

Research Council of Canada and the Sloan Foundation is gratefully acknowledged.

## References and Notes

- (1) Alfred P. Sloan Research Fellow, 1974–1976.
- (2) P. Baybutt, *Mol. Phys.*, **29**, 389 (1975).
- (3) P. Baybutt, *Chem. Phys. Lett.*, **30**, 293 (1975).
- (4) D. L. Willite and L. Splinter, *J. Am. Chem. Soc.*, **95**, 2100 (1973).
- (5) A. Dedieu and A. Vellard, *J. Am. Chem. Soc.*, **94**, 6730 (1972).
- (6) R. F. W. Bader, A. J. Duke, and R. R. Messer, *J. Am. Chem. Soc.*, **95**, 7715 (1973).
- (7) W. Th. A. M. Van der Lugt and P. Ros, *Chem. Phys. Lett.*, **4**, 389 (1969).
- (8) C. D. Ritchie and G. A. Chappell, *J. Am. Chem. Soc.*, **92**, 1819 (1970).
- (9) J. J. C. Mulder and J. S. Wright, *Chem. Phys. Lett.*, **5**, 445 (1970).
- (10) L. P. Lowe, *J. Am. Chem. Soc.*, **93**, 301 (1971).
- (11) P. Cremaschi, A. Gamba, and M. Simonetta, *Theor. Chim. Acta*, **25**, 237 (1972).
- (12) D. K. Bohme and L. B. Young, *J. Am. Chem. Soc.*, **92**, 7354 (1970).
- (13) L. B. Young, E. Lee-Ruff, and D. K. Bohme, *J. Chem. Soc., Chem. Commun.*, 35 (1973).
- (14) D. K. Bohme, G. I. Mackay, and J. D. Payzant, *J. Am. Chem. Soc.*, **96**, 4027 (1974).
- (15) J. I. Brauman, W. N. Olmstead, and C. A. Lieder, *J. Am. Chem. Soc.*, **96**, 4030 (1974).
- (16) D. K. Bohme, R. S. Hemsworth, H. W. Rundle, and H. I. Schliff, *J. Chem. Phys.*, **58**, 3504 (1973).
- (17) G. Giourmoussis and D. P. Stevenson, *J. Chem. Phys.*, **29**, 294 (1958).
- (18) E. R. Lippincott and J. M. Stutman, *J. Phys. Chem.*, **68**, 2926 (1964).
- (19) E. W. Rothe and R. B. Bernstein, *J. Chem. Phys.*, **31**, 1619 (1959).
- (20) D. K. Bohme, E. Lee-Ruff, and L. Brewster Young, *J. Am. Chem. Soc.*, **94**, 5153 (1972).
- (21) H. I. Schliff and D. K. Bohme, *Int. J. Mass Spectrom. Ion Phys.*, **16**, 167 (1975).
- (22) N. C. Barford, "Experimental Measurements: Precision, Error and Truth", Addison-Wesley, London, 1967.
- (23) J. I. Brauman, J. R. Eyley, L. K. Blair, M. J. White, M. B. Comisarow, and K. C. Smyth, *J. Am. Chem. Soc.*, **93**, 6360 (1971).
- (24) This is a lower limit since our experimental technique discriminates against the athermal channel:  $D^- + SiH_4 \rightarrow SiH_4D^- \rightarrow SiH_4 + D^-$ .
- (25) An energy barrier of 8.6 kcal mol<sup>-1</sup> should, at the thermal energies of these experiments, give rise to an activation energy >8.6 kcal mol<sup>-1</sup>.<sup>26</sup>
- (26) M. Menzinger and R. Wolfgang, *Angew. Chem., Int. Ed. Engl.*, **8**, 438 (1969).
- (27) Our measurements which were all made at a single temperature do not provide a direct measure of the activation energy which would, of course, require measurements at several temperatures.
- (28) B. DeB. Darwent, *Nat. Stand. Ref. Data Ser., Nat. Bur. Stand.*, **31** (1970).
- (29) JANAF Thermochemical Tables, 2d ed, *Nat. Stand. Ref. Data Ser., Nat. Bur. Stand.*, **37** (1971).
- (30) K. J. Reed and J. I. Brauman, *J. Chem. Phys.*, **61**, 4830 (1974).
- (31) D. K. Bohme in "Interactions between Ions and Molecules", P. Ausloos, Ed., Plenum Press, New York, N.Y., 1975.

