Fluorescence Spectra of 1,1′-Binaphthyl and Related Compounds at High Pressures

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Relative to the related compounds 2,2′-binaphthyl (I) and 2,2′-dimethoxy-1,1′-binaphthyl (II), the pressure dependence of the fluorescence of crystals of 1,1′-binaphthyl (III) is complex. Compression to 30 kbar at room temperature shifts the ^{1}La fluorescence spectra of all three compounds to longer wavelength but, for I and II does not change the intensity profile, except for some 0-0 reabsorption. For III, this red shift characteristic of ^{1}La fluorescence spectra is dominated by growth of new bands about 3.5 to 5.0×10^3 cm^{-1} to lower energy. Similar new bands are observed when 1,1′-binaphthyl crystals are compressed at 90 K or resolved crystals are compressed at room temperature, but are not found to 30 kbar for dilute solutions of 1,1′-binaphthyl in polyacrylonitrile. The planes of adjacent naphthyl residues along $\vec{b}$ in the crystal are parallel but offset, the normal distance between planes being 3.55 Å; Raman spectra provide no evidence for a structural phase transformation upon compression. These new bands are assigned as the binaphthyl excimer.

The molecular spectroscopy of 1,1′-binaphthyl is unusual in many respects due to the strong dependence of the energies of its excited electronic states on the angle, θ, between the planes of the two naphthyl residues. In the crystal or rigid matrices (methyltetrahydrofuran or methanol glass) at low temperatures, the fluorescence and first absorption band are mirror images and closely resemble comparable spectra of naphthalene.[1-4] These observations are interpreted to imply that the equilibrium value of θ for both the ground and lowest excited state is approximately $\pi/2$; the X-ray structure of the crystal suggests $\theta=68°$ at room temperature.[5] In fluid solutions, the structure of the fluorescence spectrum resembles more closely the ^{1}La absorption of naphthalene and the fluorescence decay rate ($\approx10^9$ s^{-1}) is more typical of the ^{1}La fluorescence of anthracence and larger linear polyacenes. This transformation of the fluorescence has been interpreted in terms of a thermally-activated crossing from the ^{1}Lb to a ^{1}La excited state which can be stabilized relative to ^{1}Lb by rotation of the naphthyl residues toward $\theta=0$ or $\theta=\pi$.[1,4]

This report describes yet another fluorescence transformation observed for crystalline 1,1′-binaphthyl, but not for dilute solutions of 1,1′-binaphthyl in polyacrylonitrile, for crystalline 2,2′-binaphthyl or for derivative such as 2,2′-dimethoxy-1,1′-binaphthyl. Upon compression of crystals of 1,1′-binaphthyl to pressures above 5 kbar, new bands appear in the fluorescence spectra about 3.5 to 5.0×10^3 cm^{-1} to lower wave numbers from the origin of the ^{1}La fluorescence. These bands increase in intensity with compression such that, at 30 kbar, they dominate the emission spectrum. This spectral transformation is completely reversible to compression at room temperature (nominally 295 K) and at 90 K. The new spectrum is assigned as an excimer fluorescence originating from pairs of binaphthyl molecules favorably disposed along the $\vec{b}$ axis of the crystal. Both dilute solution in polyacrylonitrile and substitution at the 2 and 2′ positions prevent similar intermolecular naphthyl residue interactions between 1,1′-binaphthyl molecules.

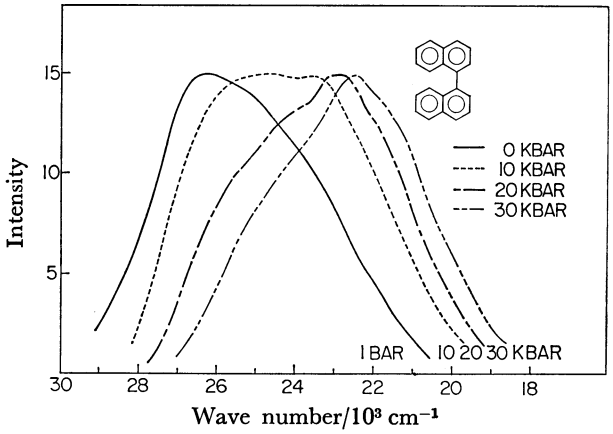

Fig. 1. Fluorescence spectra of 1,1′-binaphthyl at 295 K as a function of pressure.

