The X-Ray Photoelectron Spectra of 1:1 and 1:2 Salts Formed from Triethylammonium and 7,7,8,8-Tetracyanoquinodimethane

Jun Okubo, Toshihiko Hoshi,* Isao Ono, Kaori Karube, and Michio Kobayashi†
Department of Chemistry, College of Science and Engineering, Aoyama Gakuin University, Setagaya-ku, Tokyo 157
†Department of Chemistry, Technological University of Nagaoka, Nagaoka 940-21
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The X-ray photoelectron spectra of the 1:1 and 1:2 salts formed from the triethylammonium cation ($TEAH^+$) and 7,7,8,8-tetracyanoquinodimethane (TCNQ) have been measured and analyzed in order to investigate the electronic structures and conformations of the salts. The N 1s band (398.2 eV) degenerated in the free TCNQ molecule splits into two bands (398.4 eV and 400.3 eV) in the 1:1 salt. This is due to the unequal interactions of the nitrogen atoms of the TCNQ anion radical ($TCNQ^{\cdot-}$) with $TEAH^+$. In the 1:2 salt, the degenerated N 1s bands of two free TCNQ molecules split into three bands (398.5, 400.0, and 401.8 eV). This implies that the negative charge is inhomogeneously distributed over two TCNQ molecules, supporting the idea that the electronic structure of the 1:2 salt can be represented approximately as $TEAH^+$-$TCNQ^{\cdot-}$-$TCNQ^0$. It is found that, in the 1:2 salt, the neutral TCNQ molecule ($TCNQ^0$) is weakly bound to the TCNQ anion radical ($TCNQ^{\cdot-}$) of the strongly bound 1:1 salt, with their molecular planes parallel.

7,7,8,8-Tetracyanoquinodimethane (TCNQ) is a strong electron-acceptor and easily forms CT (charge transfer) complexes with such electron donors as tetrathiafulvalene and *p*-phenylenediamine.[1-13] Melby et al. have synthesized salts of TCNQ with many electron donors and investigated their physicochemical properties.[1] The ion-radical salt of TCNQ with triethylammonium ($TEAH^+$) was also synthesized by them, and its EPR, IR and UV spectra were measured. The analyses of these spectra have revealed that the electronic structure of the 1:1 salt between $TEAH^+$ and TCNQ can be described as $TEAH^+$-$TCNQ^{\cdot-}$; i.e., the TCNQ molecule exists as an anion radical in the crystal. Kobayashi et al. have determined the crystal structure of the 1:2 salt between $TEAH^+$ and TCNQ by means of X-ray diffraction and have shown that the TCNQ in the crystal has two kinds of electronic structures, $TCNQ^{\cdot-}$ and $TCNQ^0$; i.e., the negative charge is inhomogeneously distributed over two TCNQ molecules.[2] In contrast, Filhol et al. showed, by means of the neutron diffraction, that the electronic structure of the 1:2 salt is $TEAH^+$-$TCNQ^{-1/2}$-$TCNQ^{-1/2}$.[3a] However, they have since corrected the results to $TEAH^+$-$TCNQ^{-3/5}$-$TCNQ^{-2/5}$;[3b] i.e., the two TCNQ molecules in the 1:2 salt are not equivalent, but the negative charge is delocalized significantly over the two TCNQ molecules.

In this investigation we have measured and analyzed the X-ray photoelectron spectra (XPS) of the 1:1 and 1:2 salts formed from $TEAH^+$ and TCNQ in order to investigate the electronic structures and conformations of these salts.

Experimental

Commercial triethylamine hydrochloride (TEA-HCl) (Wako Pure Chemical Industries, Ltd.) was purified by sublimation after several recrystallizations from ethyl alcohol. Commercial TCNQ (Tokyo Kasei Co., Ltd.) was purified by sublimation in vacuo (0.28 mmHg/220 °C; 1 mmHg=133.322 Pa). The 1:1 and 1:2 salts of $TEAH^+$ and TCNQ were synthesized according to the procedure reported by Melby et al. and purified by recrystallization from acetonitrile.[1] The salts thus obtained were identified by means of their IR and UV spectra and elemental analysis. The XPS spectra were measured with a Shimadzu ESCA-750 apparatus, employing Mg $K\alpha$ (1253.6 eV) radiation as the X-ray source. Powdered samples are fixed on an adhesive tape put on the holder. The binding energies for the XPS bands were calibrated by the use of that for the $4f_{7/2}$ band of Au powder.

