gioselectivities observed in some cycloadditions.[11,12] We propose that these arguments may be extended to form a powerful, general rule of stereoselectivity: *attack of a reagent at an unsaturated site occurs such as to minimize antibonding secondary orbital interactions between the critical frontier molecular orbital of* the *reagent and those of the vicinal bonds.*[13]

A pictorial representation of this is given in Figure 4. The top drawings represent attack of an electrophile syn-periplanar to an allylic bond. Secondary orbital interactions diminish HOMO–LUMO overlap more than in anti-periplanar attack and disfavor this type of attack at both C-1 and C-2. The lower drawings show that syn-periplanar attack by a nucleophile is disfavored at C–2, but favored at C–1, due to secondary orbital interactions. Interactions of a radical SOMO with both HOMO and LUMO are stabilizing. At C–2, both interactions favor anti attack, while at C–1 the two interactions favor opposite stereochemistries. The secondary orbital rationale is supported by similar calculations on H* plus 1,3-pentadiene: attack at C-1 or C-2 shows no stereochemical preference, while attack at C-3 or C-4 of pentadiene follows the same trends reported here for attack at C-1 or C-2 of propene.

Although we have focused on frontier orbital interactions to explain these results, the stereochemical rule found here can be stated in a much more general fashion to be a result of magnified torsional effects occurring in the transition states of addition reactions: *the tendency for staggering of vicinal bonds with respect to partially formed bonds is greater than for fully formed bonds.* Just as conformational preferences in ethane[14] and related molecules[15] can be rationalized on the basis of simultaneous minimization of closed-shell repulsion between bonds[16] and maximization of filled–vacant fragment orbital interactions,[14] the even larger transition-state conformational preferences that we have found can be attributed to enhancement of these effects when one bond is stretched.

The stereochemical rule is related to our recent discovery of a general pattern of alkene pyramidalization induced by asymmetric substituents.[17] That is, asymmetrically substituted alkenes or carbonyls pyramidalize so as to produce a partially staggered conformation.[17,18] This small pyramidalization (e.g., 2.1° for propene optimized in a conformation where one $HC_3C_2C_1$ dihedral angle is constrained to 90°) has a significant influence on the preference for anti-periplanar attack: anti-periplanar attacks of $H^+$ and $H^-$ on planar propene are favored by 3.3 and 3.7 kcal/mol, respectively. For pyramidalized propene, the preference increases to 4.5 and 5.0 kcal/mol, respectively. That is, the slight pyramidalization of the alkene enhances the anti–periplanar preference by 1.2–1.3 kcal/mol.

Aside from providing an explanation for the stereochemical preference for exo attack on norbornene by all types of reagents,[19,20] and giving another viewpoint on the theoretically thoroughly trodden $S_N2'$ reaction,[21] this stereochemical rule has ramificiations in the reactivity realm, as well. For example, (1) the anomalously high reactivities of norbornene derivatives (Huisgen's "factor *x*")[22] can be attributed to the fact that the forming bond(s) in additions or cycloaddtions to norbornenes are more perfectly staggered with respect to allylic bonds than in additions to molecules such as bicyclo[2.2.2]octane. (2) The unusually low reactivities of cyclohexenes relative to cyclopentenes in cycloaddition reactions[20] may be attributed to the $\sim$6 kcal/mol of strain[23] required to distort cyclohexene into a boat conformation which has allylic bonds staggered with respect to forming bonds in cycloaddition transition states. (3) The differences in reactivities of geometrical isomers of acyclic alkenes may be attributed to the differences in energy required to rotate allylic bonds into geometries preferred in transition states,[24] which our model calculations imply will differ from preferred ground-state conformations. (4) The "eclipsed alkene model", which rationalizes the stereochemistry of electrophilic attack on asymmetric alkenes,[1b] should be modified since the preferred geometry of an alkene differs in the isolated molecule and in transition states.

Full details of these effects as well as studies of the influence of polar substituents and reagent structure on magnified torsional effects in addition transition states will be reported in future publications.

**Acknowledgment.** We are grateful to the National Science Foundation and the NATO Research Foundation for financial support of this research, Professor E. M. Burgess for extensive discussions, and Professor John A. Pople for the use of GAUSSIAN 80 for MP2 calculations.

