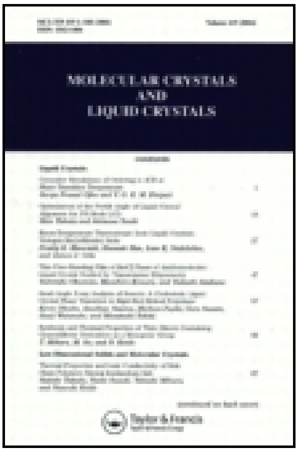

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

Polarized Reflectance Spectra of DCNQI Salts

Kyuya Yakushi [a] , Akito Ugawa [a] , Gen Ojima [b] , Takashi Ida [b] , Hiroyuki Tajima [b] , Haruo Kuroda [b] , Akiko Kobayashi [b] , Reizo Kato [c] & Hayao Kobayashi [c]

[a] Institute for Molecular Science, Okazaki, Aichi, 444, Japan

[b] Department of Chemistry, Faculty of Science, the University of Tokyo, Hongo, Tokyo, 113, Japan

[c] Department of Chemistry, Faculty of Science, Toho University, Funabashi, Chiba, 274, Japan

To cite this article: Kyuya Yakushi , Akito Ugawa , Gen Ojima , Takashi Ida , Hiroyuki Tajima , Haruo Kuroda , Akiko Kobayashi , Reizo Kato & Hayao Kobayashi (1990): Polarized Reflectance Spectra of DCNQI Salts, Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 181:1, 217-231

To link to this article: http://dx.doi.org/10.1080/00268949008036006

Mol. Cryst. Liq. Cryst., 1990, vol. 181, pp. 217–231
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

POLARIZED REFLECTANCE SPECTRA OF DCNQI SALTS

KYUYA YAKUSHI and AKITO UGAWA
Institute for Molecular Science, Okazaki, Aichi 444, Japan

GEN OJIMA, TAKASHI IDA, HIROYUKI TAJIMA, HARUO KURODA, and AKIKO KOBAYASHI
Department of Chemistry, Faculty of Science, the University of Tokyo, Hongo, Tokyo 113, Japan

REIZO KATO and HAYAO KOBAYASHI
Department of Chemistry, Faculty of Science, Toho University, Funabashi, Chiba 274, Japan

Abstract Temperature dependence of the polarized reflectance spectra have been measured on the single crystals of $(DMe\text{-}DCNQI)_2Ag$, $(DMe\text{-}DCNQI)_2Na$, $(MeBr\text{-}DCNQI)_2Cu$, and $(DMe\text{-}DCNQI)_2Cu$ (DCNQI stands for dicyanoquinonediimine). The optical spectra evidence one-dimensional band structures of Ag- and Na-salts and anisotropic three-dimensional ones of Cu-salts. The dimensionality crossover is found in $(MeBr\text{-}DCNQI)_2Cu$ around the metal-insulator phase transition.

INTRODUCTION

In the past few years, considerable effort has been devoted to the electrical,[1-6] magnetic,[9-12] structural,[13-16] and optical[17-19] studies of the organic radical salts of 2, 5-substituted dicyanoquinonediimine (*XY*-DCNQI). The substituted DCNQIs were synthesized by Aumuller and Hunig for the first time,[20-21] and the copper salt, $(DMe\text{-}DCNQI)_2Cu$, attracted attention because of keeping the metallic behavior down to 1.3 K without showing a Peierls transition.[1] From the chemical viewpoint, unique is the architecture that organic stacks are bridged by coordinate bonds through copper cations. In this respect the copper salts of DCNQIs are regarded to shed light on the field of organic metals. Apart from this chemical aspect, copper salts of DCNQI showed several unusual solid state properties: the pressure-induced metal-insulator phase transition,[2,3,4,6] the re-entrant behavior in the p–T phase diagram,[4,5] and the coexistence of conduction electrons and a magnetic order at low temperature[3,14]. These properties originate from the interaction between the π-conjugated organic stack and the $3d$-orbitals of copper cation. In this paper, we present the temperature-dependent reflectance spectra of the single crystals of four DCNQI salts ($(\mathrm{DMe\text{-}DCNQI})_2\mathrm{Ag}$, $(\mathrm{DMe\text{-}DCNQI})_2\mathrm{Na}$, $(\mathrm{DMe\text{-}DCNQI})_2\mathrm{Cu}$, $(\mathrm{MeBr\text{-}DCNQI})_2\mathrm{Cu}$), and discuss the charge-transfer interaction between the DCNQI stack and the bridging copper cation.

EXPERIMENTAL

The procedure on the crystal growth of DCNQI salts were described elsewhere.[16] Polarized reflectance spectrum was measured with two spectrometers using a microspectro-photometric technique. The spectrum from 4500 cm^{-1} to 25000 cm^{-1} was measured with the instrument composed of the optical microscope, Olympus MMSP-RK, the monochromator, JASCO-CT50, and the cryostat, Spectrim™. The spectrum from 450 cm^{-1} to 5000 cm^{-1} was measured with the infrared spectrometer of dispersive type, JASCO MIR-300, which was extensively modified in the University of Tokyo to conduct an automatic measurement and a low-temperature experiment. Solution spectrum was measured with Hitachi U-3400 using carefully purified acetonitrile as a solvent.