MO Calculation

MO calculation for the π-electron system of TCNQ was performed by using a modified PPP method[14] which can deal, at the same time, with mutually perpendicular π and π' systems as presented in the triple bonds of the cyano groups of TCNQ.

Results and Discussion

The XPS spectra for TEA-HCl, TCNQ, and the 1:1 salt between $TEAH^+$ and TCNQ are compared in Fig. 1, while the spectrum for the 1:2 salt is shown in Fig. 2. According to Ikemoto et al., the N 1s band of the TCNQ salt changes in shape upon X-ray irradiation.[4] In order to confirm this fact, we have measured the XPS spectra of the TCNQ salts at various accumulation times. As a result, the shape of the spectra was found not to change within three accumulation times, but the band shape did vary slightly at five accumulation times. Thus, in this investigation, the spectra accumulated three times are used. The dotted lines shown for each XPS band are the reduced spectra, which are obtained assuming Gaussian curves. The peak positions and integrated intensities (in percent) of these reduced spectra are summarized in Table 1 for all of the compounds investigated here.

XPS Spectra of TEA-HCl and TCNQ. TEA-HCl shows a fairly wide C 1s band at 285.4 eV, the half-width being 2.5 eV. This band consists, therefore, of

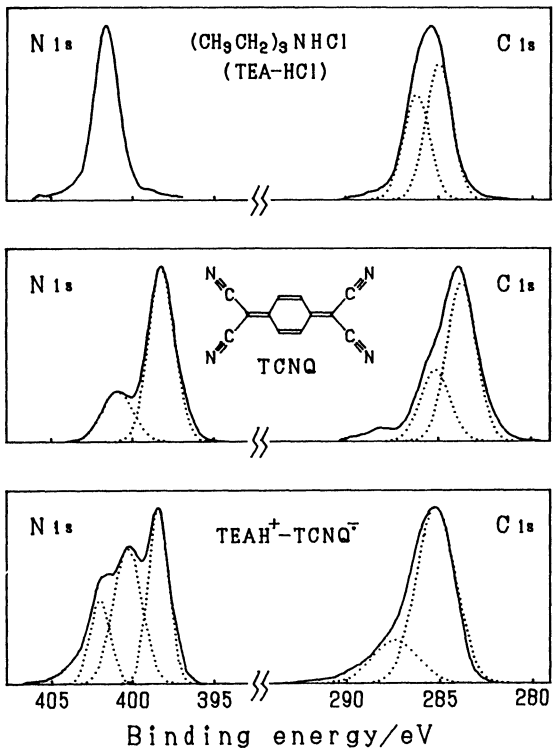

Fig. 1. Comparison of XPS spectra of TEA-HCl, TCNQ, and the 1:1 salt between $TEAH^+$ and TCNQ.

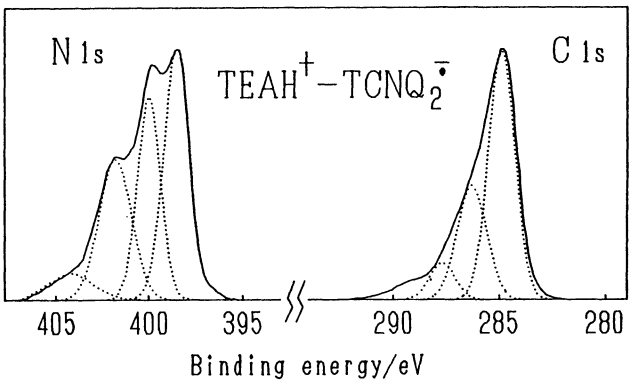

Fig. 2. XPS spectrum for the 1:2 salt between $TEAH^+$ and TCNQ.

two bands with nearly equal intensities whose peak positions are, as determined from the reduced spectra, at 285.0 and 286.2 eV. The higher-energy band at 286.2 eV is assigned to the 1s orbital of the electron-deficient carbon atom adjacent to the electron-withdrawing nitrogen atom with the higher electronegativity, and the lower energy band at 285.0 eV, to that of the outer methyl carbon atom. The N 1s band of TEA-HCl is positioned at 401.6 eV, with a narrow half width.

