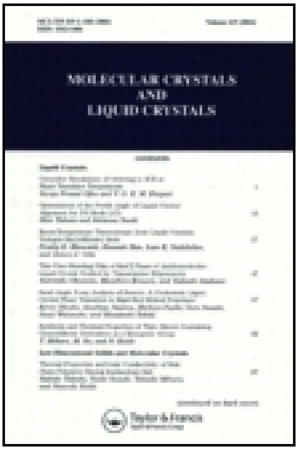


Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

# X-Ray Evidence for Molecular Dimerization at Neutral-Ionic Transition in TTF-Chloranil

Seiichi Kagoshima [a], Yasuyuki Kanai [a], Masato Tani [a], Yoshinori Tokura [b] & Takao Koda [b]

[a] Department of Pure and Applied Sciences, University of Tokyo, Komaba 3-8-1, Meguro-Ku, Tokyo, 153, Japan

[b] Department of Applied Physics, University of Tokyo, Hongo 7-3-1, Bunkyo-Ku, Tokyo, 113, Japan

To cite this article: Seiichi Kagoshima , Yasuyuki Kanai , Masato Tani , Yoshinori Tokura & Takao Koda (1985): X-Ray Evidence for Molecular Dimerization at Neutral-Ionic Transition in TTF-Chloranil, Molecular Crystals and Liquid Crystals, 120:1, 9-15

To link to this article: http://dx.doi.org/10.1080/00268948508075753

*Mol. Cryst. Liq. Cryst.* 1985, Vol. 120, pp. 9-15
0026-8941/85/1204-0009/$15.00/0

Printed in the United States of America

# X-RAY EVIDENCE FOR MOLECULAR DIMERIZATION AT NEUTRAL-IONIC TRANSITION IN TTF-CHLORANIL

SEIICHI KAGOSHIMA, YASUYUKI KANAI, MASATO TANI
Departmentof Pure and Applied Sciences, University of Tokyo,
Komaba 3-8-1, Meguro-Ku, Tokyo 153, Japan

YOSHINORI TOKURA, TAKAO KODA
Department of Applied Physics, University of Tokyo,
Hongo 7-3-1, Bunkyo-Ku, Tokyo 113, Japan

Abstract An abrupt change of some Bragg reflections occurs near the neutral-ionic transition temperature($T_{N-I}$) in TTF-chloranil. We performed intensity analyses of (3 k $\ell$) Bragg refrections below $T_{N-I}$ and found that donor ($TTF^+$:D) and acceptor (chloranil$^-$:A) molecules form D-A dimers below $T_{N-I}$.

## INTRODUCTION

The title compound, tetrathiafulvalene-chloranil(TTF-CA) , is unique material that undergoes a neutral-ionic(N-I) transition not only under high pressures but also at ambient pressure when the temperature is lowered.[1,2] The nature and the mechanism of the N-I transition have been investigated by various kinds of experiments.[3-7] Optical studies suggest that donor ($TTF^+$: D) and acceptor (chloranil$^-$: A) molecules form D-A dimers below the N-I transition temperature ($T_{N-I}$) 84K.[3,5,6] Recently, a possibility has been proposed that soliton excitations in the dimerized state may account for conductivity and ESR data below $T_{N-I}$.[8,12] Indeed, a previous X-ray study has found an abrupt change in lattice constants near $T_{N-I}$.[9,10] However, no structural evidence has been given for the formation of D-A dimers.

We made intensity analyses of (3 k $\ell$) Bragg reflections at low temperatures and found a structural evidence for the formation of D-A dimers in TTF-CA below $T_{N-I}$.

## EXPERIMENTS AND RESULTS

Needle-like crystals were obtained from an acetonitrile solution. Their typical dimension is 5x0.2x0.1 $mm^3$ . We used the Cu-$K_\alpha$ radiation monochromatized by a singly bent graphite ((0 0 2) reflection) , a position-sensitive proportional counter and a continuous-flow type cryostat. Sample crystals were glued onto an aluminium sample holder by a vacuum grease in a sample chamber filled with He gas. Temperature was measured by a Au-Fe vs. chromel thermocouple attached to the sample holder.

