

266. *Infra-red Spectroscopic Studies of the Structure of Molecular Complexes.*

By W. R. BURTON and R. E. RICHARDS.

The infra-red spectra of some molecular complexes and their pure components have been studied in the solid state and in solution. It is shown that two factors affect the stability of these complexes. The attraction factor largely determines the stability of complexes which exist in solution as well as in the solid state, but the packing factor accounts predominantly for the stability of some complexes which occur only in the solid state.

ABUNDANT evidence has been obtained in recent years, mainly from *X*-ray measurements (*e.g.*, Powell and Huse, *J.*, 1943, 435; Powell, Huse, and Cooke, *J.*, 1943, 153; Saunder, *Proc. Roy. Soc.*, 1946, *A*, 188, 1) that the constituents of molecular complexes formed between polar molecules such as picric acid, trinitrobenzene, and tricyanobenzene and polarisable molecules such as certain amines and hydrocarbons, are not held together by a normal chemical bond. Theories have been suggested by Briegleb (*Z. physikal. Chem.*, 1935, *B*, 31, 58) and Pauling (*Proc. Nat. Acad. Sci.*, 1939, 25, 577) which give explanations of much of the experimental data. During infra-red measurements on certain molecular complexes, however, we have found, as pointed out by Rapson, Saunder, and Stewart (*J.*, 1946, 1110), that these theories alone do not satisfactorily explain the properties of all these substances.

Experimental.—The complexes studied were very kindly supplied by Dr. Stewart of Capetown University, except the complex of dimethylaniline and *s*-trinitrobenzene, which was prepared by mixing a hot solution of *s*-trinitrobenzene in alcohol with hot dimethylaniline. The crystals which were deposited on cooling had *m. p.* 108° (Hepp, *Annalen*, 1882, 215, 344).

Two infra-red spectrometers were used; in the region 15 to 6 μ . a single-beam instrument with a rock-salt prism (Whiffen and Thompson, *J.*, 1945, 268) and from 6 to 2 μ . a double-beam spectrometer with fluorite prism (Thompson, Whiffen, Richards, and Temple, Report 17, Hydrocarbon Group, Institute of Petroleum). The spectra of solids were studied both by the Nujol method (Richards, *J.*, 1947, 978) and by allowing the solid to crystallise from the melt between two rock-salt plates. Solutions were studied in the usual kind of absorption cell.

Results.—The spectra of typical complexes measured are shown with the spectra of their pure components in Figs. 1, 2, and 3. The 3 : 1-complex of *pp'*-dinitrodiphenyl and diphenyl (complex *A*) has an absorption spectrum corresponding to simple addition of the spectra of its components, except in the region 750–850 cm^{-1} , where some of the bands occur at different frequencies. These bands are due to the out of plane vibrations of the C-H links of the benzene rings. Similar small shifts in these absorption bands are observed in the 3 : 1-complex of *pp'*-dinitrodiphenyl with *p*-hydroxydiphenyl (complex *B*). The strong band near 3 μ ., which corresponds to the stretching vibration of the O-H link of *p*-hydroxydiphenyl, appears to be sharper in the molecular compound than in the pure material. This is reminiscent of the effect of intra-molecular hydrogen bonding, which usually causes the corresponding band to be sharper than is the case with inter-molecular hydrogen bonding. A small, though quite definite, peak appears at 1763 cm^{-1} in the complex, which is not present in either component, and the interpretation of which is unknown. In contrast to these two examples, the spectrum of the 1 : 1-complex of *s*-trinitrobenzene and dimethylaniline (complex *C*) differs very considerably from the spectra of its constituents.

Further information is obtainable from measurement of the intensities of certain absorption bands. If a band occurs in the spectrum of a component of a molecular compound in a region where there is no absorption by the other component, by the molecular compound, or by the solvent, the peak height of this band, previously calibrated by measuring solutions of the pure constituent of known strength, will serve as a measure of its concentration in a solution of a mixture. In the system *p*-hydroxydiphenyl-*pp'*-dinitrodiphenyl in acetone, the band at 766 cm^{-1} may be used to characterise the *p*-hydroxydiphenyl, since the corresponding bands of *pp'*-dinitrodiphenyl and the complex occur at 788 and at 777 cm^{-1} , respectively. The results obtained with this mixture are shown in the table.

