Structure and properties of α-cyclo[*N*]thiophenes as potential electronic materials – A theoretical study[†]

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ABSTRACT: Density functional theory (DFT) calculations of ring-shaped α-cyclo[N]thiophenes with $N = 2$ to $N = 18$ have been performed for ideal structures of high symmetry (point groups C_{nv} and D_{nh}) and for optimum energy structures of lower symmetry (D_{2d}, C_s, C_{2v}, C_i or C_1). Whereas the first three members of the series behave exceptionally the higher members are typical cyclothiophenes consisting of weakly interacting thiophene rings. In contrast to neutral compounds, cations and dications of cyclothiophenes with N ≥ 5 exhibit pronounced electron delocalizations along the carbon backbone. However, if the functional B3LYP is replaced by BH cations of large ring-size cations show polaron-type charge defects. According to broken symmetry DFT calculations dications with $N = 14$ and $N = 18$ have biradical character. These structures correspond to two-polaron-type structures rather than to dipolarons. The calculated vertical ionization energies of cyclo[N]thiophene are comparable with those of oligo[N]thiophenes of the same number of thiophene rings but the calculated absolute energies are probably too low at large ring size. Cyclothiophenes absorb light of lower energies than the related oligothiophenes. Cyclothiophenes belong to the strongly absorbing organic chromophores. In case of high molecular symmetry some of the excited states of cyclothiophenes are degenerate. The degeneracy is lifted with lower symmetries but the general absorption feature remains. The theoretical results are discussed with respect to recent experimental findings. Copyright © 2007 John Wiley & Sons, Ltd.

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KEYWORDS: cyclothiophenes and ions; restricted and unrestricted DFT calculations; time-dependent DFT calculations; molecular structure; light absorption; ionization energies; electron affinities

INTRODUCTION

Among the conjugated oligomers α-oligo[N]thiophenes $\mathbf{1_N}$ constitute a particularly attractive class of compounds.[1] They have been extensively investigated for optoelectronic and microelectronic applications, such as organic materials for light-emitting organic diodes (OLED),[2] organic field-effect transistors (OFET),[3] and organic solar cells (OSC).[4] Efficient methods are known for the preparation of oligothiophenes $\mathbf{1_N}$ (Scheme 1). The most syntheses make use of the thiophene-thiophene coupling reaction starting from the easily available metallated thiophenes and using heavy metal catalysts.[5] This synthetic strategy, however, failed in the synthesis of α-cyclo[N]thiophenes $\mathbf{2_N}$. Cyclothiophenes have been

synthesized only recently. Bäuerle at al. obtained cyclo[N]thiophenes of the ring sizes $N = 8$, 12, 16, and 18 using the template-mediated coupling reaction of bisethinyl-substituted oligothiophenes.[6]

Cyclothiophenes exhibit several interesting properties. They show self-assembly properties and may therefore pave the way to novel molecular circuits.[7] Fullerene undergoes complexation on a cyclothiophene monolayer template.[7] Cyclothiophenes display bright yellow to red colors and are dedicated for oxidation reactions to form cationic or dicationic compounds. They may also be useful models for infinitely long chain-type polythiophene compounds.[8] A theoretical study examined the application of cyclothiophenes as building blocks for complex structures such as catenanes and knots.[9] Giant macrocylic oligothiophenes linkage of thiophenes through acetylenic bonds have been prepared very recently.[10] Scheme 1.

Semiempirical AM1- and PM3-calculations of Tol[8], Bäuerle *et al.*[6,11] and Mena-Osteritz[7] predicted all-*syn*

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[†]Dedicated to Prof. Dr h.c. Roland Mayer on the occasion of his 80th birthday.
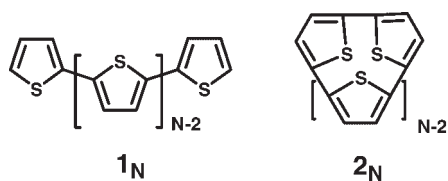
Scheme 1

(all-s-*trans*)-configured ring-shaped structures with an inner concave surface of sulfur atoms and an outer convex backbone of carbon atoms. Cyclododecithiophene 2_{12} shown in Fig. 1 was described as planar and with a delocalized π-system.[8] According to semiempirical calculations interring bonds are relatively long reminiscent to the corresponding bonds of open-chain oligothiophenes. The weak linkage between the substructures allowed a discussion of spectral properties in terms of constituent parts.[11]

The cyclothiophenes 2_N considered in this study are exclusively *syn*-configured in contrast to oligothiophenes 1_N with *anti*-configuration (cf. Fig. 1). A recent extensive study of Zade and Bendikov of a series of even-numbered cyclothiophenes has also paid attention to *anti*-cyclo[N]thiophenes and to their structural and spectral characteristics in comparison to *syn*-isomers.[12] Whereas *anti*-cyclo[N]thiophenes are energetically disfavored with respect to *syn*-isomers up to ring sizes to $N = 20$ the strain-free *anti*-isomer with $N = 30$ is significantly more stable than
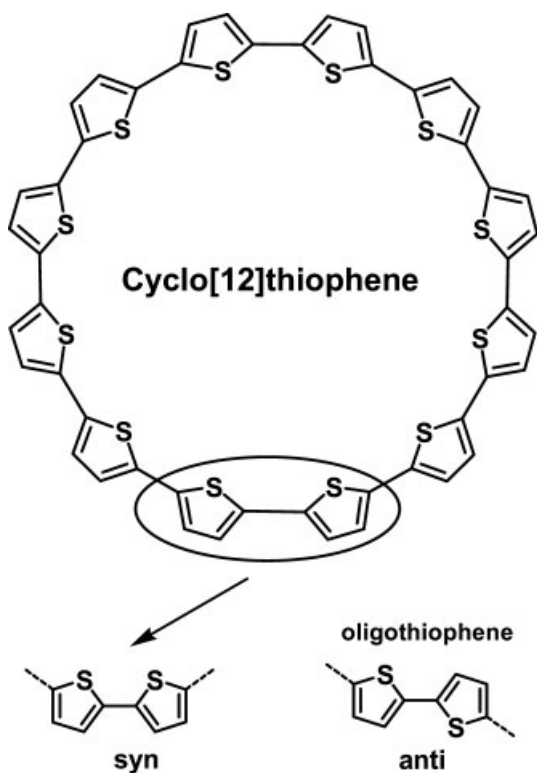

Figure 1. α-Cyclo[12]thiophene (2_{12}) and basic structural components of cyclo- and oligothiophene structures

the *syn*-isomer. The change of KS-MO-energies and of other theoretical parameters were studied depending on the ring size.[12]

The aim of this study is to calculate the molecular and electronic structure of *syn*-configured parent α-cyclothiophenes of small and middle ring size by first-principles methods. The density functional theory (DFT) and the time-dependent DFT (TD-DFT) are employed in calculating the structure and ionization and excitation energies. The alternative binding in β-position or both in α- and β-position of the thiophene substructures is discussed for some selected compounds.

The molecular geometry is expected to be sensitive to the ring size. It may change with the molecular symmetry. Therefore, it appeared advisable to delineate the molecular structure and structure-property relationships in a uniform way on an equal footing. For this purpose high symmetry cyclo[N]thiophene structures were consistently defined first. The relaxed structures of optimum energy were generally found to be of reduced symmetry. These real structures may be considered as perturbation idealized structures of high-symmetry. The reference structures of high symmetry are characterized by *n*-fold symmetry axis ($n = N$).

COMPUTATIONAL

Standard DFT calculations[13] were performed using the GAUSSIAN03[14] suite of programs. Three hybrid xc-functionals were employed in the calculations: The popular Becke-3-Lee-Yang-Parr functional (B3LYP),[15] the later proposed Becke98 (B98) functional[16] and the parameter-free PBE0 (PBE1PBE) functional.[17] The Half&Half exchange functional, designated as BHandH or BH functional,[18] in conjunction with the Lee-Yang-Parr (LYP) correlation functional was used to promote symmetry-breaking and bond localization. This exchange functional is based on one half of the HF exchange including local LSDA and gradient corrected (Becke88) terms. Calculation with the BHandHLYP functional provided more realistic bond characteristics of various open-chain[19] and ring-closed polymethine structures.[20]

To handle the compounds 2_N of the entire homologous series including larger compounds consistently Pople's small split valence double-zeta basis set 3-21G* was used in general. Additional calculations with extended basis sets were performed to examine the effect of the basis set incompleteness and to achieve more accurate numerical results.

DFT calculations were carried out with the spin-restricted RDFT model of DFT for closed shell and with the spin-unrestricted UDFT model for open shell systems. UDFT was employed in calculating radical and biradical species. The use of different spatial orbitals for α- and β-subsystems resulted in spin polarized or broken

symmetry (BS) solutions. BS-UDFT calculations cover to some extent static correlation and multi-reference effects.[21] This approach was successfully applied to describe reactive biradical intermediates and transition structures[22] and more stable conjugated organic biradicals.[23] BS-UDFT calculations revealed a change of the oligoacene structure from the conventional to the biradical one when passing from small to large compounds.[24] Based on this theoretical model biradical ground states have been found for extended dicationic oligothiophene parent compounds[25,26] and derivatives.[27] A breaking of the spin symmetry was observed.

