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From thiophene to Sulflower

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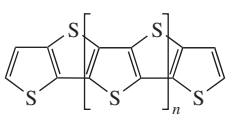
Several new approaches toward annulated oligothiophenes, including Sulflower, the first fully heterocyclic circulene, have been proposed.

The structural, electronic and optical properties of conjugated organic molecules and their oligomers and polymers have attracted widespread attention. Such π-conjugated systems as polyacetylene,[1,2] poly(*p*-phenylenevinylene)s[3–5] and polythiophenes[6,7] have received the most attention. Organosulfur compounds such as tetrathiafulvalenes and annulated oligothiophenes hold much promise in this respect due to their potential applications as organic thin-film transistors,[8] OLED[9] *etc*.[10] Annulated oligothiophenes are a rare type of π-conjugated systems. Obviously, this is due to the absence of effective methods for the synthesis of annulated oligothiophenes. For a long time, highly annulated oligothiophenes remained practically unexplored because of the lack of a suitable synthetic methodology. This article is devoted to an overview of our efforts in this field.

Thiophene can create three homological series of regular structures analogously to benzene (Table 1). Regular [3,2-*b*] junction results in linear structures, the most famous of them being dithieno[3,2-*b*:2′,3′-*d*]thiophene **1** ($n = 0$). The latter and its higher homologues attract much attention recently as potential candidates for material science.[11–13] Fully thiophenic helicenes **2** are a patrimony of the Rajca group since their first report on the synthesis of fully thiophenic [7]helicene **2** ($n = 4$).[14] Soon



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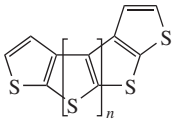

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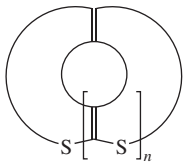

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Table 1 Annulated oligothiophenes with regular junction.

Compound	Junction	Termination	Shape	Composition
1	[3,2-*b*]	open	linear	C_2S, when $n \to \infty$
2	[2,3-*b*]	open	helical	C_2S, when $n \to \infty$
3	[2,3-*b*]	close	macrocyclic (circulene)	C_2S

Konstantin Yu. Chernichenko was born in 1982 in Kharkov, Ukraine. He is a member of the Professor Nenajdenko research group since 2001. After graduation from the Department of Chemistry of M. V. Lomonosov Moscow State University in 2006 (Diploma 'Synthesis of the first fully heterocyclic circulene'), he continued research in this field as a post-graduate student. His research interests include contemporary methods of organic synthesis. Research specialization: heterocyclic chemistry, polar organometallics and organic catalysis.

Elizabeth S. Balenkova was born in Moscow in 1926. She graduated from M. V. Lomonosov Moscow State University in 1950 and then she was a postgraduate student at the Department of Chemistry of this university. She received her PhD degree under the supervision of Academician B. A. Kazansky in 1953 for the research concerning medium ring hydrocarbons. Since that, she has been working as a senior researcher (1959) and full professor (1986). She was a supervisor of 27 postgraduate and 63 diploma works. Her research interests are in the area of organic synthesis, electrophilic addition reaction and the chemistry of heterocyclic and sulfur compounds.

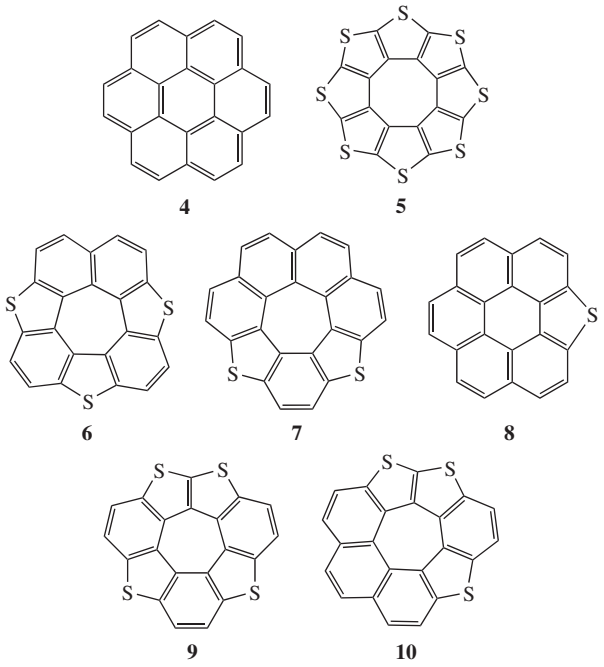
Valentine G. Nenajdenko was born in 1967 in Ivanovo, Russia. He graduated from M. V. Lomonosov Moscow State University in 1991. He received his PhD degree under the supervision of Professor E. S. Balenkova in 1994 researching the synthesis and application of unsaturated CF_3 ketones. In 2000, he received Doctor of Chemistry degree concerning chemistry of sulfonium and iminium salts. In 2003, he became a full professor of organic chemistry at the Department of Chemistry of M. V. Lomonosov Moscow State University. The field of his scientific interests includes organic synthesis, asymmetric catalysis, the chemistry of sulfur and fluorine-containing compounds and the chemistry of heterocycles. He was a supervisor of nine postgraduate works. Valentine G. Nenajdenko is head of Scientific Committee and Jury of International Mendeleev Chemistry Olympiad. He was the winner of the Academiae Europeae Award in 1997, the Russian President Award in 1996 and 2004, the Prize for the best scientific work at the Department of Chemistry of Moscow State University 2001 and 2007, Shuvalov Award 2001, Russian Science Support Foundation Award in 2005.

after that they broke their own record with the synthesis of fully thiophenic [11]helicene **2** ($n = 8$).[15] Moreover, a successful attempt was made to resolve fully thiophenic helicenes onto enantiomers along with partially successful attempts of its asymmetric synthesis.[15,16] The macrocyclic type of oligothiophenes **3**, fully thiophenic circulenes, was a missing link among these compounds.

There is no strict definition of such a class of compounds; nevertheless, circulenes are a special class of condensed polyaromatics in which a closed loop of angularly annulated benzene or heterocyclic rings surrounds an inner ring (a 'cavity').[17] The best known circulene is coronene – [6]circulene **4**.

Previously, we started a synthesis of fully heterocyclic circulene based on thiophene. Due to the systematic name of thiophenic circulene is very complex and long we called it Sulflower (from Sulfur and Flower) **5**. The molecule is both organic and inorganic because it has a belt of eight annulated thiophenic cycles and contains no hydrogen at all. Its composition $C_{16}S_8$ (or just C_2S) allows one to classify it as a novel form of carbon sulfide. The highly symmetric planar structure resembles the bloom of sunflower or eight-point star.

