POLARIZATION SPECTRA IN STRETCHED POLYMER SHEETS—IV

BENZO[k]FLUORANTHENE AND ITS AZA ANALOGS[1]

J. MICHL*[2]

Department of Chemistry, University of Utah, Salt Lake City, Utah 84112, U.S.A.

and

J. H. EGGERS

Department of Chemistry, Aarhus University, Aarhus, Denmark

Abstract—Polarized spectra of benzo[k]fluoranthene and two of its aza analogs are obtained from measurements of dichroism in stretched polyethylene sheets and interpreted by means of Pariser–Parr–Pople calculations. Aza substitution in the solute has a curiously large effect on the degree of orientation.

INTRODUCTION

In this paper, we continue a systematic investigation of polarization directions of $\pi\pi^*$ transitions in large conjugated molecules using dichroism in stretched polyethylene sheets. An outline of the method and comparison with other methods have appeared previously.[1,3]

The choice of the benzo[k]fluoranthene (1) chromophore was influenced by our continuing interest in spectra of non-alternant hydrocarbons, by the promise of high dichroic ratios which a molecule of such shape held, and by the availability of 7 - azabenzo[k]fluoranthene 2 and 7, 12 - diazabenzo[k]fluoranthene 3. If the method is to be eventually generally useful for determination of polarization directions in molecules of low symmetry, one will need to predict orientation factors from molecular properties such as shape.[1] It is at present not clear which other properties will play a role. Aza substitution leaves shape almost intact, yet we

found significant differences in the orientation of anthracene and acridine.[3] One of the aims of the present investigation was to compare the orientation of 1 and 3.

There has been little previous experimental or theoretical work on excited states of benzo[k]fluoranthene. The absorption spectrum has been measured and tentatively assigned by analogy with benzenoid hydrocarbons.[4] It has been shown that the energy of the first intense band, tentatively identified as due to HOMO → LUMO excitation, fits the correlation with HMO excitation energies found for benzenoid and other fluoranthene-like hydrocarbons.[5] A calculation by the Pariser–Parr–Pople method[6] confirmed the assignment of the first transition as HOMO → LUMO, accounted correctly for the overall shape of the absorption curve at higher energies and predicted the first transition as well as the strong transition near 33000 cm^{-1} to be z-polarized, with three weak y-polarized transitions

1   2   3
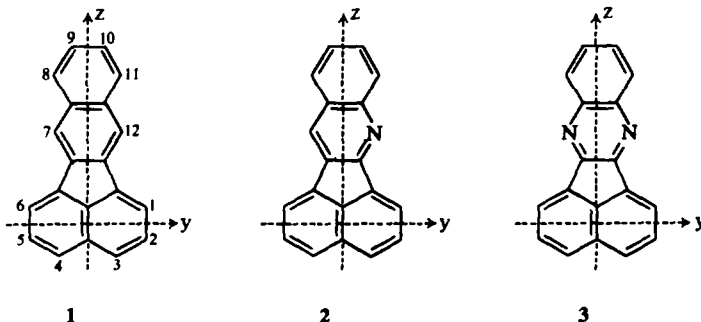
between the two.[7] A semiempirical random-phase calculation has yielded similar results for excitation energies and oscillator strengths.[8]

EXPERIMENTAL

Compounds. The sample of **1** was that described in Ref 9a and was obtained through the courtesy of Professor Keith D. Bartle, The University of Leeds, England. The sample of **2** was that described in Ref 9b and was a generous gift from Professor Jan Moszew, The University, Krakow, Poland. A sample of **3** was synthesized by the method of Ampola and Recchi,[9c] m.p. 235–6° on a hot stage, reported 234°,[9c] 241°.[9d] Before use, all samples were chromatographed on alumina.

Emission measurements. Emission and excitation spectra were taken on a Turner 210 instrument both in cyclohexane and alcohol solutions, 10^{-5}–10^{-7} M. Excitation spectra agreed with absorption spectra in all fine features.

Stretched sheet measurements. Several measurements on different numbers of sheets were performed on each compound. Each measurement was an average of three scans in each position of the Glan prism, as described in Ref 3, which also gives all other details.

