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Raman and Luminescence Spectra of Dianthracene at High Pressures

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Raman spectra of single crystal and powdered samples of dianthracene have been recorded at temperatures from 77 to 410 K and at pressures to 32 kbar. The Raman and infrared spectra of dianthracene dispersed in KBr demonstrate the apparent stability of dianthracene under these conditions, contrary to other reports. At pressures above 10 kbar, however, a fluorescence background appeared with the Raman spectra excited with Ar and He-Ne lasers. This fluorescence is attributed to direct excitation of close-coupled sandwich-like dimer defects created and trapped in the crystal under pressure.

The photodimerization of anthracene in both the solid state and solution is well known.¹⁻³ The relationship between anthracene and dianthracene is of fundamental interest, and considerable research has been reported on the excited intermediary state and on the role of topochemical factors in the dimerization.³⁻¹³ However, very few physical properties of the dimer have been described, other than that it is unstable at high temperatures and under compression.^{5-7, 13} This study was motivated by the interest as to whether the monomer or the dimer is the stable form at high pressures and by the fact that the Raman spectrum of dianthracene does not appear to have been reported. This work attempts to characterize the principal features of the Raman and infrared spectra and to employ the former as a probe to study the stability of dianthracene under static compression to 32 kbar. The luminescence background observed in the Raman studies at high pressures using 547.9, 488.0, 514.5 and 632.8 nm laser excitations is also reported.

In the dimerization process, two anthracene molecules are joined at the 9 and 10 position as shown in fig. 1.^{14, 15} The two original anthracene molecules have lost their planarity, and bonds close to tetrahedral arrangement are formed at C₉ and C₁₀ positions. The resulting dimer looks like two anthracene "butterflies" facing each other. The bond distance (C₉—C_{9'} and C₁₀—C_{10'}) of 1.62 Å between the two anthracene components is much larger than the usual single bond value of 1.55 Å. This is believed to arise from the repulsive forces that hinder the close approach of the two half-molecules. Despite the large C—C distance, the dimerization gives rise to a 2.7 % volume contraction. The dimer in fig. 1 has *D*_{2h} molecular symmetry and crystallizes to form an orthorhombic structure of *D*_{2h}¹⁵(*P*_{bca}) space group. The four

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dimer molecules of the primitive cell have different orientations and are situated on C_i sites. In this symmetry, the librational motions along the three principal axes of each molecule give rise to twelve Raman active motions, three each of A_g , B_{1g} , B_{2g} and B_{3g} species. All 276 possible internal modes of *gerade* character are also Raman active. Fortunately, many internal modes are either accidentally degenerate or too weak to detect. The infrared active modes are of the B_{1u} , B_{2u} or B_{3u} type; modes of A_u symmetry are inactive.

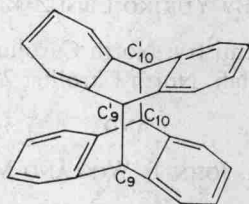


FIG. 1.—The structure of the dianthracene molecule.

The photodimerization mechanism of anthracene and other anthracene derivatives involves the encounter of a molecule in its first excited singlet state with another in its ground state.^{4, 5, 16} It is commonly believed that the excimer is the excited intermediary complex. Ideal conditions for the formation of an excimer must be met if the reaction is to proceed through the photoassociated state. The experimental studies on the relationship between crystal structure and fluorescence have shown that most planar aromatic molecules are capable of forming an excimer when there is sufficient coupling between adjacent molecules in an appropriate geometry.^{17, 18} In crystalline anthracene, the geometric and coupling requirements are not ideal; however, this crystal indicates unexpected photoreactivity. Owing to these difficulties, many investigators have turned to the study of the photodecomposition process in dianthracene for obtaining information on the dimerization process. The primary step in the photodegradation of the dimer is believed to provide a sandwich or pair-wise arrangement in which the intermolecular spacing is small enough for large intermolecular coupling. The sandwich modification, stable only at low temperatures, exhibits excimer fluorescence. The sandwich-like structure has also been interpreted to be consistent with the anthracene fluorescence under pressure.^{9, 19-21}

EXPERIMENTAL

Synthetic anthracene (Eastman H480) was the starting material for photodimerization of anthracene in cyclohexane solution. A solution of anthracene in a Pyrex tube was degassed by the freeze-thaw technique and was irradiated in a photochemical Hg vapour reactor until the characteristic purple luminescence from anthracene was no longer visible and fine white powder of dianthracene was obtained. The powder was washed in cyclohexane and was vacuum dried. Cyclohexane was the preferred solvent since dianthracene samples prepared in benzene required considerably more effort to remove the residual anthracene and benzene. Dimer prepared in cyclohexane and benzene gave identical Raman spectra with no observable monomer peaks. Dianthracene was also prepared from anthracene (Eastman X480) of different purity from that of the basic sample in order to check for possible impurity effects on the high pressure luminescence spectra. Dianthracene- d_{20} was prepared from anthracene- d_{10} (Merck, Sharp and Dohme of Canada) dissolved in nondeuterated cyclohexane solution; the contamination by the nondeuterated dimer was believed to be quite small since no C—H stretching frequency could be detected in the Raman spectrum,