RESULTS AND DISCUSSION

Figure 1 shows the spectra of DMe-DCNQI (dotted line) and $(\mathrm{DMe\text{-}DCNQI})_2\mathrm{Li}$ (solid line) dissolved in acetonitrile solution. The absorption spectrum of $(\mathrm{DMe\text{-}DCNQI})_2\mathrm{Li}$ involves three absorption bands, A, B, and C. The band C containing two shoulders at both sides of the main peak is attributed to the intramolecular transition of DMe-DCNQI neutral molecule as obviously seen from the comparison with the spectrum of DMe-DCNQI. Thus the peaks, A and B, are assignable to the intramolecular transition of DMe-DCNQI$^-$ radical. Incidentally the shape of the band A and the energy separation between the bands A and B are similar to those of TCNQ$^-$ radical.[22] We thus consider that the electronic structure of DMe-DCNQI resembles TCNQ as well as the molecular skeleton does.

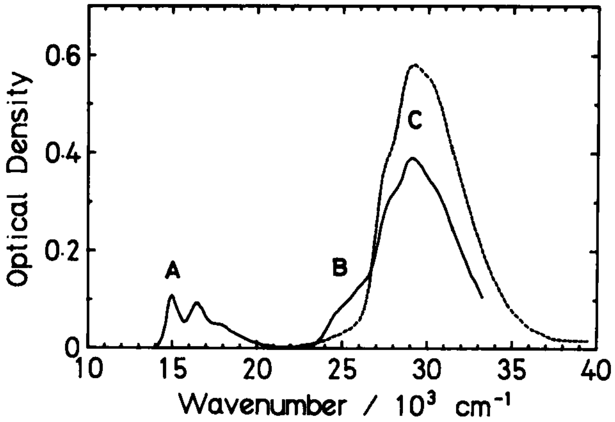

FIGURE 1 Absorption spectra of DMe-DCNQI (dotted line) and $(DMe\text{-}DCNQI)_2Li$ (solid line) dissolved in acetonitrile solution.

$(DMe\text{-}DCNQI)_2Ag$

$(DMe\text{-}DCNQI)_2Ag$ exhibits a metal-like electrical conduction with the room-temperature conductivity of 100 Scm^{-1}, a conductivity maximum at *ca.* 100 K, and a sharp decrease with an activation energy of 0.1 eV at lower temperature. As shown in Fig. 2(a), the //*c* spectrum drawn by open circles shows a large dispersion in the infrared region, whereas we cannot find any strong dispersion in the //*a* spectrum drawn by triangles. This spectrum obviously indicates the existence of a one-dimensional intermolecular interaction along the stacking direction (*c*-axis) of DMe-DCNQI. The Ag····N≡C distance is comparable with those of the coordination compound such as $[Ag(CH_3CN)_4]ClO_4$.[13] However the absence of dispersion in the infrared region of the //*a* spectrum, except due to weak vibrational transitions, demonstrates that a strong interaction is not present between the silver cation and the DCNQI stack. Further evidence for the absence of the Ag-DCNQI interaction is provided by the resemblance to the spectrum of $(DMe\text{-}DCNQI)_2Na$ where coordinate bond cannot be formed between metal cation and DCNQI (*vide infra*)[17]. This one-dimensional electronic structure is consistent with other experiments on the X-ray diffuse scattering,[15] ESR,[10] and electrical conductivity[10].

Despite the metallic behavior reported in the transport experiments of $(\mathrm{DMe\text{-}DCNQI})_2\mathrm{Ag}$, the //*c* spectrum in the infrared region is not Drude-like. This optical behavior is often observed in one-dimensional organic conductors such as $(\mathrm{TMTTF})_2X$, being ascribed to the formation of a band gap by strong electron-electron correlation.[23] Schutz *et al.* explained the electrical conductivity of this Ag-salt on the basis of "metal like" semiconductor model with the activation energy of 245 cm^{-1} where a temperature-dependent mobility is introduced.[6] The conductivity spectrum calculated through the Kramers-Kronig transformation is illustrated in Fig. 2(b). This spectrum also suggests the presence of the band gap in the low-wavenumber region already at room temperature.

The integrated intensity of the 2950 cm^{-1} absorption band is related to the magnitude of the transfer integral between the adjacent DCNQI molecules in the stack. Since the exact solution of the extended Hubbard model is not known, we tentatively estimate the transfer integral using the model of the $U = V = 0$ limit. In the case of quarter-filled tight-binding band, the transfer integral

