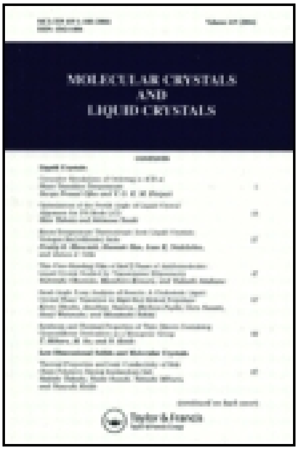

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Organic Metals: N,N'-Dicyano-1,4-benzoquinonediimines as Acceptors in Charge-Transfer Complexes

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Version of record first published: 17 Oct 2011.

To cite this article: Giovanni D. Andreetti , Silvia Bradamante , Paolo Costa Bizzarri & Giorgio A. Pagani (1985): Organic Metals: N,N'-Dicyano-1,4-benzoquinonediimines as Acceptors in Charge-Transfer Complexes, Molecular Crystals and Liquid Crystals, 120:1, 309-314

To link to this article: http://dx.doi.org/10.1080/00268948508075808

Mol. Cryst. Liq. Cryst. 1985, Vol. 120, pp. 309-314
0026-8941/85/1204-0309/$15.00/0

Printed in the United States of America

Organic Metals: *N*,*N*'-Dicyano-1,4-benzoquinonediimines as Acceptors in Charge-Transfer Complexes

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Abstract The synthesis of the title compounds is reported, together with the crystal structure of the parent system (**1a**): charge transfer complexes obtained therefrom show conductivities in the range of semiconductors.

Tetracyanoquinonedimethane (TCNQ) is the acceptor component in many charge transfer (CT) complexes endowed with high electrical conductivity.[1] We report the synthesis of the bis-aza-analogue of TCNQ, *viz*, *N*,*N*'-dicyano-1,4-benzoquinonediimine (**1a**), its 2,5-dichloro congener, together with conductivities of a selected number of their CT complexes. Cyanogen bromide and *p*-phenylenediamine (2:1 molar ratio, r.t. in H_2O in the presence of $NaHCO_3$) give the bis-cyanamide (**2a**, 75%, slowly decomposed above 300°C); lead tetraacetate (LTA) oxidation (r.t., in AcOH, usual procedure[2]) affords the parent *N*,*N*'-dicyanoquinoneimine (**1a**, m.p. 158-160°C, dec., from AcOH, 62%, ^{1}H nmr, DMSO: AA'BB' system, $\delta_{AA'}$=7.28 ppm, $\delta_{B,B'}$=7.56 ppm, J_{AB}=$J_{A'B'}$=13.5Hz). The *trans*-configuration is proved by X-ray analysis.* Figure 1 shows the numbering of the atoms. The molecule lies on the crystallographic centre of symmetry with relevant geometric parameters: N(1)-C(1)=1.150(2), C(1)-N(2)=1.334(2), N(2)-C(2)=1.303(2), C(2)-C(3)=1.450(2), C(2)-C(4)=1.446(2), C(3)-C(4)'=1.336(2)Å; N(2)-C(1)-N(1)=172.8(2), C(1)-N(2)-C(2)=119.5(2)°; N(1)-C(1)-N(2)-C(2)=13.5(2), C(1)-N(2)-C(2)-C(3)=176.9(2)°. The molecular packing is shown in Figure 2, and main contacts, in the range$>$3.20 Å are given by the N-cyano groups with the benzoquinone rings and with N-cyano group generated by the screw axes, and by the glides planes respectively.

2,5-Dichloro-p-phenylenediamine (3)[3] does not react with cyanogen bromide. However the required bis-cyanamide (2b) could be obtained by the following sequence: (3) was reacted with thiophosgene ($CHCl_3$, r.t., 48 hrs) and Et_3N to give, as the chloroform soluble fraction, the bis-isothiocyanate (4,m.p.115°C from AcOH, 50%). Reaction of (4) with aq. NH_3 in THF gave the bis-thiourea (5, m.p.232°C,dec., 80%). Lead (II) acetate in aq. KOH at re-

