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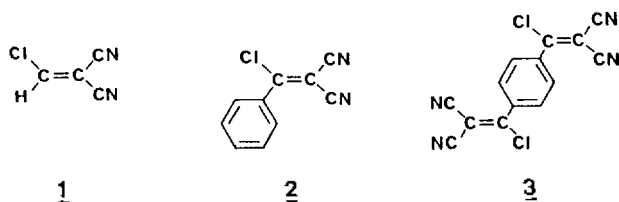
Synthesis of Enaryloxynitriles (Aryl dicyanovinyl ether) by Vinylic Nucleophilic Substitution Reaction

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A close analogy of chemical reactivity between the dicyanomethylidene group ($=C(CN)_2$) and the carbonyl oxygen atom was pointed out by Wallenfels.¹ The two units have similar inductive and resonance effects, and many well-known reactions with carbonyl groups have been shown to have close parallels with the dicyanomethylidene group. If this analogy holds, then the dicyanovinyl chloride in this study can be linked to carboxylic acid chloride.²



1-Chloro-1-phenyl-2,2-dicyanoethene (**2**) is in many ways similar to 1-chloro-2,2-dicyanoethene (**1**).^{3,4} One of the most notable reaction of **1** is its condensation with alcohol to give enalkoxynitriles, whereas **2** shows no reactivity toward alcohol.⁵ The nucleophile, which possesses a pK_a value of 10, can show an appreciable reactivity to the dicyanovinyl compound **2**.

Nucleophilic vinylic substitution reactions occur by various mechanistic pathways. In the most investigated addition-elimination route (designated by S_NV by Kosower),⁶ the primary nucleophilic attack on the double bond is followed by a expulsion of the leaving group.

The enamionitriles derived from aliphatic or aromatic amines were readily prepared and the related reaction was reported to be applied to the synthesis of poly(enamionitriles).^{7,8} However, phenoxide anions have been rarely employed as nucleophiles for the dicyanovinyl chloride² and β -chloro- α -cyano cynamate.⁹ The studies of reactivities of phenoxide anions to dicyanovinyl chloride can provide a possibility of the preparation of model compounds resembling repeating unit of poly(enaryloxynitriles) and a feasibility of polymer formation.

We now report the synthesis of enaryloxynitriles by the reaction of **2** and *p*-bis(1-chloro-2,2-dicyanovinyl)benzene (**3**) with various phenoxide anions in the presence of phase transfer catalyst and their chemical properties will be also investigated.

Experimental

1-Chloro-1-phenyl-2,2-dicyanoethene (**2**) and *p*-bis(1-chloro-2,2-dicyanovinyl)benzene (**3**) were prepared by the method previously reported by Moore and Coworkers.⁶ *p*-Cresol, *p*-methoxyphenol, 3-(4-hydroxyphenyl)-1-propanol, *p*-hydroxybenzaldehyde, ethyl 4-hydroxybenzoate, β -naphthol, catechol, resorcinol and hydroquinone were purchased from Aldrich Chemical Co. and used without further purification. The sodium salts were prepared by the reaction of the corresponding phenol derivatives with NaOH for 2h before use. 1,2-Dichloroethane was purified by the conventional method. The IR spectra were obtained with a Midac FT-IR spectrophotometer and ¹H and ¹³C NMR spectra were recorded on either a Bruker Am-300 or Varian EM-360A spectrometer. Elemental analysis data were obtained with a Yanaco MT-3, CHN-Analyzer.

General Procedure of preparation of enaryloxynitriles

Method A. A mixture of **2** (1.89 g, 10 mmol) dissolved in 1,2-dichloroethane (20 ml), sodium phenoxide (1.16 g, 10 mmol) and *tetra-n*-butylammonium chloride (5 mol%) in water (20 ml) was stirred vigorously for 3 min by mechanical stirrer. After the reaction mixture was separated and the organic layer was evaporated, the white solid was filtered and washed with distilled water several times. Crystallization from 1,2-dichloroethane gave enaryloxynitriles as needles (2.1 g, 85.0%). Other enaryloxynitriles **4b-4d**, **5a-5c** and **6** were prepared by the similar procedures.

Method B. A solution of **2** (1.89 g, 10 mmol) in 20 ml of 1,2-dichloroethane and sodium phenoxide (1.16 g, 10 mmol) and 5 mol% of *tetra-n*-butylammonium chloride in 20 ml of water was placed in a round bottomed flask. The reaction mixture was stirred vigorously with magnetic stirrer for 8h. After the reaction was completed, the organic layer was evaporated. The solid product was washed with distilled water and recrystallized from 1,2-dichloroethane to give 2.21 g (89.4%) of compound **4a**.