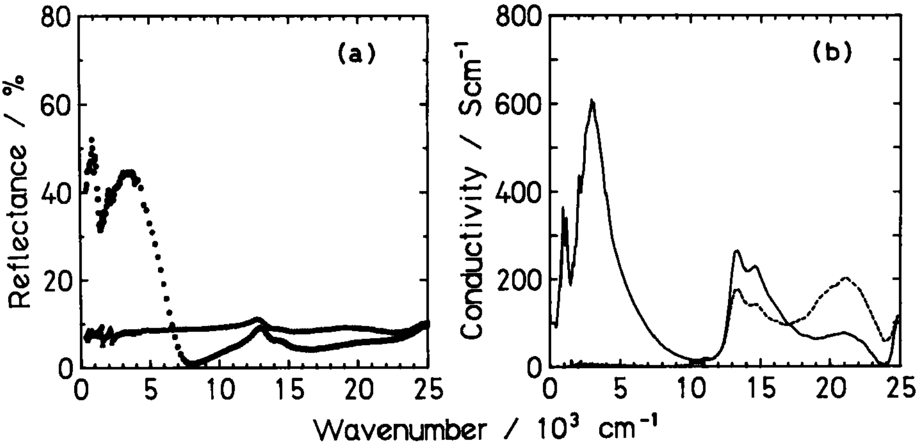

FIGURE 2 Polarized (a) reflectance and (b) optical conducivity spectra of $(\mathrm{DMe\text{-}DCNQI})_2\mathrm{Ag}$. The //*c* and //*a* spectra are respectively drawn by circles and triangles in (a), and by solid and broken lines in (b).

is related to the integrated area of conductivity spectrum by the following equation,

$$\int \sigma(\omega)\,d\omega = \sqrt{2}\,e^2 c^2 Nt/\hbar^2$$

where e is the electron charge, c the lattice constant along the stacking axis, N the site number per unit volume, t the transfer integral. The transfer integral thus calculated is 0.1 eV. The peak energies appeared in the conductivity spectrum are listed in TABLE I.

The strong vibrational bands at 900, 1150, and 2050 cm^{-1} is attributed to a_g modes induced by an electron-molecular vibration coupling.[23] This transition is optically allowed when the DMe-DCNQI molecules are dimerized or tetramerized in the stack. Thus the appearance of these vibrational bands is regarded as evidence for the presence of the fluctuating lattice distortion in the regularly stacked average structure. This interpretation is consistent with the observation of the X-ray diffuse sheet at room temperature.[15]

TABLE I Peak energies (10^3 cm^{-1}) observed in the solid spectrum of $(DMe\text{-}DCNQI)_2Ag$.

$//c$	0.90,	1.15,	2.05,	2.95,	13.4,	14.6,	21.2
$//a$	1.55,	2.29,			13.4,	14.6,	21.0

Since the absorption band at 13400 cm^{-1} has vibrational structure similar to the band A in Fig. 1, it is ascribed to the lowest intramolecular transition of $DMe\text{-}DCNQI^-$. Another band at *ca.* 21000 cm^{-1} is probably assigned to the second lowest intramolecular transition of $DMe\text{-}DCNQI^-$, the counterpart of which is found as the band B in solution spectrum. These absorption bands are also observed in the solid state spectrum of $(DMe\text{-}DCNQI)_2Na$.[17] We therefore conclude that any indication to show the interaction of DMe-DCNQI and silver cation is not found in this material.

$(DMe\text{-}DCNQI)_2Na$

The electrical, magnetic, and structural properties of $(DMe\text{-}DCNQI)_2Na$ are almost exactly the same as those of $(DMe\text{-}DCNQI)_2Ag$.[3] Figure 3 shows the temperature dependence of the reflectance and conductivity spectra polarized parallel to the stacking direction. The low-temperature spectrum shows no substantial change except the sharpening of the vibrational structures. This temperature dependence strongly indicates that the band gap is already present at room temperature. If the band gap is opened by the lattice distortion, the spectrum should change concomitantly with the the evolution of the lattice distortion on lowering the temperature. This is not the case in this material, so that we consider that the band gap already present at room temperature is formed mainly by the Coulomb interaction between the adjacent molecules in the DCNQI stack. Incidentally a_g modes are found at 980, 1100, 1200, 1300, 1600, and 2100 cm^{-1} at 20 K.

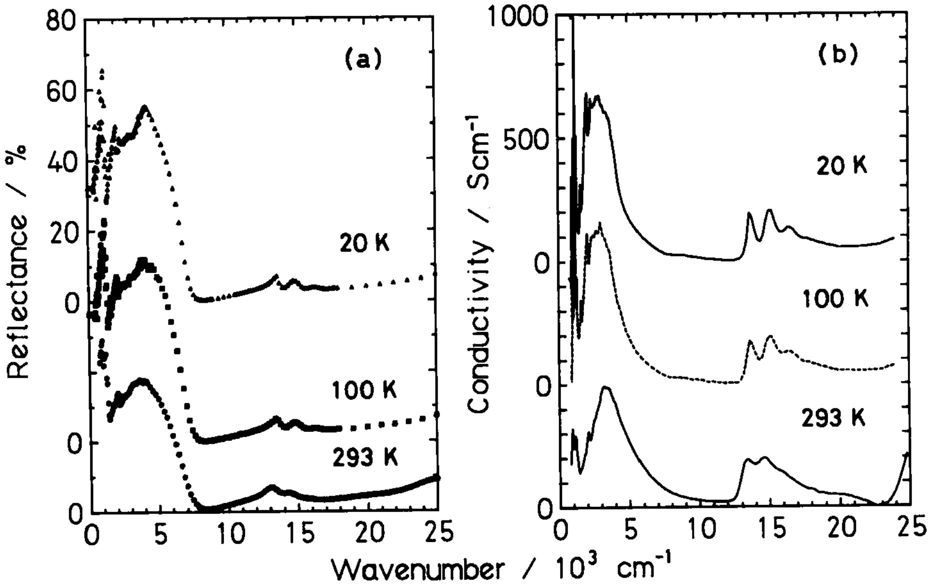

FIGURE 3 Temperature dependence of (a) the reflectance and (b) conductivity spectra of $(DMe\text{-}DCNQI)_2Na$.

