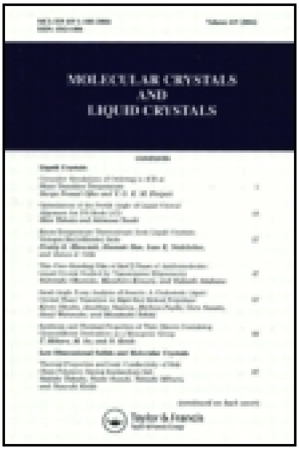


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Why Do Highly Conducting DCNQI Copper Salts Stay Metallic?

Peter Erk [a]

[a] Farbenlabor, BASF AG, 67056, Ludwigshafen/Rh., Germany

To cite this article: Peter Erk (1994): Why Do Highly Conducting DCNQI Copper Salts Stay Metallic?, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 242:1, 91-102

To link to this article: http://dx.doi.org/10.1080/10587259408037741

Mol. Cryst. Liq. Cryst. 1994, Vol. 242, pp. 91–102
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

WHY DO HIGHLY CONDUCTING DCNQI COPPER SALTS STAY METALLIC?

PETER ERK
Farbenlabor, BASF AG, 67056 Ludwigshafen/Rh., Germany

Abstract Structure and conductivity of [2-R^1,5-R^3-DCNQI]$_2$Cu salts are described. The origin of the metallic behavior shown by DCNQI copper salts is discussed. A computational study of the pressure dependence of the crystal structures is presented which indicates that the stability of the metallic state is mainly dependent on the compactness of the crystal packing.

INTRODUCTION

Organic conductors are usually characterized by the high anisotropy of their properties due to their columnar structures. They behave as quasi-1-dimensional systems, and subsequently all of their physical properties are dominated by this feature. Therefore they act as semiconductors with a thermally activated number of free charge carriers causing the conductivity to decrease at low temperatures[1].

Radical anion salts of 2,5-substituted N,N'-dicyanoquinonediimines (DCNQIs) match, in spite of their columnar packing, only partly with this concept. The compounds [2-R^1,5-R^3-DCNQI]$_2$M (R = Cl, Br, I, Me, MeO; M = Li, Na, K, Rb, Tl, NH_4, Ag, Cu) are all isostructural and crystallize as shiny black needles. However, while all non-copper salts are to be described as metal-like semiconductors, the copper salts show unprecedented metallic behavior attracting the attention of several research groups.

In this paper a condensed state-of-the-art picture on DCNQI copper salts based on literature data is drawn[2,3,4]. Furthermore, the phenomenological approach to understand the basic driving forces behind the physical properties of the DCNQI copper salts in reference[5] is extended by a modeling study using force field potentials to calculate and optimize the crystal structures.

CONDUCTIVITY

So far eight DCNQI copper salts retaining their metallic properties down to T < 10 K has been reported, based on DCNQIs substituted by Me/Me, Me/MeO, MeO/MeO, Br/MeO, I/Me, Cl/I, Br/I and I/I (group-M salts)[5]. They exhibit room temperature conductivities in the range of 200-2,000 Scm^{-1} and reach upon cooling conductivities up to 500,000 Scm^{-1}, as observed for $[2,5\text{-}Me_2\text{-}DCNQI]_2Cu$ (Figure 1)[6].

