

Multistability in a BEDT-TTF Based Molecular Conductor

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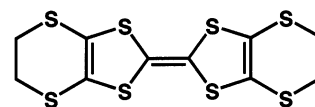
Abstract: The low dimensional organic conductor (BEDT-TTF)₂Br_{1.3}I_{1.1}Cl_{0.6} [BEDT-TTF = bis(ethylenedithio)-tertathiafulvalene] is shown to be a unique molecular solid that exists in three crystalline polymorphic forms (α' -, α''' -, β'' -phase) and, surprisingly, is able to adopt the same metal-like β'' -phase at both low ($T < 185$ K) and high ($T > 395$ K) temperatures. Several crystals of the α' - and α''' -phases have been studied using three different techniques: dc-conductivity measurements, ESR spectroscopy, and X-ray diffraction analysis. All these techniques show the existence of the reversible semiconductor \leftrightarrow metal ($\alpha''' \leftrightarrow \beta''$) phase transition at both high and low temperatures as well as the $\alpha' \leftrightarrow \alpha'''$ phase transition at high temperatures. The phase transitions of these polymorphs are characterized by huge hysteresis and dramatic changes in the transport and magnetic properties. Based on *ab initio* calculations, it is suggested that dipole–dipole interactions can play a key role in the rich polymorphism of this molecular solid.

Introduction

There is a considerable interest in obtaining and understanding multifunctional molecular materials existing in two (or more) stable/metastable states that interconvert reversibly under certain stimuli, such as temperature, pressure, light irradiation, and so forth.^{1–6} The reasons for this interest are the potential applications of these molecular materials for novel electronic devices such as thermal sensors, switching units, information storage, and processing media.

Bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) salts containing trihalide ions form a very interesting family of molecular solids that shows a rich polymorphism along with a large variety of physical properties. Thus, these salts exist in at least eight crystalline modifications (α -, α' -, α''' -, θ -, κ -, β -, β' -, and β'' -phase) possessing different transport properties such as semiconductor, metal, or superconductor and a large variety of both electronically and structurally reversible phase transitions which

can be induced by changes of pressure and/or temperature.^{4–8} The fine balance between various types of structural and electronic instabilities showed by the BEDT-TTF trihalides makes them attractive as model compounds for studying fundamental aspects of phase transitions in molecular solids.



BEDT-TTF

Recently, we have reported the preparation of a new BEDT-TTF based organic conductor, the (BEDT-TTF)₂Br_{1.3}I_{1.1}Cl_{0.6} salt,⁹ existing as two semiconducting polymorphic phases, the α' -¹⁰ and α''' -phase.⁹ The crystals of both phases contain the same set of nonpolar (Br–I–Br)[–] and (Cl–I–Cl)[–] as well as polar (Br–I–I)[–] and (Br–I–Cl)[–] anions, as ascertained by X-ray, energy dispersion X-ray (EDX), and Raman spectroscopies.⁹ We reported on the unique and very interesting property of the semiconducting α''' -phase that reversibly transforms to the metallic β'' -phase¹¹ at temperature as low as 185 K,⁹ but no studies of the (BEDT-TTF)₂Br_{1.3}I_{1.1}Cl_{0.6} mo-

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lecular organic conductor from the point of view of its structural and functional multistability in a wider temperature range have been performed. Here, we describe for the first time a series of remarkable phase transitions discovered in the $(\text{BEDT-TTF})_2\text{Br}_{1.3}\text{I}_{1.1}\text{Cl}_{0.6}$ salt at high temperature. The transitions are characterized by huge thermal hysteresis and associated large changes in their transport and magnetic properties. In particular, this study shows that $(\text{BEDT-TTF})_2\text{Br}_{1.3}\text{I}_{1.1}\text{Cl}_{0.6}$ salt is able to adopt the same metal-like β'' -phase not only at low ($T < 185$ K) but also at high ($T > 395$ K) temperatures, with distinct crystal modifications being favored between those limiting temperatures, a phenomenon that is unprecedented in molecular organic conductors. This study has been performed using three different techniques: dc-conductivity, ESR spectroscopy, and X-ray diffraction analysis on several crystals of the α' - and α''' -phase.

