with the molecular interpretation of Davies and Evans[5] concerning the oxidative metabolism of naphthalene by microbial enzymes.

This communication reports some of the salient features of a more rigorous investigation which we have made of the enzymatic attack of naphthalene crystals produced in two distinct ways. Type I single crystals of 'scintillation grade' naphthalene were grown from the melt using the Bridgman technique by Thorn Electronics, Ltd. (Surbiton, Surrey). Type II single crystals were produced by slow sublimation of polycrystalline 'molecular weight grade' naphthalene. The etchant used consisted of an aqueous solution of the cell-free enzyme derived from pseudomonads as follows. Cells grown in a naphthalene–mineral salts medium under forced aeration were sonically disrupted in a phosphate buffer of *p*H 7 (0·05 M) to yield a supernatant (after centrifuging at 25,000*g*) which was active on naphthalene in the presence of reduced niacin adenine dinucleotide (NAD) as cofactor. Etch patterns on the {00*l*} faces only could be studied by transmission optical microscopy—a restriction imposed largely by the cleavage behaviour of naphthalene crystals.

In Fig. 1, which shows a {00*l*} face of a type I crystal after etching for 30 sec, there are numerous flat-bottomed etch-pits which tend to be hexagonal in outline and all of which are of the same crystallographic orientation. Fig. 2 is an enlargement of part of the surface shown in Fig. 1: the tendency for hexagonal etch-pits to be produced is more evident here. Type II crystals behave in essentially the same way, although there does appear to be rather more aptitude for triangular (flat-bottomed) pits to be produced than with type I crystals.

We are of the opinion that it is unlikely, but not impossible, that the etch-pits in Figs. 1 and 2 are nucleated at the termini of dislocations that glide in {0*l*0} planes (and would emerge at {00*l*} faces). (Gordon[6] has recently shown

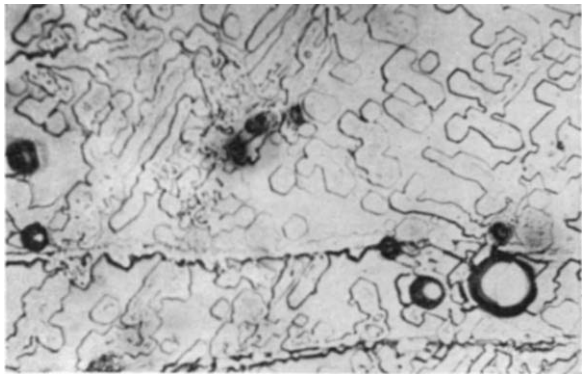

Fig. 1. Etch pattern on 00*l* face of naphthalene crystal after 30 sec exposure to enzymatic etchant (× *c*. 103)

Fig. 2. Magnified area of another region of the crystal face shown in Fig. 1 (× *c*. 206)

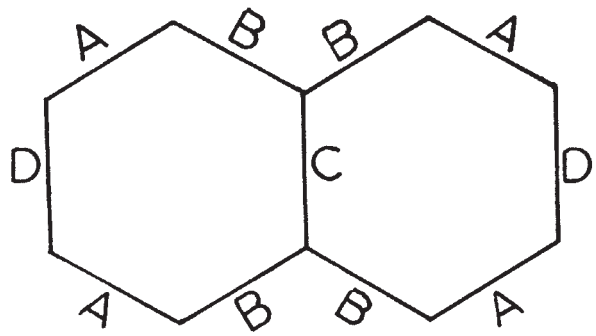

Fig. 3. The various bond types in naphthalene

that there is a greater likelihood for dislocations in naphthalene to glide in {00*l*} rather than in {010} planes.) We feel that they are more likely to be undersaturation etch-pits[7] which have been nucleated randomly on the {00*l*} faces. So far as the crystallographic orientation of the pits is concerned, it is possible to explain the results obtained with both types of crystals in terms of the anisotropy of reaction rates at various crystallographic planes of the naphthalene lattice. This anisotropy, in turn, devolves on differences of reactivity at various sites in the naphthalene molecule. In essence, our conclusions are that bonds *A* and *B* (see Fig. 3) are more susceptible to attack by pseudomonads than bonds *C* and *D*. A full account of this work is to be published elsewhere.

