Angewandte Chemie

Eine Zeitschrift der Gesellschaft Deutscher Chemiker

Supporting Information

"Sulflower": a new form of carbon sulfide

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

Carbon sulfide forms.

Stable at usual conditions:

2. C_3S_8[1] C_4S_6[2] C_4S_6[3] C_4S_6[4]

C_5S_7 C_6S_8[5] C_6S_8[6] C_6S_8[5] C_6S_{10}[7]

C_6S_{12}[1] C_8S_8[8] C_9S_9[9, 10]

Polymeric forms:

1. Black CS_2[11] $(CS)_n$[12] $(C_3S_2)_n$[13] $(C_3S_5)_n$[5] C_8S_8[6]
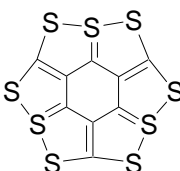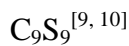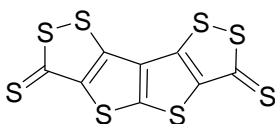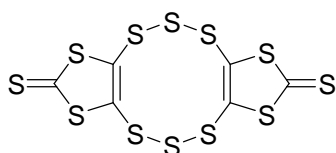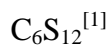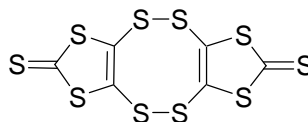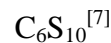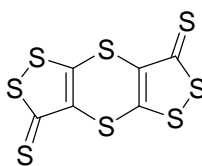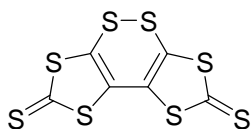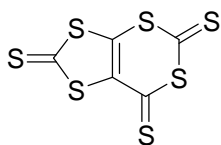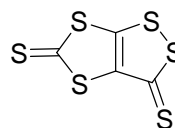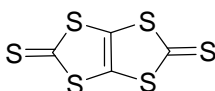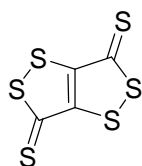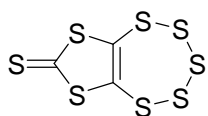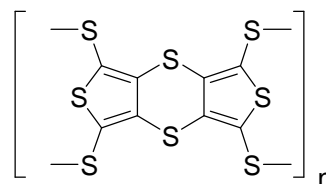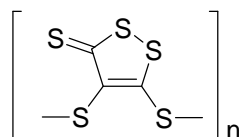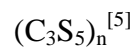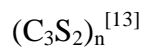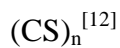
Quantum chemical calculations:

Density-functional calculations were performed within Perdew–Burke–Ernzerhof generalized gradient approximation[14] using scalar-relativistic[15] one-electron Hamiltonian and extended basis sets of Gaussian functions as implemented in a recent version of the original computer code.[16] We have used a preliminary version of scalar-relativistic basis sets of TZ2p, finite nucleus model was used. Fast riMP2 method[17] was used with cc-pVDZm basis set.

