

# ELECTRON ENERGY STRUCTURE OF THE TETRACYANOQUINODIMETHANE MOLECULE IN THE NEUTRAL AND ANION-RADICAL STATES

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The absorption spectra of tetracyanoquinodimethane (TCNQ) solutions and TCNQ films have been studied in the spectral range of 1.4–5.6 eV at room temperature. Making use of the results obtained and the literature data, the energy structures of the electronic levels of a neutral molecule  $\text{TCNQ}^{\circ}$  and an anion-radical  $\text{TCNQ}^{\cdot-}$  have been analyzed. Their excited states have been ascertained to belong mainly to the  $\pi\pi^*$ -type. In a condensed state, the absorption bands at 2.85 and 3.65 eV are caused by  $\text{TCNQ}^{\cdot-}$ , the band at 3.08 eV by  $\text{TCNQ}^{\circ}$ , and the band 5.25 eV by both  $\text{TCNQ}^{\cdot-}$  and  $\text{TCNQ}^{\circ}$ . The absorption spectra of the TCNQ solutions in water and acetic acid in the range of 1.4–4.1 eV consist of dimer bands only, while they are a superposition of the absorption bands of  $\text{TCNQ}^{\circ}$ ,  $\text{TCNQ}^{\cdot-}$ , and  $\text{TCNQ}^{\cdot-}$  dimers for the solutions in ethanol and dimethylformamide.

Researches of optical, electric, and magnetic properties of TCNQ and its salts were carried out with the purpose to obtain the organic metals that can pass into a superconducting state at comparatively high temperatures [1–9].

The synthesis of TCNQ was described for the first time in [10]. Cyanogroups (CN) are electron acceptors and, in complexes with metals or organic electron donors, this compound exists in the form of anion-radical  $\text{TCNQ}^{\cdot-}$ .

In works [11–15], the electron absorption bands of TCNQ in the spectral region of 0.3–4.5 eV were systematized, and an assumption about the existence of linear (one-dimensional) stacks of molecules in the crystals of TCNQ salts was made. The internal structure of those packages and the probable mechanism of charge transfer were considered in [16] in the framework of the one-dimensional band model.

Despite a plenty of theoretical and experimental data, the nature of the absorption bands and the energy structures of the electronic states of a neutral molecule  $\text{TCNQ}^{\circ}$  and an anion-radical  $\text{TCNQ}^{\cdot-}$  were not investigated enough. To study them in more detail is the aim of this work.

The absorption spectra of the TCNQ solutions in benzene, acetic acid (AA), dimethylformamide (DMFA), water, and alcohol and of the thin TCNQ films were

measured with a Hitachi spectrophotometer with the spectral width of a slit of 2 nm and at room temperature. The TCNQ films were thermally sputtered onto quartz substrates in a VUP-2K unit at a pressure of 6.5 mPa.

## Experimental Results and Their Discussion

The structural formula of TCNQ is depicted in Fig. 1. The position of hydrogen atoms are not indicated here. The X-ray diffraction analysis showed that this molecule is flat and possesses the  $D_{2h}$  symmetry, and the angles between its bonds are close to 120 or 180° [17]. The  $\pi$ -system of TCNQ is formed by an overlapping of the  $2p_z$ -orbitals of C and N atoms and consists of the  $\pi$ -systems of cyanogroups and a benzene ring, which are connected by the double bonds  $\text{C}_5=\text{C}_7$  and  $\text{C}_6=\text{C}_8$ . Provided such a configuration, the delocalization of an electron and, accordingly, the transfer of its excitation energy from a benzene ring onto cyanogroups and vice versa are possible.

In the spectral range of 1.4–4.1 eV,  $\text{TCNQ}^{\circ}$  [the molar extinction coefficient  $\varepsilon = 6.36 \times 10^4$  l/(mole · cm)] and  $\text{TCNQ}^{\cdot-}$  [ $\varepsilon = 2.15 \times 10^4$  l/(mole · cm)] absorb simultaneously at 3.14 eV. The latter has also the bands at 1.46 [ $\varepsilon = 4.5 \times 10^4$  l/(mole · cm)], 1.62 [ $\varepsilon = 1.8 \times 10^4$  l/(mole · cm)], and 1.66 eV [ $\varepsilon = 2.2 \times 10^4$  l/(mole · cm)] [1, 2]. The absorption spectrum of  $\text{TCNQ}^{\circ}$  was determined in those works by the spectral subtraction method applied to TCNQ salts with different stoichiometric compositions. As a result of calculations, a conclusion about the absorption by  $\text{TCNQ}^{\circ}$  only at 3.14 eV was made. In this work, the absorption spectra of TCNQ in solvents of different polarity were measured to specify the position of that maximum. TCNQ was found not to dissolve in liquid alkanes (saturated hydrocarbons).

