

Copper Salts of Rigid *N,N'*-Dicyanoquinone Diimine Derivatives

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DEDICATED TO THE MEMORY OF DR. BARUCH ZINGER UPON HIS UNTIMELY DEATH AT THE AGE OF 51 (1950–2001)

INTRODUCTION

Synthetic metals generally involve donor and acceptor components, which may contain organic donors and organic acceptors (e.g., TTF/TCNQ) (1), organic donors and inorganic acceptors [Bechgaard salts, e.g., (TMTSF)₂⁺X⁻ (2)], organic acceptors and metal donors [e.g., (DCNQI)₂M (3)], and organic donors and transition metal complexes as acceptors [e.g., (TTF)[M(dmit)₂] (4). Transition metals, such as Pt, Pd, Ni and Au in (4,5-dimercapto-1,3-dithiole-2-thione) (dmit) salts, and Cu and Ag in DCNQIs (*N,N'*-dicyanoquinone diimine) salts, play an important role in synthetic conductors. Several bis(ethylenedithio)tetrathiofulvalene (ET) salts, involving Cu, Ag, Hg or Au, have shown superconductivity at ambient pressure, and a number of “dmit” salts, involving Ni and Pd, have shown superconductivity under pressure (5).

It has been found that there are a number of prerequisite properties for achieving electrical conductivity in molecular organic compounds (6). Among them are partial degree of charge transfer, rigidity, stoichiometric control and segregated stacking in the solid state. Stoichiometric control may be achieved by preparing single molecular entities, in which both donor and acceptor units are chemically linked by spacers, e.g., methylene groups (7) or heteroatoms (8).

Initially, most neutral acceptors published in the literature involved a TCNQ (tetracyanoquinodimethane) moiety. Rigid molecules containing a TCNQ acceptor moiety covalently linked to a donor moiety by heteroatoms (O, S) are also known (9). Later, Aumüller and Hunig introduced a new acceptor, *N,N'*-dicyanoquinone diimine (DCNQI) and its substituted derivatives (10). Molecules containing this type of acceptor, covalently linked to a

donor unit, were also prepared (11), among them rigid derivatives (12). This type of molecules contain some of the important features which are necessary for conducting properties such as: a prefixed D:A stoichiometry in which the degree of CT can be tuned by varying the nature of different substituents; rigidity, which may improve intermolecular connectivity in the crystal packing in the solid state; and the presence of heteroatoms which may reinforce the intermolecular interactions in the solid state. Some of these features may be achieved by forming a complex with metal ions and a rigid acceptor molecule.

The existence of rigid transition metal salts of polycyclic acceptors, containing *N,N'*-dicyanoquinone diimine moiety, has no precedent. The present paper deals with the preparation of copper salts of this type of acceptors, and their spectral and electrical conductance properties.

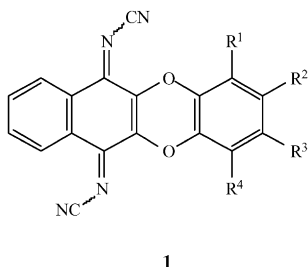
RESULTS AND DISCUSSION

Some years ago we reported (13) the synthesis of a series of rigid molecules, based on substituted benzo[*b*]naphtho[2,3-*e*]dioxin-6,11-*N,N'*-dicyanoquinone diimines] (1) (Scheme 1). Some of these (1a–1d) contain a donor linked to an acceptor by two oxygen bridges. The acceptor moiety involves *N,N'*-dicyanonaphthoquinone diimine derivatives and the donor moiety is composed of a substituted benzene ring, with electron-withdrawing groups.

All derivatives exhibited two 1e⁻ reversible reduction waves, corresponding to the successive formation of anion-radical and dianion. Comparison of the electrochemical results of compounds of type 1 with those of *N,N'*-dicyano-1,4-naphthoquinone diimine indicated that the negative charges in the former are mostly localized on the quinone diimine ring and that the charges are spatially remote from each other.

A large number of radical anion salts derived from 2,5-disubstituted DCNQIs have been prepared (3). All those

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1	R¹	R²	R³	R⁴	E_{red(1)}^a	E_{red(2)}^a
a	H	H	H	H	+0.07	-0.44
b	H	Me	H	H	+0.02	-0.45
c	H	t-Bu	H	H	-0.03	-0.43
d	t-Bu	H	t-Bu	H	+0.02	-0.43
e	H	NO ₂	H	H	+0.17	-0.34
f	H	CN	H	H	+0.11	-0.38

^a Redox potentials of reversible waves in Volts (vs. Ag/AgCl), on glassy carbon working electrode, in CH₂Cl₂-0.1M n-Bu₄NClO₄

SCHEME 1.

