

## Crystal spectra of methiodides of some nitrogen heteroaromatics

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**Abstract.** The longest wavelength bands of methiodides of some nitrogen heteroaromatics, which originate from a charge transfer (CT) transition, have been investigated in the solid state at liquid nitrogen temperature. The appearance of vibrational structure in the CT band has been established. Polarised crystal spectra have also been studied.

**Keywords.** CT band; vibrational structure; polarisation.

### 1. Introduction

Though charge transfer (CT) bands have been investigated extensively since 1952 some problems still remain unsolved. One of the problems is whether the multiplicity of a CT band occasionally observed is due to involvement of more than one donor (or acceptor) states or due to multiplicity of conformation. This problem has recently been discussed by us (Bagchi and Chowdhury 1979) with methiodide of diazenes as example, where we explained that the two CT bands  $\approx 8000 \text{ cm}^{-1}$  apart are due to multiplicity of donor final states in contradiction with the previous explanation that the two CT bands in methiodides of some pyridine derivatives are due to the presence of more than one acceptor level (Verhoven *et al* 1969; Mackay *et al* 1971; Kosower *et al* 1972). If close lying levels exist in both donor and acceptor, four bands instead of two should be observed. Since solution spectra are broad and featureless one way to study these is to increase the resolution by crystal spectra at low temperatures. Another reason for studying the crystal spectra is to resolve the vibronic contribution to CT bands, studies on which are relatively very few (Mulliken and Person 1969). Crystal spectra are also expected to yield polarisation of the CT band where again the controversy is not fully resolved. In the present work the CT absorption bands of the methiodides of pyrazine, pyridazine, quinaldine and acridine have been studied in the crystal state both at room and liquid N<sub>2</sub> temperatures.

### 2. Materials and methods

The amines were quaternised with methyl iodide and the compounds thus formed were purified by repeated crystallisation from dry ethanol. Crystals were grown from ethanol solution and polished by solvent. Some experiments were performed with identically oriented thin films of these compounds deposited on a quartz plate from ethanol

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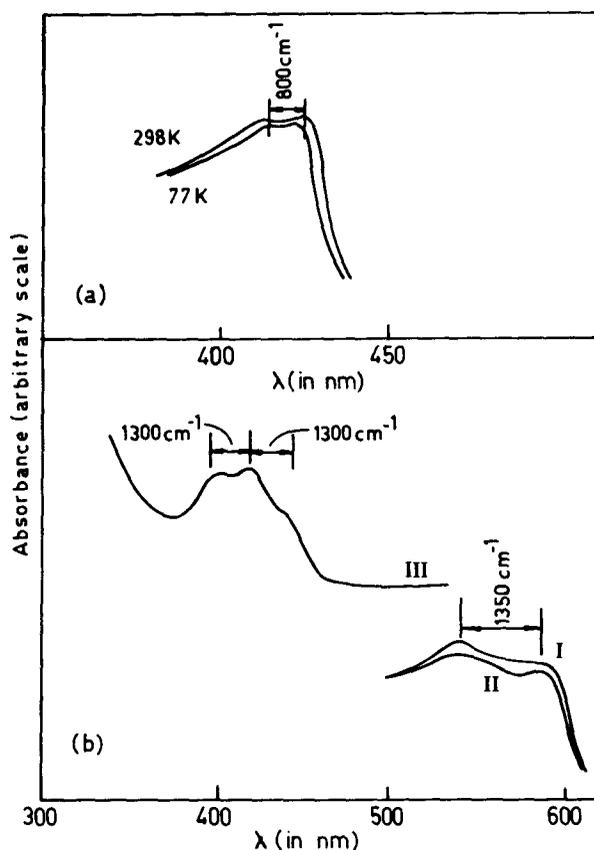
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solution. The experimental set-up for the measurement of absorption spectra of the crystals have been described previously (Bagchi and Chowdhury 1976). A cold finger type of Dewar was used for recording the spectra at low temperatures. A quartz Wallaston prism was used to polarise the light incident on the crystal (Bera *et al* 1969).

### 3. Results and discussion

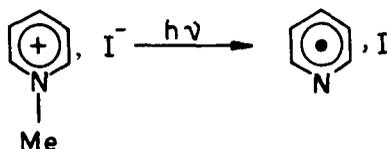
The longest wavelength bands for the crystals at 77°K are shown in figure 1. The bands for these compounds are very similar to those observed in solutions (Bagchi and Chowdhury 1979). Absence of similar bands in the corresponding nitrate and perchlorate derivative indicate that the bands originate due to an interaction between the iodide and the organic cation.

