monomeric *N*-vinylcarbazole (NVCA). Related observations were published inde-

pendently at about the same time by Scott, Miller, and Labes.⁷

These early disclosures stimulated research studies of the formation and photoelectrical properties of CT complexes of PVCA, leading ultimately^{8,9} to a commercial process for electrophotography based on compositions formed from PVCA and 2,4,7-trinitrofluorenone (TNF). In complete contrast, and despite extensive studies by several groups of workers,¹⁰ the reactions of NVCA with organic electron acceptors have not yet resulted in developments significant in other than a purely mechanistic sense; a critical survey of the scope and value of such studies has been given recently by Hyde and Ledwith.¹¹

Reactions of NVCA and chloranil have been extensively investigated. Originally it was claimed by Ellinger⁶ that chloranil was a useful initiator for cationic polymerization of NVCA in toluene, but subsequently other workers¹² found that purified chloranil was inactive in this particular system. Rather, it was shown that the strong protonic acid, 1,4-dihydroxy-2,3,5,6-tetrachlorobenzene (the dihydro reduction product of chloranil), thought to be an impurity in chloranil, was the true initiator. In more polar solvents the situation is even more confused.¹³ Another original observation by Ellinger⁶ was that mixtures of NVCA and chloranil in acetone gave rise to formation of the cyclodimer of NVCA when exposed to uv light or strong sunlight. This result has been amply confirmed by subsequent studies^{14,15} and it is now known that cyclodimerization of NVCA oc-

curs by a novel chain reaction¹⁶ in which the photoexcited chloranil (or other suitable oxidant) undergoes an electron transfer reaction with NVCA to produce NVCA cation radicals, which then function as chain carriers. There have been extensive studies of the effects of solvent and other variables on the chloranil sensitized cyclodimerization and polymerization of NVCA.¹⁷

For interpretations of photoelectrical properties of complexes of PVCA and of photoinduced and thermal reactions of NVCA with acceptors such as chloranil, the energies and types of CT transitions play a crucial role. It is surprising therefore that the very obvious asymmetry of CT spectra of carbazole complexes has not been the subject of serious comment. The two highest energy filled molecular orbitals of carbazoles are separated by only approximately 0.5 eV¹ and it is a reasonable assumption (vide infra) that the asymmetric nature of CT spectra of carbazole derivatives arises from CT transitions involving the highest and second highest energy occupied molecular orbitals of the carbazole moiety with a common lowest energy empty molecular orbital of the acceptor molecule. Multiple CT transitions, with similar origins, are not uncommon for aromatic donor molecules, with the best known example involving naphthalene and tetracyanoethylene.^{4,18}

For CT spectra which are asymmetric it is particularly misleading to treat the experimentally observed ν_{\max} as a measure of the energy of the CT transition and some kind of band analysis is necessary before making correlations. Nevertheless the values of ν_{\max} (or more usually corresponding values of λ_{\max}) have been used in several studies of CT spectra of carbazole derivatives,¹⁹ including PVCA,²⁰⁻²⁴ resulting in some erroneous conclusions. It is the purpose of the present paper to clarify the nature and origins of CT spectra of carbazoles with chloranil and to indicate how conformational preferences (especially in the case of PVCA) affect the relative intensities of available multiple CT transitions producing in consequence a dramatic effect on the wavelength sensitivities of such combinations.

Since this work was completed two important publications have appeared relating to multiple CT transitions. The first²⁵ deals with relative intensities of CT transitions in phenylpentamethyldisilane-tetracyanoethylene complexes and is notable for a proper band analysis by a computer assisted resolution of experimental curves into skewed Gaussian components. A second publication by Okamoto et al.²⁶ gives information as to the thermodynamics constants of CT complex formation of carbazoles, including PVCA, with a series of acceptor molecules and makes clear the different shapes of CT spectra for common symmetrical acceptor molecules with low molecular weight carbazoles and PVCA, respectively.

The more general results reported by Okamoto et al.²⁶ are entirely complementary to the specific data reported herein for chloranil containing systems and provide strong support for a theoretical explanation of the origins and intensities of CT transitions of carbazole derivatives.

