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Thiaheterohelicenes 3. Donor Properties of a Series of Benzene-Capped Thiaheterohelicenes. Structure of a Tetrathianonahelicene and its TCNQ Salt

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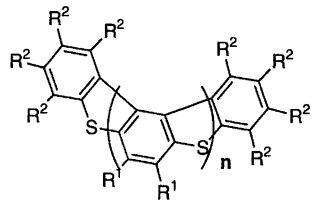
The donor properties of a series of thiaheterohelicenes have been investigated by cyclic voltammetry. The thiaheterohelicenes are oxidised to the corresponding cation radicals at potentials from 1.03 to 1.45 V vs. SCE. The structure of racemic 5,8,11,14-tetrathia[9]helicene **1** was solved. Compound **1** crystallizes in the orthorhombic system, space group *Pbca*, with $a = 8.304(2)$, $b = 15.842(3)$, $c = 33.400(8)$ Å, $V = 4394(2)$ Å^3. Compound **1** can be oxidised to a rather unstable semiconducting salt, $(\mathbf{1})_2PF_6$. Treatment of racemic **1** with 7,7′,8,8′-tetracyanoquinodimethane (TCNQ) gave an insulating solid, **1**: TCNQ. The structure of **1**:TCNQ was solved. **1**:TCNQ crystallizes in the monoclinic system, space group *C2/c*, with $a = 20.049(5)$, $b = 15.258(3)$, $c = 10.960(1)$ Å, $\beta = 103.78(2)°$, $V = 3256(1)$ Å^3. The compound crystallizes in a so-called mixed stack structure.

Polycondensed heteroaromatic structures are expected to exhibit relatively low oxidation potentials and are thus of interest as potential building blocks for organic metals. By combining the redox-properties with the chirality of helicenes one can expect to obtain chiral conducting materials, which may exhibit interesting properties under polarization with external electrical or magnetic fields.

Previously a few systems with chiral donors have been investigated.[1] Also a few materials such as $TSeT_2I$ [Tetraselenatetracene)$_2$I] have been reported.[2] In this material the particular space group is asymmetric. Metallic selenium and tellurium also crystallize in asymmetric space groups.[3]

The heterohelicenes reported (see Fig. 1) combine thiophene and benzene units and are designed to be benzene-capped in order to avoid thiophene-type oxidative polymerization.[4] The compounds carry sulfur on the outside of the helix in order to promote intermolecular electronic interactions. Methyl groups were attached in some structures to lower oxidation potentials and/or decrease inter-stack interactions.

The new thiahelicenes reported were prepared as reported elsewhere.[5,6]



1 : n = 3, $R^1 = R^2 = H$
2 : n = 5, $R^1 = R^2 = H$
3 : n = 3, $R^1 = CH_3$, $R^2 = H$
4 : n = 1, $R^1 = R^2 = H$
5 : n = 1, $R^1 = R^2 = CH_3$

Fig. 1.

Results and discussion

Donor properties of the compounds. The redox properties of the thiaheterohelicenes were investigated by cyclic voltammetry. Compounds **1–5** all exhibited one reversible one-electron oxidation at potentials above + 1 V versus the standard calomel electrode in dichloromethane. For compounds **1–3**, a second reversible wave was also observed. The results are collected in Table 1. We have noticed that the oxidation potentials are relatively high and that radical salts derived from these molecules should be handled with care to avoid reductive degradation. The oxidation potentials de- creased, as expected, with an increasing

Table 1. Cyclic voltammetry data for **1–5**, in CH_2Cl_2, $Bu_4N^+PF_6^-$ (0.1 M), at 100 mV s^{-1}, with SCE as the reference electrode.

Donor	$E_1^{1/2}$/V	$E_1^{1/2}$/V	ΔE/V
1	1.30	1.50	0.20
2	1.10	1.30	0.20
3	1.11	1.52	0.41
4	1.45	–	–
5	1.03	–	–

number of rings in the donor molecule. The highest oxidation potential was observed for compound **4** (1.45 V) decreasing to 1.30 V for **1** and 1.10 V for **3**. Likewise, owing to the electron-donating effect of the substituents, the oxidation potential decreased with an increasing number of methyl groups as seen by comparing the potential for **4** (1.45 V) with the permethylated version **5** (1.03 V) and by comparing compound **1** (1.30 V) with **3** (1.11 V).

