

# “Sulflower”: A New Form of Carbon Sulfide\*\*

Konstantin Yu. Chernichenko, Viktor V. Sumerin,  
Roman V. Shpanchenko, Elizabeth S. Balenkova, and  
Valentine G. Nenajdenko\*

Besides the many aesthetic aspects of chemistry,<sup>[1]</sup> such as molecular complexity,<sup>[2]</sup> self-organization, and nonlinear dynamics, the sheer beauty and elegance of molecular structures has always played an important role in the development of chemistry.<sup>[3]</sup> A classic example is buckminsterfullerene, a molecule whose name is dedicated to a great architect. Starting from the idea of an elegant highly symmetrical C<sub>60</sub> structure and its theoretical analysis, fullerene chemistry now lies in the mainstream of contemporary science.<sup>[4]</sup> The rapid growth of modern nanoscience and materials science has stemmed to an extent from the discovery of fullerenes.<sup>[5]</sup> Herein, we describe the investigation of a first representative of the new class of highly symmetric molecules with unusual electronic properties, namely the octathio[8]circulene (**1**)—the first fully heterocyclic circulene.<sup>[6]</sup> This molecule, which we have named “sulflower” (from sulfur and flower) has several remarkable features: It is both organic and inorganic as it has a belt of eight annulated thiophenic cycles and contains no hydrogen atoms. Its molecular formula C<sub>16</sub>S<sub>8</sub> (or simply (C<sub>2</sub>S)<sub>8</sub>) allows one to classify it as a novel form of carbon sulfide. Its highly symmetric planar structure resembles the bloom of a sunflower or an eight-pointed star (Figure 1).

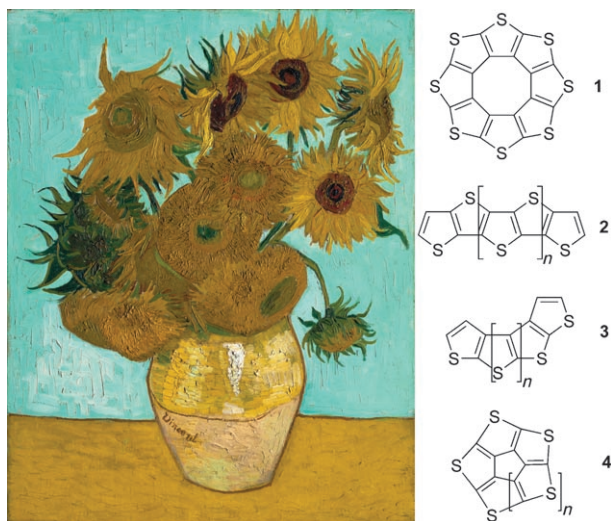
Several binary carbon–sulfur compounds are known besides CS<sub>2</sub> and its polymeric form, such as C<sub>3</sub>S<sub>2</sub>, C<sub>3</sub>S<sub>8</sub>, C<sub>4</sub>S<sub>6</sub>, C<sub>5</sub>S<sub>7</sub>, C<sub>6</sub>S<sub>8</sub>, C<sub>6</sub>S<sub>10</sub>, C<sub>6</sub>S<sub>12</sub>, C<sub>8</sub>S<sub>8</sub>, and C<sub>9</sub>S<sub>9</sub>.<sup>[7]</sup> The hypothetical polymer (–C=C–S–)<sub>n</sub> is also an isomeric form of C<sub>2</sub>S and some lower representatives of this have been synthesized.<sup>[8]</sup> Annulated oligothiophenes represent another form of carbon sulfide with the formula (C<sub>2</sub>S)<sub>n</sub>. There are two types of thiophenic ring annulation, namely 2,3-*b* and 3,2-*b*, that allow the formation of oligomeric annulated structures. Combination of these annulation types gives essentially an infinite

[\*] K. Y. Chernichenko, V. V. Sumerin, Dr. R. V. Shpanchenko, Prof. Dr. E. S. Balenkova, Prof. Dr. V. G. Nenajdenko  
Department of Chemistry  
Moscow State University  
Leninskiye Gory, 119992 Moscow (Russia)  
Fax: (+ 7) 495-932-8846  
E-mail: nen@acylium.chem.msu.ru