Results and Discussion

Single crystals of both the α' - and α''' -phase of the $(\text{BEDT-TTF})_2\text{Br}_{1.3}\text{I}_{1.1}\text{Cl}_{0.6}$ salt were obtained together as black plates in the same reaction by oxidizing the neutral BEDT-TTF donor at high temperature (120 °C) using the $\text{Bu}_4\text{NBr}_{0.6}\text{I}_{1.4}\text{Cl}$ salt, which contains a combination of the I_2Br^- , IBr_2^- , BrICl^- , and ICl_2^- anions, as the oxidant reagent.⁹ In contrast, only single crystals of the α' -phase were obtained when the electrocrystallization method, employing $\text{Bu}_4\text{NBr}_{0.6}\text{I}_{1.4}\text{Cl}$ as electrolyte and nitrobenzene as the solvent, at room temperature was used. The crystal composition of both phases was determined by EDX, being the same for all crystals obtained in different batches and with the two different methodologies. The crystals of the two phases have the same color and morphology, and the easiest way to distinguish them is by comparing their ESR parameters.^{9,12} Indeed, the ESR spectra at room temperature of single crystals of the α' and α''' -phase, oriented with the largest dimension of crystals perpendicular to the external magnetic field, consist of an anisotropic single Lorentzian line which shows line widths ranging from 70 to 45 G and 51 to 32 G, respectively (see Table 1).

The room-temperature conductivities of single crystals of the α' - and α''' -phase, measured by the dc four point method, are very similar. Thus, their conductivities amount to approximately $4 \Omega^{-1} \text{cm}^{-1}$ (in-plane) and $5 \times 10^{-3} \Omega^{-1} \text{cm}^{-1}$ (inter-plane), demonstrating the quasi-two-dimensional electronic nature of both phases. The temperature dependence of the resistance, $R(T)$, for the α''' -phase between 300 K and about 400 K in heating reveals a semiconductor-like behavior with an activation energy of $\Delta \approx 95$ meV (Figure 1a). At approximately 400 K, a dramatic drop of the resistance occurs and the $R(T)$ dependence changes from the semiconductor-like to a metallic behavior. The metal-like behavior remains stable when the sample is cooled to 378 K, at which temperature a sudden jump up of the resistance is observed. Further cooling reveals again a semiconductor-like behavior, with practically the same activation energy as that associated with the as-synthesized α''' -phase (see inset in Figure 1a).

Thus, this kind of dramatic change in the $R(T)$ behavior at high temperatures can be considered as an obvious indication

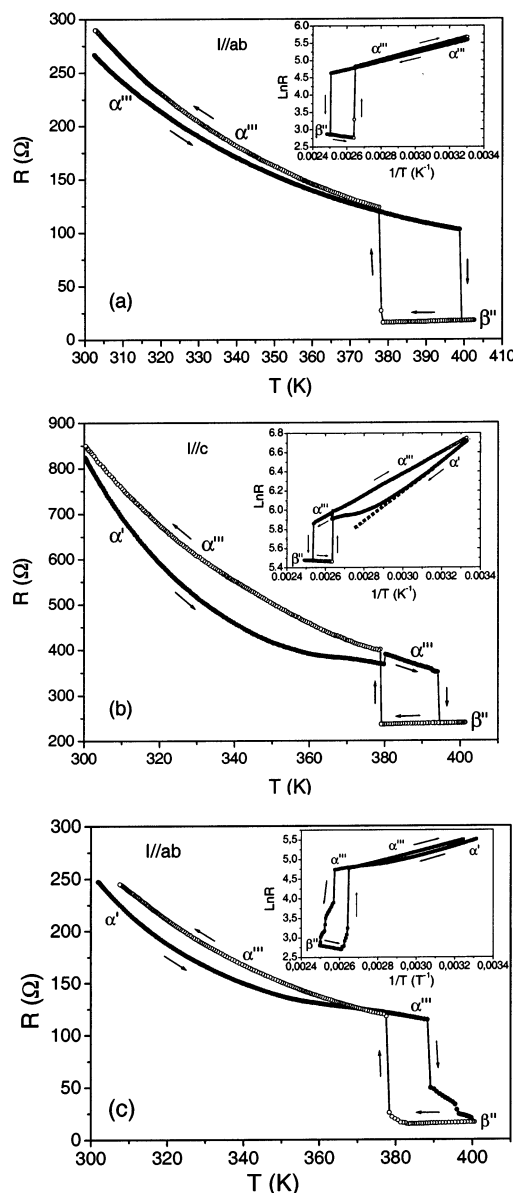


Figure 1. Temperature dependence of the resistance for as-synthesized (a) α''' - and (b and c) α' -phase crystals of the $(\text{BEDT-TTF})_2\text{Br}_{1.3}\text{I}_{1.1}\text{Cl}_{0.6}$ salt, measured with the current, I , running parallel to the ab plane (a and c) and to the c axis (b). Insets show plots of the logarithm of the resistance versus inverse absolute temperature for the same samples. The straight dotted line in the inset of part b is the Arrhenius fit.

