Spectral manifestations of aggregates structure of heteroaromatic molecules at low temperatures

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Abstract

The results of investigation of temperature influence on spectral-luminescence properties of ethanol solution of N,N-dibutyl-3,8-diazapyran-5,10-dione (DPD) in an interval of temperatures of 300–77 K and concentrations of 1.6×10^{-3}–8.0×10^{-6} mol/l are discussed. The room-temperature absorption and fluorescence spectra of DPD remained constant in a broad interval of concentration. The lowering of temperature of a solution to 148 K leads to the reduction of the long wavelength band and the formation of two maxima (at $\lambda = 374$ and 377.5 nm). It was found that their intensities' ratio depend on concentration as well as on the method of freezing the solution. The low-temperature fluorescence spectra are short-wave shifted at 35 cm^{-1}. The spectral modifications of rigid ethanol solutions of DPD were attributed to the formation of the associated forms of molecules due to van der Waals forces. Absorption spectra analysed at different cooling rates revealed a "sandwich" structure of associates at a fast rate of freezing and "foot" structure (angle 90°) at a slow rate of cooling. The distance between the associated molecules of DPD was estimated to be about 11 A. The nature of spectral modifications due to associations of DPD molecules is discussed. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

It is known [1–3] that very often it is not the isolated molecules, but their associated species, that are responsible for the spectral-luminescence properties of organic compounds. The so-called molecular excimers serve as such associates [4]. Excimers are dimers that are unstable in the ground state, with the complexes being formed only when the system is excited. The specific spectral manifestation of excimers is the emission band with an abnormally large Stokes shift (3000–5000 cm^{-1}). This phenomenon is not accompanied by any qualitative changes in the absorption spectra of the systems being studied, which indicates the lack of aggregation in the ground state.

The spectral study of the aggrågation of heteroaromatic molecules, including the problem of solvent microenvironment influence on aggregates structure dyes has received considerable attention [5–9]. The temperature dependence of the fluorescence self-quenching of tertiary amines in hydrocarbon solvents was investigated by transient decay measurements. The mechanism of quenching involves the intermediacy of bound excited-state-quenching molecular complexes, like exciplexes and excimers [10]. The formation of van der Waals dimers between heteroaromatic molecules (benzofuran, dibenzofuran, fluorene) in a supersonic jet provides a way to study excimer/exciplex formation in the gas phase [11]. The ion-pair dimer formation is evidenced through the appearance of isobestic points in the absorption spectra of the pyrylium derivatives of tetrafluoroborates as a function of concentration or temperature [12]. The low-temperature fluorescence of 2-acetylantracene was investigated in methylcyclohexane and ethanol [13]. The

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unusually large-site splitting caused by the formation of aggregates was observed when the temperature was dropped from 300 to 77 K. The influence of temperature on the aggregation process is rather complicated and not well understood.

2. Experimental part

The samples used for the studies of temperature and cooling rate dependence were prepared by solidifying of N,N-dibutyl-4,9-diazapyren-5,10-dione (DPD) in ethanol in a temperature-controlled liquid-helium cryostat. The accuracy of the temperature determination was 0.05 K. Glassy samples of DPD solution were obtained by immersing 3-mm-i.d. quartz tubes rapidly in liquid nitrogen. During the slow freezing of the solutions, the tubes were placed in cryostat for about 10 min. The investigated interval of concentration was 1.6×10^{-3}–8.0×10^{-6} mol/l. Spectral measurements were carried out using a SDL-2 spectrometer.

3. Results and discussion

Fig. 1 shows the absorbance spectra of ethanol solutions of DPD at 293–148 K. The absorbance spectra have two intensive bands at 350–380 and 230–270 nm and a less intensive band at 290–320 nm. At room temperature the absorbance spectra of DPD remain constant in a broad interval of concentrations 1.6×10^{-3}–8×10^{-6} mol/l. The lowering of temperature to 172 K was accompanied by the formation of a shoulder on the long wavelength edge of the absorbance band. At the temperature of 148 K, we observed the splitting of the band and
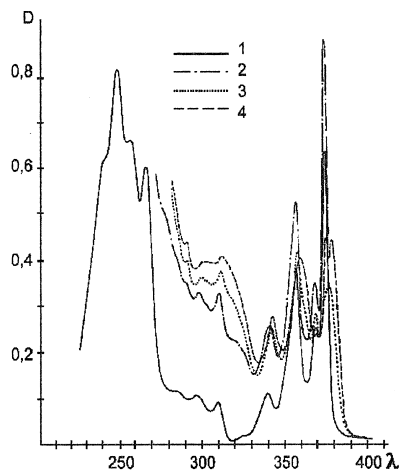

