nearly as sharply as in other (TMTSF)$_2$X salts.[15] This indicates that spin pairing does not develop effectively in (TMTSF)$_2$ClO$_4$.

The resistivity of six crystals from three different batches were measured by a conventional four probe technique.[17] Figure 3 shows a plot of resisitivity vs. T for two crystals. For all (six) crystals a fairly broad transition into a nonresistive state is observed between 1.5 and 1.2 K. These results, strongly supported by the depression of the transition temperature by small magnetic fields,[18] indicate that the crystals below 1.2 K are superconducting. These findings have been confirmed independently.[19]

The occurrence in the present system of superconductivity, at ambient pressure, demonstrates the sentivity of organic conducting solids to small chemical modifications of the constituent molecules. We emphasize that the isomorphous (TMTSF)$_2$ReO$_4$[20] is insulating below 182 K.[21] We do, however, expect the perrhenate to show ordering of the anions at low temperature.

In conclusion, we have presented evidence for a metallic state at ambient pressure in (TMTSF)$_2$ClO$_4$ and for superconductivity below 1.3 K. We tentatively ascribe the suppression of the metal to insulator transition observed in similar compounds to (a) close packing and (b) disorder effects.

Acknowledgment. It is a pleasure to acknowledge helpful discussions and a long collaboration with D. Jérome. C.S.J. and H.J.P. thank the Danish Natural Science Research Council for financial support.

Supplementary Material Available: Full structural details of (TMTSF)$_2$ClO$_4$ (3 pages). Ordering information is given on any current masthead page.

---

(17) Measurements below 4 K were performed in the mixing chamber of a ^{3}He–^{4}He dilution refrigerator.

(18) Bechgaard, K.; Carneiro, K.; Olsen, M.; Rasmussen, F. B.; Jacobsen, C. S. *Phys. Rev. Lett.*, in press.

(19) Jérome, D., personal communication and ref 5.

(20) (TMTSF)$_2$ReO$_4$: triclinic $P\bar{1}$; $a = 7.281$, $b = 7.748$, $c = 13.484$ Å; $\alpha = 83.22$, $\beta = 86.57$, $\gamma = 70.10°$.

(21) Jacobsen, C. S., to be published.

Degree of Charge Transfer in Organic Conductors by Infrared Absorption Spectroscopy

J. S. Chappell, A. N. Bloch,*,† W. A. Bryden, M. Maxfield,
T. O. Poehler,‡ and D. O. Cowan

Department of Chemistry, The Johns Hopkins University
Baltimore, Maryland 21218

Received December 17, 1980

In order that metallic conductivity occur in an organic molecular crystal of the TTF–TCNQ family, the electronic conduction bands must be populated through transfer of charge between the constituent donor and acceptor molecules.[1] The degree of charge transfer, Z, bears heavily upon the crystal binding energy[2] and the character of the Peierls transition to a periodically distorted semiconductor at low temperatures.[3] Experimentally, Z can be determined from the wavelength of this distortion by using X-ray scattering techniques[4] or from the frequencies of totally symmetric intramolecular vibrations by using resonance Raman spectroscopy.[5] Here we show that the same determination can be made more conveniently by using simple infrared-absorption spectroscopy upon small amounts of material.

The coupling between conduction electrons and intramolecular phonons takes rather different forms for totally symmetric and nontotally symmetric vibrational modes. For totally symmetric modes the coupling term in the Hamiltonian is proportional to the occupancy n_c of the conduction band, the phonon amplitude u along the normal coordinate, and $(\partial E/\partial u)_{u=0}$, where E is the energy of the molecular orbital upon which the conduction band is based. The effect of this term is to mix electron and phonon states, shifting the frequencies of both. Spectroscopically, there results a transfer of oscillator strength to the phonon when the latter's frequency, ω_0, lies in the electronic gap[6] or a Fano[7] line shape when ω_0 overlaps the electronic continuum.[8]

For nontotally symmetric modes, the derivative $(\partial E/\partial u)_{u=0}$ vanishes, and these effects do not occur. Instead, the lowest order coupling term gives rise to a simple shift $\Delta\omega$ in the phonon frequency, proportional (for $kT \ll \hbar\,\omega_0$) to $(\partial^2 E/\partial u^2)_{u=0}$ and n_c.