We succeeded in preparing a 2:1 radical salt of compound **1** with PF_6^- as the counter-anion. The salt $(\mathbf{1})_2PF_6$ is semiconducting, but measurements were not reproducible owing to surface degradation of the sample. Single crystals were subjected to ESR spectroscopy. At room temperature a single line of Lorenzian shape is observed at $g = 2000$. The linewidth is about 6 G. The single line is an indication of spin delocalization throughout a stack. Had hyperfine interactions in a single molecule dominated the spectrum one would have expected a broader (convoluted) line.

When compound **1** was treated with TCNQ a crystalline solid of 1:1 stoichiometry was obtained. The crystals were insulating and were of sufficient quality for structure determination. The structure was solved and revealed a so-called mixed stack structure (see below).

Crystal structures. A full X-ray analysis was carried out for the neutral 5,8,11,14-tetrathia[9]helicene **1** and for the charge-transfer complex **1**:(TCNQ). Both crystallize in non-chiral space groups (*Pbca* and *C2/c* respectively). Therefore enantiomers *P* and *M* are found in the unit cell and the structures are those of the neutral racemate and of the racemic charge-transfer complex. Final atomic coordinates and isotropic parameters are listed in Tables 2 and 3, selected bond lengths and angles in Tables 4 and 5. The atom numbering scheme and the ring labelling

Table 2. Atomic coordinates and equivalent isotropic thermal parameters for **1**.

	x	*y*	*z*	U_{eq} [a]
S(1)	0.9527(2)	0.6214(1)	0.69103(6)	0.0435(7)
S(2)	0.3639(3)	0.1180(1)	0.17992(6)	0.0460(7)
S(3)	0.1810(2)	0.4541(1)	0.01211(5)	0.0387(6)
S(4)	0.8093(3)	0.1753(1)	0.10366(7)	0.0516(8)
C(1)	0.687(1)	0.4387(4)	0.0821(2)	0.034(2)
C(2)	0.577(1)	0.3996(5)	0.0576(2)	0.043(3)
C(3)	0.462(1)	0.3468(5)	0.0737(2)	0.044(3)
C(4)	0.447(1)	0.3354(5)	0.1142(2)	0.040(3)
C(5)	0.776(1)	0.4803(4)	0.2281(2)	0.037(3)
C(6)	0.595(1)	0.0351(4)	0.2259(2)	0.040(3)
C(7)	0.241(1)	0.3836(5)	0.6024(2)	0.046(3)
C(8)	0.234(1)	0.4176(5)	0.5649(2)	0.042(3)
C(9)	0.501(1)	0.6942(5)	0.5110(2)	0.046(3)
C(10)	0.590(1)	0.7530(5)	0.5315(2)	0.042(3)
C(11)	0.621(1)	0.8068(5)	0.6850(3)	
C(12)	0.537(1)	0.7679(6)	0.7153(2)	0.059(3)
C(13)	0.436(1)	0.7004(5)	0.7055(2)	0.043(3)
C(14)	0.431(1)	0.6675(4)	0.6678(2)	0.037(2)
C(15)	0.978(1)	0.2960(4)	0.1372(2)	0.032(2)
C(16)	0.888(1)	0.2231(5)	0.1459(2)	0.043(3)
C(17)	0.973(1)	0.3159(4)	0.0949(2)	0.031(2)
C(18)	0.901(1)	0.2508(4)	0.0726(2)	0.036(2)
C(19)	0.034(1)	0.3862(4)	0.0733(2)	0.028(2)
C(20)	0.061(1)	0.3749(4)	0.0321(2)	0.035(2)
C(21)	0.414(1)	0.5306(4)	0.5862(2)	0.031(2)
C(22)	0.318(1)	0.4914(4)	0.5571(2)	0.035(2)
C(23)	0.050(1)	0.5152(4)	0.1220(2)	0.031(2)
C(24)	0.346(1)	0.0837(4)	0.1310(2)	0.035(2)
C(25)	0.932(1)	0.5036(4)	0.1540(2)	0.030(2)
C(26)	0.523(1)	0.0475(4)	0.1889(2)	0.034(2)
C(27)	0.716(1)	0.5413(4)	0.6555(2)	0.029(2)
C(28)	0.782(1)	0.5562(4)	0.6931(2)	0.034(2)
C(29)	0.817(1)	0.5750(4)	0.6237(2)	0.028(2)
C(30)	0.944(1)	0.6239(5)	0.6386(2)	0.033(2)

[a] $U_{eq} = 1/3\Sigma_i\Sigma_j U_{ij} a_i * a_j * \mathbf{a}_i\mathbf{a}_j$.

