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Structural characterization of 2,3,5,6-tetramethyl-*p*-phenylenediamine radical cation and its dimer in molecular crystals



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HIGHLIGHTS

- We reported the crystal structures of two reaction products between DDA and bromanile.
- X-ray crystal analyses showed that these are 1:1 CT complexes and bromide salts.
- The electronic structures of DDA complexes were investigated by UPS, and the results were discussed with the DFT calculations.
- The degree of charge-transfer was estimated to be about 0.7 for the CT complex.

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ABSTRACT

Reaction between 2,3,5,6-tetramethyl-*p*-phenylenediamine (DDA) and bromanil (BA) gave two different crystalline products, needle-like and block-shaped crystals. The former was an alternate-stack 1:1 charge-transfer complex between DDA and BA with an electron-transfer ratio of about 0.7. The latter was a bromide salt of DDA, which was crystallized simultaneously with the decomposition of BA anions. The DDA molecules in the salt were dimerized even at room temperature. The similar products were obtained by a reaction between DDA and chloranil. The molecular and electronic structures are discussed with the calculation results of the density functional theory. This report has two additional meanings on the synthesis of charge-transfer complexes with using haloanils, which are commonly used as electron acceptors: (1) special attention must be paid for contaminating halide ions in characterizing reaction products and in discussing their properties, and (2) a new moderate synthetic root of halide complexes becomes available when using haloanils.

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Introduction

Aromatic amines are strong electron donors and used as electron-donating components of charge-transfer (CT) complexes. Among the aromatic amines, *p*-phenylenediamine (PPD) and its *N*-methyl derivatives, such as *N*,*N*-dimethyl-*p*-phenylenediamine (DMPD) and *N*,*N*,*N'*,*N'*-tetramethyl-*p*-phenylenediamine (TMPD) are known as Würster's dyes. Würster radicals show remarkably interesting magnetic properties: they are usually paramagnetic at high temperatures and diamagnetic at low temperatures [1]. These phenomena are explained by the formation of Würster radical



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dimers in low temperature phases. The formation of dimers has also been reported in solutions of these radicals by Raman [2,3] and absorption [4–9] spectroscopies. Thus, theoretical calculations performed on cationic dimers have become available including those for 2,3,5,6-tetramethyl-*p*-phenylenediamine (durendiamine; DDA) [10–12].

On the other hand, benzoquinones and their halogensubstituted derivatives are used widely as electron acceptors of CT complexes, and the physical properties of resulting CT complexes have also been studied rigorously. A series of tetrahalo-*p*-benzoquinones (haloanils) are important for investigating the physicochemical properties of CT complexes, because their electron accepting abilities can be altered systematically by changing the substituted halogens. Complexes between haloanils and PPD [13,14], TMPD [15] or DDA [16] show relatively high conductivities against the ionic nature of their ground state [17,18]. These complexes sometimes show non-stoichiometric molar ratios of components [19] and sometimes the adoption of solvent molecules [20]. This may cause these materials to be investigated on their physical properties with some difficulties.

Experimental information on molecular structures and their stacking is crucial for discussing the physical properties of CT complexes; however, structural information for halide complexes with both PPD and DDA are still lacking due to their crystal qualities. To our knowledge, among aromatic amine and haloanil complexes, a crystal structure has only been reported on the TMPD-tetra-chloro-*p*-benzoquinone (chloranil; CA) complex [21].

In this paper, we carried out X-ray analyses on complexes of DDA bromide (DDA–Br) and DDA-tetrabromo-*p*-benzoquinon (bromanil; BA), which are reaction products of DDA and BA. The columnar structure and a third type of the molecular stacking in DDA–Br will be discussed with the aid of the density functional theory (DFT). The similar reaction products were obtained between DDA and CA. The electronic structures of these DDA complexes were investigated by ultraviolet photoelectron spectroscopy (UPS), and the results were also discussed with the DFT calculations for model systems based on the crystal structures. In addition to these results, part of our aims here is to emphasize a new synthetic root for halide complexes using haloanils.

