Molecular Crystals and Liquid Crystals

High Pressure Study on Intramolecular Excited Complex and Role of Ground-State Conformation

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The effects of high pressure on the luminescence properties of bichromorphic compounds, *i.e.*, (9-anthryl)-$(CH_2)_n$-(9-anthryl) systems and p-$(CH_3)_2 NC_6 H_4$-CH_2-(9-anthryl), were investigated. They were studied in a polymeric environment in order to eliminate intermolecular interactions. Two types of intramolecular interactions, *i.e.*, "through-bond interaction" and "through-space interaction," are distinguished by the different pressure effects, depending on the ground-state molecular conformations.

INTRODUCTION

As the primary effect of pressure is to increase overlap between adjacent molecular orbitals, the formation of excited molecular complexes is expected to be highly pressure dependent. The application of high pressure also offers a useful means of determining whether an emission band is from a $(\pi\pi^*)$ state or from an excited complex state, because it has been established that the vibronic bands in a given electronic band display identical pressure dependence.[1,2] Excimers have been observed at high pressures even in a crystal such as anthracene[3-6] which has not a dimer arrangement in the unit cell. Some intramolecular CT compounds have been also studied at high pressures.[7] The physical and chemical nature of these formation processes have been extensively studied. However, of particular inter-

est is the role of geometric effects, *i.e.*, the relative orientations of the two interacting molecules.

For bichromorphic compounds in which two chromophores are linked by a flexible atomic chain, a rotational motion is required to bring them into a favorable conformation to form the "through-space" excimer-like interaction. In a rigid matrix, however, rotations are restricted, so that it seems to be necessary that the pairs of chromophores be favorably oriented to a certain degree in the ground state.
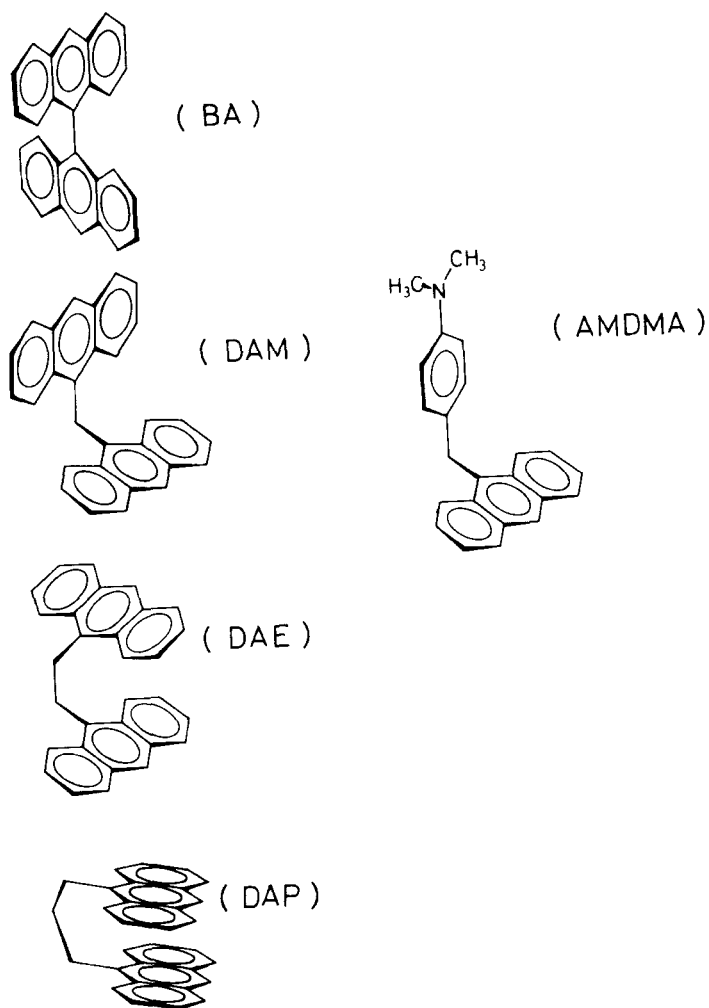

FIGURE 1   Structure of the studied compounds that form intramolecular excited complex (IEC).