DCNQI-radical salts are one-dimensional semiconductors, except for the isomorphous Cu-salts, which display (quasi-three-dimensional) metallic properties. The black needles display conductivities of ca. 100–1000 S cm⁻¹, at room temperature. Whereas most of the TCNQ radical salts can only be obtained in an 1:1 stoichiometry (weakly conduct-

TABLE 1
Properties of Copper Salts (2) of Acceptors (A) of Type 1

Cu salt (Cu _n A _m)	Stoichiometry ^a	CN (cm ⁻¹)	Conductivity (S cm ⁻¹) ^b
2a	None		
2b	CuA ₂	2139	0.1
2c	Cu ₃ A ₂	2148	10 ⁻⁴
2d	Cu ₂ A	2110, 2138	10 ⁻⁵
2e	CuA	2140, 2145	0.1
2f	CuABr · MeCN ^c	2157	~1

^a Determined by elemental analysis for C, H, N.

^b Room temperature measurement on pressed pellets; four-probe technique.

^c Determined by X-ray analysis.

ing), the DCNQI radical salts provide 2:1 ([DCNQI]₂M) stoichiometry with partly filled band, a prerequisite for conductivity (3).

Copper salts (**2**) of **1** have been prepared electrochemically by a known method (14). The results, which include stoichiometric ratios, the stretching frequencies of the cyano groups in the IR and conductivities, are described in Table 1. It appears that different substituents on the acceptor ring dictate the stoichiometry of the radical salt obtained, thus ratios of 1:1, 2:1, 1:2 and 3:2 (Cu:1) were observed. As expected, all the listed copper complexes show a decrease in the stretching frequency of the cyano group in the “C–NC” moiety compared to the same group in the uncomplexed acceptor (13). However, we have no explanation for the observation that in some cases two

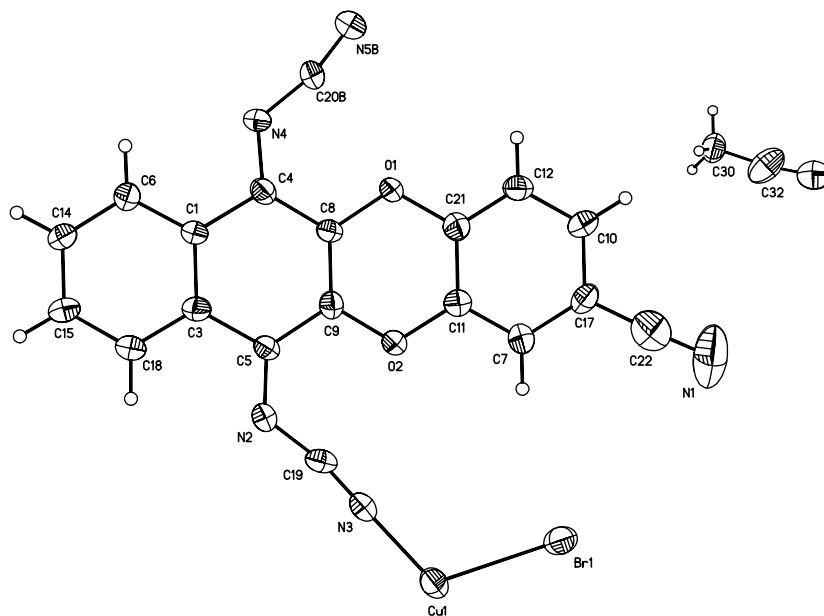


FIG. 1. ORTEP drawing of **1f** (R² = CN), including the acetonitrile solvent molecule and the atomic numbering.