Actual concn. of <i>pp'</i> -dinitrodiphenyl (moles/ml.), $\times 10^5$	0.9	1.2	2.1
Actual concn. of <i>p</i> -hydroxydiphenyl (moles/ml.), $\times 10^4$	0.8	1.6	2.2
Concn. of <i>p</i> -hydroxydiphenyl deduced from peak height, $\times 10^4$	0.9	1.7	2.25

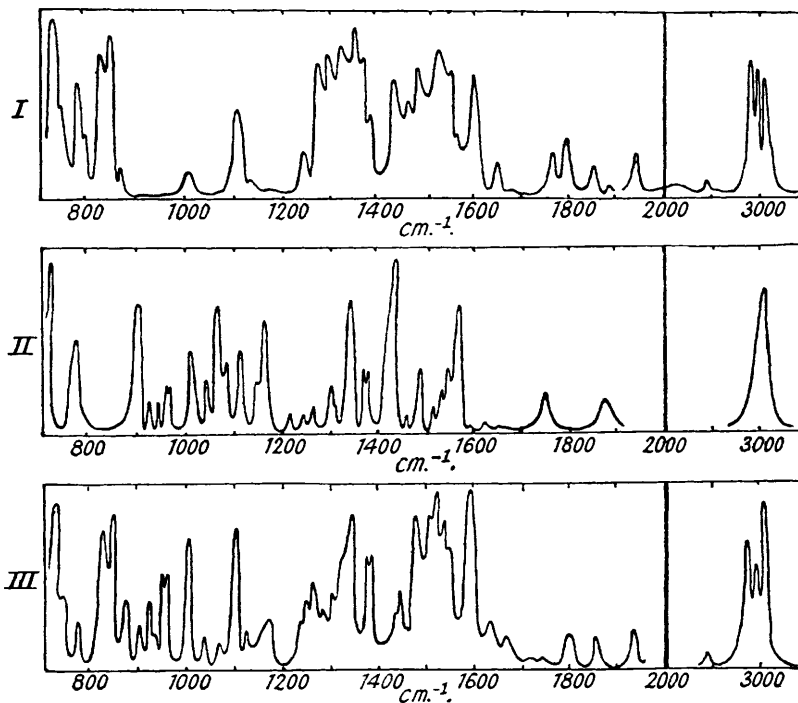
The presence of *pp'*-dinitrodiphenyl does not decrease the free *p*-hydroxydiphenyl concentration as would be expected if the complex existed in solution. Although the estimation of the *p*-hydroxydiphenyl can only be considered to be very approximate in view of the proximity of other bands, the results clearly indicate that complex formation in this solution can occur only to a very small extent, if at all.

Similar measurements on the system acenaphthene-*m*-dinitrobenzene in bromoform solution showed appreciable complex formation, since the concentrations of *m*-dinitrobenzene and acenaphthene, as measured from the peak heights of the bands at 787 and 808 cm^{-1} , were always considerably less than the concentrations expected from the amounts of these compounds put into the solution. Although quantitatively the results were only very approximate, they suggested the formation in solution of a complex of the 1 : 1-type. The existence of a complex in solution is also indicated by the yellow colour

formed on mixing the constituents in solution (see von Halban and Zimpelmann, *Z. physikal. Chem.*, 1925, **117**, 461).

Discussion.—In complexes *A* and *B* it seems clear that the interaction between the polar and polarisable components is very small, if not absent. Indeed, much greater shifts of frequencies than were recorded in the formation of these complexes are often observed during changes of state in pure compounds (see, for example, Breit and Salant, *Physical Rev.*, 1930, **36**, 871; Hettner, *Z. Physik*, 1937, **107**, 549; Halford and Carpenter, *J. Chem. Physics*, 1947, **15**, 99; Richards and Thompson, *J.*, 1947, 1260; *Proc. Roy. Soc.*, 1948, *A*, **195**, 1). The absence of the complex *B* in solution, as deduced from the intensity measurements, also implies that the intermolecular attraction must be weak.

FIG. 1.