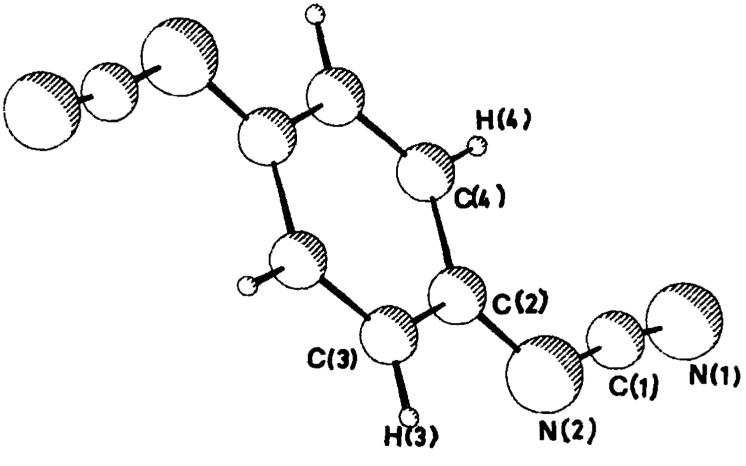


FIGURE 1 Atomic Numbering

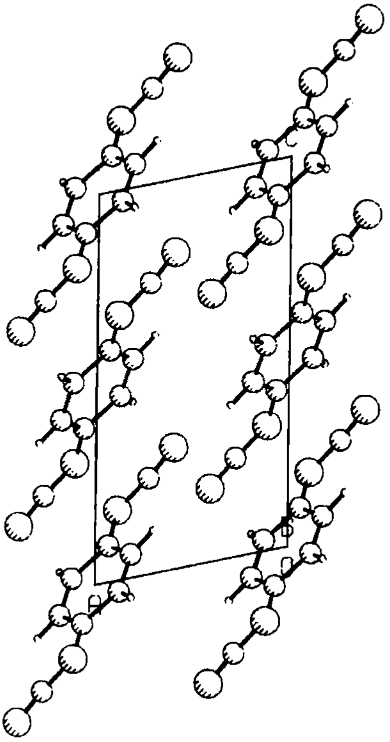
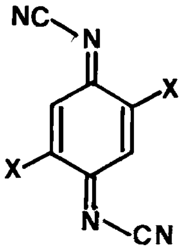
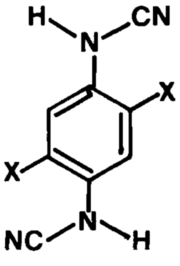


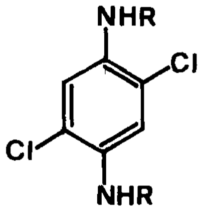
FIGURE 2 Molecular packing



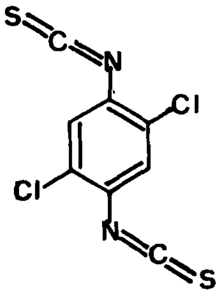
1a: X=H (DCNQI)
1b: X=Cl (DClDCNQI)



2a: X = H
2b: X = Cl



3: R = H
5: R = -C(S)-NH$_2$



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flux (6 min) trasformed (5) into the bis-cyanamide (2b, 93%, slowly decomposes above 300°C). LTA oxidaton in AcOH (r.t.) afforded (1b, m.p. ca 200°C, dec., 91%). *N*,*N'*-dicyano-1,4-benzoquinone diimines (1) could not be crystallized from AcOH without,at least partial, decomposition. Crystals of (1a), suitable for X ray analysis, were obtained by careful and rapid dissolution of a small sample (0.5g) of the row product in AcOH at 60°-70°C and leaving the solution aside for two days in the dark.

Polarography (MeCN solution 0.5 M in LiClO$_4$) revealed clean one and two electron reductions: half-wave potentials (relative to the calomel electrode) of (1a) and (1b) are respectively: $E^1_{1/2}$=+0,18; $E^2_{1/2}$=-0,14; $E^1_{1/2}$=+0,04; $E^2_{1/2}$=-0,13. These data compare rather favourably with reduction potentials of TCNQ[4] ($E^1_{1/2}$= +0.19; $E^2_{1/2}$=-0,35).

CT complexes of quinoneimines (1) were prepared by adding clear filtered MeCN solution of (1) to MeCN solutions of the donor and were obtained as black microcrystalline powders.The Table reports room temp. conductivities (compressed pellets,6000 Kgcm^{-2}) of a number of CT complexes.

Experiments are in progress to further enhance the acceptor properties of substituted *N*,*N*'-dicyanoquinoneimines and toward the obtainment of large crystals of the complexes.

This work was supported by the Italian C.N.R. (Progetto Finalizzato Chimica Fine e Secondaria).

Table. Conductivities (Ω^{-1} cm^{-1}) of some CT complexes of *N*,*N*'-dicyano-1,4-benzoquinonediimines

DCNQI · TTF	4.2×10^{-4}
DClDCNQI · TTF	5.0×10^{-3}
DCNQI · PDA[a]	1.7×10^{-6}
DClDCNQI · PDA	4.9×10^{-5}
DClDCNQI · DCl PDA	4.1×10^{-5}

[a] PDA = *p*-phenylenediamine

* Crystal data. $C_8H_4N_4$, *M*=156.7, monoclinic, *a*=5.598(4), *b*=6.201(5), *c*=11.055(8) Å, β=101.53(4)°, V=375.8(9) Å^3, *Z*=2 D_c=1.380 g cm^{-3}, space group $P2_1/c$. Intensity diffraction data were collected up to θ 70° by using the w-29 step-scanning mode with Ni-filtered Cu-$K\alpha$ radiation. The reflection profiles were analysed with the Lehman-Larsen algorythm (R.H. Blessing, P. Coppens, P. Becker, J. Appl. Cryst., 1974, 7, 488). A total of 863 reflections was collected, 615 of which, after merging the equivalent ones, were considered observed [$I>2\sigma(I)$] and used in the structure analysis and refinement. The structure was solved by direct methods and refined by full-matrix aniso-

tropic least-squares techniques. Hydrogen atoms were found in a ΔF map and refined isotropically. The final $\underline{R}$-index was 0.048 ($\underline{R}_w$=0.047), $w=1/\sigma^2(F)$). Atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Center, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

REFERENCES

1. A.F. Garito and A.J. Heeger, Accounts Chem. Res., 7, 232, J.B. Torrance, Accounts Chem. Res., 12, 79, (1979); J. Ferraris, D.O. Cowan, V.V. Walatka and J. H. Perlstein, J. Am. Chem. Soc., 95, 948, (1973)
2. Org. Synth. Coll. Vol. 4, 172
3. A. T. Peters, F. M. Rowe and D. M. Stead, J. Chem. Soc., 233, (1943)
4. J. R. Anderson, J. O. Orgensen, J. Chem. Soc. Perkin Trans. 1, 3095, (1979)