The bands are broad even at 77°K although the width is slightly less than that observed in solution. In solution, a number of possible conformation may exist for such ion pair complexes and as such the bands are likely to be broad. But such a possibility is



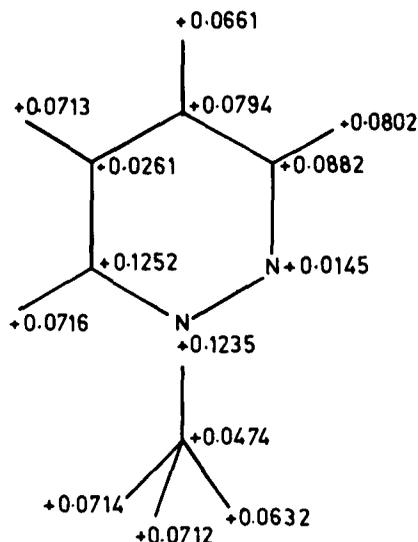
**Figure 1.** CT bands of the crystals of various methiodides: Vibrational features and polarisation characteristics (a) pyridazine methiodide, (b) acridinium methiodide (I =  $e_1$  needle axis II =  $e_2$  needle axis III = acridinium nitrate in water).

unlikely in the solid state and thus multiple conformation has no role to play as regards the width of the band. Moreover, the bands are asymmetrical with greater breadth on the high frequency side. The facts are in conformity with the assignment of  $\sigma_T$  nature to these bands where the equilibrium distance between the donor and the acceptor in the excited state is different from that in the ground state (Mulliken and Person 1969). Thus, like in the solution spectra, this band in the crystals presumably originates due to a transfer of charge from the iodide ion to the organic cation:

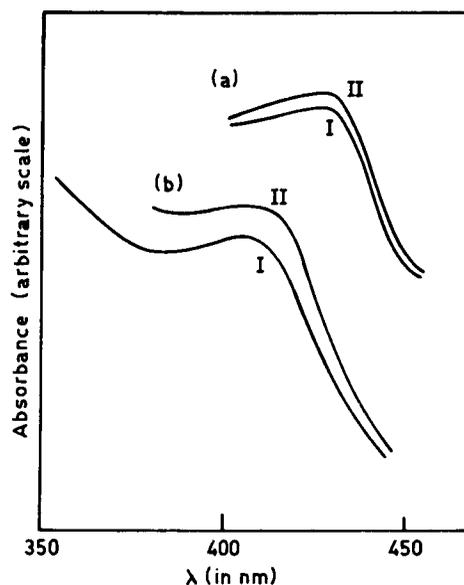


### 3.1 Vibrational features

The longest wavelength bands of pyridinium and acridinium iodide show structure [figure 1 (a) and (b)]. This may be either due to the presence of more than one electronic state (or configuration) of the complex in the solid state, or due to vibrational structure. It appears that the distribution of charge density in the cation (figure 2) may lead to more than one geometry of the complex. In the event that the band structures are due to the presence of more than one electronic state (or configuration), the relative polarisation of the components would have been different. Whereas in the case of vibronic interaction one expects similar relative polarisation for the components. Polarisation studies of acridinium methiodide (figure 3) supports the latter view (we have not been able to prepare a single crystal of pyridazine methiodide and as such



**Figure 2.** Distribution of charge densities in pyridinium cation calculated by CNDO/2 method (Pople and Segal 1966) using standard programme QCPE 29.



**Figure 3.** Polarised spectra of a single crystal of (a) pyrazine methiodide; (b) quinaldine methiodide (I =  $e_{\parallel}$  needle axis; II =  $e_{\perp}$  needle axis).

no polarisation studies have been made for the compound). In fact the potential energy curve for ion-pair complexes has a deep, rather than a shallow minimum, and the vibrational characteristic of the excited state is very likely to appear in the crystal spectrum at low temperature. Another possibility that the appearance of such structures without distinct polarisation is due to any crystal field effect of the neighbouring ions, probably does not apply because this would demand the existence of a degeneracy in the energy levels of the donor and/or the acceptor in the absence of a crystal field. We thus tentatively suggest that the lower energy band is the (O—O) band and the separation ( $800\text{ cm}^{-1}$  for pyridazinium methiodide and  $1350\text{ cm}^{-1}$  for acridinium methiodide) corresponds to excited state vibrational separation of the cation. It may also be pointed out that the vibrational structure observed in the  $\text{CT}$  spectrum of the acridinium compound has close similarity to that observed in the solution spectrum ( $\pi\text{-}\pi^*$  transition) of the corresponding cation. Thus it appears that during the process of charge transfer the electron goes to a  $\pi$  centre rather than to any localised centre of the cation.

### 3.2 Polarisation

The polarised spectra of the single crystals of the methiodides of pyrazine, acridine and quinaldine are shown in figure 3. For 1-1 complexes the theory predicts that the  $\text{CT}$  band should be polarised along the line joining the  $\text{I}^-$  ion and the centre of charge of the cation (Mulliken 1952, 1964). Lack of structural data for acridinium and pyrazinium iodide, however, prevented us from drawing any conclusion from the observed polarisations. Ethyl quinaldinium iodide is known to crystallise in monoclinic form (space group  $P 21/C$ ) with four formula units cell (Sakanoue *et al* 1970). The iodide and

the planar cation lie roughly on a plane, the planar cations forming an endless column along the *a* axis. Unfortunately, the  $\sigma$  band of the ethyl derivative overlaps the  $\pi$ - $\pi^*$  band of the cation and as such could not be studied. The  $\sigma$  band of the methyl derivative appears at a longer wavelength permitting the polarisation to be studied. The methyl derivative may be assumed to have the same crystalline structure. It is expected that the spectrum of the *bc* but not the *ab* plane should show sharp polarisation. We worked with thin films grown from solutions where we could only locate the *b* axis which coincides with the needles axis. The spectrum hardly shows any polarisation effect. The desired plane was probably not obtained. Further work on similar crystals at still lower temperatures is being planned.

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