Experimental Section

Materials. Poly(*N*-vinylcarbazole) (PVCA) obtained from BASF (Luvicon) was dissolved in tetrahydrofuran and precipitated with methanol seven times. The PVCA was redissolved in benzene and freeze dried. The molecular weight was determined by membrane osmometry and intrinsic viscosity, whereas the molecular weight distribution was determined by gel permeation chromatography. The polymer sample used had an $\bar{M}_n = 2.53 \times 10^5$ and an MWD = 5.61.

Poly(*N*-ethyl-2-vinylcarbazole) (P2VCA) was prepared anionically by conventional high-vacuum techniques. Syntheses of the monomer²⁷ and polymer²⁸ have been described previously. Molec-

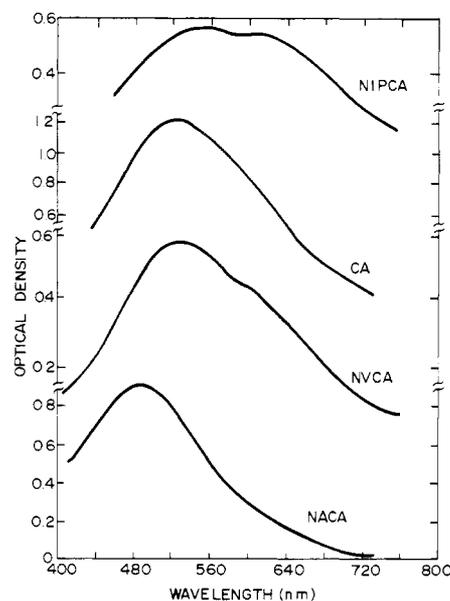


Figure 1. Charge transfer absorption spectra of *N*-isopropylcarbazole (NIPCA), carbazole (CA), *N*-vinylcarbazole (NVCA), and *N*-acetylcarbazole (NACA) with chloranil.

ular weight characterizations were determined as for PVCA and for this polymer sample $\bar{M}_n = 1.0 \times 10^6$ and MWD = 2.19.

Poly(*N*-ethyl-3-vinylcarbazole) (P3VCA) was prepared by cationic polymerization of the monomer *N*-ethyl-3-vinylcarbazole and details of the synthesis have been reported.²⁹ $\bar{M}_n = 3.3 \times 10^5$ and MWD = 2.97 were determined for the polymer sample used in these experiments.

Carbazole (CA) and *N*-isopropylcarbazole (NIPCA) (Eastman Organic Chemicals) were purified prior to use by multiple recrystallizations from ethanol. *N*-Ethylcarbazole (NECA) and *N*-phenylcarbazole (NPCA) (Aldrich Chemical Co.) were also purified by recrystallizations from ethanol. *N*-Acetylcarbazole (NACA) and a number of dicarbazoylalkanes in which carbazole groups are separated by ethane (DCAE), propane (DCAP), butane (DCAB), pentane (DCAPE), and decane (DCAD) bridges were synthesized in the Xerox laboratories and purified by multiple recrystallizations.³⁰ Two dicarbazoylcyclobutane compounds, *trans*-1,2-dicarbazoylcyclobutane (1,2-DCACB) and 1,2-dicarbazoyl-*trans*-3,4-dimethylcyclobutane (3,4-DMDCACB) were synthesized in the Donnan laboratories and purified prior to use.³¹ The electron acceptor used in this study, *p*-chloranil, was purified by multiple recrystallizations from ethanol, followed by careful drying in vacuum. Dichloromethane was the solvent used for all CT spectral measurements. It was obtained without preservatives from Burdick and Jackson, distilled from phosphorus pentoxide, and stored in the dark.

Spectral Measurements. Solution electronic absorption spectra were obtained on a Cary 15 recording spectrophotometer. The spectrophotometric data were presented via mechanical encoding to the analogue inputs of a spectrophotometer interface (Data Graphics 9158). Data converted to digital form were available at the output as parallel BCD (binary coded decimal) for processing, serialization, and decoding by a programable interface (Data Graphics 305), which output the data in USASCII coding suitable for automatic send-receive terminals (Texas Instruments ASR 733). The ASR stored data on magnetic tape cassettes and transmitted data to a Sigma 9 computer for processing and plotting.

A interactive computer curve resolving program was used to deconvolute the observed spectral envelopes into a minimum number of Gaussian bands that represent the various CT transitions. The program performs successive iterations to obtain the best possible fit between predicted and observed spectra. The standard deviation for the fits was generally less than 0.001. The experiments were generally done at room temperature, 298 K; however, a few were performed at 313 and 213 K.

