Vol. 88 (1995) *ACTA PHYSICA POLONICA A* No. 2

ELECTRONIC STATES AND STRUCTURE OF DIBENZO[j, lm]PHENANTHRO[5,4,3-*abcd*]PERYLENE

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(Received March 24, 1995; in final form May 22, 1995)

Dedicated to Professor Zdzisław Ruziewicz on the occasion of his 70th birthday[*]

Electronic absorption and emission, fluorescence anisotropy and linear dichroism techniques were applied to dibenzo[j, lm]phenanthro[5,4,3-*abcd*]-perylene in order to determine its electronic structure and check the possibility of existence of conformational isomers. The results indicate the presence of only one conformer. Its structure is proposed on the basis of the experimental data as well as molecular mechanics and quantum chemical calculations.

PACS numbers: 33.10.-n, 33.20.-t, 07.65.-b

1. Introduction

It is not always realized that most aromatic hydrocarbons are nonplanar [1]. One of the simplest examples is dibenzo[g, p]chrysene, of which the nonplanarity has been revealed by measuring linear dichroism (LD) in stretched polyethylene [2, 3]. The analysis of the LD results made it possible to assign the D_2 symmetry to the dominant conformer [3]. The work in Shpol'skii-type matrices led to the detection of two stereoisomers [4]. Similar studies on another sterically-crowded, nonplanar molecule, dinaphtho[1,2-a:1′,2′-h]anthracene have been performed by Ruziewicz and coworkers [5].

For many larger hydrocarbons it was observed that the intensities of vibronic components in the absorption spectra vary in different solvents [6–10], which indicates the presence of several forms. For tetrabenzo[a, cd, f, lm]perylene, a discrepancy between absorption and fluorescence excitation spectra was interpreted

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[*] Submitted on invitation of the Institute of Physical and Theoretical Chemistry, Technical University of Wrocław, Wrocław, Poland.

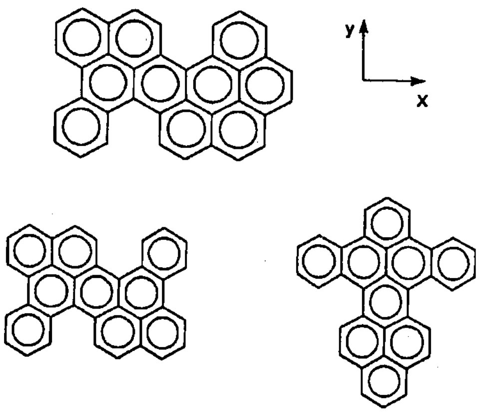

Fig. 1. Top, dibenzo[j, lm]phenanthro[5,4,3-$abcd$]perylene and the coordinate system used for calculations. Bottom, tetrabenzo[a, cd, j, lm]perylene (left) and tetrabenzo[a, cd, f, lm]perylene (right).

as evidence of more than one conformer present at room temperature [11]. This was corroborated by absorption and fluorescence study in Shpol'skii matrices [12]. Interestingly enough, the isomeric tetrabenzo[a, cd, j, lm]perylene does not seem to exist in more than one form [11].

In this paper, we study dibenzo[j, lm]phenanthro[5,4,3-$abcd$]perylene (DPP), a molecule differing from tetrabenzo[a, cd, j, lm]perylene only by the presence of one additional ring (Fig. 1). The purpose is to check the possibility of conformational equilibria, and to determine the properties of the lowest excited singlet states.

2. Experimental and computational details

The synthesis and purification of DPP has been described [13]. Absorption spectra were recorded on a Shimadzu UV 3100 spectrophotometer. For LD measurements, either Glan or sheet polarizers (Oriel) were placed in both the sample and reference beams.

Due to very small amount of the compound at our disposal and poor solubility in polyethylene (PE), a standard procedure of introducing the substance into PE from a chloroform solution could not be used. Instead, we placed small amounts of powdered sample on top of a stretched PE sheet and repeatedly added small droplets of chloroform. It took about 20 hours to obtain the concentration sufficient for reliable LD analysis (optical density of the order of 0.05). Before measuring the LD spectra, the sheet was washed with methanol in order to remove traces of the compound that could have been left on the surface.

Fluorescence was measured on a Jasny spectrofluorimeter [14], emission anisotropy on a new model of Jasny spectrofluorimeter, optimized by the use of Wollaston polarizers, for recording low-noise polarization spectra.

Quantum yields of the emission were determined using quinine sulphate in

0.1N H_2SO_4 as a standard ($\phi_{fl} = 0.51$). Fluorescence decay times were obtained by the sampling technique, with an MSG350 nitrogen laser as the excitation source.

