Disappearance, on Freezing, of the Colour of Systems that exhibit Weak Molecular Complexing

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A PHENOMENON peculiar to the electronic spectra of molecular interactions is the appearance in solution of an additional absorption even when the acceptor and donor components do not appear to associate.[1] We seek to show that such weak interactions are common and to describe an additional property, namely that the colours of the pure mixed samples vanish when the mixtures are frozen.

The red, magenta, and violet colours of mixtures of the strong electron donor tetrakis(dimethylamino)ethylene with the perhalogenobenzenes,[2] acridine,[3] or the nitrobenzenes[3,4] vanish when the systems are frozen in liquid nitrogen and re-appear when they are melted. Solution equilibrium studies[2,3] show near-zero equilibrium constants for these interactions. Tinkler[5] described colour disappearance for some diphenylamine mixtures and found no evidence for complexing with *p*-chloronitrobenzene from density, viscosity, or melting-point measurements, even though the melt was orange.

The Table shows a number of these systems together with the colour differences between the melt and the solid. The mixtures were examined mainly on the basis that bulky substituents on π-donors or π-acceptors markedly reduce their complexing ability. All of the systems show small spectrophotometric equilibrium constants in the region $-0{\cdot}2$ to $+0{\cdot}2$ l. mole^{-1} in the inert solvents hexane, cyclohexane, carbon tetrachloride, or dichloromethane.

TABLE. *Colour changes for some donor–acceptor systems*

Donor	Acceptor	Solution of melt colour	Solid colour
Tetrakis(dimethylamino)ethylene	Hexafluorobenzene	Orange-red	Very pale cream
Tetrakis(dimethylamino)ethylene	Acridine	Red	White
Tetrakis(dimethylamino)ethylene	Nitroanisole	Red	White
Tetrakis(dimethylamino)ethylene	Nitrobenzene	Magenta	White
Tetrakis(dimethylamino)ethylene	*p*-Chloronitrobenzene	Violet	White
Tetramethyl-2-tetrazene	*p*-Dinitrobenzene	Orange	White
Diphenylamine	*p*-Chloronitrobenzene	Orange	White
Diphenylamine	*p*-Dinitrobenzene	Red	White
Diphenylamine	*p*-Chloranil	Blue	Pale cream
Triphenylamine	*p*-Dinitrobenzene	Red	White
Triphenylamine	1,3,5-Trinitrobenzene	Red	Very pale pink
Triphenylamine	*p*-Chloranil	Blue-green	Pale cream
p-Di-t-butylbenzene	Tetracyanoethylene	Orange-red	White
Tetraisopropylbenzene	Tetracyanoethylene	Violet	White
Anthracene	Trinitromesitylene	Yellow	White
NN-Dimethylaniline	Trinitromesitylene	Yellow-orange	White
Pyrene	Hexanitrodiphenyl	Red	Pale cream
Anthracene	Hexanitrodiphenyl	Magenta	White
Hexamethylbenzene	Tetranitromethane	Orange-red	White
Naphthalene	Tetranitromethane	Yellow-orange	White

The reason for the colour loss may be seen by comparing the anthracene–trinitromesitylene and anthracene–trinitrobenzene systems. A simple eutectic phase diagram of the former contrasts with 1 : 1 compound formation[6] found for the second, and the melt and solid of the latter are orange. The random structure of the liquid permits intermolecular contacts, whereas for the eutectic system, acceptor and donor components become separate phases in the solid. Those acceptor and donor molecules in contact, and hence capable of contributing to the absorption intensity, are the relatively few at the crystal interfaces. Simple eutectics occur for tetranitromethane–benzene[7] and for triphenylamine–*p*-dinitrobenzene systems. *X*-Ray diffraction patterns confirm that these and the tetraisopropyl-benzene–tetracyanoethylene system are mixtures.

In summary, systems whose absorbances decrease according to the inverse square of the dilution, freeze to colourless solids for pure mixed samples. This requires that the net forces of interaction in solution should be the same for a very different environment, *i.e.* the crystal lattice, and exceptions are to be expected. Other, important exceptions will occur for systems tending to produce glasses or solid solutions. Here colour changes will be sensitive to factors impeding crystallization, such as the rapidity of freezing or a molecular geometry which does not lend itself to packing easily into a lattice structure.

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