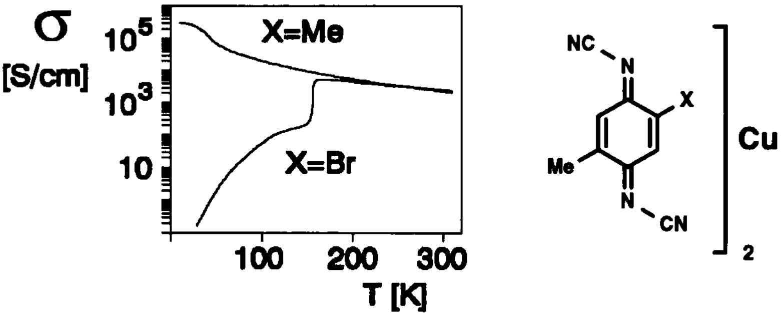


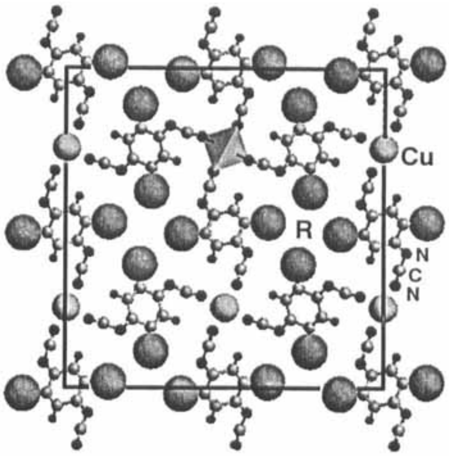
FIGURE 1 Examples for temperature dependent conductivities of group-M (X=Me) and group-M/I (X=Br) salts.

Group-M/I salts start within the same conductivity range at room temperature, but undergo phase transitions from the metallic into an insulating state at lower temperatures[5]. The metal-insulator transition temperatures (T_{M-I}) vary with the substituents, e.g. Cl/Cl (230 K), Cl/Br (205 K), Br/Br (160 K), Cl/Me (210 K), Br/Me (160 K), Cl/MeO (165 K), and most striking CD_3/CD_3 (82 K) and CH_3/CD_3 (58 K), as described recently by Hünig et al.[7].

STRUCTURE

All DCNQI copper salts crystallize in space group I $4_1/a$, with the DCNQI positioned on the center of inversion and the copper cations lined up along the 4-fold axis. In fact the asymmetrically substituted systems are statistically disordered, and the copper spine is surrounded by four stacks of DCNQIs (Figure 2).

Due to the tilt of the DCNQIs towards the c-axis of about 33-37°, they stack like other quinoid acceptors in the ring-overbond arrangement thus maximizing the overlap between the DCNQI LUMO states that form the conduction band.



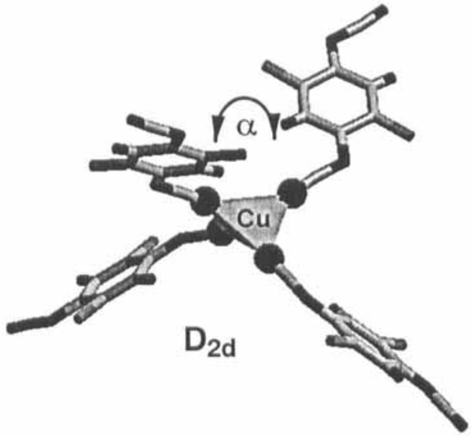


FIGURE 2 a,b-projection of the unit cell of $[2,5\text{-}R_2\text{-DCNQI}]_2Cu$.

FIGURE 3 Distorted tetrahedral ligand sphere of copper.

The copper atoms are coordinated by the CN-groups of four DCNQI molecules in a distorted tetrahedral arrangement (Figure 3). The metal-nitrogen distances of 196-200 pm indicate strong metal-ligand interactions comparable to complexes of other π-acceptor ligands.

As a result of the metal-ligand binding between the DCNQIs and copper, the salts form a close packed (Kitaigorodski packing coefficient ≥ 0.77) interwoven polymeric network to be described in terms of a sevenfold diamondoid superstructure as pointed out by Ermer[8].

THE ORIGIN OF THE METALLIC BEHAVIOR

Conductivity, XPS, IR, ESR, NMR, and susceptibility measurements indicate that copper takes part in the conduction mechanism.

During the phase transition of group-M/I salts a discontinuous shortening of the c-axis is observed. This contraction of the crystal in c-direction affects the ligand sphere of the copper, expressed by an abrupt increase of the coordination angle α at $T_{M\text{-}I}$[4].

According to these results the metallic state of DCNQI copper salts strongly depends on electron transfer between DCNQI stacks mediated by the copper and therefore on the overlap of the DCNQI π^*-LUMOs with the Cu-d-orbitals (Figure 4)[4,9].

