

On the spectral properties of the family of complex TCNQ salts with substituted pyrazines

B. Barszcz^{a,*}, B. Laskowska^a, A. Graja^a, D.V. Ziolkovskiy^b, V.A. Starodub^c

^a *Institute of Molecular Physics, Polish Academy of Sciences, ul. Smoluchowskiego 17, 60-179 Poznań, Poland*

^b *V. Karazin Kharkiv National University, 61077 Kharkiv, Ukraine*

^c *Institute of Chemistry, Jan Kochanowski University, 25-406 Kielce, Poland*

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ABSTRACT

The group of six TCNQ salts with *N*-methyl derivatives of pyrazine, bearing up to four methyl groups in various pyrazine sites, was selected for the spectral studies. The influence of the spatial structure of the donors on the charge distribution on the acceptor as well as spectral features of adequate TCNQ salts were deduced. The stretching vibrations of the C=C bonds (mode ν_4) were used for the evaluation of the charge density on the TCNQ⁻ anions but the stretching vibrations of the C≡N bonds (mode ν_2) indicate a diversity of the neighborhood of TCNQ species. It was shown that for the salts containing nonequivalent TCNQ anions the band ν_2 is splitted; each component of the multiplet seen in the IR and Raman spectra represents various environment of the anion. On the other hand the splitted mode ν_4 indicates an existence of TCNQ⁻ anions differently charged. Thus, it was shown that the spectral methods are suitable for indicating nonequivalence of the TCNQ in their salts.

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1. Introduction

The planar ion radicals of the electron accepting species, e.g. 7,7',8,8'-tetracyanoquinodimethane (TCNQ), stack in quasi-one-dimensional highly conducting molecular solids to form conducting linear chains. These charge-transfer (CT) molecular complexes create a unique opportunity for studies of intermolecular interactions, in particular donor-acceptor interactions. The overlap of electronic wave functions along the stacks greatly exceed interstack coupling, and therefore sharp anisotropy can be expected. Indeed, optical reflectance is small and almost frequency independent when the electric vector of external radiation is perpendicular to the stacks, but for parallel polarization one observes an overdamped electronic CT band and a number of lines with half-width about 100 cm^{-1} at frequencies close to those of totally symmetric (A_g) modes of isolated molecules [1–3]. Electron-molecular vibration (e-mv) coupling mentioned above determines all the optical properties of low-dimensional organic conductors in the middle infrared region. It leads to the activation of modes that are normally nonactive in the IR and these modes dominate the spectrum. For TCNQ and other symmetrical molecules, π molecular orbitals occupied by the radical electron are nondegenerated, so linear e-mv coupling is possible only for the totally symmetric modes. However, in the case of nonlinear e-mv coupling it is pos-

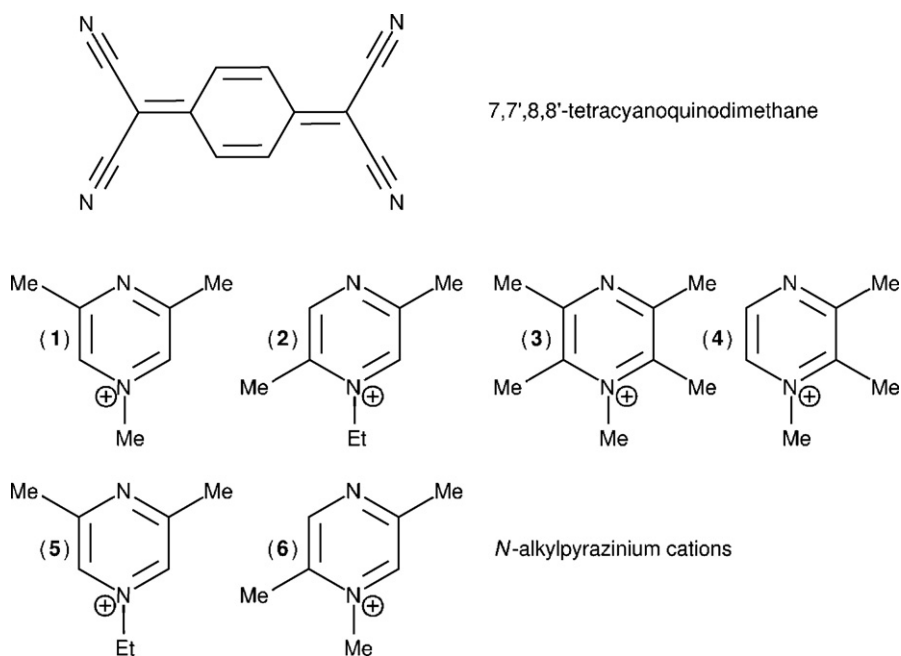
sible to observe vibronic modes with lower symmetry (e.g. B_{3g}) in the IR spectra [4]. Planar and symmetrical TCNQ molecule has 54 normal modes, among which only 10 are the A_g modes. They are Raman active and cover a range of frequencies from about 130 cm^{-1} to about 3050 cm^{-1} [5].

