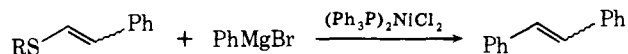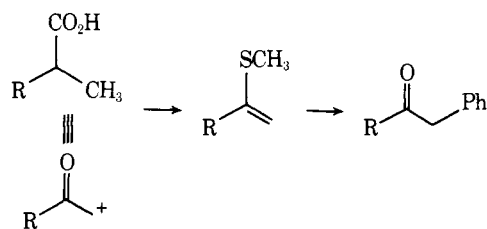**17**   **18**

acetates and enol ethers also give the reaction special merit. The intermolecular palladium-catalyzed reaction of enol thioethers contrasts with the recent report of the nickel-cata-

lyzed reaction of these compounds where the opposite regiochemistry was observed. Thus, the two methods complement one another.

The utility of these observations is demonstrated by the very mild cyclization conditions and the net arylation α to a carbonyl group.[9,10] The widespread availability of enol thioethers by addition of sulfur-stabilized anions to carbonyl groups,[11] addition of RSX to olefins followed by elimination of HX,[12] reaction of vinyllithium reagents with disulfides,[13] isomerization of allyl sulfides,[5] metalation and alkylation of phenylvinyl sulfide,[14] rearrangement of 1-phenylthio-1-vinylcyclopropanes,[15] oxidative decarboxylation of α-thio acids,[6] etc., allows a whole host of substrates to serve as enolonium equivalents. This is shown explicitly for one case below (see entry 6, Table I). The unique role of sulfur in organometallic reac-

tions appears to be an exciting one for further exploitation.

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Structure and Dynamic Behavior of *n*-Propyllithium from ¹³C, ⁷Li, and ⁶Li NMR

Sir:

Alkyllithium compounds in hydrocarbon solvents exist as tetramers[1] and hexamers[2] and undergo a variety of dynamic processes including fast inversion at carbon[3] and carbon-lithium bond exchange.[3,4]
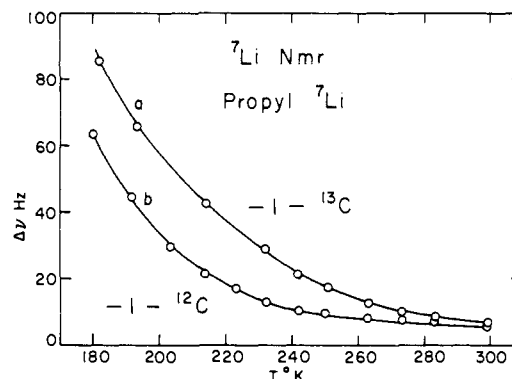

Figure 1. ⁷Li NMR, 23.37 MHz, line widths for *n*-propyllithium (lower) and *n*-propyllithium-*1*-¹³C (upper), both 0.6 M in cyclopentane.
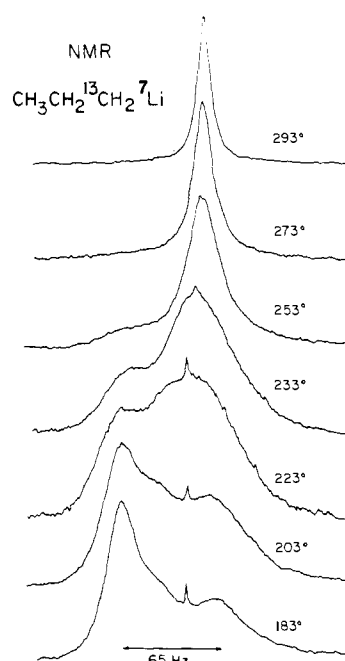

Figure 2. ¹³C NMR, 22.03 MHz, of C₁ of *n*-propyllithium-*1*-¹³C, 0.6 M in cyclopentane, different temperatures.