Time-dependent density functional theory (TD-DFT) is a proper approach for the calculation of transition energies and transition probabilities of larger molecules.[28] This approach is based on the linear response of the charge density to an applied field allowing direct computation of excitation energies and oscillator strengths. The deviation of the calculated transition energies for sulfur-containing compounds may be as low as $0.1\,eV$ as found for small clusters of sulfur[29] and amounts generally to 0.21[30] to 0.27 eV[31] for more heterogeneous series of sulfur compounds. TD-DFT results with the 3-21G* basis set are not much inferior to those with the 6-31 + G* basis set employed in previous studies.[30,31] The mean average deviation of 0.38 eV was reported for oligomers without scaling.[32] TD-DFT calculations were generally performed with the B3LYP functional in this study, but the PBE0 functional is an alternative suitable choice. The TD-DFT transition energies are calculated vertically at the equilibrium energy of the ground state.

In the strict sense, vertical energies cannot be recorded by experiment. However, transition energies are actually related to the recorded band maxima. The absorption intensity of TD-DFT was evaluated by the oscillator strength f according to the formula $f = (8\pi^2/3)(m_e \, \nu/he^2)A$-$e\int\Psi_0 r\Psi_i drA^2$, where the symbols have their usual meaning. The dimensionless oscillator strength is directly related to the integral extinction coefficient by $\varepsilon(\nu) = \int\varepsilon(\nu)d(\nu)$.

For comparison, transition energies and oscillator strengths were also calculated by the semiempirical ZINDO-CIS ('ZINDO/S')[33] and PPP-CIS[34] methods with an active space of 10 occupied and 10 unoccupied orbitals. PPP and ZINDO-CIS calculations were performed by the WPSIN3[35] and GAUSSIAN03 program,[14] respectively.

RESULTS AND DISCUSSION

Isomeric compounds of low ring size

As detailed in the next section, the first three members of the homologous series 2_N with $N = 2$ to $N = 4$ are exceptional. The dimer ($N = 2$) represents a sandwich-
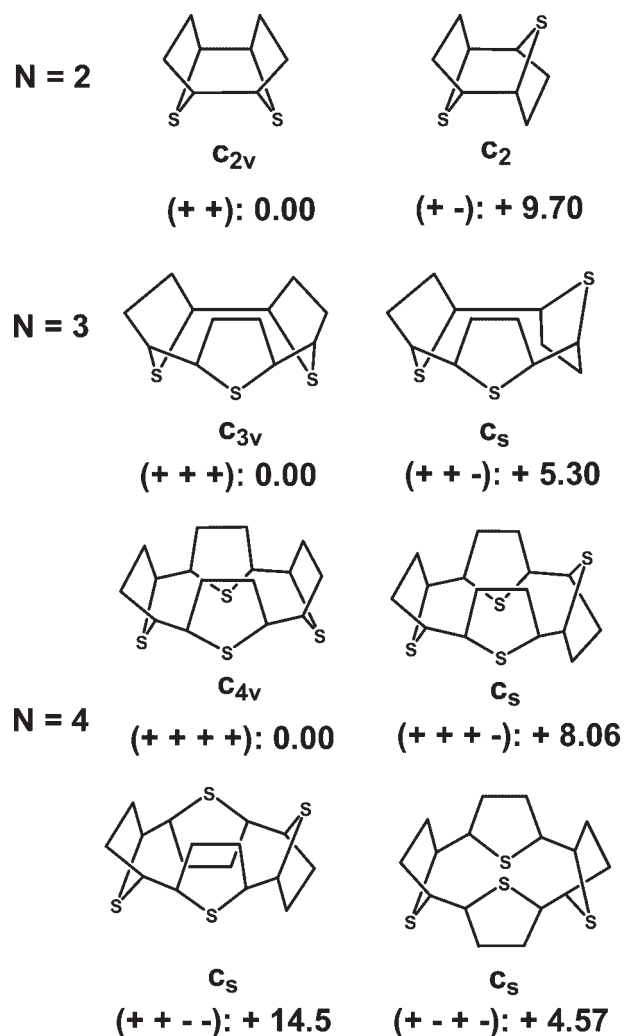

Figure 2. Schematic presentation of the geometric isomers of 2_N with low ring size and the destabilization energies in kcal/mol with respect to the all-*syn* optimum structures

like compound defined by two stereoisomers. The isomers belong to different point groups (see Fig. 2). The lower energy isomer has the point group C_{2v}. The carbon atoms of the interring bonds are located on a common plane. The same holds for the trimer and tetramer structures. In all cases structures of cofacial alignment of the sulfur atoms (*syn*-isomers) have the lowest energy. The most stable trimer and tetramer belong to the point groups C_{3v} and C_{4v}, respectively. Structures of C_{nv} symmetry also encounter with cyclothiophenes of larger ring size.

For small compounds the number of stereoisomers is restricted. As shown in Fig. 2, there are two structural isomers of 2_N with $N = 2$ and $N = 3$ and four with $N = 4$. In analogy to a calix[N]arene terminology[36] the molecular shape may be designated simply by a symbolic representation based on a sequence of signs. In this way the lowest-energy structures are designated as $(++)$, $(+++)$ and $(++++)$. The stereoisomers higher in energy

than the global minimum are characterized by sequences with both positive and negative signs. The adjacent CS bonds are fully in plane (dihedral angles SCCS $=0$) in the lowest energy conformations.

The number of possible stereoisomers increases considerably with the size of the ring structures. For ring compounds larger than $N=4$, the low energy of all-*syn* structures are only considered.

A simplified approach to larger ring structures

If the molecular symmetry differs the description of relationships between properties and structure is less clear. It is therefore useful to give a more general description of the cyclothiophenes 2_N in terms of idealized structures before examining individual real structures. High symmetry C_{nv} structures encounter with the above mentioned lowest-energy stereoisomers of the three members of the cyclothiophene series. The C_{nv} symmetry was chosen as the general reference system.

High symmetry oligothiophene structures of the point group C_{nv} are generated in the calculations by excluding a twisting between the adjacent thiophene rings. This is achieved by setting the interring angles ω_{CCCC} to zero. In an extreme case, all rings are aligned parallel to the molecular axis giving rise to a bracelet-type structure. In another extreme configuration the thiophene rings are aligned perpendicular to the axis resulting in a planar necklace-type structure (Fig. 3). If the angle ϕ is
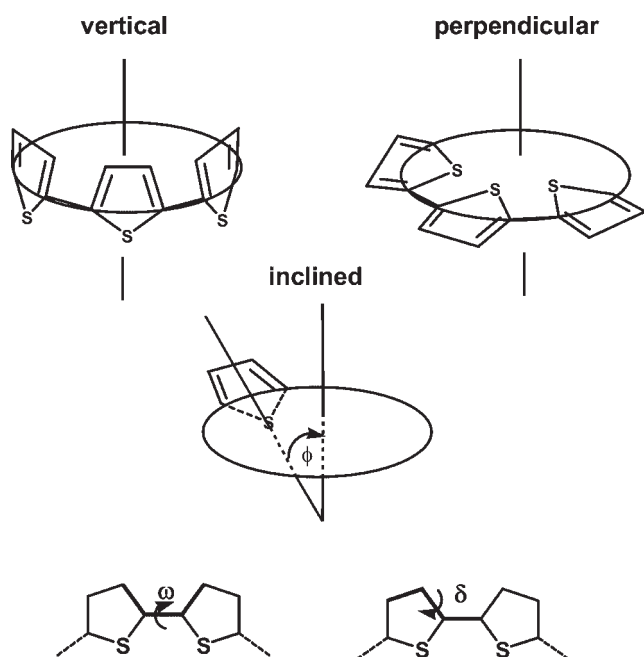
introduced between the main axis of the cyclothiophene 2_N and the symmetry axis of the thiophene subunit the angle $\phi=0°$ stands for the parallel and $\phi=90°$ for the perpendicular arrangement. In all intermediate structures the thiophene rings are inclined to the molecular axis with angles between 0 and $90°$. These cyclothiophene structures are cone-shaped. Another measure of the curvature of the cylothiophene 2_N is the dihedral angle δ_{CHCHCC} such as defined in Fig. 3. The angle amounts to $180°$ for planar structures but is less than for $180°$ for cone-shape structures.

Because of the ring strain, the small cyclothiophenes are cone shaped with sulfur directed toward the apex of the cone. As mentioned above these structures exhibit the point group C_{nv}. With increasing ring size the cone-shaped structure is becoming flat finally to pass over to a fully planar structure of the point group D_{nh}. According to the calculations the angle ϕ of the pentamer decreases from $71°$ to $0°$ in the decamer while the angle δ_{CHCHCC} increases from 140 to $180°$. The coaxial parallel alignment with $\phi=90°$ is not realized in the cyclothiophene series.

Except for compounds 2_N of the ring sizes $N=2$ to $N=4$ the high symmetry structures are not the lowest energy ones. These structures are rather saddle points of higher energy on the potential energy surface. If the constraints are lifted global or local minima of lower symmetry are obtained.

Optimized structures and their bond characteristics in ground and ionized states

Results of DFT-calculations of cyclothiophenes 2_N calculated with symmetry constraint are assembled in Table 1 along with results of lower symmetry compounds obtained by full geometry optimization. The high symmetry structures possess n-fold symmetry axes and belong to the point group C_{nv} for cone-type and to D_{nh} for planar compounds exemplified as in Fig. 4. Passing from $N=5$ to $N=9$ the angle ϕ drops down from $71°$ to $2°$. Within the theoretical model used the crossover from the high symmetry cone-type to the planar structures occurs from $N=9$ to $N=10$. Whereas the frequency analyses of the high symmetry structures ascertain saddle points lower energy structures are minima with all frequencies positive.

