is an irreversible process[1, 7, 8]. The material, when recovered (in milligram quantities) is reddish-brown instead of the normal bluish-black colour of ordinary pentacene. Its x-ray spectrum contains very few lines. It is non-volatile and totally insoluble in non-destructive solvents, so its characterization is difficult. One can obtain electronic and molecular spectra. The electronic spectrum appears in *Figure 3*, compared with that of ordinary pentacene. The most striking feature is the disappearance of the low-lying peaks which correspond to orbitals conjugated around the entire molecule. There are still excitations which correspond roughly to those in benzene and naphthalene.

The molecular spectrum appears in *Figure 4*. The portion between 600 and 2500 cm^{-1} is very different from that of pentacene; peaks are broadened, new peaks appear and some of the original peaks have disappeared. The most easily identifiable feature, however, is in the C—H stretching region near 3000 cm^{-1}. In pentacene there is a single peak corresponding to a typical aromatic C—H stretching frequency. In the product there is a new peak of comparable size corresponding to a typical paraffinic
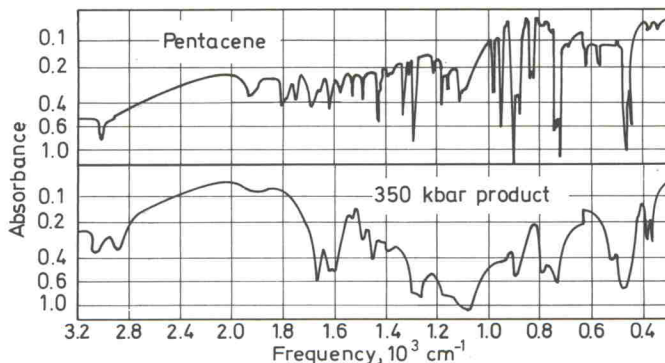

Figure 4. Infra-red spectra of pentacene and reacted pentacene

C—H frequency. Evidently the molecule has polymerized. The structure of the product is very speculative, but there must be numerous intermolecular bonds.

From the standpoint of electronic transitions, the mechanism is of interest. As illustrated in *Figure 5*, at high pressure the π orbital has increased in energy until the empty π^* orbital is available for thermal electron transfer or mixing of orbitals by configuration interaction. There may also be self-complexing between molecules in this state. This combination of events constitutes the electronic transition. Since this new state is a reactive one, the polymerization follows as a consequence of the electronic transition. Similar reactivity has been observed in a few other hydrocarbons[7, 8].
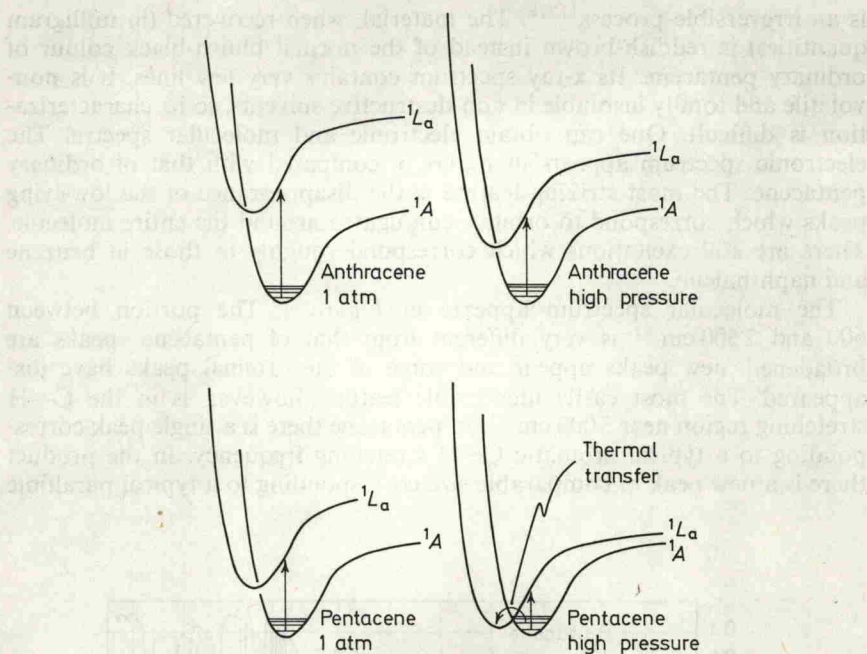
Figure 5. Configuration coordinate diagrams demonstrating the electronic transaction in pentacene

ELECTRON DONOR–ACCEPTOR COMPLEXES

A related form of chemical reactivity has been observed in a large number of electron donor–acceptor complexes. These complexes, which have been analysed in some detail by Mulliken[9], form between aromatic hydrocarbons (or related materials) as donors and such acceptors as iodine, tetracyanoethylene and halogenated hydrocarbons. The ground state is largely a 'no bond' state with a small admixture of charge transferred state, while in the excited state an electron has been transferred from the donor to the acceptor. These complexes typically have intense broad absorption peaks in the region $1\frac{1}{2}$–$2\frac{1}{2}$ eV. These peaks shift rather rapidly to lower energy with increasing pressure; a typical example is shown in *Figure 6*. They also broaden. Calculations using equation (1) indicate that for many such complexes E_{th} is reduced to zero by about 100 kbar. Some 20–30 such complexes have exhibited irreversible behaviour at high pressure as determined by electrical resistance[1, 10, 11]. Unfortunately, in most cases the products are complex and only modest attempts at characterization have been made.

Here we discuss two complexes where characterization of the products has been carried out to a reasonably complete degree. These are the complexes of pyrene and perylene with iodine. These complexes have a well-established stoichiometry (2 perylene $\cdot$ $3I_2$ and pyrene $\cdot$ $2I_2$) and crystal structure[12, 13]. *Figure 7* illustrates the irreversible electrical behaviour. In

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