Even if successful, however, they will almost certainly have to be combined with other modalities such as surgery, radiation, and conventional chemotherapy to effect cures. The discovery of oncogenes and their products holds the promise of new targets for drug design that may allow the development of truly specific anticancer agents based on exploitable biochemical differences between normal and neoplastic cells.

Effects of Electron-Transfer Processes on Conformation

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The energy profiles of conformational change processes in unsaturated hydrocarbons are important for many chemical and structural considerations. A classical example is the rotation in biphenyl derivatives (see structure 1). Mislow demonstrated that the angle of
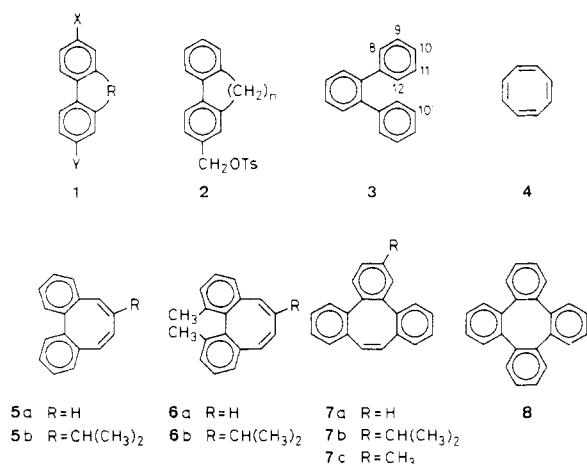

torsion between the benzene rings in 1 increases with the length of the o,o′ linkage.[1] A chemical consequence of the biphenyl conformation was described by Paquette, who found that the rate of solvolysis of the tosylates 2 depends critically on the ring size n and thus on the inter-ring torsional angle.[2] The conformational properties of the biphenyl species are controlled by a subtle interplay of electronic substituent effects, non-

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Scheme I.
The Ring Inversion of Dibenzo[a,c]cyclooctene (5a)
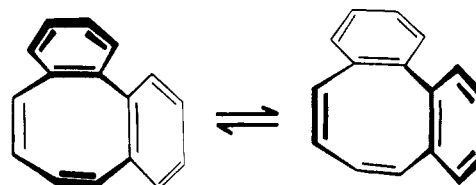
bonding interactions between ortho hydrogens, and ring strain. Is there a simple way of separating the various steric and conjugational influences?

One method of changing a molecule A in a controlled fashion is ion formation via a redox reaction. A single electron transfer creates a radical anion, A·⁻ (or cation A·⁺), which in a subsequent step can transform into a dianion, A^{2-} (or dication A^{2+}).[3,4] Monocyclic annulenes are particularly promising substrates for this area of research since change of the π-electron configuration, e.g., the interconversion of $4n$ and $(4n + 2)$ π-systems, affects the π-bonding. Spectroscopic characterization of π-charge-delocalized mono- and polycyclic ions is also relevant for synthetic purposes, in particular for reductions or reductive alkylations in liquid ammonia.[5–7] The reason is that knowledge of the spin density or charge density distribution in the anionic intermediates is essential for understanding the remarkable regioselectivity of these reactions.

Imagine that there is rotation about a CC single bond with a partial π-bond character. Ion formation actuates a new frontier orbital which may be either bonding or antibonding with respect to the CC bond, thereby inducing a change of the energetics of rotational isomerization in comparison with the neutral compound.

[†] Institute für Physikalische Chemie der Universität.
[‡] Institute für Organische Chemie der Universität.
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Providing that the doubly occupied HOMO (highest occupied molecular orbital) of the dianion A^{2-} is the same as the singly occupied MO in the corresponding radical anion $A^{\cdot-}$, the conformational behavior of $A^{\cdot-}$ should be "intermediate" between that of A and A^{2-}. It follows that a comparison among A, $A^{\cdot-}$, and A^{2-} and, if accessible, even more highly charged species should be informative.

Consider three examples of electron-transfer-induced conformational change: The first involves rotation about a single bond in ionic biphenyl, oligo(phenylene),[8] and related phenylenevinylene species.[9] The second case concerns ring inversion in ionic π-systems, of which the flattening of the tub-shaped cyclooctatetraene ring 4 upon radical ion and dianion formation is a textbook case.[10,11] It is advantageous for the purpose of the present Account to "combine" the biphenyl and cyclooctatetraene types of conformational isomerism by including the benzo-fused derivatives 5–8.[12-14] As is seen from Scheme I, an inversion of the eight-membered ring (that is, a rotation about the four single bonds) also involves a biphenyl rotation.