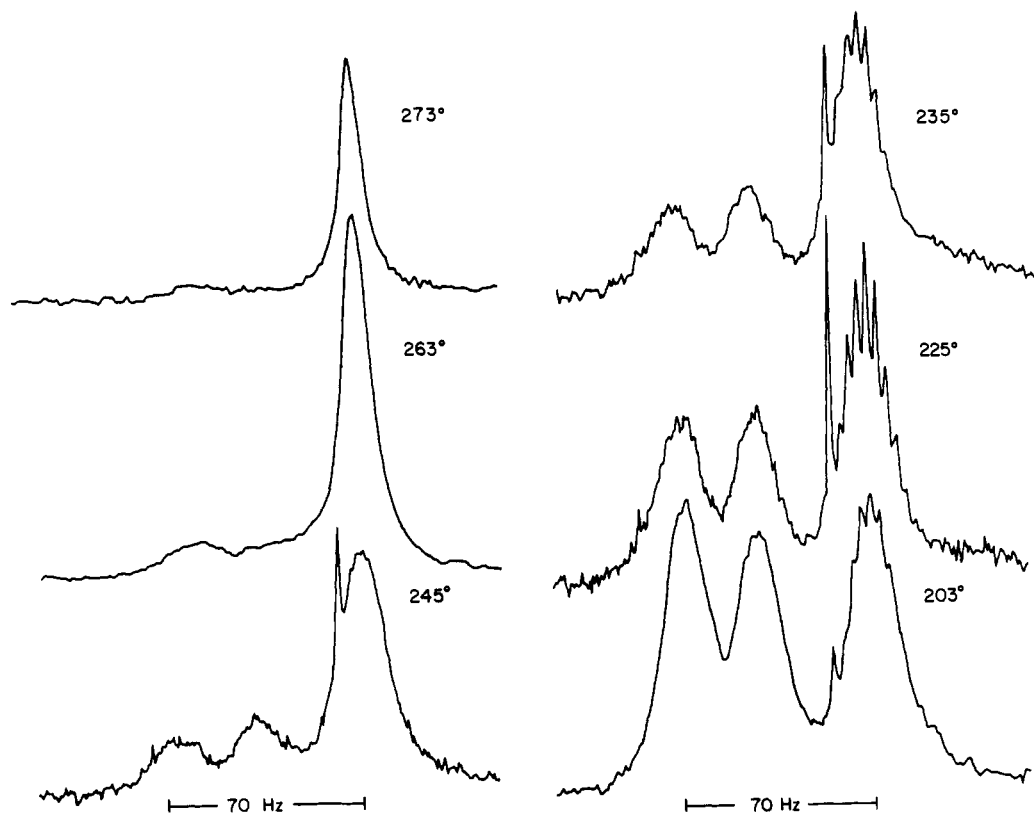**Figure 3.** ^{13}C NMR, 22.03 MHz, of C_1 of n-propyllithium-1-^{13}C-^6Li, 0.6 M in cyclopentane, different temperatures..

It is well known that the C_1 ^{13}C NMR of alkyllithiums in hydrocarbon solvents undergoes broadening[5] at low temperatures and often does not exhibit the splitting due to ^{13}C,^{7}Li coupling, seen using ether solutions.[6] This behavior is best ascribed to averaging of the ^{13}C,^{7}Li coupling by a combination of carbon–lithium bond exchange and lithium-7 quadrupole relaxation.[7] We have now confirmed this proposal using NMR of samples of n-propyllithium variously enriched in ^{13}C and ^{6}Li. It will be shown below that ^{6}Li quadrupole relaxation[8a] in these species is too slow to perturb the spectra; hence, these provide clear information on ^{13}C,^{6}Li coupling, RLi association, and dynamic behavior.[8b]

