(16) R. L. Hilderbrandt and J. D. Wieser, *J. Mol. Struct.*, **22**, 247 (1974).
(17) R. G. Rawson and I. T. Harrison, *J. Org. Chem.*, **35**, 2057 (1970).
(18) V. S. Mastryukov, O. V. Dorofeeva, L. V. Vilkov, and A. V. Golubinskii, *J. Mol. Struct.*, **32**, 161 (1976).
(19) K. Kimura and M. Kubo, *J. Chem. Phys.*, **32**, 1776 (1960).
(20) K. Tamagawa, T. Iijima, and M. Kimura, *J. Mol. Struct.*, **30**, 243 (1976).
(21) J. H. Schachtschneider and R. G. Snyder, *Spectrochim. Acta*, **19**, 117 (1963).
(22) O. Bastiansen, F. N. Fritsch, and K. Hedberg, *Acta Crystallogr.*, **17**, 538 (1964).
(23) R. C. Lord and T. B. Malloy, Jr., *J. Mol. Spectrosc.*, **46**, 358 (1973).
(24) J. D. Lewis, J. Laane, and T. B. Malloy, Jr., *J. Chem. Phys.*, **61**, 2342 (1974).
(25) W. C. Hamilton, "Statistics in Physical Science", Ronald Press, New York, N.Y., 1964.
(26) R. L. Hilderbrandt and J. D. Wieser, *J. Mol. Struct.*, **15**, 27 (1973).
(27) R. K. Bohn and Y. H. Gai, *J. Am. Chem. Soc.*, **92**, 6447 (1970).
(28) J. F. Chiang, *J. Am. Chem. Soc.*, **93**, 5044 (1971).
(29) C. S. Wang and M. D. Harmony, *J. Am. Chem. Soc.*, **98**, 1108 (1976).
(30) B. Andersen and R. Srinivasan, *Acta Chem. Scand.*, **26**, 3468.
(31) R. D. Suenram and M. D. Harmony, *J. Am. Chem. Soc.*, **95**, 4506 (1973).
(32) R. Karl and S. H. Bauer, *J. Mol. Struct.*, **25**, 1 (1975).
(33) R. K. Bohn, K. Mizuno, and K. Kuchitsu, *Bull. Chem. Soc. Jpn.*, **46**, 1395 (1973).
(34) (a) S. Chang, D. McNally, S. Sharg-Tehrany, M. J. Hickey, and R. H. Boyd, *J. Am. Chem. Soc.*, **92**, 3109 (1970); (b) P. v. R. Schleyer, J. E. Williams, and R. R. Blanchard, *ibid.*, **92**, 2377 (1970).
(35) M. I. Davis and T. W. Muecke, *J. Phys. Chem.*, **74**, 1104 (1970).
(36) A. Yokozeki and K. Kuchitsu, *Bull. Chem. Soc. Jpn.*, **44**, 2356 (1971).
(37) A. Yokozeki, K. Kuchitsu, and Y. Morino, *Bull. Chem. Soc. Jpn.*, **43**, 2017 (1970).
(38) L. Van Den Enden, H. J. Geise, H. P. Figeys, P. Geerlings, and C. Van Alsenoy, *J. Mol. Struct.*, **33**, 69 (1976).
(39) R. R. Karl, Y. C. Wang, and S. H. Bauer, *J. Mol. Struct.*, **25**, 17 (1975).
(40) K. Mizuno, T. Fukuyama, and K. Kuchitsu, *Chem. Lett.*, 249 (1972).
(41) K. Hagen and M. Traetteberg, *Acta Chem. Scand.*, **26**, 3636 (1972).
(42) V. A. Naumov and V. M. Bezzubov, *Dokl. Akad. Nauk SSSR*, **186**, 599 (1969).
(43) B. Bak, J. J. Led, L. Nygaard, J. Rastrup-Andersen, and G. O. Sorensen, *J. Mol. Struct.*, **3**, 369 (1969).
(44) J. F. Chiang and S. H. Bauer, *J. Am. Chem. Soc.*, **91**, 1898 (1969).
(45) (a) H. Oberhammer and S. H. Bauer, *J. Am. Chem. Soc.*, **91**, 10 (1969); (b) G. Dallinga and L. H. Toneman, *J. Mol. Struct.*, **1**, 117 (1967).
(46) N. L. Allinger and J. T. Sprague, *J. Am. Chem. Soc.*, **94**, 5734 (1972).
(47) D. J. Mjoberg, W. M. Ralowski, S. O. Ljunggren, and J. E. Backvall, *J. Mol. Spectrosc.*, **60**, 179 (1976).
(48) G. Dallinga and L. H. Toneman, *Recl. Trav. Chim. Pays-Bas*, **88**, 185 (1969).
(49) W. J. Lafferty, *J. Mol. Spectrosc.*, **36**, 84 (1970).

Application of Linear Dichroism to the Analysis of Electronic Absorption Spectra of Biphenyl, Fluorene, 9,9′-Spirobifluorene, and [6.6]Vespirene. Interpretation of the Circular Dichroism Spectrum of [6.6]Vespirene

Jacob Sagiv,*[1a] Amnon Yogev,[1a] and Yehuda Mazur[1b]

Contribution from the Department of Isotopes and Department of Organic Chemistry, The Weizmann Institute of Science, Rehovot, Israel.

Received February 23, 1976

Abstract: The electronic absorption spectra of biphenyl and three of its derivatives, fluorene, 9,9′-spirobifluorene, and [6.6]-vespirene, are separated into bands of different polarizations by the technique of linear dichroism in stretched polyethylene films. A semiempirical analysis of the polarization resolved spectra leads to a reassignment of part of the observed transitions. The circular dichroism of [6.6]vespirene is interpreted in terms of a dipole-dipole interaction mechanism based on the present polarization data.

The chiral derivatives of 9,9′-spirobifluorene synthesized by Prelog and Haas are interesting model compounds for the study of optical activity.[2a] Comprehensive circular dichroic studies of some vespirenes (see Figures 13 and 14) and other related chiral compounds have been carried out in order to elucidate the mechanism of optical rotation in this type of molecules and to determine their absolute configurations from chiroptical properties.[2a,b] Both the PPP-CI method[2b] and the exciton model[2a] led to results which could not account for the longest-wavelength band observed in the vespirene CD spectrum, and spiroconjugation was invoked as an additional important mechanism of interaction in the distorted spirobifluorene system. Since the exciton-type interaction implies a well defined relationship between the direction of polarization of a certain transition and the sign of its Cotton effect,[2a] an experimental determination of these polarization directions could, eventually, help to elucidate the question of how important are the contributions of other interaction mechanisms to the optical activity of chiral spirobifluorene compounds.

The present work deals with the application of linear dichroism (LD) of molecules oriented in stretched polyethylene films to this problem. Our treatment comprises four compounds, representing successive stages in the evolution of the basic biphenyl chromophoric system. It is noteworthy that much previous work, mostly theoretical, has already been published about biphenyl and fluorene. However, our experimental results show that part of the absorption bands observed in the spectra of these compounds were not given correct assignments. Employing the LD data as a basis for a semiempirical spectral analysis, a thorough understanding of the properties of chromophoric systems is achieved.

Results and Discussion

1. Biphenyl. Molecular Orientation in the Stretched Film. The linear dichroic spectrum of biphenyl and its calculated dichroic ratio,[3] $d_0 = \mathrm{OD}_\parallel/\mathrm{OD}_\perp$, as a function of wavelength are shown in Figure 1. The separation of this spectrum into bands of different polarizations relative to molecular coordinates necessitates the previous knowledge of the orientation of biphenyl molecules in the film.

