

## The Crystal and Molecular Structure of Bi(1,2,4,5,6-pentahydro-1,3-ditellurapentalen-2-ylidene) (Hexamethylenetetratellurafulvalene): the Shortest Observed Intermolecular Te–Te Contact

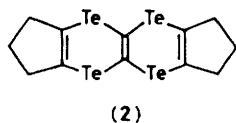
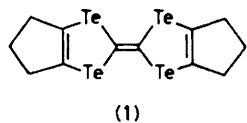
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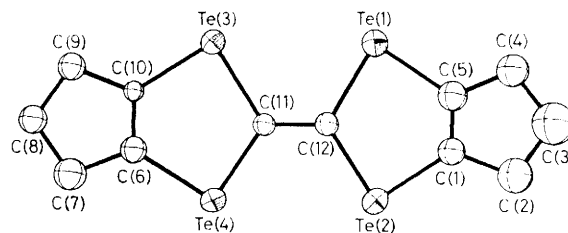
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The reaction between cyclopentene-1,2-ditelluroolate and tetrachloroethylene produces bi(1,2,4,5,6-pentahydro-1,3-ditellurapentalen-2-ylidene) (hexamethylenetetratellurafulvalene), and not its six-ring isomer, as determined by single crystal *X*-ray analysis; the latter revealed that the title compound is, surprisingly, almost identical to its selenium analogue in intramolecular dimensions but is quite different in its mode of packing, giving rise to the shortest (3.583 Å) *intermolecular* tellurium–tellurium contact yet observed.

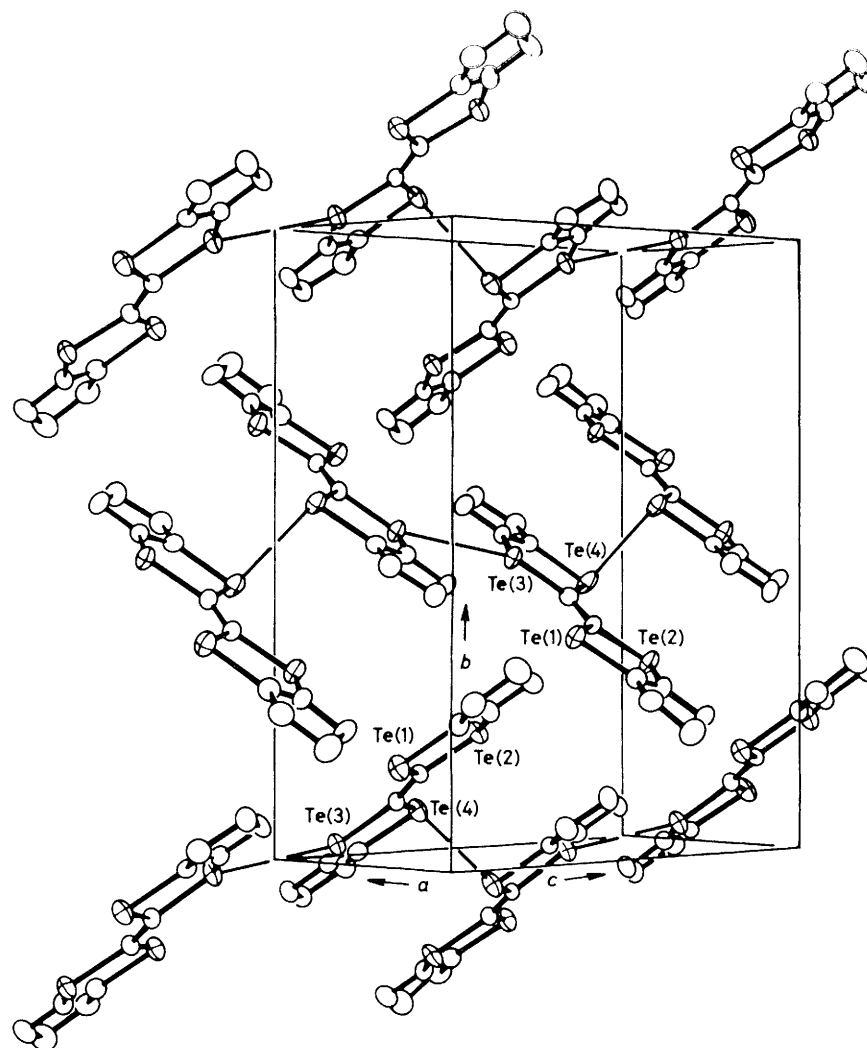
The preparation of the first tetratellurafulvalene was reported recently.<sup>1</sup> The synthetic method employed could have produced either the tetratellurafulvalene derivative (1) or the tetratelluradicyclopenta[*b,g*]naphthalene (2). We had concluded that the structure of the product was (1), based mainly on mass spectral fragmentation patterns and i.r. spectroscopy, but felt that the ultimate proof of structure rested with *X*-ray crystallography. At first, that technique proved impossible because the crystals, although of perfect morphology, apparently were fraught with internal disorder.<sup>2</sup> Eventually, single crystals devoid of disorder and twinning were obtained on crystallization from refluxing butyl acetate. In this paper we present the structure determination of bi(1,2,4,5,6-pentahydro-1,3-ditellurapentalen-2-ylidene) (1) (trivially called hexamethylenetetratellurafulvalene, HMTTeF). A crystal of HMTTeF prepared as described<sup>1</sup> and recrystallized by Soxhlet extraction in butyl acetate, and of dimensions 0.40 × 0.06 × 0.07 mm, was chosen for unit cell determination and intensity data collection.