The ^{7}Li NMR spectrum[9] of n-propyllithium (**1**, 0.57 M in cyclopentane) consists of a single line which broadens with decreasing temperature; see Figure 1. Under the same conditions, a sample of n-propyllithium-1-^{13}C (90% enriched, **2**) behaves in a similar manner (Figure 1) except the line is *always broader* than that of the unlabeled compound. The ^{13}C NMR of the enriched sample, **2**, shows shifts (TMS) at 17.0 (C_1), 23.28 (C_2), 23.04 ppm (C_3) ($J(C_1$, H$) = 96.7$ and $J(C_1,C_2) = 22.7$ Hz). As seen in Figure 2, the C_1 ^{13}C NMR of **2** broadens with decreasing temperature to $\sim$40 Hz by -40 °C. Below this temperature a second absorption (indicative of a new RLi aggregate) appears to lower field and its area increases at the expense of the first-mentioned peak as the sample is cooled further. At no point is there any line splitting indicative of ^{13}C,^{7}Li coupling. However, the ^{7}Li NMR data in Figure 1 implicate the operation of ^{13}C,^{7}Li coupling. The results just described are most consistent with a system wherein fast interaggregate carbon–lithium bond exchange averages the ^{13}C,^{7}Li coupling at the higher temperatures, thus narrowing the ^{13}C resonance of C_1 while lithium-7 quadrupolar relaxation, faster at lower temperatures, causes partial averaging of the ^{13}C,^{7}Li coupling when exchange is slow. The large ^{7}Li line widths seen for **1** support this proposal. One might expect very fast quadrupole relaxation to decouple ^{7}Li from

$^{13}C_1$ entirely. Evidently, this temperature is lower than can be practically reached in our experiments.

The scheme, given above, has now been confirmed by use of n-propyllithium-1-^{13}C-^6Li (^{13}C enriched by 90%, ^{6}Li, by 95%) (**3**). Accordingly, **3** and **4** (enriched only in ^{6}Li) were both prepared as 0.6 M solutions in cyclopentane using a sample of lithium enriched in ^{6}Li (96% Li, the rest ^{7}Li). These samples were purified by distillation on a vacuum system. The ^{6}Li NMR[9] of **4** is a single narrow line, <1 Hz wide indicating slow relaxation. The ^{13}C NMR of **3** (enriched in $^{13}C_1$) (Figure 3) shows similar behavior to that of **2** except now the upfield resonance is clearly split into more than nine lines, separation 3.5 Hz, and the new resonance to lower field consists of two main absorptions, each with many overlapping lines. The intensity ratios of the upfield multiplet are most consistent with a system wherein each $^{13}C_1$ is coupled to six ^{6}Li's, that is, a hexameric[11] aggregate undergoing fast internal carbon–lithium bond exchange.[12] This would give the intensity ratio 1:6:21:50:90:126:140:126:90:50:21:6:1. Counting shoulders one can see nine lines. The other four would be too weak to detect.

Altogether we have found propyllithium to undergo fast intraaggregate carbon–lithium bond exchange to at least -80 °C and interaggregate exchange at higher temperatures. Evidence has been uncovered for different species which become dominant at the lower temperatures. NMR of organolithium compounds enriched in ^{6}Li and ^{13}C (at C_1) is by far the superior of alkyllithiums. It should apply in similar fashion to all lithium compounds containing at least partially covalent carbon·lithium bonds.

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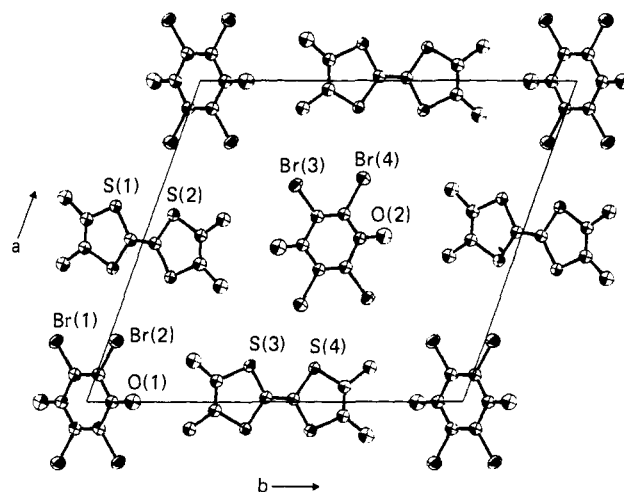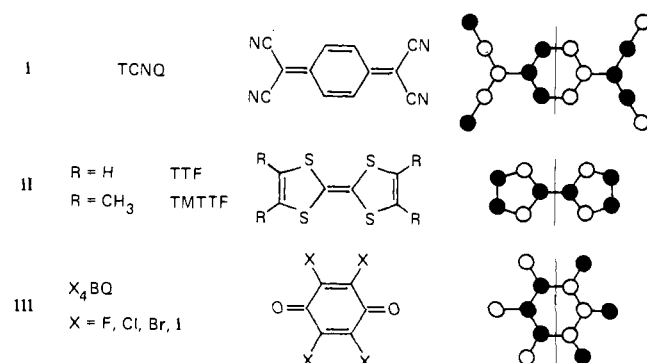Department of Chemistry, The Ohio State University
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Figure 1. Projection of the structure of TMTTF-bromanil onto the a–b plane, showing the relationships between the segregated stacks of TMTTF and bromanil (coming out of the plane of the figure).