Ground state geometries were computed using molecular mechanics (MMX force field, PCMODEL). The results served as input for INDO/S calculations of excited state energies, oscillator strengths and transition moment directions. The lowest 200 singly excited configurations were taken into account in the CI procedure.

3. Results and discussion

Room temperature absorption and fluorescence spectra are shown in Fig. 2. The spectra in heptane and ethanol are very similar. The fluorescence band is a mirror image of the absorption. Fluorescence excitation spectra were found to coincide well with absorption. This was not the case for tetrabenzo[*a*, *cd*, *f*, *lm*]perylene, in which two conformers were detected: the mirror image relationship was only observed between fluorescence and fluorescence excitation, but not for the absorption [11].

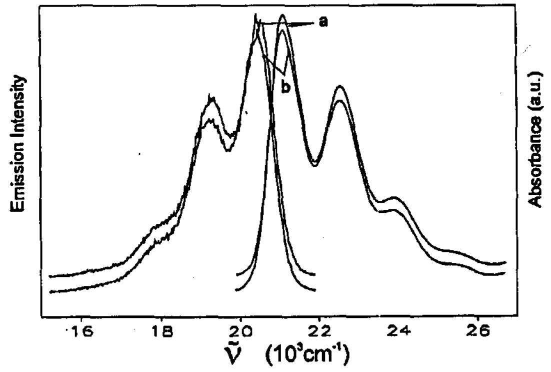

Fig. 2. Absorption and fluorescence in heptane (*a*) and ethanol (*b*) at 293 K.

The quantum yields at 293 K are high and the same in nonpolar and protic solvents (0.37 ± 0.08 in heptane and propanol). Fluorescence decay times are also the same (3.3 ± 0.3 ns in heptane and 3.4 ± 0.3 ns in propanol). The decays in both solvents are purely monoexponential. The value of the radiative constant, 1.1×10^8 s^{-1}, obtained from the decay time and quantum yield, indicates an allowed character of the emitting state and is about the same as that of perylene [15].

Thus, no evidence was found for the presence of more than one conformer. In order to propose its ground state structure, we have performed molecular mechanics calculations. The computed geometry of two low-energy forms is presented in Fig. 3. Conformer *A* was predicted to have the energy about 3.5 kcal/mol lower than the conformer *B*. This is very similar to the case of tetrabenzo[*a*, *cd*, *j*, *lm*]perylene, where the calculated difference between two low-energy conformers amounted to 3.8 kcal/mol and the "propeller-like" structure was calculated to be more stable [11].

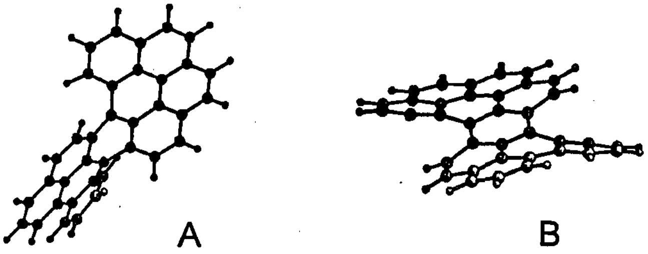

Fig. 3. The structure of two low-energy conformers calculated by MMX.

The excited state properties of both conformers of DPP, calculated by the INDO/S method, are presented in Tables I and II. The results of calculations were then compared with the data obtained by polarized spectroscopy.

Figure 4 shows the absorption spectrum in propanol along with the corresponding anisotropy of fluorescence excitation. The angle α formed by the transition moment of a particular excited state with that of the emitting state was calculated using the formula

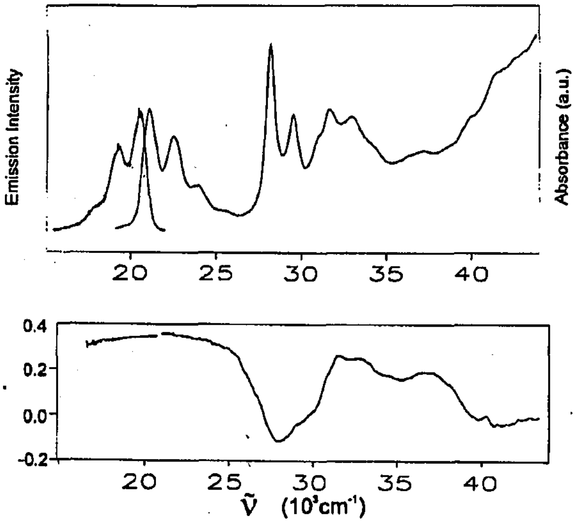

Fig. 4. Top, room temperature absorption and fluorescence; bottom, fluorescence anisotropy (excited at 22 000 cm^{-1}) and anisotropy of fluorescence excitation (monitored at 20 600 cm^{-1}) in propanol at 113 K.

$$r = (3\cos^2\alpha - 1)/(\cos^2\alpha + 3). \tag{1}$$

TABLE I

Excited state parameters for the conformer A calculated by INDO/S. R_x, R_y and R_z are the transition moment components. For the axes definition, see Fig. 1. In bold, the transitions which are candidates for the assignments (see text).

