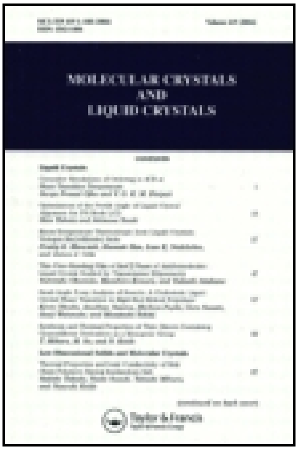

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Hypochromism in Two Low-Energy Transitions of B_2 (B_{2u}) Symmetry in the Electronic Spectrum of the Carbazole Crystal

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Hypochromism in Two Low-Energy Transitions of B_2 (B_{2u}) Symmetry in the Electronic Spectrum of the Carbazole Crystal

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The effect of intermolecular interactions on oscillator strengths of individual electronic transitions of B_2 ($\boldsymbol{B_{2u}}$) symmetry in the carbazole crystal was studied. We have shown that the two lowest-energy transitions of this symmetry exhibit very strong hypochromism—only 22% of the molecular oscillator strength is retained in the crystal spectrum. Polarized transmittance spectra of thin (~0.1 μ) carbazole monocrystals were obtained in the near UV region at normal and oblique incidence of light on the sample. An expression for transmittance *as a function of oscillator strengths of the B_2 ($\boldsymbol{B_{2u}}$) symmetry electronic transitions in the crystal, and of the angle of incidence of light on the ac face of the crystal, was derived. The* experimental *oscillator strengths were obtained by fitting the measured transmittance spectra with the derived function. Local field theory was employed to calculate the* theoretical *values of the oscillator strengths of five individual electronic transitions in the carbazole crystal. The calculations are in agreement with the oscillator strengths sum rule. The theoretically predicted and experimentally obtained values of oscillator strengths of the two lowest B_2 ($\boldsymbol{B_{2u}}$) symmetry transitions in the carbazole crystal are in very good agreement.*

Keywords: carbazole crystal; hypochromism; oscillator strengths; transmittance spectra

INTRODUCTION

Numerous experimental and theoretical studies of intensity distribution in electronic spectra of molecular associations (such as biopolymers, polymers with aromatic pendants, dimers, and higher

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aggregates of aromatic molecules) are reported in the literature. It was demonstrated that substantial intensity changes can occur in a given dipole-allowed electronic transition when molecules join to form a molecular aggregate (*hypochromism*: diminished intensity, and *hyperchromism*: increased intensity of a transition in question) [1–15]. Several different approaches have been used for theoretical interpretation of hypochromic and hyperchromic effects in molecular associations. The first-order perturbation theory was originally employed by Tinoco [1] and Rhodes [2] to explain the experimentally observed hypochromism in helical DNA. For low-energy electronic transitions, this theory predicts hypochromism, if the transition dipoles of the monomers are perpendicular to the line connecting the monomers (sometimes referred to as *parallel* arrangement of transition dipoles), and hyperchromism in case of collinear arrangement of the monomeric transition dipoles. Local field theory was applied by DeVoe [3] and others for predicting the absorption spectrum of an aggregate of monomeric units such as a molecular crystal, macromolecular polymer, *etc*. Each monomer in the aggregate is considered to have a polarizability, which depends on the local electric field at the monomer. This local field is a superposition of the incident (average) field and the field from polarizations of all other monomers in the aggregate. The predictions of the local field theory agree with those of the first-order perturbation theory. McLachlan and Ball [4] obtained similar results by means of the time-dependent self-consistent field theory. Rhodes and Chase [5] employed the method of linear response functions [6] for predicting the effect of molecular interactions on intensities in electronic absorption spectra. The authors conclude that all previously reported theories of hypo/hyperchromism are mutually compatible and are contained in the results of the linear response function method. Second quantization methods have been employed by Agranovich [7] for calculating absorption intensities in molecular associations. Hoffmann [8] applied the latter theory to calculation of the hypo/hyperchromic effect in a one-dimensional crystal with one molecule per unit cell. The prediction of the second quantization method are qualitatively similar to those of the previous theories but it was shown by Hoffmann [8] that the magnitude of hypo- or hyperchromism calculated in the approximation of the first-order pertubation theory could differ by around 50% from that predicted by the more inclusive second quantization method.

Experimentally, hypochromism was studied in biopolymers—DNA and proteins [1,9], in dimers and other associations of aromatic molecules in amorphous [10,11] and Shpol'sky matrices [12], in poly(N-vinylcarbazole) [13,14], and in other polymers with aromatic pendants [13]. Hypochromism was also observed in the absorption spectrum of molecules with a carbazole moiety after their incorporation into circular DNA [15].