Except for the first members of the series, the symmetry of the structures of optimum energy differs from that of idealized high symmetry structures. With full geometry optimization the symmetry is reduced from C_{nv} or D_{nh} to D_{2d}, C_s, C_i or C_1. Larger ring structures with $N=10$, $N=14$, and $N=18$ display a centre of symmetry. However, the low symmetry structures are still close to all-*syn*. The structural features found for the cyclothiophenes are similar to those of B3LYP/6-31G* calculations reported by Zade and Bendikov[12] who considered

Figure 3. The selected dihedral angles are the angle of inclination of the axis of thiophene towards the molecular axis (ϕ), the torsional angle around the interring bond (ω_{CHCCCH}) and the angle of the curvature (δ_{CHCHCC}) of the thiophene ring along the perimeter

Table 1. Symmetry und relative stability of cyclo[N]thiophenes 2_N with N = 5 to N = 18 and of the related cyclic compounds with N = 3 to N = 4 in kcal/mol calculated by DFT without and with constraint (ω_{CCCC}=0). Topologically analogous compounds with the ring size N = 3 and N = 4 are included (Becke3LYP/3-21G*)

| N | High symmetry structures | | | | Low symmetry structures | | | Stabilization energy | |
	Symm.	ω_{CCCC}	δ_{CCCHCH}	ϕ^a	Symm.	ω_{CCCC}	δ_{CCCHCH}	ΔE^b
2	C_{2v}	0	80	—	C_{2v}	0	80	—
3	C_{3v}	0	114	—	C_{3v}	0	114	—
4	C_{4v}	0	130	—	C_{4v}	0	130	—
5^c	C_{5v}	0	140	71	C_s	0–45	133–152	−7.5
6	C_{6v}	0	149	60	C_s	45	144–161	−10.0
7	C_{7v}	0	157	50	C_1	26–60	151–177	−8.7
8	C_{8v}	0	163	36	D_{2d}	43	163–178	−7.2
9	D_{9v}	0	179	2	C_1	29–41	168–179	−5.9
10	D_{10h}	0	180	0	C_i	19–33	175–179	−2.8
14	D_{14h}	0	180	0	C_i	19–26	179	−2.3
18	D_{18h}	0	180	0	C_i	17–32	178–179	−22.8

[a] For the definition of the angles see Fig. 2. Because of the nonplanarity of the thiophene rings of 2_N with N = 2 to N = 4 the angles ϕ are not defined.
[b] Gain in energy in passing from high to low symmetry structures.
[c] The calculation of 2_5 at MP2/6-31G* level resulted in the following angles $\omega_{CCCC} = 0°$, $\delta_{CCCHCH} = 141°$ and $\phi = 65°$ The MP2 stabilization energy amounts to 8.5 kcal/mol in passing from the higher (C_{5v}) to the lower symmetry structure (C_s). Extension of the basis set from 3-21G* to 6-31G* at the DFT level led to a lower rather than higher stabilization energy (5.0 kcal/mol).
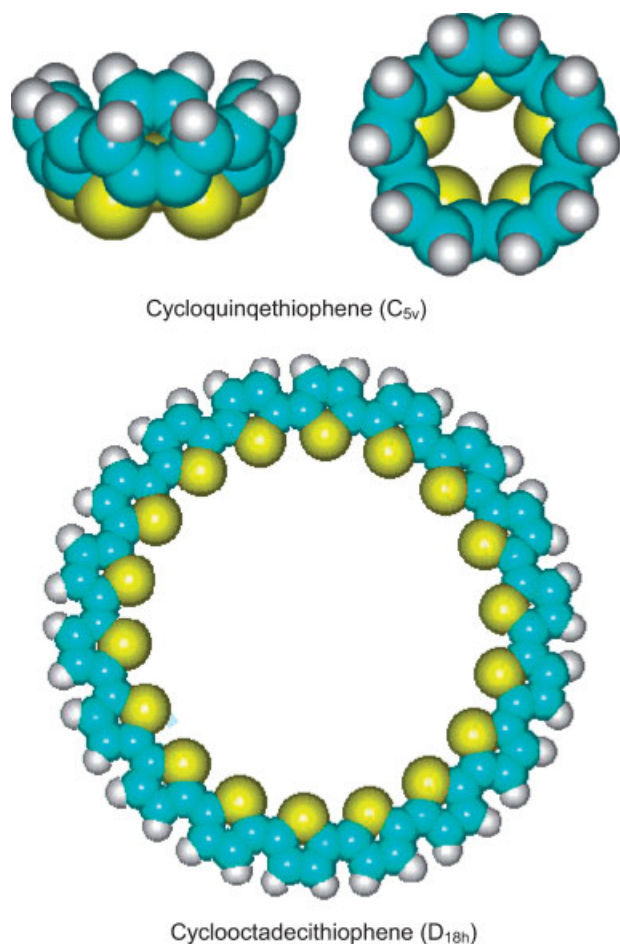

Cycloquinqethiophene (C_{5v})

Cyclooctadecithiophene (D_{18h})

Figure 4. The cone-type cyclo[N]thiophene 2_N with N = 5 in two different views (on top) and the planar compound with N = 18 calculated with zero-interring-torsion angles (at the bottom)

s-cisoid even-numbered oligomers from $N = 8$ up to $N = 30$.

The calculated stabilization energies arising from the geometrical relaxation are relatively low in the most cases. The stabilization energy is only remarkably large for $N = 18$ with 22.8 kcal/mol (see Table 1). In the latter case the structure relaxes from a planar to a twisted structure (see Fig. 5). A twisted structure with a centre of inversions was also calculated for $N = 14$ (C_i-symmetry). However, the energy of this structure is only about 0.2 kcal/mol higher than the energy of the planar isomer.

To compare *ab initio* MP2 calculations have been performed for cylo[5]thiophene (2_5). As mentioned in a footnote of Table 1, the structural data are similar to those of the DFT calculations. The gain in energy in passing from the high symmetry to the low symmetry structure is 8.5 kcal/mol compared to 7.5 kcal/mol by DFT.

The inspection of the bond parameter of Table 2 shows that the first three members of the series take an exceptional position with respect to the bond characteristics. Whereas the thiophene fragments of cylothiophenes 2_N with N ≥ 5 are weakly bound between the rings with bond lengths of about 1.45 Å the compounds with of $N = 2$ to $N = 4$ exhibit essential double bonds with lengths of about 1.35Å. Thus, there is a drastic change of the CC bond lengths in passing from $N = 4$ to $N = 5$ accompanied by a crossover from a heteroquinoid to a heterobenzoid bond system. The CS bonds of small ring compounds are about 0.08 Å longer than the bonds of the intrinsic cyclothiophenes of larger ring size (cf. Table 2). Moreover, the sulfur atoms of the small ring compounds are placed out of the ring plane by 40° on the average. Consequently the first three members of the homologous series cannot be considered as true cylothiophenes.
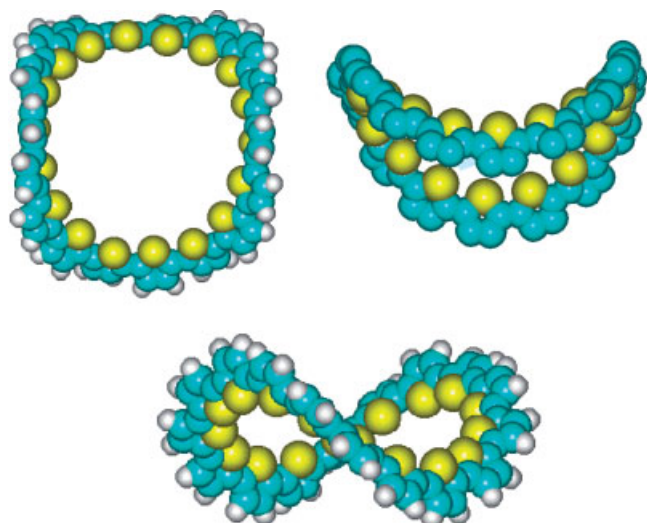
Figure 5. Optimum structures of cycloocatadecithiophene **2₁₈** in three views (N = 18, Cᵢ-symmetry)

Figure 6. The dimer **2_N** considered as substituted cycloctaetraene or 1,4-dihiin

The strange *syn*-configured dimer structure derived from **2₂** with long CS-bonds may be understood as episulfide of cyclotetraene or, alternatively, as substituted 1,4-dithiin (cf. Fig. 6). The large CS bonds of 1.779 Å and the short bonds of 1.333 Å calculated for 1,4-dithiin correspond to bond lengths of 1.879 Å and 1.362 Å of the dimer.

The bond lengths of cyclo[N]thiophenes with N > 5 and their alternation in lengths are consistent for all members of the series. The interring bond lengths amount to about 1.45 Å. Thus cyclothiophenes consist of weakly bound thiophene units. The bond lengths of high symmetry structures slightly decrease in going from
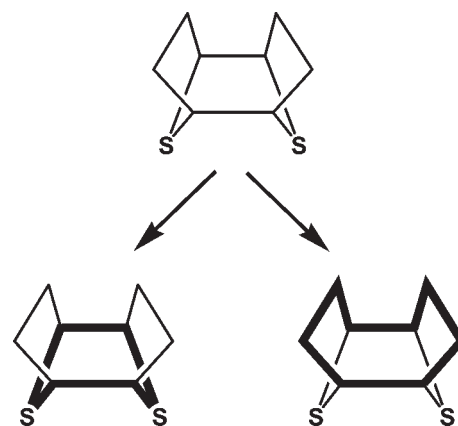
the pentamer **2₅** (1.47 Å) to the octadecamer **2₈** (1.44 Å). The averaged 'double' and 'single' bonds of the thiophene substructures are 1.39 and 1.43 Å, respectively. They do not differ much from the corresponding values of the parent oligothiophenes **1_N** (1.37 and 1.44 Å, respectively). As shown for **1₅** extension of the basis set from 3-21G* to 6-31G* hardly affects the calculated bond lengths whereas the MP2/6-31G* calculation results in a slight contraction of CS and interring CC bonds and a larger bond length alternation within the thiophene substructures (see footnote of Table 2).

