

infrared and the Raman bands in dianthracene (table 1 and 2) indicate no coincidence in the wavenumbers of peaks with appreciable intensity with the possible exception of the band at 3065 cm^{-1} . Since coincidence of wavenumber is excluded for this crystal symmetry, the mode at 3065 cm^{-1} is assigned as a combination. The division

TABLE 2.—BANDS OF THE RAMAN SPECTRUM OF DIANTHRACENE AT 296 K

| wavenumber/cm ⁻¹ (1 bar) | intensity ^a (1 bar) | wavenumber/cm ⁻¹ (10 kbar) | $\frac{d\nu}{dP}$ /cm ⁻¹ kbar ⁻¹ | assignment | |
|--|-----------------------------------|--|--|-----------------------------|-------------------|
| lattice modes | | | | | |
| 28. ₅ | vs | 37 | 0.73 | libration | |
| 37. ₁ | m | 55 | 1.6 | | |
| 53. ₆ | vs | 73 | 1.9 | | |
| 71. ₃ | w, br | 91 | 2.0 | | |
| [91] ^b | m, sh | 103 | 1.6 | | |
| 101 | s | 120 | 1.9 | | |
| 110 | s | 138 | 2.8 | | |
| 133 | vs | 147 | 1.4 | | |
| 141 | vs | 166 | 2.6 | | |
| 167 | m | 185 | 1.8 | | |
| 172 | m | 192 | 2.0 | | |
| internal modes | | | | | |
| 258 | vw | | | | (C—C deformation) |
| 327 | vs | 339 | 1.2 | | |
| 361 | m | 365 | 0.52 | | |
| 378 | vw | 384 | + | | |
| 510 | m | 516 | + | | |
| 516 | w | 525 | + | | |
| [555] | vw | | | | |
| 584 | m | 586 | + | | |
| [637] | vw | | | | |
| 711 | vs | 717 | 0.5 | (aromatic C—C stretch-bend) | |
| 760 | vw | 770 | + | | |
| [820] | vw | | | | |
| 851 | vw | | + | | |
| 885 | m | 889 | + | | |
| 890 | m, sh | 896 | + | | |
| 950 | vw | 956 | + | | |
| [996] | vw | | | | |
| [1024] | vw, sh | | | | |
| 1036 | m, sh | | | | |
| 1038 | vs | 1041 | 0.46 | | |
| 1158 | w | | | | |
| 1178 | s | 1176 | -0.18 | | |
| [1187] | w, sh | 1189 | 0.2 | | |
| 1200 | w | 1206 | 0.5 | | |
| 1228 | s | 1236 | 0.6 | | |
| 1246 | vw | | + | | |
| 1263 | vw | 1268 | + | | |
| 1265 | vw | (unresolved) | + | | |
| [1302] | vw | | | | |
| 1320 | vw | | | | |
| [1338] | vw | | | | |
| 1464 | vw | | | | |

TABLE 2.—*contd.*

| wavenumber/cm ⁻¹ (1 bar) | intensity ^a (1 bar) | wavenumber/cm ⁻¹ (10 kbar) | $\frac{dv}{dP}$ /cm ⁻¹ kbar ⁻¹ | assignment |
|--|-----------------------------------|--|--|-----------------------------|
| 1582 | vw | 1588 | 0.7 | (aromatic C—C ring stretch) |
| 1592 | vw, br | 1599 | 0.7 | |
| 1603 | w | 1613 | 1.1 | |
| 2951 | w, br | 2971 | 2.0 | (aliphatic C—H stretch) |
| 3006 | vw, br | 3020 | 1.4 | (aromatic C—H stretch) |
| 3022 | vw, sh | | | |
| 3030 | w | 3041 | 1.2 | |
| 3046 | w, br | 3058 | 1.2 | |
| 3050 | w, br | 3076 | 2.6 | |
| 3065 | w, br | | | |
| 3078 | w, br | 3099 | 2.1 | |

^a The following abbreviations have been used: s, strong, m, medium; v, very; w, weak; br, broad; sh, shoulder. ^b [] values with large uncertainty.

between the lattice and the internal modes in dianthracene is placed at the 175-258 cm⁻¹ wavenumber gap. Although this division is rather arbitrary, the smallness of the isotope effect (table 3) for the low frequency librational modes, their large wavenumber shift (dv/dP) with pressure, and finally a comparison of the present results with those on benzene and other aromatics support this division.²³⁻²⁵ The spectrum of the low frequency peaks at 77 K indicates that the lattice phonons reported in table 2 all appear to arise from one-phonon processes.

The spectrum of dianthracene-d₂₀ powder is shown in fig. 4, and the wavenumbers of the Raman bands reveal several interesting changes in the number of observed peaks and in the relative intensity in several spectral regions. For example, the central (1569 cm⁻¹) of the three peaks in the ring carbon-carbon stretch region (1500-to-1600 cm⁻¹) of dianthracene-d₂₀ is the strongest, while the highest wavenumber mode at 1603 cm⁻¹ is the strongest in the nondeuterated compound. This intensity shift may very well arise from Fermi-resonance phenomena in a manner similar to that observed in benzene.²³ Unlike the benzene case, however, no significant change of intensity could be observed when interatomic distances were changed with pressure (fig. 5 and 7). In the spectral region of the aromatic carbon-hydrogen stretch (3000-to-3100 cm⁻¹) of dianthracene, seven peaks are resolved of which the 3030 cm⁻¹ peak is most intense. In dianthracene-d₂₀, only three peaks are resolved in the aromatic C—D stretch region with the highest wavenumber band (2290 cm⁻¹) being most intense. One possible reason for the change in the number of bands in the carbon-hydrogen stretching region is the removal of combination peaks upon deuteration, while the change in the intensity change can arise from Fermi resonance.²³ In the lower wavenumber region, the intensity of the peak at 327 cm⁻¹ is larger than that at 361 cm⁻¹ in dianthracene; on the other hand, an apparent reversal of intensity occurs in dianthracene-d₂₀ where the 336 cm⁻¹ peak becomes stronger than that of the peak at 306 cm⁻¹. The large asymmetry of the 1178 cm⁻¹ peak in dianthracene was used as a guide to locate the corresponding peak (1126 cm⁻¹) in dianthracene-d₂₀. This mode is assigned as a C—C ring vibration. Deuteration affects only the wavenumber, and there is no change in the relative position, intensity or in the line shape for the low-wavenumber lattice modes. When heated from 296 to 410 K, the dianthracene bands, especially the lattice modes,