Infrared Studies of Charge-transfer Complex Formation of Polynuclear Aromatic Hydrocarbons in the Bending Vibration Region

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POLYNUCLEAR aromatic hydrocarbons and their alkyl homologues behave as good donors in the presence of a strong acceptor such as tetracyanoethylene or a polynitroaromatic, such as *p*-dinitrobenzene (PDNB), *m*-dinitrobenzene (MDNB), or symmetrical trinitrobenzene (STNB).[1] The i.r. C–H out-of-plane bending vibrations are especially rich and interesting for the polynuclear fused-ring hydrocarbons.[2] In the case of charge-transfer involving a π-donor and a π-acceptor, the vibrations represented by 1-γ (isolated C–H), 2-γ (2 C–H adjacent), 3-γ (3 C–H adjacent), 4-γ (4 C–H adjacent) *etc.* for both components are discernible for single frequency as well as the frequencies of coupled oscillators (2-γ to 5-γ).

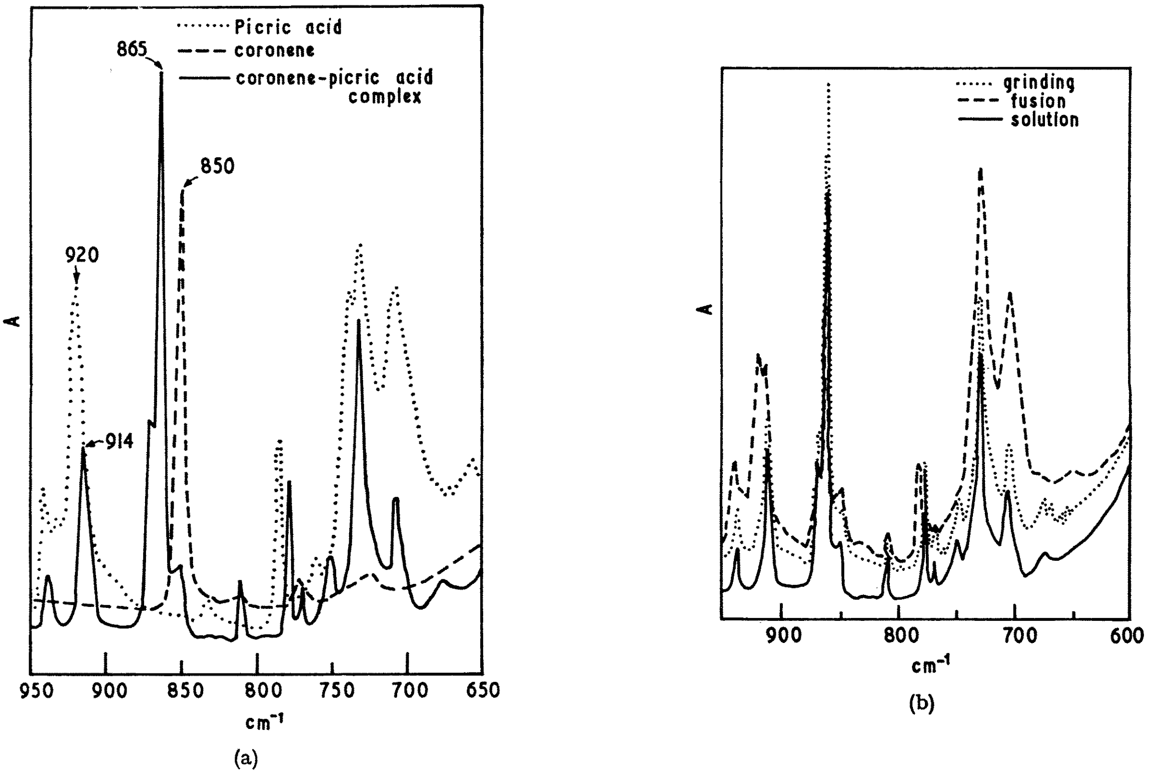


FIGURE 1

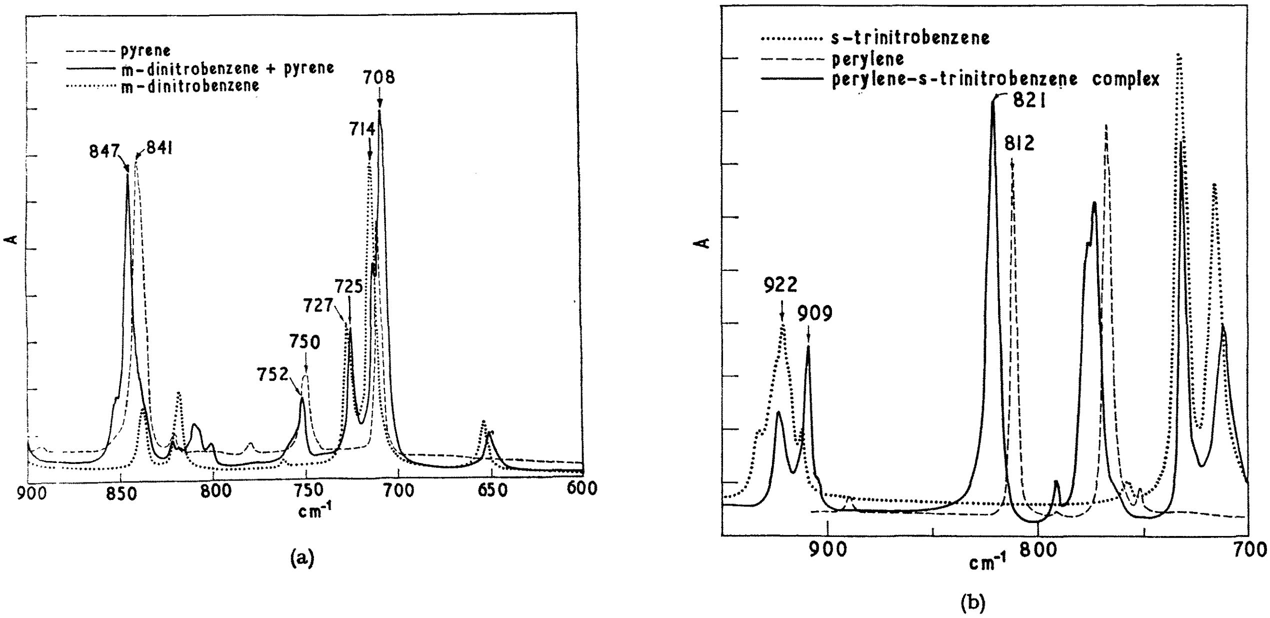
(a). *I.r. spectra of picric acid, coronene, and coronene–picric acid complex in the range* 950—650 cm.$^{-1}$. *The complex was prepared from an* o-*dichlorobenzene solution of equal mole ratio of coronene and picric acid.*

(b) *Donor–acceptor i.r. spectra of coronene–picric acid complexes in the range* 950—650 *cm.*$^{-1}$. *The dotted line indicates that the complex was formed by grinding equal molar quantities of donor and acceptor, the broken line the fusion of equal molar quantities of donor and acceptor. The solid line indicates the solution method as in* (a).

We have examined the C–H out-of-plane bending vibrations of a large number of polynuclear aromatic hydrocarbons, and their values have been compared with those obtained from the corresponding molecular complexes. During this work, two methods have been developed in order to obtain results with those fused