Elongated, rod-like molecules exhibit a uniaxial orientation, being uniformly distributed in respect to the rotation about their longitudinal molecular axes. These axes have preferred orientation parallel to the stretching direction of the film.[4] A molecular distribution of this type may be described by a single orientational parameter, f, which is related both to the dichroic ratio, d_0, and to the polarization direction of the electronic

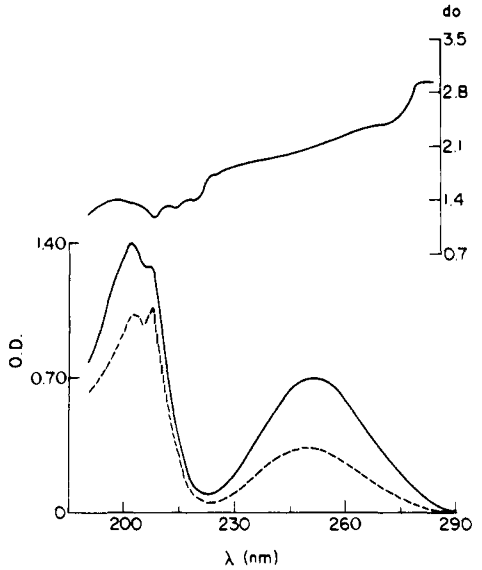

Figure 1. LD spectrum of biphenyl: lower part, (—) the curve of optical density obtained with light polarized in the direction of stretching; (- - -) the curve obtained with light polarized perpendicular to the direction of stretching; upper part, the plot of the dichroic ratio, d_0 vs. λ.

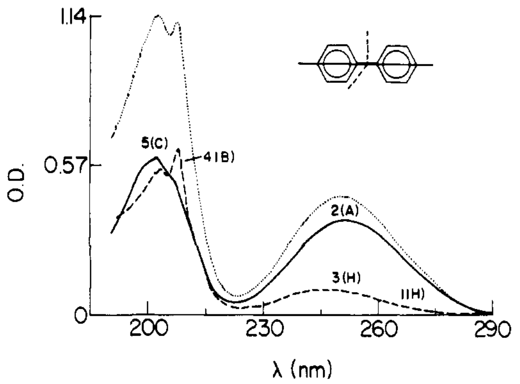

Figure 2. Isotropic spectrum and resolved spectrum of biphenyl: (···) the UV isotropic spectrum in the stretched film;[8] (—) the component polarized parallel to the axis of orientation (longitudinal); (- - -) the component polarized perpendicular to the axis of orientation (transversal).

transition, expressed by eq 1[4,5]

$$d_0 = \frac{\mathrm{OD}_{\parallel}}{\mathrm{OD}_{\perp}} = \frac{f\cos^2\alpha + \dfrac{1-f}{3}}{\dfrac{1}{2}f\sin^2\alpha + \dfrac{1-f}{3}} \qquad (1)$$

where d_0 is the dichroic ratio, f is the orientational parameter, and α is the angle between the transition moment vector and the longitudinal axis of orientation.

Biphenyl in solution has its benzene rings tilted around the central C–C bond with a twist angle, γ (Figure 3), between 20 and 40°, the intermediate value of 30° corresponding to a shallow minimum of the torsional potential.[6,7] Twisted biphenyl is obviously an elongated, rod-like molecule for which eq 1 is applicable, its longitudinal axis being the unique molecular direction of orientation in the polyethylene film. According to symmetry selection rules, in twisted biphenyl (symmetry point group D_2), only transitions polarized parallel or perpendicular to the long axis of the molecule are permitted. Since in the former transitions, the angle α equals 0°, their d_0 value is the highest, whereas in the latter transitions α equals 90° and their d_0 value is the lowest. The values of d_0 between these extremes are indicative of overlapping transitions, polarized in orthogonal directions. The upper curve in Figure 1 (d_0 vs. λ) shows that d_0 reaches a maximal and constant value of $d_0 = 2.9$ in the spectral range of 275–290 nm. Thus, at these wavelengths a pure transition may be assumed whose direction is parallel to that of the long axis of biphenyl. (α in eq 1 equals 0°.) Substitution of $d_0 = 2.9$ and $\alpha = 0$ into eq 1 results in $f = 0.38$. Using this value of the orientational parameter, we have calculated the corresponding angles α for each of the d_0 values obtained from the linear dichroic spectrum, also by means of eq 1. Bands representing pure transitions polarized parallel and perpendicular to the long axis of biphenyl result in $\alpha = 0°$ and 90°, respectively. Other values of α are due to bands of overlapped orthogonal transitions, their relative intensities being given by $\cos^2\alpha$ and $\sin^2\alpha$, respectively. The resolution of the UV spectrum into its long and short-axis polarized components is done by multiplying the OD values of the isotropic spectrum (in stretched film) by $\cos^2\alpha$ and $\sin^2\alpha$, respectively.[8]

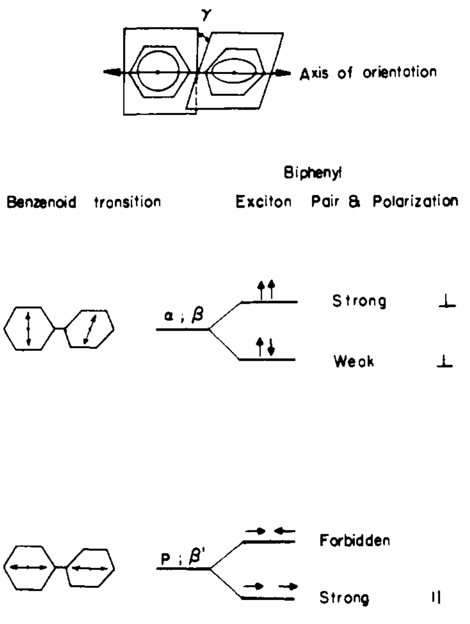

Figure 3. Biphenyl: molecular geometry and preferred orientation; schematic representation of exciton interactions in twisted biphenyl. The polarizations of resulting transitions are relative to the molecular axis of orientation.

Analysis of the Resolved Spectrum of Biphenyl. The absorption spectrum of biphenyl resolved into orthogonal polarizations, obtained from the LD spectrum using the above described resolution method, is shown in Figure 2.

Four distinct band systems, A, B, C, and H (notations used by Suzuki)[6] are observed in this spectrum: H-band, $\lambda_{\max}$ ~269 nm, short-axis polarized, (no. 1);[9] $\lambda_{\max}$ 252 nm, long-axis polarized, (no. 2); B-band, $\lambda_{\max}$ 208 nm, short-axis polarized, (no. 4); C-band, $\lambda_{\max}$ 202 nm, long-axis polarized, (no. 5). The H-band system (hidden band) consists of two overlapping components, the stronger one with maximum at 248 nm, and the weaker one appearing as an inflection at ca. 269 nm.

We have compared in the scheme in Figure 4 the experimental polarization and energies of the biphenyl transitions determined by our method with those previously reported, which all but for one, of Edwards and Simpson, are based on calculations only. The transitions in this scheme are denoted by α, p, β, and β′ (Clar)[10] and correspond to the ^1L_b, ^1L_a, ^1B_b, and ^1B_a benzenoid transitions in Platt's notation.[12] The results of Edwards and Simpson,[13] based on polarized emission measurements, agree with ours on the polarizations and locations of bands A, B, and C, but not on the location of the strong H-band component and on the polarization of its weak component. However, in view of the new results on emission from two close lying excited states we think that the latter assignments should be reinterpreted.[14] Platt's semiempirical correlation of benzenoid transitions[12] as well as Warshel's QCFF/PI method[11] lead to generally correct descriptions of biphenyl spectrum. However, in both treatments, the weak long wavelength component of the H band is not accounted for.[11] The other theoretical treatments lead to predictions which are incompatible, or only partly in agreement with the present experimental data. Finally, we have to mention that the hidden bands revealed in the spectra of solidified melts of biphenyl (Dale[6]) and in the solution spectra of sterically hindered biphenyls (Mislow, Hyden, Schaefer and Everitt, Hall, Turner[6]) seem to be only the weak low energy components of the respective H bands, while the strong ones, still underlying the A bands at a higher energy, could not be detected.