We have calculated energy of unstrained C_2S fragment from linear dependence of full energies of 2,3-*b*-annulated oligothiophenes $C_{2+2n}S_nH_4$ (n=1…5) – starting from thiophene to helical pentathiophene:
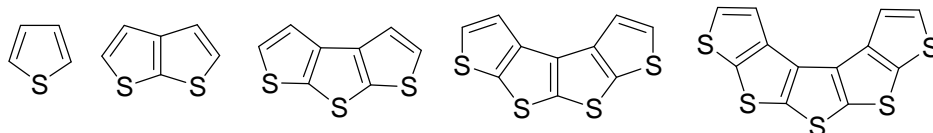
n	Full energies, Hartree	
	PBE	**riMP2**
1	-553.91315	-552.03413
2	-1029.26725	-1025.7063
3	-1504.62259	-1499.38155
4	-1979.97749	-1973.05662
5	-2455.33167	-2446.73137
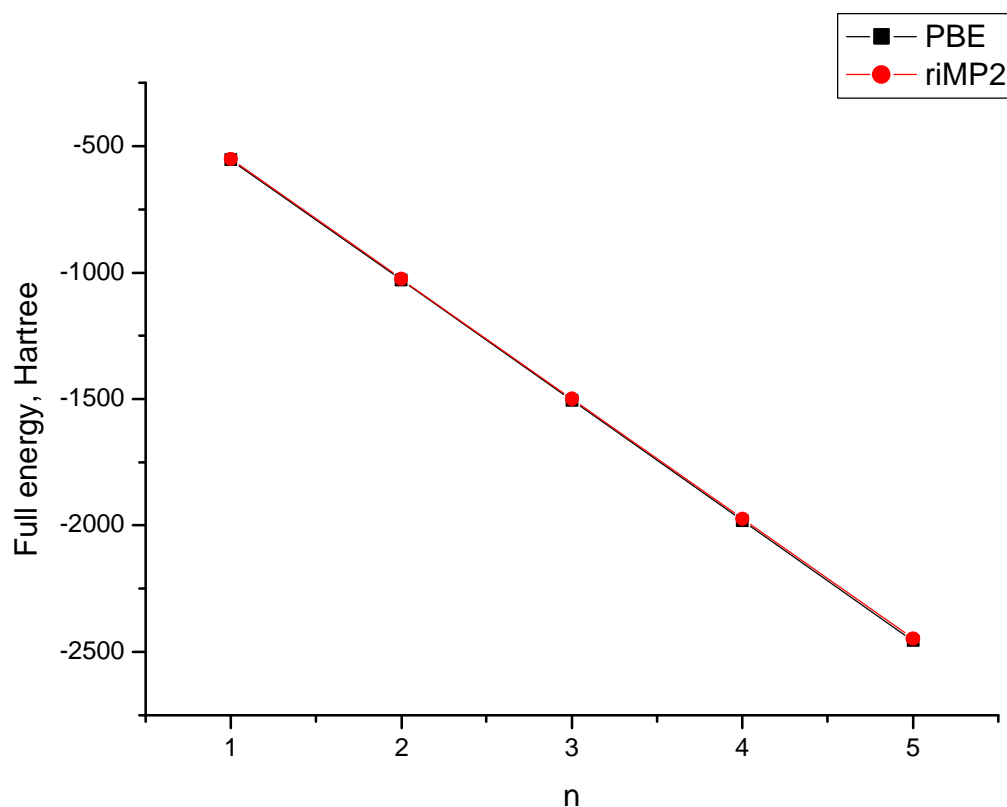
Graph linearizations give the energy of unstrained C_2S unit in 2,3-*b* annulated oligothiophenes:

E= -78.55825 - 475.35473·n (SD=3.72905E-4), **PBE**

E= -78.35856 – 473.67448·n (SD=1.01E-3), **riMP2**

A good correlation between two methods has been achieved.

Then full energies for circulenes $(C_2S)_n$ containing from 5 to 12 fused thiophenic rings have been calculated. Strain energies have been calculated as difference between circulenes full energies and corresponding number of energies of unstrained C_2S fragments.

n	Full energy of n C_2S unstrained fragments, PBE, Hartree	Full energy of circulene, PBE, Hartree	Strain energy, PBE, kcal·mol^{-1}	Full energy of n C_2S unstrained fragments, RIMP2, Hartree	Full energy of circulene, RIMP2, Hartree	Strain energy, RIMP2, kcal·mol^{-1}
5	-2376.77365	-2376.54739	142.0	-2368.3724	-2368.13367	149.8
6	-2852.12838	-2851.99176	85.7	-2842.04688	-2841.9027	90.5
7	-3327.48311	-3327.41941	40.0	-3315.72136	-3315.65428	42.1
8	-3802.83784	-3802.83243	3.4	-3789.39584	-3789.39142	2.8
9	-4278.19257	-4278.18569	4.3	-4263.07032	-4263.066	2.7

10	-4753.5473	-4753.48138	41.4	-4736.7448	-4736.67909	41.2
11	-5228.90203	-5228.77807	77.8	-5210.41928	-5210.29412	78.5
12	-5704.25676	-5704.0965	100.6	-5684.09376	-5683.93389	100.3