Experimental

Acetonitrile was dehydrated with calcium hydride and purified by distillation over phosphoric oxide. BA and CA were recrystallized from an acetonitrile solution before succeeding reactions. DDA and toluene with a purity better than 98% and 99%, respectively, were used as received.

DDA was reacted diffusively with a molar equivalent of BA in acetonitrile using an H-shaped glass apparatus in the dark. Needle-like crystals started to grow for several days, and after two weeks block-shaped crystals appeared. Both crystals were removed from the reaction tube by filtration after one week and one month, respectively, and dried over silica gel in a desiccator. The former product contained a mixture of both types of crystals, but the latter seemed to be uniform under a microscope. If the solvent was changed to toluene, the needle-like crystalline product became to be uniform. Typical images of both crystals under a microscope are shown in Fig. S1 of Electronic Supplementary Data. Chemical analysis results for needle-like and block-shaped crystals, which were obtained in toluene and acetonitrile, respectively, are given in Table 1 along with typical yields and theoretical values for some products that are expected under the experimental conditions described herein. The values for the mixture, which was obtained in acetonitrile, are also listed in the table by way of example.

Table 1

Elemental analysis for reaction products between DDA and BA.

Compounds	Analyses (%)			Yield (%) ^b
	С	Н	Ν	
Needle-like crystal	32.85	2.64	4.69	48.6
Block-shaped crystal	49.33	6.61	11.50	13.3
Mixture as obtained	34.30	3.09	5.41	-
$DDA-BA (C_{16}H_{18}N_2O_2Br_4)^a$	32.69	2.74	4.77	-
$DDA-Br (C_{10}H_{16}N_2Br)^a$	49.19	6.61	11.47	-

^a Calculated values for products expected under the reaction conditions.

^b Based upon starting DDA.

DDA was also reacted diffusively with CA in toluene or acetonitrile as a solvent. Contrary to the case of BA, it took a long time for the reaction between DDA and CA. Needle-like and block-shaped crystals were taken away from the reaction tube by filtration after three months and one year, respectively, and dried over silica gel in a desiccator. The former product was seemed to be uniform, but the latter was a mixture of both types of crystals from an observation through a microscope. The results of chemical analyses for the needle-like crystal and a typical mixture, which were obtained in toluene and acetonitrile, respectively, are given in Table 2 along with the theoretical values for some expected products under the experimental conditions.

Infrared absorption spectroscopy was performed with a potassium bromide disk method. Raman spectra were measured by a quasi-back scattering alignment with excitation of 514.5 nm. The electronic absorption spectra were also measured by a pressed disk diluting with potassium bromide. UPS spectra were measured and analyzed with the same system and the same method as the previous report [22]. Thin films were obtained by scrubbing the sample on the polished copper substrate in air. All UPS measurements were performed under the base pressure of less than 10^{-4} Pa. The sample films were characterized by Raman spectra after UPS measurements.

X-ray crystal analyses were performed on the reaction products of DDA and BA. Block-shaped crystals were used as obtained. In the case of needle-like crystals, a portion of the crystalline parts was selected, excised and used in further analyses because of its poor quality. Positions of hydrogen atoms were mapped by difference Fourier syntheses, and refined by the least squares method using an isotropic temperature factor. The structural data of these materials have been deposited to the Cambridge Crystallographic Data Centre (CCDC Nos. 668457 and 668458).

The unrestricted DFT method with the B3PW91 [23–28] functional was applied to a radical cation of DDA (DDA⁺). The geometry was optimized under three types of molecular symmetries; C_1 (without symmetry restriction), C_s and D_{2h} symmetries. Any remarkable differences were not observed in the total energy among these three symmetries, where relative energies of both C_s and D_{2h} geometries were 0.004 kcal/mol higher than that of the C_1 structure. We used the higher symmetric D_{2h} geometry for

Table 2	
Elemental analysis for reaction products between DDA and CA.	

Compounds	Analyses (%)			Yield (%) ^b
	С	Н	Ν	
Needle-like crystal	47.00	3.92	6.71	47.8
Mixture as obtained	53.40	7.90	12.75	-
DDA-CA $(C_{16}H_{18}N_2O_2Cl_4)^a$	46.62	4.40	6.80	-
$DDA-Cl (C_{10}H_{16}N_2Cl)^a$	60.14	8.08	14.03	-

^a Calculated values for products expected under the reaction conditions.