As far as molecular crystals are concerned, a great deal of literature is devoted to experimental investigations of the effect of molecular interactions in these crystals on their energy spectra (excitonic properties, positions and shapes of electronic bands, vibronic interactions, localized states, *etc*.). Experimental studies of intensity redistribution between dipole-allowed electronic transitions in the spectra of molecular crystals, with respect to the corresponding spectra of noninteracting molecules, are scarce. Data on oscillator strengths of individual electronic transitions, obtained from transmittance spectra of thin crystals with incident light polarized in all three crystallographic directions, hardly exist in the literature. Similar data obtained from reflectance spectra of bulk crystals, using Kramers–Kronig transformation, is also scarce, and sometimes such data are in contradiction with data obtained from transmittance spectra of thin crystals.

The notion that molecules in a molecular crystal retain their individuality, and the lack of reliable experimental data on oscillator strengths of individual electronic transition in these crystals, led to frequent assumptions that there is no intensity redistribution between dipole-allowed electronic transitions in the spectra of molecular crystals. The implication of this assumption is that the expression $f_a + f_b + f_c = 3f_{mol}$ would be valid for each individual electronic transition in the crystal (f_a, f_b, and f_c are the oscillator strengths of a given electronic transition, excited with electric field vector directed along the three crystallographic axes *a*, *b*, and *c* in the crystal, and f_{mol} is the oscillator strength of the same transition when the molecules are noninteracting and randomly oriented in a solution).

Accumulating data on total oscillator strengths of individual electronic transitions in molecular crystals ($f_{total} = f_a + f_b + f_c$) both by transmittance and by reflectance spectra measurements would address the thus far unresolved fundamental problem in spectroscopy of molecular solids concerning the effect of intermolecular interactions on intensities of individual electronic transitions in a molecular crystal. (From a quantum-mechanical point of view, it is the problem of changes in the molecular wave function when molecules join in a crystal.) Obtaining such data may also contribute to elucidation of the reason for differences in oscillator strength deduced from transmittance spectra measurements of thin crystals on the one hand and from reflectance spectra measurements of bulk crystals on the other hand.

The spectroscopy of carbazole is of renewed interest because of the numerous applications of molecules and polymers with carbazole moieties. Among the latter, poly(N-vinylcarbazole) exhibits photoconductive and photorefractive properties [16]. These properties make PVK (poly-N-vinylcarbazole) a candidate for applications in holography, electro-optics, electroluminescence, nonlinear optics, and electronic data storage [17,18].

Studies of interactions between carbazole molecules in the crystalline state may contribute to understanding the interactions between carbazole (and other) pendants in polymers. Molecules with carbazole moieties such as rebeccamycin and its derivatives (indolocarbazoles) are extensively studied for use as anticancer drugs [15,19]. Some of these molecules exhibit hypochromism after their incorporation into DNA [15]. Comparative studies of hypochromism in all these molecular associations may eventually contribute to the elucidation of the mechanism of interaction of drugs (such as indolocarbazoles and other aromatic compounds) with biological polymers.

The effects of intermolecular interactions on the redistribution of oscillator strengths in the electronic transmittance spectrum of the carbazole crystal was previously studied semiquantitatively; it was shown that there is a dramatic increase of transmittance in the region of the lowest B_2 ($\mathbf{B_{2u}}$) symmetry transitions in the electronic spectrum of this crystal [20,21]. In this work, we undertook theoretical and quantitative experimental studies of changes in the oscillator strengths of individual low-energy electronic transitions of B_2 ($\mathbf{B_{2u}}$) symmetry in the carbazole crystal (as compared to a molecularly dispersed solution). To our knowledge, this is the first work in which a theoretical calculation of the hypochromic effect in a specific molecular crystal is performed, and the corresponding experimental oscillator strength of an individual electronic transition is obtained from transmittance spectra measurements.

