

Extended π -systems in conjugated oligomers and polymers—the longer, the better?

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ABSTRACT

Homologous series of extended oligomeric and polymeric π -chains with arylene and arylenevinylene repeating units are investigated as a function of the chain length. Depending upon the nature of the building blocks and the mode of linking the chain-length dependence leads to fundamentally different chemical and physical consequences. An increase in dimensionality appears as a crucial step in the design and synthesis of molecular and supramolecular structures.

INTRODUCTION

The active - biological or physical - function of organic compounds is becoming an increasingly important motivation for synthesis. Considering the physical properties of organic compounds creates, as an attractive consequence, an interdisciplinary connection between organic chemistry and materials science. This trend can best be demonstrated for unsaturated species with extended π -systems because they act as chromophores and electrophores, i.e. they can serve as a medium for energy and charge transport or for energy and charge storage.

The tailoring of particular physical properties such as a long wavelength optical absorption requires a systematic increase in the size of a molecule. The design and synthesis of homologous series is, indeed, a major concept of organic chemistry. The series of $[4n]$ - and $[4n+2]$ annulenes (ref. 1) with different ring sizes and of linear oligoenes, models for the electron in the box (ref. 2), are classical examples. Extending a π -system into a series of oligomers will, naturally, create a contact between organic and macromolecular synthesis, and there is no meaningful barrier separating both approaches.

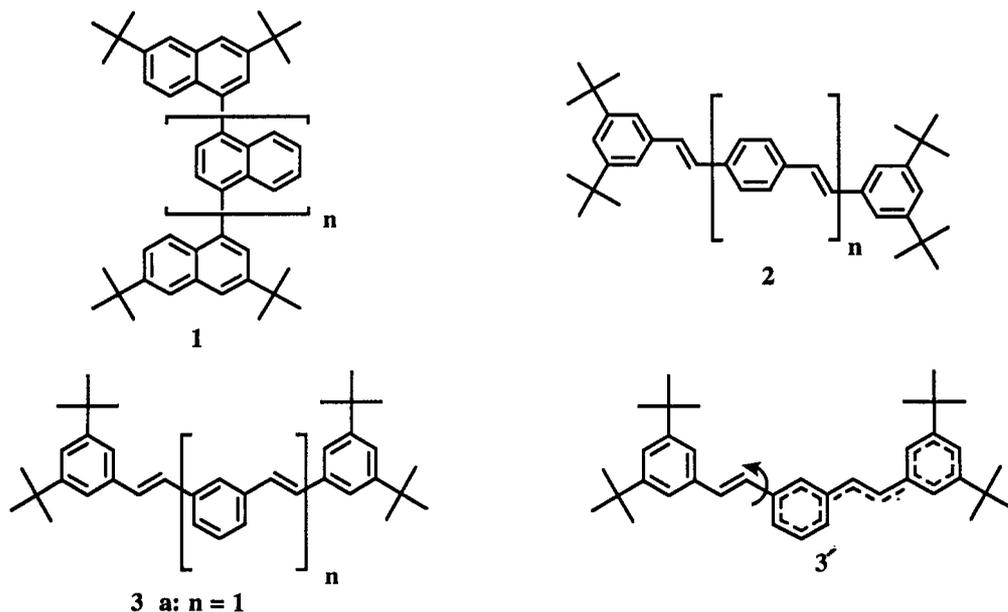
Following the physical properties of conjugated π -systems as a function of ring size or chain length or of the number of repeating units can provide deep insight into the bonding situation. Furthermore, if certain requirements are met, the information gathered can be extrapolated toward the behavior of the related polymer. It will therefore become possible to control the optical, electrical and magnetic properties via the π -topology and via the way in which electrophoric and chromophoric building blocks are linked to oligomeric and polymeric systems.

HOMOLOGOUS SERIES OF CONJUGATED π -SYSTEMS: THE ROLE OF THE CHAIN LENGTH

Conjugated polymers such as polyarylenes or polyarylenevinylenes play an important role in the search for e.g. photoconducting or light emitting materials (ref. 3,4). The investigation of such extended π -chains is often inhibited by their insolubility in organic solvents and the presence of structural defects. We have synthesized various

homologous series of soluble, monodisperse oligoarylenes and oligoarylenevinylenes (ref. 5-7). Solubility is brought about by alkyl substituents. Care has been taken in their positioning to avoid a steric inhibition of resonance. Examples are oligo-1,4-naphthylenes 1, oligo-para-phenylenevinylenes 2 and oligo-meta-phenylenevinylenes 3. The monodisperse character of any member of these series allows a systematic investigation of the physical properties as a function of chain length. Particularly important is the structure of ions resulting from partial electron transfer because the resulting polaronic and bipolaronic defects play an important role in the occurrence of electrical conductivity or ferromagnetism (ref. 8,9).