The number of π-electrons of cyclothiophenes **2_N** along the carbon backbone amounts to 4n which suggest anti-Hückel systems. However, since the related hydrocarbons are actually Jahn-Teller distorted with a pronounced bond length alternation the reference to

Table 2. Bond lengths of thiophene substructures, interannular bonds (2–6) in Å, bond lengths alternation indices (BLA) in Å and angles of out-of-plane deformation ¹of the sulfur atoms in degrees calculated by DFT B3LYP/3-21G*[a]

N	Thiophene bonds			Interring bonds		Dieder angles out-of-plane
	1–2	2–3	3–4	2–6	BLA[b]	
2[c]	1.879	1,522	1.359	1.362	0.16	31
3	1.823	1.505	1,345	1.345	0.16	45
4	1.803	1.483	1.350	1.353	0.13	33
5	1.764	1.386	1.431	1.472	0.07	0
8	1.753	1.386	1,427	1.451	0.05	0
18	1.758	1.389	1.403	1.440	0.03	0
5⁺	1.764	1.407	1.407	1.441	0.02	0
8⁺	1.753	1.400	1.410	1.432	0.02	0
18⁺	1.758	1.395	1.397	1.432	0.02	0
5⁺⁺	1.767	1.432	1.384	1.411	0.03	0
8⁺⁺	1.755	1.416	1.393	1.414	0.01	0
18⁺⁺	1.758	1.395	1.397	1.444	<0.01	0
5⁻	1.871	1.405	1.421	1.444	0.03	0
8⁻	1.763	1.397	1.416	1.434	0.03	0
18⁻	1.768	1.394	1.398	1.432	0.02	0

[a] High symmetry cyclothiophene structures.
[b] The bond length alternation index BLA is defined by the difference between the average lengths of single and double bond in the conjugated system.
[c] DFT B3LYP/6-31G* and *ab initio* MP2/6-31G* calculations of the pentamer (**2₅**) resulted in the following bond lengths:1.763, 1.385, 1.427, 1.470 and 1.743, 1.398, 1.413, 1.467 Å, respectively.

anti-Hückel systems is less founded. However, this classification may useful to understand the change of the electronic structure in passing from neutral compounds with the formal 4n π-perimeter to the corresponding dications with the $(4n + 2)\pi$-perimeter. In contrast to the neutral compounds 2_N dications 2_N^{2+} display a lower bond length alternation. According to Table 2 the bond length alternation (BLA) within the thiophene ring practically vanishes with ionization. As shown for $N = 5$, $N = 8$ and $N = 18$, BLA is lower for cations $2_N^{+\cdot}$ and dications 2_N^{2+} than for the neutral compounds 2_N. The CC-bonds of monoanions $2_N^{-\cdot}$ alternate slightly more than those of monocations $2_N^{+\cdot}$.

The magnetically based NICS value is useful to probe the aromatic or antiaromatic character of a ring system. This quantity is defined as the negative shielding at the center of the ring and given in p.p.m.[37] NICS(0) values are calculated for the centre of molecule in the ring plane. As exemplified with cyclononithiophene (2_9), the neutral compound exhibits a NICS value near to zero at the centre of the ring (cf. results in Ref. [5]). A value like that is characteristic neither for an antiaromatic system nor for an aromatic system. But the same calculations on the dicationic species 2_N^{2+} resulted in relative large negative NICS values indicating an aromatic character of the ring. In analogy to studies on polycyclic rings.[38] NICS values of the partial rings were also calculated.[38] As it was expected, the aromatic character of the thiophene substructures is principally retained. The NICS values are, however, lower than the value of the isolated thiophene calculated at the same level of theory (−12.97 p.p.m.).

To eliminate the effect of the conjugatively bound sulfur the σ-bivalent sulfur of cyclothiophene was replaced by CH_2. Structures of this type are unknown so far. Result of these calculations are exemplified with $N = 9$ in Fig. 7. The bond length alternation of the neutral

hydrocarbon is increased with respect to that of cyclothiophenes. In contrast, the CC bonds of the dications are nearly constant along the perimeter. The NICS-value of the cyclothiophene dication 2_9^{2+} is considerably lower than that of the neutral compound thus signalizing a higher aromatic character.

Polaron, two-polaron, and dipolaron structure of the ions

Cyclothiophenes $2_N^{+\cdot}$ ion radicals deserve particular attention. However, the radicals might undergo disproportion according to equation

$$2\ 2_N^{+\cdot} \rightarrow 2_N^{2+} + 2_N$$
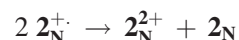
This phenomenon was extensively studied by Hünig et al. for various dyes.[39]

According to DFT calculations two cyclothiophene cation radicals $2_N^{+\cdot}$ are significantly more stable than one dicationic cyclothiophene 2_N^{2+} and one neutral cyclothiophene 2_N together. With full geometry optimization the relative stabilization energy of the cations decreases from 73.6 ($N = 5$) to 36.5 kcal/mol ($N = 18$). Thus, disproportion of cyclothiophenes is not expected for free molecules up to $N = 18$. Knowledge about the reactivity in the condensed phase requires the study of the medium effect. It should be mentioned that linear oligothiophenes also show a relative high stability of the ion radical with respect to disproportion.[27]

Cyclothiophene cations $2_N^{+\cdot}$ may be charge carriers in the condensed phase. They are involved in the hole transport phenomenon decribed by a hopping type mechanism between adjacent thiophenes. Such radical cations (or anions) are designated as polarons in solid state physics. In the case of oligothiophene the transport
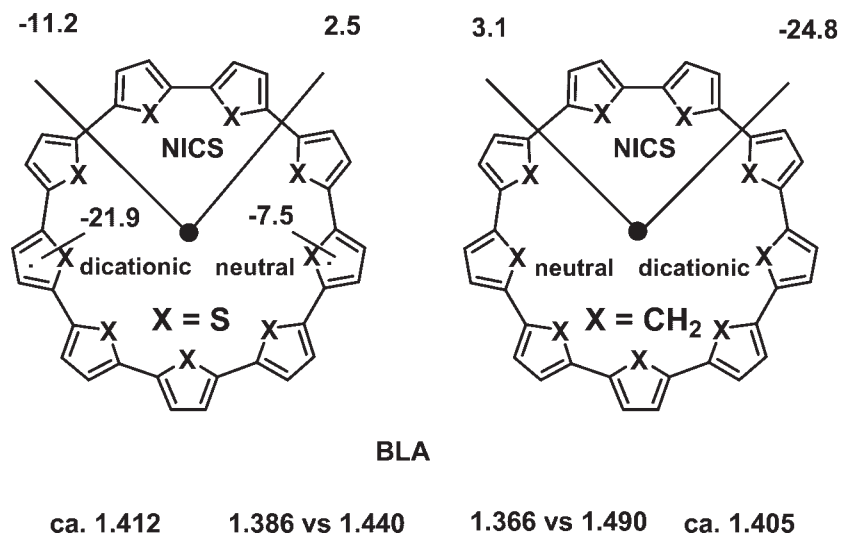

Figure 7. Bond lengths alternation indices (BLA) and NICS(0) values in p.p.m. of the planar cyclononithiophene (2_9) (on the left) and its related hydrocarbon (on the right) calculated of the whole and the partial rings by DFT GIAO B3LYP/3-21G*

process has been recently studied in terms of the single electron transfer of a mixed valence systems.[40]

Radical structures may experience geometry relaxation and symmetry breaking.[41] Because of strong electron-phonon interactions symmetry breaking is favored in extended π-conjugated systems. This effect may be underestimated in DFT calculations when functionals such as BLYP and B3LYP are used. These functionals favor the electron delocalization.[19] In the case of long chain oligothiophenes 1_N Moro *et al.*[42] calculated localized polaron structures at the restricted open shell *ab initio* level of theory whereas Bredas *et al.*[43] obtained polaronic effect at the DFT level by increasing the amount of Hartree-Fock-exchange in the exchange functional.

Calculations on cyclothiophene radical cations ($2_N^{+\cdot}$) with $N = 14$ and $N = 18$ were performed in this study by the last mentioned approach. The 'half and half' exchange functional (BHandHLYP) was used.[18] This functional is known to diminish the electron delocalization favoring solitonic defects. Bond localization is in fact indicated in the bond length characteristics of the largest considered cyclothiophene $2_{18}^{+\cdot}$. Considering the C3-C4 bonds of the cations, for example, five adjacent thiophenes display markedly shorter bonds than the remaining fifteen thiophene rings. Concomitantly, the five adjacent thiophenes bear 68% of the total charge and, in addition, 85% of the total spin density. A similar result was obtained for the cationic cyclo[14]thiophene ($2_{14}^{+\cdot}$). Thus, similar to oligothiophenes geometry localization and charge defects are expected for cyclothiophenes of large ring size.

Usually dicationic dipolarons are formed at high doping concentrations. The nature of the dipolaron of oligothiophenes 1_N was studied as a function of the chain length by first-principle methods. Dipolarons were found to be instable with respect to separation into two polarons at longer chain lengths.[44,45] This particularity was also found for oligothiophene dications (1_N^{2+}).[25,26]

In this study the same effect was observed with cyclothiophene dications 2_N^{2+} of larger ring sizes.

