ARTICLES

Effect of Environment on Pressure-Induced Emission of Benzophenone, 4,4′-Dichlorobenzophenone, and 4-(Dimethylamino)benzaldehyde in Solid Media

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The pressure-induced emission of three aromatic carbonyls—benzophenone (BP), 4,4′-dichlorobenzophenone (DCBP), and 4-(dimethylamino)benzaldehyde (DMABA)—dissolved in solid polymers and also in their crystalline state has been studied. Under pressure all compounds dissolved in polymers reveal a significant enhancement of the luminescence emission in the low-pressure region. The degree of increase is strongly dependent on the type of polymer. DMABA exhibits both fluorescence and phosphorescence, whereas BP and DCBP molecules show only phosphorescence. For all these molecules a model based on the increase with increasing pressure of the amount of π,π^* character in the initially predominately n,π^* triplet state is proposed to account for the observed increase of the emission intensity. In the case of DMABA it is proposed that the increase of the π,π^* character in the triplet state increases the emission intensity in two concurrent steps: by an increase of the radiative rate from the triplet state and by a decrease of the intersystem crossing rate between singlet and triplet states. The first factor increases phosphorescence intensity, and the second one effects the fluorescence. In the case of BP and DCBP, where the intersystem crossing process is very fast, the increase of pressure increases mainly the radiative rate of the lowest triplet state. In contrast to the polymer matrices, the emission intensity of these compounds strongly decreases under pressure in their crystalline environment. This is explained in terms of the increasing role of the nonradiative processes due to a strong coupling of the vibronic states of the triplet to the environment. The observed decrease in luminescence intensity in the polymers at high pressures has the same explanation.

Introduction

It has been demonstrated that high pressure as a perturbing variable can be a very useful tool in the study of electronic states, changing the environment of molecules in a continuous and controlled fashion. In contrast to solvent methods, the high-pressure technique allows one to select a single medium and vary its volume over a very significant range, producing in this way major changes in density and dielectric properties without alteration of its chemical nature. In this paper we employ the ability of high pressure to enhance the interaction of aromatic carbonyl molecules with their surroundings in order to mix the character of the electronic states and thus modify their radiative and nonradiative characteristics.

The emissive characteristics of aromatic carbonyl compounds have been a subject of considerable interest in the past (see, e.g., refs 1−7), including studies under high pressure.[8−10] In typical aromatic carbonyls such as benzophenone or benzaldehyde, a metastable triplet was considered to be a “pure” n,π^* state, and this fact was believed to lead not only to the characteristic phosphorescence but also to the high photochemical reactivity of these compounds. Moreover, solvent studies have shown that the character of this lowest triplet is highly environmentally dependent. The processes involved are still under considerable debate.

The most recent studies of the optically detected magnetic resonance (ODMR)[11] and electron spin resonance (ESR)[12] of benzophenone and its derivatives indicate that the lowest excited triplet state of aromatic carbonyls may not be a pure n,π^* state because both the n and π^* orbitals of carbonyl group are mixed with the aromatic π system. In other words, the triplet may have both n,π^* and π,π^* character with a degree of mixing depending on the conformation of the phenyl rings with respect to the carbonyl group. Thus, a perturbation by a suitable substituent or solvent may produce a change in the lowest triplet state from primarily n,π^* to primarily π,π^* type, and this change is expected to be accompanied by an essential change in both the spectral and chemical behaviors of the carbonyl compounds as well as in their molecular geometry.

Since in aromatic carbonyls (specifically in ketones) the compression of medium may modify the twist of the phenyl rings relative to the carbonyl frame,[13] one would expect a substantial change in the character of the triplet state and so in phosphorescent properties. Indeed, our recent studies on a series of aromatic ketones and aldehydes as well as nitriles dissolved in rigid polymers show that these systems exhibit a strong dependence of their luminescence properties on external pressure.[14−16] In all these cases, the primary result of increasing pressure is a remarkable increase in the phosphorescence emission intensity.

In the present paper we extend our study to several media, polymeric and crystalline, to test the effect of environment on pressure-induced luminescence (PIL) of three aromatic carbon-

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yls: benzophenone (BP), 4,4′-dichlorobenzophenone (DCBP), and 4-(dimethylamino)benzaldehyde (DMABA). The molecules studied differ in the electronic character of the their component groups. All compounds possess the electron-accepting carbonyl group, but DCBP has additionally electron-accepting chloride groups and DMABA the electron-donating dimethylamino groups. It is believed that these differences in the molecular structures might be reflected in the pressure-induced interactions between these molecules and their solid media. We incorporate carbonyl molecules into polymeric matrices, since they are commonly considered as an efficient and attractive environment for the study of room temperature phosphorescence. For comparison to rigid polymers, some results in crystalline environments are also presented.