Experimental

Commertially available reagent grade of 1,1′-binaphthyl from Eastman Kodak Co. was recrystallized from acetic acid and identified by infrared spectra.[6] 2,2′-dimethoxy-1,1′-binaphthyl were kindly provided by Dr. R. Helgesson of this department. The high pressure techniques for room[7,8] and low[9] temperatures are described elsewhere. The fluorescence from the samples which were excited at 3130 Å emission from 120W PEK Labs. Inc. high pressure mercury arc lamp was measured by means of front surface illumination in order to minimize reabsorption. The fluorescent intensities obtained at high pressures are normalized to that at 0 kbar. For Raman spectral measurement, a Spectra-Physics Model 165 argon laser was used for excitation. A Spex double monochrometer and photon-counting techniques were used to analyze the spectrum.

Results and Discussion

Fluorescence spectra of polycrystalline samples of 1,1′-binaphthyl at room temperature and 90 K at 1 bar, 10, 20, and 30 kbar are shown in Figs. 1 and 2. A typical pattern of other aromatics emerges from the spectra. The high wave number edge of the spectra appear to shift by -50 cm^{-1} kbar^{-1}, although reabsorption and the changing spectral profile make this value difficult to determine. For more important is the growth of intensity of new bands at low wave num-

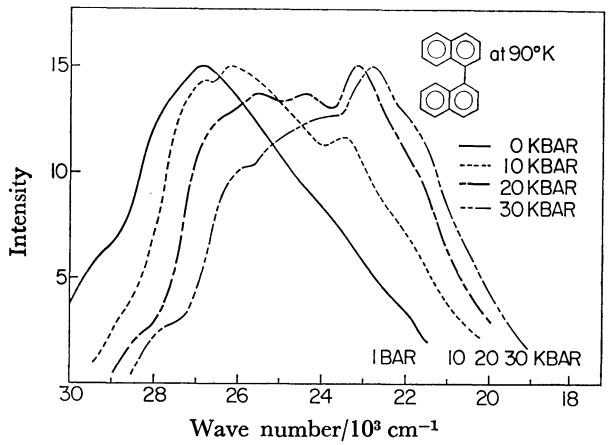

Fig. 2. Fluorescence spectra of 1,1′-binaphthyl at 90 K as a function of pressure.

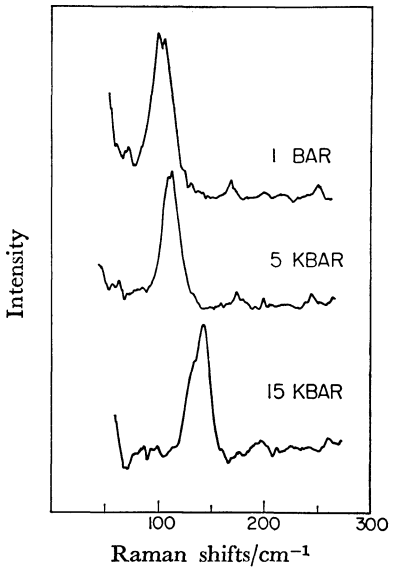

Fig. 3. Raman spectra of 1,1′-binaphthyl at 1 bar, 5 and 15 kbar.

bers, 3.5—5.0×10³ cm⁻¹ below the shifted 0-0. These transformation are completely reversible upon decompression. Similar new bands are observed when crystals of partially resolved 1,1′-binaphthyl are compressed.

Figure 3 shows the Raman spectra of polycrystalline 1,1′-binaphthyl at several pressures. These indicate that possibility of phase transition is very minor up to 15 kbar.

The new bands at low wave numbers in the fluorescence spectra of 1,1′-binaphthyl resemble in many respects new bands observed in the spectra of other crystalline aromatics at high pressures.[10–12] These spectra have been assigned to excimers formed by suitably oriented pairs of molecules at defect sites.

Figures 4 and 5 display the fluorescence spectra of 2,2′-binaphthyl and 2,2′-dimethoxy-1,1′-binaphthyl as a function of pressure. The primary effect of compression is to shift the fluorescence to lower wave numbers, by −30 cm⁻¹ kbar⁻¹ for 2,2′-binaphthyl and by about −40 cm⁻¹ kbar⁻¹ for 2,2′-dimethoxy-1,1′-binaphthyl. Except for some increased reabsorption of the 0-0

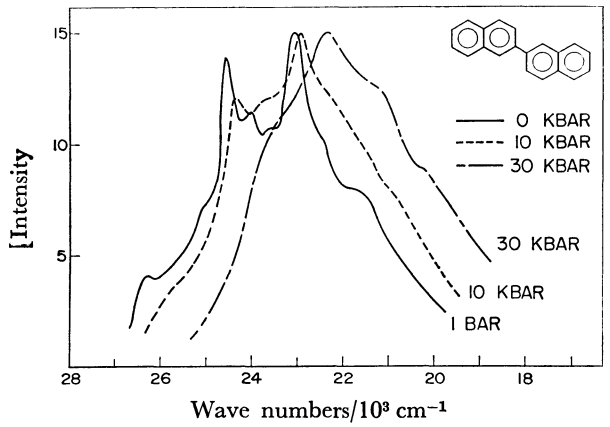

Fig. 4. Fluorescence spectra of 2,2′-binaphthyl at 1 bar, 10 and 30 kbar.