The absorption spectra of the TCNQ solutions are shown in Fig. 2. In the case of the benzene solvent (curve 1), only one intensive band at 3.12 eV, which can be regarded as characteristic of  $\text{TCNQ}^{\circ}$ , is observed in the

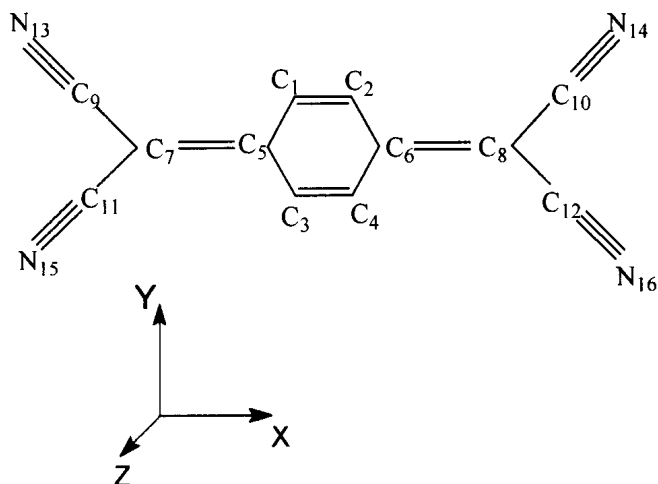


Fig. 1. Structural formula of a tetracyanoquinodimethane molecule

spectral range of 1.4–4.1 eV. This is in agreement with [1, 2].

In the case of the DMFA solvent (curve 2), this band shifts up to 3.08 eV, and the bands at 2.60 and 3.70 eV arise on its both sides. Furthermore, the structural absorption is observed in the range of 1.40–2.20 eV, which is depicted in Fig. 3 for different concentrations of TCNQ. Its long-wave and most intensive band at 1.46 eV has a vibrational structure with the frequency of  $483\text{ cm}^{-1}$ . The same vibrational structure over the frequency, but with another distribution of peak intensities of individual vibronic recurrences, is observed also for the band at 1.66 eV. The absorption spectrum in the range of 1.70–2.20 eV is formed by two bands, at 1.80 and 2.04 eV. For DMFA, the intensity of the first band is larger, while the second band prevails in alcohol. The average energy distance between the first three long-wave structural bands equals  $0.17\text{ eV}$  ( $1369\text{ cm}^{-1}$ ) and is close to fully symmetric vibrations of the TCNQ molecule [18]. The vibration frequency of  $483\text{ cm}^{-1}$  may be caused by the variations of the valence angles between  $\text{—C=N}$  bonds, whose vertices are at atoms  $\text{C}_7$  and  $\text{C}_8$  (Fig. 1). Such vibrations are called deformation ones.

In [12], the absorption spectra of  $\text{TCNQ}^\circ$  and  $\text{TCNQ}^-$  in acetonitrile are presented. In the spectral range of 1.40–4.1 eV, only the structural band at 3.14 eV is observed in the  $\text{TCNQ}^\circ$  case, and, in the  $\text{TCNQ}^-$  one, it is bathochromically displaced by 0.09 eV. In addition, the structural bands at 1.48 and 1.67 eV and the low-intensity band at 1.80 eV are also characteristic of  $\text{TCNQ}^-$ . The spectra of TCNQ in a non-polar benzene and  $\text{TCNQ}^\circ$  in a polar acetonitrile are identical with respect to the band position, in spite of the fact that the