Being unable to correlate all of our experimental results on biphenyl transitions with any of the previous assignments, which also differ from each other, we have attempted to rationalize them using a semiempirical simple qualitative version of the "composite molecule" method. We have used the same procedure also for the rationalization of the polarized spectra of the other compounds, derived from biphenyl. According to this method the electronic states of biphenyl, which is regarded as a composite molecule, arise from the interaction between the electronic states of two perturbed phenyl units. The Coulomb interaction between the transition densities localized on each of the molecular fragments is approximated by a dipole–dipole interaction term. The advantage of this treatment lies in the fact that the theoretical spectrum of a molecule can be directly obtained from the experimental polarized resolved spectra of molecular fragments composing this molecule, and thus can be directly compared with the experimental polarized resolved spectrum of the same composite molecule obtained from LD measurements. The first step in this method involves, in the case of biphenyl, assignment of the transition moment vectors to the substituted benzene fragments and constructing of an exciton scheme as done previously by Edwards and Simpson.[13] The second step involves correlation of the spectral bands in the experimental resolved spectrum with transitions derived theoretically from the exciton scheme. Charge transfer contributions are not accounted for by this approach which does not lead to any change in the predicted directions of polarization, and does not affect the orders of magnitude of the predicted intensities. Thus when aiming at a simple qualitative rationalization of experimental observations, with a particular emphasis on polarization it is sufficient to consider only the exciton-type interactions. However, in a quantitative theoretical treatment charge transfer contributions must not be neglected.

Since there are differences between the previous[13] results and ours, we shall discuss them in the following. In the molecule of biphenyl each benzene moiety is monosubstituted by a phenyl group.

According to Sklar and Platt,[17] a substituent induces transition moments perpendicular to its direction for the α band (B_{2u} symmetry) and parallel for the p-band (B_{1u} symmetry).[18] In general, the weak α-band is much more affected than the more intense p-band. The effect of a substituent on the intensity of the very strong, allowed β-band (E_{1u} symmetry) is minimal. On the other hand, the substitution removes the degeneracy, resulting in two orthogonally polarized transitions of different energies.

The H system of biphenyl (Figure 2) is attributed to the exciton pair originating in the α-benzenoid transition (Figure 3). The lower energy member (band no. 1) is weak (forbidden in planar biphenyl), while the higher-energy member (band no. 3) is allowed and thus moderately intense. Both transitions (no. 1 and 3) are polarized perpendicularly to the longitudinal axis of the molecule (Figures 2 and 3). Our measurements confirm the previous assignment[6,12,13] of band A (no. 2) to the low-energy p-exciton member, involving the in-phase excitation of the p states of the two phenyl fragments. The higher-energy member, representing the out-of-phase excitation, is forbidden (Figure 3). The interaction patterns for β' and β benzenoid transitions are similar to those of the p and α-bands, respectively (Figure 3). Band C of biphenyl (no. 5) corresponds to the allowed member of the β' exciton pair, while band B (no. 4) probably contains both members of the β-exciton pair (Figure 2). According to Edwards and Simpson,[13] band B represents only the weak low-energy member of the β exciton pair. However, its high intensity, which is similar to that of the strong C-band (Figure 2), and particularly the polarization of the corresponding band in fluorene (see the analysis of fluorene spectrum) strongly support the present assignment.

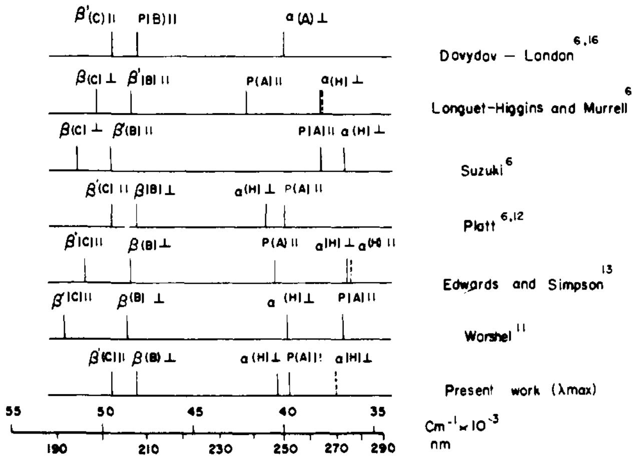

Figure 4. The location of biphenyl's transitions in the 180-300-nm region as given by various authors: (—) intense transitions; (- - -) the weak member of H band. The polarizations are relative to the longitudinal axis of biphenyl.

2. Fluorene. Molecular Orientation in the Stretched Film. Fluorene is, according to the x-ray single crystal determination,[19] a planar molecule. Its two phenyl rings are bent in respect to each other, forming an angle of 12° between the longitudinal molecular axis and the directions passing along the phenyl rings (Figure 6). The fluorene molecule belongs to C_{2V} symmetry point group and its π–π^* transitions are polarized in the molecular plane along either its C_2-symmetry axis or perpendicular to it.

The linear dichroic spectrum of fluorene in the stretched film and its dichroic ratios as a function of the wavelength are shown in Figure 5. In the long wavelength part of this spectrum, between 240 and 310 nm, the dichroic ratio has an almost constant value with a maximum of $d_0 = 2.7$ which is the highest value in the entire spectrum. This behavior indicates that the transitions in this spectral region are polarized along the direction of long axis of the molecule, which is preferentially oriented parallel to the direction of the film stretching. (This direction coincides with the direction perpendicular to the C_2 axis.) Substitution of $\alpha = 0°$ and $d_0^{\max} = 2.7$ into eq 1 leads to $f = 0.36$. This value is similar to the respective one of biphenyl ($f = 0.38$), indicating a similar distribution pattern of these two compounds in the stretched film. It follows that, although fluorene is a planar molecule, its orientation is determined, like that of biphenyl, only by the alignment of its longitudinal molecular axes in the direction of film stretching.[20] Using a similar procedure as described above for biphenyl, we have separated the spectrum of fluorene into orthogonal long and short axis polarizations (Figure 7).

Analysis of the Resolved Spectrum of Fluorene. We divide the spectrum fluorene into four band system A, B, C, H as described above for the spectrum of biphenyl. The A, B, and C bands in the two compounds are similar in shape, wave-

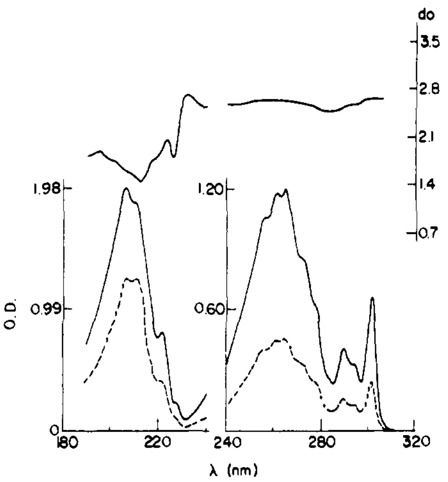

Figure 5. LD spectrum of fluorene; lower part, (—) the curve of optical density obtained with light polarized in the direction of stretching; (- - -) the curve obtained with light polarized perpendicular to the direction of stretching; upper part, the plot of the dichroic ratio, d_0 vs. λ. Note that the scales of OD are different for the long and short-λ spectral regions.

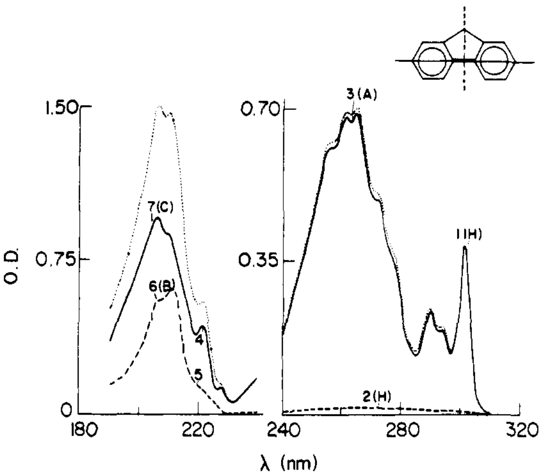

Figure 7. Isotropic spectrum and resolved spectrum of fluorene: (· · ·) the UV isotropic spectrum in the stretched film;[8] (—) the component polarized parallel to the axis of orientation (longitudinal); (- - -) the component polarized perpendicular to the axis of orientation (transversal).