RESULTS

Methods. The method used for the evaluation of the experimental data has been published in detail elsewhere,[1,3] and shall only be described briefly.

For molecules of C_{2v} symmetry, such as **1** and **3**, $\pi\pi^*$ transition moments can only be directed along the long (z) or short (y) in-plane axis. Let $A_z(\lambda)$ stand for z-polarized and $A_y(\lambda)$ for y-polarized absorption. The experimental dichroic curves $E_{\|}(\lambda)$ and $E_{\perp}(\lambda)$ are linear combinations of $A_z(\lambda)$ and $A_y(\lambda)$

$$\begin{pmatrix} E_{\|}(\lambda) \\ E_{\perp}(\lambda) \end{pmatrix} = \begin{pmatrix} K_1 & K_2 \\ K_3 & K_4 \end{pmatrix} \begin{pmatrix} A_z(\lambda) \\ A_y(\lambda) \end{pmatrix}$$

where the orientation factors K_1 – K_4 are related to average molecular orientation in the stretched sheet. We have shown previously[1] that under our experimental conditions all directions perpendicular to the stretching direction are equivalent (uniaxial stretching). Then, $K_3 = (1 - K_1)/2$ and $K_4 = (1 - K_2)/2$, so that only two orientation factors are independent. The first of these, K_1, is related to the average of the deviation β of the long orientation axis (z axis) from the stretching direction: $K_1 = \langle\cos^2 \beta\rangle_{av}$. The other, $K_2 = \langle\sin^2 \beta \cdot \cos^2 \gamma\rangle_{av}$, describes the alignment of the short (y) axis with the stretching direction and, as pointed out previously,[1] is in general independent of the first since it also reflects the γ-distribution: given a deviation β of the z axis from the stretching direction, the molecule can still be rotated about the z axis by an angle γ and thus assume a variety of orientations, some of which may be preferred. For flat molecules one can expect the values near $\gamma = 0$ or $\gamma = 180°$ to be favored since the molecular plane is then parallel to the stretching direction and the smallest molecular cross-section is exposed when viewed along the stretching direction. This is in agreement with experimental results.[1] For rod-shaped molecules the γ-distribution should be uniform, $K_2 = K_3 = (1 - K_1)/2$, and only one orientation factor is independent. The assumption of uniform γ-distribution is made frequently for molecules of any shape without attempts at justification,[10,11] but its invalidity in the general case has been pointed out by other authors as well.[12] Experimental data support the assumption for instance for anthracene or phenazine,[1] but not for perylene or fluoranthene, which are apparently not sufficiently rod-like.* Clearly, although useful, the simplification should not be made automatically.

Determination of the reduction factors $d_{\perp}^o = K_3/K_1$ and $d_{\|}^o = K_2/K_4$ is based on the inspection of families of curves $E_{\perp} - d_{\perp} \cdot E_{\|} (0 < d < 1)$ and $E_{\|} - d_{\|} \cdot E_{\perp} (0 < d < 1)$. For a certain value of $d_{\perp}$, all features due to z-polarized absorption just disappear from the former ($d_{\perp}^o$); for a certain value of $d_{\|}$, all those due to y-polarized absorption are absent in the latter ($d_{\|}^o$). The remaining spectral features are due to y-polarized transitions in the former case $[(E_{\perp} - d_{\perp}^o E_{\|}) \cdot n_0 = \text{const. } A_y]$ and to z-polarized transitions in the latter $[E_{\|} - d_{\|}^o \cdot E_{\perp} = \text{const. } A_z]$. The normalization factor $n_0 = K_1/K_4$ is needed to ensure that the proportionality constant in both equations is the same so that both reduced spectra are on the same scale. It can be derived from measurements on unstretched sheets. Under our experimental conditions (uniaxial stretching), $K_4 = (1 - K_2)/2$, and it can then be shown[1] that $n_0 = (2 + d_{\|}^o)/(2 d_{\perp}^o + 1)$.

