encompassing both units. Indeed, one can envisage an appropriate combination of the b_{1u} π-orbitals, in which the unpaired electrons in TTF^+ presumably lie,[12] thus leading to a net bonding interaction in this configuration.

These $(TTF^+)_2$ units are connected in the structure by neutral TTF molecules along both the [010] and [001] directions in the monoclinic unit cell, resulting in a two-dimensional network of TTF units parallel to the (100) plane.

Four-probe dc conductivity measurements were carried out as a function of both temperature and crystallographic direction in this material. The conductivity was found to be thermally activated and to exhibit a linear log σ vs. $1/T$ dependence with a thermal activation energy of 0.23 ± 0.02 eV along both the [010] and [001] directions. The dc conductivities at 25° along [010] and [001] are 7.4×10^{-3} and 2.7×10^{-4} ohm^{-1} cm^{-1}, respectively, both of which are appreciably higher than the conductivities of either TTF[13] or $NiS_4C_4H_4$[4] alone. The conductivity perpendicular to the (100) plane has not yet been accurately determined but appears to be at least an order of magnitude lower than that in the (100) plane.

The interactions between TTF units suggested by the structural and property studies reported herein appear to be unprecedented both in the context of prior experience with TTF derivatives and with organic molecular solids in general. Further studies of these unusual materials are in progress.

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Crystal Structure of $(TTF)_2NiS_4C_4H_4$

Sir:

In the preceding paper[1] the synthesis and properties of some new donor–acceptor compounds of tetrathiafulvalene (TTF) with bis(dithiolene) (BDT) metal complexes are described. We report here preliminary information regarding the crystal structure of one of these compounds, $(TTF)_2NiS_4C_4H_4$.

The three-dimensional structure determination was made with crystals grown by slow cooling from acetonitrile solution and utilizing 1491 independent X-ray intensities collected on an automated GE 490 diffractometer with monochromatized Mo Kα (λ 0.71069 Å) radiation.

The crystal system is monoclinic with $a = 25.80$ (2) Å, $b = 10.67$ (1) Å, $c = 9.990$ (5) Å, $\beta = 119.67$ (5)°, and space group $C2/m$. There are four $(TTF)_2NiS_4C_4H_4$ formula units per unit cell. The structure was solved by Patterson and Fourier syntheses and refined by least-squares calculations.

The locations of the centers of the molecules are shown in Table I. At the present level of refinement ($R = 0.12$ (F^2 basis)) all structural parameters (except for hydrogen atoms) are adequately known for a proper description of the arrangement of the constituent molecules. In particular the nickel and sulfur positions are indicated to be determined to within 0.01 Å. Further refinement incorporating additional data is underway to enable precise specification of intramolecular bond distances and angles involving the carbon and hydrogen atoms.

The structure consists then of three crystallographically distinct types of TTF units that occur in strips parallel to (100) and which alternate with strips containing $NiS_4C_4H_4$ units (Figure 1). The molecular planes of the crystallographically equivalent $NiS_4C_4H_4$ units are themselves parallel to (100) and the long dimension of the molecule is parallel to [001]. Two of the different TTF units are contained in a columnar stacking (Figure 2) along [010] with their planes at $y = 0$ (type I) and $y = 0.34$ and 0.66 (type II). While the molecular planes of these TTF units are all perpendicular to [010], those at $y = 0.34$ and $y = 0.66$ are rotated by about 60° with respect to those at $y = 0$. The two units at $y = 0.34$ and $y = 0.66$ are then in a fully eclipsed configuration with somewhat short intermolecular S–S contacts of 3.48 Å.

This unusual eclipsed arrangement of TTF units with S–S contacts appreciably shorter than the usual van der Waals separations is strongly suggestive of an appreciable intermolecular association. The significance of this "dimer unit," particularly in aiding the understanding of some of the unusual physical properties, is discussed in the preceding paper.[1]

A similar eclipsed arrangement of planar units has been observed in a crystal structure study of the $[MS_4C_4H_4]_2$ (M = Pd, Pt) complexes[2] where, interplanar S–S separations of about 3.0 Å occur to yield an approximately cubic array of S atoms. This close analogy in molecular structure also extends to the component planar units which differ

Table I

	x	y	z
Ni	± (0.197	0	0.170)
(center of $NiS_4C_4H_4$ unit)	± (0.697	½	0.170)
TTF (I)	0	0	½
	½	½	½
TTF (II)	± (0	0.337	½)
	± (½	0.837	½)
TTF (III)	0	½	0
	½	0	0

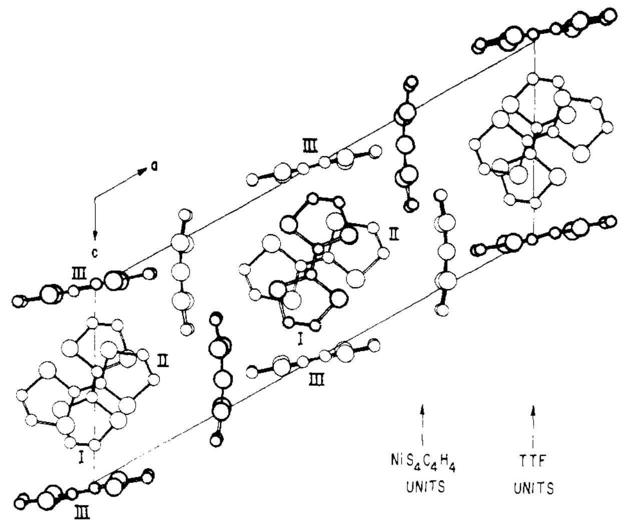

Figure 1. The unit cell of the $(TTF)_2NiS_4C_4H_4$ crystal structure viewed down [010]. The molecules whose centers are at $y = \frac{1}{2}$ are darkened; except for molecules labeled II, all other molecules have their centers at $y = 0$. The three types of TTF units discussed in the text are identified by Roman numerals.