of a first-order reversible phase transition from the semiconducting α''' -phase to a new metallic phase with a large hysteresis (about 20 K). It is worth noting the spectacular single jump down and up of the resistance (Figure 1a) which points to a cooperative (martensitic) nature of the transitions. As we will show in the following, the metallic phase existing at high temperature is the β'' -phase. Even more remarkable is the fact that crystals of the α''' -phase previously submitted to the high temperature $300 \rightarrow 400 \rightarrow 300$ K thermal cycle show in the conducting measurements (see Figure 2), when cooled to 130 K,¹³ the same $\alpha''' \rightarrow \beta''$ phase transition at ~ 185 K as previously reported for freshly obtained α''' -crystals.⁹

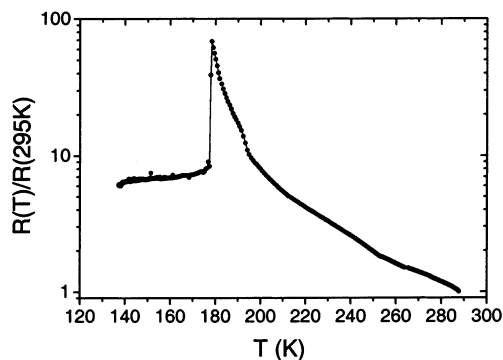
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(12) The polymorphic phase of all studied single crystals was always checked by means of their ESR spectra before and after measuring its conductivity and X-ray diffraction.

Table 1. ESR Parameters for Phases of the (BEDT-TTF)₂Br_{1.3}I_{1.1}Cl_{0.6} Salt at Different Temperatures^a

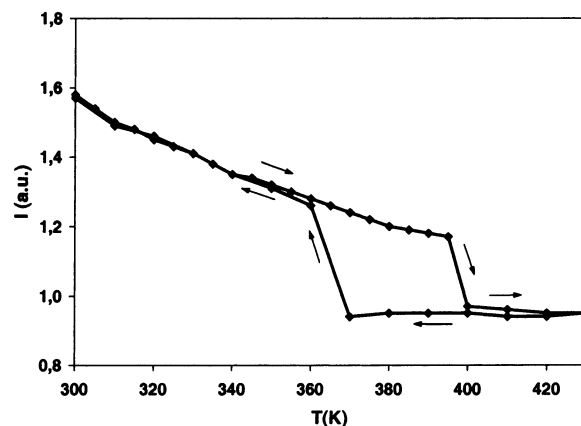
T (K)	phase	ΔH_{pp}^{max} (G)	g -factor (max)	ΔH_{pp}^{min} (G)	g -factor (min)
300	α'	70	2.0118	45	2.0040
	α'''	51	2.0120	32	2.0038
420	β''	55	2.0119	43	2.0032
170	β''	29	2.0120	20	2.0030
	α'	51	2.0120	33	2.0035

^a Maximum and minimum values have been obtained by the rotation of a single crystal oriented with the largest axis perpendicular to the external magnetic field.

**Figure 2.** Low temperature dependence of normalized resistance for the α' crystal (as-synthesized α''' crystal after heating to 430 K and cooling to room temperature) of the (BEDT-TTF)₂Br_{1.3}I_{1.1}Cl_{0.6} salt.

In contrast to the α''' -phase, the $R(T)$ dependence for the α' -polymorph shows a semiconductor-like behavior during heating to 330 K with an activation energy of $\Delta \approx 135$ meV (Figure 1b and c). Further heating results in some upward deviation from the Arrhenius fit (see insets in Figure 1b and c) and a subsequent small sharp rise of the resistance at ~ 380 K which is better displayed when the current is running parallel to the c axis. We suggest that both the deviation and rise are associated with a very broad thermal activated phase transition from the α' -phase to another semiconducting polymorph. The estimation of the activation energy of the latter gives a value of ~ 95 meV which is characteristic of the α''' -phase. Therefore, we were not surprised when at higher temperatures we have also found dramatic changes in the $R(T)$ behavior (see Figure 1b and c) that are similar to those observed when started with the as-synthesized α''' -polymorph (Figure 1a) and are associated with the transition from the α''' - to the metallic β'' -phase. In addition, cooling the resulting β'' -phase down to room temperature produced the same $R(T)$ behavior as that when this crystalline phase was obtained starting from the α''' -phase. Thus, when the α' crystals were heated from 300 to 420 K and then cooled to room temperature, they appeared to show the following series of first-order phase transitions: $\alpha' \rightarrow \alpha''' \rightarrow \beta'' \rightarrow \alpha'''$. Note that the ascription of the α''' -phase in this case was made based on its activation energy value. The α''' -phase obtained after the thermal cycle is metastable even at room temperature, revealing a huge (about 100 K) hysteresis, since it converts to the α' -polymorph at room temperature over a few days (see the following text). For the sake of clarity, the α' - and α''' -phase