For molecules of lower symmetry such as **2**, $\pi\pi^*$ transition moments can be anywhere in the molecular plane. The angles between them and the orientation axis can be determined if the molecular orientation factors K_1 and K_2 can be estimated from molecular shape or otherwise.[1]

Reduction factors. The above method was applied to the dichroic spectra of **1–3**. The degree of dichroism is very high as might be expected from the rather elongated shape of the molecules. Experience with other available data[1,3] leaves little doubt that the orientation axis z is located as indicated in formulas **1–3**.

For **1** and **3**, the determination of $d_{\perp}^o$ (listed on p. 813) is easy since a multitude of well-developed features due to A_z is available in the spectra. Moreover, A_y is negligible at most wavelengths, so that $d_{\perp}^o$ can be also simply obtained as the inverse dichroic ratio $E_{\perp}/E_{\|}$ at these wavelengths. Determination of the other reduction factor, $d_{\|}^o$, is much less accurate since the only spectral region where A_y is

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*If the assumption is made nevertheless, e.g. for fluoranthene,[13] an incorrect value of K_2 results, so that the "reduced" spectrum $A_z(\lambda)$ is not fully reduced and still contains contributions from $A_y(\lambda)$.

large also contains considerable A_z absorption. In this case, the usual approach, namely inspection of the y-polarized peak near 40000 cm^{-1} as $d_\parallel$ is varied in $E_\parallel - d_\parallel \cdot E_\perp$, was supplemented by determination of n_0 from measurements on unstretched sheets, which combined with the $d_\perp^\circ$ value also provides a value for $d_\parallel^\circ : d_\parallel^\circ = n_0 - 2(1 - d_\perp^\circ n_0)$.

The values of d° are among the lowest we have observed so far. The difference between 1 and 3 is surprisingly large, considering that molecular models would lead one to expect almost identical molecular shapes. A similar but smaller difference exists between anthracene and acridine, suggesting that this is a possibly general phenomenon. As far as the relatively low accuracy allows us to tell, in this particular case the values of $d_\parallel^\circ$ are those expected for rod-shaped molecules ($K_2 = K_3$), namely $d_\parallel^\circ = 2d_\perp^\circ/(1 + d_\perp^\circ)$.

A similar investigation of the dichroic curves for the less symmetric molecule 2 showed that within experimental error, most observable spectral features disappear simultaneously from $E_\perp - d_\perp \cdot E_\parallel$, namely when $d_\perp = 0.3$, with the exception of a shoulder at 28500 cm^1 which disappears at $d_\perp = 0.4$, and two peaks at 41000–42000 cm^{-1}, which are eliminated from $E_\perp - d_\parallel \cdot E_\perp$ when $d_\parallel = 0.3$–0.5. Assuming that 2 can also be considered rod-shaped, and given $d_\perp^\circ = 0.3$, $d_\parallel^\circ = 0.45$ would be expected for a y-polarized transition. Thus, within experimental error, the two peaks at 41000–42000 cm^{-1} are polarized along the y-axis. Similarly, the value $d_\perp^\circ = 0.3$ observed for most of the transitions in 2 is about half-way between the values $d_\perp^\circ = 0.2$ and $d^\circ = 0.35$ observed for 1 and 3 and thus equal to that expected for purely z-polarized transitions. Within our experimental accuracy all the other observed transitions in 2 are thus z-polarized, except possibly for the weak shoulder at 28500 cm^{-1}, which may deviate from the z direction by about 20° (experimental error precludes a determination of the angle with any great accuracy). In view of this, we assume in the following discussion of the reduced spectra that 2, like 1 and 3, only has y- and z-polarized transitions, in spite of its lower molecular symmetry.

The final set of reduction factors used to produce reduced spectra in Fig 1 was $d_\perp^\circ = 0.2$, $d_\parallel^\circ = 0.35$, $n_0 = 1.65$ for 1, $d_\perp^\circ = 0.3$, $d_\parallel^\circ = 0.45$, $n_0 = 1.6$ for 2, and $d_\perp^\circ = 0.35$, $d_\parallel^\circ = 0.5$ and $n_0 = 1.5$ for 3.