Results and Discussion

In this work we have been concerned with the energetics and origins of CT spectra for carbazole derivatives and not

Table I
Wavelength Maxima for CT Transitions between Chloranil and Carbazole Derivatives^d

Carbazole derivative	Carbazole concn, [M]	Chloranil concn [M]	D/A	CT max 1, nm	CT max 2, nm	
CA	Carbazole	0.0542	0.0132	4.11	540	504
NIPCA	<i>N</i> -Isopropylcarbazole	0.0416	0.0257	1.62	609 ± 10	508 ± 3 ^a
NVCA	<i>N</i> -Vinylcarbazole	0.0548	0.0132	4.15	567	504
NACA	<i>N</i> -Acetylcarbazole	0.0584	0.0130	4.49		483
NPCA	<i>N</i> -Phenylcarbazole	0.0530	0.0132	4.02	609	500
3,6-DMCA	3,6-Dimethylcarbazole	0.0253	0.0133	1.90	611	531
1,2-DCACB	1,2-Dicarbazolylcyclobutane	0.0530	0.0132	4.02	597	503
3,4-DMDCACB	3,4-Dimethyl-1,2-dicarbazolylcyclobutane	0.0530	0.0133	4.00	600	490
NECA	<i>N</i> -Ethylcarbazole	0.0530	0.0133	3.98	600 ± 5	506 ± 2 ^b
NE2ECA	<i>N</i> -Ethyl-2-ethylcarbazole	0.0361	0.0137	2.66	629	538
NE3ECA	<i>N</i> -Ethyl-3-ethylcarbazole	0.0482	0.0130	3.71	645	524
DCAE	Dicarbazoylthane	0.0271	0.0137	1.98	572	511
DCAP	Dicarbazoylpropane	0.0464	0.0137	3.39	579	505
DCAB	Dicarbazoylbutane	0.0476	0.0137	3.47	578	506
DCAPE	Dicarbazoylpentane	0.0500	0.0137	3.65	613	497
DCAD	Dicarbazoyldecane	0.0482	0.0137	3.52	614	505
PVCA	Poly(vinylcarbazole)	0.0548	0.0132	4.15	604 ± 12	501 ± 10 ^c
P2VCA	Poly(<i>N</i> -ethyl-2-vinylcarbazole)	0.0494	0.0117	4.22	616 ± 8	532 ± 12 ^b
P3VCA	Poly(<i>N</i> -ethyl-3-vinylcarbazole)	0.0494	0.0117	4.22	648 ± 6	523 ± 10 ^b
PVCACI	Chlorinated poly(vinylcarbazole)	0.0660	0.0212	3.11	579	450

^a Average of eight experiments. ^b Average of two experiments. ^c Average of nine experiments. ^d All spectra determined at 298 K in methylene chloride with chloranil and solvent as a reference. Charge transfer maxima were determined by curve fitting analyses; standard deviations, σ , for the fitting were less than 0.002.

with values of thermodynamic association constants. The latter may be estimated by the Benesi–Hildebrand procedure, as was done by Okamoto et al.,²⁶ but it is well known that such methods of analysis can give misleading information as to the true formation constants.⁴ In contrast, the values of λ_{\max} or ν_{\max} for CT absorption spectra are easily determined and provide a reliable estimate of the transition energies.

Multiple CT absorptions have been obtained for the interactions of chloranil with carbazole-containing materials. The results for carbazole (CA), *N*-isopropylcarbazole (NIPCA), *N*-vinylcarbazole (NVCA), and *N*-acetylcarbazole (NACA) are presented in Figure 1 and in Table I. These CT spectra which occur between 400 nm and 800 nm, have small extinction coefficients and are distinctly *asymmetric*. This asymmetry, as we shall show, is characteristic of all carbazole-containing molecules, with the exception of NACA.