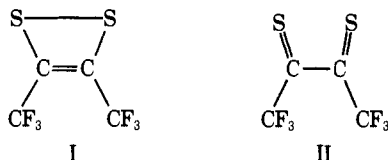
# Molecular Structure of 1,2-Bis(trifluoromethyl)dithiete by Vapor Phase Electron Diffraction

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**Abstract:** The molecular structure of 1,2-bis(trifluoromethyl)dithiete has been determined in the vapor phase by electron diffraction. The results confirm the dithiete structure, in which the principal geometrical parameters, based on  $C_2$  symmetry, are:  $r_g(C-F) = 1.326 \pm 0.003$ ,  $r_g(C=C) = 1.40 \pm 0.03$ ,  $r_g(C-C) = 1.50 \pm 0.01$ ,  $r_g(S-C) = 1.73 \pm 0.01$ ,  $r_g(S-S) = 2.05 \pm 0.01$  Å;  $\angle(C=C-S) = 100.8 \pm 0.6$ ,  $\angle(C=C-C) = 122.9 \pm 0.7$ ,  $\angle(F-C-C) = 110.8 \pm 0.6^\circ$ . The rotational parameter  $\tau(S-C-C-S) = 0.4 \pm 3.4^\circ$  indicates no significant deviation from planarity in the  $C_2S_2$  ring excluding shrinkage effects which were not included in the analysis. The  $CF_3$  groups are semistaggered, rotated about the C—C bonds by  $34 \pm 6^\circ$  relative to planar trans F—C—C=C. The quoted uncertainties represent the estimated limits of experimental errors. A comparison with other structures suggests delocalization of the carbon-carbon  $\pi$  system to include the sulfur atoms, but without appreciable participation of the S—S bond.

1,2-Bis(trifluoromethyl)dithiete was the first compound synthesized in which the unusual dithiete ring<sup>1</sup> could be postulated. Infrared and <sup>19</sup>F NMR spectra<sup>2</sup> revealed the presence of a C=C bond, and showed that the  $CF_3$  groups are attached to a doubly bonded carbon atom, but the red color of the compound prevented any observation of the sulfur-sulfur vibrations by Raman spectroscopy. Simple molecular orbital calculations<sup>3</sup> showed that structure (I), involving a dithiete ring, is more stable than the acyclic dithione structure (II).



The title compound has been extensively used in the preparation of dithiolene complexes of a number of transition and main group metals.<sup>4</sup> It is apparent that in all of these complexes, ring opening allows the 1,2-bis(trifluoromethyl)dithiete to act as a bidentate ligand, and a number of x-ray crystallographic structure studies of compounds with transition metal ions have been reported (see below). We have now determined the structure of the par-

ent compound in the vapor phase by electron diffraction, and find that I is indeed the correct formulation under these experimental conditions.

## Experimental Section

A sample of 1,2-bis(trifluoromethyl)dithiete, kindly provided by Dr. A. T. Berniaz of Simon Fraser University, showed no impurity bands in its infrared spectrum and was used without further purification.

Sector electron diffraction patterns were recorded on the University of Windsor apparatus<sup>5</sup> on Kodak 4 × 5 in. electron image plates. The experimental conditions for the dithiete exposures are presented in Table I. In each experiment, separate  $CS_2$  patterns were recorded for the  $s$  scale calibration using the standard  $CS_2$  structural parameters reported by Kuchitsu<sup>6</sup> ( $s = (4\pi/\lambda) \sin(\theta/2)$ ;  $\lambda$  = electron wavelength;  $\theta$  (diffraction angle) =  $\tan^{-1}(r/L)$  where  $r$  is the radius and  $L$  is the camera length).