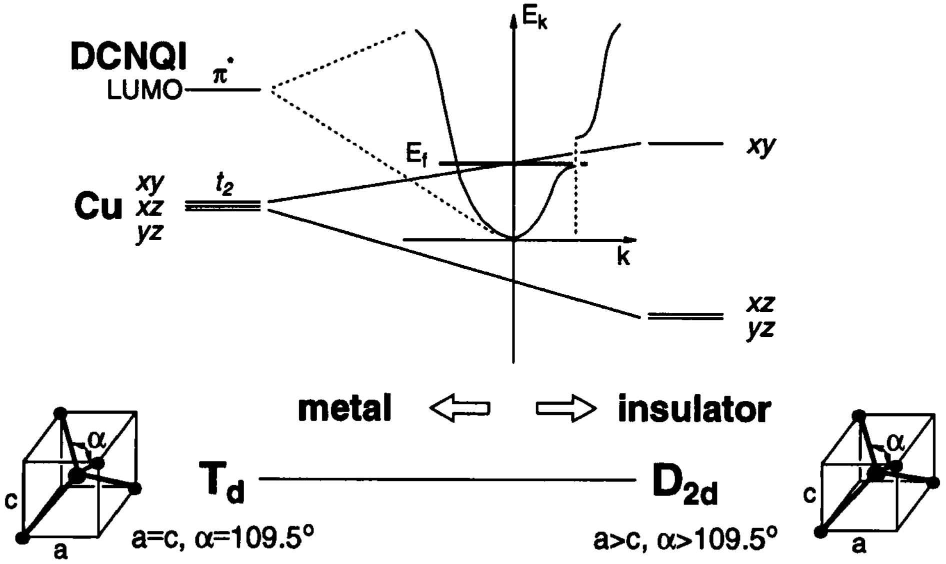


FIGURE 4 Qualitative description of the $p\pi$-d-overlap in $[2,5\text{-}R_2\text{-}DCNQI]_2Cu$ salts with respect to the distorted coordination sphere of the copper.

In agreement with this view on the conduction mechanism, the phase transition can be explained as a cut-off of the Cu-DCNQI interactions.

At room temperature copper is in an intermediate oxidation state ($+1 < q < +1.33$), thus supporting the electron transport between the DCNQI stacks by switching its oxidation state between +I and +II. At this point the charge carriers are mobile in 3 dimensions, and no simple lattice distortion can open up a gap affecting all conduction pathways.

The compression of the tetrahedral ligand environment upon cooling leads to a rise of the Cu-d_{xy}-orbitals' energy, causing electron density to be transferred from Cu to the DCNQIs LUMO-band, connected with a slight increase of the charge on the copper (q → +4/3). At T_{M-I} the charge on the copper reaches +4/3, and the system becomes unstable with respect to a trimerisation of the unit cell in the c-direction, accompanied by simultaneous formation of a charge density wave and a Jahn-Teller distortion of the ligand sphere (Figure 4). Subsequently a gap opens up at the Fermi level and below T_{M-I} the salts become 1-D semiconductors.

REASONS FOR THE PRESERVATION OF THE METALLIC BEHAVIOR

The first model to explain the unusual behavior of $[2\text{-}R^1,5\text{-}R^3\text{-DCNQI}]_2Cu$ salts was given by Kobayashi et al. who showed the transition temperature T_{M-I} to be dependent on the crystal field splitting of the Cu-d-orbitals[4]. But this model completely failed to explain the stable metallic state of the group-M salts.

An analysis of 15 DCNQI copper salts revealed the stability of the metallic state to be dependent on the compactness of the crystal packing[5]. The latter is related to the size of the substituents that have to fit into the Procrustean bed of the Cu-DCNQI-framework.

Group-M salts are characterized by extremely dense crystal packings. Group-M/I salts are less dense packed, and show a quadratic dependence between T_{M-I} and the density of the packing which indicates that a loss of packing energy during the phase transition occurs which has to be compensated by the energy the electronic/vibronic system gains via the Jahn-Teller distortion of the ligand sphere around the copper and the CDW-formation on the DCNQI stack.