In general, the absorption maxima of the CT spectra for carbazole molecules with chloranil occur near 500 nm together with a broad shoulder having a maximum in the vicinity of 600–650 nm. The maxima of the CT bands do not change position with changes in temperature between 213 and 313 K although the intensity of the CT interaction does increase with decreasing temperature as expected. The CT maxima positions are invariant with respect to the donor/acceptor (D/A) ratio. Ratios were varied from as low as 1.5 to as high as 75 with no apparent effect upon the positions of the band maxima. This strongly suggests that for the D/A ratios employed, a 1:1 CT complex results. In Figure 1, two CT bands are clearly evident in the spectra for NIPCA and NVCA and are less evident in the spectrum for CA, and only one maximum near 500 nm is present for NACA. A series of α,ω -di-*N*-(carbazyl)alkanes, CA-(CH₂)_{*n*}-CA, where *n* = 2, 3, 4, 5, 10, gave very similar asymmetric CT spectra with chloranil (Figure 2) giving further evidence that the spectral components do not arise from com-

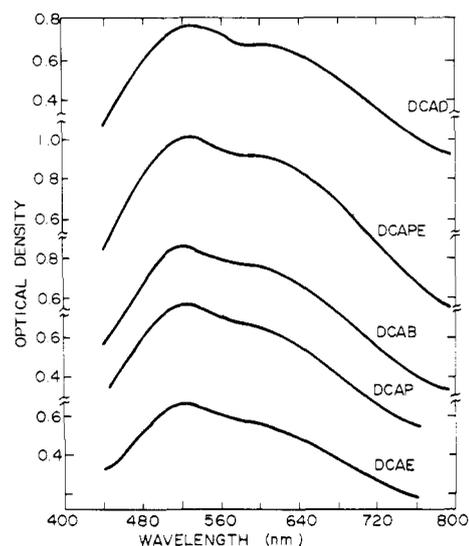


Figure 2. Charge transfer absorption spectra of α,ω -di(*N*-carbazoyl)alkanes, CA-(CH₂)_{*n*}-CA, where *n* = 2 (DCAE), *n* = 3 (DCAP), *n* = 4 (DCAB), *n* = 5 (DCAPE), and *n* = 10 (DCAD) with chloranil.

binations of CT complexes having varying compositions such as 1:1 and 2:1 D/A ratios. Putting aside for the moment the special case of PVCA, inspection of the spectra reported in this paper together with the additional examples, reported by Okamoto et al.,²⁶ reveals that all low molecular weight *N*-alkylcarbazoles (including very low molecular weight PVCA) give rise to very similar CT spectra with chloranil and related symmetrical acceptor molecules in which the *energy separation* between the two apparent CT maxima is essentially independent of acceptor molecule and is approximately 3800–4400 cm⁻¹, corresponding to approximately 0.4 eV. Highly significant exceptions to this

Table II
Energies for CT Maxima of Carbazole Derivatives with Chloranil and Ionization Potentials for Carbazole Derivatives

Carbazole derivative	λ_{CT1} , cm^{-1}	λ_{CT2} , cm^{-1}	$\Delta\lambda_{CT}$, eV	IP(HOMO), ^c eV	IP(HOMO2), ^c eV	Δ IP, eV
Carbazole				7.68	8.08	0.40
<i>N</i> -Ethylcarbazole	15 222	19 114	0.47	7.36	7.82	0.46
<i>N</i> -Acetylcarbazole		20 857		$\sim 8.0^a$	$\sim 8.0^a$	0^a
Poly(<i>N</i> -vinylcarbazole)	15 442	18 755	0.42			0.40^b

^a Peaks not resolvable. ^b Difference in energies of 1L_b and 1L_a transitions. ^c Data for carbazole, ref 1.

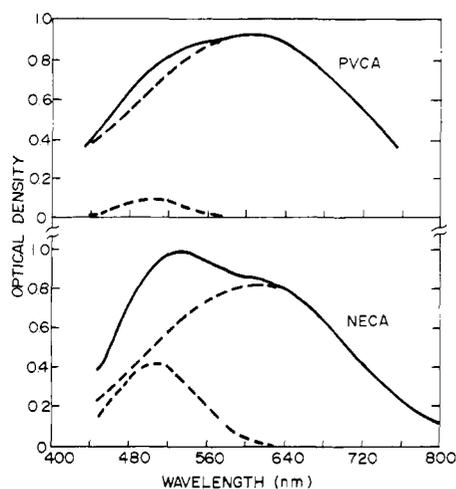


Figure 3. Charge transfer absorption spectra for poly(*N*-vinylcarbazole) (PVCA) and *N*-ethylcarbazole (NECA) with chloranil drawn with a solid line. Dashed line indicates two Gaussian subcomponents.