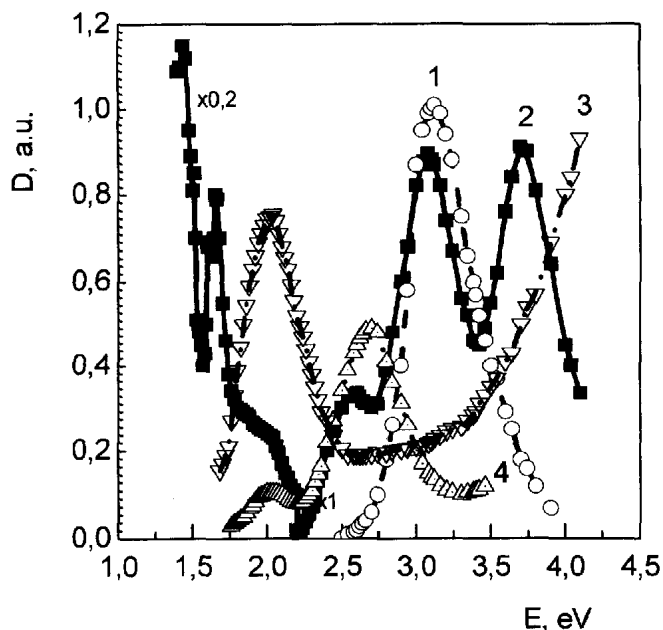


Fig. 2. Absorption spectra of the TCNQ solutions in benzene (1), DMFA (2), water (3), and acetic acid (4)

dielectric constants of the solvents differ more than by an order. One can assert that only  $\text{TCNQ}^\circ$  molecules are made up when TCNQ dissolves in benzene.

The absorption spectra of TCNQ in DMFA and  $\text{TCNQ}^-$  in acetonitrile are identical in the range of 1.40–2.20 eV, except for the band at 2.04 eV, which is not observed in the acetonitrile case. The band at 3.08 eV is formed due to the superposition of the absorption by  $\text{TCNQ}^\circ$  and that by  $\text{TCNQ}^-$ . Therefore, both  $\text{TCNQ}^\circ$  and  $\text{TCNQ}^-$  are formed in DMFA.

The absorption spectra of the TCNQ solutions in alcohol are close to those in DMFA with respect to the band position. Here, the band at 3.70 eV has the largest peak intensity, being by an order of magnitude greater than that of the 3.08-eV band. It testifies to that  $\text{TCNQ}^-$  is formed mainly in alcohol. Thus, the bands at 1.46, 1.66, 1.80, 3.08, and 3.70 eV are characteristic of  $\text{TCNQ}^-$ .

According to [5], the generation of TCNQ dimers in water is three-stage. It starts with a protonization of  $\text{TCNQ}^-$  monomers that dimerize at the second stage owing to the Van der Waals and resonant (exchange) interactions. At the third stage, the protonized dimers dissociate into  $\text{TCNQ}^-$  dimers and protons. An extrapolation leads to dimer bands at 1.94 and 3.36 eV.

TCNQ is not dissolved in distilled water. While adding a certain amount of a TCNQ solution in DMFA

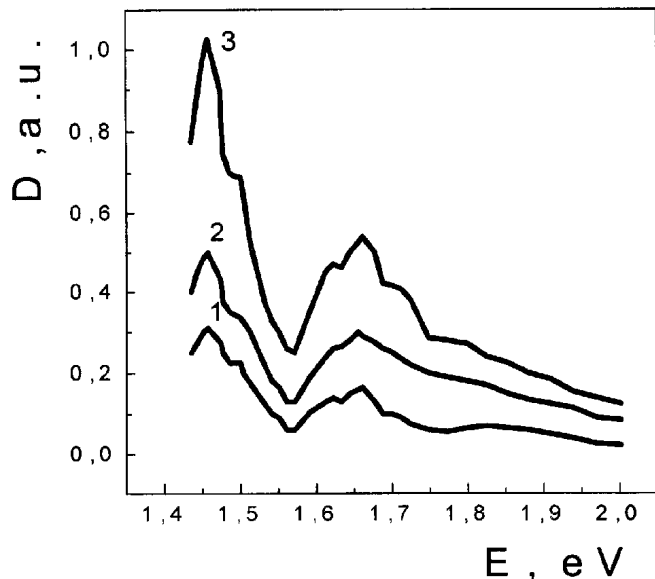


Fig. 3. Absorption spectra of the TCNQ solutions in DMFA. The larger spectrum number corresponds to a larger solution concentration

into water, a slow modification of the solution color from light brown to blue is observed. For a blue-colored solution, a broad unstructured dimer band at 2.03 eV was observed in the spectral range of 1.40–4.10 eV (Fig. 2, curve 3). The second dimer band has low intensity and does not reveal itself against the background of short-wave absorption. For the AA solvent (the donor of protons), the position of the long-wave dimer band is the same as for water (Fig. 2, curve 4). A more intensive band at 2.70 eV, in our opinion, is a short-wave dimer one. The processes of  $\text{TCNQ}^-$  dimerization in alcohol proceed in the same way as in water. In accordance with that, the bands at 2.00 and 2.60 eV of the TCNQ solution in DMFA (Fig. 2, curve 2) belong also to dimers. A comparison of spectra shows that the dimerization in DMFA proceeds less intensively than in water, alcohol, and AA.