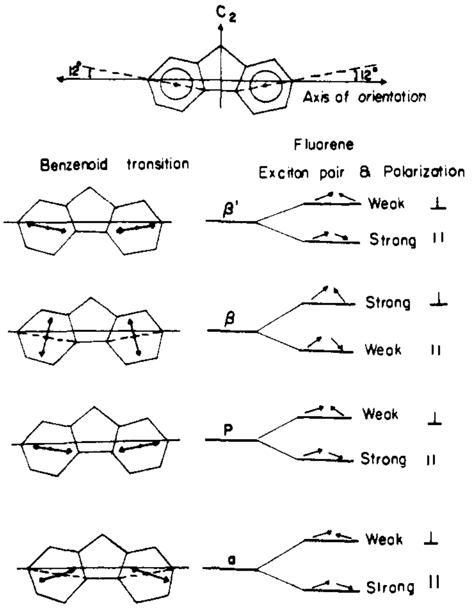

Figure 6. Fluorene: molecular geometry and preferred orientation; schematic representation of exciton interactions for the planar fluorene molecule. The polarizations of resulting transitions are relative to the molecular axis of orientation.

length, and polarization. However, the long wavelength component of the H-band in fluorene is intense, well separated from the A band and long axis polarized, contrary to that of biphenyl. The short wavelength H band component is short axis polarized, hidden under the A band as in biphenyl, but much weaker in intensity. The long axis polarizations of both H and A bands in the spectral region 240–310 nm observed by us are in accord with previous experimental results obtained from the polarized absorption and emission measurements.[21,22] On the other hand, MO calculations predicted, in analogy with biphenyl, a transversal polarization for the H transition appearing in this spectral region.[2a,23]

The striking differences between the H bands of biphenyl and fluorene indicate that different substitution patterns of the benzene fragments have a marked influence on the α-transition moments. It is thus impossible to draw a direct analogy between fluorene and biphenyl, without proper consideration of the substituent effect. On the other hand, it will be shown that by taking this effect into account even a simple qualitative exciton model leads to predictions which are in complete accord with the experimental results. For the α benzenoid transition each substituent on a benzene ring induces, according to Sklar and Platt,[17] a spectroscopic moment perpendicular to the bond axis of that substituent, of magnitude and relative phase depending on its nature. The two substituents of the benzene rings in the fluorene molecule are not identical and no experimental estimate of their relative spectroscopic moments is available. It is possible, however, to compare the results obtained by assuming plausible hypothetical values with the experimental polarizations of the bands in the resolved spectrum of fluorene. Assuming that the contributions of the two subsituents are of similar magnitude and of equal signs—and considering the bent shape of fluorene molecule—we arrive at an angle of ca. 18° between the resultant α-transition moments of each substituted phenyl fragment and the longitudinal molecular axis. Using these two moments in our exciton coupling scheme (Figure 6) we obtain a low-energy, long-axis polarized intense transition and a high-energy, short-axis polarized weak transition. This result is in good agreement with the observed bands in the resolved fluorene spectrum, while other computed resultants of the transition moments (using different relative magnitudes or signs) are incompatible with the experimental values. The former transition appears in the spectrum as the band no. 1 (H band, ∥) and the latter as the hidden weak band no. 2 (H band, ⊥). (See Figure 7.)

The polarizations of the p-transitions in fluorene are analyzed like the α-transitions. However, in this case the effect of the substituents is to induce transition moments parallel to the substitution direction. The strong long axis polarization shown by the A band indicates that the two transition moments of the benzene units are nearly parallel with the long axis of the molecule. Thus the substituent effect of the methylene bridge is much weaker than that of the directly connected benzene unit. The lesser influence of a substituent on the more intense p-transition than on the weak α-transition is a general phenomenon.[17,18] Moreover, in the case of fluorene the α-transition remains essentially a local excitation of benzenoid type, while the p-transition is strongly mixed with a charge resonance transition.[6] The interaction of the two dipoles in the exciton pair (Figure 6), will thus result in an intense band long-axis polarized (no. 3), the A band, and a weak band (no. 5), short axis polarized, which is visible as a shoulder on the B band (Figure 7).

As indicated above, the intense β-transitions are differently

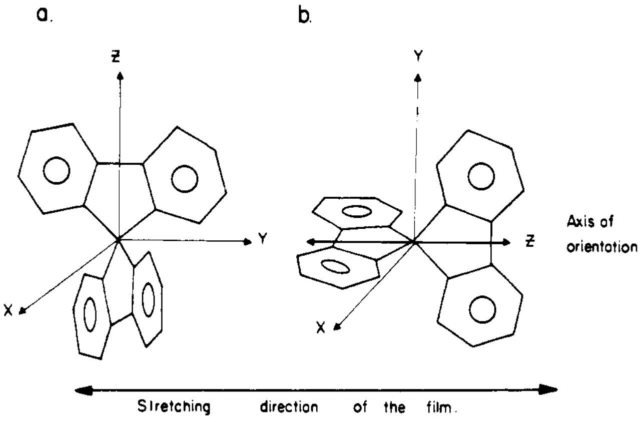

Figure 8. The orientation of 9,9′-spirobifluorene molecule in the stretched polyethylene film: (a) hindered orientation; (b) preferred orientation.

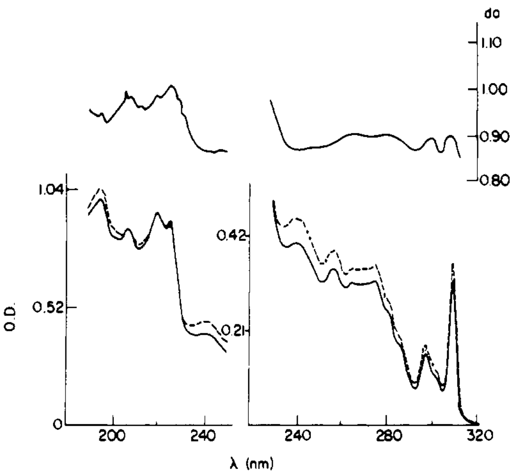

Figure 9. LD spectrum of 9,9′-spirobifluorene: lower part, (—) the curve of optical density obtained with light polarized in the direction of stretching; (- - -) the curve obtained with light polarized perpendicular to the direction of stretching; upper part, the plot of the dichroic ratio, d_0 vs. λ. Note that the scales of OD are different for the long and short-λ spectral regions.

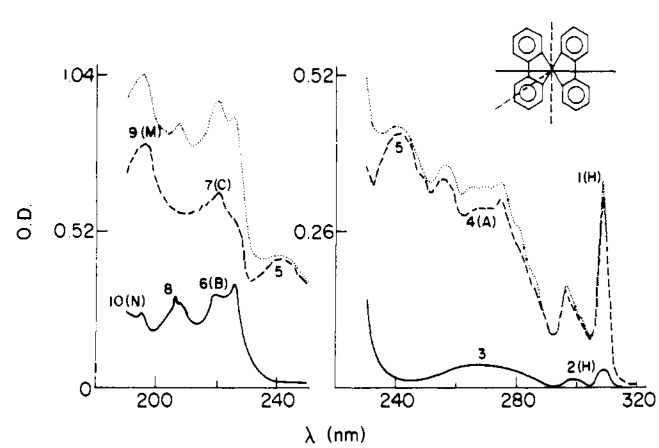

Figure 10. Isotropic spectrum and resolved spectrum of 9,9′-spirobifluorene: (···) the UV isotropic spectrum in the stretched film;[8] (—) the component polarized parallel to the axis of orientation; (- - -) the component polarized perpendicular to the axis of orientation.

influenced by substitution than the α and p-transitions. The similarity between bands B and C in fluorene and in biphenyl suggests the methylene bridge in the former compound has only a small influence on the β transitions (Figures 2 and 7). However, there is a small but significant change in the exciton coupling scheme for the two compounds caused by their different conformations (see Figures 3 and 6). From these four expected β transitions, only three are visible in the polarized resolved spectrum (Figure 7). The low energy β transition is probably the shoulder on the C band (no. 4, 11) while the high energy β transition is represented by band B (no. 6,). Band C (no. 7, 11) correlates with the low energy β′ transition. The high energy β′ member is probably in the far-UV and thus not observed in our spectrum.