Experiment

BP (99%+), DCBP (99%), and DMABA (99%) were purchased from Aldrich Chemical Co. Before being used the compounds were additionally purified: BP was sublimed twice in vacuum, DCBP and DMABA were recrystallized several times from alcohol. The compounds were dissolved in poly(ethyl methacrylate) (PEMA, 250 000 MW, Polysciences), poly(vinyl chloride) (PVCl, HMW, Aldrich), and polystyrene (PS, 250 000 MW, Aldrich) using as solvents Spectranalyzed methylene chloride (MCl) for PEMA and PS and tetrahydrofuran (THF) for PVCl. Polymers and solvents were used without further purification, since they showed no emission when exposed to the laser line. After dissolving components the solutions were poured into a flat dish, and the solvent was allowed to evaporate at room temperature (MCl) and at elevated temperature (THF). Then the films were placed in a vacuum oven for a few days at temperature higher than 50 °C. Since it is known that atmospheric oxygen can very often be involved in the evolution of the long-living excited states, some solutions were degassed by bubbling nitrogen during evaporation of the solvent and stored in vacuum. Samples prepared in this way behaved like the samples prepared in the ordinary way, showing no effect of the deoxygenation. In general, concentrations of 10^{-3} mol of compound per mole of monomer unit were employed. However, in the case of BP and DCBP, because of the low initial (atmospheric pressure) emission intensity, most of the experiments were performed at a concentration of 10^{-2}. All films obtained, approximately 50−100 μm thick, were optically clear.

The spectroscopic experiments were performed in a gasketed Merrill-Bassett diamond anvil cell (DAC) at room temperature, utilizing low fluorescent and UV transmitting diamonds. A light mineral oil served as a pressurizing medium, and pressure was determined by the ruby fluorescence technique. Over our experimental pressure range (0−100 kbar) the ruby R_1 peak fluorescence wavelength is linearly dependent on pressure with a slope of 0.0365 nm/kbar.[17] The samples were excited with the 325 nm line of a He−Cd laser in conjunction with various filter combinations. The output laser intensity was estimated to be 8×10^{15} photons/s, and the maximum effective intensity at the sample was 2 orders of the magnitude lower (see Ref 18 for details). Almost all the experiments were performed with incident intensity about 2×10^{12} photons/s unless mentioned otherwise.

The application of the DAC to high-pressure luminescence experiments as well as the experimental setup for the luminescence spectra and UV/vis absorption measurements has been described before.[19−20]

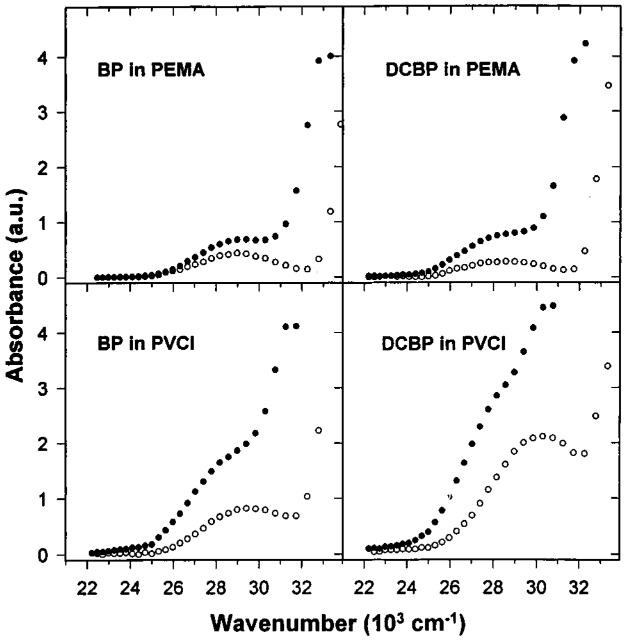

Figure 1. Absorption spectra of BP and DCBP in polymers at low and at elevated pressure: (○) BP in PEMA and PVCl at 5 kbar, DCBP in PEMA at 10 kbar, and DCBP in PVCl at 0 kbar; (●) BP in PEMA and PVCl at 53 kbar and DCBP in PEMA and PVCl at 50 kbar.

Results

Spectra. In the region of laser excitation, i.e., 30.77×10^3 cm^{-1} ≡ 325 nm, both BP and DCBP exhibit a broad band with low absorption coefficient and small shift to lower energy with increase of pressure (Figure 1). However, the shape of this band is considerably perturbed by overlap with a strong high-energy band. The significance of the overlap increases with increasing pressure as well as polarizability of the polymer (see PEMA versus PVCl). Moreover, DCBP shows a stronger overlap of both bands than BP does, at either atmospheric or elevated pressure. The pressure and matrix dependence of the low- and high-energy band confirm their well-known assignments as $S(n\rightarrow\pi^*)$ and $S(\pi\rightarrow\pi^*)$ transitions, respectively.