The objective of this research is to examine the intramolecular interaction between the two chromophores which may interact in the excited state and the rearrangement of the molecular conformation which may contribute by the application of high pressures. The compounds studied are (9-anthryl)-$(CH_2)_n$-(9-anthryl), $n = 0, 1, 2, 3$ i.e., 9,9'-bianthryl (BA), di(9-anthryl)-methane (DAM), 1,2-di(9-anthryl)ethane (DAE), and 1,3-di(9-anthryl)propane (DAP), and p-$(CH_3)_2NC_6H_4$-(9-anthryl) (AMDMA), which are listed in Figure 1 together with the abbreviations used. The measurements were carried out in poly(methyl methacrylate) (PMMA) matrix at sufficiently dilute conditions. Further, a more consistent discussion will be offered by referring to the reanalyzed results of our previous paper.[8]

EXPERIMENTAL SECTION

All the compounds were synthesized by a slight modification of the published procedure[9] and were purified by several recrystallizations as well as sublimation in vacuo. The methods of preparing PMMA and forming sample films, as well as the high pressure luminescence techniques have been described elsewhere.[8,10] Dichloromethane was used in the preparation of the sample films.

Relative quantum yields were determined by integrating the intensity of emitted light. The fluorescence measurements were made under photostationary state conditions at 298 K. The 27300 cm^{-1} band of a Hanovia 200 W Hg-Xe arc lamp was used to excite the anthracene moiety. Quinine sulfate 0.1 N sulfuric acid was used as a calibration of sensitivity depending on wavelength. Each spectrum consisted of approximately 60 time-averaged data points spaced 3.0 nm apart. The spectra were fit to four Gaussians; three for locally excited state and one for excited complex state. Experimental observables include the peak location and the ratio of the quantum yields in excited complex to locally excited state up to 50 kbar.

RESULTS AND DISCUSSION

Every compound examined exhibited a characteristic broad emission band which can be attributed to the intramolecular excited complex (IEC). They are lower in energy by 2000-3000 cm^{-1} with respect to the locally excited (LE) bands corresponding to the anthracene ^1L_a emission. The effects of pressure on the fluorescence peak location are shown in Figure 2. The pressure shifts of LE bands, except for BA,

correspond to 0–1 emission of anthracene, which is also included in the Figure for the sake of comparison. The IEC bands showed a slightly larger red-shift than the LE bands. For BA both bands are anomalously sensitive to pressure.

No changes of the fluorescence excitation spectra were observed with pressure except for the peak shift. The intermolecular contribution is eliminated entirely, since the aromatics are dispersed unimolecularly in PMMA matrix. In addition, the emission spectra showed no difference among the solvents used for the preparation of the sample films.
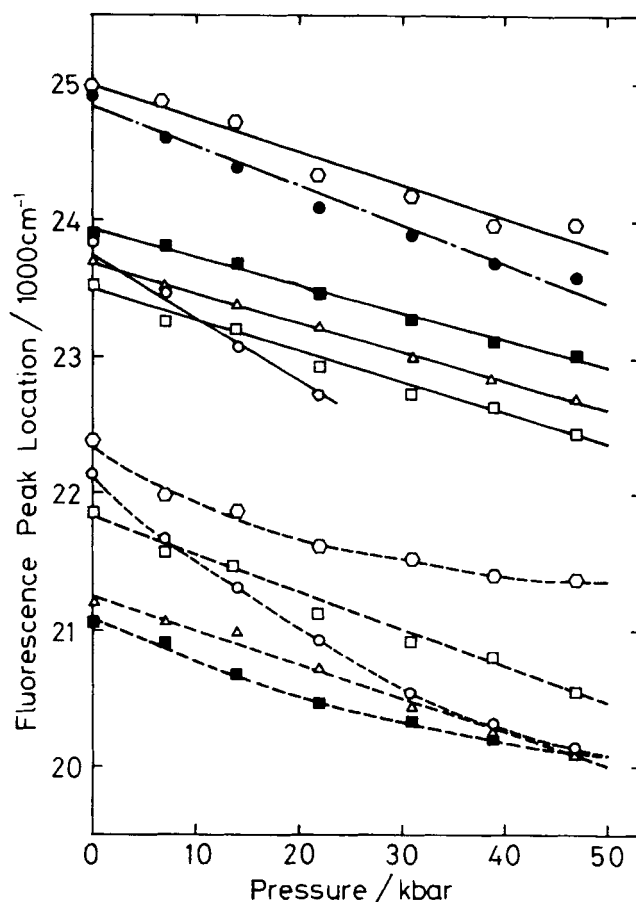