TCNQ has a C 1s band consisting of a main peak at 283.8 eV and a weak band (a shoulder in the original spectrum) at 285.2 eV. To assign these bands in the reduced spectrum, we have performed a modified PPP

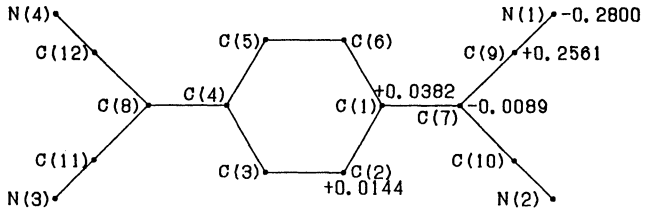

Fig. 3. The formal charge on each atom of TCNQ estimated by a modified PPP calculation.

Table 1. The C 1s and N 1s Binding Energies and Intensities for TEA-HCl, TCNQ, $TEAH^+$-$TCNQ^-$, and $TEAH^+$-$TCNQ_2^-$, as Estimated from the Reduced Spectra

Compound	Core level	Binding energy/eV	Intensity (in percent)
TEA-HCl	C 1s	288.0	57
		286.2	43
	N 1s	401.6	100
TCNQ	C 1s	283.8	69
		285.2	31
	N 1s	398.2	74
		400.9	26
$TEAH^+$-$TCNQ^-$ (1:1)	C 1s	285.2	78
		287.4	22
	N 1s	398.4	37
		400.3	40
		402.0	17
$TEAH^+$-$TCNQ_2^-$ (1:2)	C 1s	284.8	60
		286.2	31
		278.6	9
	N 1s	398.5	39
		400.0	27
		401.8	27
		404.2	7

calculation (as explained in the previous section) and have estimated the formal charge on each atom of TCNQ, the results being illustrated in Fig. 3. The formal charges on the central carbon atoms C(1)-C(8) constituting the quinodimethane skeleton are small in magnitude, but those on carbon atoms C(9)-C(12) constituting the cyano groups are large (positive values). From the viewpoint of potential depth, the lower-energy band at 283.8 eV and the higher-energy band at 285.2 eV are assigned to carbon atoms C(1)-C(8) and C(9)-C(12), respectively. This assignment predicts the intensity ratio of the 283.8 eV band to the 285.2 eV band (which is equal to the ratio of the numbers of carbon atoms assigned to each band) to be 2:1, in considerable agreement with the observed value (69:31) given in Table 1.

The N 1s band of TCNQ consists of a main band at 398.2 eV and a sub-band at 400.9 eV. The band contour and band positions agree well with those reported by Ikemoto et al.[5] They have suggested that the sub-band is attributable to a shake-up process involving intramolecular transitions between the π-electron

molecular orbitals.

XPS Spectrum of the 1:1 Salt between $TEAH^+$ and TCNQ. As may be seen from Fig. 1, the N 1s band of the 1:1 salt shows a complex band contour not explained by the simple addition of the N 1s band of $TEAH^+$ to that of TCNQ; i.e., an extra or new N 1s band has emerged on the formation of the salt. This extra band is too intense to be assigned to only a shake-up band,[4,5] i.e., the shake-up band is considered to be buried in the intense extra band. It is, therefore, demonstrated that the N 1s band is sensitive to the salt formation; in other words, the interaction between $TEAH^+$ and $TCNQ^{\cdot-}$ in the 1:1 salt is manifest in the behavior of the N 1s band. This may be due to the fact that the salt is in such a conformation that $TEAH^+$ interacts entirely with the nitrogen atoms located on the outer part of the TCNQ molecule, as will be discussed below in detail. The N 1s band of the 1:1 salt consists of three bands —at 398.4, 400.3, and 402.0 eV (Table 1) which are now assigned on the basis of the previously proposed ionic structure ($TEAH^+$-$TCNQ^{\cdot-}$) of the salt.[1]

