J. Am. Chem. Soc. **1996,** *118,* 13081−13082 13081

A Pressure Sensitive Two-Dimensional Tetracyanoquinodimethane (TCNQ) Salt of a Stable Free Radical

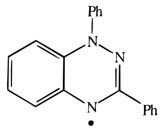
Katherine A. Hutchison, Gordana Srdanov, Reghu Menon, Jean-Christophe P. Gabriel, Brian Knight, and Fred Wudl*

Institute for Polymers and Organic Solids and
Departments of Chemistry and Materials
University of California, Santa Barbara, California 93106

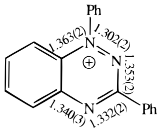
Received September 10, 1996

Organic charge-transfer (CT) salts based on open-shell donors are rare, with very few reports appearing only in the recent past,[1−3] probably due to the scarcity of stable radicals and the molecular design requirements for stabilizing a neutral radical. Here we report the preparation and full characterization (UV, IR, X-ray structure, ESR, magnetic susceptibility, and conductivity) of a salt with uncommon stoichiometry,[4] $(TCNQ)_5(DPBT)_2$, resulting from the interaction between a neutral, stable free radical and tetracyanoquinodimethane (TCNQ). The solid is a two-dimensional semiconductor exhibiting an unusual pressure dependence of its conductivity at ca 2 kbar.

The open-shell donor selected for this study was DPBT$^\bullet$[5] (**1**). This compound was chosen for two reasons: (1) with the exception of the out-of-plane twist of the 4-phenyl group, the cation and the radical should be planar, allowing for stacking and concomitant conductivity and (2) the oxidized radical would be a 10π electron aromatic cation.



(DPBT•) 1



(DPBT$^+$)

DPBT is an unexpectedly better donor[6] ($E_{1/2} = +0.103$ V vs SCE) than tetrathiafulvalene ($E_{1/2} = +0.30$ V vs SCE)[7] and a considerably weaker acceptor ($E_{1/2} = -0.960$ V vs SCE) than C_{60} ($E_{1/2} = -0.42$ V vs SCE).[8] Both redox processes were chemically and electrochemically reversible.

Large crystals of the CT complex used for the conductivity measurements were grown by slow cooling a hot acetonitrile solution of both components.

The salt is triclinic, space group $P\bar{1}$ with 2 ($DPBT\cdot TCNQ_{2.5}$) per unit cell: $a = 7.696(4)$ Å, $b = 16.428(3)$ Å, $c = 16.706(2)$ Å; $\alpha = 91.96(1)°$, $\beta = 103.16(2)°$, $\gamma = 97.36(3)°$; $V = 2035(1)$ Å^3; $R = 0.059$, $R_w = 0.062$.

A striking feature of the structure is that the TCNQ molecules do not form the usual stacks or dimerized stacks,[9,10] instead they are arranged as a set of two dimers separated by a "skewed" TCNQ molecule. Since there are no discrete stacks, the acceptors are arranged in layers[4] (Figure 1). In good agreement with the three crystallographically observed distinct TCNQ molecules (two/dimer plus one/skewed), the solid state FTIR spectrum showed three strong, sharp stretching vibrations at 2208, 2193, and 2178 cm^{-1}, indicating three different types of TCNQ molecules in the solid. Like Bryce et al.,[10] we also failed to see a correlation between the stretching vibration of the nitriles of TCNQ and degree of charge.[11] The layers (or sheets) of acceptor molecules are separated by more sparse layers of donor molecules. The DPBT exists entirely as DPBT$^+$ (see X-ray data-based (DPBT)$^+$ structure, above). Judging from the bond lengths of the exocyclic C═C bonds of the acceptor molecules,[12] one of the two dimer molecules is most negatively charged (C═C, 1.406(2) Å) and the skewed TCNQ is essentially neutral (C═C, 1.378(2) Å). On the basis of these data, the charge-based stoichiometry is $DPBT^{(+)}(TCNQ)_2{}^{(-)}TCNQ^{(0)}$.