Reduced spectra. The reduced spectra of 1–3 are presented in Fig 1. Multiplication of A_y by the factor n_0 has been performed to bring both A_z and A_y to the same scale. A grouping of the observed peaks and shoulders corresponding to individual electronic transitions is indicated in those cases which can be assigned relatively safely. This is based on shapes, intensities and spacings of the peaks (a tentative vibrational analysis is indicated), upon consideration of the mirror-image relationship between fluorescence and the first absorption band, which is

quite well developed and helps to establish the location of the 0–0 component of the first absorption band and to discern the onset of the second absorption band, upon shifts and intensity changes due to protonation of 2 and 3 in acidic media, and last, but not least, upon similarities between the spectra of 1, 2 and 3. At least one more transition is clearly present in the region 35000–40000 cm^{-1}, but the vibrational structure is insufficiently developed for a clear-cut assignment. Additional transitions are present at higher energies (> 42000 cm^{-1}).

Calculations. Fig 1 also contains results of calculations by the usual simple version of the SCF–CI
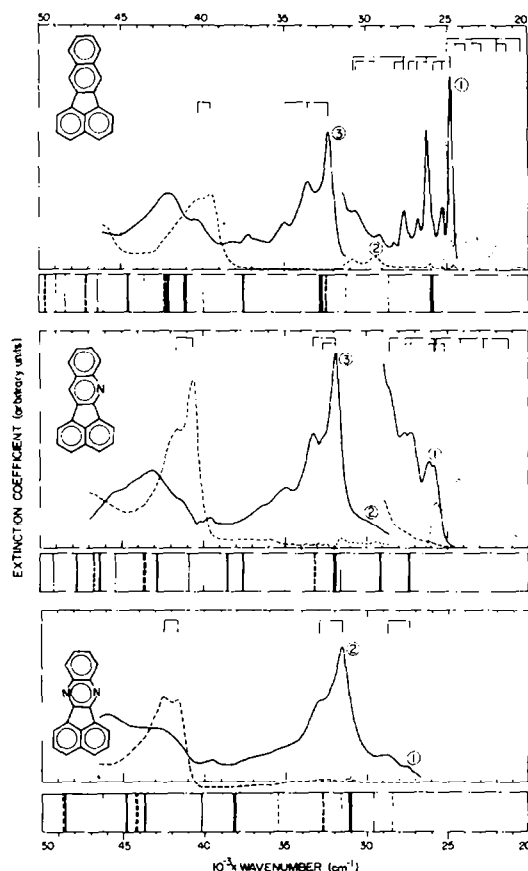

Fig. 1. Reduced polarized absorption spectra from measurements in stretched polyethylene: $A_z(\lambda)$ (z-axis polarized, full lines) and $A_y(\lambda)$ (y-axis polarized, dashed lines). Fluorescence emission spectra of I and II in cyclohexane are also shown (dotted, not corrected for instrumental response). Tentative vibrational analysis is shown above the curves, calculated pure electronic transitions below (oscillator strength above 0.5, thick lines; between 0.1 and 0.5, medium lines; below 0.1, thin lines; z-polarization, full lines; y-polarization, dashed lines). In II, the calculated polarization directions deviate slightly from the z and y axes; this is not shown. The two dotted lines indicate transitions with polarization directions calculated to lie about half-way between y and z axes.

Pariser–Parr–Pople method:[6] neglect of penetration integrals, equal bond lengths (1·40 Å), regular hexagons for benzene rings, Mataga–Nishimoto[14] repulsion integrals, singly excited configurations up to 8 eV (about 40 in all) or up to 7·6 eV (about 30 in all), with virtually identical results. Parameters for C and N were those used in Ref 15. Transition moments were obtained from the dipole length formula.

DISCUSSION

There is not much superficial similarity between the spectrum of fluoranthene[15] and that of benzo[k]fluoranthene (Fig 1). Nevertheless, the two spectra can still be related relatively straightforwardly, assuming simply that all z-polarized bands of fluoranthene have been shifted to the red and intensified in the benzo analog, whereas the y-polarized bands have not been affected.