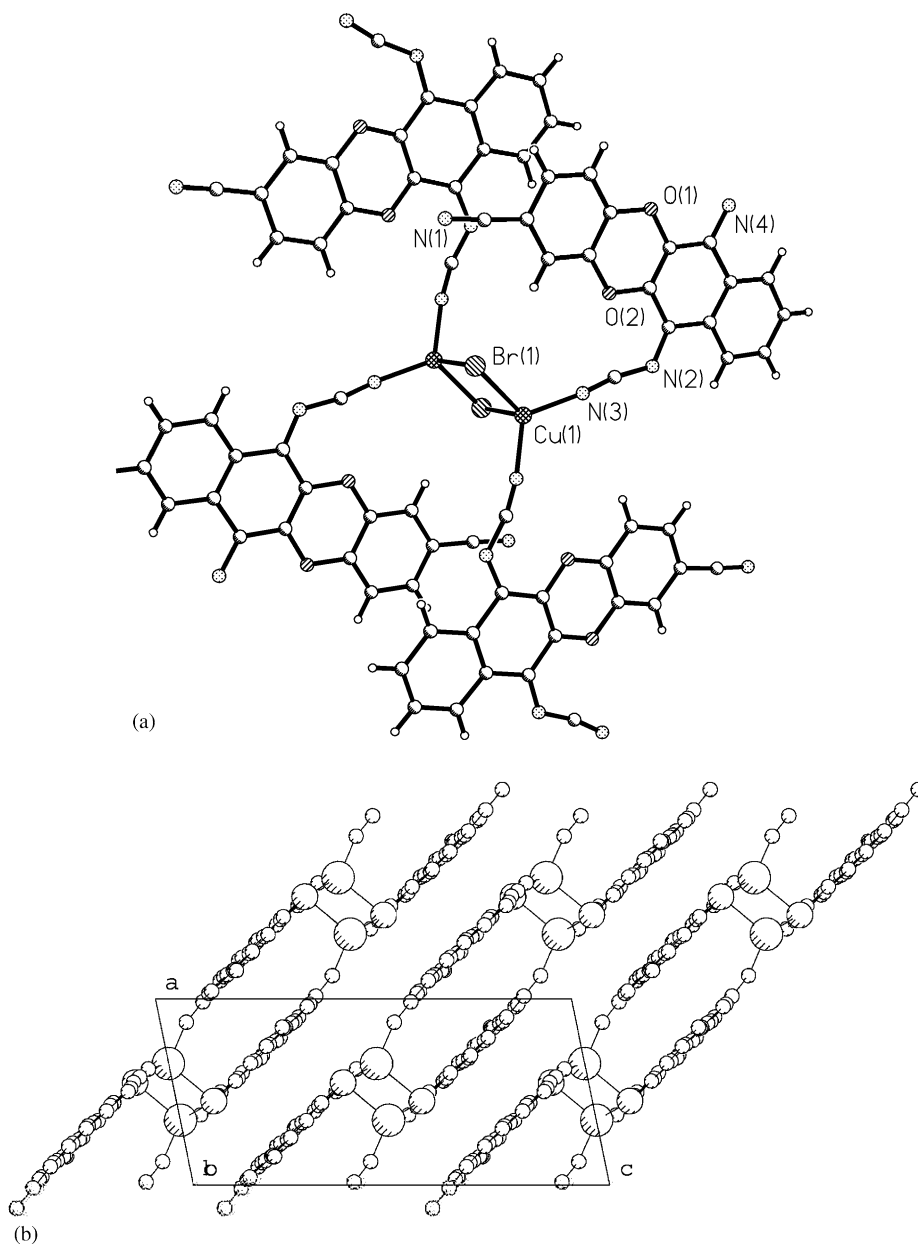


FIG. 2. Packing diagram of the structure of **1f** ($R^2 = \text{CN}$) showing (a) the tetrameric unit containing two Cu(I) ions, two bromide anions and four dicyanodiimino units, and (b) the bilayered sheets described in the text, the largest circles represent bromide anions, and the next largest Cu^+ cations.

absorption bands were observed, and in some only one. Also, contrary to TCNQ salts we have not found a correlation between the stretching frequencies of the cyano groups and the degree of charge transfer. All conductivity measurements were carried out on pressed pellets except for **2f**, which afforded good quality crystals, suitable for X-ray measurements. Surprisingly, no copper salt (**1a**) was formed from the unsubstituted acceptor. It appears that all copper salts obtained are semiconductors. **2f** appears to exhibit the highest conductivity among the prepared salts.

It is noteworthy that the conductivity value could be misleading, since it is well known that pressed pellets tend to give conductivity readings that are 2–3 orders of magnitude lower than their corresponding single crystals.

