

Crystal Spectra of Tetracene and Rubrene under Pressure*

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Pressure-induced spectral shifts (0–20 kbar) are compared for the absorption and fluorescence of tetracene and rubrene as crystals or embedded in polystyrene matrices. At 20 kbar the red shift of the tetracene crystal absorption is two to three times larger than either the red shift of tetracene in polystyrene or rubrene in both crystal and solid-solution environments. The crystal shifts and increased Davydov splitting at high pressure are related to calculations on compressed anthracene by Rice and Jortner. The spectral shifts indicate that crystal-field effects are negligible for rubrene due to steric factors. Strong specific interactions in the excited state between the phenyl substituents of rubrene and the phenyl groups of polystyrene are indicated from the fluorescence spectra at atmospheric pressure. The influence of pressure on tetracene crystal luminescence can be described in terms of excitation-energy transfer to tetracene dimers at defects. High pressures enhance the transformation of excitation energy into heat, probably by increasing non-radiative exciton trapping at imperfections.

INTRODUCTION

Molecular crystals of aromatic hydrocarbons have been frequent subjects of solid-state spectroscopy and have provided information against which theoretical models of crystal states can be checked.¹ Theories of singlet exciton states in aromatic crystals are dependent upon the magnitude and nature of intermolecular interactions. Drickamer² pioneered the use of the pressure parameter in the study of organic crystals,² and Rice and Jortner³ first computed pressure shifts for anthracene. Several laboratories are now measuring the influence of high pressure on molecular excitons in aromatic crystals by luminescence spectroscopy.^{4–9}

The observed pressure effects on crystal luminescence cannot be explained in terms of a gradual decrease in intermolecular separation.^{4–9} Far more important appear to be changes in molecular orientation and defect formation in the determination of luminescence spectra at higher pressures. The objective of this work is to discern the importance of orientation and defects in compressed crystals by comparing crystalline and solution environments of two molecules with similar spectra but different geometries. Tetracene (naphthacene) and rubrene (5,6,11,12-tetraphenylnaphthacene) crystals were chosen for this study. The substituents in rubrene should severely modify crystal interactions compared to tetracene at high pressures. The results described below show this to be the case and give some

information about Davydov splitting and exciton interactions in unsubstituted tetracene. Also, the small influence of pressure on steric effects in rubrene is noted in this comparative study.

EXPERIMENTAL

Rubrene (Aldrich Chemicals) was vacuum sublimed at 130°C in the dark. Tetracene (K and K Chemicals) was purified by column chromatography and microsublimation.¹⁰ The absorption spectra were obtained for rubrene or tetracene powders dispersed in sodium chloride by standard pellet techniques of infrared spectroscopy. Front-surface fluorescence was measured from precompressed powdered samples under 3660-Å radiation. Both chemicals were also embedded ($<10^{-3}M$) in the polymer-matrix polystyrene (PS) to form solid solutions. The PS films were prepared by removing the solvent from benzene solutions containing solute and polymer. The high reactivity of the solutes required that samples were prepared in the dark and, in the case of tetracene, under a nitrogen atmosphere. The plastic films were degassed before use. The high-pressure apparatus is described elsewhere.^{8,9,11} The bulk contraction of the crystals and the PS matrix are not very different at 20 kbar,^{12,13} although the initial pressure dependence of the compressibility may be very different for an anisotropic crystal and polymer. The observed spectral shifts under pressure are gradual and reversible (except for the crystal fluorescence in pellets).

RESULTS AND DISCUSSION

Absorption Red Shift

The absorption spectra of pellets containing tetracene and rubrene crystals are shown in Fig. 1 for two isobars.