THEORETICAL

Local field theory [3] was employed for theoretical calculations of the oscillator strengths of individual electronic transitions of B_2 ($\mathbf{B_{2u}}$) symmetry in the carbazole crystal. The local field $\mathbf{E}^{\mathrm{i}}_{\mathrm{loc}}$ at a given molecule i in the crystal was calculated as the sum of the average field $\mathbf{E}$ and the field due to polarization of the crystal. The latter consists of two terms: one is the field due to polarized molecules in a small sphere surrounding the molecule in question, which can be calculated following Refs. 3 and 4, and the other term, $4\pi\mathbf{P}/3$, is the contribution from more distant molecules [22]:

$$\mathbf{E}^{\mathrm{i}}_{\mathrm{loc}} = \mathbf{E} + \Sigma'_j G_{ij}\mathbf{p}_j + 4\pi\frac{\mathbf{P}}{3} \qquad (1)$$

where G_{ij} is the interaction term, which depends on the geometry of the crystal, $\mathbf{p}_j$ is the transition dipole moment of molecule j, and $\mathbf{P}$ is the polarization of the crystal.

Because the transition dipoles for the B_2 ($\mathbf{B_{2u}}$) symmetry transitions in the carbazole crystal are all in the same direction (along the b axis in Fig. 1), all vector quantities in Eq. (1) can be replaced by scalars. For the same reason, the polarizabilities and oscillator strengths that appear in Eqs. (2)–(7) should be written with an index b, however, for brevity the index b is omitted. Also, the magnitudes of the local field $\mathrm{E}^{\mathrm{i}}_{\mathrm{loc}}$ and of the dipole moments p_j are the same for every molecule in the crystal. Therefore $E^{\mathrm{i}}_{\mathrm{loc}} = E_{\mathrm{loc}}$, $p_j = p$, and the polarization of the crystal $P = Np$, where N is the number of dipoles (molecules) per unit volume. By using these relations, Eq. (1) becomes

$$E_{\mathrm{loc}} = E + \left(\Sigma'_j G_{ij} + 4\pi\frac{N}{3}\right)p = E + Gp, \qquad (2)$$

where $G = \Sigma'_j G_{ij} + 4\pi N/3$.

The polarizability of a molecule in the crystal $\alpha(\omega)$ and that of an isolated molecule $\alpha^0(\omega)$ are defined by

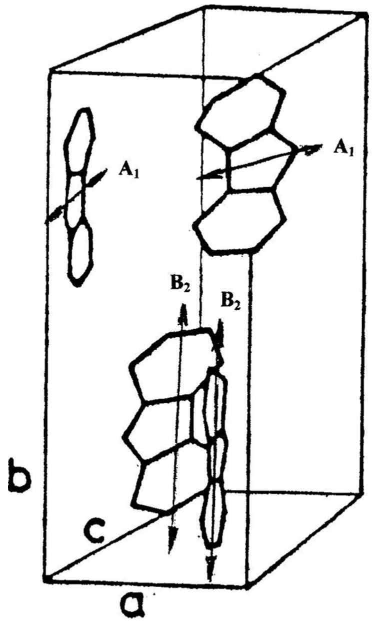

FIGURE 1 Unit cell of the carbazole crystal [23–25].

$$\mathbf{p}(\omega) = \alpha^0(\omega)\mathbf{E}_{\text{loc}} = \alpha(\omega)\mathbf{E} \tag{3}$$

From Eqs. (2) and (3), one finds

$$\frac{1}{\alpha(\omega)} = \frac{1}{\alpha^0(\omega)} - G. \tag{4}$$

The polarizabilities $\alpha^0(\omega)$ and $\alpha(\omega)$ are related to the oscillator strengths f_n^0 and f_n and the frequencies ω_n^0 and ω_n of the individual electronic transitions in an isolated molecule and in a molecule in the crystal. Respectively, they are

$$\alpha^0(\omega) = -\left(\frac{e^2}{m}\right)\Sigma_n \frac{f_n^0}{\omega^2 - (\omega_n^0)^2} \tag{5}$$

$$\alpha(\omega) = -\left(\frac{e^2}{m}\right)\Sigma_n \frac{f_n}{\omega^2 - \omega_n^2} \tag{6}$$

where the summation is over all transitions of a given symmetry.

By substituting Eqs. (5) and (6) into Eq. (4) and introducing dimensionless variables $x = (\omega/\omega_r)^2$, $x_n = (\omega_n/\omega_r)^2$, and $x_n^0 = (\omega_n^0/\omega_r)^2$, where ω_r is an arbitrary reference frequency, we find

$$\left[\Sigma_n \frac{f_n}{(\omega^2 - \omega_n^2)}\right] = \left[\Sigma_n \frac{f_n^0}{(x - x_n^0)}\right] + A = U(x), \tag{7}$$

where $A = Ge^2/m\omega_r^2$.