	Energy [10^3 cm^{-1}]	R_x	R_y	R_z	Oscillator strength	α^a [deg]
1	**22.49**	**−3.57**	**−0.21**	**0.22**	**0.878**	**0**
2	23.08	0.94	0.17	−0.09	0.065	7
3	27.79	−0.03	0.09	−0.13	0.002	84
4	29.98	0.33	−0.95	0.33	0.101	77
5	**31.17**	**−1.59**	**2.68**	**0.17**	**0.922**	**63**
6	31.31	0.60	−1.27	0.12	0.189	69
7	31.91	0.81	−0.97	0.07	0.156	54
8	32.59	0.11	−0.14	−0.07	0.004	57
9	**32.97**	**2.09**	**0.55**	**0.23**	**0.474**	**15**
10	**33.69**	**−1.45**	**−1.11**	**−0.04**	**0.342**	**34**
11	**33.99**	**1.50**	**0.62**	**0.17**	**0.275**	**21**
12	34.68	−0.31	0.96	−0.95	0.202	82
13	35.11	0.62	−0.13	−0.61	0.082	43
14	36.03	0.74	−0.36	−0.13	0.076	30
15	**36.48**	**−1.51**	**−0.50**	**−0.12**	**0.282**	**17**
16	37.08	0.38	0.76	0.18	0.086	62
17	38.20	0.00	−0.11	−0.35	0.016	88
18	38.68	0.00	−0.20	0.42	0.025	86
19	38.74	−0.81	0.33	0.40	0.108	32
20	39.86	−0.49	−0.13	−0.08	0.032	16
21	40.08	−0.52	0.19	0.09	0.039	24
22	40.64	−0.41	−0.25	0.45	0.053	47
23	41.03	−0.54	0.10	−0.27	0.047	32
24	41.31	0.11	−0.32	0.08	0.015	76
25	41.84	−0.54	1.12	0.20	0.203	67
26	42.09	−0.10	0.27	0.12	0.013	73
27	42.62	0.09	1.06	0.12	0.149	82
28	42.66	0.47	−2.35	0.03	0.743	82
29	43.24	−0.35	0.53	−0.21	0.058	63
30	43.52	−0.33	0.04	0.44	0.040	50

[a] The angle between the transition moment of a given transition and that of S_1.

TABLE II
Excited state parameters for the conformer *B* calculated by INDO/S. See caption to Table I for details.

	Energy [10^3 cm^{-1}]	R_x	R_y	R_z	Oscillator strength	α^a [deg]
1	23.08	−0.61	0.24	−0.04	0.030	28
2	**23.49**	**3.41**	**0.39**	**0.16**	**0.840**	**0**
3	27.76	−0.03	−0.01	0.01	0.000	28
4	30.30	−0.07	0.85	0.03	0.067	88
5	**31.23**	**1.77**	**−2.28**	**0.08**	**0.791**	**59**
6	**31.50**	**1.80**	**−1.75**	**−0.04**	**0.605**	**51**
7	32.11	0.87	−0.38	0.09	0.088	30
8	**32.60**	**2.37**	**1.41**	**0.11**	**0.757**	**24**
9	32.97	0.82	0.83	0.06	0.137	39
10	33.69	−0.92	−1.03	0.04	0.195	42
11	34.09	−0.76	−0.55	0.10	0.091	30
12	34.99	−0.39	0.86	−0.07	0.096	72
13	35.22	−0.06	0.31	−0.06	0.011	86
14	36.48	0.47	−0.47	−0.17	0.052	54
15	**36.65**	**−1.53**	**0.02**	**0.46**	**0.284**	**20**
16	37.38	0.31	0.73	0.14	0.073	61
17	38.12	−0.25	−0.01	−0.13	0.009	25
18	38.60	−0.03	0.03	0.06	0.001	75
19	38.89	−0.71	0.46	0.42	0.105	48
20	39.71	−0.61	0.05	0.23	0.052	26
21	39.93	0.01	0.02	0.12	0.002	81
22	40.52	0.48	−0.12	−0.04	0.030	22
23	41.25	0.66	−0.22	−0.42	0.083	41
24	41.56	0.27	−0.97	0.16	0.130	81
25	41.67	0.22	−1.18	−0.11	0.183	86
26	42.04	−0.10	−0.35	0.05	0.017	68
27	42.26	−0.32	2.30	0.06	0.691	89
28	42.68	0.03	−0.88	−0.15	0.104	85
29	43.12	0.14	−0.57	−0.13	0.048	84
30	43.48	−0.84	0.09	0.05	0.095	14