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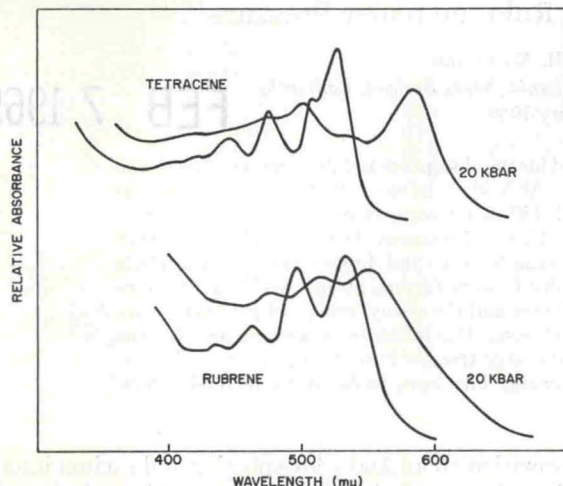


FIG. 1. Absorption spectra of tetracene and rubrene crystals in NaCl pellets at 1 atm and 20 kbar.

It is found that the longest-wavelength 1L_a bands of the parent^{14,15} and substituted aromatic hydrocarbon have similar intensities and vibrational structure and occur at similar energies. This observation supports the view that the phenyl rings cannot be coplanar with the central skeleton in rubrene.^{16,17} The triclinic crystal structure of tetracene¹⁸ is closely related to the naphthalene-type structure, which is also the space group for rubrene.¹⁹ The red shift in the 0, 0 band of rubrene relative to tetracene at atmospheric pressure is 2130 cm^{-1} in liquid solution,¹⁷ $\sim 2000 \text{ cm}^{-1}$ in the PS matrix, and $\sim 600 \text{ cm}^{-1}$ in crystals. These results clearly show that the periphenyl groups are responsible for weaker crystalline interactions in rubrene, hence a smaller solution-crystal red shift in rubrene than in tetracene. Absent from the rubrene crystal spectrum is any indication of Davydov splitting which is clearly evident in the 0, 0 band of the tetracene pellet spectrum (Fig. 1). The steric factors diminish the crystalline forces in rubrene such that the environment may be said to resemble that of a solid solution rather than a crystalline array of identical molecules.

This difference in the environment due to orientational effects also explains the pressure shift in the absorption bands shown in Fig. 2 and illustrated at 20 kbar in Fig. 1. The pressure shifts are compared in Fig. 2 for crystals and the solutes in PS matrices. The pressure shift in solution can be discussed in terms of the red-shift expression of Longuet-Higgins and Pople,^{20,21}

which gives a dependence on intermolecular separation ($\sim R^{-6}$), polarizability of solvent and solute, oscillator strength, and transition energy. For rubrene and tetracene in PS, only the solute polarizability is expected to be different for the two systems, while the intermolecular separation might be decreased by the same scale factor at high pressure. Although the magnitude of the pressure shift is similar at 20 kbar, the rate of shift at lower pressures is slightly different. This may be interpreted to mean that the larger red shift expected for rubrene on the basis of dispersion forces is not observed, because pressure enhances ring distortion which reduces π conjugation in the planar skeleton and the interaction between the nearly perpendicular π -electron systems.¹⁷ An additional pressure shift due to environmental interactions in the crystal is expected, because "solvent" states are closer to the excitation energy than in the PS matrix. The small additional red shift in rubrene crystals may be ascribed to this source. By contrast, Fig. 2 reveals a threefold increase in $-\Delta\nu(20)$ of the tetracene crystal absorption relative to the solid solution.

The pressure shift of the tetracene crystal absorption has been measured previously to be at 20 kbar about 1600 cm^{-1} ²¹ and 1400 cm^{-1} ²² by single-beam methods. When the spectral shift is plotted against the physically more meaningful density ρ parameter, Drickamer^{2,22} observes that the polyacenes show a greater-than-linear density dependence. In the lower-pressure region (0–30 kbar),²¹ the dependence is greater than ρ^2 . This density dependence is consistent with the view of Rice and Jortner,³ who calculate for anthracene that the major source of the red shift is environmental $R^{-6}=\rho^2$ interactions with minor contributions from exciton interaction and negligible exchange-interaction effects. Experimental support is provided by the fact that in anthracene, the pressure shift in the crystal is not much larger than in the plastic at 20 kbar.²¹ In the case of tetracene however, the density dependence is still greater,^{2,22} and a comparison with the PS matrix and rubrene crystals indicates that the crystal shift is the major contributing factor to the observed red shift. Rice and Jortner³ neglected crystal-field mixing with the strong upper π - π^* state which in the case of tetracene may become very significant. It is difficult to see why exciton interaction and/or exchange interaction in tetracene should be so much larger than in anthracene crystals²³ unless the stronger coupling in tetracene¹⁴ results in significant vibronic mixing of states. Charge-resonance interactions²³ are considered small for allowed transitions. From the limited information on the anisotropic compressibilities of C_{2h}^5 aromatic crystals, it was concluded⁸ that crystal symmetry is unaffected by pressure and that the linear anisotropic compressibilities along the crystal directions are similar for different aromatics. Tetracene only approximates a