Table 3. Atomic coordinates and equivalent isotropic thermal parameters for **1**: (TCNQ).

	x	*y*	*z*	U_{eq} [a]
1				
S(1)	0.37408(5)	0.5922(1)	0.2509(1)	0.0625(4)
S(2)	0.6062(1)	0.9809(1)	0.0869(1)	0.0656(4)
C(1)	0.4531(2)	0.7507(2)	0.0399(3)	0.046(2)
C(2)	0.4643(2)	0.6974(2)	−0.0545(3)	0.055(1)
C(3)	0.5483(2)	0.6077(3)	0.5537(4)	0.063(2)
C(4)	0.4255(2)	0.5710(2)	0.0383(4)	0.060(2)
C(5)	0.3475(2)	0.7245(2)	0.4050(4)	0.067(2)
C(6)	0.3502(2)	0.8105(3)	0.4393(4)	0.066(2)
C(7)	0.4770(2)	1.0727(2)	0.2867(4)	0.070(2)
C(8)	0.5293(2)	0.9120(2)	0.2248(3)	0.043(1)
C(9)	0.5488(2)	0.9927(2)	0.1822(3)	0.056(1)
C(10)	0.4265(2)	0.8423(2)	0.2984(3)	0.042(1)
C(11)	0.3878(2)	0.8690(2)	0.3840(3)	0.052(1)
C(12)	0.4138(2)	0.7558(2)	0.2488(3)	0.041(1)
C(13)	0.3779(2)	0.6986(2)	0.3099(3)	0.052(1)
C(14)	0.4300(2)	0.7149(2)	0.1399(3)	0.041(1)
C(15)	0.4137(2)	0.6240(2)	0.1336(3)	0.051(1)
TCNQ				
C(16)	0.2426(2)	0.1792(3)	0.5797(3)	0.059(2)
C(17)	0.2210(2)	0.2665(3)	0.6015(3)	0.064(2)
C(18)	0.2279(2)	0.3332(2)	0.5270(4)	0.060(1)
C(19)	0.2347(2)	0.1107(3)	0.6555(4)	0.065(2)
C(20)	0.2020(2)	0.1203(2)	0.7573(4)	0.074(2)
C(21)	0.2426(2)	0.4764(4)	0.3643(4)	0.074(2)
N(1)	0.1746(2)	0.1256(3)	0.8365(4)	0.100(2)
N(2)	0.2252(2)	0.4545(3)	0.8792(4)	0.100(2)

[a] $U_{eq} = 1/3\Sigma_i\Sigma_j U_{ij} a_i * a_j * \mathbf{a}_i\mathbf{a}_j$.

Table 4. Selected bond lengths and angles in **1** (Å, °).

