

Temperature-induced neutral-ionic transition in tetramethylbenzidine-tetracyanoquinodimethane (TMB-TCNQ)

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Experimental evidence is presented that indicates the occurrence of a temperature-induced neutral-ionic transition occurring at $T_c \approx 205$ K in the mixed-stack organic charge-transfer crystal, 3,3',5,5'-tetramethylbenzidine-7,7,8,8-tetracyanoquinodimethane (TMB-TCNQ). The transition is characterized by a large first-order-like jump in the magnetic susceptibility and a dimeric distortion of the stacks similar to those observed in tetrathiafulvalene-chloranil (TTF-CA). However, contrary to the case in TTF-CA the molecular ionicity jump at T_c is comparatively small in TMB-TCNQ. The nature of this transition observed in TMB-TCNQ is discussed drawing comparisons with that seen in TTF-CA.

A number of 1:1 mixed-stack organic charge-transfer (CT) crystals, composed of donor (D) and acceptor (A) molecules, can be divided into two types, namely, quasineutral and quasi-ionic crystals, according to the degree of CT between the D and A molecules. In some of these crystals, a phase transition can occur between the neutral (N) and ionic (I) phases when a physical parameter, such as temperature or hydrostatic pressure, gives a perturbation sufficiently intense to surmount the energy gap between the N and I phases. Such a transition, known as the neutral-ionic (NI) transition, was predicted to occur by McConnell *et al.*¹ The existence of a pressure-induced NI transition (PINIT), in several mixed-stack CT crystals, was later experimentally confirmed by Torrance *et al.*² In subsequent studies, the nature of PINIT in CT crystals was investigated in greater detail.³

Soos *et al.*⁴ suggested that a temperature-induced transition (TINIT) may occur in N,N' -dimethyldihydrophenazine-tetracyanoquinodimethane (M_2P -TCNQ), at about 370 K, but the nature of this transition still remains unclear. However, Torrance *et al.*⁵ were the first to discover such a TINIT in polycrystalline tetrathiafulvalene-*p*-chloranil (TTF-CA), occurring when temperature was lowered to 81 K at ambient pressure. Subsequent studies on the TINIT have therefore been concentrated mainly on TTF-CA.⁶ As a result of the preceding work, it is thought that the effects of Coulomb interaction and electron-lattice interaction play important roles in this transition. However, at the present stage, the available evidence is still not sufficient to eluci-

date the complete model of the NI transition. Therefore, to supplement the preceding results, much effort has been made to discover a new system that exhibits genuine TINIT at ambient pressure. However, researchers have not, as yet, been successful.

In this paper, we report on experimental evidence for the occurrence of a TINIT in a new mixed-stack CT compound consisting of 3,3',5,5'-tetramethylbenzidine (TMB) as the donor and TCNQ as the acceptor. The respective molecular structures are schematically depicted in Fig. 1. Discontinuous changes were observed in the optical as well as magnetic properties at a temperature of $T_c = 205 \pm 5$ K. (T_c is defined in this paper as the transition temperature observed on a cooling cycle.) These results display the characteristic features of a first-order TINIT, as observed in TTF-CA. However, the presently discovered TINIT in TMB-TCNQ exhibits several other features that are considerably different from those observed in TTF-CA. It may be informative to compare these differing features with the aim to achieve a greater understanding of the NI transition in organic CT crystals.

Starting powder materials of TMB and TCNQ were purified by a repeated process of sublimation and recrystallization. These purified powders were sealed in a Pyrex glass tube at different positions along its length according to the respective sublimation temperatures, about 150°C for TMB and about 160°C for TCNQ, and therefore with respect to the temperature profile produced by the furnace. Single crystals were obtained near the position where TCNQ powders were placed. The typical size