$(\mathrm{DMe\text{-}DCNQI})_2\mathrm{Cu}$

The room-temperature conductivity of $(\mathrm{DMe\text{-}DCNQI})_2\mathrm{Cu}$ is *ca.* 1000 Scm^{-1}, and this material keeps the metallic property down to 1.3 K. The reflectance spectrum of $(\mathrm{DMe\text{-}DCNQI})_2\mathrm{Cu}$ is entirely different throughout the measured spectral range from those of $(\mathrm{DMe\text{-}DCNQI})_2\mathrm{Ag}$ and $(\mathrm{DMe\text{-}DCNQI})_2\mathrm{Na}$ as shown in Fig. 4. In spite of the high conductivity, the spectral shapes are far from a typical Drude-type dispersion of the reflectance spectrum. This result suggests the presence of an additional electronic transition near the plasma frequency of the intra-band transition. This additional absorption band becomes clearer at *ca.* 5000 cm^{-1} on lowering the temperature as shown in 20 K spectra of Figs. 4(a) and 4(b). The increase of the reflectivity at low temperature undoubtedly leads to the assignment that the intra-band transition by conduction electrons contributes to the dispersion of the low-wavenumber region. The strong dispersion in the *//a* spectrum is the most substantial difference from $(\mathrm{DMe\text{-}DCNQI})_2\mathrm{Ag}$ and $(\mathrm{DMe\text{-}DCNQI})_2\mathrm{Na}$. Since this dispersion becomes more remarkable at low temperature, it is assigned to the intra-band transition along the interstack direction. This result means that the conduction band of this material is formed not only in the stacking direction but also in the interstack direction. Since the crystal belongs to the tetragonal system, this material forms an anisotropic three dimensional conduction band. To obtain the degree of anisotropy, we analyzed the reflectivity curve, simulating the reflectance spectrum by the following Drude-Lorentz model,

$$\varepsilon(\omega) = \varepsilon_c - \frac{\omega_p^2}{\omega(\omega + i\gamma)} - \sum_j \frac{\Omega_{pj}^2}{(\omega^2 - \omega_j^2) + i\Gamma_j\omega}$$

where ε_c stands for the dielectric constant contributed from the high-wavenumber excitation; ω_p and γ the plasma frequency and relaxation rate of conduction electrons; Ω_{pj}, Ω_j, and Γ_j the plasma frequency, resonance frequency, and damping parameter of a j-th Lorentz oscillator. The most reliable Drude parameters are obtainable in the analysis of the 20 K spectra, these parameters being compiled in TABLE II . These parameters almost perfectly reproduce the experimental curve.[19] However, it is difficult to uniquely determine these parameters, because ω_p and Ω_{pl} are interacting on each other. Considering this situation the ambiguity of the Drude parameters is within 30 %.

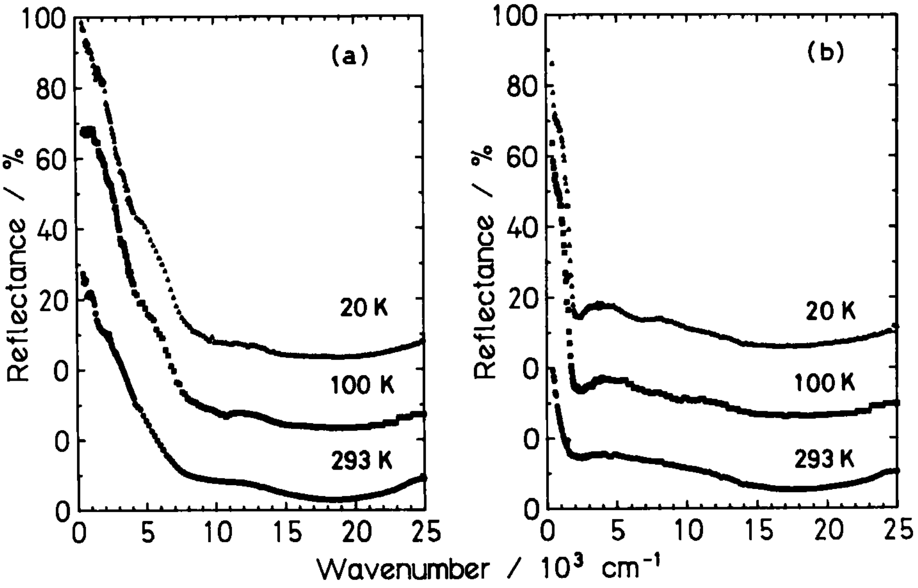

FIGURE 4 Temperature dependence of the reflectance spectra of $(\mathrm{DMe\text{-}DCNQI})_2\mathrm{Cu}$ polarized (a) parallel (//*c*) and (b) perpendicular (//*a*) to the stacking direction.