CRYSTALLOGRAPHY

The crystal structure of the neutral compound **2f** contains one molecule of acetonitrile solvent per molecular unit. The ORTEP diagram of the crystallographic asym-

TABLE 2
Crystallographic constants for CuA2

Identification code	CuA2
Empirical formula	C82 H38 Br4 Cu4 N23 O8
Formula weight	2047.15
Temperature	297(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	<i>P</i> 2(1)/ <i>c</i>
Unit cell dimensions	
<i>a</i> = 8.0294(11) Å	$\alpha = 90^\circ$
<i>b</i> = 14.064(2) Å	$\beta = 101.613(3)^\circ$
<i>c</i> = 17.585(2) Å	$\gamma = 90$
Volume	1945.2(5) Å ³
<i>Z</i>	1
Density (calculated)	1.748 Mg (m ³)
Absorption coefficient	3.208 mm ⁻¹
<i>F</i> (000)	1011
Crystal size	0.2 × 0.45 × 0.5 mm ³
Theta range for data collection	1.87–23.28°
Index ranges	−8 ≤ <i>h</i> ≤ 8, −15 ≤ <i>k</i> ≤ 15, −19 ≤ <i>l</i> ≤ 19
Reflections collected	10006
Independent reflections	2787 [<i>R</i> (int) = 0.0830]
Completeness to theta = 23.28°	100.0%
Absorption correction	Empirical
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	2787/0/281
Goodness-of-fit on <i>F</i> ²	1.076
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0666, <i>wR</i> ₂ = 0.1962
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0890, <i>wR</i> ₂ = 0.2114
Largest diff. Peak and hole	1.930 and −0.843 e Å ⁻³

TABLE 3
Bond Lengths (Å) and Angles (deg) for CuA2

Br(1)–Cu(1)#1	2.499(2)
Br(1)–Cu(1)	2.532(2)
Cu(1)–N(3)	1.930(8)
Cu(1)–N(5)	1.955(8)
Cu(1)–Br(1)#1	2.499(2)
O(1)–C(8)	1.373(10)
O(1)–C(21)	1.382(10)
C(1)–C(6)	1.391(12)
C(1)–C(3)	1.402(12)
C(1)–C(4)	1.475(12)
O(2)–C(9)	1.357(10)
O(2)–C(11)	1.385(10)
C(3)–C(18)	1.397(12)
C(3)–C(5)	1.468(12)
C(4)–N(4)	1.306(11)
C(4)–C(8)	1.419(12)
N(2)–C(5)	1.291(10)
N(2)–C(19)	1.325(13)
C(5)–C(9)	1.430(12)
C(6)–C(14)	1.384(13)
C(7)–C(11)	1.355(12)
C(7)–C(17)	1.401(13)
N(4)–C(20)#2	1.308(11)
C(8)–C(9)	1.368(12)
C(10)–C(17)	1.386(13)
C(10)–C(12)	1.383(12)
C(11)–C(21)	1.413(12)
C(12)–C(21)	1.349(12)
C(14)–C(15)	1.338(13)
N(3)–C(19)	1.157(12)
C(15)–C(18)	1.385(13)
C(17)–C(22)	1.378(16)
N(1)–C(22)	1.214(17)
N(5)–C(20)	1.150(11)
C(20)–N(4)#3	1.308(11)
C(30)–C(32)	1.350(2)
N(6)–C(32)	1.180(2)
Cu(1)#1–Br(1)–Cu(1)	80.07(5)
N(3)–Cu(1)–N(5)	118.1(3)
N(3)–Cu(1)–Br(1)#1	108.9(3)
N(5)–Cu(1)–Br(1)#1	104.7(3)
N(3)–Cu(1)–Br(1)	113.8(2)
N(5)–Cu(1)–Br(1)	109.4(2)
Br(1)#1–Cu(1)–Br(1)	99.93(5)
C(8)–O(1)–C(21)	117.0(6)
C(6)–C(1)–C(3)	119.7(8)
C(6)–C(1)–C(4)	120.5(7)
C(3)–C(1)–C(4)	119.6(7)
C(9)–O(2)–C(11)	117.1(6)
C(18)–C(3)–C(1)	119.1(8)
C(18)–C(3)–C(5)	120.1(8)
C(1)–C(3)–C(5)	120.8(7)
N(4)–C(4)–C(8)	125.3(8)
N(4)–C(4)–C(1)	116.6(7)
C(8)–C(4)–C(1)	118.0(7)
C(5)–N(2)–C(19)	125.8(8)
N(2)–C(5)–C(9)	125.3(8)
N(2)–C(5)–C(3)	117.3(7)
C(9)–C(5)–C(3)	117.4(7)
C(14)–C(6)–C(1)	119.5(8)