We have developed several approaches toward annulated oligothiophene and finally succeeded in the synthesis of Sulflower.[18]

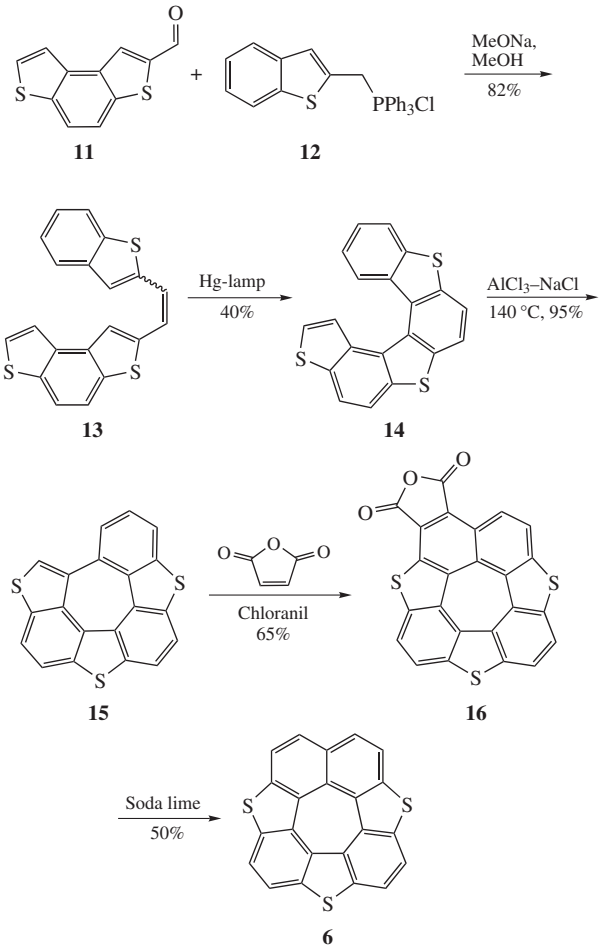


The choice falling on thiophene was not unexpected as its nucleus is the most aromatic and chemically stable among five-membered heterocycles. Partially heterocyclic circulenes containing both benzene and heteroarene rings **6–10** were known before Sulflower. Wynberg and Dopper synthesized these molecules and coined the term circulene.[19]

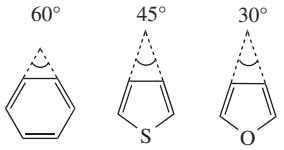
They synthesized various thiohelicenes by a sequence of the Wittig reaction followed by UV dehydrocyclization (as a key step) of the resulting stilbenes,[20–22] a perfect method for benzohelicenes synthesis. Heterohelicenes heated with $AlCl_3$/NaCl macrocyclized into dehydrohelicenes.[23] The latter were involved into the Diels–Alder reaction with maleic anhydride/chloroanil followed by decarboxylation with soda lime.[19] A typical synthetic route is illustrated by preparation of circulene **6** from **11** and **12**.

Circulene stability

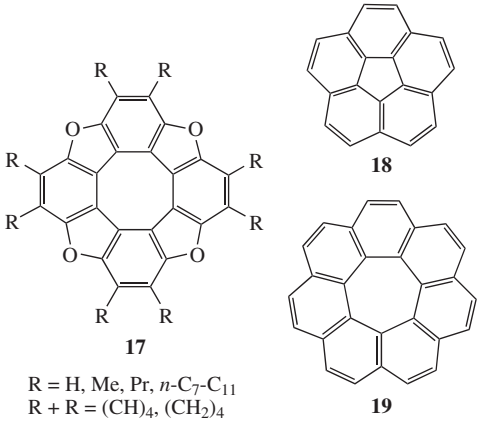
Interestingly, Wynberg and Dopper also proposed a very simple model for estimation of the circulenes strain. Circulene



is a macrocyclic ring composed of aromatic nuclei cutting off the corresponding sector of the ring. The sector angle is characteristic of every arene or hetarene:



If the angles totally are close to 360°, the circulene is flat and stable. The examples are coronene **4**, tetraoxo[8]circulenes **17**[24] ($\Sigma = 360°$), dithio- and trithio[7]circulenes by Wynberg **6–10** (Σ ranged from 345° to 390°). A stronger deviation from 360° leads to a distortion of the molecule and increases the strain. The bowl shape of corannulene **18** ($\Sigma = 300°$), as well as the saddle shape of [7]circulene **19** ($\Sigma = 420°$), can be attributed to this effect.



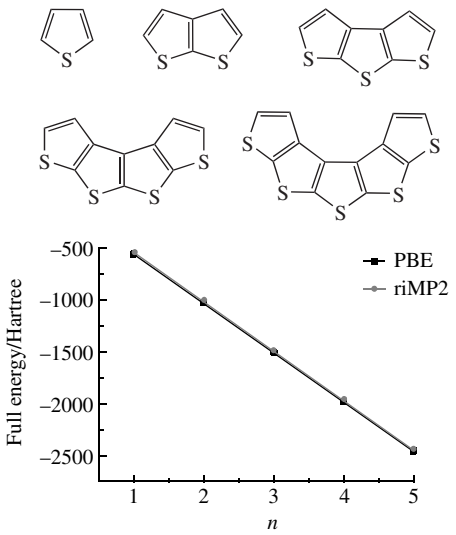


Figure 1 Calculated full energies for [2,3-*b*]-annulated oligothiophenes.

According to this model, the most stable fully thiophenic circulene should contain eight rings (Sulflower). Contemporary quantum calculations allow revaluating this result with a more reliable technique. We have calculated the energy of an unstrained C_2S fragment from the 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 (Figure 1).

Graph linearization gives the energy of an unstrained C_2S unit in [2,3-*b*]-annulated oligothiophenes:

$$E = -78.55825 - 475.35473n \text{ (SD} = 3.72905\times10^{-4}\text{), PBE}$$
$$E = -78.35856 - 473.67448n \text{ (SD} = 1.01\times10^{-3}\text{), riMP2}$$

A good correlation between two methods (PBE and riMP2) has been achieved. Then, full energies for circulenes $(C_2S)_n$ containing from 5 to 12 fused thiophenic rings have been calculated. Strain energies can be found as difference between circulene full energies and the energy of corresponding number of unstrained C_2S fragments. Strain energies have been referred to the numbers of thiophene rings in corresponding circulene (Figure 2).

It is clear from the graph that both the eight-membered and nine-membered circulenes are flat and unstrained. Accordingly, the seven-membered circulene has a bowl shape, whereas ten-membered and other higher circulenes should be saddle.

*Dithieno[2,3-*b*:3′,2′-*d*]thiophene*

One of the most convenient precursors for the synthesis of Sulflower is polythiophene **21**, which hoped to be prepared by dimerization of two 'halves', dithieno[2,3-*b*:3′,2′-*d*]thiophenes **20**.