TABLE II Parameters of Drude-Lorentz fit of $(\mathrm{DMe\text{-}DCNQI})_2\mathrm{Cu}$ at 20 K.

	ε_c	ω_p	γ	Ω_j	Ω_{pj}	Γ_j
		(10^3 cm^{-1})		(10^3 cm^{-1})		
//*c*	3.07	10.7	0.42	4.3	11.9	7.1
				12.9	9.3	7.5
//*a*	3.46	5.0	0.67	4.4	5.6	3.3
				10.2	13.6	9.7

The optical mass is calculated to be $1.7m_e$ for the stacking (*c*-axis) direction and $7.9m_e$ for the interstack (*a*-axis) direction. The tight binding band calculated by extended Huckel method predicts a pseudo-one-dimensional band structure.[16] As compared with other organic conductors such as $(TMTSF)_2PF_6$[24] and β-$(BEDT-TTF)_2I_3$[25], this anisotropic ratio is much smaller than the former ($1.2m_e$ and $46m_e$ at 30 K) which has a warped open Fermi surface and rather comparable with the latter ($2.0m_e$ and $7.0m_e$ at 26 K) which has a two-dimensional closed Fermi surface. This anisotropic ratio of $(DMe\text{-}DCNQI)_2Cu$ insists upon the strong three-dimensionality, presenting a striking contrast with the one-dimensional electronic structure of $(DMe\text{-}DCNQI)_2Ag$. This outstanding contrast is attributed to the accidental proximity of the energy levels of the copper $3d$-orbitals and DMe-DCNQI's LUMO, since the Cu and Ag-salts are isostructural to each other. In other words, the admixture of the $3d$-orbitals of copper cation with the DMe-DCNQI's LUMO is responsible for the strong interstack interaction.[2a,6] Indeed, XPS and X-ray diffuse scattering show the mixed valent state of copper cation ($Cu^{1.3+}$), that is, a back charge transfer occurs from copper to DMe-DCNQI through this admixture.

The conductivity spectrum at each temperature is shown in Fig. 5. The spectrum is unusually broad for an organic material (see Fig. 2 as to a typical spectrum of an organic crystal), indicating that several absorption bands overlap each other in this spectral region. The clue to interpret the broad spectrum might be obtained by comparing with the spectrum of $(DMe\text{-}DCNQI)_2Na$, in which metal orbitals are not mixed with the DMe-DCNQI's molecular orbital (MO). The conductivity spectrum at 20 K shown in Fig. 5 does not involve the sharp vibrational structure characteristic of the lowest intramolecular transition of $DMe\text{-}DCNQI^-$. This observation leads to the view that an admixture with the copper $3d$-orbitals considerably disturbs the original one-dimensional band structure and the electronic transitions of Cu-salt involves this copper $3d$-orbitals. This interpretation is supported by the spectral change synchronized with the structural phase transition of $(MeBre\text{-}DCNQI)_2Cu$ which will be discussed in the next section. The copper cation stands in the D_{2d} distorted tetrahedral crystal field, so that Cu^{1+} has fully occupied $3d$-orbitals(d^{10}) split into three levels: topmost $b_2(d_{xy})$, higher $1e(d_{xz}$ and $d_{yz})$, and lower $2e(d_{z2}$ and $d_{x2+y2})$.[2a,16]

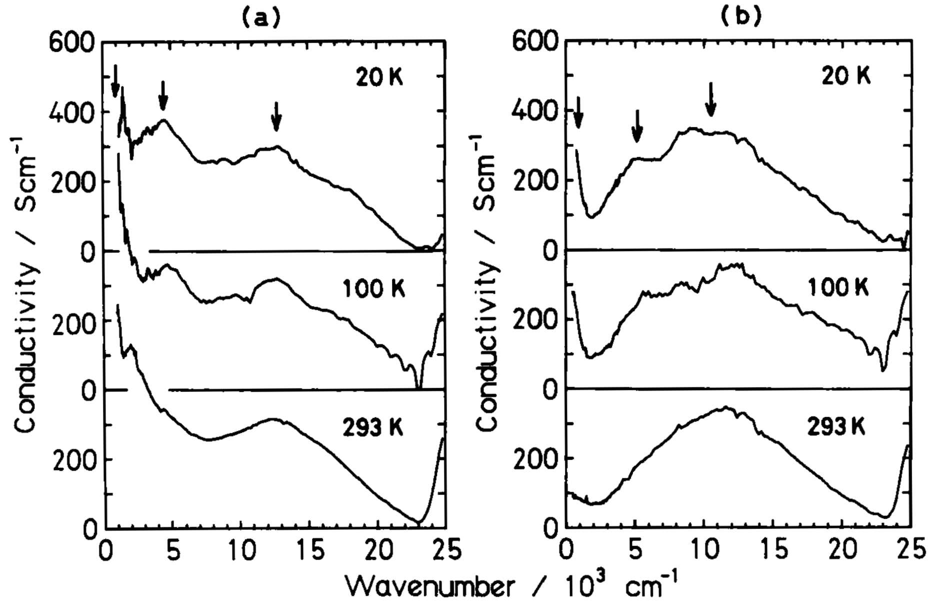

FIGURE 5 Temperature dependence of the conductivity spectra of $(DMe\text{-}DCNQI)_2Cu$ polarized (a) parallel (//*c*) and (b) perpendicular (//*a*) to the stacking direction.