1-Phenoxy-1-phenyl-2,2-dicyanoethene (4a). Yield 85.0%, mp. 139.5 °C; IR (KBr) 3020 (C-H), 2219 (C≡N), 1585 (C=C), 1250-1100 (C-O) cm^{-1} ; ¹H NMR (CDCl₃) δ 7.6 (m, 5H, -Ph), 7.2 (m, 5H, -O-Ph); ¹³C NMR (CDCl₃) δ 71.2 (=C(CN)₂), 111.3, 113.1 (-CN), 122.5, 128.0, 129.6, 130.1, 132.8, 151.5 (aromatic C's), 180.7 (=C-O).

1-(*p*-Methylphenoxy)-1-phenyl-2,2-dicyanoethene (4b). Yield 96% (recrystallized from 2-propanol), mp. 131 °C; IR (KBr) 3022 (C-H), 2221 (C≡N), 1580 (C=C), 1250-1120 (C-O) cm^{-1} ; ¹H NMR (CD₃CN) δ 7.5 (m, 5H, -Ph), 7.1 (s, 4H, -Ph-CH₃), 2.3 (s, 3H, CH₃-Ph).

1-(*p*-Methoxyphenoxy)-1-phenyl-2,2-dicyanoethene (4c). Yield 95% (recrystallized from carbon tetrachloride), mp. 111 °C; IR (KBr) 3018, 2980 (C-H), 2223 (C≡N), 1580 (C=C), 1300-1100 (C-O) cm^{-1} ; ¹H NMR (CDCl₃) δ 7.5 (m, 5H, -Ph) 7.0 (s, 4H, CH₃O-Ph), 3.6 (s, 3H, CH₃-O-Ph-O).

1-(*p*-Ethoxycarbonylphenoxy)-1-phenyl-2,2-dicyanoethene (4d). Yield 72% (recrystallized from carbon tetrachloride), mp. 148 °C; IR (KBr) 3022, 2830 (C-H), 2218 (C≡N), 1740 (C=O), 1582 (C=C), 1300-1120 (C-O) cm⁻¹; ¹H NMR (CDCl₃+DMSO-d₆) δ 7.7 (d, 4H, *J*=5.4, -O-Ph-CO-), 7.1 (d, 2H, *J*=5.4, -O-Ph-CO-), 7.5 (s, 5H, -Ph), 3.7 (q, 2H, -OCH₂CH₃), 1.2 (t, 3H, -OCH₂CH₃).

***p*-Bis(1-phenoxy-2,2-dicyanovinyl)benzene (5a).** Yield 86% (recrystallized from 1,2-dichloroethane), mp. 238 °C; IR (KBr) 3025 (C-H), 2220 (C≡N), 1580 (C=C), 1300-1120 (C-O) cm⁻¹; ¹H NMR (CDCl₃+DMSO-d₆) δ 7.7 (s, 4H, -Ph-), 7.0 (m, 10H, 2 Ph-O-).

***p*-Bis[1-(4-hydroxypropylphenoxy)-2,2-dicyanovinyl]benzene (5b).** Yield 90% (recrystallized from 2-propanol), mp. 214 °C; IR (KBr) 3510 (O-H), 3020, 2890 (C-H), 2220 (C≡N), 1580 (C=C), 1300-1120 (C-O) cm⁻¹; ¹H NMR (DMSO-d₆) δ 7.4 (s, 4H, -Ph-), 6.8 (s, 8H, 2 -O-Ph-), 4.0 (s, 2H, 2-OH), 3.2 (t, 4H, 2 -Ph-CH₂CH₂CH₂O-), 2.3 (t, 4H, 2 -Ph-CH₂CH₂CH₂-), 1.7 (m, 4H, 2 -Ph-CH₂CH₂CH₂-).

***p*-Bis[1-(4-formylphenoxy)-2,2-dicyanovinyl]benzene (5c).** Yield 39% (recrystallized from acetonitrile), mp. 285-286 °C; IR (KBr) 3030 (C-H), 2230 (C≡N), 1760 (C=O), 1585 (C=C), 1300-1120 (C-O) cm⁻¹; ¹H NMR (DMSO-d₆) δ 9.1 (s, 2H, 2 formyl), 7.2 (s, 4H, -Ph-), 7.1 (d, 4H, *J*=7.2, 2 -Ph-CHO), 6.7 (d, 4H, *J*=7.2, 2 -Ph-CHO).