Calculated by BS-UB3LYP the largest dications with $N = 14$ and $N = 18$ proved to be Kohn-Sham instable. The biradicaloid two-polaron (polaron pair) state is the molecular ground state. The lowering of energy with respect to the energy of the conventional spin-pure structure amounts to 0.27 kcal/mol for $N = 14$ and increases to 1.52 kcal/mol for $N = 18$. Whereas the CC bond lengths of the polaron with $N = 18$ are nearly constant the bond lengths of the corresponding two-polaron state vary between 0.01 to 0.02 Å. The numerical differences in bond length are small but show a systematic change: The thiophene rings of two opposite regions of the 18-membered ring are slightly heteroquinoid and those in between them are more heteroaromatic. Based on a completely different theoretical model this structural feature was first shown by Tol.[8] In the two heteroquinoid parts of the ring the charge is larger than of the two heteroaromic parts.

Ionization energies and electron affinities

Since important applications of π-conjugated polymers are based on electron transfer processes redox properties deserve particular interest. The ionization potential of oligothiophenes 1_N has to be kept low in OLEDs to facilitate electron transfer of holes from the anodes to the emitting layer whereas an increased electron affinity may reduce the electron injection barrier in the layer.

Ionization energies were calculated by the energy difference method (ΔSCF). As long as the ionized states are not relaxed vertical ionization energies are obtained. The vertical ionization energies should better correspond to experimental ionization energies measured by photoelectron spectroscopy than the adiabatic ones. Results of DFT calculations are listed in Table 3.

Except for structures of small cyclo[N]thiophenes 2_N with $N = 2$ to $N = 4$ vertical ionization energies of the low symmetry structures are larger than those of high symmetry structures. However, the general trend is the

Table 3. Vertical ionization energies IE_n of single and twofold ionization of cyclo[N]thiophenes 2_N of different symmetry in eV calculated by DFT (Becke3LYP/3-21G*)

2_N	IE_1	IE_2	Sym.	IE_1	IE_2
N, Sym.	With symmetry constraint			Without symmetry constraint	
2, C_{3v}	7.51	21.21	C_{3v}	7.51	21.21
3, C_{3v}	7.67	20.01	C_{3v}	7.67	20.01
4, C_{4v}	6.59	17.76	C_{4v}	6.59	17.76
5, C_{5v}	5.88	15.55	C_s	6.18	18.18
6, C_{6v}	5.79	14.99	C_s	6.22	15.83
7, C_{7v}	5.73	14.53	C_1	6.26	15.61
8, C_{8v}	5.67	14.17	C_{4v}	6.13	15.07
9, C_{9h}	5.66	13.92	C_1	5.88	14.36
10, D_{10h}	5.53	13.49	C_i	5.70	13.82
14, D_{14h}	5.22	12.82	C_i	5.44	12.82
18, D_{18h}	5.04	11.69	C_i	5.40	12.49

Table 4. Effect of the theoretical model on the first ionization energies of the parent thiophene and of oligo[N]thiophenes ($N = 2$ to $N = 5$)

Model	$N=1$	$N=2$	$N=3$	$N=4$	$N=5$
B3LYP/3-21G[*)]	8.88	7.43	6.77	6.40	6.15
B3PW91/3-21G[*]	9.00	7.55	6.91	6.53	6.28
PBE0/3-21G[*]	9.36	7.75	6.73	6.55	6.36
B95/3-21G	8.88	7.44	6.97	6.42	6.18
B3LYP/6-31G[*]	8.70	7.28	6.64	6.31	6.02
B3LYP/6-311++G[**]	8.94	7.54	7.00	6.54	6.30
Exp. (PES)[a]	8.87	7.95	7.43	7.28	7.11

[a] Ref. [47].

same in both series. Ionization energies less than 6 eV were calculated with $N = 9$ and larger ring sizes. Vertical ionization energies lower than 6 eV were also reported recently for 2_N with N larger than 10 calculated by DFT B97-1/3-31G[*].[9] However, the National Institute of Standards and Technology (NIST) databank[46] does not contain ionization energies less than 6 eV of organic compounds. On the other hand, ionization energies of small and middle-sized molecules are normally in error by about 0.2 eV only.[13]

To discuss this discrepancy, vertical ionization energies of the open chain oligothiophenes 1_N were calculated. In contrast to cyclothiophenes 2_N experimental ionization energies are available up to $N = 5$ in series 1_N[47] As shown in Table 4, DFT B3LYP calculations reproduce the experimental ionization energies only for the parent thiophene. The calculated ionization energies of the oligomers with $N = 2$ to $N = 5$ are significantly lower than the experimental energies. The deviation between theory and experiment grows to about 1 eV with $N = 5$. Replacement of the B3LYP by other hybrid xc-functionals or an extension of the basis set did not reduce the deviation.

It should be mentioned that the error is not restricted to sulfurorganic π-electron systems. For example, the hydrocarbon pentacene is calculated to undergo ionization at 5.83 eV at the DFT level B3LYP 6-31G[*] level whereas the experimentally determined value is 6.61 eV.[48] This same type of error has also been reported for compounds of the oligoacene series.[49] The error was attributed to a shortage of electron correlation.[49] In fact,

ab initio MP2 calculation with extended basis sets provided excellent results.[50]

The comparison of the ionization energies of the ring-shaped and open-chain compounds of Tables 2 and 3 suggests that the ionization energies of the ring closed cylothiophenes 2_N may be comparable with those of the open-chain compounds 1_N with the same number of thiophene rings (e.g., IPs for the pentamer 2_5 6.18 eV vs 6.15 eV for 1_5).

In contrast to the thiophene parent compound, anion radicals of cyclothiophenes (2_N^-) are more stable than the neutral compounds. According to the DFT calculations the adiabatic electron affinity (EA) of the pentamer 2_5 amounts to 1.33 eV (cf. Table 5) but increases considerably if diffuse functions are taken into account. With the more extended basis set 6-31 + G[**] the adiabatic EA value increases to 1.74 eV. To draw a comparison, the experimentally recorded electron affinities of 9,10-antraquinone, 1,4-napthoquinone and 1,4-benzoquinone are 1.591, 1.81 and 1.91 eV, respectively.[51]

Electronic excitation energies

Neutral high symmetry cyclothiophenes 2_N of the point groups C_{nv} or D_{nh} have twofold degenerate excited states which entails two intense A_1 (A_{1g}) $\rightarrow$ E electronic transitions of the same energy in the visible region. An additional transition of lower energy is situated in the near infrared region ($A_1 \rightarrow A_2$). This transition is dipole-forbidden. The term levels are qualitatively shown in Fig. 8. The allowed transitions are originated from four one-electronic transitions: They take place from the degenerate-occupied orbitals (e_1) to the lowest energy unoccupied orbital (a_1) and from the highest occupied orbital (a_2) to degenerate unoccupied MOs (e_1). The forbidden transition is essentially due to an electronic transition from the highest occupied molecular orbital (HOMO) of a_2 to the lowest unoccupied molecular orbital (LUMO) of a_1 symmetry.

As shown in Table 6, the wavelengths of the first intense absorption of the high symmetry cyclopolymethines display a regular bathochromic shift with ascending ring size. The absorption wavelengths are slightly lower when the functional B3LYP is replaced by

Table 5. Adiabatic ionization energies and electron affinities of neutral cyclo[N]thiophenes (2_N) and transition energies in eV and oscillator strengths f of the first intense electronic transitions of neutral and ionic cyclo[N]thiophenes (Becke3LYP/3-21G[*])

N	ΔE_{DFT}[a]			ΔE_{TD-DFT}[b] (f)			Dication
	IE$_1$	IE$_2$	EA	Sym.	Neutral	Cation	
5	5.92	15.04	1.33	C$_{5v}$	3.10 (0.41)	2.83 (0.49)	2.89 (0.42)
8	5.79	14.00	1.37	C$_{8v}$	2.95 (1.27)	1.06 (0.14)	2.43 (1.57)
18	5.29	12.05	—	D$_{18h}$	1.98 (3.85)	0.73 (1.04)	1.64 (3.42)

[a] Fully optimized structures of the neutral and ionized cyclothiophenes. Calculation of 2_5 with the 6-31 + G[**] basis set resulted in IE$_1$ = 5.97, IE$_2$ = 15.05 and EA = 1.74 eV.
[b] Degenerate excited states of the high symmetry structures. If 2_5 is calculated by the more extended basis set 6-31 + G[**] the transition energies are only slightly lower: neutral 2.92 (0.41), cation 2.73 (0.49), dication 2.82 eV (0.45).