metric unit is given in Fig. 1. Except for the somewhat high anisotropic thermal parameters of the cyano group (C22–N1) [which is not unusual for the behavior of cyano groups (15)] the structure solution and refinement otherwise have no unusual features. The basic building block of the crystal structure may be described as a centrosymmetric dimeric Cu complex with tetrahedral geometry about each of the Cu⁺ ions (Fig. 2a). The two “external” ligands on each of the Cu⁺ ions are two of the rigid *N,N'*-dicyanoquinone diimine moieties and the dimer is formed through Br[−] linkages leading to a planar “Cu₂Br₂” unit with the additional two ligands on each Cu. This stoichiometry and geometry suggest that the Cu is in the (I) oxidation state.

The crystal packing of the compound is shown in Fig. 2. It is readily seen that the “Cu₂Br₂” units form the repeating unit of the structure. Each Cu is also bonded to two dicyanodiimine units, leaving the second cyano imine group available for bonding to another Cu ion. The result is an extended “bilayer sheet” where the links between the two layers of rigid dicyano diimine molecules are provided by the “Cu₂Br₂” units. The crystal structures of some other (2,5-disubstituted-DCNQI)₂Cu salts have been described (3) as having “the copper ions... arranged along the *c*-axis

TABLE 3—Continued

C(11)–C(7)–C(17)	118.6(8)
C(4)–N(4)–C(20)#2	124.8(8)
O(1)–C(8)–C(9)	122.2(7)
O(1)–C(8)–C(4)	115.5(7)
C(9)–C(8)–C(4)	122.3(8)
O(2)–C(9)–C(8)	122.3(8)
O(2)–C(9)–C(5)	115.7(7)
C(8)–C(9)–C(5)	122.0(7)
C(17)–C(10)–C(12)	120.2(8)
C(7)–C(11)–O(2)	118.8(8)
C(7)–C(11)–C(21)	120.3(8)
O(2)–C(11)–C(21)	120.9(7)
C(21)–C(12)–C(10)	119.1(8)
C(15)–C(14)–C(6)	120.9(9)
C(19)–N(3)–Cu(1)	167.6(9)
C(14)–C(15)–C(18)	121.5(9)
C(10)–C(17)–C(22)	117.2(9)
C(10)–C(17)–C(7)	120.5(8)
C(22)–C(17)–C(7)	122.3(10)
C(15)–C(18)–C(3)	119.2(8)
N(3)–C(19)–N(2)	169.8(10)
C(20)–N(5)–Cu(1)	164.6(8)
C(12)–C(21)–O(1)	118.4(8)
C(12)–C(21)–C(11)	121.1(8)
O(1)–C(21)–C(11)	120.4(7)
N(1)–C(22)–C(17)	176.6(16)
N(5)–C(20)–N(4)#3	166.9(9)
N(6)–C(32)–C(30)	172.0(2)

like a string of pearls to which four stacks of the organic acceptor are attached in nearly tetrahedral geometry. Electrons are transported through these stacks along the *c*-axis. However, along the *a,b*-plane, the copper ions are connected by bridging ligands which now can shift electrons between the copper ions, which are supposed to occur with an average charge of $\text{Cu}^{1.33}$ (Cu^+ , Cu^+ , Cu^{++}) (16)". In those structures the "string of pearls" of copper ions resulting from the stacking allows for the mixed valence state and electrical conductivity along the string. In the structure presented here the Cu ions are isolated in the "Cu₂Br₂" units with little or no interaction between them due to lack of distance proximity, and the stoichiometry requires the maintenance of a Cu(I) oxidation state.

The structural features of this complex suggest that its relatively high electrical conductivity compared to other copper dicyanodiamine complexes cannot be due to interactions through a chain of copper ions. Another possible mechanism for the electrical conductivity would be through the pi system of the dicyanodiamine moiety and the connecting copper ions (i.e., "–N–CN–Cu–NC–N–") within one of the sheets of the bilayer system. Such a mechanism would lead to a significant anisotropy in the conductivity with a high value along the approximately [101] direction compared to other directions in the crystal. Unfortunately, the crystals were not of sufficient size or

