

## Preparation, Crystal and Molecular Structure and Properties of 5,5'-Bis-(1,3-dithiol-2-ylidene)[bicyclopenta-1,3-dien-1-yl]-2,2',3,3'-tetracarbonitrile

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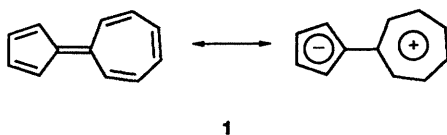
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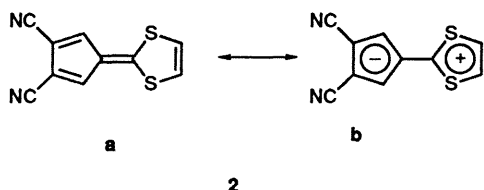
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The synthesis and properties of 2-(3,4-dicyanocyclopenta-2,4-dienylidene)-1,3-dithiole **2** have been previously reported. NMR spectral data of that compound imply a large contribution of the dipolar form to its electronic structure. Two-solvent diffusion recrystallization, in the presence of O<sub>2</sub>, yields the title compound **3**, the crystal structure of which is reported here. This appears to be the first crystal structure of a compound containing the dicyanocyclopentadiene moiety. The space group is *P*1̄, and the lattice parameters are *a* = 8.3617(19), *b* = 11.1196(23), *c* = 12.8159(20) Å,  $\alpha$  = 96.587(15)°,  $\beta$  = 103.103(15)°,  $\gamma$  = 109.917(16)° and *V* = 1066.9(4) Å<sup>3</sup> for *Z* = 2. We also discuss a plausible mechanism for the formation of compound **3**, and its spectral properties.

Organic compounds in which several equivalent structures can be drawn are of interest to both theoretical and experimental chemists. The reasons for such interest centre around the possibility that such materials are amenable to study by spectroscopic methods to determine their true electronic descriptions. One such compound is the hydrocarbon sesquifulvalene **1**. This compound can be described in terms of two principal resonance forms. It appears to be unstable and not isolable by normal chemical methods.<sup>1</sup>



One method of enhancing the stability of such hydrocarbons is to prepare heteroanalogues which are isoelectronic with the parent compound. This has been done in the case of the sesquifulvalenes.<sup>2</sup> One interesting variation of this approach is the addition of electron-withdrawing cyano groups to the cyclopentadienyl moiety to aid in stability.<sup>3-5</sup> In our own work, we have combined the latter technique with the addition of heteroatoms to the rings to prepare the stable species 2-(3,4-dicyanocyclopenta-2,4-dienylidene)-1,3-dithiole **2**.<sup>6</sup>



From the NMR data for this compound, it was reasoned that the electronic structure was due in large measure to the dipolar component **2b**. The initial purpose of this work was to investigate the crystal and electronic structure of compound **2**. However, when we attempted to grow single crystals of compound **2**, in the presence of oxygen, the product that was obtained had properties significantly different from those of the starting material. It is the crystal and molecular structure of that product **3** which is the subject of this paper.

**Table 1** Experimental data for the X-ray diffraction study

(A) Crystallographic parameters at 20 °C (293 K)

<i>a</i> = 8.3617(19) Å	crystal system = triclinic
<i>b</i> = 11.1195(23) Å	space group = <i>P</i> 1̄ (No. 2)
<i>c</i> = 12.8159(20) Å	<i>Z</i> = 2
$\alpha$ = 96.587(15)°	formula = C <sub>20</sub> H <sub>6</sub> N <sub>4</sub> S <sub>4</sub> ·CH <sub>3</sub> CN
$\beta$ = 103.103(15)°	formula wt. = 471.6
$\gamma$ = 109.917(16)°	<i>D</i> <sub>calc</sub> = 1.47 g cm <sup>-3</sup>
<i>V</i> = 1066.9(4) Å <sup>3</sup>	$\mu$ (Mo-K $\alpha$ ) = 4.5 cm <sup>-1</sup>