CALCULATION OF THE CRYSTAL STRUCTURES

Up to now, no direct relation between substituent dependent changes of the crystal packing and the distortion of the coordination sphere around the copper (which finally governs the behavior of the electronic system of $[2\text{-}R^1,5\text{-}R^3\text{-DCNQI}]_2Cu$ salts) have been demonstrated.

In order to enable a separation of packing effects from an intrinsic Jahn-Teller distortion the crystal structures of the symmetrically substituted [2,5-R_2-DCNQI]$_2$Cu salts (R = Cl, Br, I, Me, MeO) have been calculated using the crystal packer facility of the program CERIUS 3.1[10].

Calculation Setup

Molecular geometries of the neutral DCNQIs were optimized using MOPAC6.0 with the AM1-Hamiltonian under application of C_2-symmetry[11]. Crystals were built up using the symmetry operators of space group I $4_1/a$, and the DCNQI molecules as well as the copper atom were placed according to the observed structures. No charges were put on the DCNQI molecule except for the cyano nitrogen that was set to -0.2 in order to mimic the coordinative bond towards the copper atom that was subsequently set to +0.8.

The packing energy was calculated taking van-der-Waals and Coulomb interactions into account. Lennard-Jones parameters of the DREIDING-II force field were used and modified with respect to the LUMO-LUMO overlap of stacking neighbours[12]. Isotropic pressure was simulated by adding a pV term where V is the cell volume.

Minimization was carried out using a modified Newtonian method varying the lattice parameters, the orientation of the DCNQI molecule, and the methyl groups were allowed to rotate without applying a torsional potential.

Results at Ambient Pressure

The optimized ambient pressure structures of [2,5-R_2-DCNQI]$_2$Cu salts fit fairly with the experimental structures. The calculated lattice constants a and c exceed the experimental ones by 2.3% maximum. For both axes calculated and experimental data are linear dependent with correlation coefficients of 0.98 and 0.89, respectively. The increase of the lattice constants is mainly due to a slight oversize (ca. 20 pm) of the optimized DCNQI molecule structures.

The copper-nitrogen bond lengths are within 0.2% deviation from the observed values, whereas the calculated

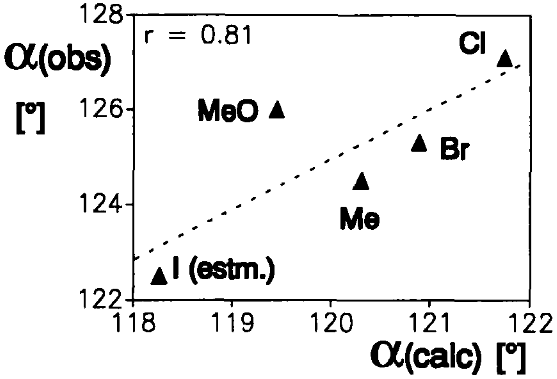


FIGURE 5 Correlation of calculated and observed coordination angles α (I estimated from Me/I structure[13]).

Coordination angles α fall short of the experimental ones by ca. 4.4°, but apparently show a linear dependency on the latter (Figure 5). The larger deviation of 6.5° in the MeO-substituted structure is probably due to the neglect of Coulomb forces and the failure of the potential functions to describe C-H···O and C-H···N interactions correctly.

Pressure Dependence of $[2,5\text{-}R_2\text{-DCNQI}]_2Cu$ Structures

The pressure sensitivities of the five compounds under investigation have been simulated up to 20 kbar (Figure 6). Applying pressure to the crystal structures yields in a contraction of the unit cell with a significantly pronounced shrinkage of the c-axis compared to a minor shortening in the a-direction. This behavior has also been observed experimentally[14], and results - as pointed out previously in this context - in an increase of the coordination angle α.

In the case of the halogen-substituted derivatives calculations show that the angle α widens continuously with applied pressure up to 20 kbar. The average rate of the pressure dependence of α amounts to ≈0.3°/kbar, which is also found for the Me-substituted compound in the region up to 13 kbar. The pressure dependence of α in the MeO-substituted salt is much weaker (≈ 0.12°/kbar), and in the high pressure region α approaches a limit of 120.9°.