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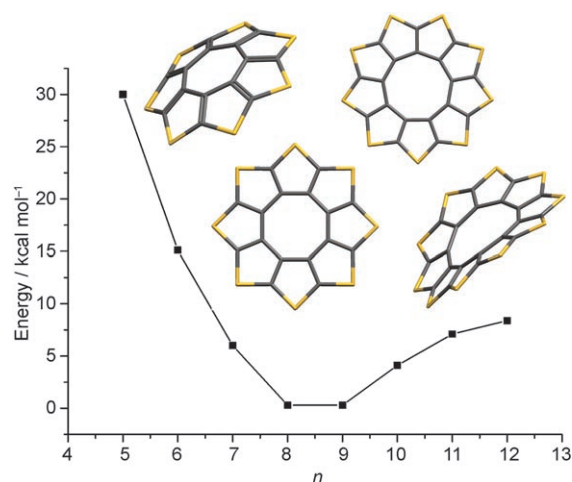


**Figure 1.** Left: “Sunflowers” by Vincent van Gogh (Copyright, Neue Pinakothek, Munich). Right: Types of annulated oligothiophenes: sulflower (**1**), linear **2**, helical **3**, and circulenic **4**.

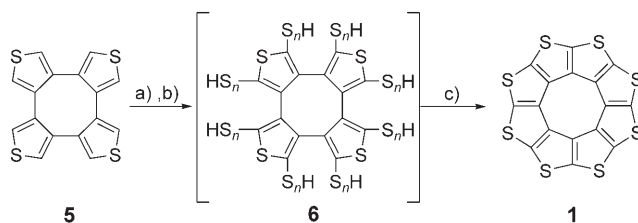
variety of annulated oligothiophene forms, while the most interesting are structures with regular annulation, such as linear oligothiophene **2** and helical oligothiophene **3** (Figure 1). Examples of these classes have been successfully synthesized recently.<sup>[9]</sup> Frameworks **2** and **3** reach the empirical formula  $C_2S$  when  $n \rightarrow \infty$ , that is, in the case of a polymer, thus giving rise to a new form of carbon sulfide. A helical structure could be closed to give a macrocycle, thus forming the circulene **3**, which consists of thiophenyl rings with an empirical formula  $C_2S$  for any number of rings.

Initially, we used quantum chemical calculations to estimate the stability of thiophenyl circulenes and to choose the most promising candidate for synthetic preparation. According to the calculations, the strain is minimized in the flat, fully thiophenyl circulenes that contain eight or nine thiophene rings (**4**,  $n = 4, 5$ ; Figure 1). To cope with the strain, lower members distort into crown-shaped structures analogous to the previously synthesized corannulene and trithia-coronene,<sup>[10]</sup> while circulenes, which contain larger number of units, create corrugated structures as was predicted<sup>[11]</sup> and confirmed by the structure of [7]circulene.<sup>[12]</sup> All calculated structures are highly symmetric, with circulenes that contain up to nine rings exhibiting an  $n$ -fold symmetry axis ( $n$  is the number of rings; Figure 2).

Of the two almost unstrained circulenes, the octathio[8]-circulene **1** was chosen as a synthetic target. For a long time, highly annulated oligothiophenes remained practically unexplored because of the lack of suitable synthetic methodology. Although significant progress in this area has been made in the last two years,<sup>[13]</sup> the nontrivial structure of sulflower presented a unique challenge which required the development of a new synthetic strategy that proved to be quite effective, simple, and straightforward. We chose tetrathiophene **5** as the most perspective precursor to **1** and envisioned that effective introduction of sulfur could be achieved through the lithium salts of **5** (Scheme 1). The essential innovation in our approach involved simultaneous treatment



**Figure 2.** Calculated strain and geometries for fully thiophenic circulenes ( $n$  = number of thiophene rings). S yellow, C gray.