At room temperature, the solid state ESR line of a powder sample of $(TCNQ)_5(DPBT)_2$ had a symmetric shape with $\Delta H_{pp} = 1.86$ G and a g factor of 2.0028 ± 0.0002 due to the TCNQ radical anion. Spin quantitation vs DPPH gave one spin per salt unit.

Results of static magnetic susceptibility of a 7.2 mg sample over the temperature range of 2−300 K, calculated using a value of 400×10^{-6} emu/mol for Pascal's corrections for diamagnetism,[13] are shown in Figure 2. The data in the figure were collected at 100 G on a field-cooled, polycrystalline sample. The χT vs T plots from the ESR and susceptibility measurements exhibited essentially identical magnetic susceptibility behavior; the salt was found to be paramagnetic down to ~20 K, whereupon a transition to an antiferromagnetically ordered state occurred (Figure 2). For temperatures between 100 and 300 K, in a field of 100 G, the data followed the Curie−Weiss law with θ approximately −31 K, indicating strong antiferromagnetic interactions between the TCNQ radical anions within the layers. Figure 1 shows the TCNQ dimer [$(TCNQ)_2$] within the layers of TCNQs. If each dimer is considered as an $S = {}^1/_2$ "molecule", then the static susceptibility data could be fit[14] using an isolated pair model with the exchange energy chosen such that the maximum lies at 20 K.[15] The fit (solid line, Figure 2) required $J = -30.8$ K, scaling factor = 0.91, $\langle g \rangle = 2.0028 \pm 0.0002$, and one spin per salt unit ($(TCNQ)_5(DPBT)_2$). The excellent fit demands that an unpaired spin be localized on each $(TCNQ)_2$ within the layer.

The pressed pellet conductivity (σ) of $(TCNQ)_5(DPBT)_2$ in a simple press[16] was $\sigma_{cp} \approx 10^{-4}$ S cm^{-1}. Surprisingly, the dc conductivity of single-crystal samples, using the standard colinear four-probe method, was $\sigma_a = 3 \times 10^{-5}$ and $\sigma_c = 7 \times 10^{-5}$ S cm^{-1}. The salt exhibited activated conductivity. The measured current direction for the first value of the conductivity was along the crystal a axis and the second value along the crystal c axis. The typical value of current was approximately

---

[1] Bryan, C. D.; Cordes, A. W.; Fleming, R. M.; George, N. A.; Glarum, S. H.; Haddon, R. C.; Oakley, R. T.; Palstra, T. T. M.; Perel, A. S.; Schneemeyer, L. F.; Waszczak, J. V. *Nature* **1993**, *365*, 821−823.

[2] Bryan, C. D.; Cordes, A. W.; Haddon, R. C.; Hicks, R. G.; Kennepohl, D. K.; MacKinnon, C. D.; Oakley, R. T.; Palstra, T. T. M.; Perel, A. S.; Scott, S. R.; Schneemeyer, L. F.; Waszczak, J. V. *J. Am. Chem. Soc.* **1994**, *116*, 1205−1210.

[3] Sugimoto, T.; Tsujii, M.; Suga, T.; Hosoito, N.; Ishikawa, M.; Takeda, N.; Shiro, M. *Mol. Cryst. Liq. Cryst.* **1995**, *272*, 183−194.

[4] Only one other case is reported to date: Ueyama, K.; Matsubayashi, G.-E.; Shinohara, I.; Tanaka, T.; Nakatsu, K. *J. Chem. Res.* **1985**, 48−49.

[5] Neugebauer, F. A.; Umminger, I. *Chem. Ber.* **1980**, *113*, 1205−1225.

[6] BAS instrument at room temperature, using 1 mM analyte concentration in acetonitrile with 0.1 M Bu_4NBF_4, 0.5 mM ferrocene as an internal reference, Pt disk as the working electrode, and $Ag/AgNO_3$ (nonaqueous) as the reference electrode.

[7] Bard, A. J.; Faulkner, L. R. *Electrochemical Methods Fundamentals and Applications*; John Wiley & Sons: New York, 1980.

[8] Dubois, D.; Moninot, G.; Kutner, W.; Jones, M. T.; Kadish, K. M. *J. Phys. Chem.* **1992**, *96*, 7137.