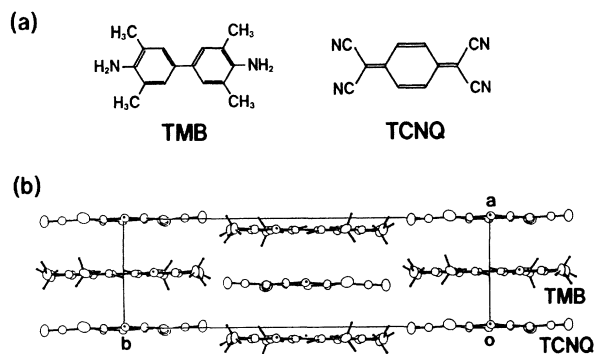


FIG. 1. (a) Molecular structures of TMB and TCNQ. (b) Crystal structures of monoclinic TMB-TCNQ.

of the crystals was $2 \times 0.5 \times 1 \text{ mm}^3$. According to a crystal structure analysis, the single crystals obtained by the present cosublimation method are monoclinic, as shown in Fig. 1. The space group was found to be $P2_1/n$, and the lattice constants were $a = 6.722 \text{ \AA}$, $b = 21.873 \text{ \AA}$, $c = 8.108 \text{ \AA}$, $\beta = 100.19^\circ$, and $Z = 2$. The number of unique reflections was 1224, and the final R factor was 8.9%. This structure is different from that of TMB-TCNQ crystals prepared by the solvent method, which were reported to have a triclinic structure.⁷ In the monoclinic structure shown in Fig. 1, TMB and TCNQ molecules form mixed-stack columns in the direction parallel to the a axis. Such a stacking structure is similar to that found in TTF-CA.⁸

Optical reflection spectra were measured on the as-grown (011) surface at various temperatures. Figure 2 shows the visible electronic excitation spectra. The main peak at 2.2 eV is attributed to intramolecular excitation

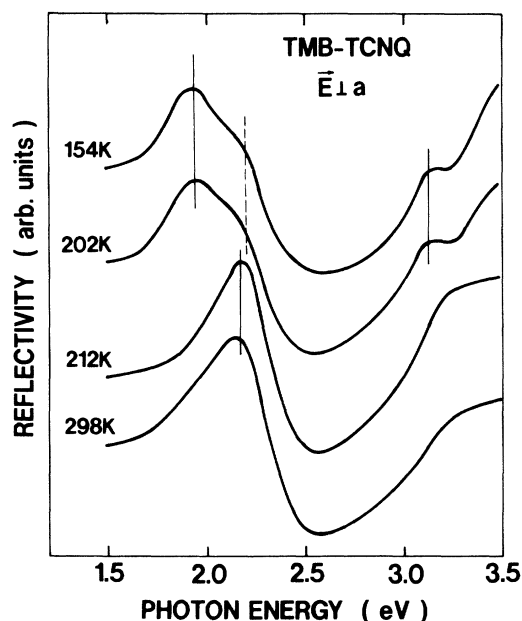


FIG. 2. Polarized visible reflection spectra of TMB-TCNQ observed at the (011) surface.

in TCNQ. This structure is strongly polarized for $E \perp a$, since the molecular planes are nearly perpendicular to the a axis, as shown in Fig. 1. When temperature is lowered, this spectrum's maximum shifts discontinuously to 1.9 eV. The 2.2 eV peak remains as a shoulder structure in the low-temperature phase. The high-energy region structure displays a discontinuous change at the same temperature. These features indicate the occurrence of a sharp change in the molecular ionicity, as observed at the TINIT in TTF-CA.⁴