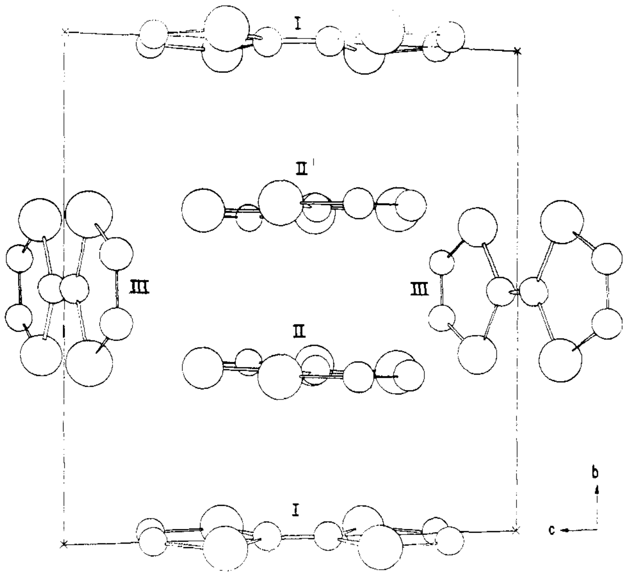

Figure 2. A view of the $(TTF)_2NiS_4C_4H_4$ structure normal to (100) showing the three types of TTF molecules (labeled I, II, and III).

principally in the replacement of a metal atom by a C=C unit.

The third type of TTF unit (type III) is centered at 0 ½ 0 and has its molecular plane oriented perpendicular to both the TTF units in the columnar stacks and the $NiS_4C_4H_4$ units. Two of the S atoms in this TTF unit make rather close contacts (3.5 Å) with S atoms of the type II TTF units on either side of the molecular plane effectively bridging the stacks of TTF molecules together along the [001] direction.

The two-dimensional character of the arrangement of TTF units is manifested in the observed variation of electrical conductivity with crystallographic direction. An appreciable electron delocalization along both [010] and [001] is indicated by such measurements.[1]

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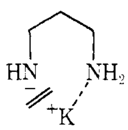
The Acetylene Zipper. An Exceptionally Facile "Contrathermodynamic" Multipositional Isomerization of Alkynes with Potassium 3-Aminopropylamide[1]

Sir:

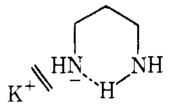
Potassium 3-aminopropylamide (KAPA), a readily prepared difunctional "superbase," exhibits exceptional activity in prototropic reactions. KAPA produces exceptionally rapid migrations of triple bonds from the interior to the terminus of the carbon chain *in seconds at 0°*.

Base-catalyzed isomerizations of 2-alkynes to 1-alkynes have been reported with very strong bases: sodium[2,3] (4.5 hr, 100°, accompanied by substantial polymerization), $NaNH_2$ in aromatic hydrocarbons[4] (1.5-2 hr, 160°), and, recently, KNH_2-NH_3-HMPA[5] (0.5-1 hr, room temperature). Migrations of two or more positions have been observed with $NaNH_2$ but required even more vigorous conditions with diminished returns. Weaker bases—even potassium *tert*-butoxide or methyl sulfinyl methide (dimsyl) in dimethyl sulfoxide—do not produce the Δ^2 to Δ^1 migration.[5-7] As the equilibrium in linear alkynes has been shown to favor heavily the internal isomers,[8,9] these internal-to-terminal migrations are "contrathermodynamic" overall, presumably reflecting formation of the stable acetylide ion assisted possibly by precipitation of the metal acetylide.

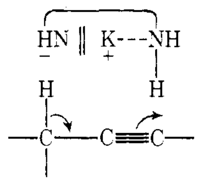
KAPA is rapidly formed by quantitative reaction of KH with excess 3-aminopropylamine (APA, trimethylenediamine). This alkylamide—in contrast to alkylamides of monofunctional amines—is quite soluble in excess amine (≥1.5 *M*), forming solutions which appear stable for at least 8 hr at room temperature. The high solubility may result from the higher solvating power of the diamine or "internal solvation" of the amide (I, II). Structures such as I and II are potentially favorable for concerted isomerizations (III).[10]



I



II



III

The KAPA-APA system proved exceptionally active both for isomerization of 2,4,4-trimethyl-1-pentene (10^4-10^5 times as reactive as KO-*t*-Bu-DMSO,[11a] based on k_ψ at 0.7 *M*) and for exchange of C-D in deuteriobenzene (10^3-10^4 times as reactive as lithium cyclohexylamide in cyclohexylamine,[11b] based on k_2).

This activity has proven exceptionally useful in "contrathermodynamic" migrations of triple bonds. In sharp contrast to the previously reported isomerizations, addition of an alkyne (IV) to KAPA (1.25 equiv, 1.0 *M* in APA) at 20° results in almost instantaneous precipitation of the potassium acetylide (V); hydrolysis yields the 1-alkyne (VI) in