

Solubility of dianthracene is very low in most solvents; large crystals are difficult to grow. Small crystals with surface area of $\sim 2 \text{ mm}^2$, however, were grown from chlorobenzene and benzene solution, with the former solvent being preferred. Microscopic examination indicated very clear and well-developed crystals. Only crystals were employed in the high pressure luminescence work, although both powder and crystals were used in the Raman scattering studies.

The near infrared (600 to 3500 cm^{-1}) spectrum at atmospheric pressure and 296 K was obtained with a Perkin-Elmer Model 421 spectrometer, using both the KBr pellets and Nujol mulls. No pulverization of the dianthracene powder was required in making the mulls or the pellets since the sample synthesized in cyclohexane was in a finely divided state. The pellets were prepared by standard KBr technique and were only pressed for a short duration at 4 kbar . Both the pellet and the mull gave identical infrared bands.

Raman data were taken with 90° geometry using a Spectra Physics (Model 165) argon ion laser (200 to 400 mW) operating at 514.5 nm in conjunction with a Spex double monochromator and ITT FW 130 photomultiplier operated in a photon-counting mode. No correction for photomultiplier response with varying wavelength was made in any of the reported spectra. All Raman spectra of dianthracene and dianthracene- d_{20} recorded at atmospheric pressure were obtained on samples sealed under vacuum in Pyrex tubes. Detailed studies of the complete Raman spectra were carried out at atmospheric pressure and in the 296 to 410 K temperature range, while only the lattice modes were examined at lower temperatures to 77 K . The high pressure Raman spectra of both the internal and the lattice modes of the dimer were obtained with the sample placed in the cavity in a NaCl crystal inside the high pressure chamber of a Drickamer type I cell. The pressure studies were carried out to 32 kbar at 296 K . The Raman scattering from dianthracene was sufficiently strong that a scan rate of several $\text{cm}^{-1} \text{ min}^{-1}$ and a 1 cm^{-1} resolution could be maintained in all regions of the spectrum.

The luminescence background observed in the high pressure Raman spectra were studied with the Raman apparatus already mentioned, however a much faster scanning rate was employed with this work. The luminescence spectra were excited with a Spectra-Physics Model 125 He-Ne laser (632.8 nm) and with the various lines of the argon ion laser (457.9 , 488.0 , and 514.5 nm), but at no time was the sample exposed to the full power of 488.0 and 514.5 nm beam. No attempt was made to "scramble" either the incident or the emitted light since the stressed NaCl windows in the high pressure cell are quite effective as polarization "scramblers". The spectra were investigated both as a function of irradiation time and pressures to 32 kbar at ambient temperatures. A Molelectron Model UV-100 nitrogen laser and Model DL-200 dye laser combination were employed at 488.5 nm to obtain the luminescence spectrum for lifetime studies. The emission was isolated with a narrow band interference filter ($514.5 \pm 3.0 \text{ nm}$) and a 0.25 m Bausch and Lomb high intensity monochromator. A RCA 1P28 photomultiplier was employed for detection and the spectrum was displayed on an oscilloscope (Tektronix Model 7904). The fluorescence lifetime was determined by comparison of the photographic traces of the excitation and fluorescence.

RESULTS

The near infrared spectrum of the dimer taken on a KBr wafer is shown in fig. 2, and the wavenumbers of the bands are listed in table 1. The KBr disc was prepared from powdered dimer synthesized in cyclohexane. Comparison of the dimer spectrum with the standard anthracene spectrum shows the absence of characteristic anthracene bands.²² The process of dispersing dianthracene in powdered KBr and pressing a pellet at 4 kbar did not cause any appreciable decomposition, and also any anthracene coprecipitated with the dianthracene must be quite small. The infrared spectrum in fig. 2 agrees with the major characteristic bands reported for a mixed monomer-dimer sample and verifies that the samples employed in this work are identical to the dimer reported previously.⁷

Fig. 3 depicts a typical Stokes Raman spectrum of dianthracene powder at atmospheric pressure and 296 K and excited by 514.5 nm radiation. The spectrum shows no visible luminescence under these conditions. The Raman frequencies obtained on small crystals were identical to those of powdered samples; however, the

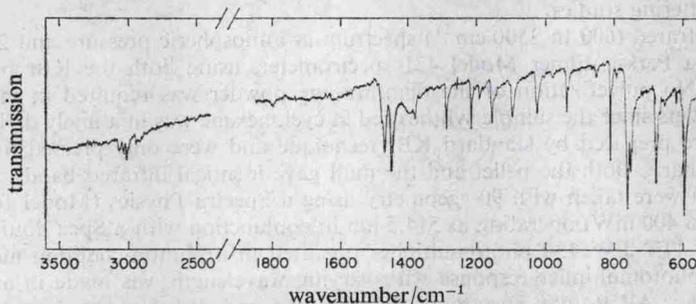


FIG. 2.—A near infrared spectrum of dianthracene at 1 bar and 296 K. The spectrum was taken with dianthracene powder in a KBr pellet pressed at 4 kbar.

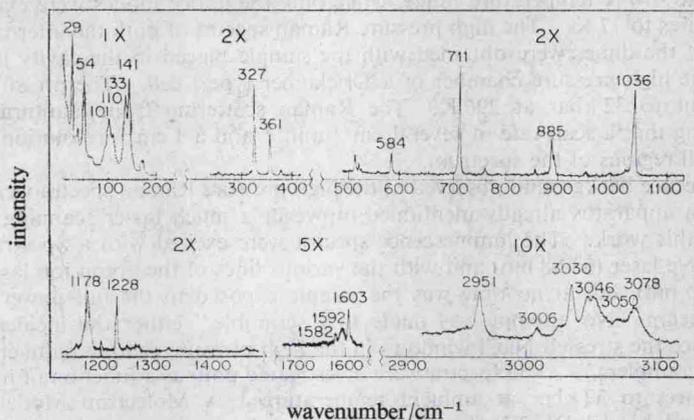


FIG. 3.—Raman spectrum of dianthracene powder at 1 bar and 296 K.

TABLE 1.—WAVENUMBERS (cm^{-1}) OF THE NEAR INFRARED BANDS IN DIANTHRACENE AT 1 bar AND 296 K

| | | | |
|-----|------|------|--------|
| 595 | 940 | 1287 | [2918] |
| 678 | 1026 | 1380 | [2944] |
| 752 | 1096 | 1394 | 3014 |
| 762 | 1154 | 1447 | 3035 |
| 812 | 1194 | 1465 | 3065 |
| 937 | 1216 | 1795 | |

[] values with large uncertainty

relative intensities were somewhat different owing to the orientation effect of the crystals. The wavenumbers of the 54 observed peaks (due to 11 lattice and 43 internal modes) are given in table 2 together with a partial assignment based on characteristic frequencies and isotope shifts; the molecule is too complex and the spectral identification too incomplete to justify a more detailed assignment at this time. A comparison of the Stokes and anti-Stokes spectra confirmed that all reported bands correspond to vibrational Raman spectra. Examination of the