When the series 1-3 are subjected to electrochemical reduction or oxidation under cyclic voltammetric control, and the redox potentials plotted as a function of chain length, the following findings are made (ref. 10-12): the chain-length dependence of the first (E_1) and second (E_2) reduction potential of 2 indicates that with increasing chain length the first excess charge is better stabilized and that the two excess charges can better avoid electrostatic interaction. Moreover, the fact that $E_2 - E_1$ approaches a minimum allows one to reliably predict how many charges can be stored in the corresponding polymer. The finding that the first oxidation potential in 1 is independent of chain length indicates that, as a consequence of the appreciable twist about the inter-ring bonds, the naphthylene units act as more or less independent electrophores. The charging process brings about a flattening of the π -chain, and thus a stronger interaction of the naphthylene units, so that a second oxidation potential is now chain-length dependent.

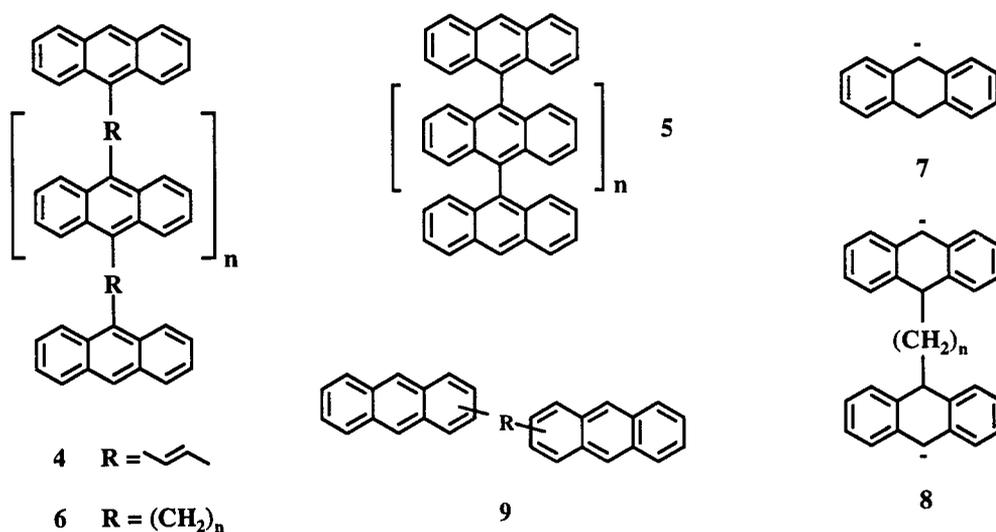


Example 3 is unique in that the first reduction potential is independent of chain length and closely corresponds to that of stilbene. Deeper insight comes from an analysis of the UV/VIS/NIR spectra of the radical anions. While in series 2 there is a bathochromic shift of the bands with increasing chain length, there is no chain-length dependence observable for the radical anions of series 3. Moreover, while the high-energy transitions correspond to those of the stilbene radical anion, there is an additional long wavelength absorption for all homologues which must be ascribed to a charge-transfer band. The immediate conclusion is that the radical anion of 3a exists as a charge-localized species according to structure 3'. It follows that a meta-phenylene unit in a conjugated chain acts as a conjugational barrier.

Tailoring the electrophoric and chromophoric properties of extended π -chains by systematically increasing the size of a molecule requires the consideration of: (1) possible steric inhibition of conjugative interaction as in 1 and (2) the π -topology of the building blocks as in 3.

OLIGOANTHRYLENES: THE ROLE OF LINKING

In order to obtain further insight into the consequences of extended π -conjugation, we have synthesized different oligo- and polyanthrylenes such as 4, 5, and 6 in which the mode of interaction of the anthracene units is systematically varied by changing the linking groups. While in the anthrylenevinylenes 4 an extended conjugation is, in principle, possible, the interaction of the anthracenes in 5 suffers from the near orthogonality of the subunits; in the alkanediyl-linked oligo- and polyanthrylenes 6, the anthracenes are supposed to exist as more or less independent chromophores and electrophores.