From the viewpoint of the potential depth on atoms for the free molecule, it is natural to expect that the N 1s band of the triethylammonium cation ($TEAH^+$) is positioned on a higher-energy side than that of the TCNQ anion radical ($TCNQ^{\cdot-}$). Therefore, the highest-energy band at 402.0 eV can be assigned to the N 1s band originating from the $TEAH^+$ of $TEAH^+$-$TCNQ^{\cdot-}$. The N 1s band originating from the $TEAH^+$ of $TEAH^+$-$TCNQ^{\cdot-}$ is on a somewhat higher-energy side than that of $TEAH^+$-Cl^-. This may be due to the fact that the effective positive charge of the proton in $TEAH^+$-$TCNQ^{\cdot-}$ is larger than that in $TEAH^+$-Cl^-; this is because the ionic radius of $TCNQ^-$ is larger than that of Cl^-. Thus, the other two N 1s bands —at 398.4 and 400.3 eV— of the salt can be attributed to the ionization from the N 1s orbital of $TCNQ^{\cdot-}$. This implies that the N 1s bands of free $TCNQ^{\cdot-}$, which are degenerated, are split into two bands because $TEAH^+$ interacts with the nitrogen atoms of $TCNQ^{\cdot-}$ unequally. The unequal interaction of $TEAH^+$ with the nitrogen atoms of $TCNQ^{\cdot-}$ just mentioned may be possible when the configuration of $TEAH^+$ and $TCNQ^{\cdot-}$ is linear in the 1:1 salt, as is illustrated in Fig. 4a. The N 1s bands (398.4 and 400.3 eV) of the $TCNQ^{\cdot-}$ of the 1:1 salt are positioned on a higher-energy side than that (398.2 eV) of the free TCNQ. This fact is rather surprising, since, in general, an XPS band of a neutral molecule is on a higher-energy side than that of negatively charged species.

As is well-known, the position of the XPS band is dependent on the potential depth on the atom. In the present case, the potential depth may be influenced by two factors: the effects of the π-electron density, and the positive charge of the proton. The increase in the binding energy of the N 1s bands of the $TCNQ^{\cdot-}$ of the 1:1 salt in comparison with that of the free TCNQ molecule may indicate that the effect of the proton is superior to that of an extra odd electron. Thus, the 400.3 eV band is assigned to the N 1s band of the nitrogen atoms 1 and 2, which interact with the proton of $TEAH^+$ directly, and the 398.4 eV band to those of the nitrogen atoms 3 and 4 (Fig. 4a). In conformity with these assignments, the observed intensity ratio (37:40:17) of the N 1s bands is in good agreement with the theoretical one (2:2:1) estimated from the number of nitrogen atoms assigned to each N 1s band. It is interesting to notice here that the 400.3 eV N 1s band of the salt has a wide half width. We have considered that this band broadening is derived from the singlet-triplet splitting due to the biradical nature of the ionized state of $TCNQ^{\cdot-}$ and/or from superimposition of the shake-up band.[5] The unpaired electron in $TCNQ^{\cdot-}$ may be localized mainly at nitrogen atoms 1

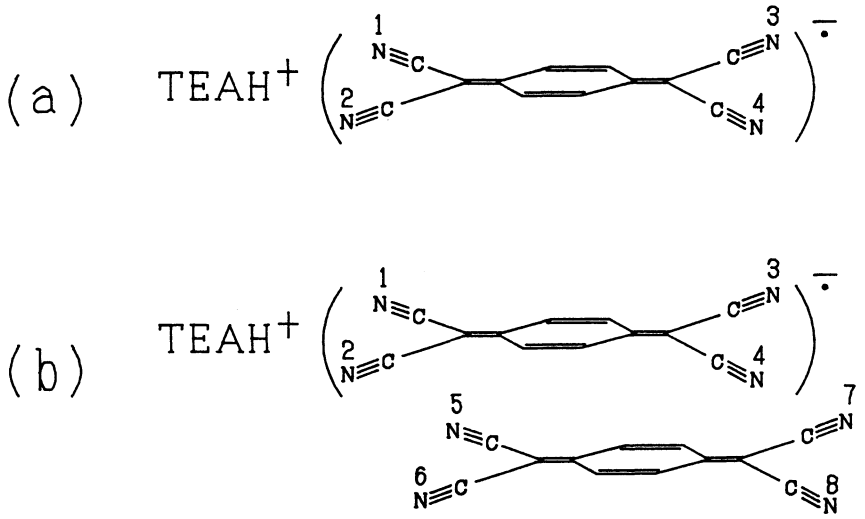

Fig. 4. Conformations of (a) the 1:1 salt ($TEAH^+$-$TCNQ^{\cdot-}$) and (b) the 1:2 salt ($TEAH^+$-$TCNQ^{\cdot-}$-$TCNQ^0$).

and 2 through the electrostatic attraction by $TEAH^+$, resulting in the concentration of the biradical nature of the ionized state of $TCNQ^{\cdot-}$ on nitrogen atoms 1 and 2 (Fig. 4a). This may be the reason why only the 400.3 eV N 1s band of the salt, which stems from the ionization of the nitrogen atoms 1 and 2, is broadened. The band broadening mentioned above may, therefore, be evidence for the presence of an unpaired electron in the CT-structure ($TEAH^+$-$TCNQ^{\cdot-}$) of the 1 : 1 salt.