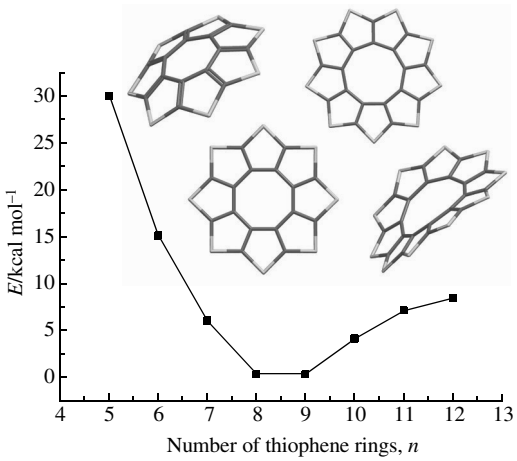
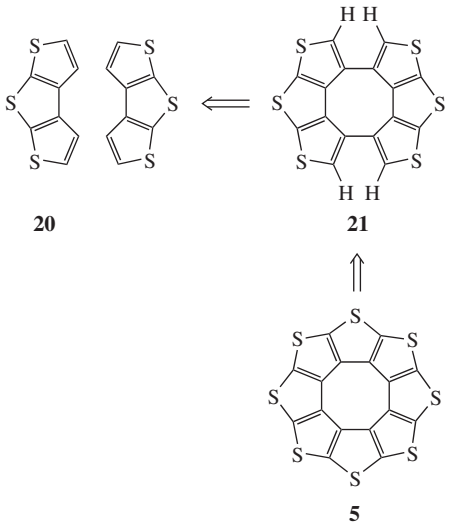
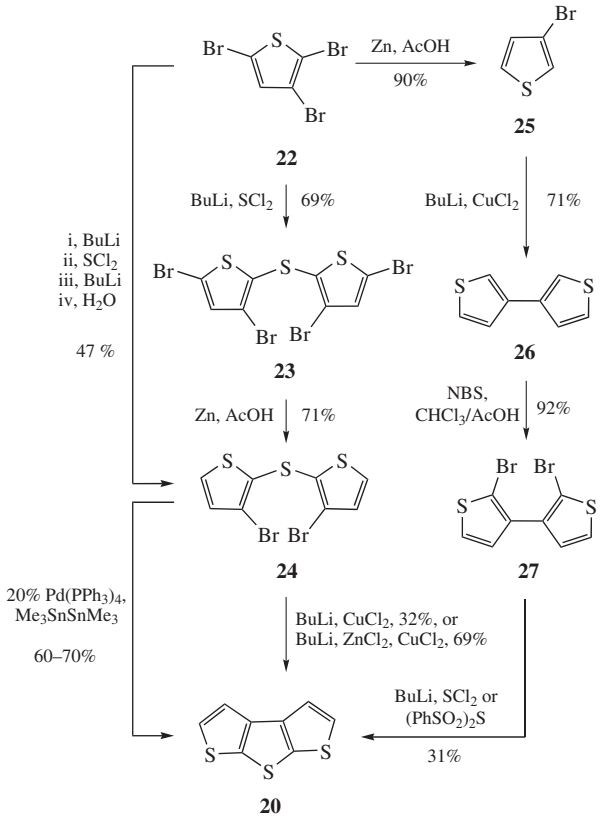


Figure 2 Strain energies of fully thiophenic circulenes.



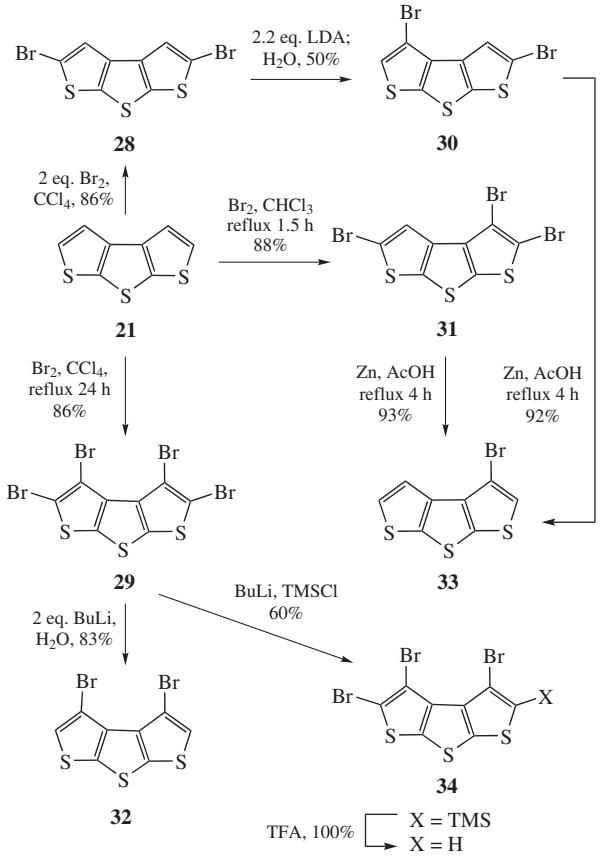
Dithieno[2,3-*b*:3′,2′-*d*]thiophene is hardly available; moreover, the yields in our hands were much lower than reported. The first part of our work on the synthesis of the heterocirculene was dedicated to an improvement of oligothiophene synthesis. Until recently, the synthetic methodology toward annulated oligothiophenes was very scarce and tedious.[25] This common methodology implies incorporation of the sulfur bridge followed by the homocoupling of two thiophene rings. The sequence is often reversed. Sulfur is usually introduced by the reaction of SX_2 (X = Cl or $PhSO_2$) with corresponding lithium salts. The homocoupling step is usually performed by the action of $CuCl_2$ on lithium salts. Despite the generality of the method, harsh reagents ($CuCl_2$, SCl_2) and necessity to work with dilithium salts result in low yields. Investigators try to improve the yields by using milder reagents, protective groups or finding better synthetic routes.

We have elaborated simple and reliable approaches toward **20**.[26] The reported synthesis of **20** involves disulfide **24** as a



precursor.[27] However, in our hands only 10–15% yields of **20** were reached. We proposed to synthesize **20** directly from 2,3,5-tribromothiophene **22** by two-step (49%) or one-pot techniques (47%). The conversion of **24** into **20** can be performed by a series of reported methods.[28,29] An alternative synthesis was based on the cyclization of **27** prepared easily from 3-bromothiophene **25**.[30] Despite low yields at the final steps, these approaches are scalable and start from commercial or easy-to-synthesize[31] reagents **22** and **25**.

Having in hand enough amounts of dithieno[2,3-*b*:3′,2′-*d*]-thiophene, we have thoroughly investigated the preparation of its derivatives. Among them the most essential for our subsequent work were bromides, iodides and organometallics. All isomeric mono-, di-, tri- and tetrabromo derivatives have been prepared.

