

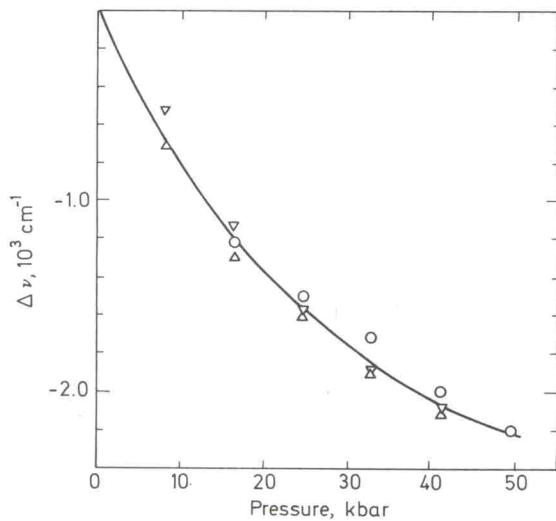


Figure 6. Shift of charge transfer peak: chloranil-hexamethyl benzene

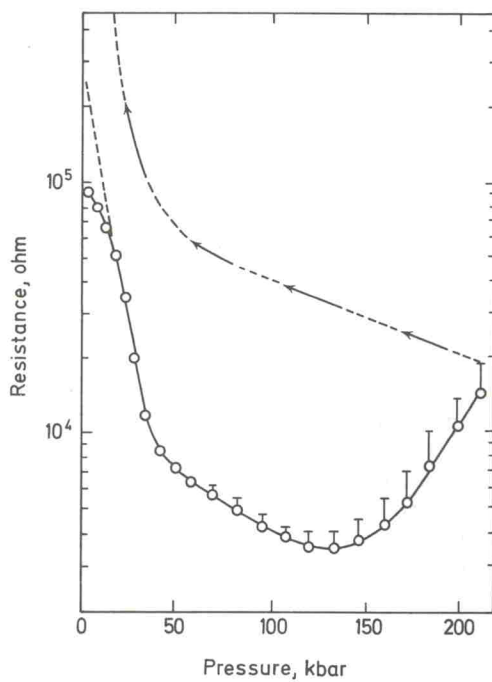


Figure 7. Resistance against pressure: pyrene · 2I₂ complex

our apparatus only a few milligrams of material can be taken to high pressure at one load, so accumulating material for analysis is something of a tour de force. From 25–30 runs of 24 h each, at 200 kbar, a batch of 140–180 mg was accumulated. At least three such batches were produced for each complex¹⁴.

The first point of interest is that the iodine can be quantitatively removed from the product. The presence of iodine is essential to the reaction. (The pure hydrocarbons have excited states near 3 eV and exhibit no irreversible behaviour or reactivity in this pressure range.) The function of the iodine is to provide a low-lying excited state (the electron transferred state) which can become the ground state at high pressure. Material pressed to 80 kbar and quickly released showed three times the number of unpaired spins as exhibited by the unpressed material. After 24 h at 80 kbar or after pressing to 165 kbar and quickly releasing, there were only twice the original unpaired spins, indicating that the reaction had proceeded. There were no free spins in the hydrocarbon product. This transfer of an electron to the iodine is the electronic transition. The subsequent reaction between hydrocarbons is the consequence.

Nothing is known about the structural details and interatomic distances in the material in the reactive state, or of the crystal structures of the hydrocarbon products discussed below.

The major portion of the recovered hydrocarbon is sufficiently soluble in ordinary solvents to be fractionated by chromatography. Two major fractions were recovered from the perylene product and two from the pyrene. These fractions were rather clean, but it is quite possible that each was a mixture of several closely related isomers. We shall consider each as a single compound. As established by mass spectroscopy and vapour phase osmometry, both perylene products were dimers, while both pyrene products were tetramers. The major structural determination was by n.m.r. using a Varian HR-220 with CAT attachments; molecular and electronic spectra were used to confirm some details. N.m.r. spectra run on samples from different batches and spectra obtained a month apart on a given sample yielded the same distribution of proton shifts. The arguments used to assign the structures are given in detail in the original reference. The results are summarized in *Table 1* for all four products. We mention here only the prominent features in the n.m.r. spectrum of perylene dimer A. (See *Figure 8* and *Table 1*.) It has 10 paraffinic, 2 olefinic and 3 aromatic protons. (Resonances in the range 6.8–8.0 p.p.m. downfield were assigned as aromatic, in the range 3.5–5.8 p.p.m. as olefinic and less than 3.0 p.p.m. as paraffinic.) The olefinic protons are divided into two classes. The proton appearing at 5.5 p.p.m. is approximately in its normal position, so it is not disturbed much by its environment. The proton at 3.7–3.9 p.p.m. is, however, shifted considerably upfield because of its location above the centre of an aromatic ring. Since three protons were aromatic, only one ring of the outer four in a perylene monomer had a benzenoid structure. This identifies the basic arrangement of the dimer as two skew layers with one olefinic proton positioned over a benzene ring.

The paraffinic protons appear above 3 p.p.m. In order to have 19 paraffinic protons, small rings must be involved in the crosslinking. The highest