Oligomeric compounds 4 are available by carbonyl olefination according to the Wittig-Horner method (ref. 7); for the direct aryl-aryl coupling in 5, the combination of lithiated anthracenes and anthraquinone species (ref. 13) appears to be superior to other more recent methods (ref. 6); the anthrylene species 6 are available via alkylation of carbanions such as 7 and 8 (ref. 14,15). The advantage of this method is that it can nicely be extended to the synthesis of higher homologues; thus the polycondensation of dianion 8 and 1,*n*-dihaloalkanes constitutes an unconventional way of preparing main-chain polyanthrylenes.

When probing the electronic interaction of the separate anthracene units in 6, various dianthrylalkane species of the general formula 9 serve as useful models (ref. 16,17); successive charging of each anthracene with one electron is again a good tool, because the potential difference for the first and second electron transfer, $E_2 - E_1$, reflects the degree of interaction of the electrophores. The radical anions of 9 can undergo a degenerate electron hopping. Interestingly, the rate of such a self-exchange in 9 (and also in 5 and 6) can be tuned by the length and conformation of the spacer, the position of the spacer at the anthracene, and the mode of ion pairing (ref. 17,18). It should be noted that in an independent approach we have been investigating the occurrence of light-induced electron hopping in the title compounds, here a related influence of the bridging groups is observed (ref. 19).

Compounds such as 4-6 serve as efficient electron-storage systems because at a final redox stage each repeating unit can accept two electrons without establishing too strong an electrostatic interaction between the redox centers. One might have anticipated that the electrostatic interaction is significantly stronger in species with extended π -conjugation such as 4, and a related argument has led to the discrimination of redox polymers and conducting polymers (ref. 20). It is noteworthy, however, that the first and second electron transfer to dianthrylethylene occur at more or less the same potential, which indicates that there is only little interaction between the separate anthracene units. This is due to an electron-transfer induced structural change including a torsion about the formal double bond (ref. 21).

In successive reduction processes the oligoanthrylenes 5 can be charged with one electron per anthracene unit. The ESR spectrum of the tetraanionic tetramer 5 (with $n = 2$), taken in the glass, leaves no doubt as to the existence of a quintet state. This indicates that spin coupling along the oligomer chain is inhibited (ref. 13). It should be noted that the stabilization of organic high-spin states is a crucial prerequisite in the search for organic ferromagnets (ref. 22). The occurrence of a TICT fluorescence (ref. 23) in higher homologues and comparison with the behavior of 9,9'-dianthryl (5, $n = 0$) will be considered elsewhere (ref. 24).

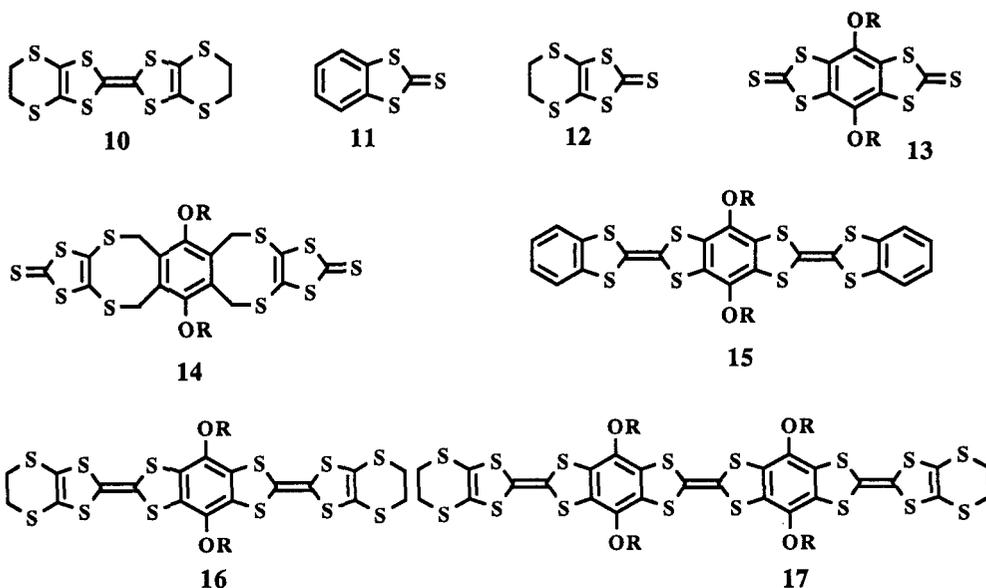
The approaches taken so far rest mainly on the topology of the π -systems: it appears that physical properties can well be controlled via the degree of interaction between the building blocks.