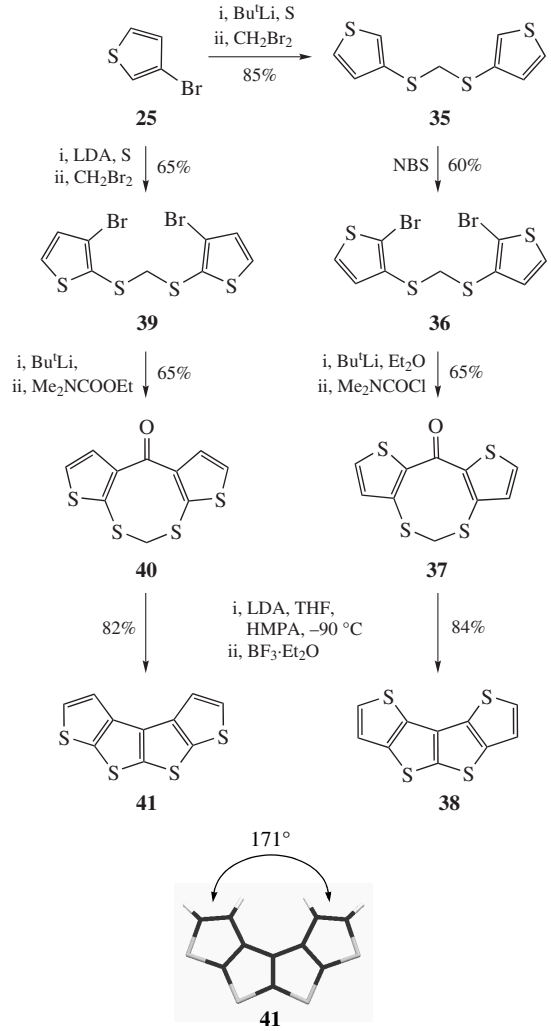


Dithieno[2,3-*b*:3′,2′-*d*]thiophene behaves similarly to thiophene and thienothiophenes. Electrophilic as well as Br–Li exchange and deprotonation reactions are directed preferably into the α-positions.

Novel approach towards annulated oligothiophenes

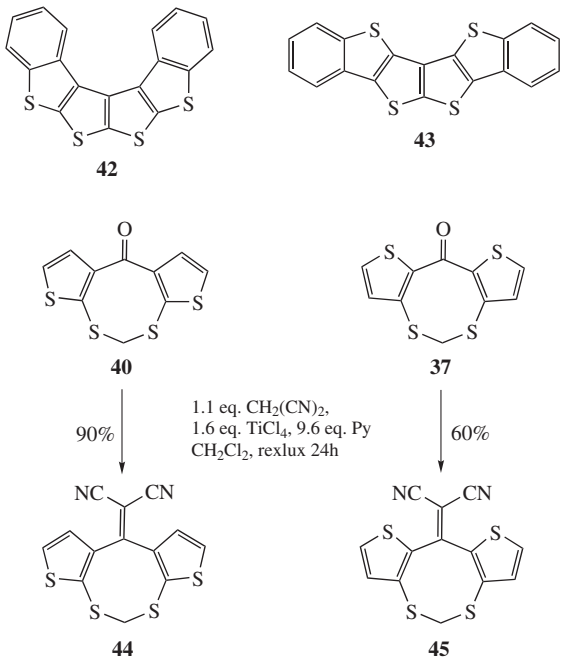
After taking experience with dithieno[2,3-*b*:3′,2′-*d*]thiophene synthesis, we proposed a nontrivial method for the synthesis of thieno[2,3-*b*]thiophene block annulated with other arenes. As a demonstration of the new strategy, two previously unknown trithienothiophenes **38** and **41** were prepared.[32] The key step involves the cyclization of corresponding 10*H*-bisthienodithiocin-10-ones **37** and **40**.

It is interesting that, from X-ray data, the angle between outer thiophenic rings in **41** is 171°, giving totally 342° for two 'halves'. Thus, the most stable configuration corresponds to about 8.5 thiophenic rings, one more confirmation for both eight- and nine-membered thiocirculenes are equally unstrained. More thorough analysis of the X-ray data for various annulated thiophenes points out that the actual value of the angle occupied by thiophene ring in annulated structures lies in the range 42.7–43.4°,[32] lower than 45° reported by Wynberg.



Trithienothiophenes **38** and **41** were subjected to further thorough spectroscopic investigations.[33]

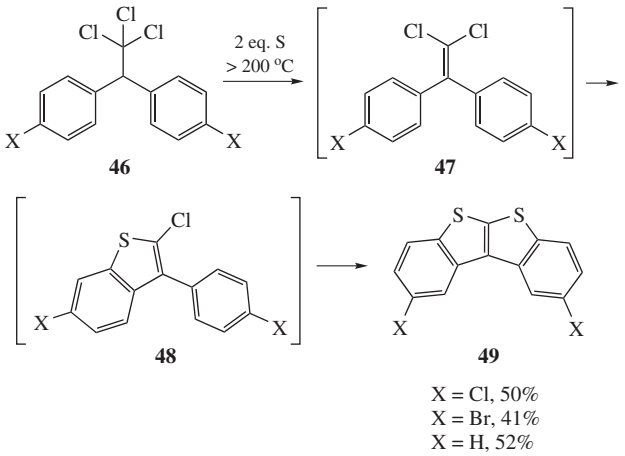
The method can be expanded to various arenes; however, it works superior for thiophenes. For example, when benzothiophene was used as a starting material, two previously unknown oligothiophenes **42** and **43** were obtained.



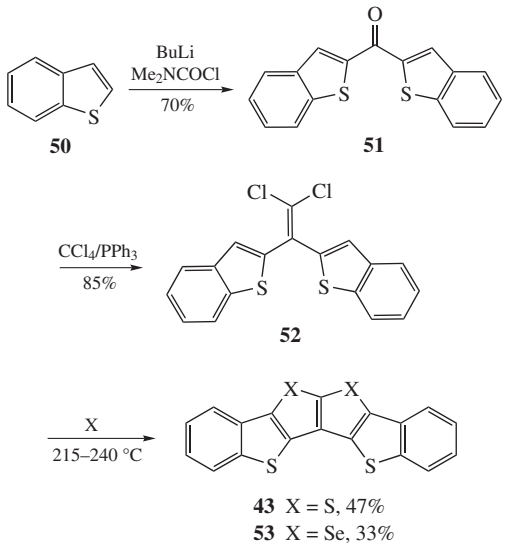
Ketones **37** and **40** have been used for the synthesis of cross-conjugated 10*H*-bisthienodithiocin-10-dicyanoethylenes **44**, **45**. The design of the structures of this type may be further improved as to provide promising advanced molecular materials with high-performance electronic and optical properties.[34]