***p*-Bis[1-(β-naphthoxy)-2,2-dicyanovinyl]benzene (6).** Yield 84% (recrystallized from 2-propanol), mp. 302-304 °C; IR (KBr) 3040, 2220, 1595, 1327, 1165 cm⁻¹; ¹H NMR (CDCl₃) δ 7.3-7.7 (s, 4H, aromatic H's in 2), 6.8-7.2 (m, 14H, naphthyl H's); ¹³C NMR (CDCl₃) δ 71.0 (=C(CN)₂), 111.5, 112.9 (-CN), 126.0, 127.4, 128.7, 129.6, 133.1, 151.2 (aromatic C's), 181.0 (=C-O-); Anal. Calcd: C, 79.4; H, 3.5; N, 10.9. Found: C, 79.1; H, 3.6; N, 10.7.

Preparation of *o*-Bis(1-phenyl-2,2-dicyanovinyl)benzene (7a). A solution of 1 g (5.3 mmol) of 2 in 20 ml of 1,2-dichloroethane was added, in one portion, to the solution of 0.29 g (2.7 mmol) of catechol dissolved in 20 ml of sodium hydroxide (0.11 g, 2.8 mmol) solution. The reaction mixture was stirred vigorously for 3 min by mechanical stirrer. After the organic solvent was separated, the greenish solid was obtained after evaporation. The solid product was washed with distilled water and recrystallized from 2-propanol.

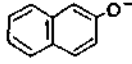



Similar procedures were applied to the synthesis of compound 7b, and 7c.

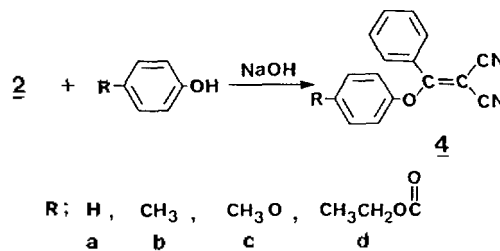
***o*-Bis(1-phenyl-2,2-dicyanovinyl)benzene (7a).** Yield 90%, mp. 194.5 °C; IR (KBr) 3050, 2220, 1570, 1500, 1330 1180 cm⁻¹; ¹H NMR (CDCl₃) δ 7.0-8.0 (m, 10H, aromatic H's in 2), 6.2-7.0 (m, 4H, aromatic H's in catechol).

***m*-Bis(1-phenyl-2,2-dicyanovinyl)benzene (7b).** Yield 86% (recrystallized from ethanol), mp. 177 °C; IR (KBr) 3055 (C-H), 2245 (C≡N), 1585 (C=C), 1380, 1220-1150 (C-O) cm⁻¹; ¹H NMR (CDCl₃) δ 7.2-7.6 (m, 10H, aromatic H's in 2), 7.1-6.8 (m, 4H, aromatic H's in resorcinol).

***p*-Bis(1-phenyl-2,2-dicyanovinyl)benzene (7c).** Yield 90% (recrystallized from 2-propanol), mp. 282 °C; IR (KBr) 3050, 2250, 1590, 1500, 1330 cm⁻¹; ¹H NMR (CDCl₃) δ 7.3-7.7 (m, 10H, aromatic H's in 2), 7.0-6.8 (m, 4H, aromatic H's in hydroquinone); ¹³C NMR (CDCl₃) δ 71.9 (=C(CN)₂), 110.5, 113.5 (-CN), 125.5, 128.0, 129.2, 130.0, 132.8, 151.5 (aromatic C's), 180 (=C-O-); Anal. Calcd: C, 77.2; H, 1.0; N,

Table 1. Results of Enaryloxynitriles prepared from Various Phenoxide anions with 2 and 3 at 25 °C for 3 min

Compound	Dicynovinyl Compound	Nucleophile	<i>pK_a</i> value	Yield (%)	mp (°C)
4a	2	PhO ⁻	10.00	85	178
4b	2	<i>p</i> -Me-PhO ⁻	10.27	96	131
4c	2	<i>p</i> -MeO-PhO ⁻	10.20	95	111
4d	2	<i>p</i> -EtOCO-PhO ⁻	9.76	72	148
5a	3	PhO ⁻	10.0	86	238
5b	3	HO(CH ₂) ₃ PhO ⁻	10.27	90	214
5c	3	<i>p</i> -OHC-PhO ⁻	7.62	39	235
6	3		9.57	84	302
7a	2		9.44 12.98	90	195
7b	2		9.44 12.32	87	177
7c	2		9.91 12.04	89	282



Scheme 1.