1 Hartree = 627.5095 kcal/mol
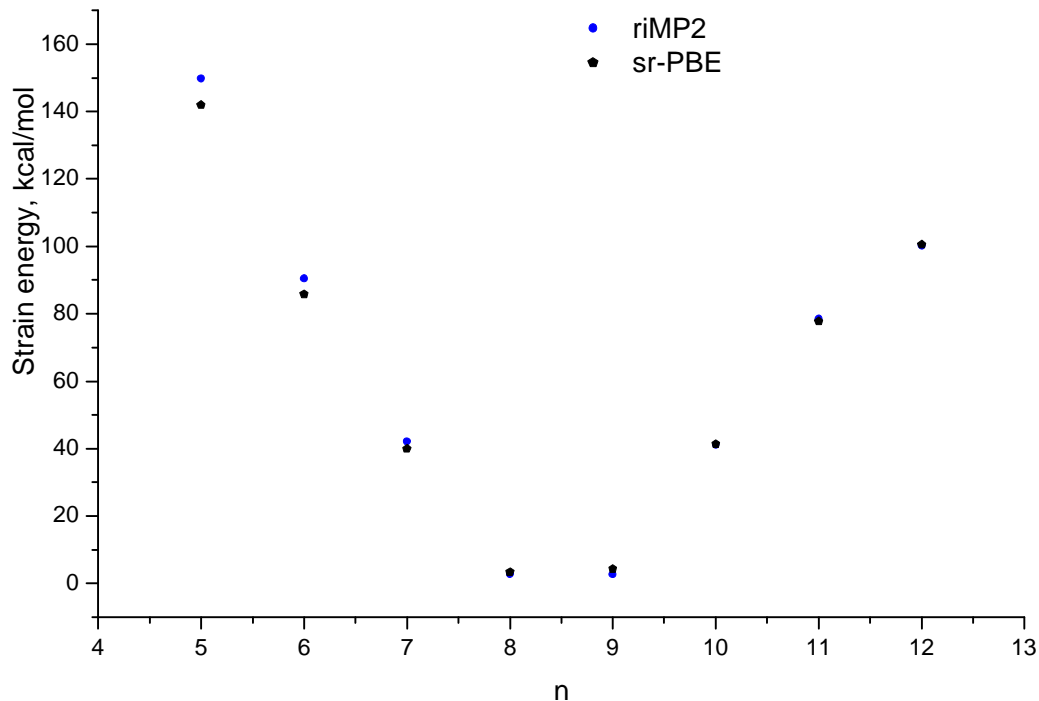
Strain energies have been referred to the numbers of the thiophene rings in corresponding circulene giving the graph in article text.

Characterization:

Elemental analysis. Elemental analysis has been carried out in the Laboratory of elemental analysis at A. N. Nesmeyanov Institute of Organoelement Compounds (Russian Academy of Sciences).

	C	S	H
Calc.	42.83	57.17	0
Exp.	42.82	57.33	-

HRMS.

Exp.		Calc.	
m/z	RI, %	m/z	RI, %
447.7760	100.00	447.776568	100.0000
448.7791	23.99	448.778851	23.7099

449.7731	36.21	449.772970	38.8445
450.7769	7.99	450.774946	8.4771
451.7704	6.56	451.769464	6.8037

NMR spectrum.