(B) Collection of X-ray diffraction data

Diffractometer: Syntex P2<sub>1</sub>  
 Radiation: Mo-K $\alpha$  ( $\lambda$  = 0.710 730 Å)  
 Monochromator: pyrolytic graphite; equatorial mode with  $2\theta(m)$  = 12.16°; assumed 50% perfect/50% mosaic for polarization correction.  
 Reflections measured: +*h*,  $\pm k$ ,  $\pm l$  for  $2\theta$  = 4.5–40.0°; 2179 total, yielding 1946 unique data.  
 Scan conditions: coupled  $\theta(\text{crystal})$ – $2\theta(\text{counter})$  from [ $2\theta(K\alpha_1) - 0.9$ ]° through [ $2\theta(K\alpha_2) + 0.9$ ]° at 4.0 deg/min in  $2\theta$ .  
 Backgrounds: stationary crystal and stationary counter at the two extremes of the  $2\theta$  scan; each for one-half of total scan time.  
 Standard reflections: 3 collected after each batch of 97 reflections; no significant fluctuations nor decay were detected.

### Results and Discussion

Several solvent systems were examined before it was determined that satisfactory crystals could be grown by the diffusion of benzene into a saturated acetonitrile solution of **2**. While growing the crystals by this method, no attempt was made to exclude oxygen. The material isolated by the use of this growth technique formed dark purple needles, whereas the starting material was orange. Because of this colour change, comparative spectroscopic analyses were performed. In Fig. 1 are presented the UV–VIS spectra of **2** and **3**. The spectrum of **3** has a long-wavelength component (shoulder at 468 nm) that is responsible for its darker appearance. In addition, the peak at 239 nm for **3** exhibits greater intensity than the corresponding peak for **2**. The Fourier transform IR spectra of **2** and **3** also show significant differences. For example, the C–H stretching mode at 3086 cm<sup>-1</sup> is quite apparent in **3**, yet is barely observable in **2**. In **3**, the strongest absorption in the spectrum is