13.9, Found: C, 76.8; H, 1.0; N, 14.0.

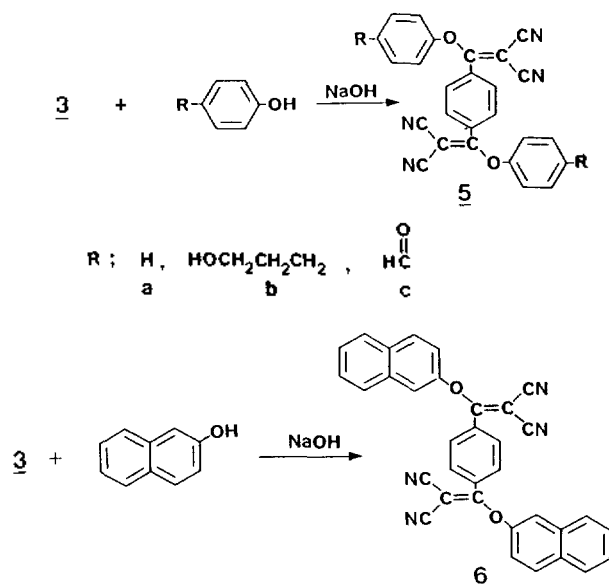
Results and Discussion

As representative compounds possessing dicyanovinyl group, the enaryloxynitriles were prepared by the reaction of 2 and 3 with the corresponding phenoxide anions in the presence of phase transfer catalyst. The reaction of anionic phenoxide with 1-chloro-1-phenyl-2,2-dicyanoethene (2) was carried out initially by interfacial technique using a high speed mechanical stirrer for a few minutes. Phenoxide anions showed a good reactivity toward 2 to give enaryloxynitriles as a stepwise condensation product. After several minutes, good yields of enaryloxynitriles were obtained.

The results and conditions of preparation of various enaryloxynitriles are summarized in Table 1.

Another synthetic method is a phase transfer reaction in the presence of a catalytic amount of quaternary ammonium salt. Two reactants were reacted rapidly and under mild conditions to give high yields of the enaryloxynitriles.

In the ¹H NMR spectrum, the phenyl protons in 2 appear as a multiplet peak at 7.5 ppm, whereas those of phenol



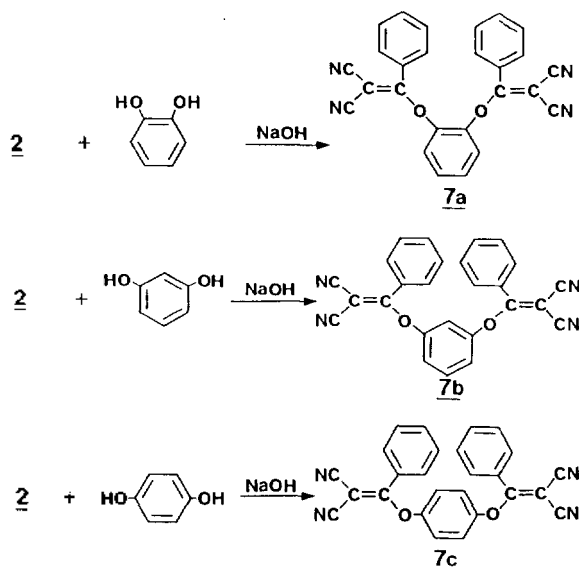
Scheme 2.

are present as a multiplet at 7.2 ppm. In ^{13}C NMR spectrum, a peak at 180.5 ppm attributable to $=\text{C}-\text{O}-$ indicates that the enaryloxide linkage was generated. The other phenol derivatives such as *p*-cresol, *p*-methoxyphenol and ethyl 4-hydroxybenzoate were chosen and reacted with **2** as indicated in Scheme 1. The reactivities of phenoxide anions were different from one another depending on the pK_a values of the corresponding phenols. *p*-Cresol, *p*-methoxyphenol and ethyl 4-hydroxybenzoate have the pK_a value of 10.23, 10.20 and 9.27, respectively.¹⁰ In case of *p*-cresol and *p*-methoxyphenol, the reaction proceeded rapidly to give the corresponding enaryloxynitriles in good yield. On the other hand, ethyl 4-hydroxybenzoate proceeded at a slower rate. Phenoxide anions derived from *p*-cresol and *p*-methoxyphenol were highly effective for nucleophilic vinylic substitution because of the enhancement of electron donation by a substituent at *para*-position. The yields are greater than 95%. However other phenoxide anions **4a** and **4d** provided a relatively low yield, 85% and 72%, respectively.