Table I. Values for the Pressed Powder Conductivities at 300 K for the TTF and TMTTF Salts of the Tetrahalo-p-benzoquinones (X = halogen) and, for comparison, those of TCNQ. For Salts with Multiple Phases, the Higher Conductivity Is Tabulated

σ(300 K)	X = F	X = Cl	X = Br	TCNQ
TTF	10	8×10^{-4}	6×10^{-4}	70
TMTTF	7	20	1	35

A New Class of Highly Conducting Organic Materials: Charge-Transfer Salts of the Tetrathiafulvalenes with the Tetrahalo-p-benzoquinones

Sir:

In organic solids with high electrical conductivity, the acceptor tetracyano-p-quinodimethane (TCNQ, I) has played a unique role in that, until now, all charge-transfer salts containing both an organic donor and acceptor in a 1:1 ratio that have exhibited high electrical conductivity ($\sigma > 1 \; \Omega^{-1} \; cm^{-1}$) have contained TCNQ or one of its close derivatives as the acceptor.[1-3]

In order to formulate guidelines for selecting other pairs of donor and acceptor molecules that would form new highly conducting salts, we have been investigating[3,4] those complementary features that the members must possess in order to meet the two essential prerequisites for high conductivity, namely, segregated stacking of donors and acceptors and incomplete transfer of charge between these species.[2,3] The requirement of segregated stacks is a difficult one to satisfy, since most charge-transfer solids crystallize[1,5] in mixed stacks, i.e.,

Scheme I

in which donor and acceptor molecules alternate. The approach[4] that we have followed is one of attempting to inhibit good donor–acceptor orbital overlap, thereby minimizing the Mulliken charge-transfer interaction that stabilizes such mixed stacks, with the idea that segregated stacks might be formed by default. One way of creating unfavorable donor–acceptor overlap is to select a pair of molecules such that the relevant frontier orbitals (HOMO of the donor and LUMO of the acceptor, shown schematically (Scheme I) for molecules I, II and III) are of different symmetry with respect to inversion. To meet the criterion of partial charge transfer, we have used[2,3] electrochemical half-wave potentials as a relative measure of the ionization potential of the donor and the electron affinity of the acceptor. These values, combined with consideration of the electrostatic crystalline binding energy, can be used as a crude guide for selecting molecules[3] such that the degree of charge transfer will be between zero (neutral molecular solid) and one (complete charge transfer, fully ionic solid).

One combination of molecules that appears to possess these complementary properties, i.e., frontier orbitals of opposite symmetry and promising match of redox properties, are the tetrathiafulvalene (TTF, II) family of donors and the tetrahalo-p-benzoquinone (III) family of acceptors. We have found[6] that TTF and TMTTF (tetramethyl-TTF) form charge-transfer compounds of 1:1 composition with each of the tetrahalo-p-benzoquinones. Furthermore, nearly every combination of donor and acceptor forms at least two distinct phases.[4,7] In this communication we shall discuss only those salts which are highly conducting.

The materials discussed here were generally prepared by mixing acetonitrile solutions of the donor and acceptor together at the boiling point of the solvent and cooling to room temperature. The pressed powder conductivities of the resulting salts are summarized in Table I, along with corresponding values measured for TTF–TCNQ[8] and TMTTF–TCNQ.[9] It should be noted that four of these new compounds (Table I)