S(1)–C(12)	1.7523(1)	C(10)–C(18)	1.3767(2)
S(1)–C(30)	1.7514(2)	C(11)–C(12)	1.3759(1)
S(2)–C(24)	1.7276(2)	C(11)–C(16)	1.3911(2)
S(2)–C(26)	1.7541(1)	C(12)–C(13)	1.4015(1)
S(3)–C(20)	1.7366(1)	C(13)–C(14)	1.3649(2)
S(3)–C(22)	1.7330(2)	C(14)–C(15)	1.3958(1)
S(4)–C(16)	1.7288(2)	C(15)–C(16)	1.4050(1)
S(4)–C(18)	1.7561(1)	C(15)–C(17)	1.4497(2)
C(1)–C(2)	1.3749(1)	C(17)–C(18)	1.4063(1)
C(1)–C(29)	1.4073(2)	C(17)–C(19)	1.4209(1)
C(2)–C(3)	1.3792(1)	C(19)–C(20)	1.4044(2)
C(3)–C(4)	1.3695(2)	C(19)–C(21)	1.4510(1)
C(4)–C(30)	1.3751(1)	C(21)–C(22)	1.4035(1)
C(5)–C(6)	1.3781(1)	C(21)–C(23)	1.4283(1)
C(5)–C(28)	1.3904(1)	C(23)–C(24)	1.4351(1)
C(6)–C(26)	1.3890(1)	C(23)–C(25)	1.4634(1)
C(7)–C(8)	1.3658(1)	C(25)–C(26)	1.4081(1)
C(7)–C(24)	1.3945(1)	C(25)–C(27)	1.4208(1)
C(8)–C(22)	1.3895(1)	C(27)–C(28)	1.3935(1)
C(9)–C(10)	1.3719(1)	C(27)–C(29)	1.4534(1)
C(9)–C(20)	1.3977(1)	C(29)–C(30)	1.4052(1)
C(10)–C(18)	1.3767(2)	C(29)–C(30)	1.4052(1)
C(28)–S(1)–C(30)	91.274(1)	S(3)–C(20)–C(9)	125.58(1)
C(24)–S(2)–C(26)	91.409(3)	S(3)–C(20)–C(19)	111.973(4)
C(20)–S(3)–C(22)	91.62(1)	C(9)–C(20)–C(19)	122.410(3)
C(16)–S(4)–C(18)	91.09(1)	C(19)–C(21)–C(22)	130.586(2)
C(2)–C(1)–C(29)	120.086(5)	C(22)–C(21)–C(23)	111.20(1)
C(1)–C(2)–C(3)	120.20(1)	S(3)–C(22)–C(8)	125.752(2)
C(2)–C(2)–C(4)	121.786(2)	S(3)–C(22)–C(21)	112.27(1)
C(3)–C(4)–C(30)	117.794(1)	C(8)–C(22)–C(21)	121.980(5)
C(6)–C(5)–C(28)	119.280(4)	C(21)–C(23)–C(24)	116.298(4)
C(5)–C(6)–C(26)	118.144(3)	C(21)–C(23)–C(25)	133.245(5)
C(8)–C(7)–C(24)	120.67(1)	C(24)–C(23)–C(25)	110.345(5)
C(7)–C(8)–C(22)	118.784(2)	S(2)–C(24)–C(7)	125.639(5)
C(10)–C(9)–C(20)	118.55(1)	S(2)–C(24)–C(23)	113.023(2)
C(9)–C(10)–C(18)	119.855(4)	C(7)–C(24)–C(23)	121.319(5)
C(12)–C(11)–C(16)	120.63(1)	C(23)–C(25)–C(26)	111.30(1)
C(11)–C(12)–C(13)	118.52(1)	C(23)–C(25)–C(27)	131.952(4)
C(12)–C(13)–C(14)	121.439(2)	C(26)–C(25)–C(27)	116.731(3)
C(13)–C(14)–C(15)	120.21(1)	S(2)–C(26)–C(6)	124.642(2)
C(14)–C(15)–C(16)	118.547(1)	S(2)–C(26)–C(25)	111.931(5)
C(14)–C(15)–C(17)	129.683(5)	C(6)–C(26)–C(25)	123.42(1)
C(16)–C(15)–C(17)	111.377(1)	C(25)–C(27)–C(28)	117.244(3)
S(4)–C(16)–C(11)	126.49(1)	C(25)–C(27)–C(29)	131.098(5)
	113.20(1)	C(28)–C(27)–C(29)	111.65(1)
C(11)–C(16)–C(15)	120.177(1)	S(1)–C(28)–C(5)	124.104(3)
C(15)–C(17)–C(18)	111.59(1)	S(1)–C(28)–C(27)	112.529(4)
C(15)–C(17)–C(19)	130.961(2)	C(5)–C(28)–C(27)	123.29(1)
C(18)–C(17)–C(19)	117.37(1)	C(1)–C(29)–C(27)	130.579(5)
S(4)–C(18)–C(10)	125.717(4)	C(1)–C(29)–C(30)	117.024(2)
S(4)–C(18)–C(17)	111.86(1)	C(27)–C(29)–C(30)	112.20(1)
C(10)–C(18)–C(17)	122.358(4)	S(1)–C(30)–C(4)	125.376(4)
C(17)–C(19)–C(20)	116.954(5)	S(1)–C(30)–C(29)	111.818(3)
C(17)–C(19)–C(21)	131.75(1)	C(1)–C(30)–C(29)	122.73(1)
C(20)–C(19)–C(21)	111.201(2)		

scheme for the thiahelicene molecule are shown in Figs. 2 and 3.

Neutral 5,8,11,14-tetrathia[9]helicene **1**. The thiahelicene molecules are located in general positions in the orthorhombic unit cell. Four thiophene and five benzene rings alternate in the molecule (Fig. 2). The entire molecule is not planar but adopts a helical geometry with more than one turn. However, individual five- and six-membered rings have fairly good planarity in order to retain the aromatic character within each ring. As already observed in carbohelicenes and in other thiaheterohelicene structures,[7–11] the distortion to planarity, and so the decrease in the C = C double bond character, is more important for the inner core region than for the outer core one. Indeed the averaged C–C bond length [1.415(13) Å] in the inner

Table 5. Selected bond lengths and angles in **1**: (TCNQ) (Å, °).