The third case stems from charge-induced conformational effects in the field of homoconjugation.[15] The formation of conjugated circuits, in spite of an "interruption" by one or more sp^3-hybridized centers, via the through-space interaction of π-units will sensitively depend on the orbital overlap and thus on the conformation. Still another example of conformation-dependent through-space interactions is provided by compounds[16] such as 9,9'-dianthrylalkanes (see below) in which two or more electroactive π-systems are connected by flexible chains. The reason is that a transformation of these systems into radical ions or dianions can change the conformation of the polymethylene chain and allow for a through-space interaction of the electroactive end groups. We anticipate that this effect will be important for the distribution of the spin or charge density.

The present approach is relevant for the construction of organic conductors and electron-storage devices.[17] An example is the chemical or electrochemical doping of poly(phenylenes) or poly(phenylenevinylenes). Monitoring this process raises the question of an electron-transfer-induced conformational change in the resulting species and the question of how the new geometry affects the transport of the charge carriers.

Rotation about CC Bonds in Oligo(phenylenes) and Oligo(phenylenevinylenes)

o-Terphenyl (3) is known to adopt a torsional angle of about 50° between the outer and inner benzene units

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in the solid state.[18] In the ^{13}C NMR spectra of 3 at very low temperatures (–150 °C), the ortho positions C-8 and C-12 are still equivalent;[8] that is, the outer phenyl rings are either orthogonal to the benzene unit or, more probably, rotation of the phenyl rings is rapid on the time scale of the experiment.

Reduction of 3 with alkali metals in tetrahydrofuran (THF) affords stable dianion salts that could be characterized by NMR spectroscopy.[8] Particularly important are temperature-dependent line-broadening effects in the ^1H NMR spectra of the dianion, which indicate a dynamic process. Analysis of the latter is much more straightforward, however, with reference to the ^{13}C NMR spectra, because any independent magnetic site is characterized by a singlet signal. At low temperatures (–60 °C) the ortho carbons are no longer equivalent, and the same holds true for the meta carbons. At higher temperatures the signals of the ortho (meta) carbons broaden and finally merge to single lines. In contrast, the resonance of the para carbons C-10 (C-10') remains sharp throughout the temperature range. This is what one would have expected for a rotation of the phenyl rings about the inter-ring single bonds, since the magnetic site of C-10 (C-10') remains unaffected. The free energy of activation of the rotation can be determined from a line-shape analysis as 13 kcal/mol.

Energetic interpretation of conformational interconversions within π-delocalized carbanions is not straightforward. In particular, one cannot restrict oneself to the properties of the pure π-system, but must also consider the roles of the σ-framework and of the ion pairing.[19,20] Despite the problems associated with such an interpretation, the above outcome is in accord with a simple π-MO model: the π-bond order of the inter-ring bond is increased upon ion formation, that is upon formation of a new frontier orbital with a bonding interaction along the inter-ring bond. Consequently, the rotational barrier is raised.

Support for our simple interpretation comes from inspection of the corresponding radical anion. As expected its rotational barrier, which has been studied by ESR spectroscopy,[21] is higher than in the neutral compound, but by 6 kcal/mol less than in the dianion.

It is well-known that the local π-charge densities of ionic π-systems can be correlated with ^{13}C chemical shifts.[22] When we calculate the π-charge q_π of the terphenyl dianion within a HMO model, we find that q_π depends critically on the choice of the resonance integrals β of the inter-ring bonds. These β-values, in turn, are related to the corresponding torsional angles ψ.[23] We observe that, within such a simple treatment, the experimentally determined sequence of ^{13}C NMR signals can only be reproduced when assuming a torsional angle ψ of about 30°.[8] In similar fashion the hyperfine coupling constants of the radical anion $3^{\cdot-}$ have been calculated as a function of ψ.[21] The predicted angle of torsion is about 50°, i.e., significantly larger

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than in the dianion and close to the value expected for the neutral compound.

We conclude from the terphenyl example that successive electron transfers increase the rotational barrier and decrease the inter-ring torsional angle. It is characteristic that the observed effects are more pronounced for the dianion than the monoanion.

The trend detected in the series of stilbenes **9**, **9·⁻**,[24] and **9²⁻**[9] is quite similar to that found for the terphenyl
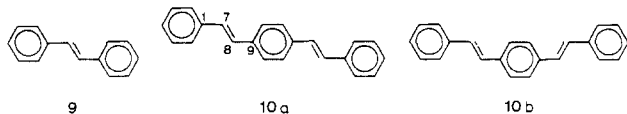
case. As before, a "frozen" phenyl rotation in **9·⁻** and **9²⁻** can be inferred from ESR and NMR spectra by simple symmetry arguments, i.e., by counting the number of hyperfine coupling constants or NMR chemical shifts in the slow-exchange domain of the experiments.