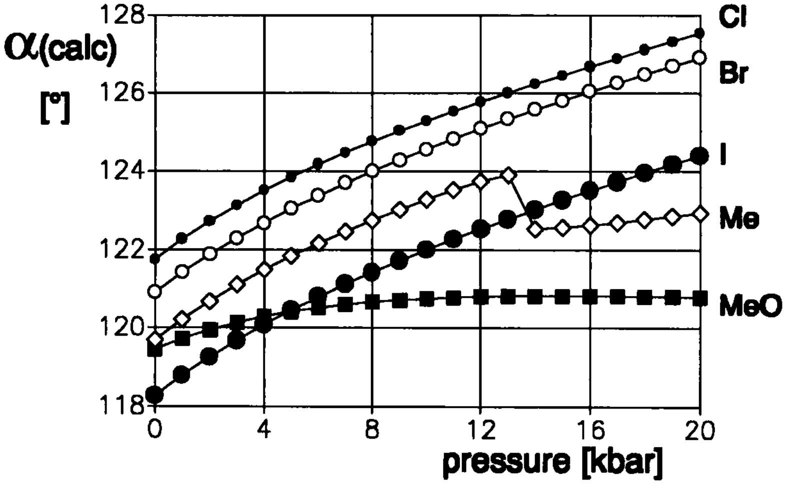


FIGURE 6 Calculated pressure dependence of the coordination angle α in $[2,5\text{-}R_2\text{-DCNQI}]_2Cu$.

In the high pressure region an anomaly for the Me-substituted derivative should be noted. Pressure induced changes of the molecular orientation cause the methyl groups of stacking neighbors to pass each other. This process results in a relaxation of the structure, combined with a drop in the coordination angle α by 1.5°. Above the anomaly the pressure dependence of α is significantly reduced compared to the halogen-substituted salts.

Influence of the Methyl-Group Size

For comparison with the behavior of the deuterated Me/Me salt[7], and with respect to the uncertainty of the calculated methyl-group size the C-H bond length of the methyl group has been varied. For C-H bond lengths of 100.4, 102.3, and 104.7 pm the pressure dependence was calculated (fig. 7). Reducing the C-H bond length results in an increase of the angle α by 0.15°/pm at ambient pressure. The pressure dependence of α in the region up to 8 kbar diminishes

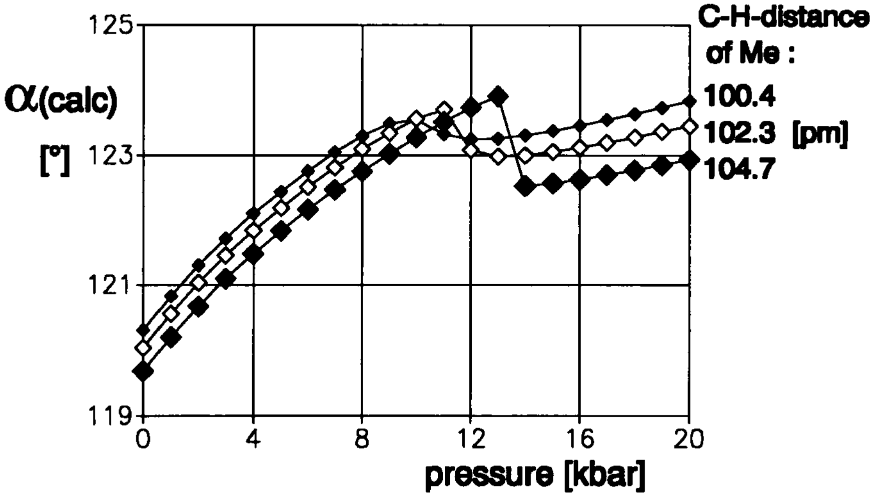


FIGURE 7 Calculated pressure dependence of the coordination angle α in $[2,5\text{-}Me_2\text{-}DCNQI]_2Cu$ under variation of the C-H bond length.

slightly with decreasing C-H bond length, whereas the anomaly observed at high pressure becomes less pronounced and shifts towards lower pressure values.