We also investigated the nucleophilic vinylic substitution by reacting **3** with nucleophiles ($^-\text{O-Ph}$, $^-\text{O-Ph-CH}_2\text{CH}_2\text{CH}_2\text{OH}$ and $^-\text{O-Ph-COH}$) at room temperature as described in Scheme 2. These reaction provided total yield up to 86% with $^-\text{O-Ph}$ and 90% with $^-\text{O-Ph-CH}_2\text{CH}_2\text{CH}_2\text{OH}$, showing high reactivity to **3**. In case of 4-formylphenoxide anion, somewhat lower yield (39%) is probably attributed to the low pK_a value (7.26) of *p*-hydroxybenzaldehyde. Higher temperatures and longer reaction time were needed to raise the conversion to enaryloxynitriles. The actual yield was observed in 75% for aldehyde derivative at a temperature of 80 °C during a 24h period.

Naphthols (pK_a of 9.57) showed lower pK_a value than phenol itself. And sodium naphthoxide is a weaker and a bulkier base than PhO^- . Thus it was expected to show slower reaction. Naphthalene derivative was obtained in 84% yield.

In the formation of dienaryloxynitriles using aromatic diol and **2**, the corresponding enaryloxynitriles (**7a-7c**) were obtained in relatively high yields as shown in Scheme 3. The 1st anion possessing higher pK_a values due to the electron



Scheme 3.

donation of a second anion reacts with **2** rapidly. But the resulting 2nd anion, which have the pK_a values of 9.5, was less reactive because of former substitution of dicyanovinyl group.

Based on these observations, it is clear that products **4-7** are enaryloxynitriles derivatives, which are formed through the vinylogous nucleophilic substitution reaction of dicyanovinyl compound.

The enaryloxynitriles were quite stable at elevated temperature in air. When a sample of enaryloxynitriles **4a** was heated to 360 °C to monitor the chemical change, it displayed a gradual change in its IR spectra and the insoluble brownish polymeric powder was formed. The band intensity at 2219 cm^{-1} corresponding to nitrile group was apparently reduced, while the absorption band at around 1580 cm^{-1} was broadened. It may be due to the chemical change of dicyanovinyl group by intermolecular addition reaction.

Further works on the details of the chemical process for the thermal curing reaction are now in progress.

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Electrical, Magnetic and Spectroscopic Properties of Tetrathiafulvalene Charge Transfer Compound with Copper(II) hexafluoroacetylacetonate, $(\text{TTF})_2\text{Cu}(\text{hfac})_2 \cdot 1.5\text{C}_2\text{H}_5\text{OH}$

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Tetrathiafulvalene (TTF) has been used as an excellent electron donor to form electrically conductive charge transfer compounds.¹ TTF salt with the square-planar bis(oxalato) cuprate anion was reported to be a dimer with weak interaction between TTF cations.² The compound exhibited semiconductor behavior with the electrical conductivity in the order of $\sim 10^{-4} \text{ Scm}^{-1}$ as compacted samples at room temperature. However, the increased interaction of TTF cations could enhance the conductivity in the stacking direction. For example, TTF-copper halides compounds having a significant interaction between partially ionized TTF radical cations showed the conductivity of $\sim 10^0 \text{ Scm}^{-1}$ at room temperature.³

Recently, we reported TTF charge transfer compound with metal halides (metal=Fe, Ru, Rh an Ir). It was concluded that the partially ionized TTF salts exhibited greater electrical conductivity than the simple salts.⁴ Therefore, it may be interesting to study the electrical properties of TTF salts in relation to the stacking of partially ionized TTF moieties. This study reports the preparation of TTF charge transfer compound with planar bis(hexafluoroacetylacetonate) cuprate anion and its electrical properties. The stacking of the TTF molecules in the compound as well as the interaction between TTF moieties is discussed based on the magnetic susceptibility measurement, and EPR, electronic, vibrational and X-ray photoelectron spectra. The electrochemical properties are also investigated in this report.