Neutral compound

Dication

Cation radical
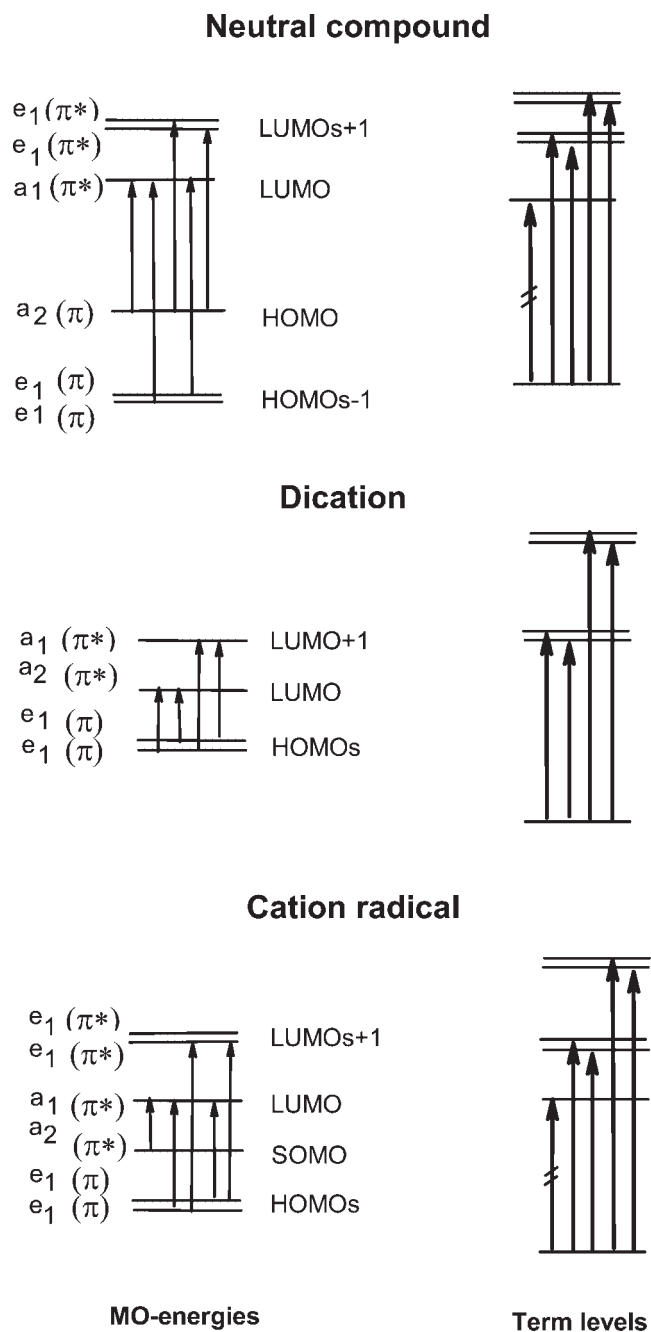

MO-energies   **Term levels**

Figure 8. Qualitative scheme of the relevant KS-frontier orbitals and the respective one-electron transitions (on the left) and of the resulting electronic states and electronic transitions between the states (on the right) of high symmetric cyclo[N]thiophenes ($\mathbf{2_N}$) The sequence of the energy levels corresponds to compounds about N = 8 in size

PBE0 (see footnotes of Table 6). Absorption wavelengths calculated by semiemipirical methods such as ZINDO/S or PPP calculated with DFT optimum geometries show absorption wavelengths comparable with TD-DFT. In the case of planar structure the electronic transitions are of the π-π^*-type. They can be calculated in the PPP approximation. This is the case for compounds of D_{nh}-symmetry.

The spectral data calculated by the different theoretical models are quite consistent.

Cyclothiophenes calculated after geometry optimization without symmetry constraint exhibit energy levels similar to those of high symmetry compounds. However, the transition energies are shifted to higher energies. Whereas the splitting of degenerate MOs of cyclo[N]thiophenes is complex and relatively large for the C_s-symmetric cycloquinqehiophene ($\mathbf{2_5}$) the D_{2d}-symmetric cyclooctithiophene ($\mathbf{2_8}$) possesses degenerate levels. Although the structure of cyclo[18]thiophene considerably changes with molecular relaxation in going from the fully planar to the non-planar (twisted) structure the splitting of the excited states after losing the degeneracy is low with about 0.05 eV. The prediction of an intense absorption of the cyclothiophene parent compounds is, in principal, in harmony with the experimental results for derivatives,[11] however, the theoretical and experimental values differ by about 100 nm. It is tempting to attribute the spectral deviation to the substituent effect not considered in the calculations. However, results of the recent TD-DFT calculations of oligoacenes [49] does not exclude a weakness of the method.

Forbidden or weak low-energy transitions may be difficult to discern in experimental absorption spectra in solution. Sometimes emission spectra provide useful information. Bäuerle *et al.* recorded fluorescence spectra of partially butyl-substituted cyclo[N]thiophenes $\mathbf{2_N}$ and of their cyclo[N]terthiophenediyne precursor compounds $\mathbf{3_N}$.[53] In the case of $\mathbf{2_8}$ and $\mathbf{3_2}$ dual fluorescence has been observed.

The calculation of cyclooctithiophene ($\mathbf{2_8}$) resulted in a weakly allowed transition at 397 nm ($A_1 \rightarrow E$, $f < 0.01$) nm and an intense transition at 379 nm ($A_1 \rightarrow E$, $f = 1.00$) (cf. Table 6).

These spectral data are calculated with the fully optimized geometry of D_{2d}-symmetry. According to DFT B3LYP/3-21G* calculations the structure $\mathbf{3_2}$ has C_{2h}-symmetry in the molecular ground state (formula in Scheme 2). Dual fluorescence of $\mathbf{3_2}$ is expected from B_u- and A_u-excited states, which are responsible for a weak and an intense spectral absorption, respectively. The calculated absorption wavelengths of $\mathbf{3_2}$ are 447 nm ($A_g \rightarrow B_u$, $f = 0.01$) and 411 nm ($A_1 \rightarrow E$, $f = 1.02$) to compare with the measured weak absorption maximum at about 470 and the intense maximum at 400nm, respectively.

Phosphorescence of cyclothiophenes has not yet been observed. Because of the efficient spin–orbit coupling of sulfur the compounds are potential candidate for light emission from triplet states. The TD-DFT calculation of $\mathbf{2_8}$ predicts the lowest energy triplet state at 1.85 eV (436 nm) and a singlet-triplet gap of 0.5 eV.

The first intense isoenergetic transition of a high symmetry cyclothiophene dication $\mathbf{2_8^{2+}}$ is again due to degenerate excited states (cf. footnote of Table 6). The absorption characteristics of the radical ions $\mathbf{2_N^{+\cdot}}$,

Table 6. Absorption wavelengths of the color-determining intense transitions of cyclothiophenes 2_N in nm (oscillator strength in parentheses) calculated by TD-DFT (Becke3LYP/3-21G*)

N	With symmetry constraint				Without symmetry constraint		
	Sym.	TD-DFT[a–c]	ZINDO/S	PPP[d]	Sym.	TD-DFT	
5	C_{5v}	400 (0.41)	527 (0.62)	—	C_s	356 (0.30)	396 (0.22)
6	C_{6v}	407 (0.72)	494 (1.16)	—	C_s	358 (0.44)	359 (0.44)
7	C_{7v}	419 (1.03)	490 (1.60)	—	C_1	359 (0.63)	371 (0.65)
8	C_{8v}	435 (1.33)	494 (1.97)	—	C_{4v}	379 (1.00)	379 (1.00)
9	D_{9v}	446 (1.50)	492 (2.31)	521 (2.99)	C_1	407 (1.29)	413 (1.29)
10	D_{10h}	470 (1.90)	518 (2.94)	545 (3.17)	C_i	442 (1.60)	442 (1.60)
14	D_{14h}	556 (2.96)	540 (3.08)	625 (4.31)	C_i	495 (2.28)	500 (2.25)
18	D_{18h}	625 (3.85)	659 (4.10)	673 (5.14)	C_i	507 (2.29)	518 (2.40)

[a] Calculated long wavelength transitions (oscillator strengths) of cyclooctithiophene ions ($N = 8$): Monocation (2_8^+)˙ 1244 (0.0) 1170 (0.14) 1170 (0.14). Dication (2_8^{2+}) 905 (0.09) 905 (0.09) 511 (1.57) 511 (1.57).
[b] For comparison: spectral data of 2_8 and 2_{18} calculated by TD-DFT PBE0/3-21G*//PBE0/3-21G*: 417 nm ($f = 1.34$) and 580 nm ($f = 4.08$), respectively.
[c] A_1–E_1 transitions (point group C_{nv}) and A_{1g}–E transitions (point group D_{nh}) of two-fold degenerate excited states.
[d] PPP parameter of sulfur derived in Ref. [52] with sulfur heterocyclic compounds.

however, are more complicated. One electron occupies a non-degenerate singly occupied molecular orbital (SOMO). This orbital may loose an electron upon excitation or accept an electron. The complex mixing of the transitions brings about a forbidden transition followed by two isoenergetic intense transitions at higher energies. (cf. footnote of Table 6). These transitions are calculated in the NIR region.

β-Cyclo[N]thiophenes

The study dealt so far with cyclothiophenes linked in the α-positions. Linkage in β-position leads to isomeric compounds as shown in Scheme 3. They are experimentally known with the first few members of the series.

The first members of series **4** with $N = 3$ and $N = 4$ are stable compounds.[54–57] According to DFT calculations the trimer 4_3 is planar whereas the following members 4_4 is puckered. The structures are depicted in Fig. 9. The theoretical structure of the tetramer 4_4 is close to the structure determined by X-ray diffraction.[58] The angle
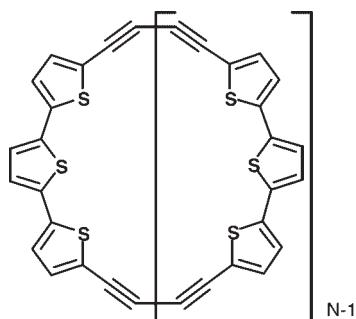
between the plane of two neighbouring thiophene rings is 54.1° calculated for the free molecule and 53.7° measured in the crystal. In contrast to the *syn*-configured cyclothiophenes 2_N with sulfur atoms in a concave inner surface the sulfur atoms of β-cyclothiophenes 3_N are placed on the outer surface. Both the trimers 4_3 and 4_4 were calculated to be significantly more stable than the strained α-linked isomers 2_3 and 2_4 discussed above. The trimer is also known as a [3]radialene in the literature. However, the bond characteristics do not show the radialene structure. The calculated bond lengths rather correspond to a thiophene structure. The delocalized nature of the thiophene substructures is supported by NICS values. The NICS(0) value amounts to -11.84 p.p.m., which is close to the value of the parent thiophene (-12.49 p.p.m.).