TABLE 4
Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for CuA2

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq)
Br(1)	4506(1)	5630(1)	902(1)	48(1)
Cu(1)	3478(2)	4248(1)	7(1)	47(1)
O(1)	8806(8)	1765(4)	3248(4)	47(2)
C(1)	6828(10)	–395(6)	2240(5)	33(2)
O(2)	6544(8)	2571(4)	1972(4)	47(2)
C(3)	5731(10)	12(6)	1601(5)	33(2)
C(4)	7922(10)	224(6)	2808(5)	33(2)
N(2)	4485(10)	1373(5)	936(4)	44(2)
C(5)	5585(10)	1049(6)	1516(5)	32(2)
C(6)	6970(12)	–1379(6)	2300(6)	43(2)
C(7)	7446(12)	4099(6)	2431(5)	40(2)
N(4)	9022(9)	–200(5)	3350(4)	39(2)
C(8)	7759(11)	1222(6)	2702(5)	35(2)
C(9)	6660(11)	1618(6)	2088(5)	35(2)
C(10)	9580(12)	4272(6)	3609(6)	43(2)
C(11)	7553(11)	3143(6)	2520(5)	38(2)
C(12)	9706(11)	3294(6)	3682(5)	41(2)
C(14)	6030(12)	–1946(6)	1726(5)	44(2)
N(3)	3766(11)	3025(6)	514(5)	51(2)
C(15)	4989(13)	–1559(7)	1114(5)	46(2)
C(17)	8472(11)	4675(6)	2985(5)	39(2)
C(18)	4809(12)	–582(6)	1031(5)	42(2)
C(19)	4197(12)	2282(7)	760(5)	44(2)
N(1)	8470(20)	6514(10)	2913(9)	136(5)
N(5)	1253(11)	4554(6)	–629(5)	48(2)
C(21)	8696(11)	2740(6)	3155(5)	37(2)
C(22)	8425(19)	5653(10)	2943(9)	91(4)
C(20)	157(12)	4764(6)	–1128(5)	38(2)
C(30)	1004(18)	7021(9)	9488(8)	63(4)
N(6)	1672(19)	7967(14)	9460(10)	90(6)

clearly defined morphology to perform such a confirming experiment.

EXPERIMENTAL

For electrochemical measurements, Princeton Applied Research (PAR) Potentiostat/Galvanostat Model 173, PAR Universal Programmer Model 175 and Yokogawa XY-recorder Model 3068 were employed. Cyclic voltammetric experiments were performed using a conventional three-electrode cell, containing a glassy carbon working electrode (ca. 3 mm diam.), an Ag/AgCl reference electrode, and a Pt wire auxiliary electrode. The concentration of **1** was 1–2 mmol L^{–1}, while that of the supporting electrolyte was 0.1 mol L^{–1}, in dichloromethane.

All copper salts listed in Table 1 were made according to a known electrochemical procedure (14), in acetonitrile, using the same concentrations of CuBr₂ and acceptor, but in quantities approximately 10% of those reported earlier. Both electrodes were Pt wires, 1 mm in diameter and 2 cm in length, immersed in a two-compartment cell, separated

by a fine glass frit. The constant current density employed was in the range of 1–5 μA .

Intensities for the crystal structure determination were measured on a Bruker Smart system. The structure was solved and refined using SHELXTL (17). Crystallographic data and refinement parameters are given in Table 2. A CIF file with the final coordinates, derived geometric parameters, thermal parameters and observed and calculated structure factors has been deposited with the Cambridge Crystallographic Data Center (Ref. No. 17828) (see Tables 3 and 4).