DISCUSSION

Pressure-temperature dependent conductivities of $[2,5\text{-}Me_2\text{-}DCNQI]_2Cu$[15], $[2\text{-}Cl,5\text{-}Me\text{-}DCNQI]_2Cu$[15], $[2,5\text{-}(MeO)_2\text{-}DCNQI]_2Cu$[16], and $[2\text{-}Br,5\text{-}Me\text{-}DCNQI]_2Cu$[16] have been investigated experimentally.

A common feature for all pressure-temperature phase diagrams of these salts is a rise in the metal-insulator transition temperature (T_{M-I}) with increased pressure (Figure 8). For $[2,5\text{-}Me_2\text{-}DCNQI]_2Cu$ a metal-insulator transition is induced at 50 K under a pressure of 110 bar. Increasing the pressure to 8.5 kbar shifts T_{M-I} to room temperature.

The calculated pressure dependence of the coordination angle α reveals the observed pressure dependence of DCNQI copper salts quantitatively. Considering α to be related to T_{M-I} and utilizing the temperature-pressure phase diagram of

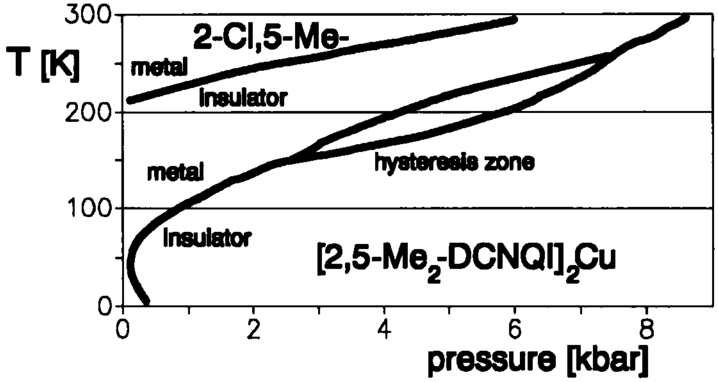


FIGURE 8 Pressure-temperature phase diagram of [2,5-Me$_2$-DCNQI]$_2$Cu and [2-Cl,5-Me-DCNQI]$_2$Cu (lit.[15]).

[2,5-Me$_2$-DCNQI]$_2$Cu to adjust calculated and experimental data enables one to predict T_{M-I} with respect to the pressure needed to achieve identical values for α.

The calculated pressure difference between [2,5-Cl$_2$-DCNQI]$_2$Cu and [2,5-Me$_2$-DCNQI]$_2$Cu for identical values of α amounts to 5-6 kbar (Figure 6). Applying pressure of 6 kbar to [2,5-Me$_2$-DCNQI]$_2$Cu shifts T_{M-I} to ≈230 K (Figure 8), which corresponds to the observed T_{M-I} of [2,5-Cl$_2$-DCNQI]$_2$Cu[4] at ambient pressure. Accordingly, for [2,5-Br$_2$-DCNQI]$_2$Cu a pressure difference of 2.5 kbar and subsequently a T_{M-I} of 160 K is evaluated, matching also the observed value.

Even for [2,5-(MeO)$_2$-DCNQI]$_2$Cu the pressure susceptibility is predicted correctly. Even at low temperatures the metallic state of this compound persists up to 8 kbar, which is reflected by the weak pressure dependence of α (Figure 6). The value for α at 8 kbar corresponds (calibration with [2,5-Me$_2$-DCNQI]$_2$Cu vide supra) to a T_{M-I} of 130 K, resembling the observed temperature range[16].

The quantitative relation of calculated pressure susceptibility to observed p/T-behavior gives rather strong evidence for the compactness of the crystal packing to be the only crucial parameter determining the stability of the metallic state in DCNQI copper salts.

The calculations performed for different C-H bond lengths in $[2,5\text{-}Me_2\text{-}DCNQI]_2Cu$ are to be considered, when reflecting on the special position of this salt[5,7]. Due to their shape, the methyl substituents of adjacent DCNQIs are dovetailed into each other that is in accordance with the high activation barrier for the methyl group rotation shown by NMR experiments. Therefore they behave differently from the isotropic ball-shaped halogens under pressure and presumably also under cooling.