[9] Huizinga, S.; Kommandeur, J.; Sawatzky, G. A.; Thole, B. T.; Kopinga, K.; de Jonge, W. J. M.; Roos, J. *Phys. Rev. B: Condens. Matter* **1979**, *19*, 4723.

[10] Obertelli, S. D.; Friend, R. H.; Moore, A. J.; Bryce, M. R.; Bates, P. *Synth. Metals* **1988**, *27*, B327−B332.

[11] Chappel, J. S.; Bloch, A. N.; Bryden, W. A.; Maxfield, M.; Poehler, T. O.; Cowan, D. O. *J. Am. Chem. Soc.* **1981**, *103*, 2442−2443.

[12] Umland, T. C.; Allie, S.; Kuhlmann, T.; Coppens, P. *J. Phys. Chem.* **1988**, *92*, 6456.

[13] König, E. In *Landolt-Bornstein New Series*; Hellwege, K. H., Ed.; Springer: Berlin, 1966; Vol II.

[14] The equation used was $\approx \chi = \{[Ng^2\mu_B^2/kT]\,(0.25 - 0.062935x + 0.0047778x^2)/(1 + 0.053860x - 0.00071302x^2 + 0.047193x^3)$ where $x = |J|/kT$, μ_B = Bohr magneton, and k = the Boltzmann constant.

[15] Kahn, O. *Molecular Magnetism*; VCH: New York, 1993.

[16] Wudl, F.; Bryce, M. R. *J. Chem. Educ.* **1990**, *67*, 717.

S0002-7863(96)03174-5 CCC: $12.00

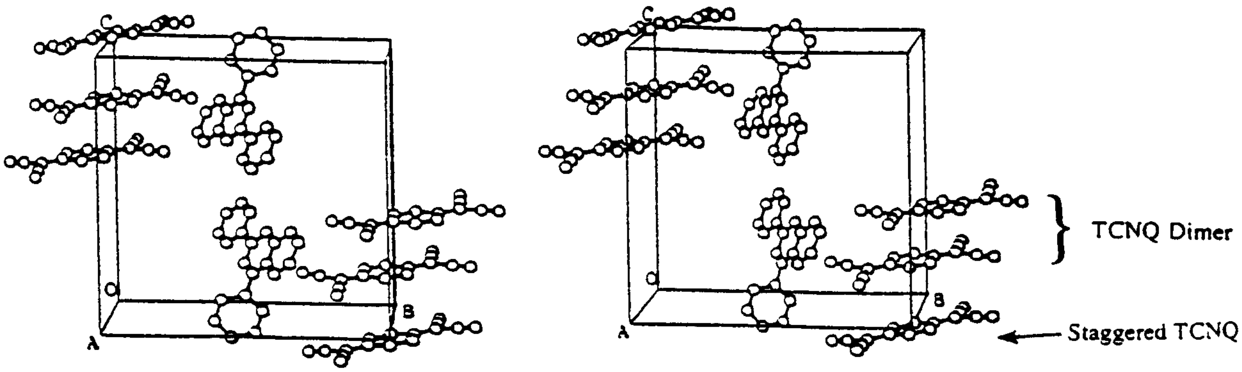


Figure 1. Stereoview of a unit cell of $TCNQ_5DPBT_2$ showing sections of the TCNQ layer and their relation to the cations. Also designated are the TCNQs which form dimers and the staggered TCNQ in the corner of the unit cell.

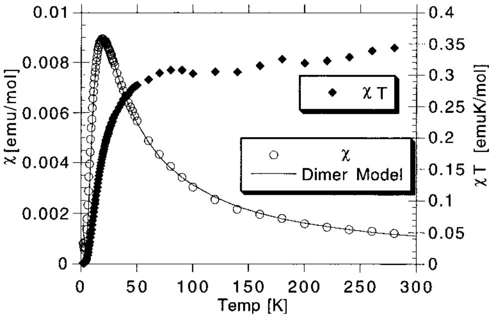


Figure 2. Static magnetic susceptibility and χT as a function of temperature on a powder sample of $(TCNQ)_5(DPBT)_2$. The line through the data points is the calculated susceptibility using the equation of ref 14. In the χT vs T curve there is a slight slope between 270 and ca 50 K which indicates a deviation from Curie−Weiss behavior, behavior usually observed in metals (Pauli susceptibility), not semiconductors.