The emission spectra of BP and DCBP in PEMA and PVCl at room temperature and atmospheric pressure show a very low emission intensity (phosphorescence) with a characteristic vibrational structure. Under pressure the spectra lose their structure and are transformed into smooth curves with high intensities and maxima shifted to lower energies (red shift) (Figure 2). The size of the pressure shift is stronger for DCBP than BP and also stronger in PVCl than PEMA.

At atmospheric pressure DMABA luminescences very inefficiently in all polymers studied, and its emission spectrum exhibits essentially one peak with a shoulder on the low-energy side. The intensity taken at the maximum of the peak is roughly an order of magnitude higher than the intensity at the shoulder (which is approximately at 20.8×10^3 cm^{-1}). The maximum of the main emission peak (fluorescence) is located at (26.7, 26.4, and 26.0) $\times 10^3$ cm^{-1} respectively for PS, PEMA, and PVCl and shifts markedly with increasing pressure to lower energies (see Figure 3). Additionally, under pressure the lower energy shoulder transforms to a strong emitting peak. This new peak that we call hereafter the low-energy band (LEB) appears to be phosphorescence with a considerably smaller shift with increasing pressure than the high-energy band (HEB) and with an approximate (decays are not exponential) rate constant of 6 s^{-1}. The absorption characteristics are discussed in a previous paper.[15]

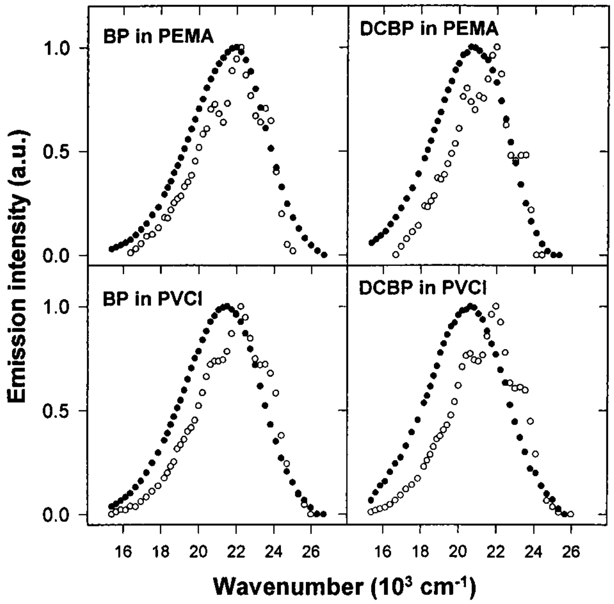

Figure 2. Emission spectra of BP and DCBP in PEMA and PVCl at 0 (○) and 60 kbar (●). All spectra are normalized to the same maximum value.

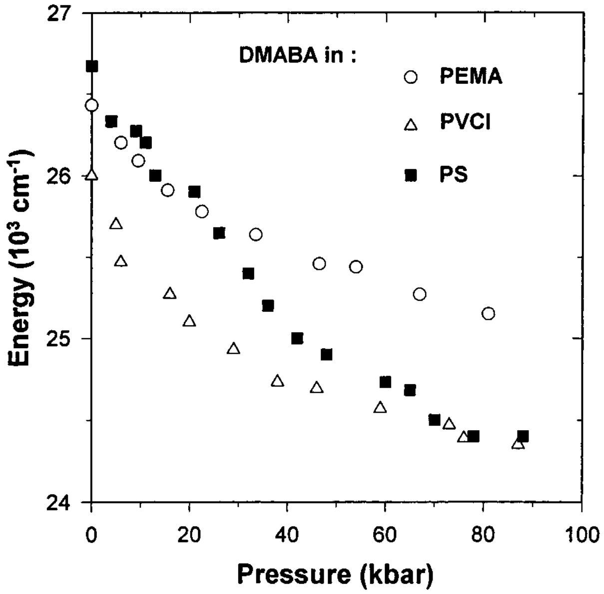

Figure 3. Pressure dependence of energy of the fluorescence peak of DMABA in PEMA (○), PVCl (△), and PS (■).

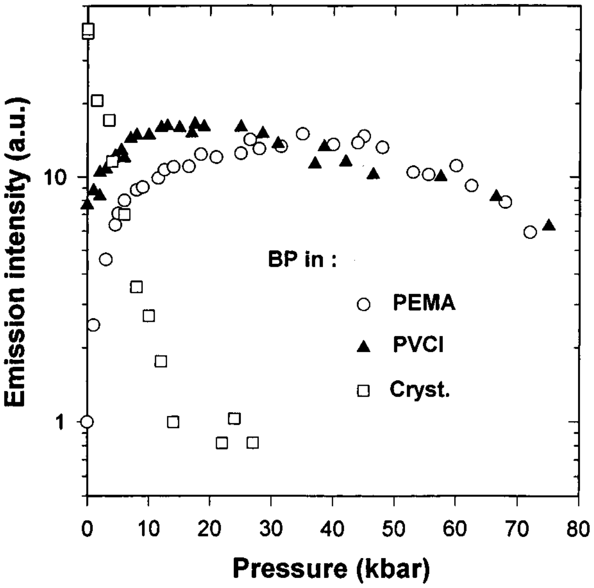

Figure 4. Pressure dependence of the relative phosphorescence intensity (at the peak maximum) of BP in PEMA (○), PVCl (▲), and crystal (□). Intensities at atmospheric pressure are normalized to the intensity of BP in PEMA.