It was found [19] that tetracyanobenzene (TCNB), which is close to TCNQ by a molecule structure, makes up charge transfer complexes (CTCs) with various organic electron donors. The absorption bands of those CTCs are in the range of 2.49–4.03 eV. Their positions are defined by the structure of donor groups. In particular, for the CTC benzene–TCNB, the corresponding absorption band is at 4.03 eV.

If the benzene solutions of TCNQ are kept in darkness for a long time, a new band at 3.95 eV appears in their absorption spectra, which testifies to a slow

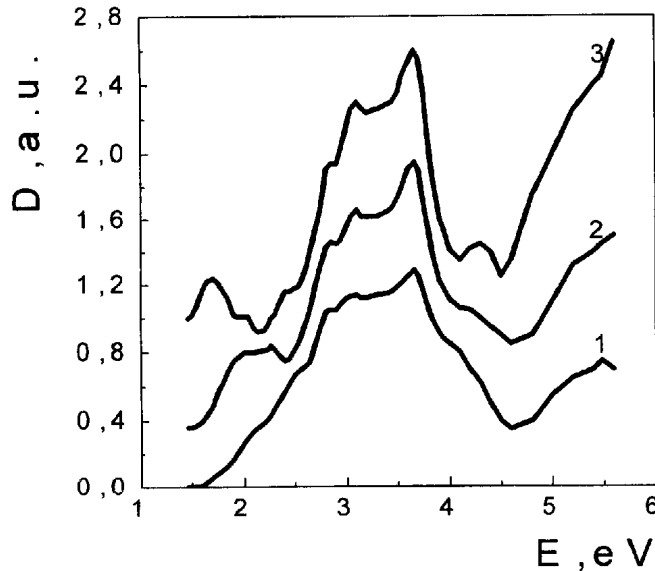


Fig. 4. Absorption spectra of the TCNQ films 0.15 (1), 0.23 (2), and 0.30  $\mu\text{m}$  (3) in thickness

formation of CTCs. In alcohol and DMFA, it is a band at 3.70 eV. Perhaps, those CTCs are formed due to the interaction of the electrons of unshared pairs in the oxygen atoms, which belong to ketonic groups of DMFA molecules or hydroxyl groups of alcohol molecules, with cyanogroups. If an electron is transferred completely onto a cyanogroup, the CTCs dissociate with a formation of  $\text{TCNQ}^-$ .

The absorption spectra of the TCNQ films 0.15 (curve 1), 0.23 (curve 2), and 0.30  $\mu\text{m}$  (curve 3) in thickness are presented in Fig. 4. In comparison with the spectrum of the TCNQ solution in DMFA, the  $\text{TCNQ}^0$  band at 3.08 eV is not shifted. Under the action of the crystalline field, the  $\text{TCNQ}^+$  band shifts bathochromically and is situated at 2.85 eV. The positions of the bands at 2.85, 3.08, and 3.65 eV do not change with increase in the film thickness.

The long-wave edge of the spectrum of the thinnest film is formed by the low-intensity bands. While the film thickness grows, it shifts bathochromically and becomes structured; and we observe new bands at 1.70 and 2.00 eV, which are close, according to their position, to the monomer (1.66 eV) and dimer (2.00 eV) absorption bands of  $\text{TCNQ}^-$ . The band at 2.4 eV (curve 3) is a short-wave dimer one. Upon a consecutive reduction of the film thickness, it is situated near 2.26 (curve 2) and 2.52 eV (curve 1).

The band at 1.46 eV either is absent from the film spectra or is displaced bathochromically, thus being situated beyond the instrument range.

The question "Why do the long-wave absorption bands of TCNQ<sup>-</sup> appear at larger film thicknesses?" remains open for discussion. The following researches will be aimed at the elucidation of this issue.

In the range of 4.00–5.60 eV, the bands at 4.25 and 5.25 eV in the film spectra are observed (Fig. 4, curve 3).