1			
		C(8)–(10)	1.4457(2)
		C(10)–C(11)	1.4113(2)
S(1)–C(13)	1.7426(3)	C(10)–C(12)	1.4262(2)
S(1)–C(15)	1.7343(3)	C(12)–C(13)	
S(2)–C(9)	1.7384(3)	C(12)–C(14)	1.4508(1)
S(2)–C(11)	1.7355(3)	C(14)–C(15)	1.3480(2)
C(1)–C(2)	1.3766(1)		
C(1)–C(14)	1.3987(2)	TCNQ	
C(2)–C(3)	1.3911(3)		
C(3)–C(4)	1.3672(2)	C(16)–C(17)	1.4376(2)
C(4)–C(15)	1.3839(1)	C(16)–C(18)	1.4432(2)
C(5)–C(6)	1.3621(2)	C(16)–C(19)	1.3671(2)
C(5)–C(13)	1.3842(2)	C(17)–C(18)	1.3330(2)
C(6)–C(11)	1.3974(2)	C(19)–C(20)	1.4305(2)
C(7)–C(7)	1.3625(2)	C(19)–C(21)	1.4385(2)
C(7)–C(9)	1.3990(2)	C(20)–N(1)	1.1357(2)
C(8)–C(8)	1.4125(2)	C(21)–N(2)	1.1336(2)
C(8)–C(9)	1.4050(2)		
1		C(10)–C(12)–C(14)	131.090(5)
		C(13)–C(12)–C(14)	111.52(1)
C(13)–S(1)–C(15)	91.562(7)	S(1)–C(13)–C(5)	123.850(3)
C(9)–S(2)–C(11)	91.034(3)	S(1)–C(13)–C(12)	112.67(1)
C(2)–C(1)–C(14)	120.09(1)	C(5)–C(13)–C(12)	123.46(1)
C(1)–C(2)–C(3)	120.90(1)	C(1)–C(14)–C(12)	131.08(1)
C(2)–C(3)–C(4)	120.802(3)	C(1)–C(14)–C12()	117.261(4)
C(3)–C(4)–C(15)	118.86(1)	C(12)–C(14)–C(15)	111.46(1)
C(6)–C(5)–C(13)	119.133(3)	S(1)–C(15)–C(4)	125.91(1)
C(5)–C(6)–C(11)	119.06(1)	S(1)–C(15)–C(14)	112.148(3)
C(9)–C(7)–C(7)	119.02()	C(4)–C(15)–C(14)	121.83(1)
C(9)–C(8)–C(10)	110.85(1)		
C(9)–C(8)–C(8)	116.92(2)	TCNQ	
C(10)–C(8)–C(8)	132.15(2)		
S(2)–C(9)–C(7)	124.912(5)	C(17)–C(16)–C(19)	121.59(1)
S(2)–C(9)–C(8)	112.64(1)	C(17)–C(16)–C(18)	117.01(2)
C(7)–C(9)–C(8)	122.45(1)	C(18)–C(16)–C(19)	121.40(2)
C(8)–C(10)–C(11)	111.15(1)	C(16)–C(17)–C(18)	121.78(1)
C(8)–C(10)–C(12)	132.41(1)	C(16)–C(18)–C(17)	121.22(2)
C(11)–C(10)–C(12)	116.40(1)	C(16)–C(19)–C(20)	122.45(1)
S(2)–C(11)–C(6)	124.71(1)	C(16)–C(19)–C(21)	121.92(2)
S(2)–C(11)–C(10)	112.448(4)	C(20)–C(19)–C(21)	115.61(3)
C(6)–C(11)–C(10)	122.84(1)	C(19)–C(20)–N(1)	177.64(1)
C(10)–C(12)–C(13)	117.35(1)	C(19)–C(21)–N(2)	179.23(1)

core is longer than the averaged C–C bond length [1.375(5) Å] in the periphery. Furthermore the moieties around rings E seem to bear the largest distortion in the molecule (maximum deviations of the ring atoms from the least-squares planes 0.10 Å) while the terminal rings A and I have good planarity (maximum deviations 0.04 Å). The dihedral angles of the least-squares best planes between the consecutive rings are given in Table 6. The major overlap in the molecule is seen between rings A and H and B and I (Fig. 2), suggesting large steric repulsion around these portions. Accordingly four C···C non-bonded contacts: C(1)–C(19) = 3.0259(2), C(14)–C(25) = 2.9819(1), C(15)–C(27) = 3.1100(1) and C(17)–C(29) = 3.1211(2) Å are significantly shorter than the sum of the van der Waals distances and the distance between the nearly coplanar (Table 6) rings A and I is quite short [3.40(1) Å].