We use known molecular transition frequencies $\omega_n{}^0$ and oscillator strengths f_n^0 (*e.g.*, [26]). Then the transition frequencies in the crystal are determined from $x_n = (\omega_n/\omega_r)^2$ of the equation $U(x_n) = 0$, and the oscillator strengths are given by $f_n = \lim[dU/dx]^{-1}$ when $x \to x_n$.

Five molecular states of B_2 ($\mathbf{B_{2u}}$) symmetry with total oscillator strength $\sum_{n=1}^{5} f_n = 7.1$ were included in the calculations. The calculated oscillator strengths and wavelengths of individual electronic transitions in the carbazole crystal are presented in Table 1 (along with experimental values for the two low-energy transitions of B_2 ($\mathbf{B_{2u}}$) symmetry). As seen in the table, theory predicts a strong hypochromic effect for the two low-energy transitions of this symmetry in the carbazole crystal and a hyperchromic effect for the fourth and fifth transition. The total oscillator strength of the five molecular transitions used for theoretical calculations of the crystal oscillator strengths is 7.1, and the calculated sum of oscillator strengths of the corresponding five transitions in the crystal is 7.1, in agreement with the oscillator strength sum rule.

TABLE 1 Results of Theoretical Calculations of Wavelengths ($\boldsymbol{\lambda_n}$) and Oscillator Strengths ($\mathbf{f_n}$) in the Electronic Transitions of B_2 ($\mathbf{B_{2u}}$) Symmetry in the Carbazole Crystal and of Experimentally Determined Wavelengths and Oscillator Strengths of the Two Low-Energy Transitions of the Same Symmetry

Transitions of B_2 ($\mathbf{B_{2u}}$) symmetry, n	Molecule (experimental)		Crystal					
			Theoretical			Experimental		
	λ_n^0nm	$\mathbf{f_n^0}$	$\lambda_n$nm	$\mathbf{f_n}$	$\mathbf{f_n/f_n^0}$	$\lambda_n$nm	$\mathbf{f_n}$	$\mathbf{f_n/f_n^0}$
1	290	0.5	286	0.12	0.23	298	0.11	0.22
2	255	0.4	253	0.08	0.20	288	0.09	0.22
3	238	1.5	213	1.46	0.97			
4	168	0.7	165	1.09	1.56			
5	87	4.0	73	4.36	1.10			

RESULTS AND DISCUSSION

Crystal Structure

Carbazole forms orthorombic crystals with four molecules per unit cell, space group D_{2h}^{16}. The optical axes of the crystal coincide in direction with its crystallographic axes; thus the interpretation of spectroscopic data is greatly simplified. The carbazole molecule has C_{2v} symmetry. The long axis of the molecule lies parallel to the long (*b*) crystallographic direction of the crystal; the short molecular axis forms an angle of around 60° with the short (*a*) crystallographic axis [23–25] (Fig. 1). The molecular B_2 symmetry transition dipoles of the four translationally nonequivalent molecules are parallel to the b-axis in the crystal (and to each other), resulting in only one crystalline state: $\mathbf{B_{2u}}$. The molecular transition dipoles of A_1 symmetry transitions lie in the *ac* plane of the crystal and give rise to $\mathbf{B_{1u}}$ and $\mathbf{B_{3u}}$ transitions (Fig. 1). Based on the mutual orientation of molecular transition dipoles of the latter symmetry (neither parallel nor collinear), substantial intensity effects are not predicted by theory for the respective transitions. The hypochromic effect predicted by theoretical calculations for the lower B_2 ($\mathbf{B_{2u}}$) symmetry transition (discussed previously in the Theoretical section) can be envisioned qualitatively from the features of the crystalline structure of carbazole. As seen in Figure 1, the molecules in the carbazole crystal form parallel layers. The distance between the molecules within the layer is around 4 Å, whereas the distance between the layers is around 10 Å. Therefore the interactions between the B_2 ($\mathbf{B_{2u}}$) symmetry transition dipoles, which are parallel within a layer, are much stronger than interaction between the dipoles in adjacent layers; thus the hypochromic effect is expected to prevail.