As examples, we choose the nitrile stretching mode of the TCNQ anion, for several reasons. First, ω_0 occurs at a frequency (ca. 2227 cm^{-1}) overlapping the strong electronic absorption in most conducting TCNQ salts. Since these are nearly one-dimensional conductors, the optical anisotropy in this region of frequency is extreme, and only light polarized perpendicular to the conducting axis is appreciably transmitted. Hence, the nontotally symmetric modes dominate the transmission spectrum of powders or thin single crystals in unpolarized light. Second, $(\partial^2 E/\partial u^2)_{u=0}$ is large for these modes, owing to the population by the conduction electrons of the locally antibonding 3b$_{2g}$ orbital. Third, since $n_c = Z$ in simple TCNQ salts, ω_0 should be a linear function of Z.

In Figure 1 we plot against Z the vibrational frequencies we obtain for powdered samples of 19 TCNQ salts, from transmission spectra measured with a Perkin-Elmer Model 521 Grating Spectrophotometer. The powders were suspended in Nujol mulls or, where material was scarce, in 1.5-mm diameter KBr pellets mounted upon a Perkin–Elmer microsampling beam condenser. No difference was observed between frequencies measured in Nujol and KBr for a given material. The spectra display a small splitting between the frequencies of the infrared active b$_{1g}$ and b$_{2u}$ modes; we consistently chose the higher frequency for Figure 1.

The linearity of Figure 1 extends to the eight measured materials for which Z is independently known; they fall on a straight line of intercept $\omega_0 = 2227$ cm^{-1} and slope $\Delta\omega/Z = -44$ cm^{-1} with correlation coefficient −0.997. We use this line to determine the previously unknown values of Z for 11 other materials, as shown on the figure.

Our analysis obtains provided that ω_0 is not significantly perturbed by the crystalline environment. In metallic TCNQ salts, where the cationic charge is fractional, distributed over an aromatic donor molecule, and screened by the conduction electrons, this is probably a good approximation. The situation is less certain, however, in the insulating alkali metal–TCNQ salts, where the cationic charge is larger, more concentrated, and less effectively screened. This may explain why ω is anomalous (2195 cm^{-1}) for the salt of Li and slightly so (2185 cm^{-1}) for that of Na, approaching the $Z = 1$ intercept of the straight line of Figure 1 only for the salt of the larger K ion (2183 cm^{-1}).

Some other materials represented on the plot deserve comments. Crystallographically, the Cs$_2$(TCNQ)$_3$ salt contains two types of TCNQ, with markedly different sets of internal bond lengths;[9] our spectra show two absorption bands corresponding, respectively,

---

[†] Corporate Research Laboratory, Exxon Research and Engineering Company, Linden, NJ 07036.

[‡] Applied Physics Laboratory, The Johns Hopkins University, Laurel, MD 20810.

(1) See, for example: Bloch, A. N.; Carruthers, T. F.; Poehler, T. O.; Cowan, D. O. "Chemistry and Physics of One-Dimensional Metals"; Keller, H. J., Ed.; Plenum Press: New York, 1977; pp 47–84.

(2) Bloch, A. N., to be published.

(3) See, for example: Lee, P. A.; Rice, M. J.; Anderson, P. W. *Solid State Commun.* **1977**, *14*, 703–708.

(4) Comès, R. "Chemistry and Physics of One-Dimensional Metals"; Keller, H. J., Ed.; Plenum Press: New York, 1977; pp 315–339.

(5) Van Duyne, R. P., private communication.

(6) Rice, M. J. *Phys. Rev. Lett.* **1976**, *37*, 36–39.

(7) Torrance, J. B.; Simonyi, E. E.; Bloch, A. N. *Bull. Am. Phys. Soc.* **1975**, *20*, 497.

(8) Rousseau, D. L.; Butler, M. A.; Guggenheim, H. J.; Weisman, R. B.; Bloch, A. N. *Phys. Rev.* [*Sect.*] *B* **1974**, *10*, 2281–2285.