(13) Due to the well-known fragility of this type of organic crystals, it is practically impossible to study the same crystal in the whole temperature range with all the techniques. In addition, in our hands to measure the dc-conductivity at high and low temperature, we must use different equipment that requires the use of different holders. For this reason, it has not been possible to record the resistance versus temperature data from 150 to 400 K with the same single crystal.

**Figure 3.** High temperature dependence of the ESR signal intensity of an as-synthesized α''' crystal of the (BEDT-TTF)₂Br_{1.3}I_{1.1}Cl_{0.6} salt.

obtained via such thermally induced phase transitions will be referred hereafter as α'_t - and α'''_t -phases, respectively.

The study of the temperature dependence of the ESR signal of the α' - and α''' -phase gives the same hysteresis loops observed in the transport measurements, confirming the occurrence and nature of the polymorphic transformations. Oriented single-crystal ESR spectra of the α' - and α''' -phase of (BEDT-TTF)₂Br_{1.3}I_{1.1}Cl_{0.6} were recorded at different temperatures. Heating to 430 K and the subsequent cooling to 120 K of both polymorphs were done at a rate of ~ 1 degree/min with the largest dimension of the crystals oriented perpendicular to the external magnetic field. These measurements reveal that at temperatures higher than 400 K the α' and α''' crystals of the (BEDT-TTF)₂Br_{1.3}I_{1.1}Cl_{0.6} are characterized by the same ESR signals showing the typical parameters of the metal-like β'' -type arrangement of BEDT-TTF based salts.^{9,14} The temperature dependence of the ESR signal intensity, $I(T)$, related directly with the magnetic susceptibilities, for the α' - and α''' -phase, is practically indistinguishable in the temperature range of 300–430 K. Thus, both samples show a sudden change at ~ 395 K on heating and around 370 K on subsequent cooling. Figure 3 shows the $I(T)$ dependence of an oriented single crystal of the α''' -phase. Worth noticing is the different temperature dependences at distinct temperature regions. Indeed, from 370 to 300 K, the intensity increases when temperature decreases, following the typical behavior of semiconductors due to the presence of highly localized and noninteracting unpaired electrons. In contrast, when the crystals are cooled from 430 to 370 K, the ESR signal, which shows a considerable less intensity, follows a Pauli-like temperature dependence in good agreement with its metallic nature. The temperature dependence in the range 120–430 K of the peak-to-peak line width for an oriented α' crystal is presented in Figure 4, showing the $\alpha' \rightarrow \alpha'''_t$ transition on heating and both $\alpha'''_t \leftrightarrow \beta''$ transitions at high and low temperatures. The most relevant ESR data for the α' and α''' crystals at 300 K as well as for the β'' -phase that appeared at both $T > 400$ K and $T < 180$ K are summarized in Table 1.

To determine unambiguously the nature of the phases as well as the structural changes resulting from the phase transitions described previously, we undertook a single-crystal X-ray diffraction analysis of the as-synthesized α' -phase from room

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Table 2. Crystallographic Data for the Various Phases of the (BEDT-TTF)₂Br_{1.3}I_{1.1}Cl_{0.6} Salt at Different Temperatures