The polarized infrared reflection spectra of the (011) surface are shown, for the $E \perp a$ component, in Fig. 3(a) and, for the $E \parallel a$ component in Fig. 3(b). The double peaks observed in the $E \perp a$ spectra are respectively attributed to the b_{2u} and b_{1u} $C \equiv N$ stretching modes in TCNQ. These modes are particularly useful for the determination of molecular ionicity, that is, the degree of CT between the D and A molecules. This is because their peak positions are sensitive to the electronic charge on TCNQ.⁹ From the peak position of the b_{1u} mode, the molecular ionicity of TCNQ at room temperature is estimated to be 0.6. This value is a little too large for denoting this phase as "quasineutral." However, it is theoretically predicted that the neutral (diamagnetic) state can have an ionicity larger than 0.5.¹⁰ Sudden shifts of the $b_{1,2u}$ peaks take place at about 200 K, indicating the onset of a first-order transition on cooling. The molecular ionicity is estimated to change from 0.59 to 0.69 at 200 K. The qualitative difference between high- and low-temperature phases is clarified by the magnetic properties presented in the following. Incidentally, note that the b_{1u} peak shows an extra shoulder structure as observed in the visible spectra.

The features observed in the $E \parallel a$ spectra in Fig. 3(b) are attributed to the totally symmetric (a_g) $C \equiv N$ stretching modes of TCNQ. These a_g modes are forbidden in regularly stacked crystals. In fact, at temperatures above 200 K, there is no observable structure at all, indicating that molecules are stacked with an equal spacing

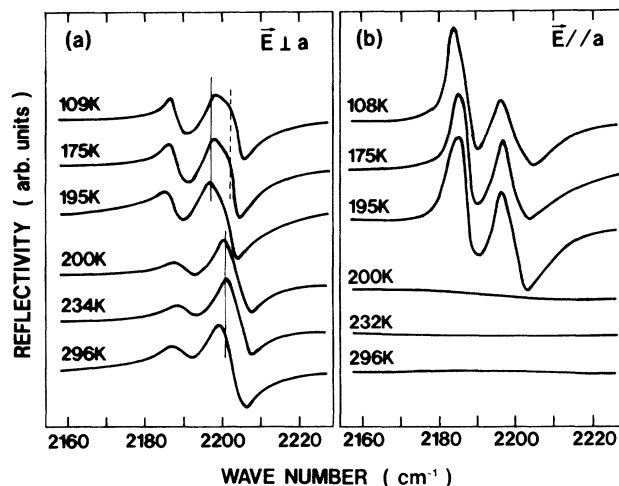


FIG. 3. Polarized infrared reflection spectra of TMB-TCNQ observed at the (011) surface, (a) $E \perp a$ and (b) $E \parallel a$, respectively.

along the stacking axis. However, when the temperature is lowered to about 200 K, structures in the $E\parallel a$ spectra suddenly appear, indicating the onset of a dimeric distortion of the stacks, as observed in TTF-CA.¹¹ These distortion-induced a_g peaks are predominantly polarized for $E\parallel a$, in agreement with an interpretation in terms of the electron-molecular vibration (EMV) coupling effect.¹² A similar a_g mode in TCNQ has been also observed in the dimerized phase of K-TCNQ and Rb-TCNQ.¹³ However, in contrast to the single a_g peak in these anion radical salts, the a_g mode in TMB-TCNQ was observed as twin peaks.

The optical data shown in Figs. 2 and 3 indicate the occurrence of a first-order phase transition at around 200 K in TMB-TCNQ crystals. Further evidence was obtained from the measurement of the electron spin resonance (ESR) on polycrystalline samples. In the low-temperature phase, only a single ESR peak of g value of about 2.00 is observed, contrary to the case of TTF-CA, where multiple peaks due to the TTF^+ and CA^- radicals are observed.¹⁴ The observed peak we attribute to the superposition of TMB^+ or $TCNQ^-$ radical spins, both having almost the same g values. The temperature dependence of the spin susceptibility χ_{spin} , estimated from the ESR signals, is plotted in Fig. 4(c). The χ_{spin} at temperatures above the critical temperature (T_c) of the transition is less than 10^{-8} emu/mol, and almost independent of

temperature, indicating that crystal is essentially diamagnetic at these temperatures. Therefore, the high-temperature phase can be regarded as neutral, in spite of the comparatively large molecular ionicity ($\rho \approx 0.59$). When temperature was lowered to about 200 K, the susceptibility shows a sudden jump to a value which is about one order of magnitude larger than that of the high-temperature phase. Below this temperature, the susceptibility shows a temperature dependence that obeys a paramagnetic Curie law. The estimated spin density is constant, and of the order of 10^{-5} spins/site below T_c . Such a susceptibility change is reproducible for repeated heating and cooling cycles centered on T_c . The hysteresis loops, observed at T_c , have widths which are somewhat sample dependent. However, the essential features of magnetic properties were not found to be dependent on samples, indicating that these features are an intrinsic property of TMB-TCNQ.

