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CHARGE-TRANSFER COMPLEXING ABILITY OF 2-CHLORO-4,6-DICYANOPYRIMIDINE

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The nature of substituents in a molecule determines whether the molecule acts as an electron donor or electron acceptor in charge-transfer complexation. The π-electron system of aromatic compounds is often an electron donor site (1), but if electron withdrawing substituents are present this property may be reversed and the electron deficient π-system may act as an electron acceptor site (2). As part of a general study of the acceptor properties of electron deficient systems we are synthesising pyrimidines and purines carrying electron withdrawing substituents. A possible site for interaction with carcinogens is at a nucleic acid and although there are some observations of chemical interaction between aromatic hydrocarbons and purines, pyrimidines, and nucleic acids which refer to the solubilisation of the hydrocarbon (3), there are only a few reports of charge-transfer complexation in the purine-hydrocarbon and pyrimidine-hydrocarbon systems. Machmer and Duchesne (4) have reported evidence for charge-transfer complexation between adenine, guanine, cytosine, and thymine and the strong acceptor chloranil in dimethylsulphoxide solution, and Duchesne and co-workers (5) have reported charge-transfer complexation between some nucleosides and chloranil. Evidence for some type of complexing between thiamine and various indoles has been obtained from n.m.r. spectroscopy (6), but no charge-transfer bands have been reported for the purine-hydrocarbon and pyrimidine-hydrocarbon systems in which the heterocyclic species is the acceptor. We have synthesised 2-chloro-4,6-dicyanopyrimidine and wish to report on the electron acceptor ability of this compound.

The ability of 2-chloro-4,6-dicyanopyrimidine to form charge-transfer complexes is indicated by the appearance of a new absorption band in the visible region of the spectrum when electron donors such as anthracene, chrysene, and pyrene are added to a solution of the compound in chloroform. A straight line plot is obtained (Fig 1) when the energy corresponding to the peak maximum of this new band, for a series of donors, is plotted against the energy of the charge-transfer transition in the corresponding complexes with 1,3,5-trinitrobenzene.

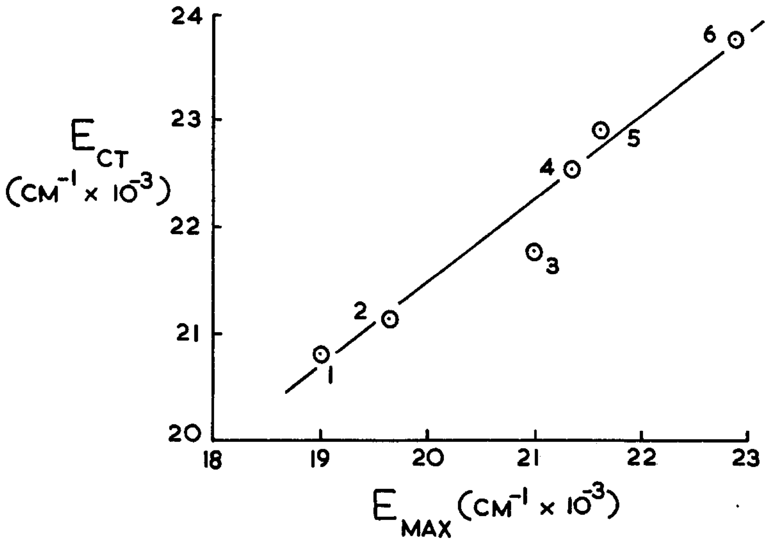

Fig. 1. Plot of energy (E_{max}, cm^{-1}) of peak maximum for a series of complexes of 2-chloro-4,6-dicyanopyrimidine against charge-transfer transition energy (E_{CT}, cm^{-1}) for the corresponding complexes of 1,3,5-trinitrobenzene.
The donors are: (1) perylene; (2) 3,4-benzopyrene; (3) anthracene: (4) pyrene; (5) 1,2-benzanthracene; (6) chrysene.

This demonstrates that the new band arises from a charge-transfer transition and, since the slope of the line is close to unity, it is evident that the complexes formed with 2-chloro-4,6-dicyanopyrimidine are of the same type as those formed with 1,3,5-trinitrobenzene, namely π,π complexes.

Association constants for complex formation are readily evaluated by the n.m.r. method developed by Hanna and Ashbaugh (7) and modified by Foster and Fyfe (8). The value of the association constant for the benzene/2-chloro-4,6-dicyanopyrimidine system in 1,2-dichloroethane at 33.5° is 0.65 kg mol^{-1}. This value may be compared with the value of 0.26 kg mol^{-1} for the association constant of the mesitylene/1,3,5-trinitrobenzene system in 1,2-dichloroethane at 33.5° (9). Since mesitylene is a more powerful electron donor than benzene (10) it is apparent that 2-chloro-4,6-dicyanopyrimidine is a better electron acceptor than 1,3,5-trinitrobenzene.

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