^{13}C MAS (Magic Angle Spinning) solid NMR spectrum has been recorded on Bruker Avance-600 at working frequency of 150 MHz and spinning rate of 5 KHz (4mm rotor). Satellite lines at *ca.* 171 ppm, 158 ppm, 105 ppm and 92 ppm are spinning sideband peaks corresponding to 5 KHz spinning rate. 600 seconds delay between pulses was used due to extremely long relaxation time for the carbons nuclei of Sulflower. Full acquisition time to record spectrum was 50 hours.
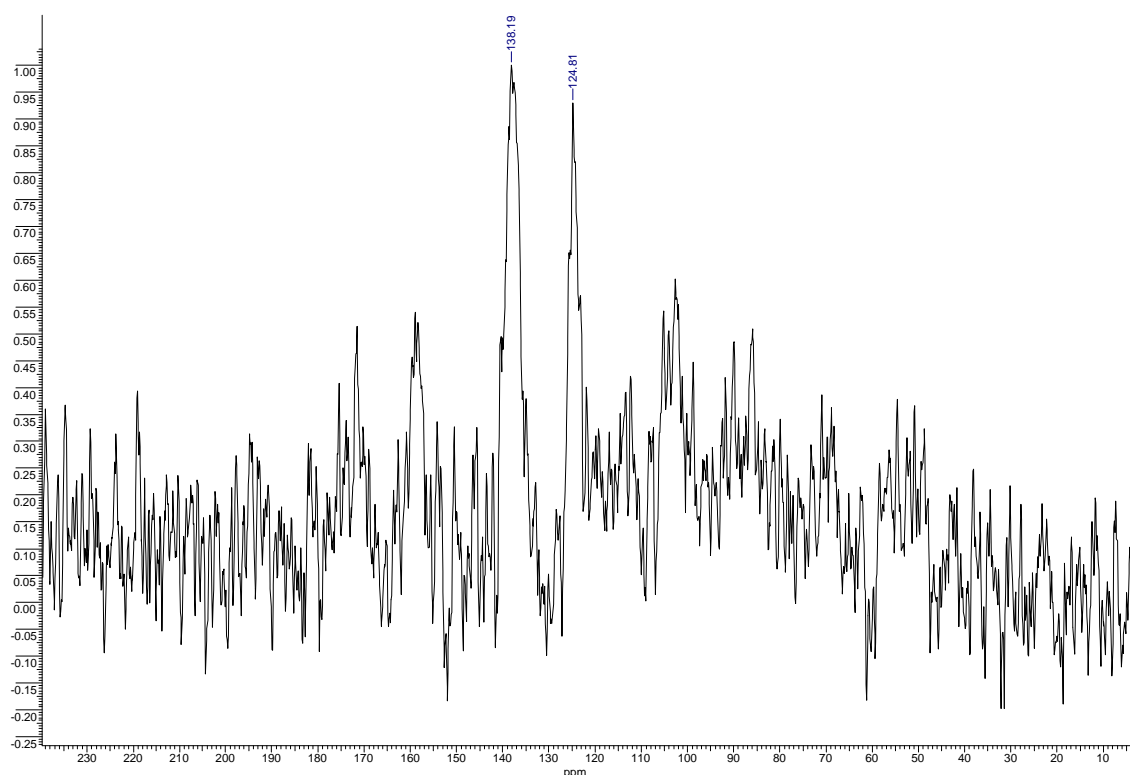
FT-IR spectrum

IR spectrum has been recorded on IR-200 Thermo Nicolet (KBr).
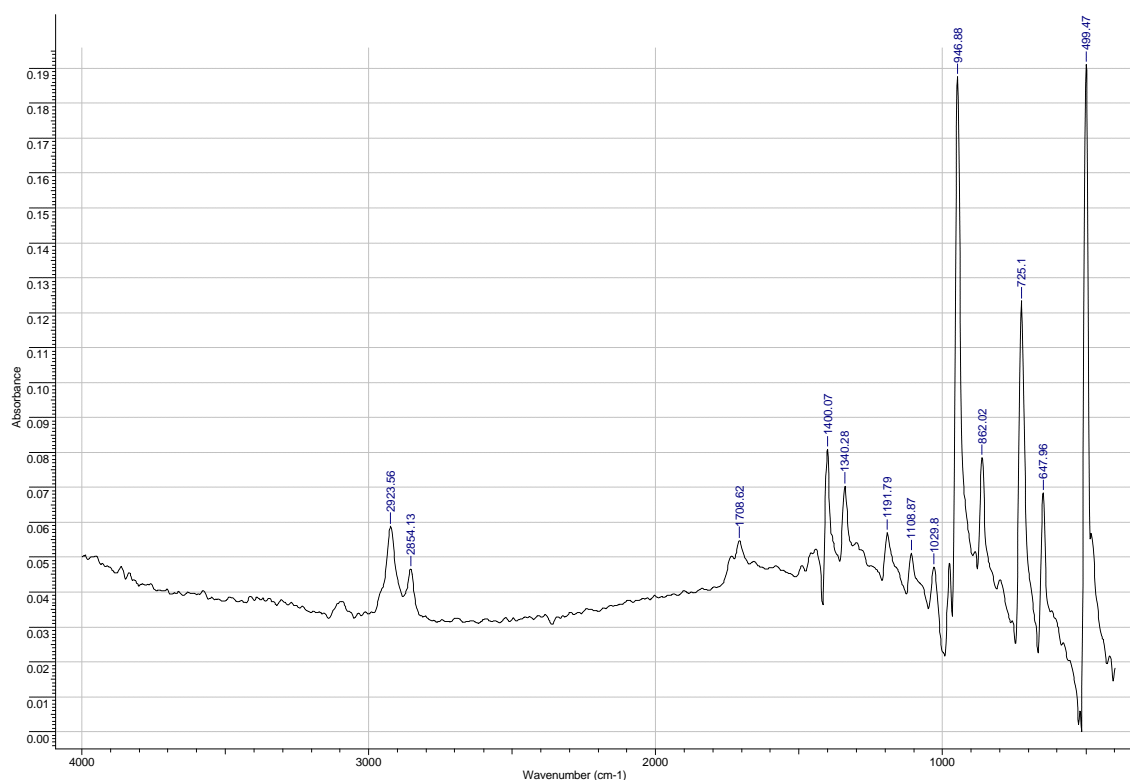
X-Ray Powder Diffraction (XRPD):