On the other hand vibrational spectra of anion radical salts contain also some bands typical for the cation though these bands are rather weak. Role of the electron donors consists not only in giving some supplementary bands to the spectrum of the salt but in the modification of the crystal structure. The changes in the spatial form of the cations can provoke some modifications in the stacks organization, in the overlapping of the π orbitals occupied by the radical electrons, and thus in the e-mv coupling [6–8]. The vibrational spectroscopy is direct and the best method of identification of these changes. The localization of the vibronic bands observed in the IR spectra of the ion radical salts depends first of all on the frequencies of the A_g modes but also on a quantity of the couplings. The former value can be directly determined from Raman studies of an acceptor but the latter – from a fitting of the appropriate theoretical expression to experimental reflectance or optical conductivity data.

It is well known, that e-mv coupling constants in the anion radical salts of TCNQ depend indirectly on the molecular structure of donors (cations). The cation structure influences indirectly other physical properties of TCNQ salts, in particular their structure and electrical conductivity. For example, it was shown for the family of TCNQ salts with *N*-methyl derivatives of pyridine [9–11]. These pyridine derived cations contained various number of methyl

* Corresponding author.

E-mail address: barszcz@ifmpan.poznan.pl (B. Barszcz).



Scheme 1.

groups, in various pyridine sites. Though all the salts show triclinic symmetry with nearly the same unit cell parameters and similar dimer structure, the d.c. electrical conductivity overcomes a range from 4×10^{-5} to $6 \times 10^{-3} \Omega^{-1} \text{cm}^{-1}$ [10].

For the present spectral studies the group of six TCNQ salts with cation based on the *N*-methyl derivatives of pyrazine was selected (Scheme 1). Recently, these complex salts have been synthesized and preliminary characterized by some of us [12–16]. All these salts have layered structure where conducting anion radical layers formed by TCNQ alternate with non-conducting cation layers. However, the anion layers consist of TCNQ anions of various organization. In such salts certain additional interactions *via* nonalkylated nitrogen atom of pyrazine between TCNQ anion-radical stacks and cations are possible, and may lead to supplementary interactions and couplings influenced their vibrational spectra.

Here we mainly discuss the infrared and Raman spectra of the family of several TCNQ salts with various *N*-alkylpyrazinium cations. The aim of the paper is to investigate the influence of the spatial structure of the cations on the spectral properties of adequate TCNQ complex salts.

2. Experimental

Synthesis of the complex TCNQ salts with various *N*-alkylpyrazinium cations was described by Kazheva et al. [14]. The single crystals of (*N*-Me-2,6-di-Me-Pz)(TCNQ)₂ (1), (*N*-Et-2,5-di-Me-Pz)(TCNQ)₂ (2), (*N*-Me-Tetra-Me-Pz)(TCNQ)₂ (3), (*N*-Me-2,3-di-Me-Pz)(TCNQ)₂ (4), (*N*-Et-2,6-di-Me-Pz)(TCNQ)₂ (5), (*N*-Me-2,5-di-Me-Pz)(TCNQ)₂ (6) selected for the spectral studies shown various habits and dimensions. For example, the crystals of 6 described previously [16], 2 and 3, show needle-like shape with length between 2 and 25 mm and black-violet colour.

The infrared reflection spectra of the crystalline samples were recorded in the frequency range from 400 to 7500 cm^{-1} , at room temperature, for two polarizations of the beam: parallel and perpendicular to the longest crystal axis; these investigations were performed with FT-IR Bruker Equinox 55 spectrometer equipped with Hyperion 1000 microscope. Infrared absorption spectra of the salts for which the reflectance spectra were of poor quality

were studied at room temperature, in the KBr pellets containing dispersed compounds using the same spectrometer. The room temperature Raman spectra of the single crystals were collected with a Horiba Jobin Yvon LabRam HR800 spectrometer with excitation beam ($\lambda_{\text{ex}} = 633 \text{ nm}$) from the He–Ne laser; supplementary investigations were performed for excitation $\lambda_{\text{ex}} = 488 \text{ nm}$ from the Ar laser. The power of the beam at the sample was less than 1 mW to avoid damages of the sample.

The *ab initio* calculations of optimal geometry and normal modes frequencies of the *N*-methyl derived pyrazine cations were performed using the Gaussian 03 program [17]. Calculations were carried out on an isolated molecules using the density functional theory (DFT) with Becke's three parameter exchange functional combined with the Lee–Yang–Parr correlation functional (B3LYP). The 6-311++G(d,p) basis set was used for optimizations and all calculations. The normal modes assignment was performed based on the experimental and theoretical data.

3. Remarks on the crystal structure and electrical properties

Salt 2 has a layered structure where conducting anion-radical layers formed by TCNQ alternate with non-conducting cation layers along the *a* axis. The TCNQ anion-radicals are packed in the stacks along the *b* axis in A··B··C··B sequence. The charge in TCNQ stacks is distributed inhomogeneously: the particles A and C have the charge of $-0.69e$ and $-0.63e$ while the B one is charged three times lower ($-0.17e$). The cation layer is formed by rows of practically planar cations along the *b* axis [13].

Crystal structure of 3 is formed by practically flat cation and two TCNQ anions (A and B), situated in special positions. The salt has a layered structure in which cation layers alternate along the *c* axis with the layers formed by TCNQ radical anions. The anions constitute regular stacks along the *b* axis, where they partially overlap. The interplanar distances are 3.23–3.25 Å [15].

The crystal structure of 6 is formed by cation in a special position and TCNQ anion in general position. The salt has layered structure, where cation layers alternate along the *c* axis with TCNQ layers. Anions in the salt form stacks along the *a* axis, where they are sit-

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