EXTENDED TETRATHIAFULVALENES: DIMENSIONALITY IN CONDUCTING CHARGE-TRANSFER COMPLEXES

The above discussion of extended π -conjugation has been restricted to the single molecules, which is not fully appropriate for magnetic and electrical properties since they depend upon the nature of the bulk material. A rational design of organic conductors, e.g. of conducting charge-transfer (CT) complexes, would therefore have to consider both molecular and supramolecular properties. The example of crystalline CT complexes is revealing, since the occurrence of electrical conductivity is bound to the formation of segregated (donor and acceptor) stacks and to a certain amount of charge transfer between the stacks (ref. 25). The charge-transport process is along the stacking axis; this one-dimensionality, however, can create lattice distortions at low temperature and thus lead to the formation of isolating states. Theory predicts that such a lattice distortion could be successfully suppressed if the dimensionality of the charge-transfer process were increased by the creation of interstack interactions. The example of 10 whose CT complexes, depending on the counterions, possess crystal structures with interstack sulfur-sulfur contacts shorter than the sum of the van-der-Waals-radii, is significant (ref. 25).

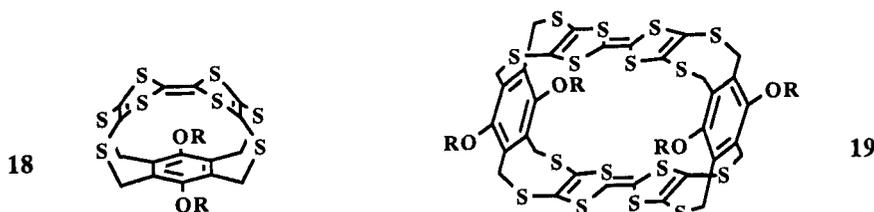
We have worked out another concept for increasing the dimensionality in conducting CT complexes, which rests upon the synthesis of extended donor molecules incorporating two or more tetrathiafulvalene (TTF) units (ref. 26-29).

Thioketones such as 11 and 12 as well as the corresponding cationic or anionic species are useful starting compounds for TTF synthesis (ref. 30). The formation of extended TTF's requires dithiones such as 13 and 14, which can give rise to cross-conjugated double bonds "in two directions". It is thereby mandatory to maintain sufficient solubility by attaching alkyl and aryl substituents (R) at the hydroquinone units. This concept has led us to the synthesis of structurally defined, extended donors such as 15 and 16. Not surprisingly in view of the redox activity of parent TTF, the "trimer" 17 can be oxidized



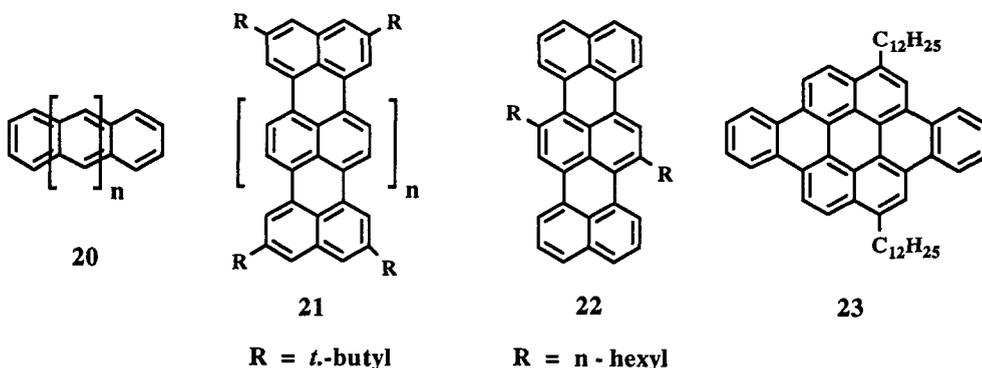
to a hexacation, whereby the interaction of the charges can again be investigated according to the above cyclovoltammetric criteria. It is also possible to subject these donors to electrocrystallization experiments resulting in the formation of single crystals of CT complexes, which can then be subjected to crystal-structure analysis and four-point conductivity measurements. It appears that the extended donors form segregated stacks like the parent TTF. The resulting "channels" for charge transfer, however, are significantly larger. Characteristically, the crystals exhibit short interstack sulfur-sulfur contacts. While it is thus possible to design molecules for the formation of a specific solid-state structure, there is no obvious correlation with e.g. the electrical conductivity. The present complexes have a relatively high room-temperature conductivity, but appear to be semiconductors according to temperature-dependent measurements.