^b Based upon starting DDA.

Table 3	
Crystallographic data for DDA-E	ßr

DDA-Br	
Chemical formula	C ₁₀ H ₁₆ N ₂ ·Br
Formula weight	244.15
Crystal system	Monoclinic
Space group	C2/m
T (K)	298
a (Å)	9.714 (5)
b (Å)	16.195 (9)
c (Å)	6.867 (4)
β(°)	109.15 (4)
V (Å ³)	1020.5 (10)
Ζ	4
$\mu ({\rm mm^{-1}})$	4.00
Measured reflections	1469
Independent reflections	1218
Reflections with $F^2 > 2\sigma(F^2)$	999
R _{int} , S	0.040, 1.03
Number of parameters	98
$R[F^2 > 2\sigma(F^2)]$	0.029
$WR(F^2)$	0.029
$\Delta ho_{ m max}$, $\Delta ho_{ m min}~(m e m \AA^{-3})$	0.40, -0.38

CCDC No. 668458.

the discussion because of its small energy difference. Using the obtained geometry of the DDA⁺ monomer, a dimer structure was also optimized without counter anions for charge compensation. The inter-plane distance between the DDA⁺ moieties and the amount of sliding along the direction of two amino groups were optimized, where the geometry of each DDA⁺ moiety was fixed as that of the DDA⁺ monomer. Analytical vibrational frequency computations at the optimized structure were then performed to confirm that the optimized structure was at an energy minimum. The Cartesian coordinates for the optimized geometries for the DDA⁺ monomer and dimer are deposited as a list in Electronic Supplementary Data. The vertical values of the ionization potential were calculated by the Δ SCF method, while the adiabatic ones were estimated from the difference of the total energies between the corresponding two charge states. The values of the electron affinity were also calculated by the Δ SCF method. All calculations were performed with using the 6–311G(d) basis set. The Gaussian 09 program package [29] was employed for these calculations. All molecular structures were drawn with the GaussView 5.0 [30].

Results and discussion

Two types of crystals obtained from reactions between DDA and CA resembled corresponding ones from DDA and BA in spectral patterns of their infrared absorption (see Figs. S2 and S3 in Electronic Supplementary Data) and in crystalline appearances such as a needle or a block; therefore, it would be expected that the two types of reaction products are similar to each other in the cases of CA and BA. The products between DDA and CA were usually obtained as powdery samples. Especially, the sample, which were kept for a long period in the reaction system, had mainly small block-shaped crystals, but contained a small portion of very tiny needle-like crystals from observation through a microscope. Contrary with this, the reaction between DDA and BA gave relatively large crystals; then, crystallographic analyses were performed to both types of crystals. Typical sizes were $0.5 \times 0.25 \times 0.06~mm^3$ and $0.2 \times 0.2 \times 0.2~mm^3$ for needle-like and block-shaped crystals, respectively. Crystal X-ray analyses clearly showed that block-shaped crystals obtained from the reaction between DDA and BA are salt complexes of DDA bromide (DDA-Br), which crystallizes in the monoclinic system, space group C2/m. Crystallographic data are listed in Table 3. This is

Table 4

Crystallograph	ic data	for	DDA-	BA
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DDA-BA	
Chemical formula	C16H16Br4N2O2
Formula weight	587.95
Crystal system	Triclinic
Space group	$P\bar{1}$
T (K)	298
a (Å)	6.704 (6)
b (Å)	7.733 (6)
c (Å)	9.027 (7)
α (°)	77.26 (3)
β (°)	72.40 (4)
γ (°)	87.99 (4)
V (Å ³)	434.8 (6)
Ζ	1
$\mu ({\rm mm^{-1}})$	9.27
Measured reflections	1971
Independent reflections	1971
Reflections with $I > 2\sigma(I)$	1615
R _{int} , S	0.0000, 1.11
Number of parameters	117
$R[F^2 > 2\sigma(F^2)]$	0.050
$wR(F^2)$	0.150
$\Delta ho_{ m max}$, $\Delta ho_{ m min}$ (eÅ $^{-3}$)	0.97, -0.76