Annulated oligothiophenes through 1,1-diaryl-2,2-dichloroethylenes

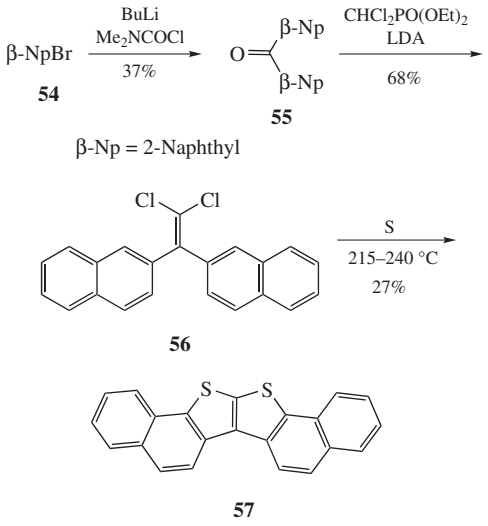
In 1968, Voronkov *et al.*[35] reported DDT and its analogues **46** when heated with sulfur in high-boiling indifferent solvent gave corresponding benzothieno[2,3-*b*]benzothiophenes **49** in moderate yields. The reaction proceeds through intermediate dichloroethylene **47** and 2-chloro-3-aryl-1-benzothiophene **48**. Despite the moderate yields and harsh reaction conditions, the availability of the starting materials and simplicity makes this approach attractive for preparative purposes.



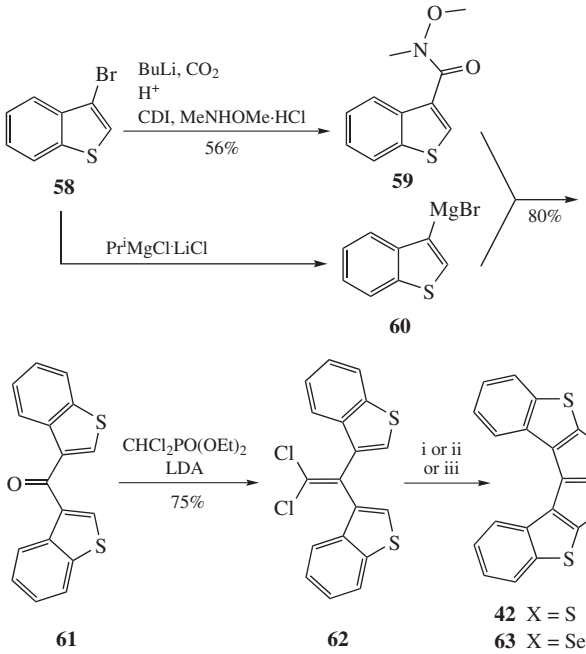
We have enhanced substrate scope of the reaction by the introduction of various symmetrical diaryldichloroethylenes with both sulfur and selenium. Dichloroethylenes **52**, **56**, **62** were prepared from corresponding diarylketones **51**, **55**, **61**, which in turn were synthesized either by the reaction of aryllithium salts with carbamoyl chloride or in a three-stage sequence through Weinreb amide **59**.



As one can see, original conditions are severe for sensitive substrates we have used especially when selenium was used instead of sulfur. The reaction was modified as follows: dichloroethylenes were simultaneously treated with LDA/sulfur or selenium, the bisthiolate (bisselenolate) thus formed was heterocyclized by heating in DMF. This allowed us to considerably increase



the yields and selectivity of the reaction. Thus, we have proposed a number of simple and effective methods for the synthesis of annulated oligothiophenes of both linear and helix types.

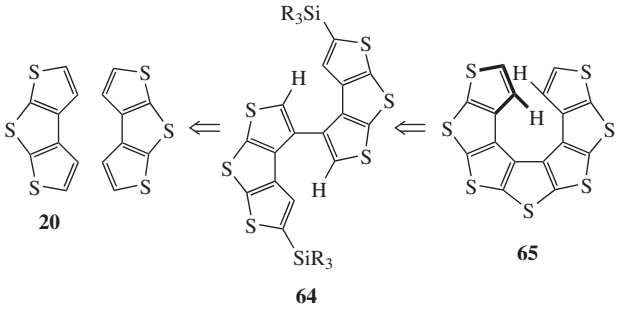


Reagents and conditions: i, S, 215–240 °C, 25%; ii, LDA/S, then DMF, 80 °C, 50%; iii, LDA/Se, then DMF, 80 °C, 25%.

Synthesis of Sulflower

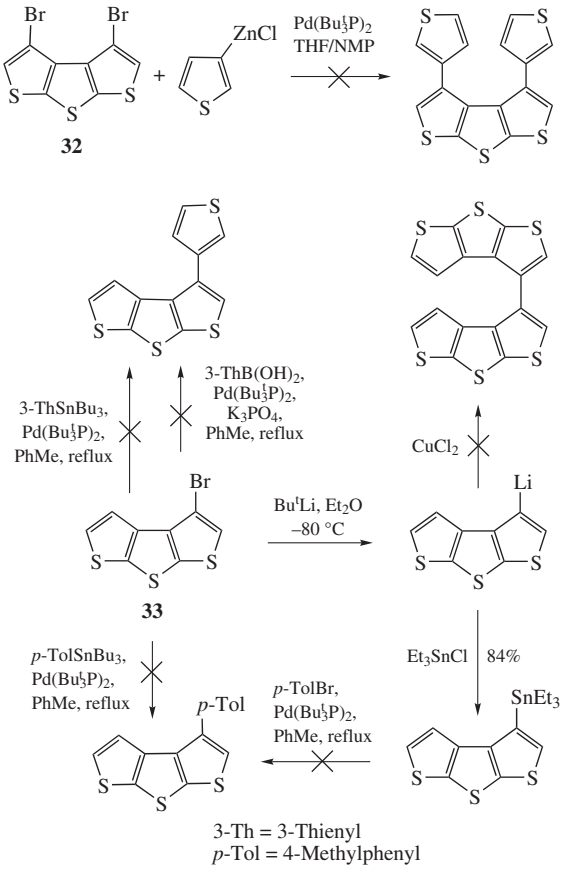
Having in our hands appropriately substituted dithienothiophene derivatives, we attempted to do cross- and homocoupling reactions with zinc, lithium, tin and boron organometallics. However, the dimerization process of dithieno[2,3-*b*:3′,2′-*d*]thiophene is counteracted by two factors: the low solubility and sterical strain of the hypothetical product **21**. The latter is due to the rigid structure along with small H···H distance. Standard methods, the oxidative homocoupling of lithium salts,[14] Pd-assisted homo-[15] or cross-coupling[36] of the dithieno[2,3-*b*:3′,2′-*d*]thiophene derivatives were used by Rajca *et al.* in the syntheses of thiophene helixes **65**. These works uncover some aspects of the chemistry of dithienothiophenes. The solubility problem was successfully solved by the introduction of lipophilic silyl or long-chain alkyl groups, whilst cross-coupling requires up to 40 mol% $Pd(Bu^t_3P)_2$ (an almost stoichiometric amount).