The optical densities of the experimental plates were sampled at 0.1095 mm intervals with the microdensitometer<sup>5</sup> described previously, with the plate spinning and moving continuously so that an annular portion, 0.075 mm, of the plate was sampled in each of 350 measurements obtained for the radial range  $0.75 < r < 4.5$  cm. Interpolation of densities at  $\pi/10$  intervals in  $s$  (by the Lagrange method) was based on six points for long camera plates, and three points for short camera plates. The interpolated optical densities were converted to relative intensities by the correction<sup>7</sup>

Table I. Experimental Conditions<sup>a</sup>

Camera length (mm)	No. of plates	Exposure time (sec)	Density range	$s$ range ( $q = (10/\pi)s$ ) ( $\text{\AA}^{-1}$ )
296.70	2	10	0.05–0.2	$10 < q < 52$
95.20	3	75	0.1–0.4	$40 < q < 110$

<sup>a</sup> Reservoir temperature 0 °C, vapor pressure about 5 Torr; nozzle temperature 21 °C, nozzle orifice 0.5 mm; background pressure 1 to  $2 \times 10^{-5}$  Torr (Torr = (101325/760) Pa); beam current  $5 \times 10^{-7}$  A; high voltage 58 kV stabilized to better than  $1 \times 10^{-4}$ .

$$I = D(1 + 0.01D) \quad (1)$$

The interpolated relative intensities were averaged to give a set of experimental intensities,  $I_x(s)$  for each camera length.

### Analysis

The averaged experimental intensities were converted to the form

$$I_0(s) = s^4 I_x(s) / \Phi(s) \quad (2)$$

where  $\Phi(s)$  is the sector function obtained from argon scattering patterns. The experimental molecular intensity was obtained for each camera length as

$$sI_m^x(s) = s \sum_k [f_k(s)^2 + S_k(s)] \cdot [I_0(s)/B_0(s) - 1] \quad (3)$$

where  $B_0(s)$  is the background,  $f_k(s)$  are the elastic scattering factors,<sup>8</sup> and  $S_k(s)$  is the inelastic scattering.<sup>9</sup> The backgrounds were hand-drawn smoothly through the  $I_0(s)$  curve. Improved backgrounds were obtained by minimizing the difference between experimental intensity and theoretical molecular intensity calculated from the model. The theoretical molecular intensity expression<sup>7</sup> was

$$sI_m(s) = 2 \sum_{i>j} C_{ij}(s) r_{ij}^{-1} \exp(-l_{ij}^2 s^2 / 2) \sin(sr_{ij}) \quad (4)$$

where

$$C_{ij}(s) = |f_i(s)||f_j(s)| \cos[\eta_i(s) - \eta_j(s)] \quad (5)$$

$r_{ij}$  is the thermal average internuclear distance,  $l_{ij}$  is the root mean square amplitude of vibration, and  $\eta_i(s)$  are the phase factors.

Refinements of the structure were carried out by the method of least-squares<sup>10</sup> based on  $sI_m^x(s)$  obtained above. A single theoretical curve was adjusted simultaneously to the data for both camera lengths. A diagonal weight matrix was used. The  $r_g$  distances were calculated from an independent set of geometric parameters, using Hilderbrandt's algorithm.<sup>11</sup>

The 1,2-bis(trifluoromethyl)dithiete molecule was assumed to have  $C_2$  symmetry, and the trifluoromethyl groups were taken as having local  $C_{3v}$  symmetry. Since no force field was available for the molecule, no corrections were made for shrinkage effects. The following parameters were assumed to give a geometrically consistent model:  $C_3-C_4$ ,  $C_4-C_5$ ,  $C_5-C_7$ ,  $C_4-S_1$ ,  $\angle S_1 C_4 C_3$ ,  $\angle C_5 C_4 C_3$ ,  $\angle F_7 C_5 C_4$ ,  $\tau F_7 C_5 C_4 C_3$ ,  $\tau C_5 C_4 C_3 S_2$ , and  $\tau S_1 C_4 C_3 S_2$ , where the  $\tau$ 's are the torsional angles. The atom numbering scheme is shown in Figure 1.