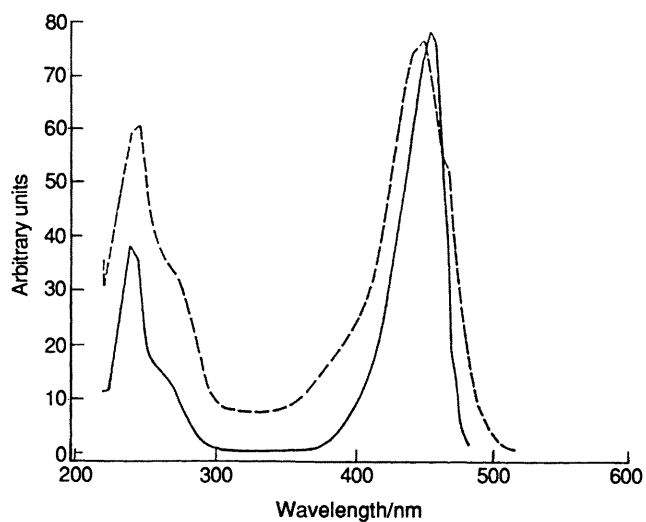


Fig. 1

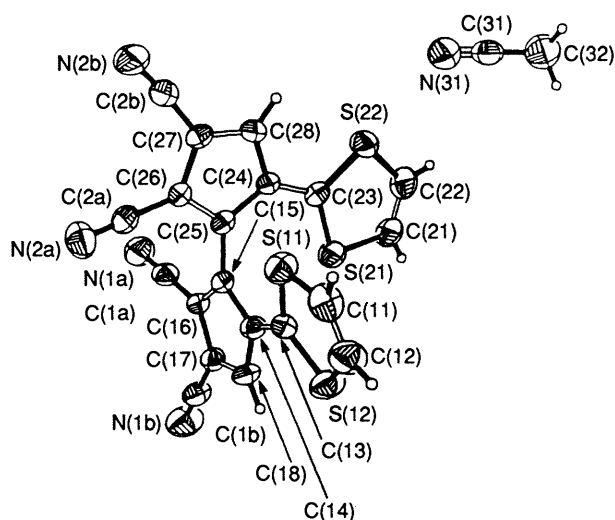


Fig. 2

at  $1434\text{ cm}^{-1}$ . This line does not appear at all in the spectrum of **2**. In addition, **3** exhibits a line at  $938\text{ cm}^{-1}$  of medium intensity, which is absent in the spectrum of **2**. Mass spectral analysis of **3**, however, gave the same spectrum as that obtained for **2**, with an  $m/z$  value of 216 for the molecular ion. While clearly there is a difference between **2** and **3**, the definitive determination of their relationship awaited a crystal-structure analysis.

**Description of the Structure.**—The crystal consists of discrete molecular units of  $\text{C}_{20}\text{H}_6\text{N}_4\text{S}_4$  and acetonitrile (in a 1 : 1 ratio), which are mutually separated by normal van der Waals' distances; there are no abnormally short intermolecular contacts. A summary of the experimental data for this X-ray study is given in Table 1. Fig. 2 shows the atomic-labelling scheme and the thermal ellipsoids. The acetonitrile molecule of solvation is identifiable from its bond lengths of  $\text{CH}_3\text{-CN}$  [atoms  $\text{C}(32)\text{-C}(31)$ ] =  $1.427(9)\text{ \AA}$ ,  $\text{C}\equiv\text{N}$  [atoms  $\text{C}(31)\text{-N}(31)$ ] =  $1.110(8)\text{ \AA}$ , bond angles of  $\text{C}(32)\text{-C}(31)\text{-N}(31)$  =  $178.4(6)^\circ$ , and the satisfactory behaviour of its parameters under least-squares refinement.

The  $\text{C}_{20}\text{H}_6\text{N}_4\text{S}_4$  molecule is composed of two equivalent dicyanodithiafulvalene units which are joined *via* a  $\text{C}(\text{sp}^2)\text{-C}(\text{sp}^2)$  linkage  $\text{C}(15)\text{-C}(25)$  =  $1.466(5)\text{ \AA}$ . Note that atoms whose first integer is '1' define the 'first half' of the molecule,

while atoms with an initial '2' define the 'second half' of the  $\text{C}_{20}\text{H}_6\text{N}_4\text{S}_4$  molecule. All bond lengths within the molecule are normal, and related distances agree to within  $0.015\text{ \AA}$  in each case. Bond types and ranges are as follows:  $\text{S-C}(\text{sp}^2)$  =  $1.702(4)\text{-}1.728(6)\text{ \AA}$ ,  $\text{C=C}(\text{isolated})$  =  $1.305(8)\text{-}1.308(8)\text{ \AA}$ ,  $\text{C=C}(\text{connecting rings})$  =  $1.412(8)\text{-}1.418(5)\text{ \AA}$ ,  $\text{C=C}(\text{in } \text{C}_5 \text{ rings})$  =  $1.363(6)\text{-}1.386(5)\text{ \AA}$ ,  $\text{C-C}(\text{in } \text{C}_5 \text{ rings})$  =  $1.419(6)\text{-}1.439(6)\text{ \AA}$ ,  $\text{C-C}(\text{between } \text{C}_{10}\text{H}_3\text{N}_2\text{S}_2 \text{ units})$  =  $1.466(5)\text{ \AA}$ ,  $\text{C-CN}$  =  $1.425(6)\text{-}1.435(7)\text{ \AA}$ ,  $\text{C}\equiv\text{N}$  =  $1.141(6)\text{-}1.151(7)\text{ \AA}$ .