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# Superconductivity in an Organic Solid. Synthesis, Structure, and Conductivity of Bis(tetramethyltetraselenafulvalenium) Perchlorate, $(TMTSF)_2ClO_4$

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Recently it was reported that a series of quasi-one-dimensional organic cation radical salts $(TMTSF)_2X$,[1] where X is a symmetrical octahedral anion, $PF_6^-$,[2,3] $AsF_6^-$,[4] $SbF_6^-$,[5] and $TaF_6^-$,[5] exhibit

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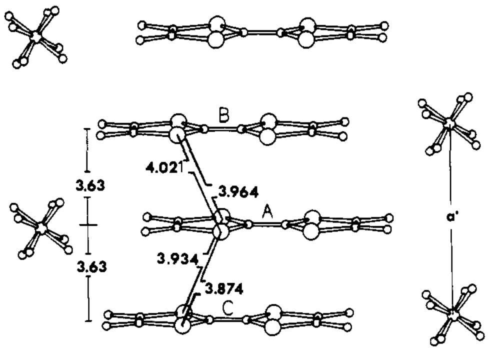


**Figure 1.** Side view of the stacks in $(TMTSF)_2ClO_4$ (tilted 10°). a' is the projection of a. Each contact between two TMTSF molecules occurs twice because of the inversion center midway between the units. The symmetry operations are A($x$,$y$,$z$), B($1 - x$, $1 - y$, $1 - z$), and C($-x$, $1 - y$, $1 - z$).

superconductivity at moderate hydrostatic pressures of 1.2 GPa in the 0.4–1.5-K region. In these materials pressure suppresses a metal to insulator transition occurring between 10 and 20 K at ambient pressure. For X = $PF_6^-$, the findings have been confirmed indpendently.[6,7]

We have prepared TMTSF salts with symmetrical, tetrahedral anions because of the following reasons: (a) The tetrahedral anions can be smaller than the above-mentioned octahedral anions, thereby resulting in a closer packing of the solid and maybe mimicking the effect of pressure. (b) In the triclinic structure of $(TMTSF)_2PF_6$,[8] $PF_6^-$ resides in a center of inversion. The tetrahedral anion will in a similar structure (by lacking the inversion symmetry) either introduce anion disorder or, by ordering, change the periodicity of the lattice. Disorder can prevent or smear the metal to insulator transition, whereas anion order may open a gap at the Fermi level.

The experimental results for tetrahedral $X^-$ are diverging. $(TMTSF)_2BF_4$[1] and $(TMTSF)_2ReO_4$ are insulating below 41 and 182 K, respectively. $(TMTSF)_2ClO_4$ in contrast remains metallic down to 1.3–1.5 K, where a transition into a superconducting state occurs in all measured crystals. The significance of this observation lies in the fact that chemical modification can stabilize a superconducting state. So far only pressure could stabilize low-temperature metallic[9] and superconducting states[2,4,5] in molecular metals.

Single crystals of $(TMTSF)_2ClO_4$ were obtained by electrochemical oxidation[10] of TMTSF[11,12] according to

$$2n\mathrm{TMTSF} + n\mathrm{ClO_4}^- \xrightarrow{ne} [(\mathrm{TMTSF})_2\mathrm{ClO_4}]_n$$

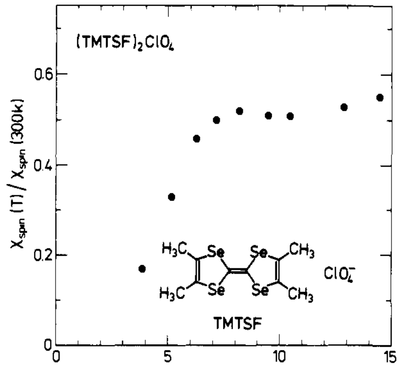
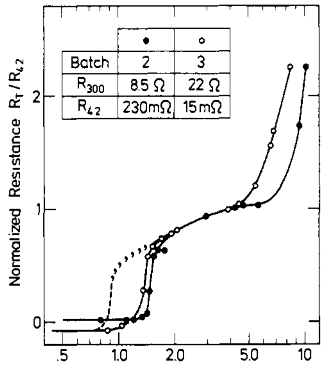


**Figure 2.** Molecular constituents and intensity of the EPR line of $(TMTSF)_2ClO_4$ normalized over the 300 K value.



|  | ● | ○ |
|---|---|---|
| Batch | 2 | 3 |
| $R_{300}$ | 8.5 Ω | 22 Ω |
| $R_{4.2}$ | 230mΩ | 15mΩ |

**Figure 3.** Normalized resistance vs. $T$ for two crystals from different batches. (The apparent negative or positive resistance below the transition is considered an artifact of the electrical contacts and circuit, due to its dependence on frequency, current, and sample.) The dashed line shows the results for $C_3$ in a perpendicular magnetic field of 0.03 T.