In contrast to the N 1s band, the C 1s band of the 1 : 1 salt has a broad and rather structureless band shape; i.e., the C 1s bands of donor and acceptor are not separated, but are overlapped to give a broad band, demonstrating that the C 1s band is insensitive to the salt formation. The broad C 1s band of the 1 : 1 salt can, however, be decomposed into two bands of the Gaussian type positioned at 285.2 and 287.4 eV, whose intensity ratio is 78 : 22 (Table 1), as is shown in Fig. 1. The intense band at 285.2 eV results, as has been explained above, from a complete overlap of the band originating from the 283.8 eV C 1s band of the free TCNQ molecule, which is assigned to the central carbon atoms C(1)-C(8) of TCNQ (Fig. 3), and that originating from the C 1s band of TEA-HCl. The weak band at 287.4 eV may originate from the 285.2 eV C 1s band of the free TCNQ molecule, which is assigned to the carbon atoms C(9)-C(12) of TCNQ; this assignment is based on the fact that the theoretical intensity ratio (7 : 2) is in good agreement with the observed one (78 : 22). According to these assignments of the C 1s bands of the salt, the two C 1s bands at 283.8 and 285.2 eV of the free TCNQ molecule are shifted to energies higher by 1.4 and 2.2 eV respectively by the formation of the salt. This rather surprising result may be also explained by the same reason as that presented for the higher-energy shift of the N 1s band of $TCNQ^{\cdot-}$.

XPS Spectrum of the 1 : 2 Salt between $TEAH^+$ and TCNQ. The N 1s band of the 1 : 2 salt shows, like that of the 1 : 1 salt, a complex band contour not explained by the simple addition of N 1s bands of the cation and the anion; i.e., at least, an additional N 1s band has emerged on the formation of the salt. Indeed, it has shown, as will be discussed below, that the splitting pattern of the N 1s bands is a good indicator of the donor-acceptor interaction in the salt or of the conformation and electronic structure of the salt.

The N 1s band of the 1 : 2 salt consists of four bands —at 398.5, 400.0, 401.8, and 404.2 eV, with the intensity ratio of 39 : 27 : 27 : 7 (Table 1). The assignment of these bands is the basis for the study of the donor-acceptor interaction in the 1 : 2 salt and for the verification of the previously proposed models for the electronic structure of the 1 : 2 salt. By analogy with the case of the 1 : 1 salt, the N 1s band of $TEAH^+$ may be expected to shift to a higher-energy side on forming the 1 : 2 salt, the 401.8 or 404.2 eV band being a candidate for the N 1s band of $TEAH^+$ in the salt. We have considered that the 401.8 eV N 1s band can not be assigned to the N 1s band of $TEAH^+$ for the following two reasons: (1) the band has, as will be discussed later, a wide half width and, hence, resembles the 400.3 eV N 1s band of the $TCNQ^{\cdot-}$ of the 1 : 1 salt, and (2) the intensity of the band is too large to be assigned to $TEAH^+$. Thus, the 404.2 eV N 1s band is assigned to $TEAH^+$, while three N 1s bands at 398.5, 400.0, and 401.8 eV must be assigned to the two TCNQ molecules in the 1 : 2 salt. In other words, it has been demonstrated that the degenerated N 1s bands of two free TCNQ molecules are split into three bands in the 1 : 2 salt. This splitting pattern of the N 1s bands is possible only when the following two conditions are fulfilled: (a) the negative charge is inhomogeneously distributed over two TCNQ molecules, and (b) the unequal, in the same sense as in the 1 : 1 salt, interaction of $TEAH^+$ with the nitrogen atoms of the one TCNQ molecule is stronger (or weaker) than that with the nitrogen atoms of the other TCNQ molecule. The first condition is necessary for the second one to be fulfilled, rather supporting the electronic structure of $TEAH^+$-$TCNQ^{\cdot-}$-$TCNQ^0$ previously determined by means of X-ray diffraction.[2] The second condition may be fulfilled when the 1 : 2 salt is in the conformation illustrated in Fig. 4b. As may be seen from Fig. 4b, $TEAH^+$ interacts strongly with $TCNQ^{\cdot-}$ with just the same conformation as that of the 1 : 1 salt, and $TCNQ^0$ interacts weakly with $TCNQ^{\cdot-}$, with their molecular planes parallel.