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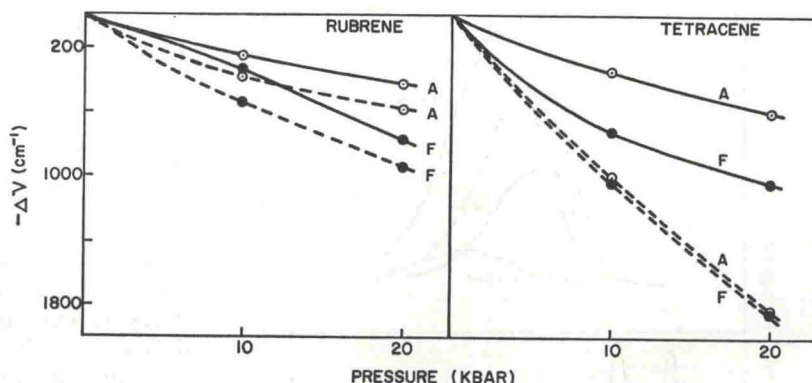


FIG. 2. Pressure shift $-\Delta\nu$ of the 0,0 absorption band A, and fluorescence-band maxima F. —, PS matrices; ---, crystal (powder). The red shift at 20 kbar is reproducible to $\pm 100 \text{ cm}^{-1}$.

monoclinic crystal structure, and this may be the origin for the predominant crystal-field shift.

Davydov Splitting

Perkampus and Pohl²⁴ observed Davydov splitting in a number of hydrocarbon films by means of unpolarized light. Ohigashi *et al.*²⁵ have noted the effect of pressure on the 0,0-band splitting of tetracene films. Since their pressure environment is hydrostatic, it is interesting to compare their results with the pressure results on pellets. The 1-atm exciton splitting of 690 cm^{-1} ²⁵ and 650 cm^{-1} in the present work represents a reasonable value compared to polarization studies of single crystals.^{14,26,27} Ohigashi *et al.*²⁵ observe the splitting S to increase by $35 \text{ cm}^{-1}/\text{kbar}$ up to 5.2 kbar, and we observe a linear increase of $\sim 50 \text{ cm}^{-1}/\text{kbar}$ up to 20 kbar under quasihydrostatic conditions. This is satisfactory agreement considering the experimental difficulties involved. The density dependence of this interaction between translationally nonequivalent molecules is roughly threefold larger than the values predicted from the dipole approximation.^{24,25} This is not surprising, since the calculations of Silbey, Jortner, and Rice²³ indicate that short-range multipole and long-range dipole-dipole interactions make significant contributions to the Davydov splitting in anthracene. Tanaka²⁶ also calculated a splitting for tetracene far smaller than observed at 1 atm and suggested that the discrepancy may be due to charge-transfer electron overlap effects. However, the latter suggestion is not consistent with calculations on anthracene crystals.^{3,23}