Another striking difference between the isomeric compounds concerns the spectral characteristics. In contrast to the α-linked compounds 2_N, compounds with β-linkage of series 4_N absorb in the near UV rather than in the visible region. The transitions are of the π-π^* type. According to TD-DFT calculations the calculated longest-wavelengths absorption wavelengths of 4_3 are 252 nm (strong) and 291 nm (weak) to compare with experimental absorption maxima of about 255 and 320 nm. A third type of cylothiophens encounters with thiophenes symmetrically linked in the α- and β-positions (5_N). Compounds of this series are unknown so far. Again, the trimer 5_3 is

3_N

Scheme 2
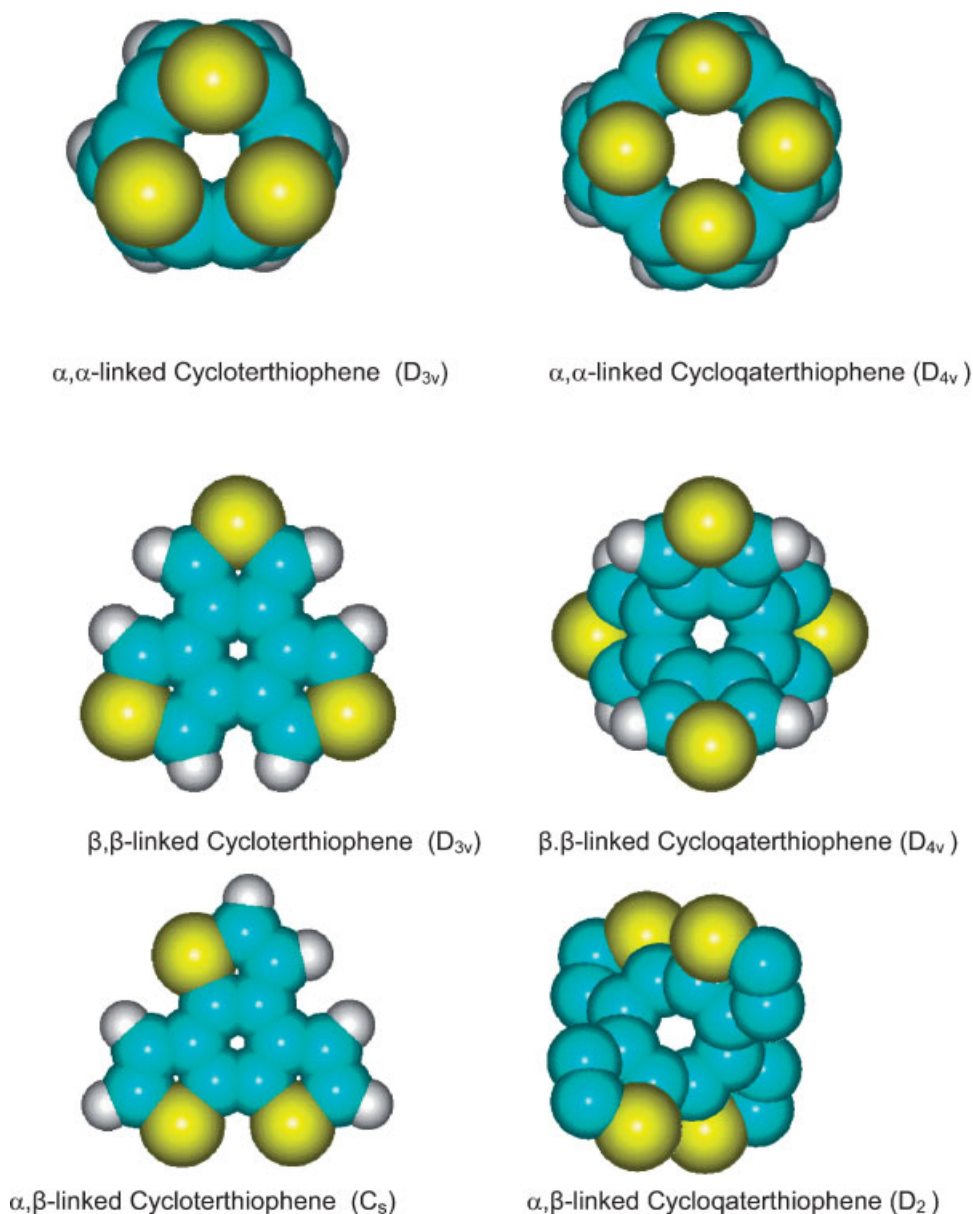

4_N 5_N
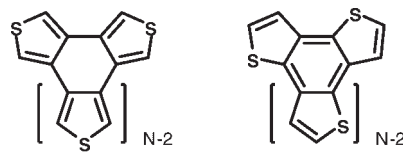
Scheme 3

Figure 9. Structures of differently linked dimers and tetramers

calculated to be planar and the tetramer **5₄** folded (see Fig. 9).

CONCLUSIONS

To get insight into structure and properties of *syn*-configured cyclothiophenes 2_N. DFT calculations were performed. The parent compounds of C_{nv} and D_{nv} symmetry were considered as reference for the minimum energy structures which are of lower symmetry. Cyclo[N]thiophenes with five to nine thiophene rings display an essential cone-type shape The compounds become increasingly planar with growing ring size. As

shown with $N = 18$ larger rings become twisted with full geometry optimization.

The electronic system of cyclothiophenes is excited and ionized at relatively low energies. Neutral cyclothiophenes 2_N have characteristic chromophoric systems. They are predicted intensively to absorb light in the visible region and, in the case of the dications 2_N^{2+}, in the near infrared region. This is in agreement with the experiment.

Similar as found for cationic linear oligothiophenes cyclothiophene cations of larger ring size show geometric defects and exhibit charge localization. These structural characteristics correspond to a polaron-type electronic structures. Dications 2_N^{2+} of larger ring size

compounds are energetically favoured in the broken symmetry two-polaron (polaron pair) structure.

The molecular and electronic structures were examined. According to the bond characteristics the first three members of the homologous series 2_N are not real α-oligothiophenes. Ring shaped oligothiophene linked in β position of the thiophene rather than in α-position also differ strongly from α-oligothiophenes in structure and properties.