The correlation between the transitions of fluorene and biphenyl is schematically represented in Figure 16. It would be interesting to note that the weak transversal β transition of biphenyl correlates with a longitudinal transition in fluorene (no. 4), while the strong β transition representing the high-energy member of the β-exciton pair is expected to be short-axis polarized in both compounds (Figures 3 and 6). The resolved spectra (Figures 2 and 7) show that band B in fluorene is short-axis polarized as in biphenyl,[24] thus confirming our assignment.[25]

3. 9,9′-Spirobifluorene (SBF). Molecular Orientation in the Stretched Film. 9,9′-Spirobifluorene (SBF) is composed of two fluorene molecules connected at the carbon atom of their methylene bridge (Figure 8). The electronic transitions of a rigid SBF molecule (symmetry point group D_{2d}) are polarized either along the C_2 axis pointing in the z direction, or are double degenerate, being polarized in the x,y directions (Figures 8, 11). Due to the orthogonal disposition of its fluorene fragments[26] and to the lack of direct conjugation of their π electronic systems, the π–π^* spectrum of SBF is expected to be, in a first approximation, the simple sum of spectra of two noninteracting fluorene molecules. Thus transitions which are long axis polarized in fluorene, should appear in SBF as pairs of degenerate transitions polarized in the x or y directions, while those which are short axis polarized in fluorene should give transitions polarized along the z direction.

The long wavelength part of SBF isotropic spectrum (Figure 10) is indeed similar to the corresponding part of the isotropic fluorene spectrum (Figure 7) and the H and A bands of the former can be easily recognized by their characteristic shapes, intensities, and positions. The 240–310-nm part of the LD spectrum of SBF (Figure 9) shows an almost constant value of its dichroic ratio, d_0, as in the corresponding part of fluorene spectrum (the A and H bands). However, the d_0 value of SBF is less than unity (~0.9) indicating the presence of pure transitions preferentially polarized in directions perpendicular to that of film stretching. Since these transitions, which correspond to the A and H bands of fluorene, are polarized in SBF along the long axes of its fluorene moieties,[27] we deduce that the SBF molecules are oriented in the film with these long axes perpendicular to the stretching direction. An orientation which fulfills this condition is depicted in Figure 8b. Both fluorene fragments are shown to have their planes parallel to the stretching direction of the film. Such a molecular distribution resembles the previously discussed planar orientation of disk-like molecules (like coronene).[4,28] However, in the case of SBF, two perpendicular planes are involved simultaneously in the orientation process. It follows that the orientation may be conveniently described in terms of the intersection line between these two planes. This line, denoted by z (Figure 8), is the unique preferred molecular direction of orientation.[29] The distribution of SBF molecules in the film should be uniform in respect to rotation about z axis, as no special preferred position of the molecule may be reached by such rotation. Equation 1 is therefore applicable also for this system, α defining now the angle between the transition moment and the z axis. It is very likely that the distribution of SBF in polyethylene is also best described by the "f" model (as in fluorene): a fraction, f, of the molecules is perfectly oriented with their planes (or the z axes) parallel to the stetching direction and

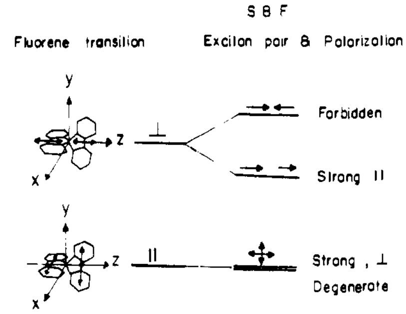

Figure 11. The schematic representation of exciton interactions in 9,9′-spirobifluorene. The polarizations of resulting transitions are relative to the molecular axis of orientation (z).

a fraction, $(1-f)$, randomly distributed.

We can determine the parameter of orientation, f, using the LD spectrum of SBF. As previously stated, the minimum value of d_0 (0.87) in this spectrum (in the 240–310-nm region) corresponds to a pure transition polarized perpendicular to the z axis of orientation. Substitution of this value and $\alpha = 90°$ into eq 1 results in $f = 0.09$. The spectrum of SBF, resolved by the previously described procedure into z and x,y polarizations, is shown in Figure 10.

Analysis of the Resolved Spectrum of SBF. Our analysis of SBF spectrum commences by considering the interaction between the two fluorene moieties. Two interaction mechanisms are operative in this molecule. The first one consists of the Coulomb interaction of localized transition densities, which may be approximated by the dipole–dipole term, leading to an exciton type scheme. The second one is the spiro-conjugation.[30] There is previous evidence from studies of polarization of fluorescence indicating that the spiro-conjugation plays only a minor role in the interaction of the two fluorene fragments in SBF.[31] Thus we correlate the spectra of fluorene and SBF using only the dipole–dipole interaction scheme. We shall also discuss the possible influence of neglecting spiroconjugation on our results. Those transitions which are long axis polarized in fluorene cannot interact (through dipole–dipole interaction) in SBF. They will lead, instead, to pairs of degenerate transitions polarized along the x and y directions which are centered at similar wavelengths as the corresponding transitions in fluorene (Figure 11). On the other hand, transitions which are short-axis polarized in fluorene are strongly interacting in SBF, since their dipole moments are collinear. The electronic excited states corresponding to these transitions should split into pairs. Transitions of the low energy member are allowed and polarized along the z direction; transitions of the high-energy member are forbidden (Figure 11). The allowed transitions should appear at the red side of the corresponding bands of fluorene.

We have numbered the bands in the resolved spectrum of SBF in the sequence of increasing energy of their $\lambda_{\max}$, and our assignment commences in the low-energy part of the spectrum (Figure 10). The correlation with the bands of fluorene is summarized in Figure 16. Comparing the resolved spectra of SBF and fluorene (Figures 7 and 10), and considering that the transitions polarized parallel to the orientational axis in the former correspond to transitions polarized perpendicular in the latter, leads to the following conclusions. In the 230–320-nm spectral regions the intense member of the H-band system is of similar shape and polarization as the corresponding band of fluorene, while the A band in SBF spectrum is slightly changed in its shape. This change is probably due to the overlap with the fairly intense band (no. 5) which in fluorene (no. 4) is much weaker and located in a shorter wavelength region. In the 190–240-nm spectral region of SBF, the bands corresponding to the B and C bands of fluorene are recognizable by their characteristic shapes and polarizations. In addition to these, three new bands have appeared in the spectrum of SBF (8, 9, and 10). These bands derive either from far-UV bands of fluorene, or have no counterpart in the spectrum of fluorene, being characteristic of SBF only. Band no. 8 may be attributed to the low energy allowed transition resulting from splitting of the high-energy transversal β' transition of fluorene, which is probably located in its far-UV. Bands no. 9 and 10 cannot be directly assigned by our semiempirical method. The notations M and N have been adopted for these two bands.

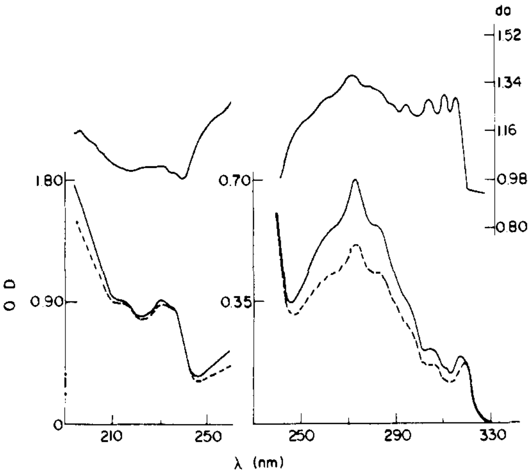

Figure 12. LD spectrum of [6.6]vespirene: lower part, (—) the curve of optical density obtained with light polarized in the direction of stretching; (- - -) the curve obtained with light polarized perpendicular to the direction of stretching; upper part, the plot of the dichroic ratio, d_0 vs. λ. Note that the scales of OD are different for the long and short-λ spectral regions.

We may conclude that the simple exciton scheme used by us gives a complete qualitative description of the gross features of SBF spectrum. This observation strongly supports the assumption, based on previous fluorescence studies,[31] that spiroconjugation is not of major importance in determining the spectral characteristics of SBF in the near-UV.