formula: C ₂₀ H ₁₆ Br _{1.6} Cl _{0.6} I _{1.1} S ₁₆	temperature (K), phase				
	295, α'	386, α _t '''	398, β''	295, ^a α _t '''	177, ^a β''
<i>M</i>	1034.03	1034.03	1034.03	1034.03	1034.03
cystal system	triclinic	triclinic	triclinic	triclinic	triclinic
space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> (param)	1202.7(1)	1725.1(3)	591.8(1)	1707.0(2)	568.8(1)
<i>b</i> (param)	887.2(1)	902.0(2)	913.6(2)	893.4(1)	895.5(8)
<i>c</i> (param)	1634.7(2)	1635.3(3)	1628.2(3)	1630.7(2)	1622.7(1)
α (deg)	88.582(6)	87.967(8)	92.07(1)	88.005(4)	92.70(2)
β (deg)	85.187(8)	84.28(1)	96.48(1)	84.217(3)	97.09(1)
γ (deg)	70.862(7)	81.38(1)	105.30(1)	81.326(2)	105.06(1)
<i>V</i> (nm ³)	1.6421(3)	2.5028(8)	0.8417(3)	2.4474(3)	0.780(3)
<i>Z</i>	2	3	1	3	1
<i>D</i> _{calc} (g cm ⁻³)	2.091	2.058	2.040		
μ (cm ⁻¹)	3.735	3.675	3.643		
ranges of <i>h, k, l</i>	-11 ≤ <i>h</i> ≤ 10 -8 ≤ <i>k</i> ≤ 0 -15 ≤ <i>l</i> ≤ 15	-16 ≤ <i>h</i> ≤ 16 0 ≤ <i>k</i> ≤ 8 -15 ≤ <i>l</i> ≤ 15	0 ≤ <i>h</i> ≤ 5 -8 ≤ <i>k</i> ≤ 8 -15 ≤ <i>l</i> ≤ 15		
2θ _{max} (deg)	39.92	39.76	39.98		
reflins collected	2923	4398	1494		
independent reflns	2097	2531	1195		
<i>R</i>	0.0485	0.0583	0.0468		
w <i>R</i> ₂	0.128	0.139	0.121		
crystal size (mm ³)	0.3 × 0.2 × 0.02	0.3 × 0.2 × 0.02	0.3 × 0.2 × 0.02		

^a The structure was not solved, since after the thermal treatment the crystals show high mosaicity.

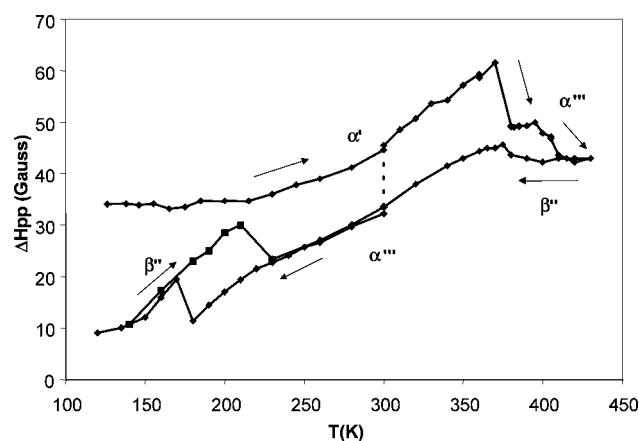


Figure 4. Temperature dependence of the ESR peak-to-peak line width for an oriented single crystal of the α'-phase of the (BEDT-TTF)₂Br_{1.3}I_{1.1}Cl_{0.6} salt. A dashed line indicates the α_t''' → α' phase transition at room temperature over a few days after the thermal cycle.

temperature up to 430 K and subsequently back down to 130 K with temperature steps of ~1–3 K for the data collection. This structural study shows that at high temperatures the unit cell of the as-synthesized α' crystal changes, adopting consecutively the α_t''' and β'' structural arrangements upon heating at *T* ≈ 380 K and 395 K, respectively, and again the α_t'''-phase at around 375 K and the β''-phase at around 183 K on cooling (Table 2). The full structure was solved at 295, 386, and 398 K, and only the cell parameters were collected at low temperature (177 K), since after the thermal cycles the crystals presented a high mosaicity. In summary, the X-ray studies definitely indicate that the spectacular changes in the transport properties (see Figures 1b,c and 2) occurring during the thermal cycle 295 → 386 → 398 → 295 → 177 K are related to the α' → α_t''' → β'' → α_t''' → β'' phase transitions. Furthermore, the X-ray, conductivity, and ESR studies showed that at room temperature the α_t'''-phase, obtained from these transformations (α_t'''), converts into the α'-polymorph (α_t') with time, while the as-synthesized α_t'''-phase is indefinitely stable at room

temperature. The differences between the α_t'- and α_t'''-phase and the as-synthesized α'- and α_t'''-phase are probably related to the presence of a high mosaicity and defects generated during the thermal treatment.

According to X-ray data, all polymorphs of (BEDT-TTF)₂Br_{1.3}I_{1.1}Cl_{0.6} are composed of layers of BEDT-TTF that alternate with trihalide anion layers along the *c*-axis. Projections of both kinds of layers for the α'-, α_t'''- and β''-phase are depicted in Figure 5. The stacking of the BEDT-TTF molecules, neutral and radical cations, along the *b*-axis forms the organic layers in all polymorphs. The overlap modes of BEDT-TTF within the stacks are identical for the three phases, while the relative orientations of the neighboring stacks along the *a*-axis are different (Figure 5, left). Interestingly, the α_t'''-phase contains the two types of relative orientations of the BEDT-TTF stacks present in phases α' and β''. There are no intermolecular S••S contacts shorter than the van der Waals distance (3.70 Å) between BEDT-TTF within the stacks, but there are several of such contacts between the stacks, each phase having its own characteristics. The trihalide IBr₂⁻, ICl₂⁻, I₂Br⁻, and BrICl⁻ anions in these polymorphs are completely disordered and arranged at different positions: (i) in a general position for the α'-phase (Figure 5a, right), (ii) centrally located at inversion centers for the β''-modification (Figure 5c, right), and (iii) in a general position and at inversion centers for the α_t'''-phase (Figure 5b, right). It is also worth noticing that anion layers of the α_t'''-phase can be considered as a combination of anion layers of both the α'- and β''-phase.