aromatic hydrocarbons which are only sparingly soluble in organic solvents. One is the direct mulling and grinding of the hydrocarbon (donor) and the acceptor in an agate mortar. The second is the direct fusion of the aromatic and the acceptor at elevated temperature (usually around the m.p. of the donor). Both procedures yielded products which gave essentially identical spectra when compared with the spectra taken from pure complex isolated from a homogenous solution phase. A typical example, coronene–picric acid, obtained by these three different methods, is shown in Figures 1a and 1b.

The 2-γ band of coronene at 850 cm.$^{-1}$ has been shifted to *ca.* 864 cm.$^{-1}$. In general, for the π–π complexes, the bending vibrations of the donor partner shift to higher wavenumbers; and those of the acceptor partner shift to lower wavenumbers. Two typical examples are shown in Figure 2: the pyrene–MDNB (Figure 2a) and the perylene–STNB complexes (Figure 2b). In both cases the C–H bending vibrations have decreased; for pyrene, 841 to 847 cm.$^{-1}$; for perylene, 812 to 821 cm.$^{-1}$. As far as the π-acceptor is concerned, the opposite effect is noticed; for MDNB, 714 to 708 cm.$^{-1}$; for STNB, 922 to 909 cm. [1].

The frequency shift due to charge-transfer is real. The exchange of electron is reflected in the respective frequency shifts of both partners in the complexes.



(a)

(b)

FIGURE 2

(a). *I.r. spectra of pyrene*–m-*dinitrobenzene complex* (*solid line*) *in* 900—600 *cm.*$^{-1}$ *region. The broken line is for the donor; the dotted line is for the acceptor.*

(b) *I.r. spectra of perylene*–s-*trinitrobenzene in* 900–650 *cm.*$^{-1}$ *region. The dotted line is for the acceptor and the broken line is for the donor.*

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[2] M. Margoshes and V. A. Fassel, *Spectrochim. Acta*, 1955, **7**, 14.