Nevertheless, by invoking the dipole–dipole interactions only, we cannot explain some of the minor spectral features of the SBF spectrum. These include the shift to the red of the degenerate x,y-polarized bands, the increase in the intensity, and the broadening of some of these bands when compared with the corresponding transitions in fluorene. It is probably that both spiroconjugations and the molecular vibrations, which destroy the strict orthogonality of the dipole moments localized on each fluorene moiety, are responsible for these spectral features.[31]

4. [6.6]Vespirene. Molecular Orientation in the Stretched Film. [6.6]Vespirene is a chiral derivative of SBF in which the two fluorene fragments are substituted by hexyl bridges. These alkyl bridges impose a distorted conformation on the molecule, causing the dihedral angle, ϕ, between the fluorene fragments in the spiro system to be smaller than 90° (Figures 1a and 14). According to symmetry selection rules, the allowed transitions of vespirene (C_2 symmetry point group) may be polarized either along its C_2 symmetry axis, or perpendicular to it. Since the degeneracy of the x,y-polarized transitions of SBF is removed in vespirene by the dipolar interaction of transition moments which are no more perpendicular to each other (Figure 14), a splitting into pairs of different polarized bands is to be expected[32] (Figure 15). The more intense components of these pairs should be polarized along the C_2 symmetry axis.

An inspection of the LD spectrum (Figure 12) shows that the dichroic ratio, d_0, is not constant in the region of bands H and A. This is an indication of different polarized transitions

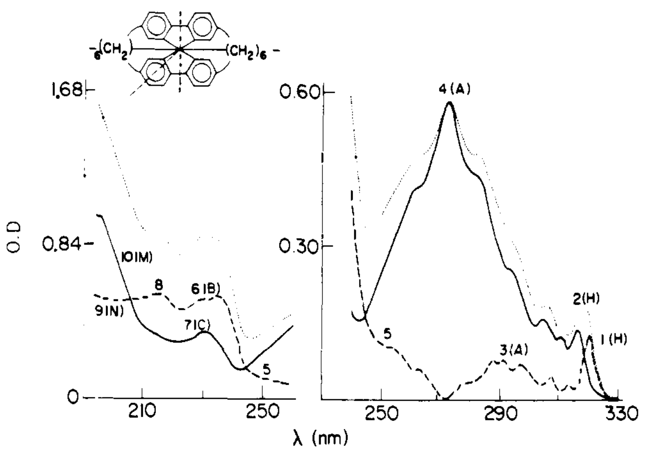

Figure 13. Isotropic spectrum and resolved spectrum of [6.6]vespirene: (· · ·) the UV isotropic spectrum in the stretched film;[8] (—) the component polarized parallel to the axis of orientation (longitudinal); (- - -) the component polarized perpendicular to the axis of orientation (transversal).

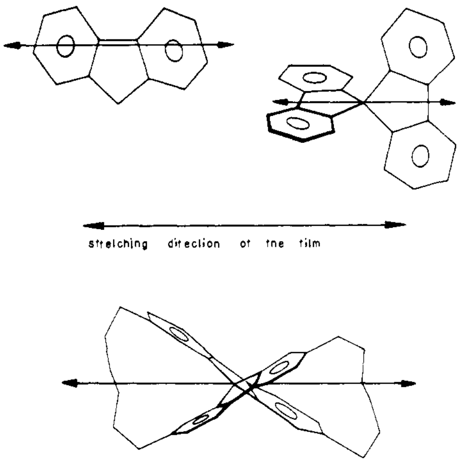

Figure 14. The preferred orientation of fluorene, SBF and vespirene in stretched polyethylene.

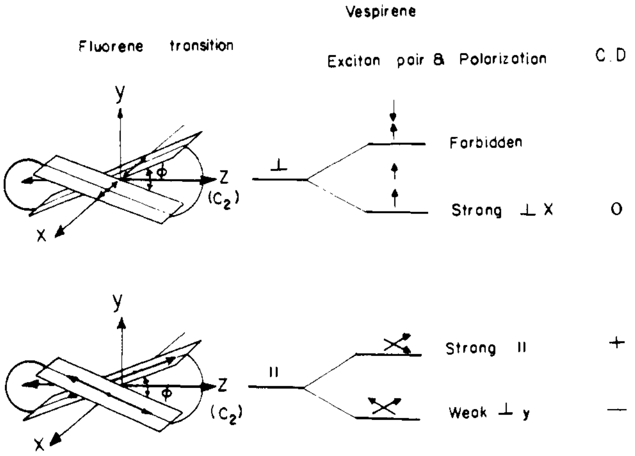

Figure 15. Schematic representation of exciton interactions in [6.6]-vespirene. The fluorene fragments are represented by two planes with a dihedral angle ϕ between them. The polarizations of resulting transitions are relative to the molecular axis of orientation, z.

which overlap with each other. The maximal d_0 value, (1.36), corresponds to maximum absorption of band A. It follows that transition moments pointing in the direction of the C_2 molecular axis are preferentially oriented parallel to the stretching direction of the film. We conclude that the C_2 symmetry axes of vespirene molecules are oriented perpendicular to the directions of orientation of the corresponding C_2 axes in SBF (Figure 14). This change in orientation is due to the alkyl bridges, causing the molecule to be elongated, while hindering the planar orientation of its fluorene fragments (Figure 14). In vespirene the C_2 symmetry axis becomes a longitudinal molecular axis of orientation. Accordingly, eq 1 may be applied to vespirene with $\alpha = 0°$ for transitions polarized along the C_2 axis, and $\alpha = 90°$ for transitions polarized perpendicular to it. The parameter of orientation, $f = 0.11$, was calculated by the substitution of $\alpha = 0°$ and $d_{0\max} = 1.36$ into eq 1. Using this f value in eq 1, the UV spectrum of vespirene was resolved into transitions polarized parallel or perpendicular to the molecular C_2 axis (Figure 13).

Analysis of the Resolved Spectrum of Vespirene. The exciton scheme of [6.6]vespirene (Figure 15) shows three types of allowed transitions originating in the longitudinal and transversal transitions of fluorene, as follows: the longitudinal fluorene transitions generate exciton pairs having weak low-energy members, polarized in the y-direction (B symmetry), and stronger high-energy members polarized along the z direction, (C_2 axis A symmetry). These pairs correspond to the degenerate x,y transitions of SBF. Allowed low energy transitions, transversally polarized in the x direction (B symmetry), and high energy forbidden transitions result from the fluorene transversal transitions, exactly in the same manner as the previously described SBF transitions of z polarization (Figure 11).

Since the molecular orientation in the polyethylene film is uniform with respect to rotation about the orientation axis (the C_2 axis, in vespirene), our LD technique does not differentiate one type of transversal transitions from another. Thus the transversal bands in the resolved spectrum may be due to combinations of both x and y types.

The assignment of vespirene spectral bands and the correlation with the spectrum of SBF are summarized in Figures 13 and 16.[33] Some of the strong transitions of vespirene retained their characteristic band shape and can therefore be assigned by a straightforward comparison with the resolved spectra of fluorene and SBF. We recognize the low-energy H band, which is now composed of two transitions polarized in orthogonal directions (no. 1 and 2), the longitudinal A band (no. 4), the transversal B band (no. 6), and the longitudinal C band (no. 7). In addition, band no. 8 may be correlated with band no. 8 of SBF and bands no. 9 and 10 with 10 and 9 of SBF, respectively. The other assignments, part of which are tentative (represented by dashed lines in Figure 16), were achieved comparing the polarization of the resolved spectra of vespirene and SBF with the predicted polarizations derived from the exciton scheme (Figure 15).

As in the case of SBF, we have obtained a good qualitative description of the vespirene spectrum using in our analysis only a dipole–dipole interaction mechanism between transition densities localized on each fluorene fragment. The validity of the present assignments is corroborated by the following analysis of the CD spectrum of vespirene.

5. Analysis of the CD Spectrum of [6.6]Vespirene. As we have mentioned above, a detailed analysis of the CD spectrum of vespirene based on the exciton model has already been performed.[2a] We present here a new interpretation of the entire CD spectrum of [6.6]vespirene in terms of Cotton effects associated with each of the transitions appearing in its resolved spectrum. The purpose of the present analysis is to show that the difficulties encountered in the interpretation of the longest-wavelength band observed in the CD spectrum are not due to the approximate nature of the exciton approach, but have to be ascribed to the previous incorrect assignment of the H band.