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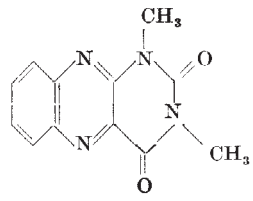
Dimethylalloxazine as an Electron Donor and Acceptor

I WISH to report that 1,3-dimethylalloxazine (I) can form molecular complexes acting not only as an electron acceptor but also as a donor. It was possible to crystallize complexes from ethylene dichloride with the following compounds: pyrene, tetracyanoethylene (TCNE), and 2,3-dichloro-5,6-dicyano-*p*-benzoquinone. The results of the elemental analysis indicate that these complexes contain dimethylalloxazine and the other component in a ratio of 2 : 1 regardless of whether the latter is a donor or acceptor. As the infra-red spectra of the complexes are very close to the superimposed spectra of the components,



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there is no appreciable change in the intramolecular bonds by complex formation. Therefore, the ground states of the complexes are essentially non-bonding. The complexes are more deeply coloured than the components. For example, the pyrene and TCNE complexes are deep yellow. On the other hand, dimethylalloxazine is pale yellow and the other two components are colourless. As shown in Fig. 1, the appearance of a new absorption is clearly seen in these complexes. It can be concluded that these complexes are of the charge transfer type; dimethylalloxazine in the pyrene complex is acting as an electron acceptor and in the TCNE complex as a donor.

In the present complexes, which have essentially non-bonding ground states, the energies of the molecular orbitals may be little different from those in the separate components. In a naïve approach, the energy of the first charge transfer band in a given complex can be considered as the energy difference between the highest occupied molecular orbital of the donor and the lowest vacant molecular orbital of the acceptor[1]. Therefore, the relative positions of the molecular orbitals associated with the complex formation can be ascribed on the basis of the energies of the excitation within the component molecules and of the first charge transfer bands in the complexes. Strong donors are expected to have their highest occupied molecular orbitals at relatively high energies and strong acceptors are expected to have their lowest vacant molecular orbitals at relatively low energies.

In Fig. 2, the lowest vacant molecular orbitals of the acceptors, including dimethylalloxazine, were located relative to the highest occupied molecular orbital of pyrene by means of the energies of the charge transfer bands in the pyrene complexes. The positions of the remaining molecular orbitals were assigned on the basis of the first excitation energies in the component molecules. As any changes in energy of the molecular orbitals in forming the complex have been ignored, the present position is only approximate. Nevertheless, it is clearly shown that the highest occupied molecular orbital of dimethylalloxazine is located between those of the donor and the acceptors, and the lowest vacant molecular orbital of the alloxazine is located again between those of the donor and acceptors. In agreement with the observation reported here, the molecular orbital diagrams given in Fig. 2 indicate that dimethylalloxazine can be an electron donor when combined with strong acceptors and can be an acceptor when combined with strong donors.