CCDC No. 668457.

consistent with results from an elemental analysis and the fact that the block-shaped crystal showed no vibrations corresponding to anionic and neutral molecules of BA (see Fig. S2 in Electronic Supplementary Data). It is obvious that there is no source of bromide anions (Br⁻) under the reaction conditions except for BA. An earlier study [31] of TMPD-CA complexes also showed that further reactions with CA anions take place in ionizing solvents. Dissociative electron attachment reactions of alkyl halides occur during photoionization processes of TMPD in organic glasses at low temperatures [32]. Coupling reactions between aromatic amines and CA have also been reported [33]. This work clearly shows that decomposition of haloguinon anions takes place and liberates halide ions in polar solvents. It could be thought that this decomposition increases slowly in concentrations of Br- anions giving good reaction fields for crystal growth. The same situation would be held at the reaction between DDA and CA. This is important when synthesizing CT complexes because haloquinons can be used as halideion source reagents. In addition to this, it is noteworthy that the quality of crystals is sufficient to determine the positions of the hydrogen atoms.

On the other hand, X-ray crystallography revealed that needlelike crystals consist of 1:1 complexes between DDA and BA, and there is no evidence of solution uptake. The complex of DDA-BA crystallizes in the triclinic system, space group $P\bar{1}$. Crystallographic data are listed in Table 4. This is also consistent with results from chemical analyses. The crystal quality of DDA-BA is usually worse than that of DDA-Br. This is due to decomposing BA⁻ anions in surface regions of crystals and due to effects from Br⁻ anions generated by the decomposition, and is the reason why reactions between DDA and BA do not give rise to a single product in a polar solvent. This situation was obvious for the case of the reaction products between DDA and CA, because decomposition of CA⁻ anions was slower than that of BA⁻ anions and the DDA-CA complexes still remained after a year. Typical data for the mixture as synthesized are shown in Tables 1 and 2. This shows that special care should be taken when characterizing structures and when discussing results from this series of the charge-transfer complexes with haloaniles.

Fig. 1 compares the molecular structure of DDA⁺ obtained by the X-ray analysis of DDA–Br to the optimized geometry of the DFT calculation. The position of each hydrogen atom in the X-ray



Fig. 1. Bond lengths given in angstroms (left) and bond angles in degrees (right) of DDA⁺: (a) experimental and (b) DFT optimized structures. A mirror plane lies perpendicular to the molecular plane; therefore, values for an asymmetric unit are shown. Thermal motion ellipsoids are also depicted for carbon (green) and nitrogen (blue) atoms in the X-ray structure. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

analysis was determined from difference Fourier syntheses, which also attests to the high quality of the crystal used. It is obvious from observed and calculated structures that the DDA⁺ molecule adopts a quinoid structure as pointed out from AM1 calculations [10]. From X-ray analyses, the central carbon ring is almost planar within experimental error, and four methyl carbon atoms and one of two amino groups also poses on this plane; however, the other amino group is slightly removed from the plane. This is partly due to interactions between DDA⁺ molecules, and in part to a hydrogen-like bonding between the amino group and the Br⁻ ion as discussed below. It should be mentioned that methyl groups do not freely rotate about their C-CH₃ axes even at room temperature. DFT calculations show that hydrogen atoms from methyl groups stay away from those of amino groups because of steric repulsion. This provides a reason as to why methyl groups do not rotate freely.

DDA⁺ molecules of DDA–Br form one-dimensional columns along the *c*-axis. The stacking manner of DDA⁺ molecules is shown in Fig. 2. All the molecules are equivalent in crystallography; therefore, there exists no evidence of doubly charged or neutral molecules in the crystal. One remarkable feature of the column is an alternation in the distance between molecular planes: shorter and longer distances are 3.1 and 3.6 Å, respectively, which correspond to intervals of 3.16 and 3.65 Å in a nearly straight line of amino carbon atoms. In addition to this column of DDA⁺ molecules, four Br⁻ anions closely locate at amino hydrogen atoms with distances of 2.65 and 2.77 Å in the asymmetric unit. This hydrogenlike bonding combines DDA⁺ columns in order to form networks in *ab* planes. It should be noted that this alternation in DDA⁺ molecules resembles the one observed for the low temperature phase of the TMPD perchlorate salt in spite of the difference in molecular overlapping [34]. The inter-planar spacing of 3.1 Å is obviously close to the van der Waals radius of a carbon atom, suggesting that there would be strong interactions between unpaired electrons of



Fig. 2. Stacking of DDA⁺ and Br⁻ (red ellipsoids) molecules in DDA–Br complexes with characteristic inter-atomic contacts given in angstroms.