Figure 4 shows the packing diagram of the molecules in the unit cell, as viewed in a projection down [100]. Homochiral molecules are stacked in [110] planes and *P* and *M* layers, related by an inversion centre, alternate along [001]. This packing pattern differs slightly from that of the pentathia[9]heterohelicene[10] and other racemic

Table 6. Selected dihedral angles (°) between the least-squares planes of the rings for **1** and **1**: (TCNQ).

Neutral thiahelicene **1**		Charge transfer complex **1**: (TCNQ)	
Ring–ring	Angle	Ring–ring	Angle
A–B	6.7(2)	A–B	6.2(1)
B–C	8.0(3)	B–C	8.5(1)
C–D	10.3(2)	C–D	9.3(1)
D–E	10.6(3)	D–E	10.0(2)
E–F	9.0(2)	A–A′	20.1(2)
F–G	10.6(2)		
G–H	11.4(3)		
H–I	8.3(3)		
A–I	16.3(3)		

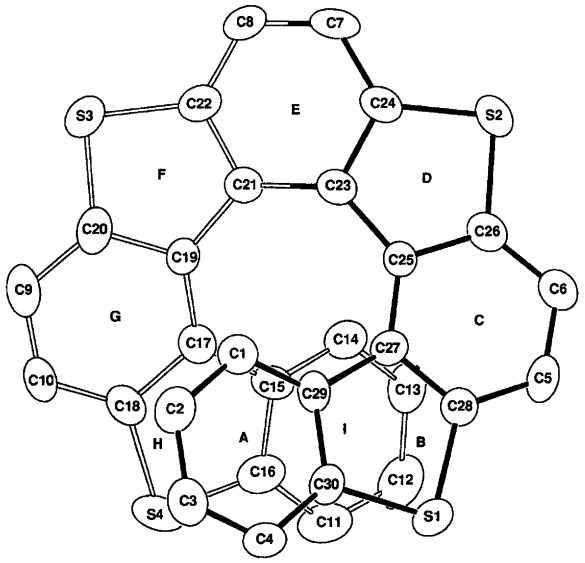


Fig. 2. ORTEP drawing and numbering scheme for **1**. The thermal ellipsoids are scaled to include 50% probability. For clarity hydrogen atoms are omitted and darkened bonds show the half of the molecule that corresponds to the other half by a pseudo C_2 symmetry axis.

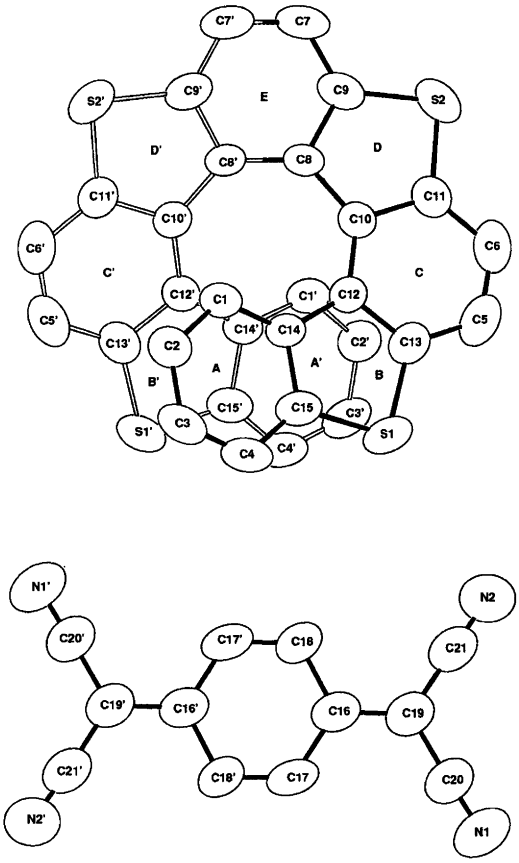


Fig. 3. ORTEP drawing and numbering scheme for **1** and TCNQ in **1**:(TCNQ). The thermal ellipsoids are scaled to include 50% probability. For clarity hydrogen atoms are omitted and darkened bonds show the half of the molecule that corresponds to the other half by a C_2 symmetry axis.