In the preliminary analysis the skeleton formed by the four carbon and two sulfur atoms was constrained to be planar. Initially  $\angle F_7 C_5 C_4$  was fixed at 109.5° while the other parameters were adjusted. In the final stages of analysis all the geometric parameters and the amplitudes  $l_{C_4 S_1}$ ,  $l_{S_1 S_2}$ , and  $l_{C_5 F_7}$  were refined simultaneously. The remaining amplitudes were grouped as indicated in Table II, and were given plausible fixed values obtained by comparison with

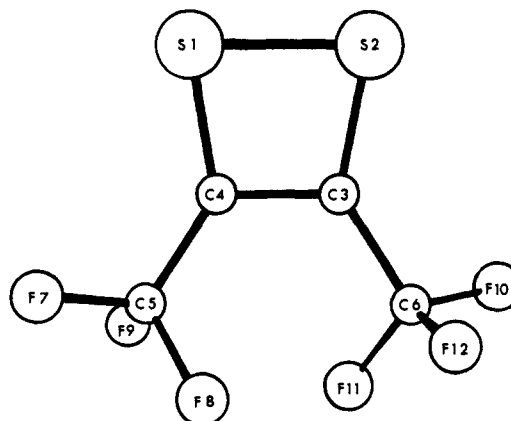


Figure 1. Diagram of 1,2-bis(trifluoromethyl)dithiete with atom numbering.

Table II. Bond Lengths (Å) and Angles (deg) for 1,2-Bis(trifluoromethyl)dithiete<sup>a, b</sup>

	$l_{ij}$
$R^c$	0.118
$C_5-F_7$	1.326 (3)
$C_3=C_4$	1.40 (3)
$C_4-C_5$	1.50 (1)
$C_4-S_1$	1.729 (10)
$\angle C_4 C_3 S_1$	100.8 (0.6)
$\angle C_5 C_4 C_3$	122.9 (0.7)
$\angle F_7 C_5 C_4$	110.8 (0.6)
$\tau C_5 C_4 C_3 S_2^d$	179 (5)
$\tau C_3 C_4 C_5 F_7^d$	146 (6)
$\tau S_1 C_4 C_3 S_2^d$	0.4 (3.4)
$S_1-S_2$	2.05 (1)
$F_7 \cdots F_8$	2.146 (9)
$C_4 \cdots S_2$	2.42
$C_5 \cdots S_1$	3.00
$C_5 \cdots S_2$	3.90
$C_4 \cdots F_7$	2.33 (7)
$C_4 \cdots C_6$	2.55
$C_5 \cdots C_6$	3.03
$S_1 \cdots F_7^e$	3.311
$S_1 \cdots F_9$	3.611
$S_1 \cdots F_8$	4.011
$C_5 \cdots F_{11}$	2.60
$C_5 \cdots F_{12}$	3.62
$C_5 \cdots F_{10}$	4.20
$C_4 \cdots F_{11}$	2.79
$C_4 \cdots F_{12}$	3.26
$C_4 \cdots F_{10}$	3.58
$F_8 \cdots F_{11}$	1.95
$F_8 \cdots F_{12}$	2.87
$F_8 \cdots F_{10}$	3.84
$F_9 \cdots F_{12}$	4.48
$F_9 \cdots F_{10}$	4.54
$F_7 \cdots F_{10}$	5.44
$S_2 \cdots F_8$	4.41
$S_2 \cdots F_9$	4.54
$S_2 \cdots F_7$	4.66
Resolution Factors (theoretical/experimental)	
Long camera	$1.99 \pm 0.04$
Short camera	$1.72 \pm 0.08$

<sup>a</sup> The  $r$  values reported are  $r_g(0) = r_{ij} - l_{ij}^2/r$ , values in angstroms, and angles in degrees. <sup>b</sup> Parenthesized values are the estimated uncertainties. No uncertainty is quoted for the  $l_{ij}$ 's which were fixed in the analysis. <sup>c</sup>  $R = \{(\sum_s [sI_m(s)_{\text{exp}} - sI_m(s)_{\text{th}}]^2) / \sum_s [sI_m(s)_{\text{exp}}]^2\}^{1/2}$ . <sup>d</sup> These parameters reflect planarity of the  $C_4 S_2$  skeleton. <sup>e</sup> The uncertainties in these parameters are estimated to be greater than  $\pm 0.05$  Å since the true rotational conformation of the  $CF_3$  groups was not determined in the analysis.

other molecules, and by trial and error adjustment. The final values of all parameters are presented in Table II. The correlation matrix for the least-squares parameters is given in Table III.

