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Charge Transfer Interaction in Homomolecular Crystals of Azacycl[3.3.3]azine Derivatives

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The electronic spectra and structure of the single crystals of azacycl[3.3.3]azine derivatives have been investigated by the reflection and absorption measurements. In addition to the π-π^* transitions of in-plane polarization, the out of plane polarized transition have been found which are due to the intermolecular charge transfer transition between the stacked molecules of the same species.

The electronic structure of azacyclazine system has been a subject of controversial discussion as regard to the concept of aromaticity.1) The ab initio SCF MO calculations were performed to discuss the electronic structure.2) The major conclusion is that the HOMO is of π-electron nature consisting of peripheral N atoms, and the LUMO is also a π-orbital being composed of the central N and C atoms. The calculation on tetraazacycl[3.3.3]azines showed that it is a polar molecule; the central N atom acts as a σ acceptor and π donor while the peripheral N atoms behave as σ and π acceptors.3)

The crystal structures of azacyclazines have been studied to find aromatic structure.3-7) However, a possibility has been indicated that self-complexes may be formed because the intermolecular contact is fairly strong and the molecule has amphoteric properties. Actually the photoelectron spectra of azacycl[3.3.3]-azines showed ionization potentials in the range of 7.3 - 9.1 eV,2,3) which may

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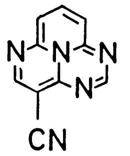

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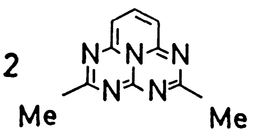

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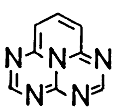

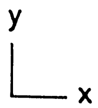

support their good donor properties. The LUMO extending over the central N and peripheral C atoms may act as a good acceptor. Recently Ashwell and Nowell[8] have presented a view on the charge transfer interaction in the homomolecular crystal of 4-cyano-1,3,6-triazacycl[3.3.3]azine 1 by showing a semi-conductivity of $5\mathrm{x}10^{-10}\mathrm{S\ cm}^{-1}$. We have been interested in the CT interaction between the same molecules and this type of CT absorption has been reported for anthracene,[9] naphthacene,[10] 2,2'-cyanine,[11] (5-dimethylamino-2,4-pentadienylidene)dimethylammonium salt,[12] squarylium dye[13] and picolyltricyanoquinodimethane.[14] This time we have measured the crystalline reflection and absorption spectra of 1 and 2,5-dimethyl-1,3,4,6-tetraazacycl[3.3.3]azine 2 and compared them with the solution spectra (Fig.1 (a)).

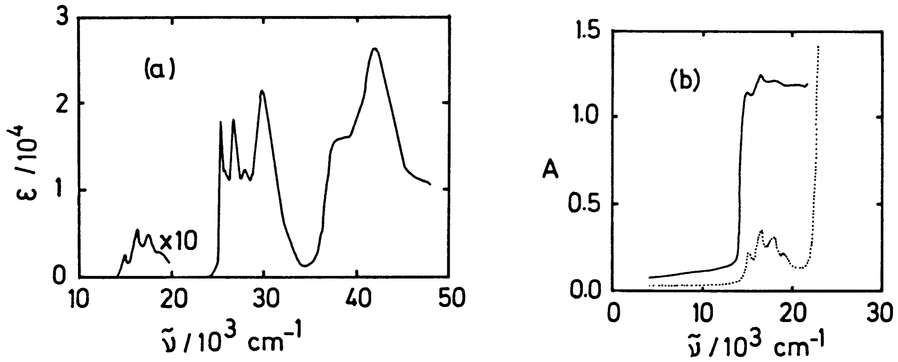

Fig.1. Absorption spectra of 1, (a) solution in CH_3CN, (b) thin crystal with polarized light: —— in plane, and ········ out of plane of the molecule.

The electronic absorption spectra of 1 and 2 consist of five bands, while MO calculation based on P-P-P method showed more than five transitions; the polarization character of these bands are assigned as follows: 15000 cm^{-1} (x), 26000 cm^{-1} (x), 30000 cm^{-1} (y), 38000 cm^{-1} (x) and 42000 cm^{-1} (y?).

The reflection spectra of 1 are shown in Fig.2 together with the projection of molecules. Broad structureless reflections were found below 14000 cm^{-1}, but these were found to be of non-absorptive nature, since the absorption spectra measured with very thin crystals (Fig.1(b)) did not show any absorption band below 14000 cm^{-1}. Origin of this broad reflectance will be discussed in a latter publication; but a possibility remains that it is due to an internal reflection effect. The positions of small humps around 14200 - 18000 cm^{-1} coincide with the crystalline absorption bands, which resemble in shape to the first band in the solution spectrum. The second strong reflection band at 24000 cm^{-1} parallel to the molecular plane corresponds to the solution band of 26000 cm^{-1}, and the weak reflection band at 31000 cm^{-1} is correlated to the solution band at 30000 cm^{-1}. The calculated transition moments agree with the observed band intensities and polarizations. The x polarized transitions were found to occur rather strongly as compared to the y bands on the (010) plane. For the out of plane direction weak humps around 15500 cm^{-1} were due to the weak band at 15000 cm^{-1} in the solution spectra. However, the broad and modest reflection band recognized at 21000 cm^{-1} may be regareded as the intermolecular CT band in this crystal.