The wave functions and the energies of the molecular orbitals (MOs) of TCNQ<sup>o</sup> and TCNQ<sup>-</sup> were calculated for the first time in [11]. This calculation showed that the effective charges at N-atoms of cyanogroups are negative and those at C-atoms positive. The charges at C<sub>7</sub>- and C<sub>8</sub>-atoms (Fig. 1) are also negative. This testifies to a probable polarization of the  $\pi$ -electron cloud of the benzene core in the direction of cyanogroups. In TCNQ<sup>-</sup>, the dipole moments of cyanogroups increase. The values of the electron transition energies, calculated in this work, agree badly with experiment. In [15], the magnitudes of the Coulomb and resonance integrals were made more accurate, and the energy diagrams of the excited electronic levels of TCNQ<sup>o</sup> and TCNQ<sup>-</sup> with respect to the level of the highest bonding MO were constructed. Nevertheless, the  $\pi$ -systems of TCNQ<sup>o</sup> and TCNQ<sup>-</sup> were not analyzed in this work, and the possible types of excited states were not specified.

TCNQ<sup>o</sup> and TCNQ<sup>-</sup> are composed of twelve C-atoms and four N-atoms, each giving away an electron to the  $\pi$ -system. Eight MOs of sixteen are the bonding ones and are occupied by two electrons each.

It was indicated above that TCNQ<sup>o</sup> and TCNQ<sup>-</sup> belong to a point group of  $D_{2h}$ -symmetry. The symmetry of the ground state is defined by a Kronecker product of the irreducible representations of all the bonding MOs and is transformed according to the totally symmetric irreducible representations  $A_{1g}$  for TCNQ<sup>o</sup> and  $B_{2g}$  for

TCNQ<sup>-</sup>. The transition polarization or the symmetry of the total wave function of the excited state were determined similarly, but here only the irreducible representations of those MOs, which interact at the transition, are included into the product.

From the structural formula of TCNQ<sup>o</sup> (Fig. 1), it follows that the  $2p_z$ -orbitals of the C- and N-atoms take part in overlapping. Therefore, all the excited states in TCNQ<sup>o</sup> and TCNQ<sup>-</sup> belong to the  $\pi\pi^*$ -type.

The oscillator strength of the absorption band was calculated according to the formula [20]

$$f = 4,3 \cdot 10^{-9} \int \varepsilon(\nu) d\nu.$$

For the Gaussian contour of the band, the area under the curve is [21]

$$\int \varepsilon(\nu) d\nu = 1,063\varepsilon_{\max}\Delta\nu,$$

where  $\varepsilon_{\max}$  is the coefficient of molar extinction at the band maximum and  $\Delta\nu$  is the half-width of the absorption band in  $\text{cm}^{-1}$ .

The main characteristics of the single-electron transitions in TCNQ<sup>o</sup> and TCNQ<sup>-</sup> are quoted in the table. In TCNQ<sup>o</sup>, the transitions from the level of the highest bonding MO (level 8) onto levels 10–13 are forbidden. The calculation predicts only two excited electronic states,  $\pi_8\pi_9^*$  and  $\pi_8\pi_{14}^*$ , with the energies of 2.83 and 5.63 eV, respectively. Their experimentally determined energies are equal to, respectively, 3.12 (a solution in benzene) and 5.25 eV (a film).

In TCNQ<sup>-</sup> transitions from the MO levels 8 and 9 are allowed, because the last level is occupied by a single electron. The calculations showed that the transitions from level 9 are forbidden by symmetry. The energy distance between levels 9 and 10 is 1.70 eV (transition

#### Main characteristics of single-electron transitions in TCNQ<sup>o</sup> and TCNQ<sup>-</sup>

N of transition	TCNQ <sup>o</sup>						TCNQ <sup>-</sup>					
	Calculations [11, 15]				Experiment		Calculations [11, 15]				Experiment	
	Transition	<i>E</i> , eV	<i>f</i>	II	<i>E</i> , eV	<i>f</i>	Transition	<i>E</i> , eV	<i>f</i>	II	<i>E</i> , eV	<i>f</i>
I	$\pi_8\pi_9^*$	2.83	0.95	X	3.12	1.00	$\pi_8\pi_9^*$	1.21	0.35	X	1.46	0.21
II	$\pi_8\pi_{10}^*$	3.67	0.00				$\pi_8\pi_{10}^*$	2.91	0.45	X	3.08	0.44
III	$\pi_8\pi_{11}^*$	4.29	0.00				$\pi_8\pi_{11}^*$	2.99	0.04	Y		
IV	$\pi_8\pi_{12}^*$	4.54	0.00				$\pi_8\pi_{12}^*$	3.44	0.10	Y	3.70	0.50
V	$\pi_8\pi_{13}^*$	5.06	0.00				$\pi_8\pi_{13}^*$	4.24	0.24	X	4.25	
VI	$\pi_8\pi_{14}^*$	5.63	0.24	Y	5.25		$\pi_8\pi_{14}^*$	4.75	0.00			
VII	$\pi_8\pi_{15}^*$	6.10	0.06	Y			$\pi_8\pi_{15}^*$	5.15	0.61	Y	5.25	
VIII							$\pi_8\pi_{16}^*$	5.21	0.05	X		
IX							$\pi_9\pi_{10}^*$	1.70	0.00		1.66	0.11
X							$\pi_9\pi_{11}^*$	1.78	0.00		1.66	0.11