The rate of increase in the crystal splitting of the 0,0 band is compared in Fig. 3 with the red shift in the vibronic bands at high pressure. If the vibronic-band maxima can be identified with the (+) component (b polarized) of the crystal spectrum, then Fig. 3 reveals that interactions in vibronic states reduce the red shift considerably. The vibronic bands of tetracene in PS show identical shifts within experimental error so

that the crystal field is responsible for the different shifts observed in tetracene crystal absorption. The vibronic bands of rubrene show similar pressure shifts, again suggesting that crystal-field effects in rubrene are minor due to steric factors. The reduced shift for higher vibronic bands was predicted by the exciton calculations of Rice and Jortner.³ The weak-coupling limit predicts $\Delta\nu(0-1) > \Delta\nu(0-2)$ which is contrary to the observation in Fig. 3. This discrepancy may be due to experimental difficulties in assigning band peaks or the expectation that crystal-field effects in tetracene should be considered in the intermediate- or strong-coupling limit.^{1,14}

Broadening

Considerable band broadening at higher pressure is shown in Fig. 1 for the absorption of both crystals. The increase in bandwidth is slightly larger than observed in PS matrices at comparable pressures. Hence crystal-

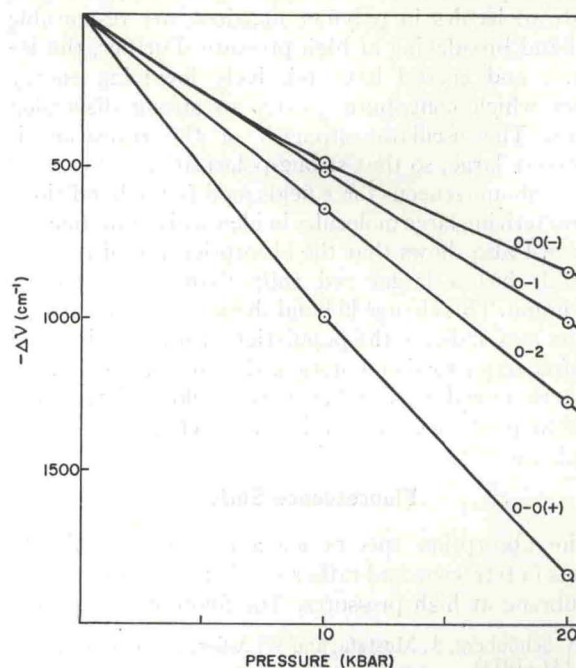


FIG. 3. Pressure shift of the tetracene crystal absorption for the 0, 1 and 0, 2 vibronic bands and the two components of the 0,0 band. The reproducibility is $\pm 100 \text{ cm}^{-1}$ at 20 kbar.

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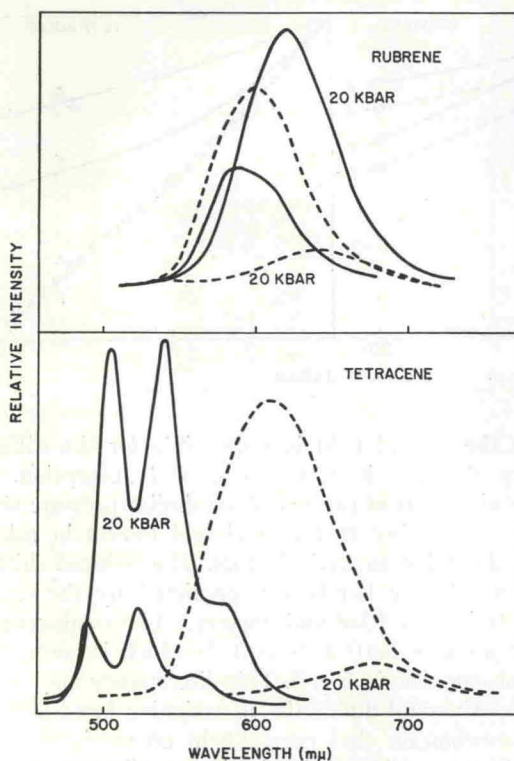


FIG. 4. Fluorescence spectra of tetracene and rubrene in PS matrices (—) and as crystalline powders (---) at 1 atm and 20 kbar.