The jump in χ_{spin} clearly shows that the spin state of each molecule is changed at T_c , which is the essential feature of the NI transition. In spite of the small change in molecular ionicity, each molecule undergoes a discontinuous change from a diamagnetic state to a magnetic state possessing $\frac{1}{2}$ spin. However, the number of spins observed in the low-temperature phase is much smaller than the molecular density in the crystal. This can be explained in terms of a spin-soliton model proposed for TTF-CA.¹⁴ When the DA stacks are dimerized below T_c , two of the adjacent DA molecules form a singlet dimer. Hence, dimerized stacks cannot contribute to the magnetic susceptibility. However, there exists a finite number of defects that have the forms of walls between domains having opposite directions of dimerization. These domain walls are regarded as solitons similar to those in polyacetylene.¹⁵ It has been observed that the ESR line width is considerably broadened as temperature is lowered below T_c , indicating a motional narrowing effect for mobile spin solitons as suggested for TTF-CA.¹⁴

The optical and magnetic properties of TMB-TCNQ are summarized in Fig. 4; the peak position of the b_{1u} $C \equiv N$ stretching mode of TCNQ at the top (a), the relative absorption intensity of the a_g $C \equiv N$ stretching mode in the middle (b), and the spin susceptibility at the bottom (c), all as a function of temperature. The major conclusions derived from Fig. 4 are as follows: The degree of CT (ρ) jumps from 0.59 (the N phase) to 0.69 (the I phase) at T_c , as estimated from the wave numbers of b_{1u} $C \equiv N$ stretching modes of TCNQ. The ionicity jump $\Delta\rho$ is thus 0.1, which is considerably smaller than $\Delta\rho \approx 0.35$ in TTF-CA. In the N phase above T_c , the crystal is regularly stacked and diamagnetic. On the other hand, in the I phase below T_c , the lattice is significantly distorted by dimerization and, at the same time, a certain amount (of the order of 10^{-5} spins/site) of paramagnetic defects (spin solitons) are generated in the lattice. The change of degree of CT, the onset of lattice dimerization, and the generation of spins are unambiguous evidence for the existence of NI transitions in TMB-TCNQ.

The loops indicated by arrows in Fig. 4 represent the hysteresis behaviors of the respective quantities at the