X-ray data also showed that the α_t'''-polymorph⁹ as well as the α_t'''-phase can be reversibly converted to the metallic β''-phase at low (*T* < 185 K) temperatures, showing the same hysteresis (60 K) observed in the ESR experiments (see Figure 4). Thus, remarkably, the α_t''' crystals of (BEDT-TTF)₂Br_{1.3}I_{1.1}Cl_{0.6} can be reversibly converted to the same metallic β''-phase at both low (*T* < 185 K) and high (*T* > 400 K) temperatures, as indicated in Scheme 1. To our knowledge, this phenomenon is unprecedented in organic molecular solids.

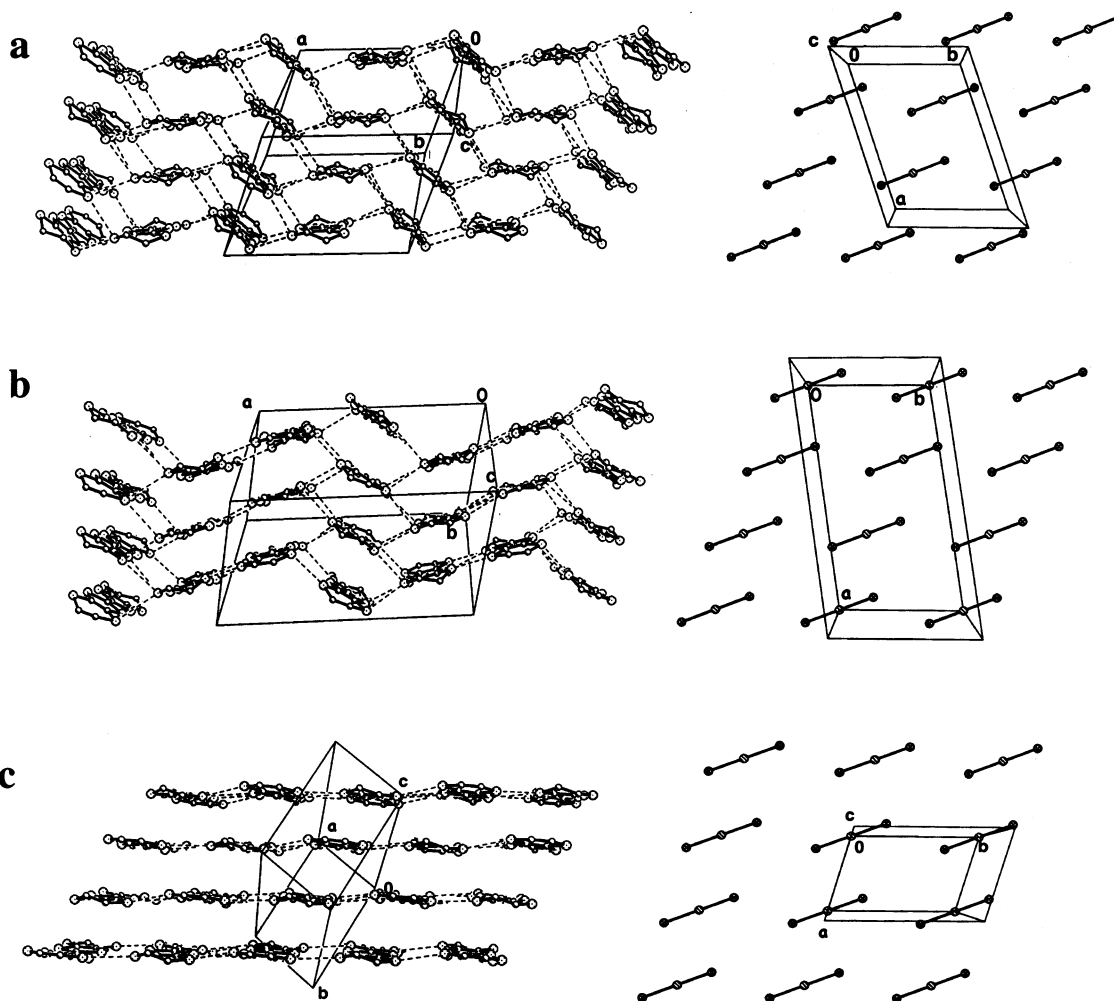
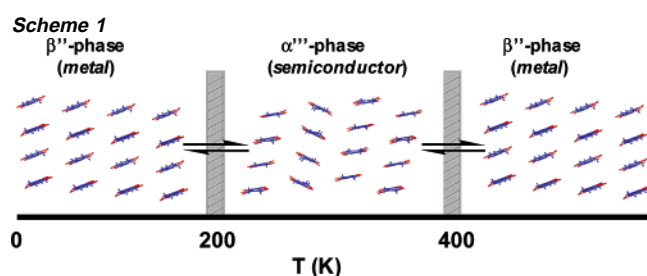