Investigation of carbazole crystals thin enough for transmittance spectra measurements ($\sim 0.1\,\mu$) on a universal stage showed that the well-developed face contained the short and intermediate axes of the index ellipsoid (*ac* face). Therefore, only electronic and vibronic bands corresponding to transitions of A_1 ($\mathbf{B_{1u}}$, $\mathbf{B_{3u}}$) symmetry appear in the polarized transmittance spectra measured at normal incidence of light on the monocrystalline sample. To obtain information on oscillator strength of transitions of B_2 ($\mathbf{B_{2u}}$) symmetry, we measured the transmittance spectrum of the sample at oblique incidence of light on the *ac* face of the crystal. First, the crystal transmittance spectra were measured at normal incidence of light on the sample with the electric field vector **E** parallel to the *a* and then to the *c* crystallographic directions. As mentioned before, the resulting spectrum contained only transitions of A_1 ($\mathbf{B_{1u}}$, $\mathbf{B_{3u}}$) symmetry, allowing unmistakable symmetry assignment of these transitions in the crystal. Consequently, by rotating the sample 60° around the *a* crystallographic axis, the electric field vector could be directed at an angle of 30° to the long crystallographic direction of the crystal, which is also the direction of the transition dipoles of the B_2 ($\mathbf{B_{2u}}$) symmetry transitions. The transmittance spectrum thus obtained should reveal all transitions of B_2 ($\mathbf{B_{2u}}$) symmetry in the spectral region studied (340–220 nm), along with transitions of A_1 ($\mathbf{B_{1u}}$, $\mathbf{B_{3u}}$) symmetry.

Assignment of Electronic Transitions

The experimental electronic transmittance spectra of a thin carbazole crystal are shown in Figure 2. The *a*- and *c*-components of the transmittance spectrum at normal incidence of light on the *ac* face of the crystal are denoted II and III respectively and at oblique incidence on the same face are denoted IV. The solution spectrum of carbazole is denoted I. For qualitative comparison, the transmittance spectra of an isotropic microcrystalline sample of carbazole in the n-nonane matrix at 77 K, and that of isotropic carbazole powder in KBr at room temperature are presented in Figure 2 (V and VI respectively).

Three molecular electronic transitions of A_1 symmetry are seen in the near UV spectrum of the carbazole molecule at around 330, 245, and 210 nm (Fig. 2-I). In the crystal transmittance spectra at normal incidence of light on the sample (Fig. 2-II and III), transitions of A_1 ($\mathbf{B_{1u}}$, $\mathbf{B_{3u}}$) symmetry are detected at around 340 and 250 nm, and the two

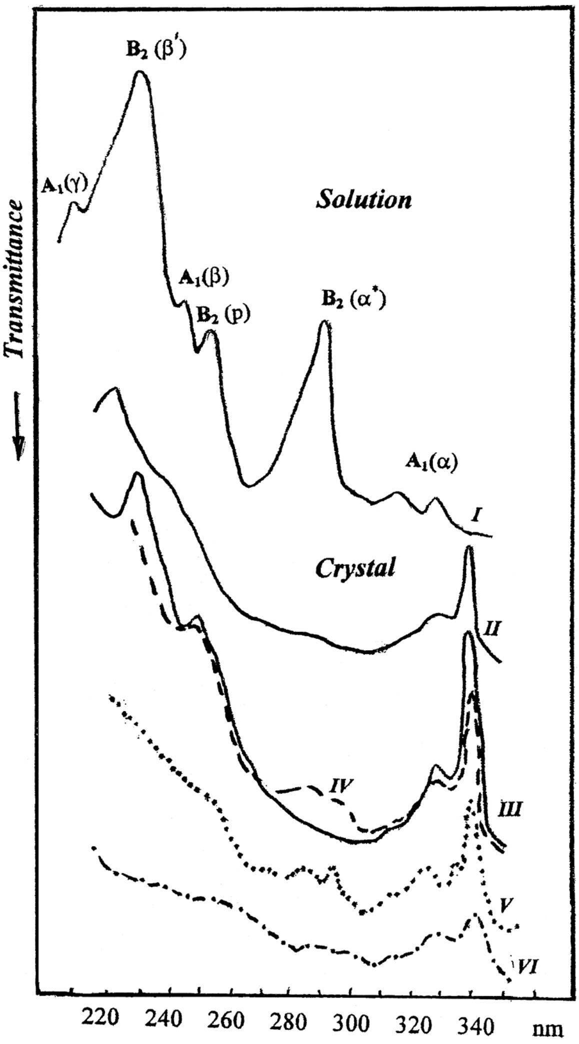

FIGURE 2 Transmittance spectra of carbazole: **I**, solution in ethanol; **II, III, IV**, *ac* face of a monocrystalline sample (thickness 0.13 μ); **II**, $(\mathbf{E},{}^\wedge a) = 0$; **III**, $(\mathbf{E},{}^\wedge c) = 0$; **IV**, $(\mathbf{E},{}^\wedge b) = 30^\circ$; **V**, isotropic microcrystalline sample (in fast frozen nonane); and **VI**, carbazole powder in KBr.

factor-group components corresponding to the third molecular transition of this symmetry (210 nm in the molecular spectrum) are at 225 nm and 230 nm. These results are in good agreement with those obtained by M. Tanaka [26] from reflectance spectra of a bulk carbazole crystal.