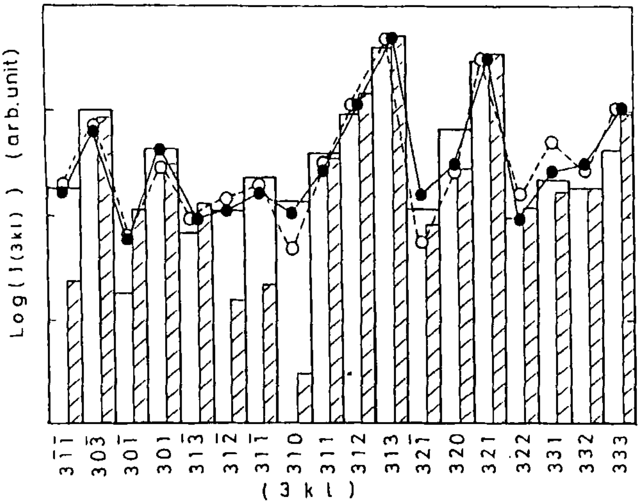


FIGURE 1 Comparison of observed and calculated intensities. Open and hatched bar graphs show intensities of (3 k $\ell$) reflections measured at 27K and 290K, respectively. Closed and open circles denote calculated intensities for the most probable pattern of molecular displacement ( Model 1 ) and for another displacement containing only the b- and the c-components ( Model 2 ), respectively. See Table I.

Bragg reflection intensities of (2 k $\ell$) , (3 k $\ell$) and (4 k $\ell$) were measured at 290K and 27K. Data were corrected for the Lorentz and the polarization factors as well as the absorption. Intensities of Bragg reflections at 290K are consistent with the previous structural analysis.[9] Intensities of (3 k $\ell$) reflections measured at 290K and 27K are shown in Fig. 1. It is evident that rather weak Bragg reflections at 290K change their intensities dramatically when the temperature is lowered to 27K. We found that the intensity change occurs abruptly near 78K. Figure 2 shows typical temperature dependence of such Bragg reflections in heating run. This abrupt change in intensity is considered to be closely related to the N-I transition. This change occurs at $T_c$=78.5±0.5K in all samples grown from the acetonitrile solution in heating run. We found a thermal hysteresis at the transition temperature; $T_c$ in cooling run is lower than that in heating by 0.5-1 K .

## DISCUSSION

In order to clarify the molecular displacement below 78K, we tried to find a suitable model of molecular displacement which reproduces the intensities of (3 k $\ell$) reflections measured at 27K. We assume

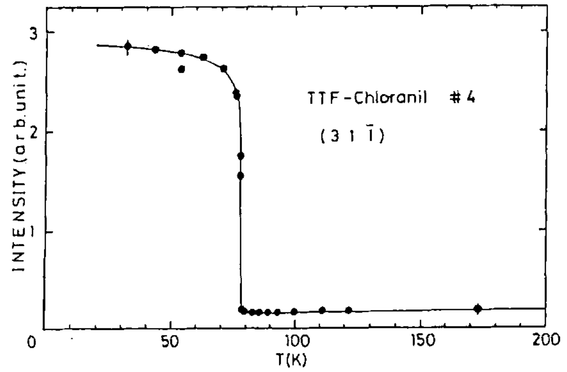


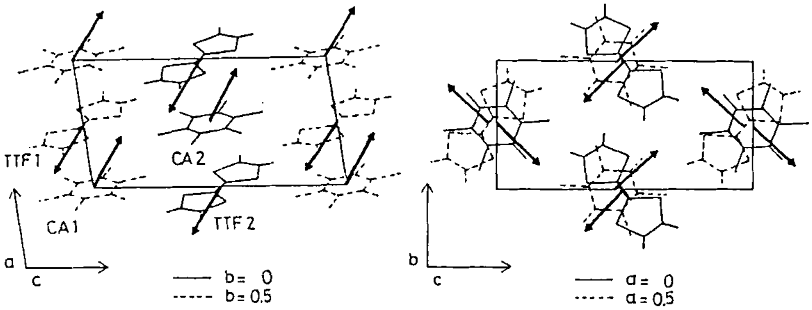
FIGURE2 Temperature dependence, in heating run, of the intensity of the (3 1 $\bar{1}$) reflection.