field effects such as resonance interactions play a minor role in causing pressure broadening. It is probable that dispersive interactions due to the inhomogeneous environment, produced by imperfections in crystals and by density fluctuations or inhomogeneous packing of solute molecules in polymer matrices, are responsible for band broadening at high pressure. Further, the PS matrix and crystal have relatively low-lying energy states which contribute greatly to strong dispersion forces. The oscillator strength of the transition is relatively large, so that strong polarization forces exist and nonhomogeneous force fields modify the bandwidth characterizing large molecules in identical environments. Figure 1 also shows that the absorption tail of rubrene crystals has a larger red shift than the first-band maximum. This change in band shape in the "hot-band" region may indicate the population of pressure-induced low-frequency torsional motions due to a pressure effect on steric crowding. Further work would be interesting to relate pressure effects to the thermochromic behavior of rubrene.^{28,29}

Fluorescence Shift

The absorption spectra suggest large crystal-field effects in tetracene and rather small crystal interactions in rubrene at high pressures. The fluorescence spectra

of compressed crystals are not so easily analyzed. Inspection of Fig. 4 reveals that only tetracene in PS possesses a fluorescence at 1 atm that can be considered a mirror image of the absorption spectrum. The other spectra are broad and 1500–2500 cm^{-1} removed from the origin of the absorption band. The fluorescence pressure shift $\Delta\nu_f$ of tetracene in PS is greater than for the corresponding transition in absorption (Fig. 2), which is the expected behavior and has been observed for pyrene⁹ and anthracene³⁰ in plastics. The condition $\Delta\nu_f > \Delta\nu_a$ may be attributed to larger polarizability differences in the equilibrium excited solute plus solvent configuration (Franck-Condon principle).

The fluorescence-band maximum of rubrene in PS matrices may be located in the region 560–600 nm depending upon sample history and temperature treatment. Figure 4 illustrates the broad, asymmetric fluorescence for a sample with a particularly large Stokes shift. Although broad rubrene fluorescence considerably removed from the absorption origin has also been reported in the literature,³¹ it is found here that the 0,0 fluorescence band of rubrene in polymethylmethacrylate (PMMA) and in benzene at 77°K occurs near 535 and 560 nm, respectively, and that the band bears some mirror-image relationship to the absorption. Since PS is observed to be a good "solvent" for rubrene, strong interactions between the phenyl groups of PS and rubrene are indicated. The magnitude of the spectral shifts of the rubrene absorption in PMMA, cellulose acetate, and PS are very similar, so that no specific interactions are evident in the ground state. Hence, strong specific interactions occur upon excitation of the rubrene-PS system.

The similarity in the fluorescence of rubrene in PS and in the crystalline form, illustrated in Fig. 4, is attributed to their similar environments. It is possible that a minute quantity of rubrene gets trapped in PS as aggregates and is solely responsible for the emission. It appears more likely that steric interactions between the phenyl groups and conformational changes in the excited state are responsible for the results. For example, one can envision a parallel arrangement of the rubrene skeleton and two polymer chains which permits four phenyl groups to be nearly coplanar on each side of rubrene and would result in strong transannular interactions.³² Detailed x-ray structure analysis is required to see if a similar arrangement can occur in the excited state. Rubrene does not form excimers in solution electrolysis,³³ because steric factors probably prevent a favorable sandwich arrangement required for excimer formation. The pressure shifts $\Delta\nu_f$ are similar for rubrene or tetracene in PS matrices at 20 kbar (Fig. 2). This

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result implies that the pressure dependence of the strong, specific interactions in the excited state of rubrene is not unusual or different from the "normal" pressure response of the fluorescence of tetracene in PS and that crystal effects are small in rubrene.