The XRPD data set for **4** was collected at an automated STADI/P (Stoe) powder diffractometer (Cu $K\alpha_1$-radiation, *l* = 1.5406 Å, Ge-monochromator, linear PSD, step 0.01° 2*q*, 20 °C). Peak positions determined by profile fitting were used for indexing with the TREOR90 program[18]. The indexing yielded a monoclinic unit cell with lattice parameters of *a* = 11.1548(3), *b* = 16.5633(4), *c* = 3.90776(9) Å, *b* = 94.180(2)°, *V* = 720.07(4) Å^3, *Z* = 16 and the only systematic extinction, namely, *00l*: *l*=2n resulting in $P2_1$ or $P2_1/m$ possible space groups.

The structure was then solved in two steps. At the first step, the starting model for Rietveld refinement was found using the FOX program[19] where the $C_{16}S_8$ scatterer was created. Insertion of rigid body instead of individual atoms resulted in the reduction of the refined atomic parameters from 72 to 6 (three positional and three rotational parameters per molecule). Interatomic distances and angles for rigid body were taken from[21]. This procedure allowed us to find approximate positions of the $C_{16}S_8$ molecule in the unit cell only for non-symmetrical $P2_1$ space group. Further refinement was carried out in the GSAS program.[20] At the beginning, the soft constrains for interatomic separations (1.40±0.03 Å and 1.76±0.05 Å for C–C and C–S bonds, respectively) were applied for the molecule. Atomic displacement parameters were fixed at 0.04 Å^2 and were not refined. Full profile refinement confirmed that found structural model is correct. After the restrains were removed the molecule conserved flat however, the distances spread increased. Since the R-factor and c^2 values remained almost unchanged the restrains were used in the final refinement. The values of the reliability factors wR_p, R_p and c^2 have been calculated at 0.036, 0.027 and 1.44, respectively. Main crystallographic data and X-ray experimental conditions are