Table III. Correlation Matrix<sup>a</sup>

$C_3=C_4/2$	$C_3-S_2$	$\angle C_4C_3S_2$	$C_4-C_5$	$\angle C_3C_4C_5$	$\tau_{C_5C_4C_3S_2}$	$C_5-F_7$	$\angle F_7C_5C_4$	$\tau_{F_7C_5C_4C_3}$	$\tau_{S_1C_4C_3S_2}$	$l_{C_5-S_2}$	$l_{S_1-S_2}$	$l_{C_5-F_5}$	
$\sigma^b$	0.005	0.004	0.202	0.004	0.225	1.717	0.001	0.200	1.881	1.127	0.003	0.008	0.001
1.000													
-0.123	1.000												
-0.907	0.010	1.000											
0.095	0.224	-0.141	1.000										
-0.712	0.105	0.585	-0.149	1.000									
-0.328	-0.076	0.243	-0.149	0.340	1.000								
0.053	0.030	-0.038	0.107	-0.096	-0.139	1.000							
-0.168	-0.215	0.251	-0.769	0.153	0.104	-0.034	1.000						
0.389	0.092	-0.340	0.177	-0.337	-0.745	0.161	-0.078	1.000					
-0.066	0.041	0.112	-0.029	-0.051	-0.389	-0.016	0.019	-0.283	1.000				
0.028	0.035	0.071	-0.118	-0.073	-0.066	-0.001	-0.033	0.005	0.023	1.000			
0.127	-0.242	0.191	-0.467	0.195	0.175	-0.357	0.764	-0.098	-0.002	-0.158	1.000		
-0.772	0.142	0.700	0.051	0.537	0.233	-0.024	0.040	-0.281	0.056	-0.108	0.055	1.000	

<sup>a</sup> Bond distances in angstroms, and angles in degrees. <sup>b</sup> Standard errors from least-squares program.

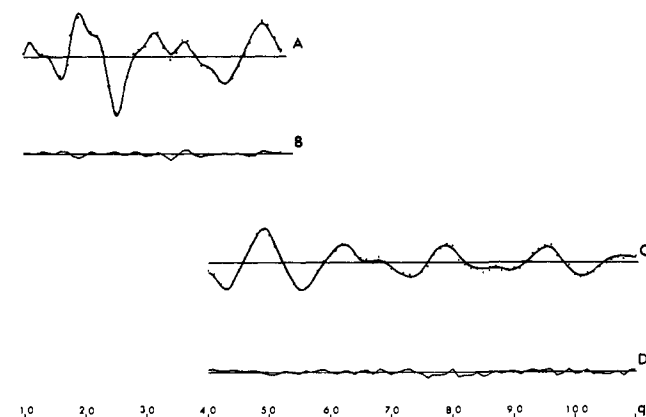


Figure 2. Molecular intensity curves in  $q = ((\pi/10)s)$ : (A) long camera intensity, experimental (dots) and theoretical (solid)  $I_m(q)$  calculated from structural parameters of Table II; (B) difference (experimental-theoretical) curve; (C) short camera intensity, experimental (dots) and theoretical (solid); (D) difference curve.

The major factors affecting the uncertainties of the geometrical parameters are the scale factor and the weight matrix. The scale factor uncertainty, about 0.10% [ $|\Delta q/q| = |\Delta(L\lambda)/(L\lambda)|$ ], implies a systematic error of approximately  $\pm 0.0015$  Å in all distances. The assumption of a diagonal weight matrix would cause the calculated uncertainties to be too small by a factor of about 1.5.<sup>12</sup> Considering these influences and other smaller errors which are discussed elsewhere,<sup>6</sup> a factor of three times the least-square values seemed a reasonable estimate of the uncertainties.