(9) Fritchie, C. J.; Arthur, P. *Acta Crystallogr.* **1966**, *21*, 139–145.

0002-7863/81/1503-2442$01.25/0

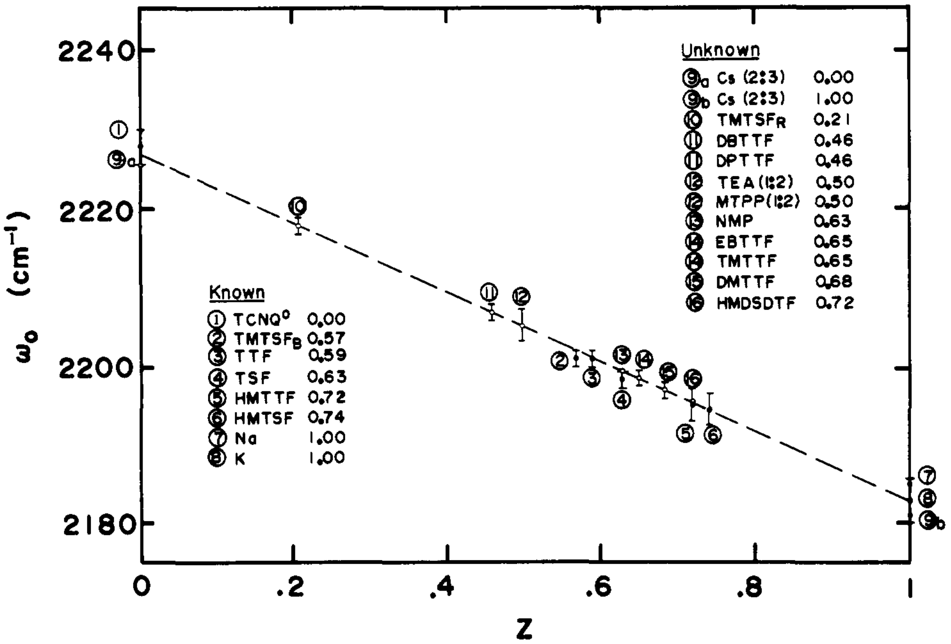


Figure 1. Nitrile stretching frequency, ω_0, vs. Z for 19 TCNQ salts. (●) Z known from independent measurements;[17,19] (○) Z previously unknown.[17]

to TCNQ^0 and TCNQ^{-1}, in 1:2 intensity ratio. On the other hand, despite the crystallographic inequivalence of two TCNQ sites in the methyltriphenylphosphonium (MTPP) and triethylammonium (TEA) salts, we find in both cases only one absorption band corresponding to $Z = 0.50$. We are thereby in agreement with conclusions based on resonance Raman spectroscopy,[5,10] but not with an analysis of X-ray bond lengths.[11]

The value of Z for NMP-TCNQ has been controversial, set at 0.67 by one X-ray diffuse scattering study,[12] at 0.91 by another,[13] and at 0.94 by an NMR analysis.[14] Our result of 0.63 is closest to the first value but must be regarded with caution because the absorption by the antisymmetric modes in our powdered samples is partially obscured by the exceptionally strong Fano effect of the totally symmetric mode in parallel polarization.[15] We suspect in any case that Z in NMP-TCNQ may depend upon the preparation of the sample, possibly because of variable protonation of the NMP.[16]

Our approach is not, of course, limited to TCNQ salts. For example, we have examined a series of salts of tetrafluorotetracyano-*p*-quinodimethan (TCNQF$_4$) and found that the TTF, DBTTF, HMTTF, and HMTSF salts[17] all have $Z = 1.00 \pm 0.04$. As discussed in detail elsewhere,[18] this is consistent with our observation that these salts are Mott insulators, whereas their isostructural TCNQ counterparts, with fractional Z, are metals. Studies of solid solutions between TCNQ and TCNQF$_4$ salts and of other systems are in progress.

---

(10) Matsuzaki, S.; Kuwata, R.; Toyoda, K. *Solid State Commun.* **1980**, *33*, 403-405.

(11) Flandrois, P. S.; Chasseau, D. *Acta Crystallogr., Sect. B* **1977**, *B33*, 2744-2750.