*Crystal data:* (1), C<sub>12</sub>H<sub>12</sub>Te<sub>4</sub>, *M* = 666.63, monoclinic, space group *P*2<sub>1</sub>/*c*, *a* = 6.623(2), *b* = 17.760(2), *c* = 12.859(3) Å, β = 99.05(3)°, *Z* = 4, λ(Mo-*K*<sub>α</sub>) = 0.71069 Å, μ(Mo-*K*<sub>α</sub>) = 77.3 cm<sup>-1</sup>. Intensities for 2965 reflections in the range 0 < 2θ ≤ 50° were measured on an Enraf-Nonius CAD4 diffractometer by the ω–2θ scan technique. Of these, 2308 unique reflections with *I* > 3σ(*I*) were used in the structure determination. The structure was solved by the use of the MULTAN79 program package (which yielded the positions of the four Te atoms) followed by weighted Fourier synthesis. Least squares refinement by block diagonal methods followed by a final three cycles of full matrix converged to *R* = 0.035 and *R*<sub>w</sub> = 0.048.



**Figure 1.** Molecular structure of HMTTeF (1). Selected bond angles (°) and distances (Å): C(5)–Te(1)–C(12) 90.2(2), Te(1)–C(5)–C(1) 122.1(4), and Te(1)–C(12)–Te(2) 115.2(2); Te(1)–C(5) 2.090(5), Te(1)–C(12) 2.098(5), and C(11)–C(12) 1.356(7).



**Figure 2.** Crystal packing for HMTTeF (1). Selected intermolecular distances (Å): Te(1)–Te(2) 4.124 ( $x, \frac{1}{2}-y, z-\frac{1}{2}$ ), Te(3)–Te(3) 3.583 ( $2-x, -y, -z$ ), Te(4)–Te(4) 3.743 ( $2-x, -y, 1-z$ ), and C(3)–C(10) 3.670 ( $1-x, y-\frac{1}{2}, -z-\frac{1}{2}$ ). (The relevant symmetry operations are in parentheses).

During refinement hydrogen atoms were included in pre-calculated positions with  $B = 6.0 \text{ \AA}^2$  and were not refined. An absorption correction was applied.†