listed in Table 1. Atomic coordinates and refinement parameters are given in the cif-file. One should note that calculated and average experimental bond length and angles (even those refined without restrains) are in a good agreement. The experimental, calculated and difference X-ray patterns for $C_{16}S_8$ are shown in Fig.1.
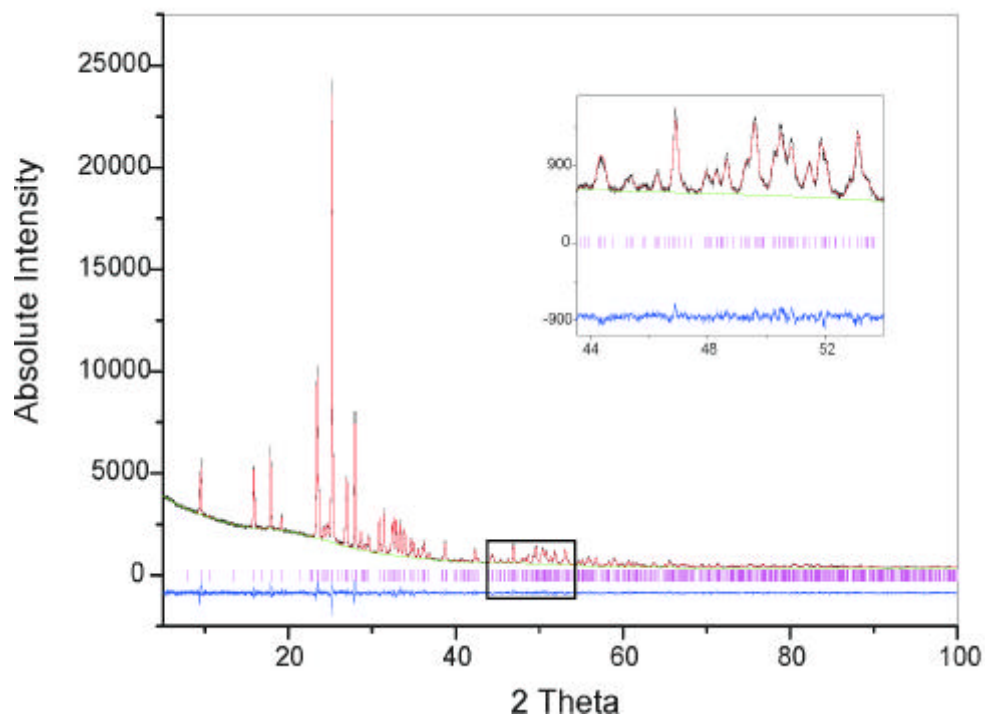
Figure 1. The Rietveld plot for the X-ray powder diffraction pattern of C_2S at 293 K: observed pattern (black), calculated (red), background (green), and difference (blue) profiles are given. The magenta bars at the bottom indicate the peak positions.

Plane geometry of **4** is in good agreement with the structure of annulated tetrathiophene synthesized recently by our group[21].

Table 1. Main Crystallographic Data for C_2S

formula	C_2S
fw	879.312
space group	$P2_1$
a (Å)	11.15402(18)
b (Å)	16.5628(3)
c (Å)	3.90742(4)
b (°)	94.180(1)

V (Å^3)	719.94(2)
Z	16
Radiation	Cu Kα_1
$\boldsymbol{l}$ (Å)	1.5406
D_{calc} (g cm^{-3})	2.070
$\boldsymbol{m}$(mm^{-1})	1.233
T (K)	293(2)
Number of atomic sites	24
$2\boldsymbol{q}$ range, step (deg)	5-110, 0.01
data collection mode	transmission
Texture parameter along 001	0.841(9)
Reliability factors	$R_p^{a} = 0.027$
	$wR_p^{b} = 0.036$
	$\boldsymbol{c}^{2\,c} = 1.44$
Restrain contribution to $\boldsymbol{c}^2$	1.3%

[a] $R_P = \mathrm{S}(|I_o - I_c|)/\mathrm{S}I_o.$

[b] $wR_P = [\mathrm{S}w(I_o - I_c)^2/\mathrm{S}wI_o^2]^{\frac{1}{2}}.$

[c] $\boldsymbol{c}^2 = \mathrm{S}w(I_o - I_c)^2/(N_{obs} - N_{var})$

[1] Yang, X., Rauchfuss, T. B. Wilson, S. R., An organometallic route to binary carbon sulfides. The structure of C$_6$S$_{12}$. *J. Am. Chem. Soc.* **111**, 3465-3466 (1989).

[2] Richter A. M., Fanghänel E., Donatorsubstituierte polyacetylene und analoga II. Notiz über die synthese einfacher derivate des neuen heterobicyclischen grundkörpers 3H,6H-1,2-dithiolo[4,3-c](1,2)-dithiol. *Tetrahedron Letters*, **24**(34), 3577-3578 (1983).

[3] Schumaker, R. R., Engler, E. M., Thiapen chemistry. 2. Synthesis of 1,3,4,6-tetrathiapentalene-2,5-dione. *J. Am. Chem. Soc.* **99**, 5521-5522 (1977).

[4] Beck, J., Daniels J., Roloff, A., Wagner, N., Isomers among the carbon sulfides C_4S_6 – synthesis and crystal structures of α,α-C_4S_6, α,β-C_4S_6, and of a second polymorph of the diiodine adduct α,β-$C_4S_6 \cdot I_2$. *Dalton Trans.* 1174–1180 (2006) and references therein.