Notations: *f* is the oscillator strength and II is the transition polarization

IX) and that between levels 9 and 11 is 1.78 eV (transition X), which is close to a position of the band at 1.66 eV (a solution in DMFA). Due to a configurational interaction between the excited states of transitions IX and X, the prohibition is cancelled and one of those transitions can be observed in absorption spectra. This band is supposed in [11] to correspond to the  $n\pi^*$ -state, that is, to be a local excitation. In our opinion, it may be a transition of one of the  $2S$ -electrons of the unshared pairs of N-atoms onto the  $\pi^*$ -levels of  $\text{TCNQ}^+$ . The elucidation of the nature of the 1.66-eV band will be the subject of the following researches. The energy diagram of the  $\text{TCNQ}^+$  levels is better coordinated with the experiment for the transitions from level 8.

Thus, the energy structure of the  $\text{TCNQ}^\circ$  and  $\text{TCNQ}^-$  electronic levels was considered in this work in detail. All the excited states were found to belong to the  $\pi\pi^*$ -type. There are sixteen levels altogether. Eight of them are occupied by two electrons. Other levels are empty, except for level 9 in  $\text{TCNQ}^+$  which contains one electron.

For  $\text{TCNQ}^\circ$ , the calculations predict two allowed transitions,  $\pi_8\pi_9^*$  and  $\pi_8\pi_{14}^*$ , with the energies of 2.83 and 5.63 eV, respectively, which result in the absorption band at 3.12 and 5.25 eV.

The energy diagram of the  $\text{TCNQ}^+$  levels is better coordinated with the experiment, if the transitions are supposed to start mainly from level 8, as it is in  $\text{TCNQ}^\circ$ .

In the solid-state case, the positions of the monomer bands at 2.85, 3.08, 3.65, 4.25, and 5.25 eV and of the long-wave dimer band at 2.04 eV do not depend on the thickness of the TCNQ film. The bands at 2.85 and 3.65 eV belong to  $\text{TCNQ}^+$ , at 3.08 eV to  $\text{TCNQ}^\circ$ , and at 5.25 eV to  $\text{TCNQ}^-$  and  $\text{TCNQ}^\circ$ .

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#### ЕНЕРГЕТИЧНА СТРУКТУРА ЕЛЕКТРОННИХ СТАНІВ НЕЙТРАЛЬНОЇ МОЛЕКУЛИ І АНІОН-РАДИКАЛА ТЕТРАЦІАНОХІНОДИМЕТАНУ

М.П. Горішній

Резюме

Досліджено спектри поглинання розчинів і плівок тетраціанохінодиметану (ТЦНХ) в області 1,40—5,60 eV при кімнатній температурі. На основі одержаних і літературних даних розглянуто енергетичну структуру електронних рівнів нейтральної молекули ТЦНХ<sup>0</sup> і аніон-радикала ТЦНХ<sup>-</sup>. Встановлено, що їх збуджені стани в основному належать до  $\pi\pi^*$ -типу. В конденсованому стані смуги поглинання 2,85 і 3,65 eV зумовлені ТЦНХ<sup>+</sup>; 3,08 eV — ТЦНХ<sup>0</sup>, а 5,25 eV — ТЦНХ<sup>0</sup> і ТЦНХ<sup>-</sup>. Спектри поглинання розчинів ТЦНХ у воді і оцтовій кислоті в області 1,40—4,10 eV складаються тільки із димерних смуг, а для спиртових і диметилформамідових розчинів вони є суперпозицією смуг поглинання ТЦНХ<sup>+</sup>, ТЦНХ<sup>-</sup> і димерів ТЦНХ<sup>-</sup>.