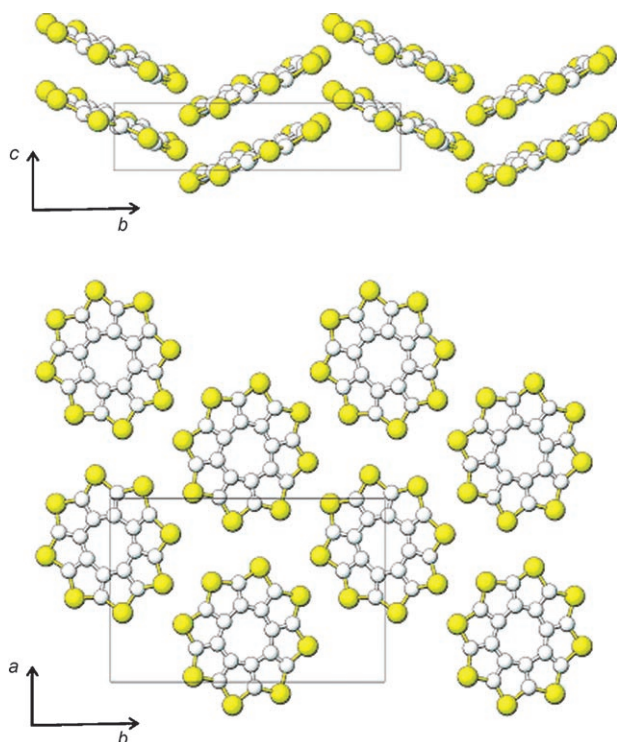


**Scheme 1.** Synthesis of circulene **1** from tetrathiophene **5** via polythiol **6** ( $n = 1$ ). Reagents and conditions: a) LDA (16 equiv), sulfur (16 equiv), room temperature, 24 h; b) aq. HCl; c) vacuum pyrolysis.

of **5** with an excess of lithium diisopropylamide and sulfur. This technique resulted in complete sulfurization of free thiophene sites and efficient formation of an intermediate polythiolate, which was then converted into polythiol **6** by acidification with HCl.<sup>[14]</sup> Subsequent vacuum pyrolysis of the crude polythiol led to elimination of the excess of sulfur through  $H_2S$  and elemental sulfur. The target circulene **1** was obtained in overall 80% yield starting from **5**, which itself is easily attained in 70% yield starting from commercially available 3,4-dibromothiophene.<sup>[15]</sup> Thus, we have developed an extremely short and effective approach to this complicated and aesthetic molecular architecture.

Sulflower (**1**) was isolated as a dark red powder that is insoluble in common organic solvents. Elemental analysis and high-resolution mass spectrometry (HRMS) revealed a perfect agreement of analytical data for **1** with the calculated values. In particular, the molecular ion multiplet at  $m/z$  448 in the mass spectrum showed the same relative intensities and  $m/z$  ratios as those predicted. The high symmetry of sulflower was confirmed by both solid-state magic-angle spinning (MAS)  $^{13}C$  NMR experiments, which revealed two signals at  $\delta = 125$  and 138 ppm, and IR spectroscopy, which showed very weak absorption (the average absorbance was less than 0.05, while maximal adsorbance of highest peaks was less than 0.2). Intense peaks at 499, 724, and 947  $cm^{-1}$  are characteristic for C–S bonds in annulated oligothiophenes.<sup>[16]</sup>

The final proof of the structure was obtained by X-ray diffraction measurements. Although good-quality single crystals of circulene **1** were not accessible, the X-ray powder diffraction data were successfully used for the final solution and refinement of the structure.<sup>[17]</sup> The results of structure refinement revealed a very good agreement between the calculated and experimental data. The sulflower molecule was found to be flat, with the average bond lengths and angles close to those values for the calculated model. Despite its high symmetry, sulflower crystallizes in a non-centrosymmetric  $P2_1$  space group. The packing of the  $C_2S$  molecules in the unit cell is shown in Figure 3. Along the  $c$  axis, the molecules are



**Figure 3.** Packing of sulflower (**1**) molecules in the unit cell. S yellow, C white.

situated one under another and separated by about 3.9 Å to result in infinite columns. Inside the columns, molecules are tilted and form the corrugated layers perpendicular to the  $c$  axis. The angle between the molecules in adjacent columns is close to 131°. The separation between the sulfur atoms in the neighboring molecules is very small ( $\approx 3.25$  Å) and close to that for two neighboring atoms inside the molecule. A reduction in the electrostatic repulsion between sulfur atoms is achieved by the mutual orientation of the molecules where three closest sulfur atoms form an almost regular triangle. One should bear in mind that the precise interatomic distances cannot be obtained from the X-ray powder diffraction technique and that further structural investigations (e.g. neutron diffraction) are needed.