The ten-atom ( $\text{C}_8\text{S}_2$ ) dithiafulvalene system of the 'second half' of the molecule [*i.e.*, atoms  $\text{S}(21)\text{-S}(22)$  and  $\text{C}(21)\text{-C}(28)$ ] is close to planar (RMS deviation from planarity =  $0.024\text{ \AA}$ ), whereas the 'first half' [atoms  $\text{S}(11)\text{-S}(12)$ ,  $\text{C}(11)\text{-C}(18)$ ], shows some substantial distortions (RMS deviation =  $0.131\text{ \AA}$ ). These latter distortions are a combination of torsion and buckling of the system about the  $\text{C}(13)\text{-C}(14)$  linkage, as indicated by the deviations of other atoms from the strictly planar (RMS deviation =  $0.006\text{ \AA}$ ) carbocyclic ring defined by  $\text{C}(14)\text{-C}(18)$ ; *viz.*  $+0.102(4)\text{ \AA}$  for  $\text{C}(13)$ ,  $+0.448(1)\text{ \AA}$  for  $\text{S}(11)$ ,  $+0.570(5)\text{ \AA}$  for  $\text{C}(11)$ ,  $+0.334(6)\text{ \AA}$  for  $\text{C}(12)$  and  $-0.038(1)\text{ \AA}$  for  $\text{S}(12)$ .

What is most interesting about this structure is the apparent bond alternation observed in the cyclopentadiene portion of the molecule. From the NMR results of **2**,<sup>6</sup> it was determined that the dipolar structure was an important contributor to its overall description (the dipolar structure is one in which both the positive and negative portions are aromatic, and therefore, little or no bond alternation in the cyclopentadiene portion would be expected). Apparently, according to our structural analysis, the dipolar form is less of a contributor in **3**. To our knowledge, no crystal structure of any molecule containing a dicyanocyclopentadienyl moiety has appeared in the literature. However, in our search for appropriate models to use for purposes of comparison, the calculated values for the bond lengths in azulene appeared reasonable.<sup>7</sup> Azulene **4** can be described as a cyclopentadienide anion fused to a tropylium cation. The anionic portion of azulene might be considered analogous to the dicyanocyclopentadienide moiety that exists in **2** and **3**. In

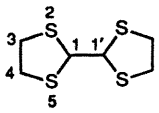


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azulene, the longest bond is at the fusion of the 5 and 7 membered rings ( $1.50\text{ \AA}$ ). The remaining bond distances range between  $1.33$  and  $1.46\text{ \AA}$  for the double and single bonds, respectively.<sup>7</sup> In comparison, the bonds in the dicyanocyclopentadienyl portion of **3** vary considerably from those calculated values for strict carbon-carbon, single-double bond alternation. None are as long as a normal single bond, nor as short as a normal double bond [dicyanocyclopentadienyl bond distance range;  $\text{C-C}(\text{intraring})$  =  $1.439(6)\text{-}1.363(6)\text{ \AA}$ ]. These data indicate that the molecule has substantial aromatic character, but is not fully delocalized.