## Results and Discussion

The geometrical parameters and root mean square amplitudes for the final model and the correlation matrix are presented in Tables II and III, respectively. The molecular intensity,  $sI_m^x(s)$ , is given in Figure 2, and the radial distribution curves are shown in Figure 3. The results substantiate the ring structure I for the molecule.

**Bond Angles.** The exocyclic valence angles  $\angle C_5C_4=C_3$  ( $122.9^\circ$ ), and  $\angle F_7C_5C_4$  ( $110.8^\circ$ ) fall within the usual ranges and deserve no further comment. The endocyclic angle  $\angle C_3C_4S_1$  ( $100.8^\circ$ ) is consistent with the conditions imposed by the ring bond lengths (i.e., S—S longer than C=C).

**Bond Lengths.** The C—C bond in the  $C_2S_2$  ring is longer than that in ethylene ( $1.337$  (1) Å)<sup>13</sup> and 3,4-dimethylcyclobutene ( $1.357$  (5) Å)<sup>14</sup> but comparable to the value for the C—C distance in benzene ( $1.396$  (3) Å).<sup>15</sup> The exocyclic C—C bond distance is close to the  $C(sp^2)-C(sp^3)$  value ( $1.515$  (3) Å) observed in  $H_2C=CCCH_3CH_2CH_3$ <sup>16</sup> but

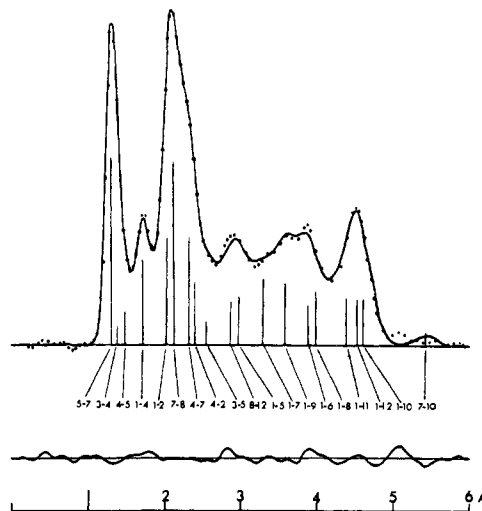


Figure 3. Radial distribution curves: Experimental (dots) theoretical (solid), and difference (lower solid) curves. The vertical bars indicate the distribution of important interatomic distances.

shorter than those in  $(CF_3)_2C=NH$  ( $1.551$  (7) Å)<sup>17</sup> and  $(CF_3)_2C=CH_2$  ( $1.535$  (6) Å).<sup>17</sup> The C—F bond length falls between that reported for  $HCF_3$  ( $1.334$  (5) Å)<sup>18</sup> and for  $CF_4$  ( $1.323$  (5) Å)<sup>18</sup> and agrees very well with the values in  $(CF_3)_2C=NH$  ( $1.326$  (3) Å)<sup>17</sup> and  $(CF_3)_2C=CH_2$  ( $1.329$  (2) Å).<sup>17</sup>

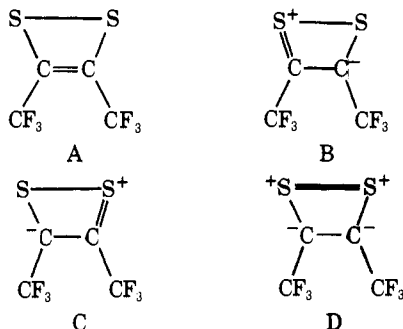
The C—S bond length of  $1.730$  (10) Å lies between the values reported for the S—C( $sp^2$ ) bond ( $1.748$  (6) Å) in methyl vinyl sulfide<sup>19</sup> ( $H_2C=CH-S-CH_3$ ) and the S—C bond distance in the aromatic thiophene<sup>20</sup> molecule ( $1.7140$  (15) Å). The S—S bond length ( $2.050$  (14) Å) is in good agreement with the S—S single bond value reported for orthorhombic sulfur ( $S_8$ )<sup>21</sup> ( $2.048$  (2) Å), and the S—S value in the  $C_3S_2$  ring of 4-methyl-1,2-dithiacyclopent-4-ene-3-thione<sup>22</sup> ( $2.047$  (7) Å).