Moreover, **9** extends nicely to **10**.[25] Clearly, compound **10** can undergo different conformational processes. Rotation about the C-1 to C-7 single bond is an isodynamic isomerization, while rotation about the C-8 to C-9 single bond produces different conformations, namely **10a** and **10b**. The NMR spectra of the neutral compound fail to indicate any dynamic behavior. However, there is no doubt from the number and relative intensities of the ^{13}C NMR signals (-60 °C) of the corresponding dianion[9] that *both* conformers are present. Above ca. -50 °C (100 MHz) one observes significant line-broadening effects, indicating the exchange to be due to the interconversion of **10a²⁻** and **10b²⁻**.

The paracyclophane tetraene **11**[26] can be regarded as a cyclic analogue of the linear oligo(phenylene-vinylenes). Upon reduction of this interesting model compound with alkali metals, **11** transforms into a
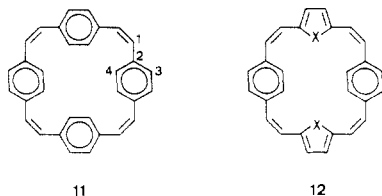
thermally stable dianion and tetraanion.[27] The most striking spectroscopic result is the extreme shift difference of protons inside and outside the macrocycle (note that an inner benzene proton in **11²⁻/2Li⁺** resonates at $\delta = -7$). This finding can be ascribed to peripheral ring current effects; i.e., the dianion exists as a strongly diatropic perimeter, and the tetraanion as a strongly paratropic perimeter.

While in the neutral compound the rotation of the benzene rings about the neighboring single bonds is extremely rapid, it becomes slow in the dianion.[27] This

is obvious from the broadening of the signals of H-3 and H-4 in NMR spectra taken above -20 °C. The rotational process, which interconverts the magnetic sites of inner and outer benzene protons, now proceeds within the NMR time scale; the activation barrier is about 15 kcal/mol. And this value is, again, about 6 kcal/mol larger than in the corresponding radical anion.[28] We conclude that the pronounced tendency toward π-charge and π-bond delocalization within the perimeter of the ions lowers the conformational mobility. Accordingly, the corresponding tetraanion is rigid: up to a temperature of +60 °C, one does not observe a rotation of the benzene rings.

The activation barrier for phenylene rotation in the radical anion of **12**, a hetero analogue of the hydrocarbon **11**, is similar to the one in **11·⁻** itself.[28] It appears, however, that a conformational description of, e.g., dianion **12²⁻** is much more straightforward than that of the neutral compound.[27] The important finding here is the pronounced deshielding of the thiophene protons in the diatropic species **12²⁻**. This reveals that the thiophene ring does not rotate and that the dianion adopts a conformation with the sulfur atoms pointing toward the center of the macrocycle. This finding appears reasonable since such an arrangement is expected to minimize the deviations of the macrocyclic π-system from planarity.

It follows from the above examples that spectroscopic studies of radical anions and dianions in solution contribute to our knowledge of the stereodynamic behavior of flexible π-systems. It should be noted that the conformation of the ionic title compounds can be different in the solid and in solution. A discussion of this aspect is beyond the scope of this Account and will be given elsewhere.[9]

Ring Inversion and Distortion in Cyclic π-Systems

Let us now invoke the additional concept of ring strain and proceed to the benzo-fused cyclooctatetraenes. The cyclooctatetraene dianion **4²⁻** is essentially planar in solution[10,11] and in the solid state,[29] as is the corresponding radical anion **4·⁻**.[30] Upon electron injection the tub-shaped, conformationally mobile ring of **4** is flattened, although this requires an enlargement of the bond angles to 135°. Similar ring-flattening processes have been observed by us upon radical anion and dianion formation from the bicyclic analogues heptalene (**13**)[31] and octalene (**14**)[32] (the neutral compounds existing as π-bond localized species).

Monitoring the conformational effects of electron-transfer processes in, e.g., cyclooctatetraene would require an exact kinetic analysis of ring inversions not only in the neutral compound but also in ions derived from it. Since this is not possible for the parent com-

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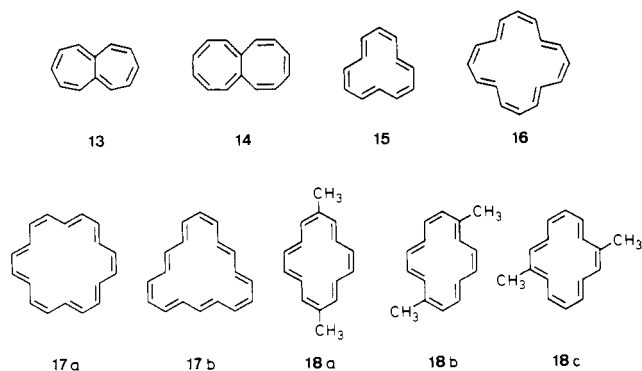
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pound, one needs cyclooctatetraene derivatives in which flattening of the ring is severely inhibited.