In the same spectral region (340–220 nm), three molecular electronic transitions of B_2 symmetry at 290, 255, and 238 nm are seen (Fig. 2-I). In the corresponding crystal transmittance spectrum, obtained at oblique incidence of light on the *ac* plane of the crystal, in addition to the transitions of A_1 ($\mathbf{B_{3u}}$, $\mathbf{B_{1u}}$) symmetry, a new weak band with two maxima at 298 nm and at 288 nm is seen (Fig. 2-IV). This band in the crystal electronic spectrum represents all transitions of B_2 ($\mathbf{B_{2u}}$) symmetry revealed in the spectral region investigated. We assign these maxima in the crystal spectrum to the first (290 nm) and second (255 nm) B_2 ($\mathbf{B_{2u}}$) symmetry molecular transitions, respectively. An alternative assignment could be that the two maxima at 298 nm and 288 nm both belong to the same electronic transition in the crystal spectrum [the first B_2 ($\mathbf{B_{2u}}$) transition], in which case the second very weak B_2 ($\mathbf{B_{2u}}$) transition in the crystal (predicted oscillator strength $f = 0.08$) is hidden under the much stronger transitions of A_1 ($\mathbf{B_{3u}}$, $\mathbf{B_{1u}}$) symmetry and its position cannot be located in our crystal transmittance spectrum.

We could not detect in the crystal spectrum (in the spectral region studied) an absorption band corresponding to the third molecular B_2 transition at 238 nm ($f = 1.5$) for which substantial intensity changes are not predicted by theory (Table 1). We assume that, because of the large oscillator strength of this transition, there is a large splitting of the factor-group components in the crystal electronic spectrum (Davidov splitting). Because of the prevalence of the interactions between parallel B_2 ($\mathbf{B_{2u}}$) transition dipoles in the crystal, predominantly the high-energy factor-group (Davidov) component is allowed by symmetry in the crystal spectrum of this transition. As a result, the band in the crystal spectrum, which corresponds to the third molecular transition of B_2 ($\mathbf{B_{2u}}$) symmetry, shifts to the far UV region beyond the spectral range investigated.

Experimental Oscillator Strength

To find the wavelengths and oscillator strengths of the electronic transitions of B_2 ($\mathbf{B_{2u}}$) symmetry in the carbazole crystal, we used transmittance measurements for light incident on the *ac* face of a thin film, as described previously. Measurements were made both at an angle of incidence $\theta = 60^\circ$ and at normal incidence, $\theta = 0^\circ$. We used expressions

$$\varepsilon_{a,b} = A_{a,b} + \omega_p^2 \sum_n \frac{f_{n;a,b}}{(\omega_{n;a,b})^2 - \omega(\omega + i\gamma_{n;a,b})} \tag{8}$$

for the dielectric constants ε_a and ε_b Here $\omega = 2\pi c/\lambda$ is the variable frequency, and $f_{n;a,b}, \omega_{n;a,b}$, and $\gamma_{n;a,b}$ are the unknown oscillator strengths, resonant frequencies, and damping factors of the electronic transitions n. The frequency $\omega_p = \sqrt{4\pi Ne^2/m}$ is the plasma frequency associated with the molecular concentration $N = 4.69 \times 10^{21}\,\mathrm{cm}^{-3}$. The constants A_a and A_b were adjusted to give the known low-frequency values $\varepsilon_a = 3.06$, and $\varepsilon_b = 4.20$.

Using a procedure similar to that described in Ref. 27, we calculated the transmittance T of the film and adjusted the unknown parameters in Eq. (8) to fit the experimental log(1/T) vs. ω curves. The transmittance is

$$T = \frac{1}{4}\left|P^{(1)} - P^{(2)}\right|^2. \tag{9}$$

where

$$P^{(1,2)} = \frac{Z^{(1,2)} - \cos\theta}{Z^{(1,2)} + \cos\theta}. \tag{10}$$

Here $Z^{(1)}$ and $Z^{(2)}$ are ratios of the tangential components E_a/H_c at a film surface if the H field has even (1) or odd (2) parity about the center of the film:

$$Z^{(1)} = -\left(\frac{i\omega}{c\beta}\right)\left(1 - \frac{\sin^2\vartheta}{\varepsilon_b}\right)\tan\left(\frac{\beta t}{2}\right), \tag{11}$$

$$Z^{(2)} = \left(\frac{i\omega}{c\beta}\right)\left(1 - \frac{\sin^2\vartheta}{\varepsilon_b}\right)\cot\left(\frac{\beta t}{2}\right), \tag{12}$$

where

$$\beta = \left(\frac{\omega}{c}\right)\left[\varepsilon_a - \left(\frac{\varepsilon_a}{\varepsilon_b}\right)\sin^2\vartheta\right]^{1/2} \tag{13}$$

is the normal component of the wave vector inside the film. The results of this fitting are shown in columns 7 and 8 of Table 1, which give the wavelengths of the first two electronic transitions $n = 1{,}2$ excited by the b component of the electric field.

For the B_2 (**B_{2u}**) transitions in the carbazole crystal $f_a = f_c = 0$, thus f_b constitutes the total oscillator strength of a given transition. It follows that for discussion of intensity effects (hypo- or hyperchromy) in transitions of this symmetry f_b should be compared to 3 f_{mol}.

As mentioned before, theory predicts strong hypochromy for the first two low-energy transitions of B_2 ($\mathbf{B_{2u}}$) symmetry. Specifically, in the crystal spectrum, the predicted oscillator strengths are $f_{\alpha^*} = 0.12$ and $f_p = 0.08$, for the α^* and the p states (in Clar's notation) respectively, and in the molecule the experimental values are $3f_{\alpha^*} = 0.5$, and $3f_p = 0.4$.

Although theory predicts no substantial intensity change for the third transition, hyperchromy is predicted for the higher (fourth and fifth) transitions of B_2 ($\mathbf{B_{2u}}$) symmetry (Table 1). The latter predictions could not be verified experimentally because the corresponding transitions in the crystal are located beyond the spectral range investigated.

We have not calculated the oscillator strengths for transitions of A_1 ($\mathbf{B_{1u}}$, $\mathbf{B_{3u}}$) symmetry in the carbazole crystal. Our experimental oscillator strength of the first A_1 ($\mathbf{B_{1u}}$, $\mathbf{B_{3u}}$) transition in the carbazole crystal (340 nm) is close to that in the carbazole molecule, although a small hyperchromic effect (17%) was detected (data not shown).

The experimental absorption bands at 298 nm (α^*-state) and 288 nm (p-state) in the crystal spectrum, assigned by us to B_2 ($\mathbf{B_{2u}}$) symmetry transitions (Fig. 2-IV), have oscillator strengths $f_{\alpha^*} = 0.11$ and $f_p = 0.09$. These experimental oscillator strengths constitute only 22% of their respective molecular oscillator strengths and are very close to the theoretically predicted values (Table 1). If we accept the alternative assignment of experimentally observed B_2 ($\mathbf{B_{2u}}$) transitions in the crystal, then the oscillator strength of the first B_2 ($\mathbf{B_{2u}}$) symmetry transition in the crystal is $f_{\alpha^*} = 0.11 + 0.09 = 0.20$, and the experimental oscillator strength of this transition constitutes 40% of the corresponding molecular oscillator strength ($f = 0.5$). In either case, the hypochromic effect in these transitions appears to be the largest reported in the literature for any kind of a molecular association.

It is noteworthy that the transmittance spectra of both an isotropic polycrystalline sample of carbazole (carbazole powder in a KBr pellet) and a microcrystalline sample of carbasole in n-nonane matrix have an intensity distribution qualitatively similar to that of the spectrum of a thin carbazole monocrystal, recorded at oblique incidence of light on the *ac* plane of the sample. (Compare Figs. 2-V and 2-VI with 2-IV.)

Comparison with Literature Data

An absorption band, similar to the one we observed at only oblique incidence of light on a thin crystal in the 290-nm region, was reported by Chakravorty and Gangulu [28] in the transmittance spectrum of a thin carbazole crystal at normal incidence of light on the sample. The intensity distribution in the region of the first A_1 ($\mathbf{B_{1u}}$, $\mathbf{B_{3u}}$) transition in their spectrum substantially differs from that in our transmittance spectrum and also from that in the reflectance spectrum of Ref. 26. Unlike our spectrum, and that of Ref. 26, the intensity of the first A_1 ($\mathbf{B_{1u}}$, $\mathbf{B_{3u}}$) symmetry pure electronic transition (340 nm) in Ref. 28 is smaller then that of the vibronic bands in both Davidov components. Conceivably, the spectrum observed in Ref. 28 was recorded from a crystal whose developed face was different from the *ac* face and thus had a nonzero projection of the of the B_2 ($\mathbf{B_{2u}}$) symmetry transition dipole on the electric field vector. As a result, the B_2 ($\mathbf{B_{2u}}$) transitions appear in their spectrum of the carbazole crystal at normal incidence of light on the sample. Some of our samples produced spectra qualitatively similar to those in Ref. 28, but we have not determined their well-developed face because we could not use them for quantitative measurements, due to their inferior quality—cracks and nonuniform thickness.