Mori *et al.* estimated the energy separations of tnese energy levels from the model calculation[3]: 9000 cm^{-1} between b2 and 1e, and 19000 cm^{-1} between b2 and 2e. The 20 K spectra in both polarizations show three absorption bands shown by arrows: the intra-band transition at 0 cm^{-1}, the absorption band at 4000-5000 cm^{-1}, and the absorption band at 10000-12000 cm^{-1}. Combining the model calculation with the optical spectra, we suggest a hypothesis that the b2-orbital is mainly hybridized with DMe-DCNQI's LUMO, the 2e-orbital is mixed with the HOMO of DMe-DCNQI, and 1e-orbital is located beween them. On the basis of this model, the lowest transition is assigned to the intra-band transition in the conduction band made by copper b2 and DMe-DCNQI's LUMO, the second one at *ca.* 4000 cm^{-1} to the charge-transfer transition from copper 1e to the conduction band, and the third one at *ca.* 12000 cm^{-1} to the interband transition from the valence band formed by the mixed orbitals between HOMO and copper 2e. In the Na-salt the one-dimensional conduction band developing along the stacking direction is four times degenerate, since four DMe-DCNQI molecules are involved in the primitive unit cell.[16] On the other hand, in the Cu-salt the admixture removes the degeneracy of these conduction bands as well as it enhances the band dispersion along the interstack direction. This situation also makes the electronic structures of this material more complicated and may bring about the broad spectrum.

(MeBr-DCNQI)$_2$Cu

(MeBr-DCNQI)$_2$Cu is metallic down to 160 K and undergoes a metal-insulator phase transition. The reflectance spectra of (MeBr-DCNQI)$_2$Cu in the metallic phase (293 K and 200 K) are almost the same as those of (DMe-DCNQI)$_2$Cu as shown in Fig. 6. The metal-insulator phase transition brings about a spectacular change in the spectrum.

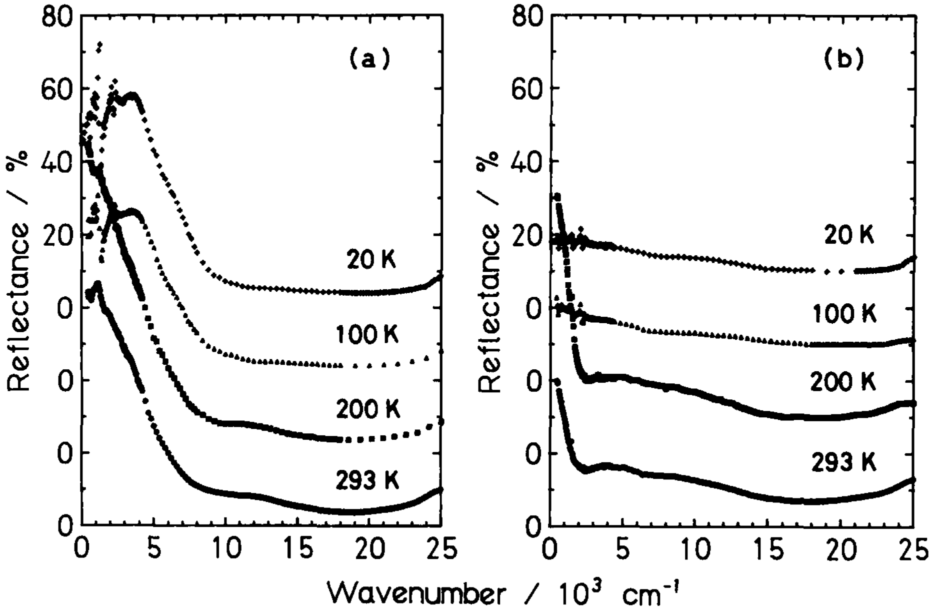

FIGURE 6 Temperature dependence of the reflectance spectra of (MeBr-DCNQI)$_2$Cu polarized (a) parallel (//*c*) and (b) perpendicular (//*a*) to the stacking direction.

TABLE III Parameters of Drude-Lorentz fit of (MeBr-DCNQI)$_2$Cu at 200 K.