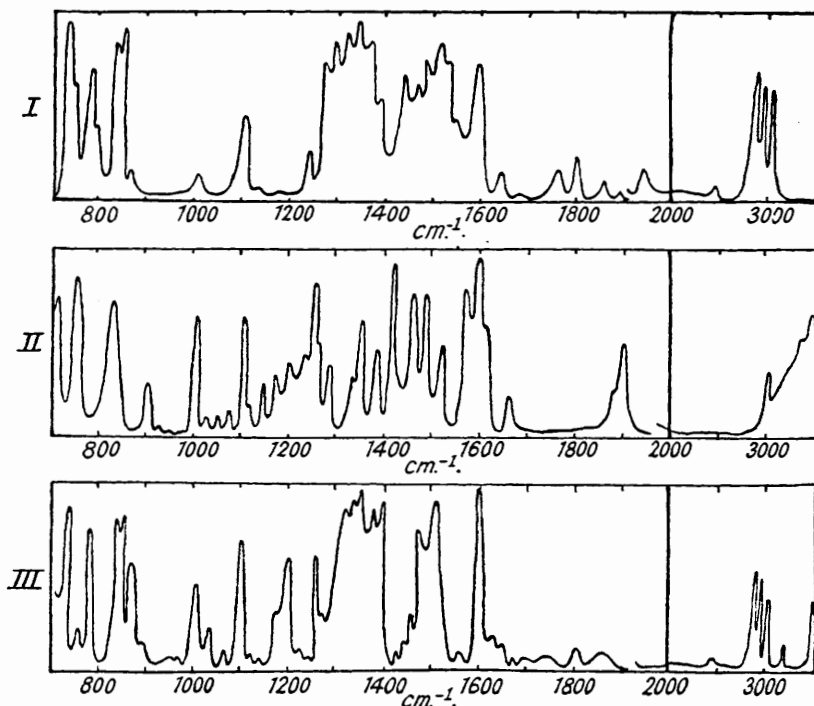
I. *pp'*-Dinitrodiphenyl (solid). II. Diphenyl (solid).
 III. 3 : 1-Complex of *pp'*-dinitrodiphenyl and diphenyl (complex *A*) (solid).

The structure of complex *C* is probably of the alternating-layer type (Briegleb, *loc. cit.*). On the Briegleb theory, the bonds of the dimethylaniline possess dipole moments induced by the *s*-trinitrobenzene, and we should therefore expect frequency shifts in the spectrum of the dimethylaniline due to the changed polarity of the bonds. On the Pauling theory (Pauling, *loc. cit.*), one would expect the frequencies of the *s*-trinitrobenzene molecules also to be altered when it forms such a complex. The spectrum of complex *C*, showing considerable shifts in the frequencies of both components, is consistent with interactions of both the Briegleb and the Pauling type.

The infra-red studies so far therefore confirm that although the theories of Briegleb and Pauling can provide an explanation of the formation of some molecular complexes, these theories are not satisfactory in explaining the properties of the complexes of types *A* and *B* described above. There is no evidence of any strong forces of attraction between the components of these complexes, but at the same time their existence implies that their crystals must be more stable than those of the separate components.

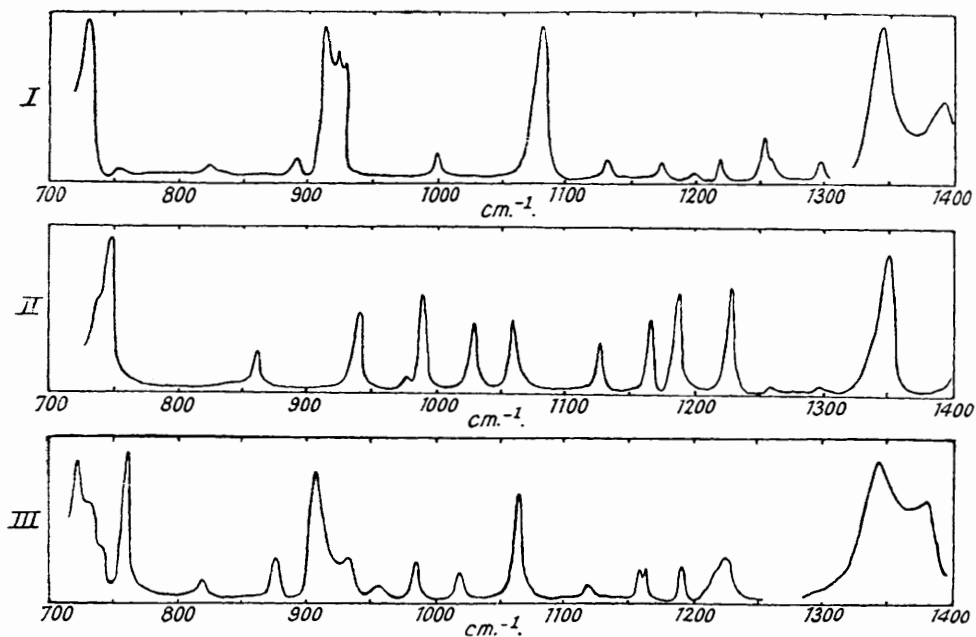
The marked dependence of the molecular ratio on the geometrical shapes of the components (Saunders, *loc. cit.*) suggests the importance of a packing factor. The reason for this can be understood if one assumes that these aromatic compounds prefer to crystallise in layer-type

FIG. 2.