Fig. 1. Absorbance spectra of N,N-dibutyl-4,9-diazapyrene-5,10-dione in ethanol at 293 (1), 223 (2), 172 (3) and 148 K (4).

the formation of two maxima at 374 and 377.5 nm. It is important to note that at concentrations of solution higher than 7.5×10^{-6} mol/l the intensity of long-wave absorbance band increases and the intensity of short-wave absorbance band decreases.

At temperature of 77 K the ratio of intensities of bands at 374 and 377.5 nm was dependent both on the concentration of solution and the dynamics of solution's freezing. At a concentration of 1.6×10^{-4} mol/l and a fast rate of cooling, the ratio of intensities was about 1.25 and upon sufficiently slow rate of cooling it was approximately 1.02. At the concentration range from 10^{-4} to 10^{-5} mol/l and a fast rate of freezing the ratio intensities increases from 1.25 to 2.6. When the concentration of solution was 8×10^{-6} mol/l, the long-wave maximum at 377.5 nm disappeared. The absence of concentration changes in absorbance spectra at 293 K suggests that in a polar solvent there is a small degree of association of DPD's molecules. We assume that the degree of association, mostly dependent on the van der Waals forces, can be increased when the temperature decreases and the concentration of solution exceeds 10^{-6} mol/l.

The above-mentioned experimental results together with the analysis of literature data [12–14] regarding the association processes in similar molecular systems allows us to suggest the "sandwich" structure of DPD's associates.

It is known [1,14] that in the case of "sandwich" associates the angle between associate molecules, θ, can be determined by the equation: $f_k/f_d = (1 + \cos \theta)/(1 - \cos \theta)$, where f_k and f_d are the oscillator forces of short-wavelength and long-wavelength absorbance bands in the spectrum of associate.

The absorbance spectrum of DPD at 77 K (Fig. 1) demonstrates approximately equal intensities of long-wavelength and short-wavelength bands, and, therefore, approximately equal values of their oscillators force. These data show that the angle θ between associate molecules is close to $90°$ which may correspond the "foot" structure of DPD associates. We assumed that at slow cooling rate when the ratio of intensities of bands at 374 and 377.5 nm was 1.02 the "foot" structure of associate was predominant. However, at fast freezing rate when this ratio was 1.25, the intensity of a long-wave band decreases and molecules have no time "to be marshalled" and the angle between them becomes smaller. The geometry of associates essentially changes in accordance with temperature and freezing rate.

We have used the following equation for estimating the distance between molecules in the associate [14]:

$$R = \left[\frac{2.14 \times 10^{10} \cos \alpha \times f}{\Delta v \times v} \right]^{1/3} \text{Å},$$

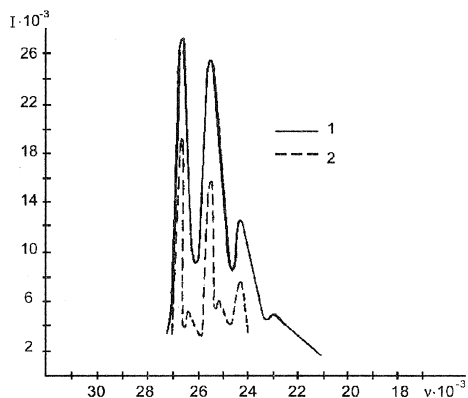where $f = 0.5$ is the oscillator force of an individual DPD molecule calculated from the absorbance spectrum at

Fig. 2. Fluorescence spectra of DPD in ethanol at 393 (1) and 77 K (2).

Fig. 3. Luminescence spectra of DPD in ethanol at 77 K and excitation 340 (1) and 375 nm (2).

300 K, $\Delta v = 250$ cm^{-1} is the value of split between two absorbance bands, $v = 2640$ cm^{-1} is the value of transition frequency and α is the angle between the transition moments.