The introduction of bulky silyl groups into the α-position of the dithienothiophene will not work in case of **21**, as it will

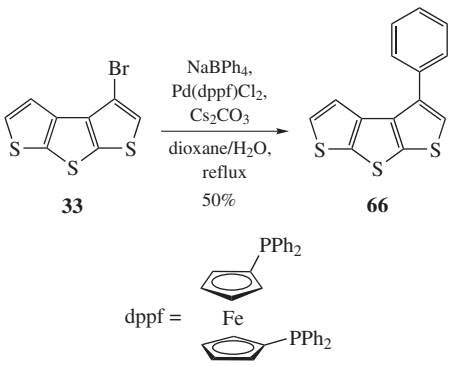


20 **64** **65**

dramatically increase the strain. Most of our efforts were unsuccessful, the only product **66** was isolated when 3-bromodithienothiophene **33** was reacted with sodium tetraphenylborate and $Pd(dppf)Cl_2$. The possible reasons were mentioned: products or intermediates insolubility and Pd catalyst inhibition by sulfur-rich heterocycle when standard load (5 mol%) is used.

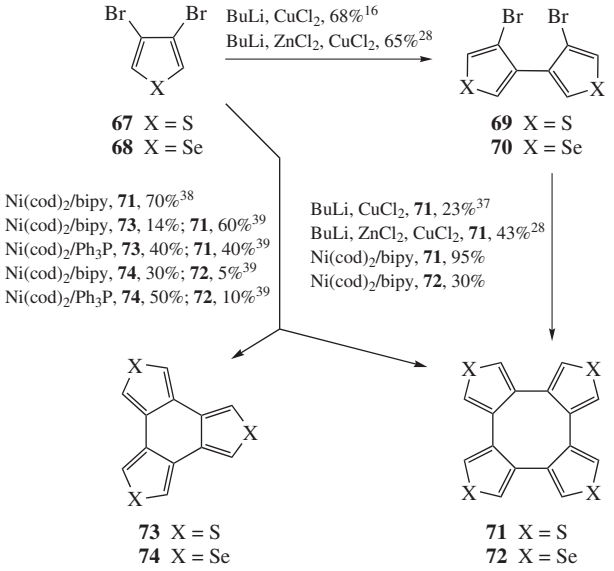


32 **33**

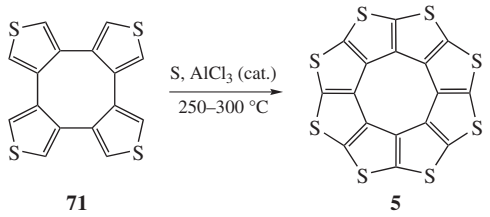


33 **66**

These failures promote us in seeking alternative routes toward heterocirculene **5**. Cyclic tetrathiophene **71** seemed to be a perfect candidate for thiocirculene synthesis. It was first synthesized from **69** by a classical approach through lithium salt homocoupling with $CuCl_2$[37] and was further improved by replacing lithium with zinc.[28] More effective is the direct coupling of 3,4-dibromothiophene **67** with an equimolar amount of $Ni(cod)_2/Ph_3P$ or $Ni(cod)_2$/bipy (2,2′-bipyridine) systems.[38] Despite its high yield and straightforwardness, it has been shown recently that tetramerization is accompanied by formation of corresponding trimer **73**. Trimerization became preferential for 3,4-dibromoselenophene **68**.[39] We have found that 4,4′-dibromo-3,3′-dithiophene **69** can be used as an attractive alternative for the preparation of **71**. This compound was converted almost quantitatively into **71** with $Ni(cod)_2$/bipy. This two-step sequence allows us to avoid the formation of trimer **73** and thus, chromatographic separation with common yield from **67** being comparable to direct tetramerization. Moreover, cyclic tetraselenophene **72** was prepared in 30% yield, which is a promising precursor for the preparation of fully selenophenic circulene.



Initial attempts of the sulfurization of **71** were made by heating with an excess of elemental sulfur. Aluminium chloride as a catalyst was found to be required for the reaction to proceed.



71 **5**

Reaction mixture was subjected to mass spectrometry analysis. Mass-chromatography analysis of the sublimation curve distinctly showed the presence of two compounds. One of them was identified as sulfur, whilst another had a molecular ion multiplet at 448, corresponding to $C_{16}S_8$. These preliminary results assured us that Sulflower **5** exists and is stable. Interestingly, **71** when treated with SCl_2 with or without $AlCl_3$ additive gives only chlorination products.

Further efforts were focused on seeking more effective synthetic ways to convert **71** into **5**. The introduction of sulfur in a thiophene ring is achieved most conveniently by metallation followed by reaction of organolithiums with sulfur. In case of **71**, this requires preparation of an octalithio derivative or multiple metallation–sulfurization steps. We proposed a novel technique based on simultaneous treatment of **71** with an excess of lithium diisopropylamide and sulfur (16 equiv. both). In ethereal solution, **71** is deprotonated rapidly by LDA. The subsequent reaction

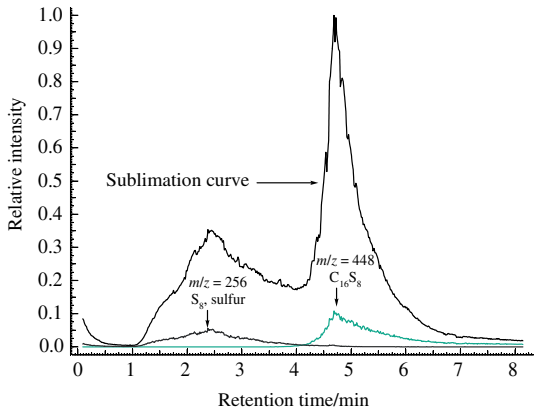
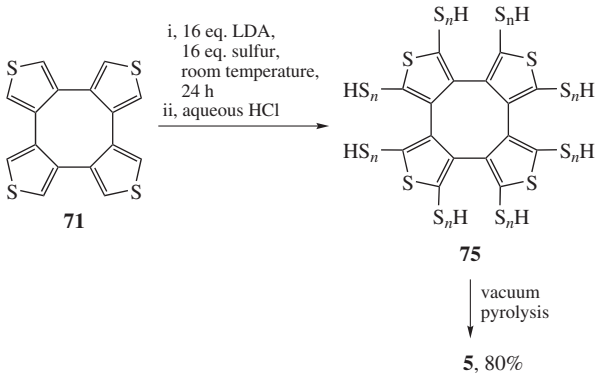


Figure 3 Mass-chromatography analysis of the products of **71** and elemental sulfur fusion.

with sulfur leads to smooth sulfurization. After acidification, the brown precipitate of polythiol **75** is subjected to vacuum sublimation. At 0.1 Torr and temperatures above 150 °C, excessive sulfur distillation is observed; over 400 °C, circulene **5** sublimates and deposits as dark red tiny needles in 80% yield.[18]



Characterization and properties of Sulflower

The substance was found to be insoluble in ordinary solvents. It was characterized by a set of standard methods, including elemental analysis and high-resolution mass spectrometry. The ^{13}C NMR spectrum has been measured as magic spin angle solid-state version due to insolubility. Two distinct signals at 125 and 138 ppm point out the molecule high symmetry. Interestingly, spectrum recording has taken several days as carbon nuclei relaxation time reached up to 10 min.