The molecular structure of HMTTeF is depicted in Figure 1, with the corresponding bond distances and angles. Crystal packing is depicted in Figure 2, with the corresponding intermolecular distances. The first observation is that the structure of HMTTeF exhibits *normal* bond lengths in the carbocyclic rings when compared with HMTSF (hexamethylenetetraselenafulvalene)<sup>3</sup> or HMTSF.TCNQ (TCNQ = tetracyanoquinodimethane).<sup>4</sup> The differences between these molecules are more pronounced when the heterocyclic rings are compared. For example, compare the angles C(5)–Te(1)–C(12) =  $90.2(2)^\circ$  vs. C(5)–Se–C(12) =  $92.6^\circ$ ,<sup>4</sup> Te(1)–C(5)–C(1) =  $122.1(4)^\circ$  vs. Se(1)–C(5)–C(1) =  $119.6^\circ$ ; the remaining angle is the same for both tellura and seleno analogues ( $115.2^\circ$ ). The differences in the first two angles are probably just a reflection

of the need to accommodate the difference in size between selenium and tellurium. In the chalcogen fulvalenes the C–X (X = S, Se, Te) bond length increases in the order C–S (1.75 Å),<sup>5</sup> C–Se (1.89),<sup>6</sup> and C–Te (2.098, *cf.* Figure 1).<sup>7</sup> The central double bond [C(11)–C(12)] is slightly longer than a normal double bond length but of the order of that observed for TMTSF (TMTSF = tetramethylselenafulvalene):<sup>6</sup> HMTTeF, 1.356(7); HMTSF, 1.383;<sup>4</sup> TMTSF, 1.352.<sup>6</sup> This is surprising since there should be a great deal of steric repulsion around this linkage due to non-bonded interactions between the four large tellurium atoms linked to these two  $sp^2$  hybridized carbon atoms.

The mode of packing is unexpected when compared with TTF<sup>5</sup> (tetrathiafulvalene), TMTSF,<sup>6</sup> and TTeT<sup>7</sup> (tetra-telluranaphthacene) in that there is no tendency for HMTTeF to form uniform stacks. HMTTeF exhibits two intermolecular tellurium contacts that are significantly shorter than the sum of the tellurium Van der Waals' radii [the Te(3)–Te(3) distance of 3.583 Å is the shortest intermolecular tellurium

† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

‡ In HMTSF.TCNQF<sub>4</sub> the donor has lost one electron and it is not surprising that the central double bond is longer in the cationic fulvalene.

contact observed to date].§ These interactions cause a zigzag-chain arrangement of adjacent molecules with neighbouring chains approximately perpendicular. The Te(3)–Te(3) interaction lies in the plane of the two contacting molecules while the Te(4)–Te(4) interaction is approximately perpendicular to the molecular planes (see Figure 2). It appears as though the driving force for crystallization of HMTTeF is formation of a tellurium network regardless of molecular shape (carbon framework) and *electronic structure*, in agreement with interpretation of solution electrochemical properties.<sup>1</sup>

We conclude that the structure of bi(1, 2, 4, 5, 6-pentahydro-1,3-ditellurapentalen-2-ylidene) (hexamethylenetetratellurafulvalene) previously assigned to the new compound is indeed correct. The unusual features discovered in this study were: (a) HMTTeF is surprisingly similar (practically identical) in size and shape to HMTSF; (b) even though the molecular structures of the selenium and tellurium fulvalenes are identical, the HMTTeF's mode of packing in the solid state is radically different from any other chalcogen fulvalene; and (c) HMTTeF is remarkably stable to elevated temperature (continuous Soxhlet extraction in butyl acetate for over 24 h, exposed to the atmosphere). This work in conjunction with that on ditellurafulvenes<sup>8</sup> leads us to conclude that divalent tellurium forms unusually strong bonds to sp<sup>2</sup> hybridized as contrasted to sp<sup>3</sup> hybridized carbon and that molecules containing divalent tellurium bonded to sp<sup>2</sup> hybridized carbon exhibit short intermolecular tellurium contacts.<sup>7,8</sup>

§ A. Bondi, *J. Phys. Chem.*, 1964, **68**, 441 gives a Van der Waals' radius for Te of 2.06 Å. The Te(3)–Te(3) intermolecular contact of 3.583 Å is 0.54 Å shorter than 4.12 Å (sum of above Van der Waals' radius).

We thank E. A. Chandross and T. J. Kistenmacher (Johns Hopkins University) for critical comments. M. P. C., P. J. C., and M. V. L. are grateful to the National Science Foundation for financial support.

Received, 8th July 1982; Com. 796

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