It remains to consider the luminescence of tetracene crystals. The appearance of the 1-atm spectra depends upon the sample preparation. For example, tetracene-NaCl pellets yield a 0, 0-band maximum located near 550 nm that approaches the appearance of tetracene film spectra.³⁴ For powders, a broad, symmetric band near 610 nm is found as soon as the 1-atm spectrum is scanned. In pellets it is observed that the application of pressure and light⁴ gives an irreversible change in the 1-atm spectrum by displacing it toward longer wavelengths where the powder spectrum appears. In this regard the 1-atm absorption spectrum shows slight additional broadening after repeated pressure applications, but no other changes are evident. The central question is the origin of the broad emission. Excimer formation was not observed in solution electrolysis,³³ but dimer absorption and emission spectra have recently been reported for matrix-stabilized tetracene.³⁵ The geometry of the tetracene dimer was not determined but may be very similar to that of the 55° anthracene dimer.³⁶ In compressed crystals, an experimental distinction between the presence of *minute* quantities of strongly coupled monomer units or weakly coupled entities of dimers or higher aggregates is difficult to make. In the case of anthracene³⁶ or tetracene, very little distortion is required within the crystal, in order that a description in terms of dimeric units becomes appropriate. Fielding and Jarnagin³⁷ find that the lifetime of defect emission from anthracene crystals corresponds to the lifetime measured for matrix-stabilized dimers. There is little doubt that pressure as well as other straining techniques^{38,39} produce annealable imperfections in molecular crystals. Some imperfections may be defects which favor dimer formation³⁷ or permit a "face-on" sandwich configuration in the excited state followed by excimer emission.^{4,6,7} Jones and Nicol⁴ conclude from their study of naphthalene, anthracene, and phenanthrene that excimer emission is responsible for the pressure effects.

A more likely explanation, at least for tetracene crystal luminescence, is an efficient trapping process of the excitation energy by dimers formed at defects in the imperfect crystal. The 2500-cm⁻¹ displacement of the emission from the electronic band origin is smaller than

usually observed in excimer formation (~ 6000 cm⁻¹) but can be explained in terms of a 1400-cm⁻¹ crystal shift of the solvent-isolated dimer emission observed by Katul and Zahlan.³⁵ The magnitude is reasonable for solution-crystal shifts. Recent work on the fluorescence of two crystalline forms of perylene suggests that pressure does not produce excimers in the case of β -perylenes.⁸ The reversible spectral shift of β -perylenes absorption and fluorescence is similar in magnitude to that of tetracene (Fig. 2) under pressure, while α -perylenes, which has a paired sandwich arrangement, shows a smaller shift and the condition $\Delta\nu_f < \Delta\nu_a$ instead of $\Delta\nu_f \sim \Delta\nu_a$.

An important clue to crystal luminescence of imperfect crystals is gained from the intensities. It is seen from Fig. 4 that the crystal environment is responsible for a drastic reduction in radiative processes. The intensities of the band maxima at 20 kbar are typically 10%–20% of that at atmospheric pressure. Surprisingly, the 1-atm intensities remain unaltered (within $\pm 10\%$) after continued pressure cycling of the crystals. In other words, the number of excitation energy traps is not increased, or an increase in dimer formation is counterbalanced by a greater number of dislocations which quench energy transfer. Lifetime studies at high pressures are required to analyze the kinetics of exciton scattering by increased concentrations of imperfections reversibly produced at high pressures. It is suspected that plastic deformation would reversibly yield dislocations, but not defects. Other "dimeric" crystals possessing excimer luminescence⁹ or charge-transfer luminescence⁴⁰ also show reduced quantum efficiencies at high pressures. The intensity data here are consistent with the view that very low concentrations of tetracene dimers are responsible for the luminescence and that pressure-induced imperfections enhance nonradiative processes by enlarged scattering cross sections of excitons.

Returning to pressure-induced shifts, it is well to remember the statement by Rice and Jortner³ that "observed spectral shifts represent only the end effects of very subtle balances between different interactions, all of which must be carefully considered." The present results can be interpreted to mean that crystal-field effects are large in tetracene and that the spectral shift of the "monomer" absorption is identical to that of the "dimer" emission. This result is not unreasonable since the arrangement of monomer and dimer units in the crystal lattice is not expected to be grossly different, if the geometrical situation is similar to anthracene.³⁶ As perhaps anticipated, the spectral shifts of rubrene in the crystal and in solid solution are not very different due to steric factors. However, rubrene in its excited state shows strong specific interactions between its phenyl substituents and the phenyl groups from PS or from neighboring molecules in the crystal.

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