[a] The angle between the transition moment of a given transition and that of the calculated second transition, assumed to correspond to the lowest excited singlet state.

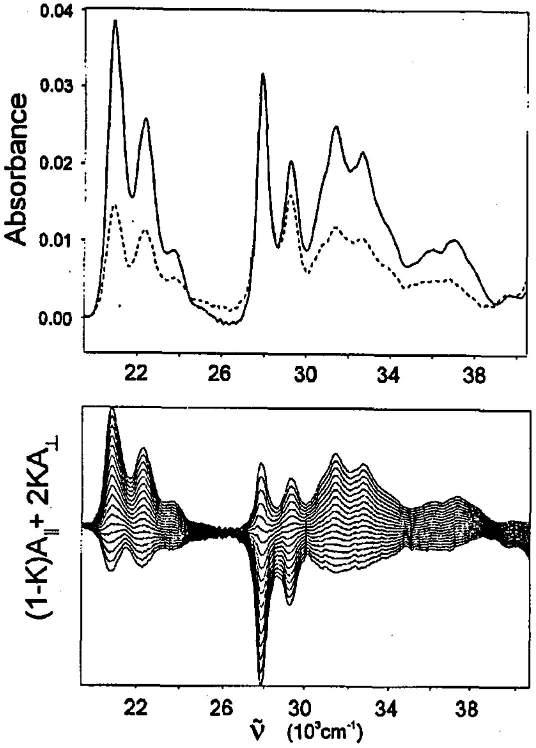

Fig. 5. Top, LD curves obtained in stretched PE: solid line, $A_{\|}$, dashed line, $A_{\perp}$; bottom, the "reduction" procedure. The values of K were varied from 0.2 to 0.71 in steps of 0.03.

Figure 5 presents the linear dichroism measurements in stretched PE. Two curves were recorded: $A_{\|}$, corresponding to the polarization of the electric vector of absorbed light parallel to the stretching direction, and $A_{\perp}$, in which the two directions are perpendicular to each other. The analysis of the LD curves was based on the so-called "reduction procedure" [16], i.e. plotting the family of curves $A_{\|} - cA_{\perp}$ and determining the value of c_k for which a particular spectral feature f (peak, shoulder) disappears from the spectrum. For this value

$$c_f = 2K_f/(1 - K_f), \tag{2}$$

or

$$K_f = c_f/(c_f + 2). \tag{3}$$

In this work, we extracted the values of K_f directly from the plots of $(1 - K)A_{\|} + 2KA_{\perp}$. K_f is the so-called "orientation factor", which can be expressed as an average value of the $\cos^2\theta_f$, where θ_f is the angle between the direction moment of the transition f and the direction of stretching.

In general, alignment in PE is related to molecular shape: the long molecular axis orients better than the short one and therefore reveals a higher value of K.

The direction in the molecular frame which, on the average, is best aligned is referred to as the "effective orientation axis". In high symmetry molecules (D_{2h}, C_{2v}, etc.), only three different transition moment directions are possible, and the effective orientation axis coincides with one of them (usually it corresponds to the longest molecular axis). In molecules of low symmetry, such as DPP, there is an infinite number of possible transition moment directions. It is generally assumed that the direction of the effective orientation axis is perpendicular to the smallest cross-section of the molecule. No matter what the symmetry is, the larger value of K indicates that the transition moment direction forms a smaller angle with the orientation axis.

TABLE III

Emission anisotropy and linear dichroism results.