generalization are NACA and CA. An essentially constant energy separation between the two CT bands is to be expected since *N*-alkylcarbazoles have first and second ionization potentials differing by approximately 0.5 eV (Table II). Corresponding ionization potentials for carbazole have a lower energy separation which should result in a rather smaller splitting between the two CT bands, as noted experimentally. Furthermore, in NACA the highest occupied MO is substantially stabilized on account of the resonance effect of the acetyl substituent on the nitrogen lone pair electrons. In consequence the first and second ionizations are almost identical (Table II) which, in the usual broad CT spectra, would be unresolvable into two components. A single Gaussian band fits the observed CT band with a standard deviation less than 0.001. The average energy of the two ionizations of NACA is very similar to that of the second highest occupied MO (ca. 8 eV) of CA and *N*-alkylcarbazoles and hence *all* such low molecular weight species should give rise to a similar *high energy* CT transition with electron acceptors. For NACA this is unambiguously assigned to the single transition near 500 nm and there is, as we have already noted, a corresponding band to be seen for all the other carbazole compounds.

A most probable position for the *lowest energy* CT transition of *N*-alkylcarbazoles (IP = 7.4 eV) with chloranil is readily estimated as $\sim 16\,000\text{ cm}^{-1}$ or approximately 600 nm by comparison with ionization potentials and CT maxima for complexes of chloranil with other donor molecules.⁴ Thus we must conclude that the apparent shoulder at around 600 nm in CT spectra of carbazoles with chloranil arises from a transition involving the highest occupied molecular orbital of the carbazole and the lowest empty mo-

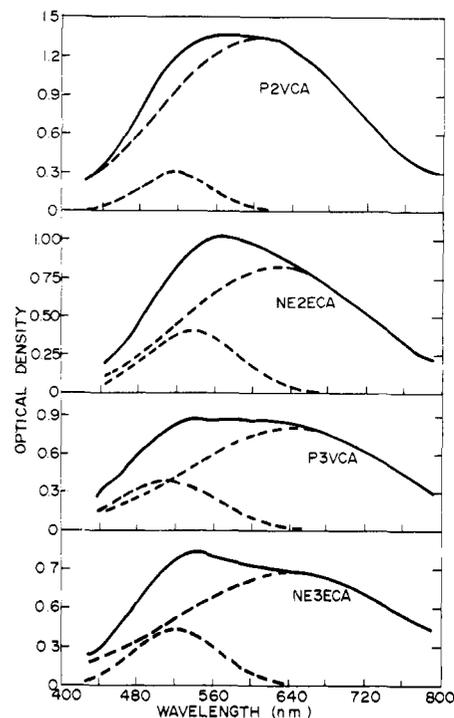


Figure 4. Charge transfer absorption spectra (solid lines) and Gaussian subcomponents (dashed lines) for poly(*N*-ethyl-2-vinylcarbazole) (P2VCA), *N*-ethyl-2-ethylcarbazole (NE2ECA), poly(*N*-ethyl-3-vinylcarbazole) (P3VCA), and *N*-ethyl-3-ethylcarbazole (NE3ECA) with chloranil.

lecular orbital of the acceptor. This is the usual condition for CT spectra and it follows that this *low energy* transition must be the *more important component* of the multiple band system observed. Examples of asymmetric CT bands for carbazole derivatives have been reported^{14-17,26,32} but no explanation has been offered. Most recently Okamoto et al.²⁶ attempted a band resolution in which the *higher energy* transition was given a dominant role. This seems highly unlikely as a result of the considerations noted above and of the more theoretical argument presented below. However, in many respects and especially the differences between PVCA and other carbazoles, our conclusions are in broad general agreement with those of Okamoto et al.²⁶ although there must be more than the usual skepticism about the validity of analyses by the Benesi-Hildebrand procedure when there is uncertainty about the band analysis.