Fig. 3. Bond lengths given in angstroms (left) and bond angles in degrees (right) for DDA and BA molecules in DDA-BA crystals. Both molecules have inversion symmetry; therefore, the values for an asymmetric unit are shown. Thermal motion ellipsoids are also depicted for carbon (green), nitrogen (blue), bromine (red), and oxygen (purple) atoms. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

these two molecules. This spacing is similar to the value of 3.15 Å for DMPD–Br [35] and is shorter than the value of 3.52 Å for TMPD–Br [36]. Overlapping of DDA⁺ molecules is smaller than in these Würster's salts. The distance and the degree of overlapping between molecules are determined by the repulsion of methyl groups, which depends on the substituted position.

We would like to consider molecular overlapping with using the results given from DFT calculations. Unpaired DDA⁺ electrons occupy $2b_{3g}$ orbitals (SOMOs) under D_{2h} molecular symmetries, which are π -orbitals (see the energy diagram and schematic drawings of several molecular orbitals depicted as Fig. S4 in Electronic Supplementary Data). The LUMO is also a π -orbital, and transitions between these two orbitals are optically allowed. Orbital characters are the same as those in Hartree-Fock calculations of PPD⁺ [37], except for contributions from hydrogen atoms to the LUMO. It is obvious from the atomic contribution to the SOMO that the most effective interaction between SOMOs of adjacent molecules is achieved when molecules stack parallel upon each other. When considering the repulsion of substituted methyl groups, the stacking manner of DMPD-Br would be the next effective structure. TMPD-Br shows the same molecular overlap to DMPD-Br; however, repulsion from dimethylamino groups distances these molecules. These two types of configurations in PPD⁺ dimers have been investigated by *ab initio* calculations [12]. A third type of configuration is seen with DDA-Br, and the closest pair of DDA⁺ molecules was deposited as Fig. S5 in Electronic Supplementary Data. Molecular overlapping is less effective in comparison to DMPD-Br due to repulsions in methyl groups substituted to central carbon rings.

The DFT method gives the optimized geometry for the singlet electron configuration of the dimeric (DDA⁺)₂ system without counter anions, while the structure for the triplet state never converged. The optimized geometry of the dimer is similar to the closest pair of DDA⁺ molecules in the DDA-Br crystal, and the closest carboncarbon distance is 3.027 Å, which is consistent to the observed value of 3.16 Å. We confirmed that a dimer with an optimized structure shows no imaginary frequencies in analytical vibrational frequency computations. The total energy of the dimer at this optimum point is larger than twice that of the monomer; however, it is interesting to note that there exists a potential minimum at the structure close to the experimental one. This is due to exchange interactions of unpaired electrons on DDA⁺ molecules, which act on attractive forces for adjacent molecules in the crystal. The energy diagram and several molecular orbitals of the DDA⁺ dimer are depicted as Fig. S6 in Electronic Supplementary Data. It is hypothesized that this attractive force and the hydrogen-like bonding between DDA⁺ and Br⁻ causes the alternate stacking of DDA⁺ molecules in the one-dimensional column.