**Bonding.** The reported bond lengths for S—S, S—C, and C=C in dithiete indicate the presence of delocalization of the carbon-carbon  $\pi$  system in the molecule. The delocalization occurs mainly among the three S—C and C=C bonds, rather than all four bonds in the ring. This feature can easily be explained by simple valence-bond structures. Of these structures, only D gives rise to any multiple bond character in the S—S bond, but this form will be very unstable because of the unfavorable charge distribution, so that presumably only structures A, B, and C contribute, and each of these involves a single S—S bond. According to Pauling's bond length-bond order criteria,<sup>23</sup> the S—C and C=C bonds have bond orders of 1.27–1.35, and 1.43–1.78,

Table IV. Comparison of Principal Bond Distances of 1,2-Bis(trifluoromethyl)dithiete and Related Molecules<sup>a, b</sup>

	Method	C=C	C—S	C—CF <sub>3</sub>	C—F	Ref
Dithiete	E.D.	1.400 (33)	1.729 (10)	1.500 (10)	1.326 (3)	This work
[AuL <sub>2</sub> ] <sup>-</sup>	X ray	1.31 (4)	1.76 (3)	1.50 (7)	1.30 (7)	25
[NiL <sub>2</sub> ] <sup>-</sup>	X ray	1.40 (2)	1.70 (2)	1.48 (3)	1.30 (3)	27
[NiL <sub>2</sub> ]	X ray	1.38 (2)	1.71 (1)	1.48 (3)	1.33 (2)	26
[CoL <sub>2</sub> ] <sub>2</sub>	X ray	1.407 (20)	1.694 (16)	1.493 (12)	1.267 (18)	24
[η <sup>5</sup> -CpCoL]	X ray	1.48	1.74	1.51	1.27	28

<sup>a</sup> Distances in angstroms. <sup>b</sup> Cp = cyclopentadienyl group.



respectively; from these bond order values, we estimate that the contribution of A, B, and C are about 50, 25, and 25%, respectively.

Alternatively, the LCAO calculations<sup>3</sup> predicted bond orders 1.474 (C—S), 1.658 (C=C), and 1.342 (S—S). The  $\pi$  electron delocalization including the  $3p\pi$  orbitals of sulfur is promoted by the electron withdrawing capacity of the CF<sub>3</sub> groups. The delocalization energy of the dithiete was about 0.25 eV greater than the bis(trifluoromethyl)dithione. The consequent lengthening of the C=C bond (by about 0.06 Å relative to ethylene) provides space in the ring to accommodate a nearly normal S—S bond.

**Dithiolene Complexes.** It is interesting to compare the results in Table II with those reported for the ring system in transition metal complexes derived from 1,2-bis(trifluoromethyl)dithiete (= L). Structures have been established by x-ray crystallographic methods for the [CoL<sub>2</sub>]<sub>2</sub><sup>24</sup> dimer, AuL<sub>2</sub><sup>-</sup>,<sup>25</sup> NiL<sub>2</sub><sup>26</sup> and NiL<sub>2</sub><sup>-</sup>,<sup>27</sup> and η<sup>5</sup>-CpCoL<sup>28</sup> (Cp = cyclopentadienyl group) (see Table IV). In the cases of the two nickel complexes, and the cobalt dimer, the C—S bonds do not seem to be significantly shorter in the complexes than in dithiete itself, and equally the C=C delocalization in the parent compound and in the complexes is apparently of the same order. The agreement with the Au(III) anionic complex is less satisfactory, especially in terms of the C=C bond lengths. The corresponding bond lengths in the C<sub>2</sub>S<sub>2</sub>M ring in η<sup>5</sup>-CpCoL have been questioned, and any comparison with the present results is therefore probably not viable.

In summary, the insignificant bond length differences between dithiete and its transition metal complexes do not suggest that complex formation is accompanied by any

great change in bond character in the S—C=C—S moiety. The driving force for this rupture of the S—S bond in complexation must therefore be the formation of two M—S bonds.