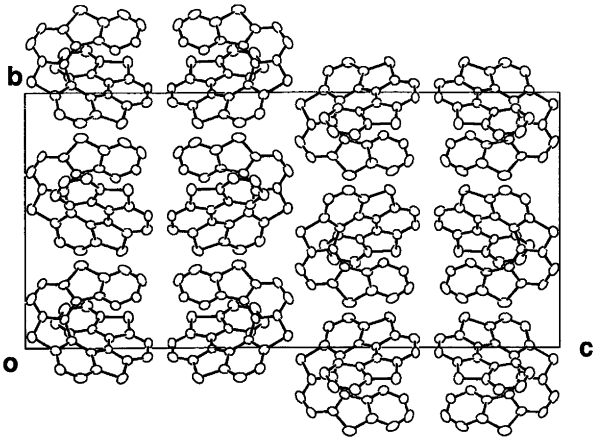


Fig. 4. Projection of the unit cell of **1** along [100].

heterohelicenes with fewer rings[11,12] as there is no direct overlap between the unlike antipodes.

Charge-transfer complex **1**:*(TCNQ).* The TCNQ molecules are located at inversion centres in the monoclinic unit cell. A noteworthy feature is the presence in the molecule of a crystallographic C_2 symmetry axis passing through C(7)–C(7)′ and C(8)–C(8)′ and parallel to the crystal [001] axis. The helical shape of the molecule is very similar to that of the neutral racemate; the aperture between the two terminal rings is 3.44(1) Å. No significant differences are noted between the intermolecular bond lengths in the neutral thiaheterohelicene **1** and in the compound **1**:(TCNQ) (Tables 4 and 5), suggesting that the helicene is not oxidized. Accordingly, bond lengths in the TCNQ moiety seem to be close to the values expected for a non-ionic TCNQ molecule.[13] Finally, **1**:(TCNQ) is a 1:1 neutral charge-transfer complex, which is not surpris-

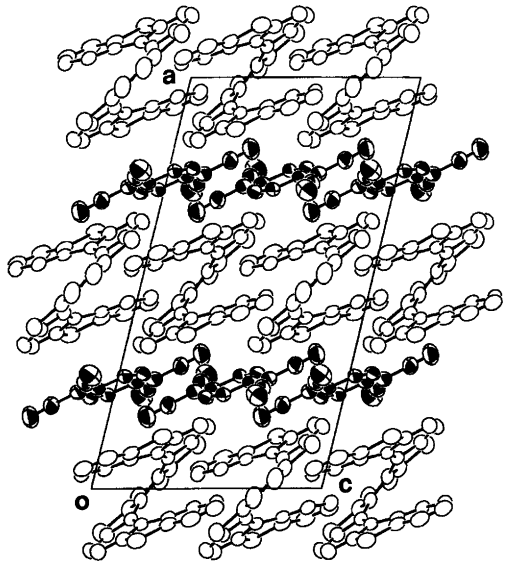


Fig. 5. Projection of the unit cell of **1**: TCNQ along [010].

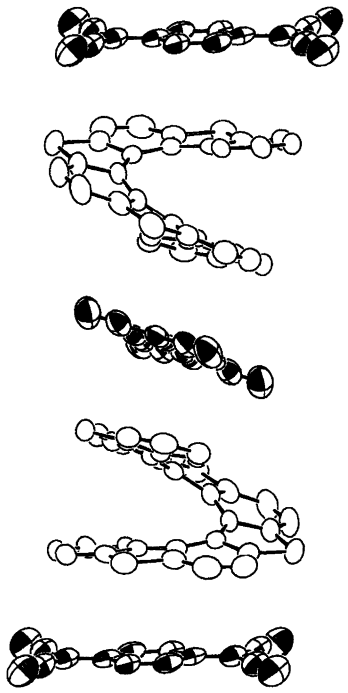


Fig. 6. The mode of stacking along [101] for **1**:(TCNQ).