that each molecule is not deformed. Then we use atomic scattering factors of constituent atoms and, in addition, anomalous dispersion corrections for S and Cℓ which are presented in the previous work.[9] However, we do not take account of thermal parameters, because they have not been evaluated at 27K. Structure factors of (3 k ℓ) Bragg reflections are calculated for several types of molecular displacement without molecular rotation. We find that the experimental results are fairly reproduced by a few types of displacement. Here we describe typical two types of models. Model 1: The displacements of $TTF^+$ and $CA^-$ molecules are mainly along the a-axis. In this case, the displacement along the a-axis is essentially important to reproduce the experimental results and the b- and the c- components improve the model. In Fig. 3, the pattern of this displacement is shown. Clearly, in this model, $TTF^+$ and $CA^-$ molecules form D-A dimers. Final molecular displacement components in Model 1 are tabulated in Table I. The calculated Bragg intensities using these values are shown in Fig. 1 as closed circles. Model 2: The displacements of $TTF^+$ and $CA^-$ molecules have only the b- and the c- components. The pattern and the components of this displacement are shown in Fig. 3 and Table I, respectively. The open circles denote calculated Bragg intensities by Model 2 in

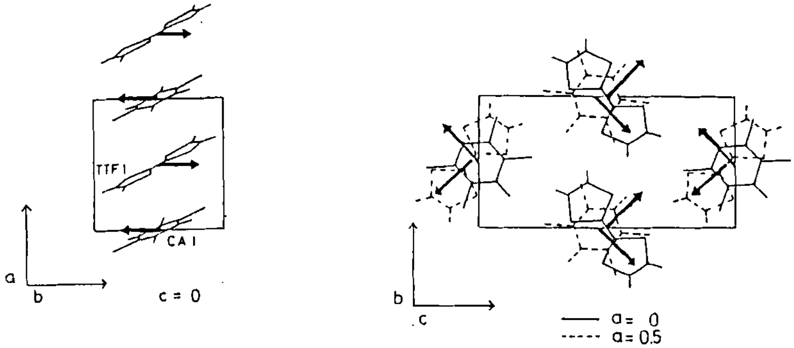
TABLE I Magnitude of the molecular displacement of TTF1, TTF2, CA1 and CA2 for Model 1, and for Model 2 containing only the b- and the c- components. Values are measured in Å. TTF1, TTF2, CA1 and CA2 are molecules shown in Fig. 3 (a).

| | | TTF1 | TTF2 | CA1 | CA2 |
|---|---|---|---|---|---|
| Model 1 | a= | -0.036 | -0.036 | 0.036 | 0.036 |
| | b= | 0.030 | -0.030 | -0.030 | 0.030 |
| | c= | -0.028 | -0.028 | 0.028 | 0.028 |
| Model 2 | a= | 0 | 0 | 0 | 0 |
| | b= | -0.075 | 0.075 | 0.075 | -0.075 |
| | c= | -0.071 | 0.071 | -0.071 | 0.071 |

Fig. 1. It is to be noted that the b- and the c- components of the displacement in Model 1 are different from those in Model 2. It seems that there are several local minima in the model fitting. Nevertheless we consider that Model 1 will be the most probable one as far as our analysis is concerned.



(a) Model 1 (b) Model 1



(c) Model 2 (d) Model 2

FIGURE 3 The molecular displacement pattern in TTF-CA at 27K. Arrows indicate the direction of the displacement. (a) and (b) are for Model 1. (a) Projection on the a-c plane. (b) Projection on the b-c plane. (c) and (d) are for Model 2. (c) Plojection on the a-b plane. Only one of stacks, consist of TTF1 and CA1, are drawn for simplicity. (d) Plojection on the b-c plane.