Organosulfur compounds display important electronic properties.<sup>[18]</sup> For example, tetrathiafulvalenes and  $\pi$ -conjugated oligothiophenes are extensively used in light-emitting

devices,<sup>[19]</sup> thin-film transistors,<sup>[20]</sup> and other applications.<sup>[21]</sup> The extremely close packing of the sulflower molecules in the solid state suggests strong intermolecular interactions both within layers and between adjacent layers. Although such interactions should be favorable for the future use of sulflower as an electron donor in materials science applications, they also result in its insolubility in common solvents and complicate the preparation of thin-film materials based on sulflower. This latter complication forced us to seek other methods to prepare a more soluble form of this molecule. Sulflower dissolves in triflic acid ( $CF_3SO_3H$ ) with the formation of deep purple solutions. ESR investigations revealed the presence of a paramagnetic species that displays a broad singlet in the ESR spectrum ( $g$  factor: 2.008), which most likely corresponds to the radical cation of sulflower. Solubility of sulflower in the form of the radical cation should allow the preparation of thin films thereof. Another possibility to prepare thin films is by vacuum sublimation owing to the high thermal stability of **1**.

In summary, sulflower is the first representative of a novel class of heterocyclic circulenes. This study illustrated the high stability of these structures and the development of an efficient synthetic methodology, which should be applicable to the new families of Se-, Te-, N-, and P-containing heterocyclic circulenes. Variation of the heteroatoms should allow the preparation of novel materials with diverse electronic properties. We have already succeeded in the preparation of a mixed thiophene-selenophene circulene,  $C_{16}S_4Se_4$  (data not shown). Further research is underway.

### Experimental Section

Starting material tetrathiophene **5** was prepared according to a described procedure.<sup>[15]</sup> Reagents were purchased from Acros Organics or Sigma-Aldrich.

**Preparation of 1:** Diisopropylamine (9.9 mL, 70 mmol) was added to a suspension of tetrathiophene **5** (0.985 g, 3 mmol) in diethyl ether (150 mL) in a 250-mL three-necked flask flashed with argon, and the mixture was cooled to  $-20^\circ\text{C}$ . A solution of  $n$ -butyllithium in hexanes (23.2 mL of 2.5 M solution, 58 mmol) was added, and the mixture was allowed to warm to about  $0^\circ\text{C}$  and then stirred at this temperature for 30 min. Powdered sulfur (1.530 g, 48 mmol) was then added, and the reaction was stirred for 24 h at room temperature. Water (100 mL) was added, and the mixture was stirred for 30 min. The aqueous layer was separated, washed with diethyl ether (50 mL), and acidified with 5 N HCl. The resulting precipitate was filtered, thoroughly washed with water, and dried in air on the filter and then under vacuum to give a solid (2.25 g). Vacuum pyrolysis was carried out at a dynamic vacuum of 0.04–0.05 torr, with the sample of polythiophene placed in the sealed end of a silica or pyrex tube and plugged with glass wool. Heating was carried out by using a flame or tube furnace. The excess of sulfur began to sublime at temperatures above  $150^\circ\text{C}$ , while circulene **1** sublimates in the temperature range  $450$ – $530^\circ\text{C}$ . The tube fragment containing the sublimed circulene **1** was cut off, and the product was purified by repeated vacuum sublimation to give pure sulflower (1.070 g).

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- [17] See Supporting Information for details of XRPD experiments. Crystal data for **1**: Dark red powder; C<sub>16</sub>S<sub>8</sub>, monoclinic, *P*<sub>2</sub><sub>1</sub>, *a* = 11.15402(18) Å, *b* = 16.5628(3) Å, *c* = 3.90742(4) Å, *β* = 94.180(1)°, *V* = 719.94(2) Å<sup>3</sup>, *Z* = 16, Cu<sub>Kα1</sub> radiation, *λ* = 1.5406 Å, *D*<sub>calcd</sub> = 2.070 g cm<sup>−3</sup>, *μ* = 1.233 mm<sup>−1</sup>, *T* = 293(2) K. CCDC 609788 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).
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