In fact the anomaly found in the high pressure region is caused by a release of Me-Me contacts. It can be related to the one observed experimentally in $[2,5\text{-}Me_2\text{-}DCNQI]_2Ag$[15], and is presumably also present in $[2,5\text{-}Me_2\text{-}DCNQI]_2Cu$ where it may be responsible for the hysteresis found in the medium pressure zone (fig. 8).

The calculations of the coordination angle α in $[2,5\text{-}Me_2\text{-}DCNQI]_2Cu$ using different C-H bond lengths reveal the pronounced sensitivity of α to this parameter (Figure 7). This might be the key for understanding the deuteration effect[7], even though the changes in bond lengths investigated here exceed the ones found for switching from C-H to C-D ($\approx$ 1%). However, it must be taken into account that the Lennard-Jones radius of deuterium is shorter due to the smaller vibrational elongation of the C-D bond.

The results of this study emphasize clearly that the stability of the metallic state in $[2,5\text{-}Me_2\text{-}DCNQI]_2Cu$ and its deuterated derivatives depends only on the space filling properties of the Me substituent.

CONCLUSIONS

The simple model presented here to describe the pressure dynamics of $[2,5\text{-}R_2\text{-}DCNQI]_2Cu$ salts takes only basic structural features into account. It is, in its present state, certainly not sophisticated enough to address questions concerning the electronic and vibrational system of these unique solids. However, comparison with all known dynamic and static solid state features of $[2,5\text{-}R_2\text{-DCNQI}]_2Cu$ salts validates the model to a satisfactory extend. Therefore it must be taken as a major hint that temperature and pressure dependencies of the electronic properties of DCNQI copper salts are determined only by the "internal pressure" the substituents provide for the DCNQI-copper network by their size and geometry.

ACKNOWLEDGEMENT

The author is grateful to Prof. S. Hünig and K. Sinzger for inspiring discussions and communicating results prior to publication.

REFERENCES

1. J. S. Miller and A. J. Epstein, Angew. Chem. Int. Ed. Engl., 26, 287 (1987).
2. S. Hünig, Pure Appl. Chem., 62, 395 (1990).
3. S. Hünig and P. Erk, Adv. Mater., 3, 225 (1991) and lit. citeted therein.
4. R. Kato, H. Kobayashi, A. Kobayashi, J. Am. Chem. Soc., 111, 5224 (1989) and lit. cited therein.
5. P. Erk, H. Meixner, T. Metzenthin, S. Hünig et al., Adv. Mater., 3, 311 (1991) and lit. cited therein.
6. A. Aumüller, P. Erk, G. Klebe, S. Hünig et al., Angew. Chem. Int. Ed. Engl., 25, 740 (1986).
7. S. Hünig, K. Sinzger, M. Jopp et al., Angew. Chem. Int. Ed. Engl., 31, 859 (1992).
8. O. Ermer, Adv. Mater., 3, 608 (1991).
9. P. Erk, S. Hünig et al., in Organic Superconductivity, edited by V. Z. Kresin and W. A. Little (Plenum Press, New York, 1990), pp. 325-334.
10. CERIUS 3.1 is a trademark of Molecular Simulations.
11. J. J. P. Stewart, MOPAC6.0, QCPE # 455.
12. S. L. Mayo, B. D. Olafson, W. A. Goddard III, J. Phys. Chem., 94, 8897 (1990). Modified LJ-parameters (radius [pm], well depth [kcal/mol]): C 185, 0.095; H 150, 0.015; N 180, 0.077; Cu 100, 0.01.
13. P. Erk, S. Hünig, J. U. von Schütz, H.-P. Werner, H. C. Wolf, Angew. Chem. Int. Ed. Engl., 27, 267 (1988).
14. R. Moret, Synthetic Metals, 27, B301 (1988).
15. R. T. Henriques, S. Tomic, W. Kang, D. Jérôme et al., Synthetic Metals, 27, B333 (1988).
16. H. Kobayashi, A. Miyamoto, R. Kato et al., Phys. Rev. B: Condens. Matter, 47, 3500 (1993).