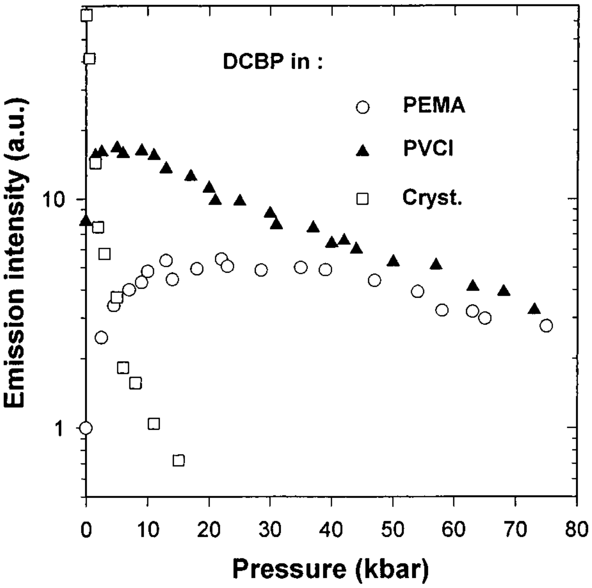

Figure 5. Pressure dependence of the phosphorescence intensity (at the peak maximum) of DCBP in PEMA (○), PVCl (▲), and crystal (□). Intensities at atmospheric pressure are normalized to the intensity of DCBP in PEMA.

Emission Intensity. Because the emission intensity of all systems studied change significantly under prolonged irradiation (see the following paper), the pressure dependence of the emission intensity has been determined at each pressure on a fresh (not previously irradiated) sample, from the measurement of the intensity at the maximum emission. This procedure allowed us to minimize the exposure of the sample and thus to avoid any influence of irradiation on the pressure dependency.

The results for the pressure effect on phosphorescence intensity of BP and DCBP molecules in polymers and crystals are presented in Figures 4 and 5. As one sees, for both molecules in the same matrices, very similar changes under pressure are observed. In both polymers, PEMA and PVCl, the phosphorescence intensity initially increases and then above a certain pressure (different in each case) gradually decreases. The increase is several times larger in PEMA than PVCl and also larger for BP than DCBP. Furthermore, the intensity maximizes sooner (at lower pressures) in PVCl than PEMA as well as for DCBP relative to BP.

In crystalline BP and DCBP in contrast to their behavior in polymer matrices, over the whole pressure range only a decrease of the intensity is observed. The effect of pressure is so spectacular that the emission from crystals practically vanishes within 15 kbar. It should be noted that this effect was essentially reversible and reproducible.

In the case of DMABA the effect of pressure on emission intensity is much larger than for BP and DCBP (see Figures 6 and 7). First of all, DMABA exhibits with increasing pressure, regardless of the type of the polymer matrix, a remarkable increase in the intensity of the LEB and a substantial increase in the HEB also. In the former, the intensity increases rapidly, 200, 50, and 700 times respectively in PEMA, PVCl, and PS within 10 kbar, but then decreases as the pressure is further

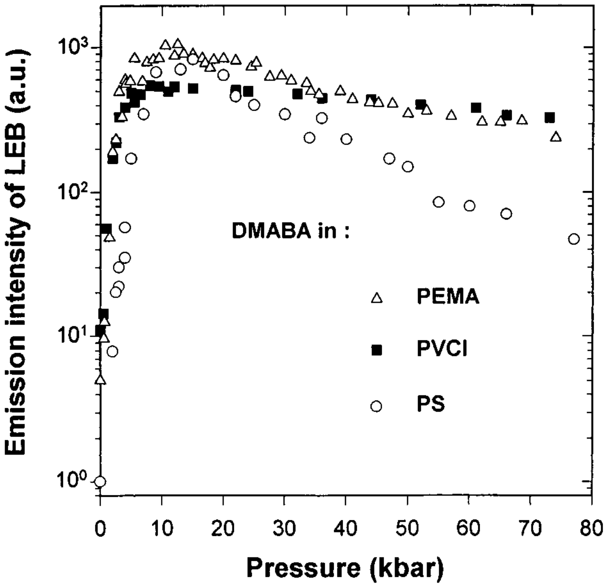

Figure 6. Pressure dependence of the relative phosphorescence intensity of DMABA in PEMA (△), PVCl (■), and PS (○).