In considering the dimensionality of TTF-based CT complexes one is normally restricted to planar building blocks. A quite unconventional increase in dimension of TTF chemistry is possible by intramolecular formation of cross-conjugated double bonds. Thus, the dithione 13 provides the TTF cage 18 in up to 70 % yield upon treatment with trialkylphosphite (ref. 31). A crystal structure of the latter reveals a strong deviation from planarity of the TTF subunit which, therefore, does not form CT complexes. The electrochemical oxidation and subsequent re-reduction of 18 provides the macrocyclic dimeric cage 19 in a unique "metathetic dimerization" (ref. 32). The resulting cage-type donor is made up of two TTF and two hydroquinone units with a high redox-activity. Since the resulting cage is large enough to act as a host it should now be possible to combine host-guest chemistry with the design of conducting CT complexes. Surprisingly in view of the structures of conventional TTF-CT complexes, in which the direct donor-donor interaction is important, some CT complexes derived from 19 have a relatively high powder conductivity of up to $3.1 \cdot 10^{-2}$ S/cm.



TWO-DIMENSIONAL "LADDER" STRUCTURES

In polymer chemistry, transition from one-dimensional, chain-type structures to two-dimensional, ribbon-type structures is known to bring about distinct advantages such as higher thermal stability and rigidity (ref. 33). An even more significant consequence is obvious when comparing one- and two-dimensional systems with extended π -conjugation. In the latter, one predicts significantly decreasing band-gaps, which might have attractive consequences such as the occurrence of intrinsic electrical conductivity. The synthesis of defect-free ribbon or ladder polymers is much more demanding than that of chain systems. An approach which has recently become most popular employs repetitive cycloaddition-reactions (ref. 34-36). We have recently shown, however, that a two-step approach, in which a linear polymer is subjected to polymer-analogous ring-closure reactions under formation of ladder structures, can also provide structurally homogeneous products (ref. 37,38).



The linear [n]acenes 20 and the rylenes 21 constitute two-dimensional subunits of graphite whereby in the former an appreciable instability is observed for higher oligomers (ref. 39). We have recently shown that rylenes can be prepared from oligonaphthylene precursors by an electron-transfer induced electrocyclic process in which neighboring naphthyl components are initially fused to perylene units (ref. 40,41). The electrocyclic reaction can be performed via both reduction and oxidation. It is essential to bring about sufficient solubility by the introduction of terminal tert.-butyl groups. The resulting products exhibit high thermal stability.

While the perylene system is yellow, the terrylene is red, quaterylene is blue and pentarylene is green-blue. The pentamer possesses a "band-gap" of ca. 1.6 eV, which is much lower than that of the above mentioned linear systems and which corresponds to that one observed for polyacetylene (ref. 42). This finding convincingly documents the role of the π -topology: the small band-gap can be brought about not only by drastically increasing the size of the π -system, but also by appropriately linking the chromophoric subunits. Not surprisingly, therefore, the rylene series proves extremely useful in studies of e.g. fluorescence, photoconductivity, and non-linear optical activity (ref. 43,44). A detailed presentation of these results is beyond the scope of the present text.

When extending the rylene series toward higher homologues, the terminal tert.-butyl groups no longer suffice to maintain solubility. It is therefore crucial to incorporate n-alkyl groups in the bay-region of the ribbon structure which will of course create an appreciable steric hindrance with neighboring hydrogen atoms. We have shown that the di-n-alkylterrylene 22 can be prepared via cyclization

of the corresponding trinaphthyl precursor (ref. 45). The crystal structures of the starting compound and of the product nicely document the prevailing steric effects, namely, that the resulting terrylene perimeter significantly deviates from planarity. This result paves the way for the analogous synthesis of soluble polymers.

When increasing the dimensionality of π -conjugation in ribbon-type structures, perylene acts as a crucial component. On the one hand, it can be extended in the "north-south" direction leading to the rylene series; on the other hand, as has already been documented by Clar (ref. 46) that it also acts as a dienophile in Diels-Alder reactions. Dialkylperylene can thus be extended in the "east-west" direction, e.g. by Diels-Alder reactions with benzyne which leads to a soluble dibenzocoronene 23 (ref. 47).

CONCLUSION

Increasing the size of a π -system proves to be a key step in probing the nature of π -conjugation. It appears, however, that depending upon the prevailing π -topology, the chain-length dependence of various physical properties in conjugated π -systems can differ drastically. It is thus possible, by linking one and the same building block in a sterically and electronically variable fashion, to bring about a broad spectrum of different physical behavior in oligomers and polymers. The tailoring of electrophores and chromophores, in particular, with respect to the band-gap energy, is a central process in the design and synthesis of organic materials.

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