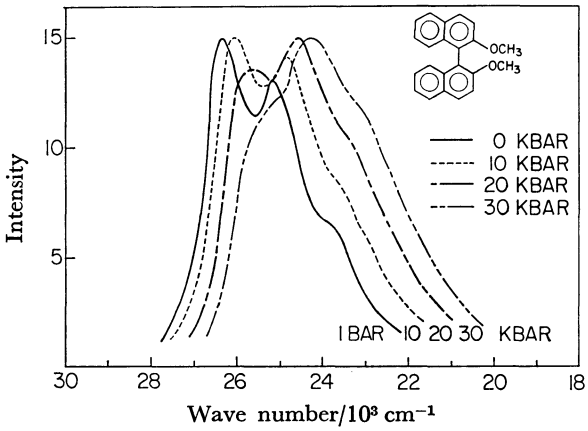

Fig. 5. Fluorescence spectra of 2,2′-dimethoxy-1,1′-binaphthyl at several pressures.

band at high pressures, the intensity profiles of these spectra change only slightly with compression which is the exception for aromatic hydrocarbons.[10–12] The interesting observation here is that the new bands are observed for 1,1′-binaphthyl but not for 2,2′-binaphthyl or 2,2′-dimethoxy-1,1′-binaphthyl. If the excimer fluorescence originated at defects, some excimer-like fluorescence would be anticipated from these compounds.

As steric hindrance between two naphthalene residues is at minimum in 2,2′-binaphthyl among various binaphthyls,[13] charge or excitonic resonance between two naphthyl residues should be maximized in 2,2′-binaphthyl. But no similar excimer fluorescence to 1,1′-binaphthyl was observed for 2,2′-binaphthyl. This indicates that the excimer fluorescence in 1,1′-binaphthyl is not originated from intramolecular interaction.

Figure 6 depicts the fluorescence spectra of dilute (≈10⁻³ M) solutions of 1,1′-binaphthyl in polyacrylonitrile at 1 bar and 30 kbar. No intensity redistribution is noted, which evidences the intermolecular nature of the excimer fluorescence.

An interesting explanation for the difference between 1,1′-binaphthyl and the other binaphthyls is suggested by examination of the structure of 1,1′-binaphthyl crystal.[5] Binaphthyl molecules with the same configuration are oriented with the planes of their naphthyl

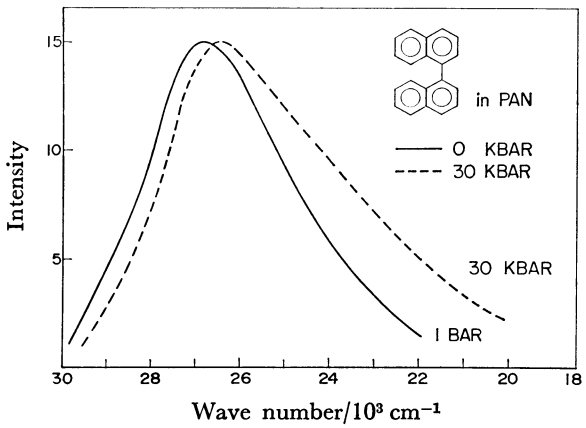

Fig. 6. Fluorescence spectra of dilute ($\approx 10^{-3}$ M) solutions of 1,1'-binaphthyl in polyacrylonitrile at 1 bar and 30 kbar.

residues parallel to each other and are separated by 6.35 Å along $\vec{b}$. For this geometry the normal distance between naphthyl planes of adjacent molecules is 3.55 Å, almost identical to the 3.53 Å separation between pyrene molecules in the dimeric structure of crystalline pyrene, the prototype excimer system.[14] Although the overlap of naphthyl residues is slightly less favorable for excimer emission, compression along $\vec{b}$ can compensate for this factor. However, substitution at the 2 position of the naphthyl residues necessarily increases the separation between binaphthyl molecules along this direction to a degree that should preclude excimer formation by this mechanism.

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