The comparison of the three spectra in Fig 1 is interesting. While the strong z-polarized band of 1 near 32000 cm^{-1} and the only relatively strong y-polarized band, near 42000 cm^{-1}, remain basically unaffected by the aza substitution, the long wavelength region of the spectrum is changed almost beyond recognition. The characteristic first band of the hydrocarbon is shifted to the blue and becomes relatively less intense. This is unusual for aza substitution in aromatic hydrocarbons and apparently must be blamed on the non-alternant nature of benzo[k]fluoranthene 1. Even so, the effects are bigger than in the closely related fluoranthene itself[15] and hard to account for without recourse to calculations.

According to our PPP calculation for 1, the first electronic transition near 25000 cm^{-1} corresponds to an almost pure excitation from the highest occupied molecular orbital to the lowest unoccupied one. At atoms 7 and 12, the expansion coefficient of the former is 0·40 and that of the latter only 0·15. This shows clearly the lack of pairing properties and the non-alternant nature of 1 in the PPP model. The HOMO→LUMO excitation thus corresponds to removal of 0·14 units of electron charge from each of the positions 7 and 12 and it then seems understandable that substitution of the more electronegative aza nitrogen for carbon in these positions should increase the excitation energy. Using the value 18750 cm^{-1} per unit of electron charge estimated by Murrell[16] the blue shift should be about 2600 cm^{-1} for each nitrogen. Experimentally, it is 1200 cm^{-1} for the first nitrogen and another 1400 cm^{-1} for the second one, only about half of what the simple argument would predict.

Actually, this simple and commonly used approach is fraught with dangers, above all when applied to substituents with a large inductive effect, such as aza. This has been discussed in detail elsewhere.[15] In particular, the configuration mixing scheme may change significantly in an often unpredictable way. Our PPP calculations on 2 and 3 show that this indeed occurs to some degree: whereas the 1 → −1 (HOMO→LUMO) configuration has 88% weight in the first excited state of 1, its weight in the lowest excited state of 2 is only 58%, due to 25% admixture of the 2 → −1 configuration. In 3, the state in which the 1 → −1 configuration predominates is second in energy. The configuration 1 → −1 (69% weight) is mixed with 2 → −2 (24% weight). In both 2 and 3, increased interaction of the 1 → −1 configuration with higher configurations lowers its energy and the calculated shifts with respect to 1 are thus smaller than would be expected from a simple argument which neglects configuration interaction: 1400 cm^{-1} for the first and 2200 cm^{-1} for the second nitrogen, still somewhat more than the experimental values. The lowest calculated transition in 3 corresponds to a 2 → −1 excitation, similarly as in fluoranthene,* and is predicted to be extremely weak (f < 10^{-3}). It might be hard to detect under the more intense 1 → −1 transition (calculated f = 0·09).

In addition to providing a rationale for the striking blue shift of the first transition, the PPP calculations also account for the decrease of its relative intensity. The results for energies, substituent shifts, relative intensities, and polarizations of strong transitions are generally in good agreement with experiment, except for the intensity of the strong transition on 3 calculated at 38000 cm^{-1} (Fig 1). In addition, many weak transitions are predicted as well. Some but not all are observed, and it is impossible to say how meaningful the calculated numbers are.

We have also considered the possibility that a nπ^* state becomes lowest in energy and thus observable as the aza substitution shifts the π–π^* absorption to higher energies, but comparisons of absorption and emission in hydrocarbons, alcohol, and alcohol-acid mixtures have failed to reveal any evidence for such a state.

Finally, we wish to point out the decrease in the degree of orientation in the stretched polyethylene in the series 1, 2, 3. The reason for this is at present not clear. It seems highly desirable to investigate the generality of this interesting phenomenon further, if only in order to ascertain how disturbing it will be for our efforts to find general shape-orientation relationships in non-polar stretched polymers, which are needed for work on molecules of low symmetry. It is also conceivable that information on the effective size of nitrogen lone pairs will result. This problem is of considerable current interest.[18]

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*There is no doubt about the authenticity of the first weak transition near 25000 cm^{-1} in fluoranthene which had been overlooked until relatively recently.[15, 17] Recent statements to the contrary made in Ref 8 are apparently based on a misunderstanding.

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