[5] Doxsee, D. D., Galloway, C. P., Rauchfuss, T. B., Wilson, S. R., Yang X., New carbon sulfides based on 4,5-dimercapto-l,2-dithiole-3-thion(β-$C_3S_5{}^{2-}$): $[C_3S_5]_n$, C_6S_8 and C_5S_7. *Inorg. Chem.* **32**, 5467-5471 (1993).

[6] Chou, J.-H., Rauchfuss, T. B., Solvatothermal routes to poly(carbon monosulfide)s using kinetically stabilized precursors. *J. Am. Chem. Soc.* **119**, 4537-4538 (1997).

[7] Galloway, C. P., Doxsee, D. D., Fenske D., Rauchfuss, T. B., Wilson, S. R., Yang X., Binary Carbon Sulfides Based on the α-C3S5 Subunit and Related C-S-O, C-S-Cl, and C-S-N Compounds. *Inorg. Chem.* **33**, 4537-4544 (1994).

[8] Gompper R., Knieler R., Polborn K., Thieno[2,3-b]thiopheno[3,2-c;4,5-c']bis(1,2-dithiole)-3,6-dithione - an octamer of carbon sulfide. *Z. Naturforsch.*, *B* 48 (11) 1621-1624 (1993).

[9] Hansen, L. K., Hordvik, A., *X*-Ray crystal structure of benzo[1,2-*c*;3,4-*c'*;5,6-*c''*]tris[1,2]dithiole-1,4,7-trithione: a sulphur analogue of coronene. *J. Chem. Soc., Chem. Commun.*, 800-801 (1974).

[10] Brown, J. P., Gay, T. B., Benzo[1,2-*c*;3,4-*c'*;5,6-*c''*]tris[1,2]dithiole-1,4,7-trithione. *J. Chem.* Soc., *Perkin Trans. 1*, 866-868 (1974).

[11] Ochiai B., Endo, T., Carbon dioxide and carbon disulfide as resources for functional polymers. *Prog. Polym. Sci.*, **30**, 183 – 215 (2005) and references therein.

[12] Zmolek P. B., Sohn H., Gantzel P. K., Trogler W. C., Photopolymerization of Liquid Carbon Disulfide Produces Nanoscale Polythiene Films. *J. Am. Chem. Soc.* **123**, 1199-1207 (2001) and references therein.

[13] Stadlbauer W., Kappe T., The chemistry of carbon subsulfide. *Sulfur Rep.*, **21** (4), 423-445 (1999).

[14] Perdew, J. P., Burke, K., Ernzerhof M. Generalized gradient approximation made simple. *Phys. Rev. Lett.* **77**, 3865–3868 (1996)

[15] Laikov, D. N. An implementation of the scalar relativistic density functional theory for molecular calculations with Gaussian basis sets, DFT200.–*Satellite Symp. 10th Intern. Cong. Quantum Chem.*, Menton, June 11–14 (2000)

[16] Laikov, D. N. Fast Evaluation of Density Functional Exchange-Correlation Terms Using the Expansion of the Electron Density in Auxiliary Basis Sets. *Chem. Phys. Lett.* **281**, 151-158 (1997)

[17] Kendall, R. A., Fruchtl, H. A., The impact of the resolution of the identity approximate integral method on modern ab initio algorithm development. *Theor. Chim. Acta* **97**, 158-163 (1997)

[18] Werner, P.-E., Eriksson, L., Westdahl, M. TREOR, a semi-exhaustive trial-and-error powder indexing program for all symmetries. *J. Appl. Crys.* **18**, 367-370 (1985)

[19] Favre-Nicolin, V.; Cerny, R. FOX, `free objects for crystallography': a modular approach to ab initio structure determination from powder diffraction. *J. Appl. Cryst.* **35**, 734-743 (2002)

[20] Larson, A. C.; Von Dreele, R. B. General Structure Analysis System (GSAS). *Los Alamos National Laboratory Report LAUR*, 86-748 (2000)

[21] Nenajdenko, V. G., Sumerin, V. V., Chernichenko, K. Yu., Balenkova, E. S. A new route to annulated oligothiophenes. *Org. Lett.* **6**, 3437-3439 (2004)