	ε_c	ω_p	γ	Ω_j	Ω_{pj}	Γ_j
		(10^3 cm^{-1})			(10^3 cm^{-1})	
//c	3.15	10.3	0.88	3.7	12.1	8.5
				13.0	10.8	9.4
//a	4.62	5.6	1.17	6.3	10.8	9.1
				11.7	13.9	9.4

This change can be taken as direct evidence that the dispersions in the infrared region, the shape of which is not Drude-like, is ascribed to the absorption by conduction electrons. The results of Drude-Lorentz fit of 200 K spectra are compiled in TABLE III . The optical masses are calculated to be 1.9m_e for the stacking direction (//c) and 6.4m_e for the interstack direction (//a). The optical anisotropy is the same as (DMe-DCNQI)$_2$Cu taking account of the ambiguity of the Drude parameters. We therefore cannot find any difference in the degree of anisotropy between this salt and (DMe-DCNQI)$_2$Cu above the phase-transition temperature.

The temperature-dependent conductivity spectra are shown in Fig. 7. The notable change of the spectrum around the metal-insulator phase transition is first the appearance of the optical gap in the //c spectrum and second the disappearance of the intra-band transition in the //a spectrum. The absorption band at *ca.* 2500 cm^{-1} resembles the 20 K spectrum of (DMe-DCNQI)$_2$Na shown in Fig. 3(b), so that it is ascribed to the inter-band transition across the band gap opened by the phase transition. This inter-band transition is strongly polarized to the stacking axis. The absence of the corresponding transition along the interstack direction means the vanishing of the charge-transfer interaction between the copper cation and DMe-DCNQI near the band gap. Therefore the electronic structure of (MeBr-DCNQI)$_2$Cu becomes one-dimensional along the stack in the insulating phase. This dimensional crossover is unusual, considering the small structural change accompanying the phase transition.[2a,14,16] Consequently we are obliged to think that the interaction between the topmost 3d-orbital (d_{xy}) and DCNQI's LUMO, so that the interaction near the Fermi level, is sensitive to the

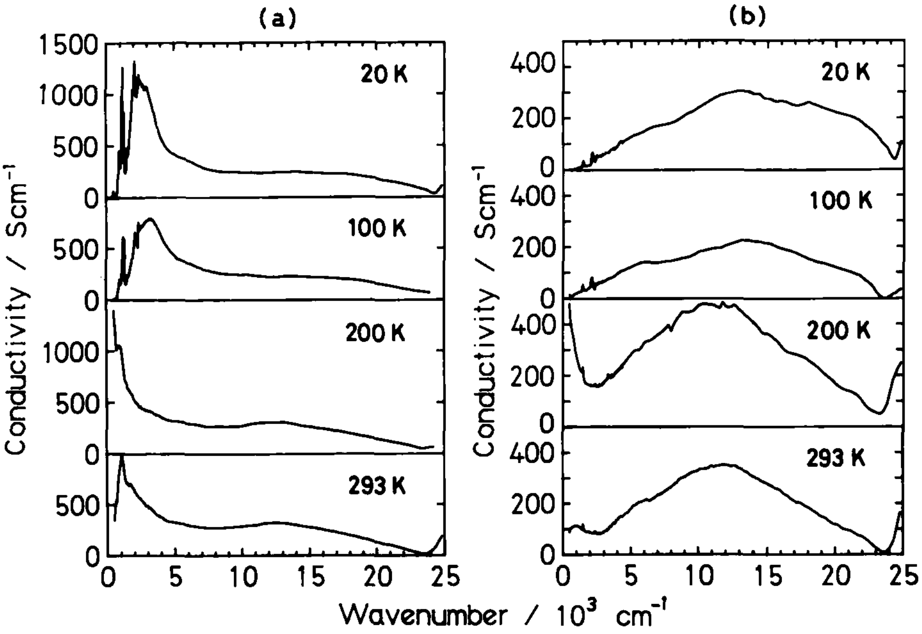

FIGURE 7 Temperature dependence of the conductivity spectra of (MeBr-DCNQI)$_2$Cu polarized (a) parallel (//*c*) and (b) perpendicular (//*a*) to the stacking direction.

configuration around the copper cation.

Another two absorption bands, which we have assigned to the charge-transfer transition from copper 1e to DCNQI's LUMO and to the inter-band transition in the preceding section, weaken and shift to blue below the metal-insulator phase-transition temperature. Comparison with the 20 K spectrum of (DMe-DCNQI)$_2$Cu manifests this spectral change more clearly. The structural change around the copper cation concomitant with the phase transition is first the shortening of the Cu···N≡C distance by 0.021 Å and second the enhancement of the D_{2d} distortion from a tetrahedral symmetry.[16] This geometrical change increases the energy separations between b_2 and 1e as well as between b_2 and 2e, so that the blue shift is consistent with this structural change. The decrease of the transition probability appears to be contradictory to the shortening of the coordinate bond. The D_{2d} distortion of cyano groups around the copper ion may possibly decrease the degree of admixture between 3*d*-orbital and *pπ* -orbital of DCNQI.