FIGURE 2   Effect of pressure on the fluorescence peak location of BA (O), DAM (△), DAE (□), DAP (o), and AMDMA (■) in PMMA matrix. Anthracene 0–1 peak (●) is presented as a comparison. Solid line: LE band. Broken line: IEC band.

The yield of the IEC emission is small at atmospheric pressure, while as the pressure is increased, it increases at the expense of the LE emission. Figure 3 shows the effect of pressure on the ratio of the fluorescence quantum yields from the IEC state (ϕ_{IEC}) and from the LE state (ϕ_{LE}). These spectral transformation are completely reversible with pressure.

According to Schneider and Lippert,[11,12] the intramolecular excited electron-transfer state of BA has been first reported in polar solvents. The state is characterized by almost complete CT-like behavior with a high dipole moment as established in our previous paper.[10] It has been suggested that a resonance interaction through the 9–9′ bond occurs at the excited state by changing the twist angle (θ) between the two anthracene molecular planes. In the ground state, however, the two chromophores are strongly twisted with respect to each other, near to
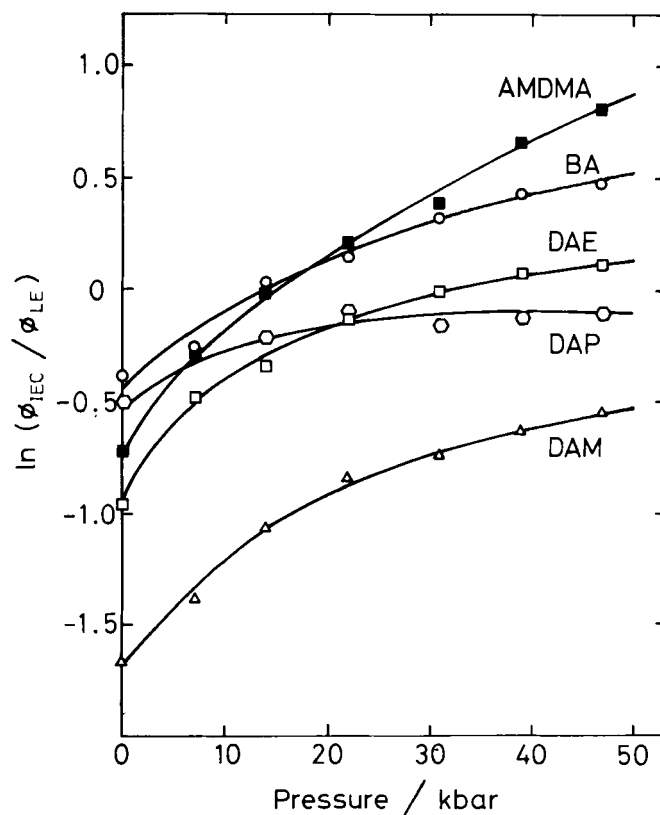

FIGURE 3   Effect of pressure on the ratio of the fluorescence quantum yield.

90°, due to nonbonding repulsions. The increase of viscosity by more than ca. 100 cP or the freezing of solvents, strictly quenches the formation of the electron-transfer state.[13] In glycerol only the LE emission is observed.