REFERENCES

1. J. Ferraris, D. D. Cowan, V. Walatka, Jr., and J. H. Perlstein, *J. Am. Chem. Soc.* **95**, 948 (1973); L. B. Coleman, M. J. Cohen, D. J. Sandman, F. G. Yamagishi, A. F. Garito, and A. J. Heeger, *Solid State Commun.* **12**, 1125 (1973).
2. K. Bechgaard, C. S. Jacobsen, K. Mortensen, H. J. Pedersen, and N. Thorup, *Solid State Commun.* **33**, 1119 (1980); D. Jerome, A. Mazaud, M. Ribault, and K. Bechgaard, *J. Phys. Lett.* **41**, L95 (1980); K. Bechgaard, K. Carnerio, F. B. Rasmussen, M. Olsen, G. Rindorf, C. S. Jacobsen, H. J. Pedersen, and J. C. Scott, *J. Am. Chem. Soc.* **103**, 2440 (1981); F. Wudl, *Acc. Chem. Res.* **17**, 227–232 (1984).
3. S. Hunig and P. Erk, *Adv. Mater.* **3**, 225 (1991); S. Hunig, *Pure Appl. Chem.* **62**, 395 (1990).
4. L. Brossard, M. Ribault, L. Valade, and P. Cassoux, *Physica B* **143**, 378 (1986); L. Brossard, M. Ribault, L. Valade, and P. Cassoux, *J. Phys. France* **50**, 1521 (1989).
5. J. M. Williams, J. R. Ferraro, R. J. Thorn, K. D. Carlson, U. Geiser, H. H. Wang, A. M. Kini, and M.-H. Whangbo, "Organic Superconductors," Chap. 1, pp. 1–10. Prentice-Hall, Englewood Cliffs, NJ, 1992.
6. J. Y. Becker, J. Bernstein, S. Bittner, N. Levi, and S. S. Shaik, *J. Am. Chem. Soc.* **105**, 4468–4470 (1983); J. Y. Becker, J. Bernstein, S. Bittner, J. A. R. P. Sarma, and S. S. Shaik, *Chem. Mater.* **1**, 412–420 (1989); J. Y. Becker, J. Bernstein, S. Bittner, and S. S. Shaik, *Pure Appl. Chem.* **62**, 467–472 (1990).
7. J. Y. Becker, J. Bernstein, S. Bittner, N. Levi, S. S. Shaik, and N. Zer-Zion, *J. Org. Chem.* **53**, 1689–1694 (1988); J. Y. Becker, J. Bernstein, S. Bittner, and S. S. Shaik, *Synth. Met.* **27**, 197–204 (1988).
8. J. Y. Becker, J. Bernstein, S. Bittner, E. Harlev, and J. A. R. P. Sarma, *Nouv. J. Chim.* **12**, 875–880 (1988).
9. P. Bando, K. Davidkov, N. Martin, J. L. Segura, C. Seoane, A. Gonzalez, and J. M. Pingarron, *Synth. Met.* **56**, 1721 (1993); E. Barranco, N. Martin, J. L. Segura, C. Seoane, P. Cruz, F. Langa, A. Gonzalez, and J. M. Pingarron, *Tetrahedron* **49**, 4881 (1993).
10. A. Aumüller and S. Hünig, *Angew. Chem. Int. Ed. Engl.* **23**, 447 (1984); A. Aumüller and S. Hünig, *Liebigs Ann. Chem.* **142**, 165 (1986).
11. J. Y. Becker, J. Bernstein, S. Bittner, Y. Giron, E. Harlev, L. Kaufman-Orenstein, D. Peleg, L. Shahal, and S. S. Shaik, *Synth. Met.* **41–43**, 2523–2528 (1991).
12. N. Martin, J. A. Navarro, C. Seoane, A. Albert, F. H. Cano, J. Y. Becker, V. Khodorkovsky, E. Harlev, and M. Hanack, *J. Org. Chem.* **57**, 5726–5730 (1992).
13. T. Czekanski, M. Hanack, J. Y. Becker, J. Bernstein, S. Bittner, L. Kaufman (Orenstein), and D. Peleg, *J. Org. Chem.* **56**, 1569–1573 (1991).
14. A. Aümüeller, P. Erk, G. Klebe, S. Hünig, J. U. von Schutz, and H.-P. Werner, *Angew. Chem. Int. Ed. Engl.* **25**, 740 (1986).
15. J. Bernstein and K. N. Trueblood, *Acta Crystallogr. B* **27**, 2078–2089 (1971).
16. H. Kobayashi, R. Kato, A. Kobayashi, T. Mori, and H. Inokuchi, *Solid State Commun.* **65**, 1351 (1988); S. Kagoshima, N. Sugimoto, T. Osada, A. Kobayashi, R. Kato, and H. Kobayashi, *J. Phys. Soc. Jpn.* **60**, 4222 (1991).
17. G. M. Sheldrick and T. R. Schneider, SHELXL (refinement), in "SHELXL: High Resolution Refinement. Methods in Enzymology" (C. W. Carter, Jr. and R. M. Sweet, Eds), Vol. 277, pp. 319–343. Academic Press, San Diego, 1997; G. M. Sheldrick, SHELXS (direct methods), (1990). Phase annealing in SHELX-90: direct methods for larger structures, *Acta Crystallogr. A* **46**, 467–473 (1990).