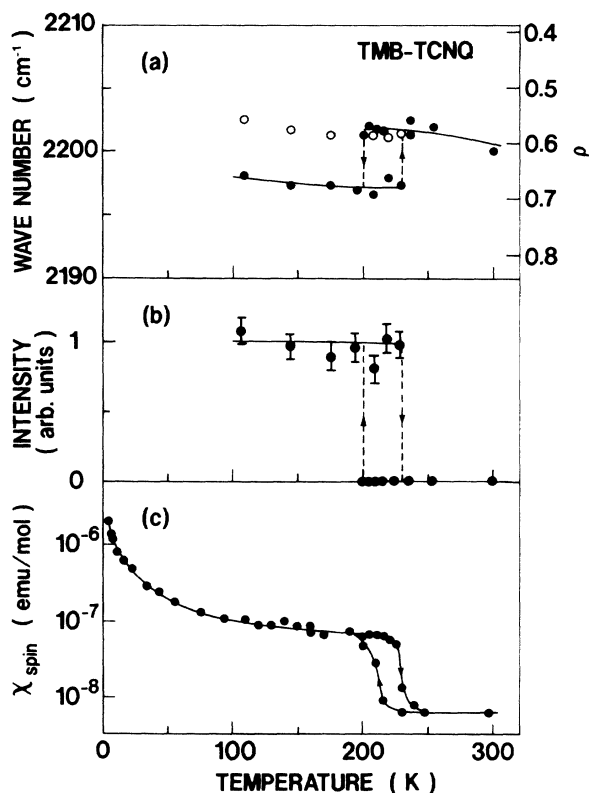


FIG. 4. Peak positions of the $C \equiv N$ stretching b_{1u} mode in (a), the intensity of the a_g mode in (b), and the spin susceptibility in (c), as a function of temperature. The open circles in (a) indicate the positions of the shoulder structures in the I phase.

TINIT. These hysteresis loops are characteristic to TMB-TCNQ and in direct contrast to the barely observable hysteresis behavior in TTF-CA. Hence, one can conclude that the first-order nature of the transition is much larger in TMB-TCNQ than in TTF-CA. The hysteresis loop in Fig. 4(c) is not so sharp as compared with the "rectangular" loops in Figs. 4(a) and 4(b). This may be attributed to the different quality of samples used; single crystals used in the optical measurements and polycrystals in the magnetic measurements.

The following characteristics of *NI* transition in TMB-TCNQ seem to give important information on the transition. Firstly, the change of degree of CT ($\Delta\rho$) is small in the *NI* transition of TMB-TCNQ in contrast to TTF-CA. This result indicates that there exists a sharp boundary between diamagnetic *N* and magnetic *I* state at around $\rho \approx 0.6$. According to the theoretical calculation,¹⁶ the small $\Delta\rho$ is attributed to the larger contribution of the intermolecular transfer energy in comparison to that of intersite Coulomb interaction. In this case, it is predicted that the boundary between the *N* and *I* phase exists at $\rho_c > 0.5$, consistent with the experimental result, and that the *NI* transition becomes indistinct. However, TMB-TCNQ crystals show a distinct hysteresis effect, and large discontinuities in observable physical properties at T_c . These large discontinuities are thought to arise from a large dimeric distortion of the stacks due to a stronger electron-lattice interaction in TMB-TCNQ than in TTF-CA.¹⁷ Therefore, the major driving force in the *NI* transition in TMB-TCNQ is thought to be the energy gain by the lattice dimerization, while the Coulomb interaction is supposed to play the main role in TTF-CA.

Another interesting feature in TMB-TCNQ is the appearance of twin peak structures observed both in the visible and infrared spectra of the low-temperature *I* phase (cf. Figs. 2 and 3). These doublet peaks indicate that there are two kinds of TCNQ molecules having different molecular ionicities coexisting in the ground state. These features are not observed in the TINIT of

pure TTF-CA crystals. The coexistence of *N* and *I* molecules in the ground state of the *I* phase may be due a "staging" effect as discussed before by Hubbard and Torrance.¹⁸ More detailed studies are necessary to confirm this conjecture.

In conclusion, we have presented experimental evidence for the occurrence of a TINIT in TMB-TCNQ crystals prepared for the first time in monoclinic form. This is the second such phenomenon to be observed in mixed-stack organic CT crystals. Nevertheless, it has significant meaning in the study of the *NI* transition in organic CT crystals, since the observed features of the transition are rather contrastive to those in TTF-CA; a fairly small ionicity change $\Delta\rho$ and a distinct hysteresis in TMB-TCNQ, against a large $\Delta\rho$ and a negligible hysteresis effect in TTF-CA. According to the existing theory, this difference may be attributed to the relative contributions of the Coulomb energy, the transfer energy *T* and the electron-lattice interaction *S*, to the *NI* transition. It is suggested that TMB-TCNQ represents a system with a relatively large *T* and *S*, while in TTF-CA the contribution from the Coulomb interaction is dominant. Further details of experimental results on temperature-induced and pressure-induced *NI* transition in TMB-TCNQ will be reported shortly.

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