Energy[a] [10^3 cm^{-1}]	r[b]	α[c] [deg]	K_f	θ_f [deg]
21.13	0.36	15	0.59 ± 0.01	40 ± 1
22.53	0.35	17	0.59 ± 0.01	40 ± 1
23.92	0.33	20	0.59 ± 0.01	40 ± 1
25.63	0.24	31		
28.16	−0.11	67	0.35 ± 0.01	54 ± 1
29.50	−0.01	56	0.40 ± 0.02	51 ± 1
30.9(sh)	0.15	40		
31.71	0.26	29	0.59 ± 0.02	40 ± 2
33.00	0.25	30	0.59 ± 0.02	40 ± 2
34.45(sh)	0.17	38		
37.21	0.19	36	0.60 ± 0.02	39 ± 2
40.11	−0.01	56		
~41	−0.04	59		

[a] Absorption in heptane, 293 K. [b] Accuracy: ±0.01. [c] Accuracy: ±2°.

The polarized spectroscopy results for DPP are given in Table III. At least five different electronic states can be located in the region below 41 000 cm^{-1}. The peak corresponding to the origin of the S_1 transition at 21 130 cm^{-1}, has the same orientation factor (0.59) as the peaks at 22 530 cm^{-1} and 23 920 cm^{-1}. We therefore assign these three peaks to the same electronic transition. Also the band at 25 630 cm^{-1}, too weak to have its LD reliably measured, most probably belongs to S_1, since it has its counterpart in the emission spectrum.

Two prominent peaks at 28 160 cm^{-1} and 29 500 cm^{-1} (and, possibly, also a shoulder at 30 900 cm^{-1}, which may be a vibronic component) belong to a state whose transition moment forms a large angle with that of the S_1 level. This is evident from both anisotropy and LD data. It should be noted that the values of θ of 40° and 54°, extracted from the orientation factors may correspond to either 14°

or 86° as the angle between the transition moments between the two states. The anisotropy result clearly suggests the latter value. Smaller values of α obtained directly from the anisotropy curve are most probably due to the spectral overlap with the next transition, which is polarized nearly parallel to S_1. This transition consists of two peaks at 31 710 cm^{-1} and 33 000 cm^{-1} and perhaps also a shoulder at 34 450 cm^{-1}.

The band observed at 37 210 cm^{-1} is again polarized nearly parallel to S_1. It is followed by a transition whose negative sign in the anisotropy curve indicates a large angle α.

A somewhat surprising result is that three of the four excited states for which the orientation factors could be determined reveal very similar polarization. However, inspection of Table I shows that the calculations reproduce such behaviour quite well for the conformer A. Four transitions calculated between 33 000 cm^{-1} and 37 000 cm^{-1} (labelled 9, 10, 11 and 15 in Table I) are predicted to have fairly large oscillator strength and the "long-axis" polarization similar to that of the first excited singlet state. Each of them may thus correspond to the experimentally found transitions at 31 710 cm^{-1} and 37 210 cm^{-1}. For the conformer B, only one calculated transition (15th in Table II) is a good candidate for such assignment.

The calculated excited states patterns in the two conformers differ also in other respects. For the conformer A two transitions (1 and 5 in Table I) are predicted to be much stronger than the other ones, whereas in the form B, four transitions (2, 5, 6 and 8) have large and similar oscillator strengths. The experimental data favour the former prediction, since the two transitions with origins at 21 130 cm^{-1} and 28 160 cm^{-1} clearly dominate the spectrum. Finally, for the conformer A, the lowest calculated excited singlet state is strongly allowed, whereas in the form B the allowed state corresponds to S_2. The experimental data leave no doubt about the allowed character of the emitting transition. Thus, the combination of theoretical and experimental results provides arguments for the assignment of the emitting and absorbing species to the conformer A.

4. Conclusions

Absorption and fluorescence data indicate that only one form of dibenzo[*j*, *lm*]phenanthro[5,4,3-*abcd*]perylene is present in solutions and low-temperature glasses. The analysis of polarized spectra, quantum chemical and molecular mechanics calculations suggests that the lowest energy conformer has a "propeller-like" structure, similar to that proposed for a related molecule, tetrabenzo-[*a*, *cd*, *j*, *lm*]perylene, which has also been shown to exist in only one form [11]. It is interesting that a smaller molecule, dibenzo[*g*, *p*]chrysene also prefers the "propeller-like" form [3].

We are currently working on some related compounds, in particular some terrylene derivatives of high symmetry, where it is probable that a strict distinction between various symmetry types will be possible on the basis of polarized spectroscopy results. These studies may also be useful in view of the use of terrylene in single molecule spectroscopy studies [17].

Acknowledgments

Dr. J.W. Downing and Prof. J. Michl are kindly acknowledged for providing us with their version of the INDO/S program. The technical assistance of G. Orzanowska and J. Karpiuk is greatly appreciated. The work was sponsored in part by the grant 2P303.089.04 of the State Committee for Scientific Research (Republic of Poland).

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