I. *pp'*-Dinitrodiphenyl (solid). II. *p*-Hydroxydiphenyl (solid).
 III. 3 : 1-Complex of *pp'*-dinitrodiphenyl and *p*-hydroxydiphenyl (complex B) (solid).

FIG. 3.



I. *s*-Trinitrobenzene (solid). II. Dimethylaniline (liquid).
 III. 1 : 1-Complex of *s*-trinitrobenzene and dimethylaniline (complex C) (solid).

lattices. Fig. 4 shows diagrammatically the arrangement of the molecules in a crystal of the 3:1 molecular complex of *pp'*-dinitrodiphenyl and diphenyl (Saunders, *loc. cit.*; Rapson, Saunders, and Stewart, *J.*, 1946, 1110). A similar complex can be formed from dinitrodiphenyl and *NNN'N'*-tetramethylbenzidine, so it follows that from size considerations alone it should be possible for the pure dinitrodiphenyl to crystallise in a similar lattice to those of its complexes, as is shown in Fig. 5. It can be seen, however, that the oxygen atoms of the nitro-groups, which carry fractional negative charges, approach relatively closely to one another, and this would cause considerable repulsion between these nitro-groups. Pure *pp'*-dinitrodiphenyl does not therefore crystallise in this way, but forms a complicated lattice in which the nitro-groups overlap as far as possible in order to produce attraction instead of repulsion (Van Nickerk, *Proc. Roy. Soc.*, 1943, *A*, 181, 314). When allowed to crystallise in the presence

FIG. 4.

Structure of complex *A*: *pp'*-dinitrodiphenyl molecules are denoted by black circles, the diphenyl molecule by plain circles (see Rapson, Saunders, and Stewart, *J.*, 1946, 1110).

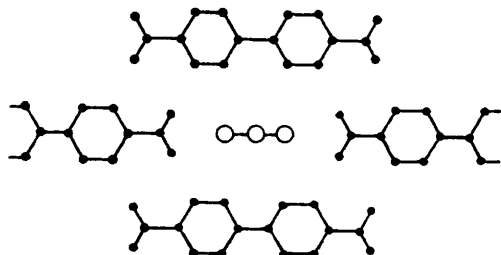
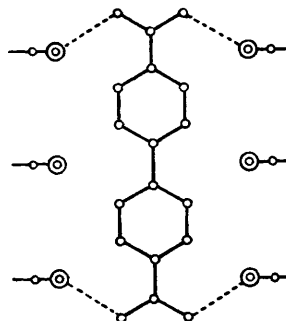


FIG. 5.

Showing repulsion between O-atoms in a hypothetical crystal of *pp'*-dinitrodiphenyl of the same structure as its complexes.



of diphenyl, however, it is able to do so in the preferred layer-type lattice, using the diphenyl molecules to separate or "insulate" the polar nitro-groups from one another.

It is concluded that the complexes *A* and *B* owe their stability not to forces of attraction between the components but rather to the lower energy of their crystal lattices compared with that of the pure *pp'*-dinitrodiphenyl.

When, in addition to the packing factor discussed above, there is also some definite force of attraction between the molecules of the components of the molecular complex, one would expect more than one type of complex to be formed, depending upon which of the two factors finally predominates. As an example, if *NNN'N'*-tetramethylbenzidine is added to a hot solution of *pp'*-dinitrodiphenyl, a 1:4-complex separates on cooling, whereas on adding *pp'*-dinitrodiphenyl to excess of tetramethylbenzidine a 1:1-complex separates immediately (Rapson, Saunders, and Stewart, *loc. cit.*; see also Sudborough and Bear, *J.*, 1910, 97, 773; Sudborough, *J.*, 1916, 109, 1339).

In conclusion we thank Dr. Stewart of Capetown University, for the provision of samples of molecular complexes, and Dr. H. W. Thompson, F.R.S., for the use of the spectroscopic equipment.

PHYSICAL CHEMISTRY LABORATORY,
SOUTH PARKS ROAD, OXFORD.

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