The structure of $(TMTSF)_2ClO_4$[13] is similar to that of the congener $(TMTSF)_2PF_6$.[8] $(TMTSF)_2ClO_4$ crystallizes in the triclinic space group $P\bar{1}$,[11] with unit cell parameters $a = 7.266$, $b = 7.678$, $c = 13.275$ Å; $\alpha = 84.58$, $\beta = 86.73$ and $\gamma = 70.43°$. The packing motif is one of segregated columns along a. Figure 1 shows a side view of the structure emphasizing the slight dimerization of the nearly planar TMTSF molecules. The dimerization leads to a gap in the band structure, but not at the Fermi level in this formally half-filled band metal.[8] The perchlorate ions are disordered, and the oxygens occupy eight nearly equivalent positions at random. Preliminary, low-temperature X-ray diffuse scattering indicates that no ordering occurs at least down to 15 K.[14] The unit cell of 694.3 $Å^3$ is smaller than that of $(TMTSF)_2PF_6$ (714.3 $Å^3$). Also a slight compression along a (7.266 Å vs. 7.297 Å) is noticed.

In several one-dimensional conductors the metal to insulator transition is the effect of an electronically driven (Peierls) structural transition. In the $(TMTSF)_2X$ series no evidence is found for a similar structural relationship.[4] In the $(TMTSF)_2X$ compounds the resistivity anomaly is reflected in the free-spin susceptibility[15] and has been shown to be related to antiferromagnetic ordering.[16] The magnetic anomaly occurs, in the previously described $(TMTSF)_2X$ salts, close to the metal to insulator transition temperature. In $(TMTSF)_2ClO_4$ the susceptibility decreases rapidly below 6 K (see Figure 2) but not

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(10) TMTSF was purified by two gradient sublimations onto Teflon (165 °C, $10^{-5}$ torr). 1,2,2-Trichloroethane (Fluka) was redestilled twice and better than 99.9% by GC. The solvent was dried by passage through basic alumina (Woelm, Super I) and deoxygenated by purging with argon. $n$-$Bu_4NClO_4$ was prepared by anion exchange from the hydrosulfate and recrystallized from methanol–water (1:1) seven times and vacuum dried. $(TMTSF)_2ClO_4$ was prepared by anodic oxidation of 10 mL of a $10^{-3}$ M solution of TMTSF in trichloroethane containing $n$-$Bu_4NClO_4$ (0.10–0.12 M) under exclusion of air, light, and moisture. Electrode area = 0.25 $cm^2$ (platinum rod), $I = 5$ μA, $T = 25$ °C, conversion < 60%. Anal. Calcd for two single crystals: C, 24.12; H, 2.42. Found: C, 23.99, 24.05; H, 2.48, 2.52. Anal. Calcd: Cl, 3.56. Found: Cl, 3.60. $(TMTSF)_2ReO_4$ was prepared under similar conditions.

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nearly as sharply as in other $(TMTSF)_2X$ salts.[15] This indicates that spin pairing does not develop effectively in $(TMTSF)_2ClO_4$.

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 $(TMTSF)_2ReO_4$[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 $(TMTSF)_2ClO_4$ 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. Jērome. C.S.J. and H.J.P. thank the Danish Natural Science Research Council for financial support.

**Supplementary Material Available:** Full structural details of $(TMTSF)_2ClO_4$ (3 pages). Ordering information is given on any current masthead page.

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

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

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# Degree of Charge Transfer in Organic Conductors by Infrared Absorption Spectroscopy

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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, $\omega_0$, lies in the electronic gap[6] or a Fano[7] line shape when $\omega_0$ 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, $\omega_0$ 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, $\omega_0$ 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 $\omega_0$ 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 $\omega$ 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,

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