The wavelength maxima for the CT bands in Table I and Figures 3 and 4 have been obtained from a computer curve resolving program. Band shapes for electronic absorption spectra have been discussed previously.^{33,34} It has been suggested that log-normal distributions, of which the Gaussian distribution is a special case, are preferred for bands exhibiting skewness. There is no obvious choice for a

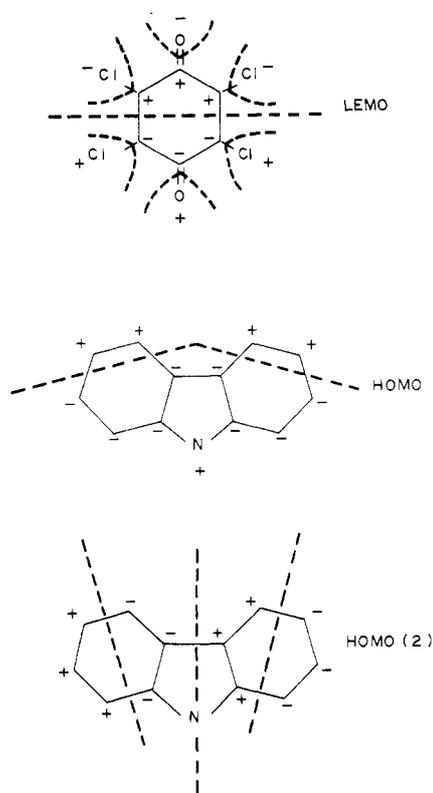


Figure 5. Signs of orbital coefficients obtained from simple HMO treatment for the highest occupied molecular orbital (HOMO) and second highest occupied molecular orbital (HOMO (2)) for carbazole and the lowest empty molecular orbital (LEMO) for chloranil. Dashed lines indicate nodal planes.

distribution function to describe CT transitions. However, since the asymmetry observed for the spectral results in Figures 1–4 are not skewed bands so much as overlapping symmetric bands, it has been assumed that a reasonable first approximation is the use of a Gaussian distribution. The qualitative results are identical even when a different distribution function is used. For example with the skewed Gaussian, only two bands are necessary, and the positions of the two maxima are almost identical with those obtained using the symmetric Gaussian function.

Results of the curve fitting analysis for PVCA and its model compound NECA are indicated in Figure 3. Charge transfer spectra of PVCA with chloranil and other symmetrical acceptor molecules are clearly different in general shape from those of the model compound NECA and similar materials. For the polymer the major transition appears to be centered around 600 nm with only a weak asymmetric influence in the high energy side of the band. As previously noted, on the basis that the major CT transition is that of lowest energy and is common to all *N*-alkylcarbazoles including PVCA, the apparent λ_{\max} (~500 nm) for CT spectra of most carbazoles with chloranil arises from a contribution by a comparatively minor CT transition involving the second highest occupied molecular orbital of the carbazole. For PVCA this minor CT band is even less intense with the apparent λ_{\max} coinciding with that to be anticipated for a donor unit having an ionization potential of ~7.4 eV (Figure 3).

In contrast, it is interesting to note (Figure 4) that for both the closely related polymers P2VCA and P3VCA and their corresponding model compounds, *N*-ethyl-2-ethylcarbazole (NE2ECA) and *N*-ethyl-3-ethylcarbazole (NE3ECA), CT spectra with chloranil are highly asymmet-

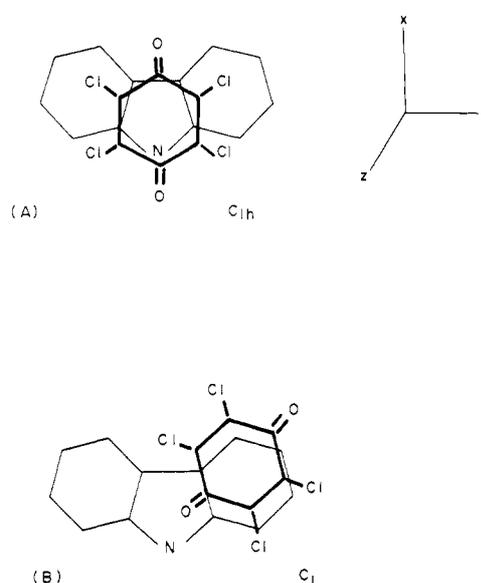


Figure 6. Conformations for carbazole/chloranil complex. *z* axis out of the plane of the paper, *x*, *y* axes in the plane of the paper. Symmetric complex (C_{1h}) point group drawn in A, unsymmetric complex (C_1) point group drawn in B.

ric exhibiting two CT transitions in the manner of most low molecular weight carbazole compounds.