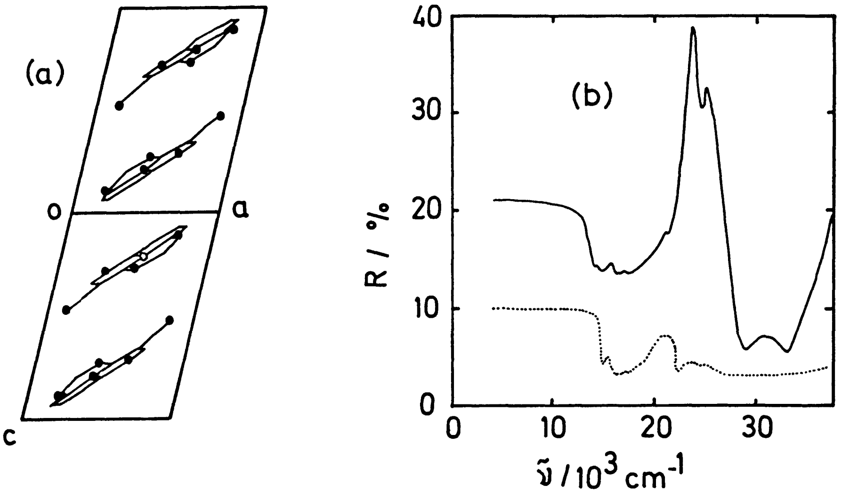

Fig.2. (a) Projection figure of 1 onto (010); (b) reflection spectra with polarization directions: —— parallel and ········ perpendicular to molecular plane.

Two types of molecular overlap were reported by Ashwell et al.,$^{7)}$ with interplanar distances of 3.09 and 3.31 A, as shown in Fig.3 (a) and (b). The intermolecular overlap integrals in these pairs were of comparable sizes, 0.0049 and 0.0034, respectively. Therefore, both types of stacking might be effective for the intermolecular CT interaction. The calculated MO coefficients for the HOMO and LUMO are shown in the same figure.

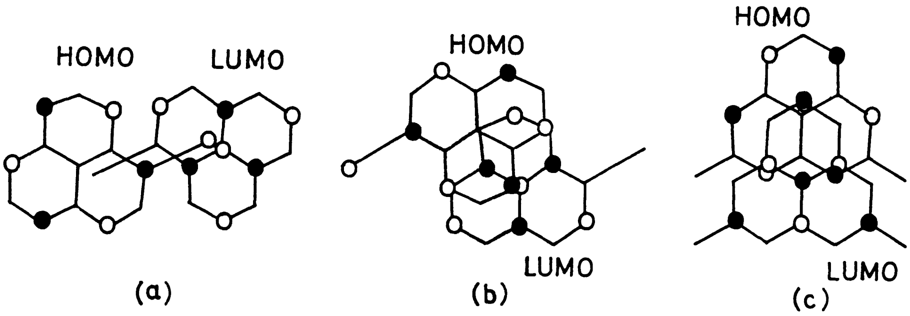

Fig.3. Frontier orbitals of the overlapped pairs in the crystals: (a) and (b) for 1 and (c) is for 2.

Another example of a self-complex is the crystal of 2. The molecules stack along the a-axis with an interplanar spacing of 3.4 A$^{6)}$ and the overlap integral is 0.0011. The overlap mode is shown in Fig.3 (c). Fig.4 illustrates the projection and reflectances on the (010) face.Non-absorptive reflections are also found for this crystal in the energy region below 16000 cm^{-1}. A sharp reflection band is observed at 31200 cm^{-1} in the inplane spectrum which may be correlated to the first y transition. This band appears feebly in the out of plane direction. However, appearance of a small but broad reflection band in the region of 23200 cm^{-1} on this plane is of particular interest since its polarization is along the out of plane direction and it may be regarded as an inter-

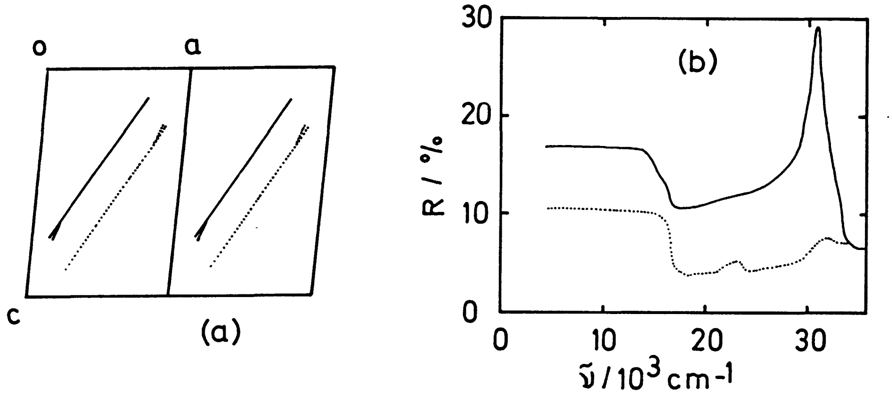

Fig.4. (a) Molecular projection of 2 onto (010), (b) reflection spectra: —— in plane, and ········ out of plane polarizations.

molecular CT band. Recognition of a CT band in the crystal of 2 may imply that an electron accepting substituent (eg.-CN) is not a profound need to exhibit an intermolecular CT. Probably, the characteristic electronic polarization in the ring and the good molecular packing have facilitated the CT interaction. Further substitution by the CN group might have enhanced the CT process, since the orbital energy of LUMO is more stable than that of 3 and 2 by 0.08—0.12 eV and the polarization energy of the crystal 1 may be larger than that of 3 and 2 by 0.1 eV. The transfer energy is apparently larger in 1 than in 2 since the overlap integrals are much large, therefore, the intermolecular CT band in 1 is red-shifted and showed stronger intensity than in 2.

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