Fig. 3 shows the molecular structures of DDA and BA in the DDA–BA crystal. DDA and BA molecules form one-dimensional columns along the *c*-axis with constant distances of 3.25 Å. This short contact shows strong interactions between adjacent DDA and BA molecules in the column (see Fig. S7 in Electronic Supplementary Data for molecular stacking and characteristic inter-atomic distances). Both molecules are nearly planar except for DDA hydrogen atoms. In contrast with DDA–Br, positions for methyl group hydrogen atoms could not be determined by difference Fourier



Fig. 4. IR absorption spectra of the CT complexes and halide salts depicted by blue and red curves, respectively. The results of the DFT calculations for DDA⁺ and (DDA⁺)₂ are also shown by black curves, where the scaling factor of 0.958 was used to fit both experimental and simulated spectra. The peaks marked by arrows could be assigned to carbonyl asymmetric stretching vibrations of BA and CA, which were used in estimation for amounts of charge transfer (see text). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

syntheses; therefore, lengths and dihedral angles of C–H bonds were fixed as 0.95 Å and 109.5°, respectively, and positions of hydrogen atoms were refined using the riding model. As shown in Fig. 3, two amino groups twist oppositely along an axis through two nitrogen atoms. This is partly due to hydrogen bonds between DDA and BA in the adjacent column. The central ring of DDA can be thought to adopt a benzene-like structure, which is apparently different from the structure of DDA⁺ in the DDA–Br crystal. BA molecules show strong quinoid structures, suggesting that DDA–BA is a molecular CT complex. It is interesting to note that all of the short inter-atomic contacts appear at atoms, which contribute largely to the HOMO of DDA or the SOMO of DDA⁺. This may imply that the large amount of the charge transfer is more likely to occur in adjacent molecules within the one-dimensional alternated column of DDA and BA.

In order to characterize the nature of the DDA–CA and DDA–BA complexes, the amounts of charge-transfer were estimated from the carbonyl asymmetric stretching vibrations of chloranil and bromanil, where we adopted an approximately linear relationship between the position of this vibration and the degree of charge-transfer [38,39]. Firstly, we compared the observed infrared spectrum of DDA–Br to that of the theoretical calculation for (DDA⁺)₂, where the scaling factor of 0.958 was used to fit both spectra to each other. Consistency between them is fairly well except for the region of N–H stretching vibration around 3300 cm⁻¹; then,



Fig. 5. UPS spectra of the CT complexes and halide salts measured at 7.75 eV (lower panel) and 9.18 eV (upper panel) in photon energies (see Figs. S8–11 in Electronic Supplementary Data for spectra obtained at other photon energies). The measurements were performed with the thin film, which was obtained by scrubbing the sample on the polished copper substrate in air.

the same factor was used for simulating the theoretical spectrum of DDA⁺ in the DDA-CA and DDA-BA complexes as shown in Fig. 4. The N–H stretching vibrations were observed at the reduced frequencies as compared to those in the simulated spectra for DDA⁺ and (DDA⁺)₂. This reduction would be due to hydrogen bonding discussed above. The situations of the hydrogen-like bonding are nearly similar to each other in two amino hydrogen atoms of DDA-Br, but are quite different in those of DDA-BA, which showed two features in each peak of the N-H stretching vibrations. It would be concluded by comparison between observed and simulated spectra that the carbonyl asymmetric stretching vibrations of CA and BA are assigned to peaks at 1691 cm⁻¹ and 1681 cm⁻¹, respectively, which are denoted by arrows in the figures. From these vibrational peaks, the degrees of charge-transfer were estimated to be 0.723 and 0.755 for DDA-CA and DDA-BA, respectively. The value for DDA-CA is quite large as compared to 0.24 for the complex between tetrathiafulvalene (TTF) and CA at 300 K [38]. Although the observed values of the ionization potential have not been reported for DDA in a gaseous phase, the DFT calculations estimated the ionization potential of DDA to be 6.29 eV and 5.77 eV for the vertical and adiabatic values, respectively, which is about 0.6 eV smaller than the observed vertical and adiabatic values of 6.92 eV and 6.4 eV, respectively, for TTF in a gaseous phase [40-42]. This small ionization potential of DDA and sufficient overlapping of electron donor and accepter molecules in the one-dimensional column would be attributed to the reason for the relatively large degree of charge-transfer.

The electronic structures of the obtained products were investigated by UPS. The UPS spectra measured at 7.75 and 9.18 eV of photon energies are compared in Fig. 5, and those measured at

Table 5

Calculated values of the vertical and adiabatic ionization potentials (I_v and I_a) and the electron affinity (E_A) in eV. The first two values are shown for I_v .