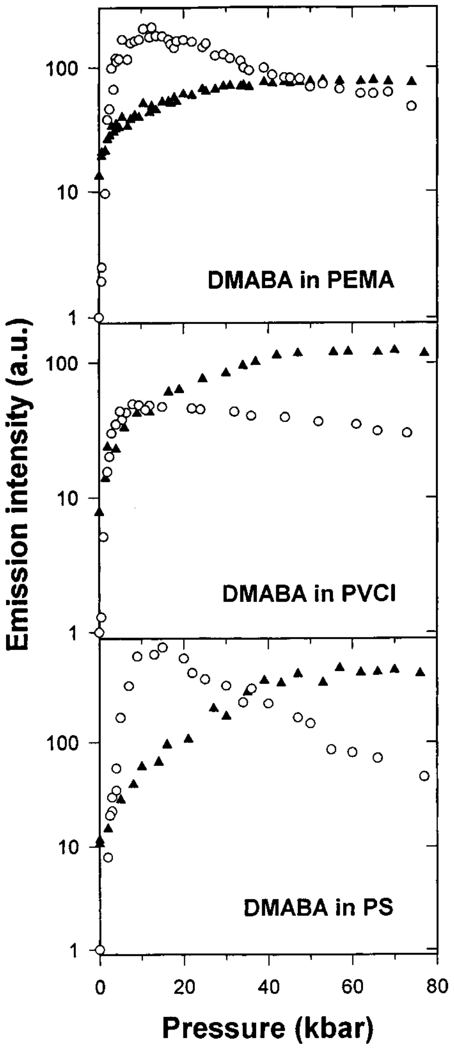

Figure 7. Pressure dependence of the phosphorescence (○) (LEB) and fluorescence (▲) (HEB) intensity of DMABA in several polymers. In each case the intensity is normalized to the initial phosphorescence intensity.

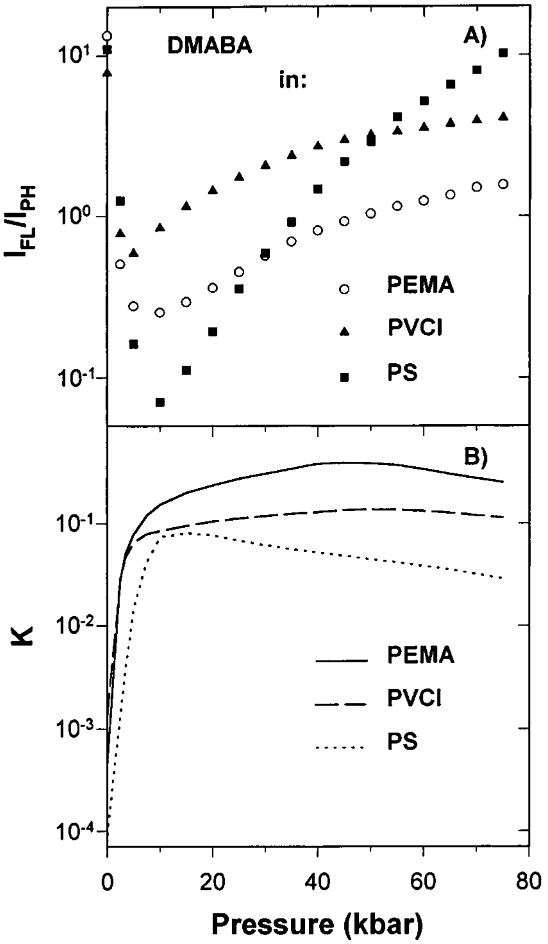

Figure 8. (A) Pressure dependence of the ratio of fluorescence (I_{FL}) to phosphorescence (I_{PH}) intensity of DMABA in several polymers. (B) Pressure dependence of $K = k_T^R/(k_T^N + \gamma_{HA})$ calculated with the initial values (at atmospheric pressure) of k_{ISC}/k_S^R and Φ_{FL}: 1.69 × 10^2 and 5 × 10^{-3} (PEMA); 0.96 × 10^2 and 10^{-2} (PVCl); 9.81 × 10^2 and 10^{-3} (PS), respectively.

increased. The degree of this decrease differs among the polymers and is estimated to be a factor of 2 in PEMA, 1.5 in PVCl, and 10 in PS. Although the initial intensities of DMABA in these polymers are spread by a factor of 10, their maximum values vary only by a factor of 2. In contrast to the LEB, the HEB intensity (fluorescence) increases less and levels off above 50 kbar with no decrease. Thus, the ratio of the fluorescence to phosphorescence intensity (I_{FL}/I_{PH}) (see Figure 8A) shows initially within 5−10 kbar a strong decrease, even 2 orders of magnitude in PS, and then above 10 kbar a significant increase. In the case of PS the final value (at 80 kbar) of the I_{FL}/I_{PH} ratio approaches its initial value.