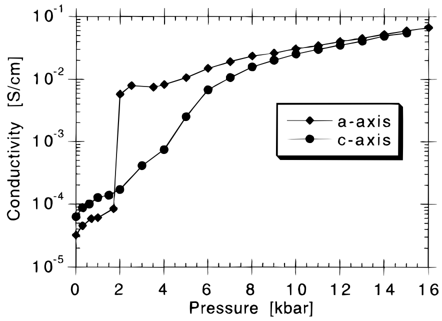


Figure 3. Four-probe single-crystal conductivity of $(TCNQ)_5(DPBT)_2$ as a function of pressure measured along the crystallographic *a* and *c* directions. The conductivity along the *a* axis exhibits a sudden jump at 2 kbar which is apparently due to a phase transition since occasionallyt the crystal broke upon traversing this pressure. The conductivity measured along the *c* axis demonstrated behavior more typical of molecular conductors.

1−0.1 μA, and the current−voltage characteristics were ohmic. It is important to note that σ_a was measured in the direction of *least overlap* of TCNQ molecular orbitals. Thus, the values reported here are those of a two-dimensional system. The σ_{cp} was *higher* than the single-crystal value; an *unprecedented result* but in agreement with pressure dependence results (see below).

High-pressure conductivity measurements showed that σ_a increased by ca. two orders of magnitude when the pressure was increased from 1.8 to 2.1 kbar at room temperature and σ_c increased more gradually. As the pressure was further increased to 15 kbar, σ_a had increased by more than 3 orders of magnitude compared to its value at atmospheric pressure (Figure 3). This large enhancement in σ_a with a minuscule (0.3 kbar) change in pressure is rather unusual in organic charge-transfer complexes, whereas the pressure dependence of σ_c has been observed before.[17−19] Moreover, this pressure-induced enhancement in conductivity is fully reversible and reproducible under pressure cycling.[20] We propose that, as pressure increases, the layers containing the $(TCNQ)_2$ are squeezed together changing the $(TCNQ)_2$ intralayer distances to a uniform intermolecular separation. The result is an increase in orbital overlap with a concomitant reduction of the band gap of the material to zero and obliteration of the built-in Peierls-type[18] intralayer gap.

In conclusion, we have prepared a $D(A)_{2.5}$ CT salt using a neutral, stable free radical as a donor. The CT solid had a structure consisting of $(TCNQ)_2$ layers. Static magnetic susceptibility and ESR measurements showed an antiferromagnetic ordering below 20 K, behavior theoretically ascribable to $(TCNQ)_2$ within the layer. The salt was a semiconductor at room temperature and atmospheric pressure, with a strongly pressure-dependent conductivity. We interpreted the unusual pressure-dependence on the equalization of distances between $(TCNQ)_2$ "molecules" within the layers, which caused an increase in the π-orbital overlap with a concomitant reduction of the band gap and/or removal of a Peierls gap.

Acknowledgment. We thank the National Science Foundation for support through the MRSEC and grants DMR-91-22536, DMR-9500888. K.A.H. thanks the DOD for a National Defense Science and Engineering Graduate Fellowship. We are also indebted to Prof. K. Holczer for help with ESR and magnetic susceptibility.

Supporting Information Available: Crystallographic data and ESR spectra for $(TCNQ)_5(DPBT)_2$ (8 pages). See any current masthead page for ordering and Internet access instructions.

JA963174I

---

(17) Jerome, D.; Schulz, H. J. *Adv. Phys.* **1982**, *31*, 299.

(18) Roth, S. *One Dimensional Metals: Physics and Materials Science*; VCH: Weinheim, 1995.

(19) Williams, J. M.; Ferraro, J. R.; Thorn, R. J.; Carlson, K. D.; Geiser, U.; Wang, H. H.; Kini, A. M.; Whangbo, M.-H. *Organic Superconductors*; Prentice Hall: London, 1992.

(20) On few occasions crystals could not be cycled past 2 kbar pressure without loss of contacts.