Compounds	E_A^a	Iv ^a		Ia ^b
DDA	-2.0	6.5	7.8	6.0
DDA ⁺	5.6	11.2	12.6	11.0
$(DDA^{+})_{2}$	8.6	13.1	14.6	-

^a Vertical values were calculated by the Δ SCF method.

^b Adiabatic values were estimated from the difference in the total energy.

other photon energies are deposited as Figs. S8-11 in Electronic Supplementary Data. All samples studied here showed the spectral features around 6 eV and 8 eV, indicating that these features could be assigned to the spectral structures along with ionization of the common components. It should be noted that any spectral differences were not observed for two crystalline types of products, indicating that the valence electronic structures of the DDA complexes are not much affected along with dimerization. This would be also confirmed from the fact that the UV-visible absorption spectra of both crystal types show a similar pattern to each other (see Fig. S12 in Electronic Supplementary Data). The calculated values of the ionization potential are summarized in Table 5, where the values for DDA⁺ and (DDA⁺)₂ were calculated without any charge compensation of counter anions. The first structure at 6 eV can be assigned to ionization from the SOMO $(3b_{3g})$ of DDA⁺ or the HOMO of (DDA⁺)₂, which is constructed by a bonding-type combination between the SOMOs of two DDA⁺ moieties in the dimer. It might be concluded that the second feature around 8 eV originates in ionization from the molecular orbital $(2b_{2g})$ next to the SOMO of DDA^+ or the molecular orbital next to the HOMO of $(DDA^+)_2$. The values of these two ionization energies were estimated by the \triangle SCF calculations to be 11.2 eV and 12.6 eV for DDA⁺ and to be 13.1 eV and 14.6 eV for (DDA⁺)₂, respectively. It should be noted from the calculations that the differences between the first and the second ionization energies are nearly constant even if DDA⁺ molecules form dimers. This is consistent with the experimental observations for the two types of reaction products between DDA and haloanile. In passing, we failed to observe the UPS spectra of DDA in the solid state because of its volatile nature and maybe of the low ionization energy. Actually, as discussed above, it might be expected from the calculated value of the ionization potential that DDA shows the lower ionization threshold than TTF, of which the value was reported to be 5.0 eV for the solid film at -38 °C [43,44].

Conclusion

Herein, we reported the crystal structures of two reaction products of DDA and BA for the first time. Both products were obtained from the same reaction pot, but at different reaction times. One structure was a complex salt of DDA–Br, which was crystallized simultaneously with decomposing BA[–] anions. Another structure was a 1:1 charge-transfer complex between DDA and BA, DDA– BA. The similar products were obtained with using CA instead of BA.

DDA molecules from DDA–Br crystals showed quinoid structures and stacked in a one-dimensional column with alternating molecular distances. The closest pair of DDA molecules was consistent with the optimized geometry of DFT calculations. Steric repulsion in methyl groups caused DDA⁺ molecules to stack in a third type of dimeric structure, which was different from that of DMPD–Br and TMPD–Br. Br⁻ anions played a role in combining columns of DDA through hydrogen bonds. Component molecules of DDA–BA also stacked in a one-dimensional column, in which DDA and BA molecules alternated. X-ray analyses showed that obtained products of DDA–BA were molecular crystals and DDA molecules adopted benzenoid structures, while the amount of the charge-transfer was estimated to be about 0.7 from infrared spectra.

The valence electronic structures of DDA complexes were investigated by UPS, and the results were compared with the theoretical calculations. Two spectral features were observed at 6 eV and 8 eV in the low binding energy region for all compounds with and without dimerization. The DFT calculations showed that the differences between the first and the second ionization energy are nearly constant during dimerization of DDA⁺, which is consistent with the UPS observations.

Finally, results from this report have two additional implications on the synthesis of charge-transfer complexes with haloanils, which are commonly used as electron acceptors: (1) special attention must be paid for contaminating halide ions when characterizing reaction products and in discussing their properties, and (2) a new moderate synthetic root for halide complexes is now available when using haloanils.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.molstruc.2014. 12.005.

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