By extrapolation of the results of BA in fluid solutions, quenching of the IEC state is expected in the compressed rigid matrix. The present results in PMMA matrix, however, indicate that an increase of pressure causes the IEC yield to increase relative to the LE yield. Since the PMMA matrix is glassy at room temperature, the IEC conformation cannot be formed by the normal diffusional rotational motion. It is to be noted that the external pressure tends to have a small decreasing effect on exciton migration.[14]

Therefore, we can conclude that the prominent increase in the yield ratio with pressure may originate from a change in the molecular conformation caused by the high external pressure. High pressure will cause a change of the twist angle. Such a deformation may be possible indeed not only at the excited state but also at the ground state. The change of θ, however, lead to a resonance interaction only at the excited state, because ^1L_a state that is the lowest excited state (S_1) of anthracene has a polarization parallel to the short molecular axis of anthracene.

Table 1 gives the value of $\ln(\phi_{IEC}/\phi_{LE})$ at 1 bar and the initial slope of $\ln(\phi_{IEC}/\phi_{LE})$ against pressure. The amount of the increase in the quantum yield ratio with pressure becomes smaller in the order of DAM, DAE, and DAP. As for DAE, an excimer type emission has been observed in a fluid solvent and a parallel pair but small overlapped conformation has been proposed.[15-17] Thus, there is a possibility for DAE to bring about a "through-space interaction," which is similar to that suggested in our previous paper.[8]

DAP has the most favorable number of linked carbon atoms for parallel pair conformation. The fluorescence bands for 1,9-DAP in 19230 cm^{-1} and 1,2-DAP in 21280 cm^{-1} have been ascribed to the

TABLE 1

The values of $\ln(\phi_{IEC}/\phi_{LE})$ at 1 bar and its initial
pressure dependency, $d \ln(\phi_{IEC}/\phi_{LE})/d P$

	BA	DAM	DAE	DAP	AMDMA
$\ln(\phi_{IEC}/\phi_{LE})$	−0.42	−1.66	−0.89	−0.37	−0.67
$d \ln(\phi_{IEC}/\phi_{LE})/d P$ ($\times 10^{-2}$ kbar^{-1})	3.15	4.68	4.44	1.82	7.59

intramolecular excimer.[18] Thus, the fluorescence of the present 9,9'-DAP in 22380 cm^{-1} can be also ascribed to the intramolecular excimer with parallel pair conformation. This is evidenced from the smallest pressure effect on the peak shift as well as on the quantum yield ratio, since the stable preformed conformation is considered to be scarcely affected by compression. Namely, such a stable excited complex as in the intramolecular excimer of DAP, which originated from a complete overlapped conformation by "through-space interaction," shows the smallest pressure dependency.

On the other hand, the larger value of ϕ_{IEC}/ϕ_{LE} for AMDMA as compared with DAM is considered to be due to the larger donor-acceptor character. Moreover, the larger increase in ϕ_{IEC}/ϕ_{LE} of AMDMA with pressure than that of dianthrylalkanes may indicate that the IEC conformation of AMDMA is accomplished by a smaller structural change. This may reflect the fact that the rotational re-arrangement occurs at the P-N, N-dimethylanilino group as proposed by Grabowski, et al.[19] The less bulky P-N, N-dimethylanilino group may also have a possibility to rotate even in the PMMA matrix.[20]

As discussed above, the preformed sites or the ground-state molecular conformations are considered to play an important role for the IEC formation in rigid media. In relation to this, also it has been suggested for dinaphthylalkane systems by the calculation of conformational energy that the similarity in the conformation between ground- and excited-state is a crucial factor for intramolecular excimer formation.[21] Probably high pressure affects them to perturb their structures favorably to form and stabilize the IEC conformation.

CONCLUSION

For BA and DAM, the IEC emission is considerably due to "through-bond interaction," whereas with increasing number of the linked carbon atom, "through-space interaction" becomes gradually effective. For DAP, the IEC emission originated from "through-space interaction," which is characterized by a small pressure dependency in the energy shift as well as in the quantum yield ratio.

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