The conformational model shown in Fig. 4b makes possible a further assignment of the three N 1s bands at 398.5, 400.0, and 401.8 eV. There seem to be formally two alternative assignments for the lowest-energy band at 398.5 eV: one is the assignment to the four nitrogen atoms of the $TCNQ^0$ positioned at 5—8, and the other, to the nitrogen atoms at 3, 4, 7, and 8 (Fig. 4b). Following the latter assignment, the highest-energy band at 401.8 eV is assigned to the nitrogen atoms 1 and 2, which are bound with the proton of $TEAH^+$ most strongly, and the band at 400.0 eV to the nitrogen atoms 5 and 6. As a result, the energy difference between the two split bands of $TCNQ^{\cdot-}$ in the 1 : 2 salt amounts to 3.3 (=401.8−398.5) eV, which is very different from that (1.9 eV) in the 1 : 1 salt; thus, the latter assignment can be ruled out. Since, however, the 401.8 eV band is assigned to the nitrogen atoms 1 and 2, and the 400.0 eV band, to the nitrogen atoms 3 and 4, the former assignment reasonably predicts the above-mentioned energy difference to be 1.8 (=401.8−400.0) eV, which corresponds well to the value (1.9 eV) observed in the 1 : 1 salt. The theoretical intensity ratio (2 : 1 : 1) for the three N 1s bands assigned as above is also in agreement, though only qualitatively, with the observed one (39 : 27 : 27). It is interesting to note that the two split N 1s bands of $TCNQ^{\cdot-}$ in the 1 : 2 salt are both shifted to a higher-energy side by ca. 1.5 eV compared with those in the 1 : 1 salt. This may be because a small amount of the unpaired electron of $TCNQ^{\cdot-}$

migrates to $TCNQ^0$, for that $TCNQ^0$ is bound to $TCNQ^{\cdot-}$ via the weak CT-type interaction ($TCNQ^{\cdot-}$ behaves as an electron donor with respect to $TCNQ^0$). The unique similarity between the N 1s bands of the 1 : 2 salt and those of the 1 : 1 salt is the existence of the broad band assigned to the nitrogen atoms (1 and 2) of $TCNQ^{\cdot-}$ directly interacting with $TEAH^+$. That is, the 401.8 eV N 1s band of the 1 : 2 salt, which is assigned to the nitrogen atoms (1 and 2) directly interacting with $TEAH^+$, exhibits a band broadening based on the same mechanism as that in the 1 : 1 salt. This is a further confirmation of the band assignment based on the conformation and electronic structure of the 1 : 2 salt presented in Fig. 4b.

The C 1s band of the 1 : 2 salt shows an ill-resolved band shape which is very similar, in spite of the presence of $TCNQ^{\cdot-}$ in the salt, to that of the C 1s band of the free TCNQ molecule. Indeed, the two lower-energy reduced bands at 284.8 and 286.2 eV, which are assigned, respectively, to the central carbon atoms of $TCNQ^{\cdot-}$ and $TCNQ^0$ and to the carbon atoms constituting the cyano groups of $TCNQ^{\cdot-}$ and $TCNQ^0$, have an energy separation of 1.4 eV and an intensity ratio of 60 : 31, comparable to those values (1.3 eV and 69 : 31) for the C 1s band of the free TCNQ molecule (see Table 1). It can, therefore, be understood that the C 1s-band positions of $TCNQ^{\cdot-}$ coincide, following the electronic structure of $TEAH^+$-$TCNQ^{\cdot-}$-$TCNQ^0$ for the 1 : 2 salt, with those of $TCNQ^0$. We have considered this coincidence to be a further confirmation of the already mentioned general tendency for the core level of the carbon atom to be scarcely affected by valence electrons.[5] The C 1s band of $TEAH^+$ in the 1 : 2 salt might be buried under the C 1s bands of $TCNQ^{\cdot-}$ and $TCNQ^0$.

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