Although we may have to keep several possibilities for the molecular displacement as it is discussed above, we can find a unique feature common to them. It is that a $TTF^+$ (or $CA^-$) molecule displaces from the center of neighbouring $CA^-$ (or $TTF^+$) molecules which are stacked on and under the $TTF^+$ (or $CA^-$) molecule (see Fig. 3 ). In this point, we can conclude that $TTF^+$-$CA^-$ dimers are formed below about 80K.

We also examined another model in which $TTF^+$ molecules rotate around the center of mass of each molecule without translational displacements.[11] We find that such a model cannot reproduce the experimental results. When parameters in this model are adjusted to reproduce the intensity change of the rather weak reflections, the model involves big changes in intensities of rather strong reflections contrary to experimental results. We conclude that main features of the intensity difference between 27K and 290K is explained by the molecular displacement which forms $TTF^+$-$CA^-$ dimers. However, we would still keep a possibility that a certain coupling of the rotation with the displacement may be present.[11]

In our measurements of four samples, the temperature at which the abrupt intensity change occurs, as shown in Fig. 2, is different from the $T_{N-I}$ which is reported to be 84K.[2-10] In samples made by cosublimation of TTF and CA,[3] we found that the intensity change occurs at 82.3±0.5K in heating run. These samples also have the hysteresis which was mentioned already for the samples obtained from the acetonitrile solution. Kikuchi et al. reported the exsistence of the hysteresis in reflectivity measurements.[4] Our result is consistent with theirs. In this point of view , this transition may be of first order. However, from the thermal measurements, Ayache et al. reported that it is not the simple first order transition.[7] These results might be explained by following ideas :(1) There is some kind of difference between crystals made by different crystallizations. (2) There are several transitions near 84K. First the N-I transition occurs at 84K and then $TTF^+$-$CA^-$ dimerization takes place or a liquid of dimers turns into a solid of them at a lower temperature.

## CONCLUSION

We found abrupt changes of Bragg intensities near $T_{N-I}$. It has a small thermal hysteresis. Intensities of (3 k ℓ) Bragg reflections below $T_{N-I}$, at least at 27 K, are explained by the formation of $TTF^+$-$CA^-$ dimers.

## ACKNOWLEDGEMENT

We would like to thank Prof. T. Mitani of Institute for Molecular Science for valuable discussions about this material.

## REFERENCES

1. J. B. Torrance, J. E. Vazquez, J. J. Mayerle and V. Y. Lee, Phys. Rev. Lett., 46, 253 (1981).
2. J. B. Torrance, A. Girlando, J. J. Mayerle, J. I. Crowley, V. Y. Lee, P. Batail and S. J. LaPlace, Phys. Rev. Lett., 47, 1747 (1981).
3. Y. Tokura, T. Koda, T. Mitani and G. Saito, Solid State Commun., 43, 757 (1982).
4. K. Kikuchi, K. Yakushi and H. Kuroda, Solid State Commun., 44, 151 (1982).
5. C. S. Jacobsen and J. B. Torrance, J. Chem. Phys., 78, 112 (1983).
6. A. Girlando, F. Marzola, C. Pecile and J. B. Torrance, J. Chem. Phys., 79, 1075 (1983).
7. C. Ayache and J. B. Torrance, Solid State Commun., 47, 789 (1983).
8. T. Mitani, G. Saito, Y. Tokura and T. Koda, to be published
9. J. J. Mayerle, J. B. Torrance and J. I. Crowley, Acta Cryst., B35, 2988 (1979).
10. P. Batail, S. J. LaPlaca, J. J. Mayerle and J. B. Torrance, J. Am. Chem. Soc., 103, 951 (1981).
11. From the ESR measurements in Ref. 8, the probability of $TTF^+$ molecular rotation is found to be much larger than that of $CA^-$.
12. B. Horovitz and B. Schaub, Phys. Rev. Lett., 50, 1942 (1983).