Figure 5. A view down the long axis of the BEDT-TTF radical cations (left) and projection of the anion layer along the c axis (right) for the (a) α' -, (b) α'' -, and (c) β'' -phase of the $(\text{BEDT-TTF})_2\text{Br}_{1.3}\text{I}_{1.1}\text{Cl}_{0.6}$ salt. Dotted lines indicate $\text{S}\cdots\text{S}$ contacts shorter than 3.8 Å.



A key question to answer is what drives such remarkable phase transitions. We suggest that the polar trihalide counterions I_2Br^- and BrICl^- present in the $(\text{BEDT-TTF})_2\text{Br}_{1.3}\text{I}_{1.1}\text{Cl}_{0.6}$ salt, the unique structural feature that differentiates this salt from other trihalide salts of BEDT-TTF, might play a crucial role in the minimization of the lattice energy due to dipole–dipole interactions. *Ab initio* calculations carried out at the MP2/LANL2DZ level (GAUSSIAN94)¹⁵ determine the electrical dipole moments of BrICl^- and I_2Br^- anions as 0.727 and 0.597

D, respectively. The difference in energy between parallel and antiparallel dipole–dipole systems of these species was found to be 1.0 kcal/mol. Consequently, the stabilization energy furnished by the dipole–dipole interaction between two polar trihalide anions can be approximately estimated as 0.5 kcal/mol. This value is comparable in energy to those provided by the van der Waals forces or weak hydrogen bonds.^{16–18} It is therefore reasonable to assume that some polymorphs of $(\text{BEDT-TTF})_2\text{Br}_{1.3}\text{I}_{1.1}\text{Cl}_{0.6}$ (for example, the unique α'' -phase) are able to exist only in a temperature range in which the dipole–dipole interactions are beneficial for the minimization of the lattice energy. In this scenario, these interactions would be collapsed at high and low temperatures due to strong heat vibrations of trihalide species and the Coulomb interanion repulsion, respectively. In this case, a new balance of intermolecular interactions can favor the generation of another more stable phase, the metallic β'' -phase.

Conclusion

X-ray diffraction analysis, dc-conductivity, and ESR spectroscopic measurements on several crystals of the two inter-

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Table 3. Analytical and Spectroscopical Data of a Few Representative Single Crystals of the (BEDT-TTF)₂Br_{1.3}I_{1.1}Cl_{0.6} Salt

synthetic procedure	phase type ^a	crystal composition ^b	Raman spectrum data at 295 K (cm ⁻¹)			
			I ₂ Br ⁻	IBr ₂ ⁻	BrCl	ICl ₂
A (batch 1)	α'''	(BEDT-TTF) ₂ Br _{1.3} I _{1.1} Cl _{0.6}	139.8, m	164.7, s	236.4, m	263.6, w
	α'	(BEDT-TTF) ₂ Br _{1.4} I _{1.0} Cl _{0.6}	136.9, m	162.4, s	233.7, m	260.1, w
A (batch2)	α'''	(BEDT-TTF) ₂ Br _{1.3} I _{1.0} Cl _{0.7}	139.0, m	166.7, s	235.1, m	263.5, w
	α'	(BEDT-TTF) ₂ Br _{1.3} I _{1.1} Cl _{0.6}	136.4, m	163.1, s	232.2, m	259.3, w
B	α'	(BEDT-TTF) ₂ Br _{1.3} I _{1.1} Cl _{0.6}	137.9, m	163.4, s	235.1, m	260.6, w

^a The type of crystalline phase was checked by ESR and X-ray spectroscopy. ^b Elemental composition of crystals was determined by using EDX spectroscopy; the experimental error of this method is ±0.1.