Certain substituent effects may be observed from the results in Table I. *N*-atom substitutions of alkyl or aryl groups generally increase the wavelength maximum of the low energy CT band. The effect on the high energy CT band is much less; its position remains essentially unchanged. Substitutions at the 2 and 3 positions of the carbazole ring result in increases in the wavelengths of both CT maxima, as can be seen for NECA, NE2ECA, NE3ECA, and the corresponding polymers. In general, the high energy CT band is less dependent upon substituent perturbation than the low energy CT band centered near 600–620 nm.

We may gain some insight into the origins of the two transitions in carbazole derivatives by a consideration of symmetry of the possible conformations of the sandwich-like overlap of donor and acceptor molecules in the complex.

The intensity I of an electronic transition is related to the initial and final electronic states of the system (with wave functions ψ_I and ψ_F , respectively) by the following expression:

$$I \propto \mu_\alpha^2 = |\langle \psi_I | M_\alpha | \psi_F \rangle|^2 \quad (1)$$

in which M is the transition dipole moment operator in the α ($\alpha = x, y, z$) Cartesian direction with reference to an arbitrary coordinate system. For closed shell systems, ψ_I is totally symmetric whereas the symmetry of ψ_F is the product of symmetries of the donor and acceptor orbitals involved in the transition. The condition for a nonzero transition probability is a totally symmetric matrix element.

The experimental evidence suggests that the observed multiple CT transitions may involve the highest and second highest occupied molecular orbitals, HOMO and HOMO(2), respectively, of the donor molecule, and the lowest empty molecular orbital (LEMO) of the acceptor molecule. A simple HMO calculation is sufficient for evaluation of the symmetry considerations. The results of these calculations for the basis orbital coefficients of HOMO, HOMO(2), and LEMO are illustrated in Figure 5. The

Table III
Symmetry Properties of the x , y , and z Components of the Dipole Moment Operator and Orbitals^a

Conformation	Transition		$\psi_1(\psi_d\psi_a\rangle)$	M_d	$\psi_F(\psi_d'\psi_a'\rangle)$	$\langle\psi_1 M_d \psi_F\rangle$
C_{1h}	HOMO	LEMO	a'	$a'(M_x, M_z)$	a'	A
C_{1h}	HOMO(2)	LEMO	a'	$a''(M_y)$	a''	A
C_1	HOMO	LEMO	a	$a(M_{x,y,z})$	a	A
C_1	HOMO(2)	LEMO	a	$a(M_{x,y,z})$	a	A

^a ψ_1 is the initial state of the complex and is given by a direct product of the ground state electronic configuration of the donor and acceptor molecules, ψ_d and ψ_a , respectively. ψ_d' and ψ_a' are the wave functions of the excited donor and acceptor molecules. ψ_d' contains a hole in the HOMO or HOMO(2) orbital and in ψ_a' the LEMO orbital is occupied.

C_{1h}	E	x, y
a'		HOMO, LEMO, M_x, M_z
a''		- HOMO (2), M_y

C_1	E
a	HOMO, HOMO (2), LEMO, $M_{x,y,z}$

Figure 7. Character tables for C_{1h} and C_1 point groups.

signs of the orbital coefficients are shown and the dashed lines represent nodal planes.

Two distinct conformations for a carbazole/chloranil complex are drawn in Figure 6. The complexes are sandwichlike structures having parallel molecular planes and differ by a rotation around the z axis (normal to the x - y plane) and a translation in the x - y plane. These two conformations are representative of the symmetry properties of all other possible parallel structures for this donor-acceptor pair. The conformation shown in Figure 6A has a plane of reflection ($\sigma_{x,z}$) which is lacking in the conformation shown in Figure 6B. The group theoretical designations for the conformation in Figure 6A is C_{1h} ; the other conformation contains only an identity element and is designated C_1 .³⁵ In the limit of weak coupling between donor and acceptor molecules, the most probable contribution to the CT transition intensity involves charge displacement in the z direction. In order to examine which transitions have an allowed z component (see Figure 6) consider the symmetry properties of the x , y , z components of the dipole moment operator and the orbitals of interest listed in the character tables in Figure 7. The results of applying these symmetry designations to 1 are summarized in Table III, in which A designates a totally symmetric product and therefore a symmetry allowed transition. From these considerations, it is apparent that the HOMO(2) \rightarrow LEMO CT transitions in the C_{1h} conformation contain no z component and are not expected to contribute appreciably to the observed spectrum. Thus totally symmetric overlap of chloranil and carbazole derivatives would lead only to a CT band near 600 nm, corresponding to transitions from the 1L_b level in the carbazole derivatives to the lowest empty molecular orbital in the acceptor. In the C_1 conformation

both transitions from HOMO and HOMO(2) are mixed, polarized with the z component, and may contribute to the observed spectrum.