According to the exciton model,[2a] bands related to the lon-

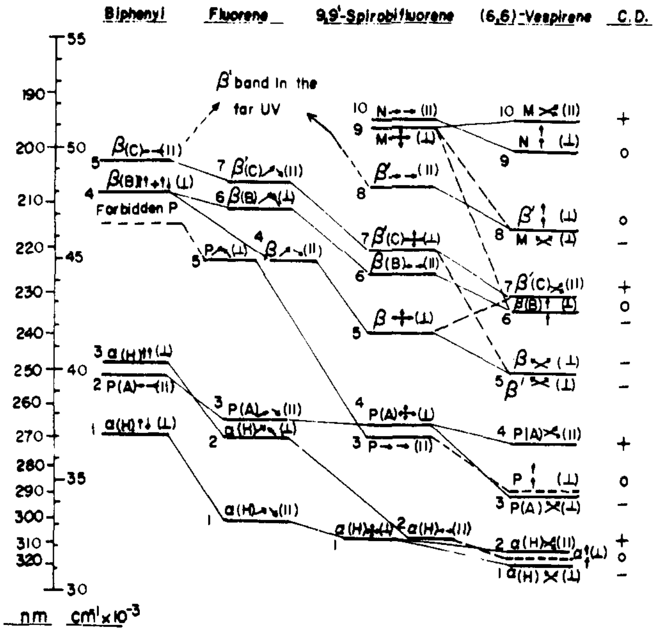

Figure 16. The correlation scheme between the spectral bands in the resolved spectra of biphenyl, fluorene, SBF and vespirene, giving the evolution of the different electronic transitions from biphenyl to vespirene: (—) the position of maximum absorption (λ_{max}); (- - -) uncertain location of λ_{max}.

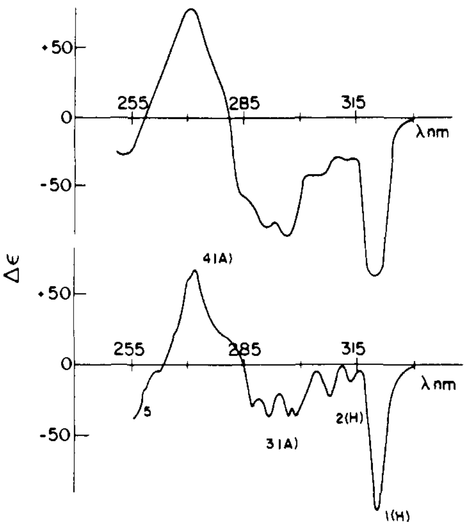

Figure 17. CD spectrum of [6.6]vespirene in the 255-330-nm spectral region: upper part, CD spectrum of vespirene in isooctane, reproduced by permission from ref 2a; lower part, CD spectrum of vespirene in stretched polyethylene film, calculated from the resolved LD spectrum. The units of the calculated spectrum are arbitrary. The two spectra were drawn at the same scale.

gitudinal fluorene transitions leading to z- and y-polarized bands should not produce optical rotation (see Figures 15 and 16). The very strong Cotton effect associated with the H band of [6.6]vespirene could not be understood on the basis of an assignment of x-polarization for this band.[2a] Our experimental results show, however, that band H is long-axis polarized in fluorene and has two components of z- and y-polarization in vespirene. It is therefore expected that two components of opposite sign will appear in the CD spectrum, as well. Since only one strong negative CD band is observed in the region of H system, we decided to perform a CD calculation to solve this problem. We have calculated a hypothetical CD spectrum for the R enantiomer of vespirene by the following procedure.

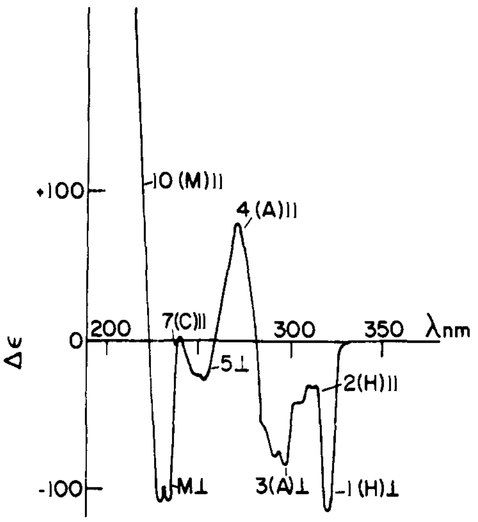

Figure 18. CD spectrum of [6.6]vespirene in the 210-330-nm spectral region, reproduced by permission from ref 2a. The notations refer to respective bands in the resolved LD spectrum (see Figures 16 and 13).

The circular dichroism of an absorption band may be conveniently characterized by an anisotropy factor, defined as $g = \Delta\epsilon/\epsilon$, where ϵ is the extinction coefficient of a racemic solution and $\Delta\epsilon$ defines the magnitude of the respective CD in one of the enantiomers.[34]

When vibronic effects are small enough to be neglected, the g factor takes on a constant value across a single pure electronic absorption band.[35] According to the exciton model, all transitions of a certain symmetry type should exhibit the same factor of anisotropy, which depends only on the dihedral angle, ϕ, between the planes of the two fluorene fragments (Figure 15). For the R enantiomer, bands of symmetry A lead to positive $\Delta\epsilon$, while bands of symmetry A lead to positive $\Delta\epsilon$, while bands of symmetry B (transversal bands of y-type) lead to negative $\Delta\epsilon$, such that

$$G = \frac{g_y{}^{\perp}}{g^{\parallel}} = -ctg^2\frac{\phi}{2} \tag{2}$$

where $g_y{}^{\perp}$ and $g^{\parallel}$ are the anisotropy factors characteristic of B-type and A-type absorption bands, respectively, and their ratio, G, is determined by the angle ϕ corresponding to the ground state equilibrium conformation of the molecule.

The CD spectrum (in arbirary units) as a function of angle ϕ may be then calculated from the resolved absorption spectrum by means of the following relation ($g^{\parallel}$ is set equal to unity)

$$\Delta\epsilon(\lambda)_{\text{arb. units}} = \epsilon(\lambda)^{\parallel} + G \cdot \epsilon(\lambda)_y{}^{\perp} \tag{3}$$

$\epsilon(\lambda)^{\parallel}$ and $\epsilon(\lambda)_y{}^{\perp}$ in eq 3 stand for the absorption curves of z and y polarizations, respectively (Figure 13).

The difficulty encountered in this calculation is that the resolved absorption curve of transversal polarization contains both y and x components which cannot be separated from one another. Due to the fact that the x-polarized traansitions are devoid of optical activity ($\Delta\epsilon = 0$), the apparent g factor characteristic of the B-symmetry bands will not be a constant but a varying function of λ. Since this function is unknown, we were unable to calculate a CD curve for the 190-260-nm spectral region which contains intense x-polarized bands overlapping with the y-polarized band. Fortunately, the transversal bands in the 260-330-nm spectral region contain only negligible contributions from two weak x-polarized transitions (see Figure 16), so that the assumption of a constant $g_y{}^{\perp}$ factor seems to be a reasonable approximation.

Performing calculations for various G's, and comparing the results with the measured CD spectrum of vespirene (in isooctane),[2a] we obtained a best fit for $G = -7.6$. The agreement of the computed with the measured CD spectrum (Figure 17) is good, although the details cannot be compared quantitatively.[36] These calculations show that the negative band at 283–305 nm and the positive band at 262–283 nm are indeed components of the A-exciton pair, but the strong negative band at 310–330 nm is only the low-energy member of the H exciton pair. The positive H member, in the 305–315-nm region, cannot be directly observed in the CD spectrum, being completely masked by its stronger neighbor bands of opposite sign.

The negative Cotton effect at $\lambda < 262$ nm corresponds to band no. 5 ($\lambda_{max} \approx 250$ nm). A tentative assignment of the observed bands in the 190–250-nm region of the CD spectrum is presented in Figure 18. Note that bands 6 (B), 8, and 9 (N) do not seem to contribute to the CD spectrum, thus confirming our predictions (Figure 16).

Summary

It was shown that the UV spectra of four biphenyl derivatives differing in their degree of complexity, as well as the CD spectrum of an optically active derivative of spirobifluorene (SBF) are best interpreted in terms of a dipole–dipole interaction mechanism. No major spectral features of SBF or vespirene may be ascribed to spiroconjugation.