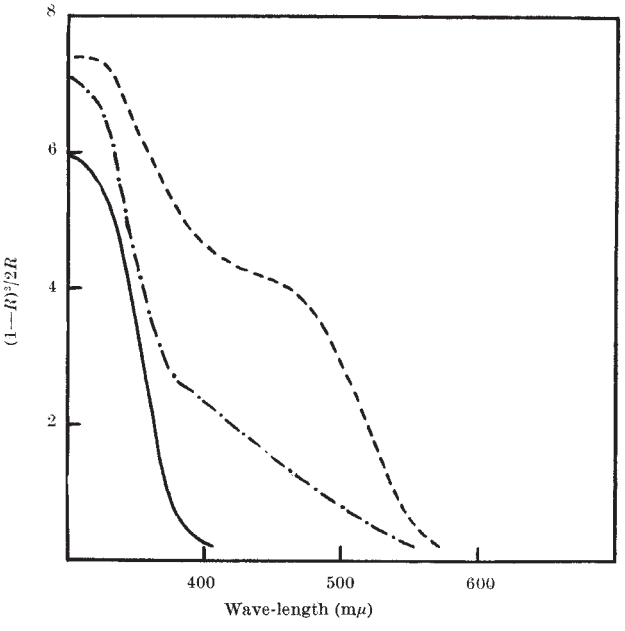

Fig. 1. Kubelka-Munk plots of diffuse reflectance spectra of dimethylalloxazine (——), the pyrene complex (- - -), and the TCNE complex (— · — · —)

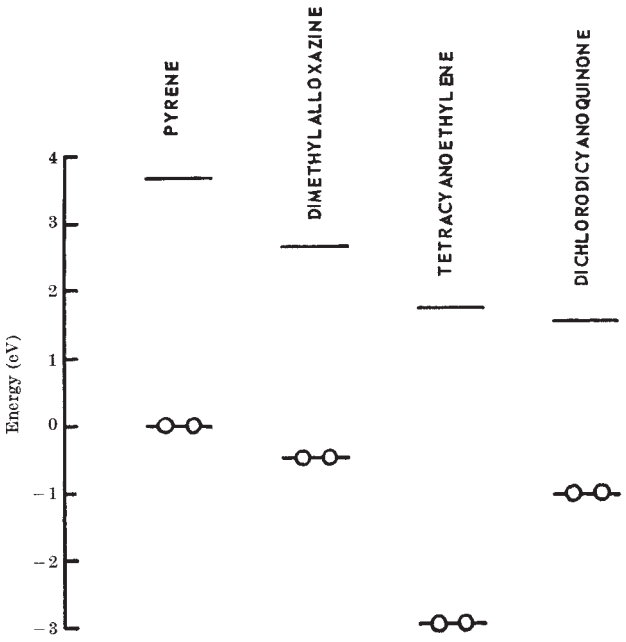

Fig. 2. Relative location of the highest occupied and the lowest vacant molecular orbitals in dimethylalloxazine and some other compounds

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Polymorphic Forms of the Diaminopyrene-*p*-chloranil and Related Molecular Complexes

I REPORTED earlier that most of the quinone complexes with electrical resistivities of 10^6 ohm cm or less have essentially dative ground states[1]. The only exceptions found were the 1,6-diaminopyrene complexes with *p*-chloranil and *p*-bromanil. It therefore seemed worthwhile to examine these complexes further. The resistivity values reported for the *p*-chloranil complex are scattered in a wide range, namely 10^3–10^4 ohm cm for the pressed polycrystalline samples[2,3] and 10^5–10^9 ohm cm in the three directions of the single crystal[4]. This communication reports the existence of some polymorphic forms of the 1,6-diaminopyrene-*p*-chloranil and related molecular complexes. The polymorphic forms are distinctly different in colour, diffuse reflectance spectrum, vibrational spectrum, X-ray diffraction, and also electrical resistivity. The scattered resistivity values appear to be well related to those of such forms.

The *p*-chloranil complex prepared in chloroform, the solvent from which Kronick and Labes grew their single crystal[4], is dark blue and green when pulverized. The composition is 1 : 1. Calculated (per cent): carbon 55·3, hydrogen, 2·5; nitrogen, 5·9; chlorine, 29·7. Found (per cent): carbon, 55·2; hydrogen, 2·4; nitrogen, 6·1; chlorine, 29·4. The diffuse reflectance spectrum shown in Fig. 1 indicates that, although the spectrum has an absorption minimum at about 530 mμ, the absorption extends to about 1·8 μ. The pressed pellet exhibits a resistivity of the order of 10^7 ohm cm. This value seems to be reasonable as the average for 10^5–10^9 ohm cm observed in the three directions of the single crystal. This green form can be transformed into the brown form (mentioned later) by recrystallization from benzene.