ing considering the following redox potentials: $E^{\circ}_{\text{helicene}^{+}/\text{helicene}} = 1.30$ V and $E^{\circ}_{\text{TCNQ/TCNQ}^{-}} = 0.19$ V vs. SCE. These redox potentials indicate that oxidation of the helicene by TCNQ is not thermodynamically favourable. As exemplified in Fig. 5, 5,8,11,14-tetrathia[9]helicene and TCNQ molecular layers are stacked along [101]. This pattern is quite usual for TCNQ complexes of helicenes.[8,14] Enantiomers *P* and *M*, related by an inversion centre and separated by a TCNQ molecule, alternate in the stack (Fig. 6). There is a direct overlap between the rings A, B and C of the helicene and the TCNQ molecule, especially between the thiophene ring B and the quinoidal ring of the TCNQ; the mean interplanar distance is 3.54(1) Å.

Conclusion

We have reported the properties of several thiahelicenes. Using a racemic mixture of 5,8,11,14-tetrathia[9]helicene **1** it was possible to prepare a racemic semiconducting 2:1 hexafluorophosphate salt and a racemic mixed stack charge-transfer TCNQ compound. Further investigations of the new donors should involve resolving the racemic mixtures of the donors in order to investigate the properties of derived solids under external polarization.

Experimental

5,8,11,14-Tetrathia[9]helicene **1**. Crystals were grown by recrystallisation from heptane.

Crystals of **1**:(TCNQ) were made by dissolving **1** and TCNQ (100% excess) in the minimum volume of hot acetonitrile whereafter the solution was left for slow cooling in a preheated Dewar vessel. The black crystals of **1**:(TCNQ) were collected by filtration and washed with a small amount of acetonitrile and ethyl ether and dried.

Crystals of $(\mathbf{1})_2PF_6$ were obtained by electrochemical oxidation (Pt rod electrodes) of a solution of **1** (10 mg) in dry CH_2Cl_2 (20 ml) with $TBAPF_6$ (0.1 M) as the conducting electrolyte using a constant current of 1 μA. The black crystals of $(\mathbf{1})_2PF_6$ were harvested after 80% conversion and washed with small amounts of CH_2Cl_2 and ether and dried.

Table 7. Crystallographic data for **1** and **1**: (TCNQ).

Compound	**1**	**1**:(TCNQ)
Formula	$C_{30}H_{14}S_4$	$C_{42}H_{18}N_4S_4$
Formula weight	502.68	706.87
λ/Å	0.71069	0.71069
T/K	293	293
Crystal dimensions/mm	0.05×0.33×0.37	0.17×0.17×0.33
Crystal system	Orthorhombic	Monoclinic
Space group	*Pbca*	*C*2/*c*
a/Å	8.304(2)	20.049(5)
b/Å	15.842(3)	15.258(3)
c/Å	33.400(8)	10.960(1)
β/°	90	103.78(2)
V/Å^3	4394(2)	3256(1)
Z	8	4
D_c/g cm^{-3}	1.52	1.44
μ/cm^{-1}	2.20	3.26
No. of independent reflections	4285	3206
No. of observed reflections	1936	1555
No. of variables	307	226
R $(F_o)^a$	0.052	0.038
$R_w(F_o)^a$	0.073	0.049
Max. and min. Δρ/e Å^{-3}	0.99	0.49

[a] $R=\Sigma(|F_o| - |F_c|)/\Sigma|F_o|$ and $w=1/[\sigma^2(F_o)+(0.03F_o^2)^2]$.

Structure determination. Crystal data and parameters of the data collection are compiled in Table 7. Unit cell parameters were determined by accurate centring of 25 strong independent reflections. The data were collected on an Enraf–Nonius CAD4-F diffractometer, using the $w/2\Theta$ scan. The numbers of total reflections measured were 5026 ($1 \leq \Theta \leq 26°$; $+h$, $+k$, $+l$) and 7000 ($1 \leq \Theta \leq 26°$; $+h$, $+k$, $+l$) giving 4285 and 3206 independent reflections for **1** and **1**:(TCNQ), respectively. The structure was solved using direct methods. The non-hydrogen atoms were refined anisotropically by full-matrix least-squares methods. $Sw(|F_o| - |F_c|)^2$ was minimized with $w = 1/[s^2(F_o) + (0.03\ F_o^2)^2]$. Hydrogen atoms were included in structure factor calculations at ideal positions and not refined. All computer programs are from Xtal 3.2.[15]

Anisotropic displacement parameters, parameters for the hydrogen atoms, tables of bond distances and angles and lists of the observed and calculated structure factors are available from the authors on request.

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