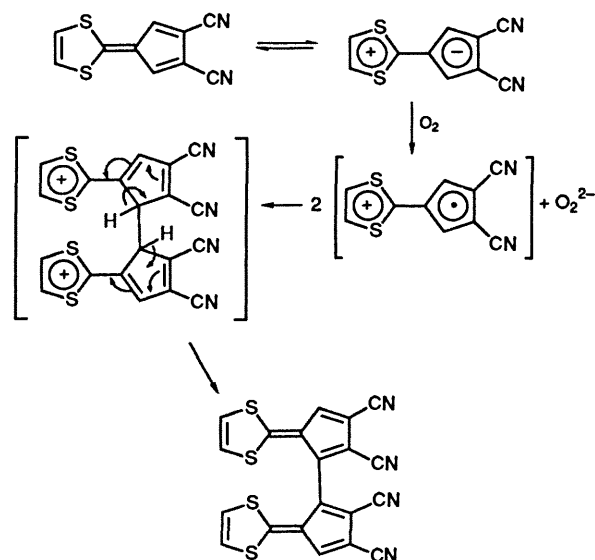
There is structural information in the literature relevant to the dithiole portion of the molecule. Crystal structures have been obtained for the neutral molecule tetrathiafulvalene (TTF),<sup>8</sup> and for salts of the radical cation of TTF, *viz.*,  $(\text{TTF}^+)(\text{HgCl}_3^-)$ <sup>9</sup> and  $(\text{TTF}^+)(\text{Cl}^-)$ .<sup>6,7,10</sup> Comparison of the bond lengths in the various TTF-containing molecules indicates that most bond lengths in the dithioethylene portion of the molecule are not dependent on the charge on the species. (See Table 2 for a summary of the various bond types in the three TTF molecules.) However, the  $\text{S-C}$  (ring junction) distance is charge dependent.

The bond length in the neutral species is  $1.757\text{ \AA}$ , significantly longer than those in the charged species. These bond lengths are

**Table 2** Bond lengths (Å) for various TTF compounds


	1-1'	1-2	2-3	3-4	
Neutral	1.349	1.757	1.726	1.314	Exptl.
HgCl <sub>3</sub> (1:1)	1.41	1.72	1.71	1.31	Exptl.
Cl <sub>0.67</sub>	1.38	1.72	1.719	1.32	Exptl.
Dication	1.425	1.701	1.755	1.328	Calc.
<b>3</b>		1.71	1.72	1.31	Exptl.

consistent with calculated values for neutral TTF and those of TTF<sup>+</sup> and TTF<sup>2+</sup>.<sup>11</sup> In compound **3**, we observe an S-C (ring junction) bond length of 1.71 Å, similar to that observed for charged dithiole species, suggesting some contribution by the dipolar resonance form. Based on these data, one can conclude that **3** appears to have some aromatic character, although bond alternation in the dicyanocyclopentadienyl portion of the molecule argues against its existence as a fully aromatic, dipolar species. The reason for this may be that the energy required to bring two negative charges (*e.g.*, dicyanocyclopentadienide anion) close together is not balanced by the gain in aromaticity. Finally, it is noted that oxygen was not excluded during our initial attempts to grow single crystals of **2**. When oxygen was excluded **3** was not formed. The presence of oxygen, therefore, clearly leads to the formation of **3**. A reasonable mechanism for this transformation is shown in Scheme 1.

**3****Scheme 1**

**Conclusions.**—The attempted growth of crystals of **2** in the presence of oxygen led to the formation of a new compound, **3**. The crystal structure of this new compound shows it to be an addition product of **2**.

To our knowledge, this is the first crystal structure of a compound containing the 3,4-dicyanocyclopentadienide moiety. As part of a heterosquifvalene structure, it appears to have some aromatic character, although bond alternation in the dicyanocyclopentadiene portion of the molecule seems to indicate that the dipolar form of **3** is not as important as NMR data suggest this form is for **2**.

## Experimental

**General.**—IR spectra were recorded on a Nicolet 5DX Fourier transform IR spectrophotometer. UV-VIS spectra were recorded on a Hewlett-Packard Diode Array spectrometer. Mass spectra were recorded on a Hewlett-Packard 5985 spectrometer operating at 70 eV. 2-(3,4-Dicyanocyclopentadienylidene)-1,3-dithiole was prepared as previously described.<sup>6</sup>

**Synthesis of 5,5'-Bis-(1,3-dithiol-2-ylidene)[bicyclopenta-1,3-dien-1-yl]-2,2',3,3'-tetracarbonitrile **3**.**—The dithiole **2** (20 mg) was dissolved in acetonitrile (20 cm<sup>3</sup>) and placed in one cell of a Landolt H-tube. The other cell was filled with benzene. The solutions were allowed to equilibrate for three weeks. Purple crystals of the title compound formed and were suitable for X-ray analysis. These were isolated by filtration, washed with benzene (5 cm<sup>3</sup>), and air dried.