According to our evaluation, at $\alpha = 0$ the distance between associated molecules is 11.7 Å. With an increase of angle values up to 30°, 45° and 60° the distance R decreases up to 11.1, 10.5 and 9.32 Å, correspondingly.

Fig. 2 shows the fluorescence spectra of ethanol solution of DPD at 293 and 77 K. It was found that the change of concentration of solution from 1.6×10^{-3} to 8×10^{-6} mol/l had no influence on the position of fluorescence bands maximum at room temperature. The fluorescence spectra at 77 K have three narrow bands with maxima at 26 850, 25 530, 24 220 cm^{-1} as well as two relatively broad bands with maxima at 26 300 and 25 100 cm^{-1}. The fluorescence maxima of DBD at 25 530 and 24 220 cm^{-1} measured at 77 K are bathochromatically shifted by approximately 45 cm^{-1}, relative to the positions of maxima in the fluorescence spectra measured at room temperature. However, the fluorescence maximum at 26 850 cm^{-1} is blue shifted as compared to its position in the fluorescence spectrum at room temperature. The values of Stokes shifts measured for short-wavelength part of absorbance spectrum and its long-wavelength part differ significantly. Thus, for the absorbance maximum at 371 nm this value was approximately equal to 104 cm^{-1}, and for the absorbance maxima at 374 and 377.5 nm these values were equal to 1208 and 2270 cm^{-1}, respectively.

Fig. 3 shows the luminescence spectra (fluorescence and phosphorescence were not separated) of ethanol solution of DPD at 77 K using two excitation wavelengths. It was fou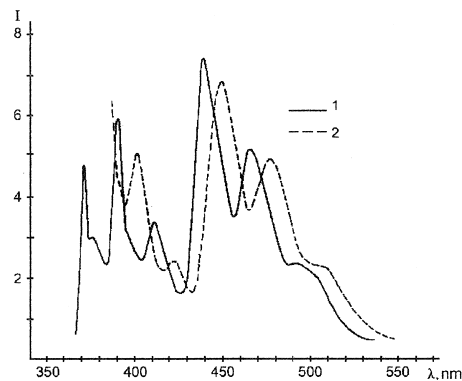nd that at excitation wavelengths shorter than 370 nm the fluorescence spectrum does not depend on the excitation wavelength. However, at excitation wavelengths longer than 375 nm the fluorescence spectra have a red shift (about 10 nm) with the following positions of maxima: 24 938, 23 641, 22 272, 21 053 cm^{-1}. These spectral observations, in our opinion, confirm the existence of two fluorescence centers representing individual and associated molecules of DPD.

References

[1] N.N. Barashkov, T.V. Sakhno, O.A. Khakhel, R.N. Nurmukhametov, Russ. Chem. Rev. 62 (1993) 579.
[2] N.N. Barashkov, O.A. Gunder, Fluorescent Polymers, Ellis Horwood, Chichester, 1994.
[3] N.N. Barashkov, T.V. Sakhno, R.N. Nurmukhametov, O.A. Khakhel, Polymer 37 (1996) 1109.
[4] M. Gordon, W.R. Ware, The Exciplex, Academic Press, New York, 1975.
[5] V.I. Ughakov, Russ. Chem. Rev. 61 (1992) 1114.
[6] M.L. Degtyar, V.M. Rozenbaum, J. Struct. Chem. 36 (1995) 189.
[7] T.P. Burghard, I.E. Lyke, K. Ajtai, Biophys. Chem. 59 (1996) 119.
[8] O.U. Rodionova, S.N. Shcherbo, V.I. Ughakov, J. Phys. Chem. 68 (1994) 48.
[9] T.T. Ndou, R. Wandrushka, J. Lumin. 46 (1990) 33.
[10] B.R. Ramachandran, A.M. Halpern, J. Photochem. Photobiol. A: Chem. 58 (1991) 1.
[11] W.T. Yip, D.H. Levy, J. Phys. Chem. 100 (1996) 11539.
[12] I. Lampre, D. Markovitsi, J. Phys. Chem. 100 (1996) 10701.
[13] E.C. Meister, G.W. Suter, U.P. Wild, J. Phys. Chem. 92 (1988) 6537.
[14] L.I. Alperovich, J. Struct. Chem. 35 (1994) 49.