At first, we were unable to grow crystals suitable for an X-ray experiment, that is why powder X-ray diffraction method was chosen as an alternative. The crystal structure was successfully solved and proved the molecular structure. Another packing was found based on the single crystal X-ray data (space group $P2_1/n$ instead of $P2_1$).[40] The mistake can be justified by very close correct packing and those stated originally by us, the authors emphasized.

The sublimation of Sulflower always starts with small amount of white coating deposition, which is further covered with dark red crystalline Sulflower. It was unclear whether the white substance is an impurity or just a peculiar crystal form inherent to a Sulflower thin film. Extensive physico-chemical investigations of both red and white samples including Raman, IR and UV-VIS spectroscopy, as well as X-ray single crystal and powder diffraction analysis, were performed. The white deposit was stated to have a crystal packing similar to red form but less ordered. The white form is metastable and transforms into the red one on standing. It is of particular interest, because quantum chemical calculations point on Sulflower should be white, as its molecule contains no suitable adsorption lines. We have shown that in the solid state due to strong intermolecular S···S interaction absorption corresponding to red colour appears.[41]

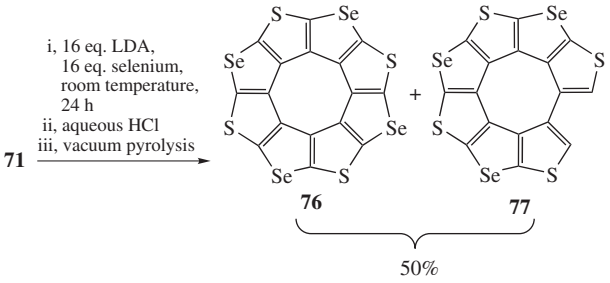
Strong S···S contacts are the characteristic feature of Sulflower. These interactions play a significant role in the physics of organic semiconductors. The design of thin-film transistor with Sulflower as semiconducting material is in progress.

Semiconducting Sulflower is one of the most obvious applications; however, based on the theoretical computations, Sulflower was speculated to be a perfect hydrogen storage material with up to ten molecules of H_2 absorbed by one Sulflower molecule.[42]

We have reported the only system to dissolve Sulflower was found to be triflic acid CF_3SO_3H. These solutions had a deep purple colour and a paramagnetic signal (g-factor of 2.008). At the same time, if the solution was diluted with water, Sulflower precipitated unchanged. The nature of Sulflower–triflic acid interactions is still a black box, though one thing is clear – reverse dissolution is practical method to cover surfaces with Sulflower thin films.

Further synthetic achievements

Besides the investigation of Sulflower properties, further synthetic work was pointed in two directions: synthesis of Sulflower heteroanalogues and heterocirculenes with a macrocyclic size other than eight.



The most obvious was to test selenium instead of sulfur under developed reaction conditions. The reaction proceeds in a similar manner giving white powder in 50% yield. However, the reaction proceeds not so smooth as in case of Sulflower. Careful analysis by mass spectrometry, elemental analysis, X-ray powder diffraction and STM showed the product to be a mixture of sulfur–selenium circulene **76** and underselenized circulene **77**. The latter is referred to as so called 'dehydrohelicenes'.[23] Similar to Sulflower the admixture products are absolutely insoluble; so, it is impossible to resolute components by crystallization or extraction. More surprising is that, according to single crystal X-ray

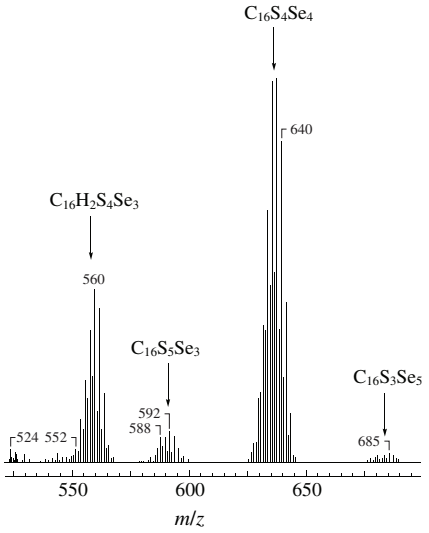
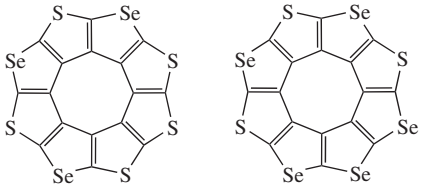


Figure 4 MS multiplets corresponding to circulenes **76**–**79**.

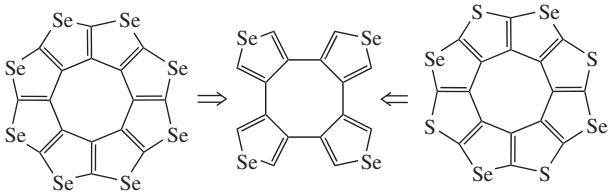
diffraction, both compounds create shared packing with the same molar ratio as in the powder sample.

The mass spectrum, as well as STM analysis, showed the presence of defected circulenes **78** and **79** with the compositions $C_{16}S_5Se_3$ and $C_{16}S_3Se_5$ as admixtures. The mechanism of its formation is yet unclear, the most reasonable is direct substitution of chalcogenes at high temperatures. Interestingly, in conditions of a large excess of selenium, not only sulfur substitutes for selenium, but also a reverse process takes place.