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**Supplementary Material Available:** Data for intensity curves (2 pages). Ordering information is given on any current masthead page.

## References and Notes

- (1) C. G. Krespan, B. C. McKusick, and T. L. Cairns, *J. Am. Chem. Soc.*, **82**, 1515 (1960).
- (2) C. G. Krespan, *J. Am. Chem. Soc.*, **83**, 3434 (1961).
- (3) H. E. Simmons, D. C. Blomstrom, and R. D. Vest, *J. Am. Chem. Soc.*, **84**, 4783 (1962).
- (4) R. Eisenberg, *Prog. Inorg. Chem.*, **12**, 295 (1970).
- (5) J. Barbe, J. L. Hencher, Q. Shen, and D. G. Tuck, *Can. J. Chem.*, **52**, 3936 (1974).
- (6) K. Kuchitsu, "Molecular Vibrations and Structure Studies", S. J. Cyvin, Ed., Elsevier, Amsterdam, 1972, Chapter 10.
- (7) L. S. Bartell, "Physical Methods in Chemistry", 4th ed, Vol. 1, A. Weissberger and B. W. Rossiter, Ed., Interscience, New York, N.Y., 1971.
- (8) L. Schäfer, A. C. Yates, and R. A. Bonham, *J. Chem. Phys.*, **55**, 3055 (1971).
- (9) C. Tavaud, D. Nicolas, and M. Rouait, *J. Chem. Phys.*, **64**, 540 (1967).
- (10) W. C. Hamilton, "Statistics in Physical Science", Ronald Press, New York, N.Y., 1964, Chapter 4.
- (11) R. L. Hilderbrandt, *J. Chem. Phys.*, **51**, 1654 (1969).
- (12) L. S. Bartell and M. G. Anashkin, *J. Mol. Struct.*, **17**, 193 (1973).
- (13) L. S. Bartell, E. A. Roth, C. D. Hollowell, K. Kuchitsu, and J. E. Young, *J. Chem. Phys.*, **42**, 2683 (1965).
- (14) A. Skancke, *Acta Chem. Scand.*, **22**, 3239 (1968).
- (15) K. Kimura and M. Kubo, *J. Chem. Phys.*, **32**, 1776 (1960).
- (16) T. Shimanouchi, Y. Abe, and K. Kuchitsu, *J. Mol. Struct.*, **2**, 82 (1968).
- (17) R. L. Hilderbrandt, A. L. Andreassen, and S. H. Bauer, *J. Phys. Chem.*, **74**, 1586 (1970).
- (18) C. G. Thornton, *Diss. Abstr.*, **14**, 604 (1954); *Chem. Soc., Spec. Publ.*, **No. 11** (1958).
- (19) H. M. Salp and S. Samdal, *Acta Chem. Scand.*, **25**, 1903 (1971).
- (20) B. Bak, D. Christensen, L. Hansen-Nygard, and J. Rastrup-Andersen, *J. Mol. Spectrosc.*, **7**, 58 (1961).
- (21) A. S. Cooper, W. L. Bond, and S. C. Abrahams, *Acta Crystallogr.*, **14**, 1008 (1961).
- (22) G. A. Jeffrey and R. Shiono, *Acta Crystallogr.*, **12**, 447 (1959).
- (23) L. Pauling, "The Nature of the Chemical Bond", 3d ed, Cornell University Press, Ithaca, N.Y., 1960, p 239.
- (24) J. H. Enemark and W. N. Lipscomb, *Inorg. Chem.*, **4**, 1729 (1965).
- (25) J. H. Enemark and J. A. Ibers, *Inorg. Chem.*, **7**, 2636 (1968).
- (26) R. D. Schmidt, R. M. Wing, and H. H. Maki, *J. Am. Chem. Soc.*, **91**, 4394 (1969).
- (27) R. M. Wing and R. L. Schlupp, *Inorg. Chem.*, **9**, 471 (1970).
- (28) H. W. Baird and B. M. White, *J. Am. Chem. Soc.*, **88**, 4744 (1966).