In this connection we will briefly discuss the preliminary results on the polarized reflectance spectrum of $(MeBr-DCNQI)_2Cu$ under high pressure up to 21 kbar in the spectral range from 4200 cm^{-1} to 25000 cm^{-1}. Upon applying pressure the reflectivity around 5000 cm^{-1} significantly increases, whereas the shoulder in the reflectance spectrum around 12000 cm^{-1} shows slight decreases rather than increase. This result suggests the increase of the intrastack interaction and the decrease of the interstack interaction. It is known that high pressure induces a metal-insulator transition.[2] If the analogous geometrical change occurs at high pressure, this result also indicates that the hybridization between copper 3*d*-orbital and DCNQI's *pπ* -orbital is sensitive to the geometrical environment of the copper ion.

In conclusion, all these results lead to the view that the three-dimensional conduction band of Cu-salts is barely sustained not only by the accidental proximity of the energy levels of copper 3*d*-orbitals to the DCNQI's LUMO but also by the specific tetrahedral coordination of cyano groups around the copper ion. The interstack interaction mediated by copper ion is easily broken by a small geometrical distortion.

REFERENCES

1. A. Aumuller, P. Erk, G. Klebe, S. Hunig, J. U. von Shutz, and H.-P. Werner, Angew. Chem. Int. Ed. Engl., 25, 740 (1986).
2. (a)A. Kobayashi, R. Kato, H. Kobayashi, T. Mori, and H. Inokuchi, Solid State Commun., 64, 45 (1987); (b)T. Mori, K. Imaeda, R. Kato, A. Kobayashi, H. Kobayashi, and H. Inokuchi, J. Phys. Soc. Jpn., 56, 3429 (1987).
3. T. Mori, H. Inokuchi, A. Kobayashi, R. Kato, and H. Kobayashi, Phys. Rev. B, 38, 5913 (1988).
4. S. Tomic, D. Jerome, A. Aumuller, P. Erk, S. Hunig, and J. U. von Shutz, J. Phys. C, 21, L203, (1988).
5. R. T. Henriques, W. Kang, S. Tomic and D. Jerome, P. Erk, S. Hunig, and J. U. von Shutz, Solid State Commun., 68, 909 (1988).
6. J. U. von Shutz, M, Bair, H. J. Bross, U. Langohr, H.-P. Werner, H. C. Wolf, D. Schmeisser, K. Graf, W. Gopel, P. Erk, H. Meixner, and S. Hunig, Synthetic Metals, 27, B249 (1988).
7. R. T. Henriques, S. Tomic, W. Kang, D. Jerome, F. Brisset, and

P. Batail, P. Erk, S. Hunig, and J. U. von Shutz, Synthetic Metals, 27, B333 (1988).

8. S. Tomic, D. Jerome, A. Aumuller, P. Erk, S. Hunig, and J. U. von Shutz, Synthetic Metals, 27, B281 (1988).
9. D. Kongeter, F. Hentsch, H. Seidel, M. Mehring, J. U. von Shutz, H. C. Wolf, P. Erk, and S. Hunig, Solid State Commun., 65, 453 (1988).
10. H.-P. Werner, J. U. von Shutz, H. C. Wolf, R. Kremer, M. Gehrke, A. Aumuller, P. Erk, and S. Hunig, Solid State Commun., 65, 809 (1988).
11. T. Mori, S. Bandow, H. Inokuchi, A. Kobayashi, R. Kato, and H. Kobayashi, Solid State Commun., 67, 565 (1988).
12. T. Mori, H. Inokuchi, A. Kobayashi, R. Kato, and H. Kobayashi, Synthetic Metals, 27, B237 (1988).
13. R. Kato, H. Kobayashi, A. Kobayashi, T. Mori, and H. Inokuchi, Chem. Lett., 1579 (1987).
14. H. Kobayashi, R. Kato, A. Kobayashi, T. Mori, and H. Inokuchi, Solid State Commun., 65, 1351 (1988).

15. R. Moret, Synthetic Metals, 27, B301 (1988).
16. R. Kato, H. Kobayashi, and A. Kobayashi, J. Am. Chem. Soc., 111, 5224 (1989).
17. K. Yakushi, G. Ojima, A. Ugawa, and H. Kuroda, Chem. Lett., 95 (1988).
18. D. Schmeisser, K. Graf, W. Gopel, J. U. von Shutz, P. Erk, and S. Hunig, Chem. Phys. Lett., 148, 423 (1988).
19. H. Tajima, G. Ojima, T. Ida, H. Kuroda, A. Kobayashi, R. Kato, H. Kobayashi, A. Ugawa, and K. Yakushi, Proc. Phys. Chem. Org. Superconductors, in press (1989).
20. A. Aumuller and S. Hunig, Liebigs Ann. Chem., 1989, 142.
21. A. Aumuller and S. Hunig, Liebigs Ann. Chem., 1989, 165.
22. Y. Iida, Bull. Chem. Soc. Jpn., 42, 71 (1969).
23. M. J. Rice, V. M. Yartsev, and C. S. Jacobsen, Phys. Rev. B, 21, 3437 (1980).
24. C. S. Jacobsen, D. B. Tanner, and K. Bechgaard, Phys. Rev. B, 28, 7019 (1983).
25. H. Tajima, K. Yakushi, H. Kuroda, and G. Saito, Solid State Commun., 57, 911 (1986).