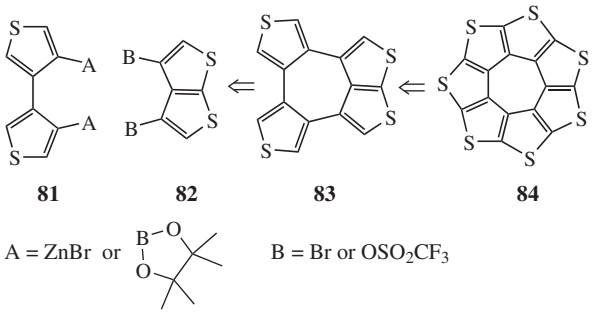
78 **79**

It is likely that incomplete selenization takes place during treatment with LDA/selenium. The possible reasons are the low solubility of the intermediate selenolate salts along with the low reactivity of selenium as against sulfur. Reaction modification leads to reducing of dehydrocirculene **77** content to at least twice; however, the most convenient way to prepare pure **76** seems to be *via* the sulfurization of tetraselenophene **72**, which is also a precursor for the preparation of fully selenic circulene **80**.



80 **72** **76**

Besides eight-membered thiocirculene, it was mentioned above that nonathio[9]circulene is also unstrained. It looks like a perfect candidate to be synthesized; however, it is difficult to propose a rational approach towards this molecule. Heptathio[7]circulene **84** is a more strained bowl shaped molecule, but the retrosynthetic analysis through polythiophene **83** seems to be realizable.

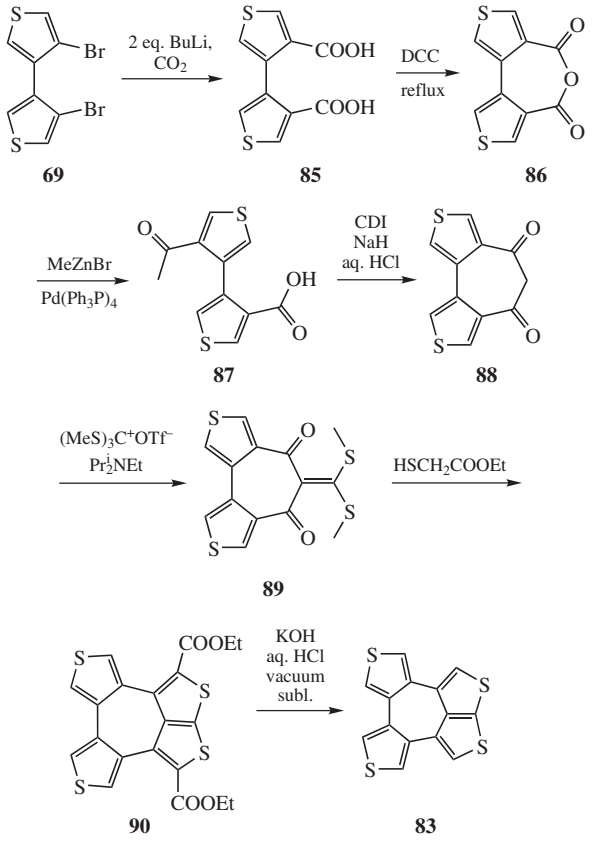


81 **82** **83** **84**

A = ZnBr or B = Br or OSO_2CF_3

The state-of-the-art synthesis of **83** implies a Pd-catalysed cross-coupling reaction between two building blocks: 4,4′-disubstituted 3,3′-bitiophene **81** and 3,4-disubstituted thieno[2,3-*b*]-thiophene **82**. The former was used in the form of corresponding dizincate or bis(pinacolatoboron) compounds, the latter in the form of dibromide or ditriflate. The GC-MS analysis of the reaction mixtures showed that the reaction took place, however, only by one end. Macrocyclization product was never detected, the remaining organometallic position being protonated.

As the convergent approach failed, polythiophene **83** was successfully prepared by a linear scheme, though it is still under revision. Cyclic anhydride **86** reacts with methylzinc bromide selectively by one carboxylic group. 1,3-Diketone **88** while reacting with CS_2 gives only resin products, obviously, due to exclusive reactivity on the enolate O-center, thus $(MeS_3)C^+OTf^-$ was used alternatively.

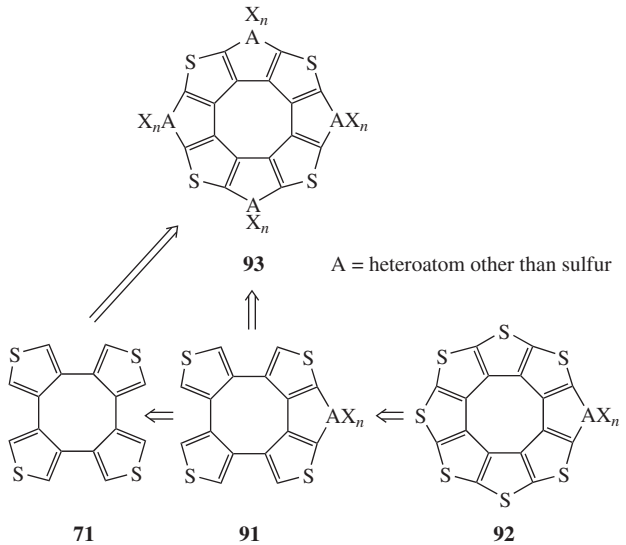


69 **85** **86** **87** **88** **89** **90** **83**

Perspectives

Contemporary organic material chemistry becomes a part and parcel of the material science. Organic materials have a plethora of advantages in comparison with inorganic ‘brothers’. The most valuable of them is the fine tuning of desired properties by varying the substituent adjacent to the active core.

Sulflower is a molecule with very strong intermolecular S···S interactions. That is why its semiconducting properties are underway. In sprite of Sulflower originality, we consider it as the first representative of the broad new class of organic materials. Tetrathiophene **71** proved oneself as a precursor for at least two heterocirculenes **5** and **76**, whilst Sulflower showed

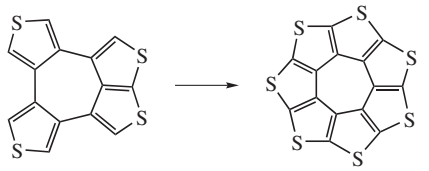


93 A = heteroatom other than sulfur

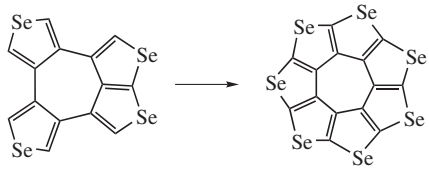
71 **91** **92**

exceptional stability of its core. Introduction of one heteroatom A with a valence of higher than 2, *e.g.*, nitrogen or phosphorus, into this core gives rise to a class of structures **92** with varied side chains. Moreover, we believe these compounds be soluble in usual organic solvents. Other possible route is the development of exhaustive substitution of **71** with a nonsulfur heteroatom leading to the structures **93**.

As mentioned above, the alternative implies the synthesis of heterocirculenes other than eight-membered ones. If, for some reason, the conversion of **83** into **84** failed, we could prepare a selenium analogue of **83** in a similar manner and try to prepare heptaseleno[7]circulene, which is flat according to quantum-chemical calculations.



83 **84**



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