**Crystallography; Collection of X-Ray Data.**—A carefully selected crystal was mounted in a thin-walled glass capillary and was aligned on a Syntex P2<sub>1</sub> automated four-cycle diffractometer at the University at Buffalo-SUNY. Determination of the unit-cell parameters, crystal-orientation matrix, and Bravais lattice were carried out as described previously;<sup>12</sup> diffraction data were collected under the conditions shown in Table 1B. The resulting data were corrected for Lorentz and polarization factors and were reduced to unscaled  $|F_o|$ -values. Any reflection with  $I(\text{net})$  less than zero was assigned a value  $|F_o| = 0$ . All data were placed on an approximately absolute scale by means of a Wilson plot.

**Solution and Refinement of the Crystal Structure.**—The positions of the four sulfur atoms were derived using MULTAN 80<sup>13</sup> on a VAX 11/780 at Allied-Signal Inc., Buffalo Research Laboratory. The remaining non-hydrogen atoms, except for the acetonitrile molecule, were located from a series of difference-Fourier syntheses. All subsequent calculations were performed using the Syntex XTL system on a Data General NOVA 1200 computer at the University at Buffalo-SUNY.<sup>14</sup>

Anisotropic refinement of all non-hydrogen atoms converged with  $R_F = 15.0\%$ , at which point an acetonitrile molecule of solvation was located. The structure was optimized by full-matrix least-squares refinement, minimizing the function  $\Sigma w(|F_o| - |F_c|)^2$  where  $1/w = [\sigma(|F_o|)^2 + (0.015|F_o|)^2]$ . All hydrogen atoms were located from a difference-Fourier synthesis. The methyl hydrogens were included in optimized positions with  $d(\text{C-H}) = 0.95$  Å.<sup>15</sup> The discrepancy indices at convergence were  $R_F = 5.0\%$ ,  $R_{wF} = 3.7\%$  and goodness-of-fit (GOF) = 1.260 for 307 variables refined against 1944 data (the reflections 036 and 072 were discarded).<sup>\*</sup> The discrepancy indices<sup>†</sup> for those 1627 data with  $|F_o| > 3.0\sigma(|F_o|)$  were  $R_F = 3.6\%$ ,  $R_{wF} = 3.5\%$  and for those 1440 data with  $|F_o| > 6\sigma(|F_o|)$  were  $R_F = 2.9\%$ ,  $R_{wF} = 3.2\%$ . A final difference-Fourier synthesis showed no significant features and tests of the weighing scheme revealed no anomalies. The structure is both correct and complete.

**Supplementary Material Available.**—Tables containing bond distances, interatomic angles, fractional atomic coordinates, thermal parameters and hydrogen positional parameters are available (6 pages) from the Cambridge Crystallographic Data Centre.<sup>‡</sup>

<sup>\*</sup> The reflections 036 and 072 were deleted from the data set because of an obvious error in their intensity measurements.

<sup>†</sup>  $R_F(\%) = 100[(\Sigma||F_o| - |F_c||)/\Sigma|F_o|]$   
 $R_{wF}(\%) = 100[(\Sigma w(|F_o| - |F_c|)^2)/\Sigma w|F_o|^2]^{\frac{1}{2}}$  where  $w = [\sigma(|F_o|)]^{-2}$ .  
 GOF =  $[\Sigma w(|F_o| - |F_c|)^2/(N_o - N_v)]^{\frac{1}{2}}$ .  
 $N_o$  = number of observations,  $N_v$  = number of variables.

<sup>‡</sup> For details of the CCDC deposition scheme see 'Instructions for Authors (1993)', *J. Chem. Soc., Perkin Trans. 2*, 1993, Issue 1.

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