Experimental

Synthesis. 1 mmol of copper(II) (hexafluoroacetylacetonate) was dissolved in a mixture of absolute ethanol (10 ml) and triethylorthoformate (2 ml). A solution of TTF (3 mmol) in a mixture of absolute ethanol (25 ml) and triethylorthoformate (5 ml) was added dropwise with stirring under argon atmosphere. TTF and copper(II) (hexafluoroacetylacetonate) were obtained from Aldrich Chemicals and used without further purification. The reaction solution changed to dark-brown color immediately. The reaction mixture was stirred for ca. 4 hrs, and then refrigerated overnight. The deep-brown colored precipitates were isolated by filtration and washed several times with absolute ethanol. The microcrystalline precipitates were dried in vacuum at room temperature (yield; 45.4%). Elemental analysis was performed by Korea Research Institute of Chemical Technology, Daejeon, KOREA. Anal. Calc. for $(\text{TTF})_2 \text{Cu}(\text{hfac})_2 \cdot 1.5\text{C}_2\text{H}_5\text{OH}$: C, 29.

57; H, 1.97. Found: C, 29.20; H, 2.22.

Physical measurements. The electrical conductivity was determined on the compressed pellets by van der Pauw's four-probe method in a temperature range of 100-300 K. The sample pellet ($2 \times 3 \times 20$ mm) was spotted with conductive silver paste (DOTITE D-500) to make a good contact. Low temperature was obtained by using CTI-CRYOGENIS model 8001 cryodine cryocooler. The temperature was measured with a DT-500K silicon diode connected to a Lake Shore Cryotronics, Inc., model DRC-82C temperature controller. Constant current was applied by using a Keithley model 227 current source and the voltage was measured with a Keithley model 181 nanovoltmeter. The EPR spectral measurements were made on powdered sample at 77 K and at room temperature by using a ESP-300S X-band EPR spectrometer. The field strength was calibrated using DPPH ($g=2.0037$). The magnetic susceptibility data were collected from 77 K to room temperature by using Faraday method with a Cahn 2000 electrobalance. The magnetometer was calibrated with $\text{HgCo}(\text{SCN})_4$. Susceptibilities were corrected for the diamagnetism of the substituent atoms using Pascal's constant. The X-ray photoelectron spectra were recorded on a Perkin-Elmer, Physical Electronics model 5400 X-ray photoelectron spectrometer equipped with a magnesium anode X-ray source and a hemispherical analyzer. The residual gas pressure was 5×10^{-9} torr. The binding energies were calibrated using the Au $4f_{7/2}$ peak at 84.9 eV and the $\text{Cu}2p_{3/2}$ peak at 932.2 eV. The adventitious C 1S line at 284.6 eV was used from charge referancing. Electronic spectra were recorded on a Shimadzu 260 spectrometer on solution and solid/nujol mulls mounted between quartz plates. Infrared spectra ($400\text{-}4,000 \text{ cm}^{-1}$) were obtained using potassium bromide pellets with a Polari's FT-IR spectrophotometer. Cyclic voltammograms were recorded on a EG-PAR Inc., model 273 Potentiostat and Galvanostat. The platinum working electrode (0.7 cm diameter) was polished with alumina prior to each run. An Ag/AgCl reference electrode was used. All potentials were reported versus to AgCl electrode and uncorrected for junction potentials. Cyclic voltammograms were recorded in DMF using 0.1 M tetraethylammonium perchlorate as an electrolyte at scanning rate of 100 mV/s.

Results and Discussion

Figure 1 shows the temperature dependence of the powder resistivity of $(\text{TTF})_2\text{Cu}(\text{hfac})_2 \cdot 1.5\text{C}_2\text{H}_5\text{OH}$. The resistivity increase with decreasing temperature in the experimental temperature range. The negative coefficient $d\rho/dT < 0$ reflects the intrinsic semiconductor behavior given by $\rho = \rho_0 \exp(E_a/k \cdot T)$. The Boltzmann factor describes the thermally activated generation of charge carriers in a narrow bandgap semiconductor, and the activation energy is calculated with $E_a = 0.083 \text{ eV}$. This value is comparable to those of several organic conductors.⁵ The room temperature conductivity is $6.28 \times 10^{-3} \text{ Scm}^{-1}$, which lies in the range of semiconductor. This value is somewhat greater than those of simple ionized TTF salts having a columnar structure ($\sim 10^{-5} \text{ Scm}^{-1}$).⁶ It is similar to those of $(\text{TTF})_n\text{SbX}_4$.⁷ TTF in $(\text{TTF})_n\text{SbX}_4$ is known to be partially ionized and columnar structures are formed. Therefore, such a relatively high electrical conductivity of