Using the stretched polyethylene LD technique it was possible to follow the evolution of individual electronic transitions from biphenyl to vespirene and to analyze the influence of various geometrical transformations and electronic effects on the respective spectra. The possibility of extending the applications of this useful experimental method also to complex electronic spectra of bulky or low-symmetry molecules is demonstrated.

Experimental Section

The LD spectra were recorded with a Cary-15 spectrophotometer using the new, accurate P.N.P. technique. The method of measurement, as well as the preparation of the stretched film matrices are described elsewhere.[4,5]

Acknowledgments, We are grateful to Professor V. Prelog for suggesting this investigation, for his comments as well as for supplying the samples of 9,9′-spirobifluorene and [6.6]-vespirene, and for the permission to reproduce the CD spectrum of [6.6]vespirene. We thank Dr. A. Warshel for his unpublished results on biphenyl. This research was supported in part by a grant from U.S.-Israel Binational Science Foundation (BSF), Jerusalem.

References and Notes

(1) (a) Department of Isotopes. (b) Department of Organic Chemistry.

(2) (a) G. Haas, P. B. Hulbert, W. Klyne, V. Prelog, and G. Snatzke, *Helv. Chim. Acta*, **54** (2), 491 (1971); (b) G. Wagniere, "Aromaticity, Pseudoaromaticity and Antiaromaticity", Proceedings of the III-d Jerusalem Symposium, 127 (1970) (calculations by the Pariser–Pople–Parr-configuration interaction method).

(3) $OD_{\parallel}$ and $OD_{\perp}$ are the optical densities for light polarized parallel and perpendicular to the stretching direction, respectively.

(4) G. Aviv, L. Margulies, J. Sagiv, A. Yogev, and Y. Mazur, *Spectrosc. Lett.*, **10**, 423 (1977).

(5) A. Yogev, L. Margulies, J. Sagiv, and Y. Mazur, *Rev. Sci. Instrum.*, **45**, 386 (1974); A. Yogev, L. Margulies, J. Sagiv, and Y. Mazur, *Chem. Phys. Lett.*, **23**, 178 (1973), and references therein.

(6) H. Suzuki, "Electronic Absorption Spectra and Geometry of Organic Molecules", Academic Press, New York, N.Y., 1967, pp 269–280, 285–290.

(7) E. Huler and A. Warshel, *Acta Crystallogr.*, in press.

(8) The isotropic spectrum of molecules incorporated in a stretched film is defined as the spectrum of an identical molecular assembly having a random distribution. This spectrum is given by: $OD(\lambda) = (1/3)[OD_{\parallel}(\lambda) + 2OD_{\perp}(\lambda)]$.[4]

(9) The bands are numbered in the sequence of increasing energy of their λ_{max}.

(10) E. Clar, "Aromatische Kohlenwasserstoffe", Springer-Verlag, Berlin, 1952.

(11) A. Warshel, The Weizmann Institute of Science, Israel, private communication. The QCFF/PI method was applied only to planar biphenyl for which the long-wavelength component of H band is a forbidden transition. For method of calculation see A. Warshel and M. Karplus, *J. Am. Chem. Soc.*, **94**, 5612 (1972).

(12) J. R. Platt, *J. Chem. Phys.*, **19**, 101 (1951).

(13) L. O. Edwards and W. T. Simpson, *J. Chem. Phys.*, **53**, 4237 (1970).

(14) Emission from more than one excited singlet state seems to be a frequent phenomenon in aromatic compounds having low-energy overlapping bands in their electronic spectrum.[15] As our resolved spectrum indicates (Figure 2), the first two excited states of biphenyl, A and h, are very close in their energies. It is therefore very probable that both A and H excited states contribute to the observed fluorescence of biphenyl. The polarization of excitation is sensitive to the relative angle between the absorbing and emitting dipoles, but since in this present case both absorption and emission have a mixed polarization character, it becomes impossible to detect the small changes in the polarization of excitation which would reveal the existence of weak transversal bands underlying the strong longitudinal A band.

(15) L. Margulies and A. Yogev, *Chem. Phys. Lett.*, **35**, 291 (1976).

(16) A. S. Davydov, "Theory of Molecular Excitons", McGraw-Hill, New York, N.Y., 1962.

(17) A. L. Sklar, *Rev. Mod. Phys.*, **14**, 232 (1942); J. R. Platt, *J. Chem. Phys.*, **19**, 263 (1950); J. Petruska, *ibid.*, **34**, 1111 (1960).

(18) A linear dichroic study concerned with the effect of various substitution patterns on the transition moments of the benzenoid transitions (J. Sagiv, to be published), and previous studies on para-disubstituted benzenes confirm the predictions of Platt–Sklar theory: A. C. Albrecht and W. T. Simpson, *J. Chem. Phys.*, **23**, 1480 (1955); E. W. Thulstrup, M. Vala and J. H. Eggers, *Chem. Phys. Lett.*, **7**, 31 (1970).

(19) G. M. Brown, M. H. Bartner, *Acta Crystallogr.*, 7, 139 (1954).

(20) The uniaxial distribution pattern characteristic of elongated molecules having one dimension considerably longer than the others is described in terms of a "*f*" model. According to this model a fraction (*f*) of the molecules in the film are perfectly aligned with their long axes in the direction of stretching, and a fraction $(1 - f)$ is at random.[4,15] It is conceivable that *f* and $(1 - f)$ represent the fractions of molecules incorporated in the oriented and unoriented domains of the polymer, respectively.[4] It is noteworthy that even if some planar component of the distribution is considered, only the relative intensities of the different polarized components in the short λ region of the resolved spectrum are modified, but the main features (sequence and polarization of transitions) remain unchanged.

(21) Von G. Hohlneicher, F. Dörr, N. Mika, and S. Schneider, *Ber. Bunsenges. Phys. Chem.*, **72**, 1144 (1968).

(22) A. Bree and R. Zwarich, *J. Chem. Phys.*, **51**, 903 (1969).

(23) C. A. Pinkham and S. C. Wait, Jr., *J. Mol. Spectrosc.*, **27**, 326 (1968).

(24) Due to their characteristic shapes and polarizations, bands B and C are easily identified in the resolved spectra of all four biphenyl derivatives (compare Figures 2, 7, and 10, and 13).

(25) The alternative assignment of band B to the low-energy member of the β-exciton pair[13] requires a longitudinal polarization for this transition in fluorene, and a much lower intensity (Figure 6).

(26) V. Prelog, private communication (x-ray measurements).

(27) Our conclusions concerning the polarizations of A and H bands of SBF are based on symmetry considerations and thus remain valid even if possible interactions between the component fluorene units are considered.

(28) A Yogev, L. Margulies, B. Strasberger, and Y. Mazur, *J. Phys. Chem.*, **78**, 1400 (1974).

(29) The preferred orientation of SBF molecule in polyethylene is a sort of "compromise" reached when each fluorene fragment tends towards its own preferred orientation. As shown in Figure 8a, the most preferred orientation of one fluorene corresponds to a most hindred orientation of the other. The compromise implies that both fluorene fragments be oriented with their planes parallel to the stretching direction (planar orientation),[4] their longitudinal axes being perpendicular to it (Figure 8b).

(30) H. E. Simmons and T. Fukunaga, *J. Am. Chem. Soc.*, **89**, 5208 (1967).

(31) H. Labhart, E. R. Pantke, and K. Seibold, *Helv. Chim. Acta*, **55**, 658 (1972).

(32) The direct electronic influence of the alkyl bridges, via the substituent effect, is expected to be small[17,18] and can be safely neglected in this treatment.

(33) Transitions polarized in the *x*-direction are represented symbolically by their dipolar pattern (↑), while those polarized in the *y*-direction by (⤪). The longitudinal transitions are represented by (⤩).

(34) W. Kuhn, *Ann. Rev. Phys. Chem.*, **9**, 417 (1958).

(35) A. Moscowtiz, "Modern Quantum Chemistry", O. Sinanoglu, Ed., Part III, Academic Press, New York, N.Y., 1965, pp 31–44.

(36) Note that $G = 7.6$ corresponds to an angle ϕ to be 63°. Most likely, this discrepancy between the calculated and the experimental value must be ascribed to various factors which have been neglected in our simple treatment (see also the discussion on SBF).