Our considerations are based on the symmetries of the donor and acceptor orbitals involved in the charge transfer transitions which can be obtained via a simple HMO calculation. The use of semiempirical molecular orbital methods for the calculation of the orientation dependence of CT stabilization in molecular complexes is complicated by the assumptions inherent to the method of calculation, as well as the neglect of dispersion forces and solvation effects. Nevertheless we have performed PPP calculations in which an HMO basis was used for the SCF refinement (the parameterization in ref 36 was followed). In this calculation the interplanar distance was allowed to vary between 3 and 6 Å and for each distance several interplanar orientations were considered. The relative charge transfer stabilization energy as a function of the geometry of the complex is maximized for nonsymmetrical conformations similar to that indicated in Figure 6B. For this minimum energy conformation of a carbazole-chloranil pair, as we have just noted, CT transitions involving the first and second highest occupied molecular orbitals would be expected. On this basis we should expect all carbazole derivatives to form complexes with chloranil having a molecular orientation similar to Figure 6B. Inspection of space filled molecular models indicates that for orientation 6B (in comparison to 6A) there is considerably more steric interference between the chlorine substituents and the groups attached to the nitrogen atom of carbazole. This interference is most pronounced in the case of PVCA and it is a reasonable conclusion therefore that the CT spectrum of PVCA with chloranil arises mainly from conformers similar to 6A rather than the more usual 6B.

In this way it is possible to understand the significant difference between PVCA and all other carbazole derivatives (including very low molecular weight PVCA) and polymers in which the carbazole unit is removed from the main chain. The rather specific stereochemical organization of substituents in the highly hindered PVCA is already apparent from studies of NMR and emission spectroscopy.²⁹

Further confirmation of these ideas arises from the highly asymmetric nature of both polymer and model compounds of ring-alkylated carbazoles. Here we are dealing with very similar donor units and the polymers have carbazole units substituted directly onto the polymer backbone. However, the carbazole derivative is no longer symmetrical as for simple N -alkylcarbazoles and similar symmetry considerations indicate that charge transfer transitions for both HOMO and HOMO(2) are likely for any arrangement of the donor-acceptor pairs.

Finally it is worth recalling that asymmetric substitution in the acceptor molecule would have a similar effect on the theoretical arguments presented. Thus a complex between a simple N -alkylcarbazole and an unsymmetrical acceptor

molecule would be expected to exhibit the two CT transitions for all molecular arrangements, and it is well known that complexes of *N*-alkylcarbazoles and PVCA all exhibit very similar multiple CT bands with the unsymmetrical acceptor 2,4,7-trinitrofluorenone.^{5,8,32} The PVCA–TNF system is important in electrophotography and the two charge transfer transitions are known to be important in extending the wavelength sensitivity.⁸

Conclusions

N-Alkylcarbazoles with chloranil give rise to two CT transitions originating in the first and second highest occupied molecular orbitals of the carbazole moiety. Theoretical arguments indicate that the most probable molecular organization for a carbazole–chloranil pair is coplanar but unsymmetrical with the chloranil lying at a significant angle to and displaced from the carbazole *z* axis (Figure 6B). In this conformation both CT transitions would be expected. An alternative symmetrical conformation in which the carbazole and chloranil *z* axis are aligned (Figure 6A) would lead to only the low energy CT transition involving the highest energy filled orbital of the carbazole. Charge transfer spectra for PVCA–chloranil combinations are significantly different from those of simple model compounds such as *N*-ethylcarbazole and it is suggested that steric hindrance in PVCA greatly reduces the probability for complex formation involving the more stable unsymmetrical arrangement. In consequence CT spectra for PVCA with symmetrical acceptors such as chloranil are comprised mainly of the lowest energy transition.

In complete contrast, the closely related polymers P2VCA and P3VCA, which are based on unsymmetrical donor components, give with chloranil, as expected, multiple CT transitions which are essentially identical in relative intensities to those of the corresponding model compounds.

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