(12) Pouget, J. P.; Megtert, S.; Comès, R.; Epstein, A. J. *Bull. Am. Phys. Soc.* **1973**, *3*, 380.

(13) Ukei, K.; Shirotani, U. *Commun. Phys.* **1977**, *2*, 159-161.

(14) Butler, M. A.; Wudl, F.; Soos, Z. G. *Phys. Rev.* [*Sect.*] *B* **1975**, *12*, 4708-4719.

(15) Torrance, J. B., private communication.

(16) Soos, Z. G.; Keller, H. J.; Moroni, W.; Nöthe, D. "Synthesis and Properties of Low-Dimensional Materials"; Miller, J. S., Epstein, A. J., Ed.; New York Academy of Sciences: New York, 1978; pp. 442-458.

(17) Abbreviations for TCNQ salts: TCNQ^0, tetracyano-*p*-quinodimethan; TMTSF$_B$, tetramethyltetraselenafulvalenium TCNQ (black form); TTF, tetrathiafulvalinium TCNQ; TSF, tetraselenafulvalenium TCNQ; HMTTF, hexamethylenetetrathiafulvalinium TCNQ; HMTSF, hexamethylenetetraselenafulvalenium TCNQ; Na, sodium TCNQ; K, potassium TCNQ; Cs (2:3), (Cs)$_2$(TCNQ)$_3$; TMTSF$_R$, tetramethyltetraselenafulvalinium TCNQ (red form); DBTTF, dibenzotetrathiafulvalinium TCNQ; DPTTF, diphenyltetrathiafulvalinium TCNQ; TEA (1:2), triethylammonium (TCNQ)$_2$; MTPP (1:2), methyltriphenylphosphonium (TCNQ)$_2$; NMP, *N*-methylphenazinium TCNQ; EBTTF, tetrahydrodithinotetrathiafulvalinium TCNQ; TMTTF, tetramethyltetrathiafulvalinium TCNQ; DMTTF, dimethyltetrathiafulvalinium TCNQ; HMDSDTF, hexamethylenediselenadithiafulvalinium TCNQ.

(18) Bloch, A. N. *Bull. Am. Phys. Soc.* **1980**, *25*, 255 and to be published.

(19) Charge-transfer references, TMTSF-TCNQ (black): Pouget, J. P. International Conference on Low Dimensional Synthetic Metals, Helsingør, Denmark, Aug 1980. TTF-TCNQ: see ref 4. TSF-TCNQ and HMTSF-TCNQ: Weyl, C.; Engler, E. M.; Bechgaard, K.; Jehanno, G.; Etemad, S. *Solid State Commun.* **1976**, *19*, 925-930. HMTTF-TCNQ: Megtert, S.; Pouget, J. P.; Commès, R. "Molecular Metals"; Hatfield, W. E., Ed.; Plenum Press: New York, 1978; pp 87-103.

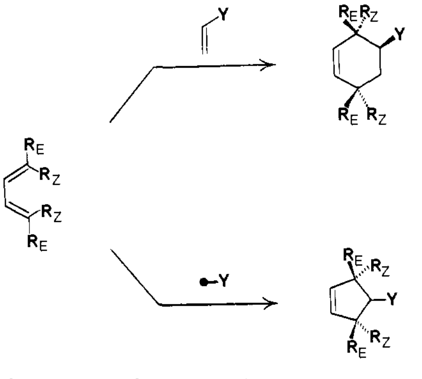
A Stereoselective Synthesis of Cyclopentene Derivatives from 1,3-Dienes

Rick L. Danheiser,* Carlos Martinez-Davila,[†]
Richard J. Auchus,[‡] and James T. Kadonaga[‡]

Department of Chemistry
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

Received December 29, 1980

The Diels-Alder reaction is widely recognized as a remarkably powerful stereoselective method for the construction of six-membered rings (eq 1). An analogous process for the conversion of



(1)

(2)

conjugated dienes to *cyclopentene derivatives* would constitute

---

[†] CONACyT (Mexico) predoctoral fellow.

[‡] M.I.T. Undergraduate Research Opportunities Program participants.

0002-7863/81/1503-2443$01.25/0 © 1981 American Chemical Society