convertible polymorphs α' and α''' of the (BEDT-TTF)₂Br_{1.3}I_{1.1}Cl_{0.6} salt show that the α'''-phase of this organic conductor is reversibly transformed to the same metallic β''-phase at both low ($T < 185$ K) and high ($T > 395$ K) temperatures, a phenomenon which is, to our knowledge, unprecedented in organic molecular solids. The rich polymorphism and the spectacular series of phase transitions discovered in the (BEDT-TTF)₂Br_{1.3}I_{1.1}Cl_{0.6} salt set a new precedent concerning multistability in molecular materials that could provide clues for understanding and even designing new bi- (or multi-) stable multifunctional molecular materials.

Experimental Section

BEDT-TTF and Bu₄NBr_{0.6}I_{1.4}Cl salt were synthesized as previously published.⁹ Nitrobenzene of analytical grade from Aldrich was used as received.

X-ray data were collected on a Nonius Kappa CCD equipped with graphite-monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å) and a nominal crystal to area detector distance of 40 mm. Intensities were integrated using DENZO and scaled with SCALEPACK. The different phases of one single crystal were measured with equal scans in ϕ direction and the same time periods. The structures were solved with direct methods SHELXS86 and refined against F2 SHELX97.¹⁹ Hydrogen atoms at carbon atoms were added geometrically and refined using a riding model. All non-hydrogen atoms were refined with anisotropic displacement parameters. Atomic coordinates and other related structural data have been deposited as Supporting Information. The EDX analysis was performed with a scanning electron microscope (SEM) HITACHI S-3000N with an EDX-NORAN instrument. For Raman spectroscopy, a Jobin–Yvon T64000 Micro-Raman spectrometer, working in a backscattering mode, was used. The measurements were performed with a 633 nm laser line and with a spectral resolution of 1 cm⁻¹. A diamond (1332 cm⁻¹) line was used for the calibration of the spectrometer. EPR spectra in the range 120–440 K were obtained with an X-Band Bruker ESP 300E spectrometer equipped with a rectangular cavity operating in a T102 mode, a Bruker variable-temperature unit, a field frequency lock ER 033M system, and an NMR gaussmeter ER 035M. The modulation amplitude was kept well below the line width, and the microwave power was well below saturation. Temperature resistance dependencies were measured using a standard four-probe dc-method. Four annealed platinum wires (20 μm in diameter) were attached to the crystals by a conductive graphite paste.

(19) Sheldrick, G. M. *SHELXL-93, Program for the Refinement of Crystal Structure*; Göttingen University: Germany, 1993.

All four contacts were placed on the same conducting surface (mainly along the *a*-axis) for measurements of the in-plane resistance. For measurements of the inter-plane resistance, on both conducting surfaces two contacts were mounted more or less in front of each other so that a current was running along the inter-plane direction (mainly along the *c*-axis).

Synthesis of (BEDT-TTF)₂Br_{1.3}I_{1.1}Cl_{0.6} Salt. A. Chemical Oxidation Method (Procedure A). Bu₄NBr_{0.6}I_{1.4}Cl salt⁹ (1.25×10^{-3} mols) was added to a hot solution (120 °C) of BEDT-TTF (0.26×10^{-3} mols) in nitrobenzene (40 mL) under argon. Then, the resulting solution was cooled to 25 °C with a rate of 1 deg/hour, and as a result, nice black shining platelike crystals of the α'- and α'''-phase of (BEDT-TTF)₂Br_{1.3}I_{1.1}Cl_{0.6} salt were obtained. The total yield of the crystals was around 70% in all batches.

B. Electrocrystallization Method (Procedure B). High quality platelike black single crystals of the α'-phase were also obtained by electrocrystallization in an H-shaped cell using Bu₄NBr_{0.6}I_{1.4}Cl as electrolyte, in approximately stoichiometric amounts, and nitrobenzene as solvent. Electrocrystallization was performed with Pt electrodes and in galvanostatic conditions at 25 °C using a constant current of 0.9 μA.

The crystallographic phase of the obtained crystals was determined by comparing the ESR spectra as well as by X-ray diffraction analysis while the composition of the obtained crystals was determined by EDX analysis and Raman spectroscopy. As a matter of example in Table 3 are given the Raman and EDX analysis data obtained in three different experiments showing that the crystals and the anion layers of the α'- and α'''-polimorph have the same composition.

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Supporting Information Available: Crystallographic information files (CIF) for the three phases of the (BEDT-TTF)₂Br_{1.3}I_{1.1}Cl_{0.6} salt. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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