Our experimental data on the position and shape of all absorption bands in the carbazole crystal spectrum corresponding to transitions of A_1 ($\mathbf{B_{1u}}$, $\mathbf{B_{3u}}$) symmetry agree with the results of Ref. 26 obtained from reflection spectra. The experimental hyperchromic effect observed in Ref. 26 in the first of these transitions is substantially larger than that observed by us.

Our theoretical predictions and experimental data on intensities (oscillator strengths) of the first two electronic transitions of B_2 ($\mathbf{B_{2u}}$) symmetry in the crystal absorption spectrum disagree with theoretical and experimental data of [26]. As possible reasons for such disagreement, we notice that similar discrepancies between absorption intensities obtained from transmission spectra measurements of a thin crystal, and from reflection spectra measurements of a bulk crystal, were reported for a dietyl-cyanine iodide compound [29] and the anthracene crystal [30]. Substantial differences in absorption intensities, obtained from the reflectance spectra of the same sample, were reported when using different software for the Kramers–Kronig transformation [31].

Hypochromism in Poly(N-vinylcarbazole)

Comparison between the hypochomic effect in the carbazole crystal with that in poly (N-vinylcarbazole) can only be made qualitatively because we do not know of theoretical calculations of intensity redistribution in the electronic spectrum of poly(N-vinylcarbazole). Qualitatively the predictions of the hypochromy theory hold for both systems. While in poly(N-vinylcarbazole) (PVK), both the short- and the long-axis polarized transitions exhibit the hypochromic effect in the carbazole crystal this effect is observed only in the long-axis polarized B_2 ($\mathbf{B_{2u}}$) symmetry transitions. This difference is a result of different arrangement of molecules in each of these molecular associations. Theory [1–5,7] predicts the hypochromic effect for lowest-energy transitions if the monomer transition dipoles are parallel in the molecular association. In PVK, the carbazole pendants "lie close to and parallel to one another" [31]. Consequently, the transition dipoles are nearly parallel for both A_1 and B_2 symmetry transitions, resulting in hypochromism for low-energy bands corresponding to transitions of both symmetries. In the carbazole crystal, only the transition dipoles of the B_2 ($\mathbf{B_{2u}}$) symmetry transitions are parallel, leading to hypochromism in the low energy bands of the corresponding transitions. The transition dipoles of the A_1 ($\mathbf{B_{1u}}$, $\mathbf{B_{3u}}$) transitions are at an angle of $\sim 120^\circ$ to each other, resulting in a small hyperchromism in the lowest-energy transition of this symmetry.

Another difference between the two types of molecular associations is the magnitude of the effect. While in PVK, 60% of molecular oscillator strength is retained in the polymer; in the carbazole crystal, it is only around 20% (40% in the alternative assignment). This difference can be qualitatively explained as due to different intermolecular distances between the carbazole monomers—around 4 Å in the carbazole crystal and around 6 Å in poly(N-vinylcarbazole).

EXPERIMENTAL

Carbazole purified by solvent extraction, zone melting, and sublimation was kindly donated by Dr. McGhie from the Laboratory of Materials Research of the University of Pennsylvania. A Cary-14 spectrophotometer equipped with polarizers and a rotating sample holder was employed for transmission spectra measurements. The thickness of crystals was determined from the known birefringence of the crystal by employing a Bereck compensator fitted to a Leitz polarizing microscope. To prepare a microcrystalline sample, a 10^{-3} M solution of carbazole in n-nonane was fast-frozen at 77 K. The thickness of samples was around 1 mm. Because of very limited solubility of the components in the solid state, phase separation takes place even at this low concentration, and microcrystals of carbazole are formed in the n-nonane matrix. To check for the possibility of preferential orientation of the carbazole microcrystals, sections were cut out from the frozen sample in three mutually perpendicular directions. The spectra of all these sections were identical (data not shown).

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