Crystalline DMABA, in contrast to its behavior in polymers, exhibited a single peak at all pressures. At atmospheric pressure the peak was located at 21.7 × 10^3 cm^{-1}, and its decay, although nonexponential, gave a lifetime in the nanosecond range. With increasing pressure the peak shifted strongly to lower energy. Both facts indicated clearly that emission in DMABA crystal was represented by fluorescence. Since there were no dramatic changes in intensity with increasing pressure, the crystal luminescence was not studied in detail.

Discussion

It is clear from the data presented that the emission intensity (efficiency) of these aromatic carbonyl molecules is very strongly affected by the external pressure. However, the size as well as the sign of pressure effect on the carbonyl molecules emission intensity varies among the matrices studied. In polymeric media the pressure increased increases significantly the emission intensity at least at low pressure while in the crystalline environment it strongly decreases. Furthermore, while BP and DCBP exhibit only phosphorescence at all pressures, the DMABA molecule shows both phosphorescence and fluorescence. To concentrate on some of these features, we divide our discussion in two parts based on the character of molecule: the aldehyde (DMABA) and the ketones (BP and DCBP). However, at the beginning we present general considerations that may be applied to both types of molecules.

Kinetic Model. It has been suggested[11] that there is a substantial mixing of $^3\pi,\pi^*$ character into the T_1 state of the carbonyls (e.g., benzophenone) due to the mixing of the "n" character of the oxygen unpaired electron with the phenyl ring π character. Since, in aromatic carbonyls, increasing solvent polarity has been shown to increase the extent of π,π^* content of the predominately n,π^* triplet state, we conclude that increasing external pressure has essentially the same effect. With increasing pressure the enhancement of the interaction between a molecule and its surroundings stabilizes further the initial mixing of the ring π orbitals with the n carbonyl orbital, contributing to an increase of the π,π^* (π ring, π^* carbonyl) character in the triplet state. Thus, the increase of the emission intensity under pressure would be essentially a manifestation of the increasing π,π^* character of the triplet state.

In looking for the kinetic reasons for the strong pressure dependence of the luminescence emission of aromatic carbonyls, we have derived[14] the following expressions for the fluorescence (I_{FL}) and phosphorescence (I_{PH}) intensity under steady state conditions:

$$I_{FL} = \alpha I_{ex}[1 + (k_S{}^N + k_{ISC})/k_S{}^R]^{-1} \tag{1}$$

$$I_{PH} = I_{Fl}(k_{ISC}/k_S{}^R)[1 + (k_T{}^N + \gamma_{HA})/k_T{}^R]^{-1} \tag{2}$$

It should be noted that eqs 1 and 2 are obtained under the following assumptions: (i) the absorption of the light (αI_{ex}) takes place to the excited singlet (S_1) state of the molecule, (ii) S_1 decays radiatively or nonradiatively to the ground (S_0) state or undergoes an intersystem crossing (ISC) transformation to the triplet state, (iii) the triplet (T_1) state decays to the ground state or participates in the reaction with the environment, and (iv) there is a negligible disappearance of the molecules in irreversible reactions (short times of excitations and low excitation intensities). The symbols $k_S{}^N$, $k_S{}^R$ and $k_T{}^N$, $k_T{}^R$ stand for nonradiative (N) and radiative (R) rates, respectively, for the singlet and triplet states. k_{ISC} is the ISC rate constant between S_1 and T_1 electronic states. $\gamma_{HA} = k_{HA}[PH]$, where k_{HA} is a bimolecular rate for the hydrogen abstraction reaction and [PH] is the concentration of reacting centers of the polymer.

Since αI_{ex} was approximately constant, in all cases, the pressure dependence of the fluorescence and phosphorescence intensities should follow the pressure changes in the rate constants. Unfortunately, reliable measurements of these rates could not be performed because of the unstable conditions in the samples during a dye laser excitation due to the light-induced effect discussed in the following paper. However, we will show that the trends in fluorescence and phosphorescence intensity under pressure are in the direction expected from the progression in modification of the electronic structure of the triplet state.

DMABA. In all polymeric matrices, pressure converts very weakly emitting DMABA to an efficiently emitting molecule, and both the fluorescence and phosphorescence intensity increase markedly. While the fluorescence intensity increases gradually and begins to level off at pressures higher than 50 kbar, the phosphorescence intensity exhibits more complex dependence: a large increase at the beginning (5−10 kbar) and then a decrease at higher pressures (above 10 kbar). These observations can be understood in terms of the pressure-induced changes in the character of the lowest triplet state of the molecule.