Acknowledgements

REFERENCES

1. (a) Bäuerle P, in *Electronic Materials: The Oligomer Approach*. Müllen K, Wegner G (eds). VCH Wiley: Weinheim, 1998; 105–197; (b) Bäurle P, in *Handbook of Oligo- and Polythiophenes*. Fichou DJ (ed). Weinheim, 1999; 89–181.
2. (a) *Organic Light Emitting Diodes, Synthesis, Properties and Applications*. Müllen K, Scherf U (eds). Wiley-VCH: Weinheim, 2006; p 1–426; (b) Kraft A, Grimsdale AC, Holmes AB. *Angew. Chem.* 1998; **110**: 416–433; (c) *Angew. Chem. Int. Ed. Engl.* 1998; **37**: 402–428; (d) Perepichka IF, Perepichka DF, Meng H, Wudl F. *Adv. Mater.* 2005; **17**: 2281–2305;; (e) Barbarella G, Favarett L, Sotgui G, Antolini L, Gigli G, Cingolani R, Bongini A. Chem Mater. 2001; **13**: 4112–4122; (f) Dini D. *Chem. Mater.* 2005; **17**: 1933–1945; (g) Otsubo T, Aso Y, Takimiya K. *J. Mater. Chem.* 2002; **12**: 2565–2575; (h) Chen CH, Shi J, Tang CW. *Macromol. Symp.* 1997; **125**: 1–48.
3. (a) Waldauf C, Schilinsky P, Perisutti M, Hauch JM, Brabec CJ. *Adv Mater.* 2003; **15**: 2084–2088; (b) Murphy AR, Fréchet JMJ, Chang P, Lee J, Subramanian V. *J. Am. Chem. Soc* 2004; **126**: 1596–1597; (c) Beng S, Wu. Y, Liu P, Gardner S. *J. Am. Chem. Soc.* 2004; **126**: 3378–3379; (d) Dimitrakopoulos CD, Malenfant PRL. *Adv. Mater.* 2002; **14**: 99–117; (e) Brown AR, Jarrett CP, de Leeuw DM, Matters M. *Synth. Met.* 1997; **88**: 37–55; (f) Horowitz G. *Adv. Mater.* 1998; **10**: 365–377; (g) Sun Y, Liu Y, Zhu D. *J. Mat. Chem.* 2005; **15**: 53–65.
4. (a) Brabec CJ, Sariciftci NS, Hummelen JC. *Adv. Funct. Mater.* 2001; **11**: 15–26; (b) Negishi N, Yamada K, Takimiya K, Aso Y, Otsubo T, Harima Y. *Chem. Lett.* 2003; **32**: 404–405; (c) Qiao Q, McLeskey JT Jr. *Appl. Phys, Lett.* 2005; **86**: 153501–153503.
5. (a) Hartwig JF. *Angew. Chem.* 1998; **110**: 2154–2177; (b) *Angew. Chem. Int. Ed.* 1998; **37**: 2046–2067; (c) Guram AS, Rennels RA, Buchwald SL. *Angew. Chem.* 1995; **107**: 1456–1459; (d) *Angew. Chem. Int. Ed. Engl.* 1995; **34**: 1348–1350; (e) Lukevics E, Arsenyan P, Pudova O. Heterocycles. 2003; **60**: 663–687.
6. (a) Krömer J, Rios-Carreras I, Fuhrmann G, Musch C, Wunderlin M, Debaerdemaeker MT, Mena-Osteritz E, Bäuerle P. *Angew. Chem.* 2000; **112**: 3623–3628; (b) *Angew. Chem., Int. Edit. Engl.* 2000; **39**: 3481–3486.
7. (a) Mena-Osteritz E. *Advan. Mater.* 2002; **14**: 609–616; (b) Mena-Osteritz E, Bäuerle P. *Adv.Mater.* 2006; **18**: 447–451.
8. Tol AJW *Synth Met* 1995; **74** 95–98.
9. Foumine S, Guadarrama P. *J. Phys. Chem. A* 2006; **110**: 10098–10105.
10. Nakao K, Nishimura M, Tamachi T, Kuwatani Y, Miyasaka H, Nishinay T, Iyoda M. *J. Am. Chem. Soc.* 2006; **128**: 16740–16747.
11. Bednarz M, Reineker P, Mena-Osteritz E, Bäuerle P. *J. Lumin.* 2004; **110**: 225–231.
12. Zade SS, Bendikov M. *J. Org. Chem.* 2006; **71**: 2972–2981.
13. Koch W, Holthausen MC. *A Chemist's Guide for Density Functional Theory (2nd edn)*. Wiley-VCH: Weinberg, 2001; 528.
14. Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheesman JR, Montgomery JA Jr, Vreven T, Kudin KN, Burant JC, Millam JM, Iyengar SS, Tomasi J, Barone V, Mennucci B, Cossi M, Scalmani G, Rega N, Petersson GA, Nakatsuji H, Hada M, Ehara M, Toyota K, Fukada R, Hasegawa J, Ishida M, Nakajima T, Honda Y, Kitao O, Nakai H, Klene M, Li X, Knox JE, Hratchian HP, Cross JB, Adamo C, Jaramillo J, Gomperts R, Stratmann RE, Yazyev O, Austin AJ, Cammi R, Pomelli C, Ochterski JW, Ayala PY, Morokuma K, Voth GA, Salvador P, Dannenberg JJ, Zakrzewski VG, Dapprich S, Daniels AD, Strain MC, Farkas O, Malick DK, Rabuck AD, Raghavachari K, Foresman JB, MC Ortiz JV, Cui Q, Baboul AG, Clifford S, Cioslowski J, Stefanov BB, Liu G, Liashenko A, Piskorz P, Komaromi I, Martin RL, Fox DJ, Keith T, Al-Laham MA, Peng CY, Nanayakkara A, Challacombe M, Gill PMW, Johnson B, Chen W, Vong MW, Gonzalez C, Pople JA. *Gaussian 03, Revision C.02, Gaussian, Inc., Wallingford, CT,* 2003.
15. (a) Becke AD. *J. Chem. Phys.* 1993; **98**: 5648–5652; (b) Lee C, Yang W, Parr RG. *Phys. Rev. B* 1988; **37**: 785–789.
16. Schneider HL, Becke AD. *J. Chem. Phys.* 1998; **105**: 9624–9631.
17. The PBE1PBE functional,also denoted as PBE0,is based on the well-known PBE generalized gradient functional that is composed by 15% HF,75% PBE (Perdew JP, Burke K, Ernzerhof M, *Phys. Rev. Letters* 1996; **77**: 3865–3868 .
18. The BH,HLYP (BHLYP) functional is implemented in Gaussian programs,has the formula $0.5,^* Ex(HF) + 0.5,^* EX(LSDA) + 0.5,^* Dex(B88) + EC(LYP)$,which is not precisely the formulation by Becke AD. *J. Chem. Phys.* 1993; **98**: 1372–1377.
19. Fabian J. *Theochem* 2006; **766**: 49–60, and referenes therein.
20. Wannere CS, Sattelmeyer KW, Schäfer HF III, von Ragué Schleyer P. *Angew. Chem.* 2004; **116**: 4296–4302; *Angew. Chem., Int. Ed. Engl.* 2004; **43**: 4200–4206.
21. Cremer D. *Mol. Phys.* 2001; **99**: 1899–1940.
22. (a) Gräfenstein J, Hjerpe AM, Kraka A, Cremer D. *J. Phys. Chem. A* 2000; **104**: 1748–1761; (b) Ochoa E, Mann M, Sperling D, Fabian J. *Eur. J. Org. Chem.* 2001; 4223–4231, and references therein.
23. Kikuchi A, Ito H, Abe J. *J. Phys. Chem.* 2005; **109**: 19448–19453.
24. Bendikov M, Duong HM, Starkey K, Houk KN, Carter EA, Wudl F. *J. Am. Chem. Soc.* 2006; **126**: 7416–7417.
25. (a) Tol AJW. *Chem. Phys.* 1996; **208**: 73–79; (b) Gao Y, Liu CG, Jiang YS. *J. Phys. Chem. B* 2002; **106**: 5380–5384.
26. Zade SS, Bendikov M. *J. Phys. Chem. B* 2006; **110**: 15839–15846.
27. Rohde D, Dunsch L, Tabet A, Hartmann H, Fabian J. *J. Phys. Chem. B* 2006; **110**: 8223–8231.
28. Serrano-Andrea L, Merchan M. Theochem. 2005; **729**: 99–108.
29. Fabian J, Komiha N, Linguerri R, Rosmus P. Theochem. 2006; **801**: 63–69.
30. Fabian J. *Theor. Chim. Acta* 2001; **106**: 199–217.
31. Fabian J, Diaz LA, Seifert G, Niehaus T. *Theochem.* 2002; **594**: 41–53.
32. Hutchison GR, Ratner MA, Marks TJ. *J. Phys. Chem.* 2002; **106**: 10596–10605.
33. Zerner MC. In *Reviews in Computational Chemistry* Vol. **2**, Lipkowitz KB, Boyd DB (eds). Wiley-VCH: New York, 1991; 313–365.
34. Suzuki H. *Electronic Absorption Spectra and Geometry of Organic Molecules*. Academic Press: New York, 1967.
35. Wagner H-U, Fabian J. WPSIN3, PPP Singlet-CI Program 97.11, 1997.
36. Ugozzoli F, Andreetti GD. *J. Incl. Phenom. Mol, Recogn. Chem.* 1992; **13**: 337–348.
37. Schleyer PR, Maerker C, Dransfeld A, Jiao H, van Eikema Hommes NJR. *J. Am. Chem. Soc.* 1996; **118**: 6317–6318.
38. Cyranski MK. *Chem. Rev.* 2005; **105**: 3773–3811, and references given therein.
39. (a) Hünig S. *Pure Appl. Chem.* 1967; **15**: 109–122; (b) Hünig S, Berneth M. *Top. Curr. Chem.* 1980; **92**: 3–44, and references given therein.
40. Lacroix JC, Chane-Ching KI, Maquère F, Maurel F. *J. Am. Chem. Soc.* 2006; **128**: 7264–7276.
41. Zuppiroli I, Bieber A, Michoud D, Galli G, Gygi F, Bussac MN, André JJ. *Chem. Phys. Lett.* 2003; **374**: 7–12.

42. Moro G, Scalmani G, Cosentino , Pitea D. *Synth. Met.* 2000; **108**: 165–172.
43. Geskin VM, Dkhissi A, Brédas JL. *Int. J. Quant. Chem.* 2003; **91**: 350–354.
44. Brocks G. *Synth. Met.* 1999; **102**: 914–915.
45. Van Haare JAEH, Havinga EE, Van Dongen JLJ, Janssen RA, Cornil J, Bredas JL. *Chem. A Eur. J* 1998; **4**: 1509–1522.
46. Institute of Standard and Technology, NIST Chemistry WebBook, Standard Reference Data Base, 2005.
47. Jones D, Guerra M, Favaretto L, Middelli A, Fabrizio M, Distefano G. *J. Phys Chem.* 1990; **94**: 5761–5766.
48. Schmidt W. *J. Chem. Phys.* 1977; **66**: 828–845.
49. Kadantsev ES, Stott MJ, Rubio A. *J. Chem. Phys.* 2006; **124**: 134901–134911.
50. Deleuze MS, Claes L, Kryachko ES, Francois JP. *J. Chem. Phys.* 2003; **119**: 3106–3119.
51. Heinis T, Chowdhury S, Scott SL, Kebarle P. *J. Amer. Chem. Soc.* 1988; **110**: 400–407.
52. Fabian J, Mehlhorn A, Zahradnik R. *J. Phys. Chem.* 1968; **72**: 3975–3985.
53. Bednarz M, Reineker P, Mena-Osteritz E, Bäuerle P. unpublished work, 2004.
54. (a) Kauffmann T, Greving B, Kriegesmann R, Mitschker A, Woltermann A. *Chem. Ber.* 1978; **111**: 1330–1336; (b) Kauffmann T, Mackowiak HP. *Chem. Ber.* 1985; **118**: 2343–2352.
55. Kabir SMH, Miura M, Sasaki S, Harada G, Kuwatani Y, Yoshida M, Iyoda M. Heterocycles. 2000; **52**: 761–774.
56. Hart H, Sasaoka M. *J. Am. Chem. Soc.* 1978; **100**: 4326–4227.
57. Zhou ZH, Yamamoto T. *J. Organometall. Chem.* 1991; **414**: 119–127.
58. Irngartinger H, Huber-Patz U, Rodewald H. *Acta Cryst.* 1985; **C41**: 1088–1089.