If $k_S{}^N$ and $k_S{}^R$ show a negligible pressure dependence, then the increase of fluorescence with increasing pressure, described by eq 1, should reflect a decrease of the ISC rate. In general, the rate of ISC can depend on the mutual electronic character of the singlet (S_1) and triplet (T_1) state, the S_1-T_1 energy gap, and vibronic factors. The effect of pressure on the ISC rate may essentially involve two important effects. The first one is the relative energetic displacement of the lowest excited singlet state and the lowest triplet state. Increased pressure is expected to decrease the energy of the excited singlet state more than it does the triplet state. Thus, the S_1-T_1 energy gap (ΔE_{ST}) would decrease, presumably increasing the rate of intersystem crossing. The second, and perhaps dominating, effect of pressure on the ISC rate is the increase of the π,π^* character in the T_1 triplet state. El-Sayed[21] has proposed selection rules for estimating the magnitude of the ISC rate constant based upon an analysis of the effect of a change in configuration (n,π^* to π,π^*, etc.) on the spin−orbit coupling operator. The result of this analysis indicates that when a change in spin multiplicity is accompanied by a change in electron configuration the process is rapid. In this case the ISC rate depends on the square of the S_1-T_1 matrix element.

A strong shift toward low energy of the fluorescence and absorption maxima with pressure indicates that the lowest singlet state of DMABA has a π,π^* character. In contrast to the singlet behavior, the triplet state shows a relatively small shift (to lower energy) and is believed to possess initially essentially an n,π^* character. In such a situation the effect of pressure on the ISC rate would consist of two factors: an increase of the ISC rate as a result of decreasing energy gap between $S_1$and T_1 and a decrease of ISC rate due to a decrease of the S_1-T_1 matrix element.

Since the fluorescence intensity increases with increasing pressure, we believe that the second factor governs the behavior of the ISC rate. In this case the k_{ISC} rate constant will decrease with increasing π,π^* character in T_1. As can be seen in Figure 8A, the ratio of I_{FL}/I_{PH} decreases initially despite the fluorescence increase. This indicates a stronger increase of the phosphorescence than of the fluorescence intensity. If one rewrites the eq 2 in the form

$$I_{FL}(p)/I_{PH}(p) = k^{-1}(p)[1 + K^{-1}(p)] \tag{3}$$

with

$$k(p) = k_{ISC}(p)/k_S{}^R \quad \text{and} \quad K(p) = k_T{}^R(p)/[k_T{}^N(p) + \gamma_{HA}(p)] \tag{4}$$

where (p) stands for the parameter under pressure, it becomes obvious that the pressure dependence of K should clearly prevail the pressure dependence of $k(p)$.

Based on the experimental results of the I_{FL} and I_{PH}, the pressure dependence of $K(p)$ can be found numerically from

$$K(p) = \{[I_{FL}(p)/I_{PH}(p)]k(p) - 1\}^{-1} \tag{5}$$

with

$$k(p) = k(0) + \Phi_{FL}{}^{-1}(0)[R^{-1}(p) - 1] \tag{6}$$

$k(0) = k_{ISC}(0)/k_S^R$, and $R(p) = I_{FL}(p)/I_{FL}(0) = \Phi_{FL}(p)/\Phi_{FL}(0)$ where Φ_{FL} is the fluorescence efficiency and (0) stands for atmospheric pressure. Because the expression for the $K(p)$ includes two unknown parameters, $k(0)$ and $\Phi_{FL}(0)$, the shape of the $K(p)$ function has been examined as a function of these two parameters. For each polymer the set of $k(0)$ and $\Phi_{FL}(0)$ has been found which gives the smoothest changes in $K(p)$. As can be seen in Figure 8B, for three matrices $K(p)$, after an initial exceptionally large increase, decreases substantially at higher pressure.[22] Although the quantitative changes on $K(p)$ depend on the choice of $k(0)$ and $\Phi_{FL}(0)$, qualitatively the same effects are obtained over a considerable range of these parameters. A strong increase can be caused by an increase of the radiative rate (k_T^R), but since the k_T^R is expected not to decrease with increasing pressure, the decrease at higher pressures may be the result of increasing dissipation of energy (an increase of the k_T^N) from the triplet. The probability of the $T_1 \rightarrow S_0$ nonradiative process has been shown to be proportional to the square of the vibrational overlap integral between the zero-point function of the triplet state and the nearby excited vibrational functions of the ground state. One of the ways of increasing the overlap integral is by displacing the two potential curves with respect to one another. This might be what is happening at higher pressures. Furthermore, in the higher pressure region a dissipation of triplet energy through an increasing vibronic and/or electronic coupling with the polymer molecules may also participate. See also the discussion below on the aromatic ketones.

The reasons for different degree of the increasing or decreasing of $K(p)$ under pressure in the matrices studied are not completely established yet. The result obtained is only an indication that processes in which the triplet state is involved are strongly environmentally dependent. Summarizing the pressure effect on DMABA emission, one can state as follows: The initial strong increase of the emission intensity of either fluorescence or phosphorescence is caused by increase of interaction of the electronic states of the triplet state with its surroundings. Due to compression, the π phenyl orbital mixes more strongly with the n carbonyl orbital, and the molecule changes its conformation to stabilize new orbital configurations with different environmental interactions. Thus, with increasing pressure the molecule loses the π plane of symmetry and adjusts its configuration to new van der Waals interactions. This process takes place until the van der Waals forces are able to influence molecular orbitals of the “transformed” molecule. We believe the pressure dependence of the fluorescence intensity reflects an attaining of a gradual balance between a new molecular configuration and the modified intramolecular forces. The phosphorescence intensity includes additional nonradiative processes, the importance of which increases with increasing pressure.

BP and DCBP. Both molecules, regardless of the type of environment, exhibit only phosphorescence emission. In the polymer matrices, under pressure BP and DCBP exhibit a remarkable but different size of phosphorescence intensity growth. However, crystals of these molecules only decrease their emission intensity as pressure increases.

It is widely recognized that the lowest excited singlet state of BP and DCBP is n,π* in character. Since the triplet has also n,π* character but with a substantial amount of π,π* character, the ISC rate should be a fast process. If $k_{ISC} \gg k_S^R$, k_S^N, then the phosphorescence intensity expressed by eq 2 can be reduced to

$$I_{Ph} \approx \alpha I_{ex}[1 + (k_T^N + \gamma_{HA})/k_T^R]^{-1} \qquad (7)$$

and I_{FL} to zero.

From eq 7, a weak phosphorescence intensity may be caused by a fast nonradiative process, i.e., $k_T^N + \gamma_{HA} > k_T^R$. In the polymers, the increase of pressure should however modify the triplet state by increasing its π,π* character, which will give the primary increase of the radiative rate, k_T^R. As a result of this, the phosphorescence intensity should gradually increase. At this point we cannot distinguish whether the increase of phosphorescence intensity is only due to the increase of k_T^R or to a change of k_{ISC} also. The last effect would participate in the case when the initial (at atmospheric pressure) quantum efficiency of ISC (Φ_{ISC}) is low. Since BP has Φ_{ISC} close to one, it seems that only the change in k_T^R is responsible for the increase of phosphorescence intensity.

In crystals as well as at high pressure in polymers the phosphorescence intensity decreases. It seems to us that this effect has its source in pressure-induced nonradiative processes due to the growing importance of the coupling of the triplet molecule states to the environment. A reasonable reversibility of the pressure effect in the crystal rather excludes an involvement of pressure-induced defects[9b] on the decrease of phosphorescence intensity. Instead of this effect we postulate that in the crystal the strong interaction of the molecule with nearest neighbors inhibits the changes in the π,π* content of the triplet state. The increase of pressure increases only the amount of dissipated energy through the coupling of vibronic states of the molecule with lattice of the crystal. Thus, the decrease of phosphorescence intensity takes place.

The variation of the size of the pressure effect among the compounds and matrices studied may have its source either in the difference in polarizability or packing of the environment as well as in the polarity of the molecule. It is worth noting that more polarizable media show a smaller, if any, increase of the phosphorescence intensity. This perhaps can be explained by variation of the initial (at 0 kbar) degree of the n,π* character in the triplet state among the media. Furthermore, the more polar molecule, DCBP, exhibits less effect than BP. Lipson et al.[12] indicate that, for aromatic ketones, an increase in π,π* character of the triplet state is accompanied by a substantial change in the dihedral angle between the phenyl rings and the plane of the carbonyl group. As the polymer is compressed, there may be an inhibition of this rearrangement which makes an increase of π,π* character more difficult. In the relatively tightly packed crystal this geometrical barrier may be operative already at atmospheric pressure. More systematic studies in this matter are however needed.

Conclusions

We have shown that under pressure DMABA, BP, and DCBP in polymeric as well as in crystalline media exhibit a remarkable change of the emission intensity. These changes are explained in terms of a model that takes a mixing of the lowest triplet state character as a controlling factor of the intensity increase and vibronic coupling of the triplet state to the environment as a factor responsible for the intensity decrease. The increase of emission intensity in polymeric environments is attributed to pressure mixing of the triplet state involving an increase its π,π* character. As a result, two concurrent effects occur: (1) an increase of the radiative rate of the triplet state (BP, DCBP, DMABA, phosphorescence increase) and (2) a decrease of the intersystem crossing rate (DMABA, fluorescence increase). A decrease of phosphorescence intensity in polymers in the high-pressure region and crystals over the whole pressure range is attributed to an increase of the nonradiative rate from the triplet state. It seems to us that this process may be controlled by an increasing role of the dissipation energy of the triplet state via vibronic coupling with surrounding molecules. Finally, we have shown that high pressure is a useful tool in rearranging and controlling the character and decay modes of the triplet state of electronically excited carbonyl chromophores.

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