This is what one expects for the cyclooctatetraene compounds 5–8, for which planar or nearly planar structures will suffer from increased bond angle strain and from nonbonding interactions of the ortho hydrogens within the biphenyl units (note that ring inversion implies a biphenyl rotation).

In all of the cases 5–8, we can prepare stable dianion salts.[8] A problem is that isodynamic ring inversion does not affect the magnetic sites of the nuclei and cannot be detected in the NMR. So, in order to observe an eventual ring inversion, e.g., in 5 or 5^{2-}, we have to introduce a prochiral group, thus arriving at 5b.[33,34] A related procedure affords the dimethyl analogue 6b in which the substituents are expected to create an additional barrier to biphenyl rotation and to ring inversion. Another model for varying the ease of a ring inversion is the tribenzocyclooctene derivative 7b, whose synthesis includes a Diels–Alder reaction between 3-isopropylfuran and dehydrodibenzo[a,e]cyclooctene.[35]

In the neutral dibenzocyclooctene derivative 5b, the methyl nuclei of the isopropyl group are diastereotopic even at +170 °C. We conclude that the molecule is nonplanar and chiral and that there is no ring inversion even at this high temperature. On the other hand, we have measured the ^{1}H NMR spectra of the dianion (as potassium salt) in dimethyl ether at temperatures as low as –145 °C. Now, we learn that the methyl groups of the isopropyl substituent are equivalent![33,34] We conclude that the dianion either is planar or undergoes an extremely rapid conformational interconversion.

The two o-methyl groups in the analogous compound 6b prevent the corresponding dianion from adopting a planar or nearly planar conformation. Not unexpectedly, its isopropyl methyl groups are diastereotopic even at +100 °C. Similarly, while the neutral tribenzocyclooctene 7b does not undergo ring inversion even at +200 °C, the dianion exhibits dynamic behavior. Coalescence of the signals of the isopropyl methyl protons occurs at –100 °C, and from an exact line-shape analysis we can determine the activation energy of the ring inversion as 7 kcal/mol.[34,35] We believe this to be the first example of a conformationally mobile dianion of a cyclooctatetraene species.

The ring inversion of the neutral compound 7a, which process interconverts enantiomeric forms, is slow within the NMR time scale. We were however able to take advantage of this slowness. The methyl derivative 7c

can be separated into its enantiomers via column chromatography and the rate constant of the racemization measured polarimetrically.[36] The free energy of activation is 41 kcal/mol. We can thus estimate that upon going from the neutral compound to the dianion the relevant activation energy is lowered by about 34 kcal/mol.

The conclusion that emerges from the above cyclooctatetraene studies is that ion formation favors highly symmetric structures with π-bond and charge delocalization. In some cases ion formation induces ring-flattening processes, even when in the corresponding neutral compounds this is opposed by severe strain.

The [12]annulene 15[37] and the [16]annulene 16[38] are the higher homologues of 8. The neutral compounds 15 and 16 are known from extensive spectroscopic studies to exist as π-bond localized, conformationally mobile species.[39] The conformational interconversions imply a rotation of trans-configurated double bonds about the neighboring single bonds. In contrast to the neutral compounds the corresponding dianions are π-bond delocalized. Not surprisingly, dianions 15^{2-} and 16^{2-} are conformationally rigid.[37,38] The reduction of the annulenes 4, 15, and 16 transforms $4n$ π- into ($4n$ + 2) π-systems and π-bond-localized into π-bond-delocalized species. (The intermediate ($4n$ + 1) π-radical anions are also π-bond-delocalized.) In all cases this increases the π-bond order of the formal single bonds and lowers the conformational mobility.

This must not necessarily hold true for the reduction of [$4n$ + 2]annulenes. The neutral [18]annulene 17[40] possesses no π-bond alternation and conforms approximately to D_{6h} symmetry. The low-temperature ^{1}H NMR spectra of the corresponding dianion, and specifically the relative signal intensities of inner and outer protons, point toward a mixture of structures 17a^{2-} and 17b^{2-}.[41] Each species is π-bond-localized and nonplanar. Increasing the temperature causes dynamic processes which bring about the equivalence of all ring protons. This finding can readily be understood if a rapid interconversion of the two conformers 17a^{2-} and 17b^{2-} occurs and if each conformer undergoes a rapid π-bond shift.

The [14]annulene 18[42] and its radical anion[43] are shown by NMR and ESR spectroscopy to exist as equilibrating mixtures of the three conformers 18a, 18b, and 18c. However, and this is another stereodynamic effect, the relative amounts of the isomers differ drastically when going from 18 to 18˙$^-$.

The activation energies of ring inversions (and π-bond shifts) in neutral and charged annulenes have been used to estimate electronic stabilization and destabilization energies.[39,41] It has been claimed that this is possible both for the rotation of trans-configurated double bonds

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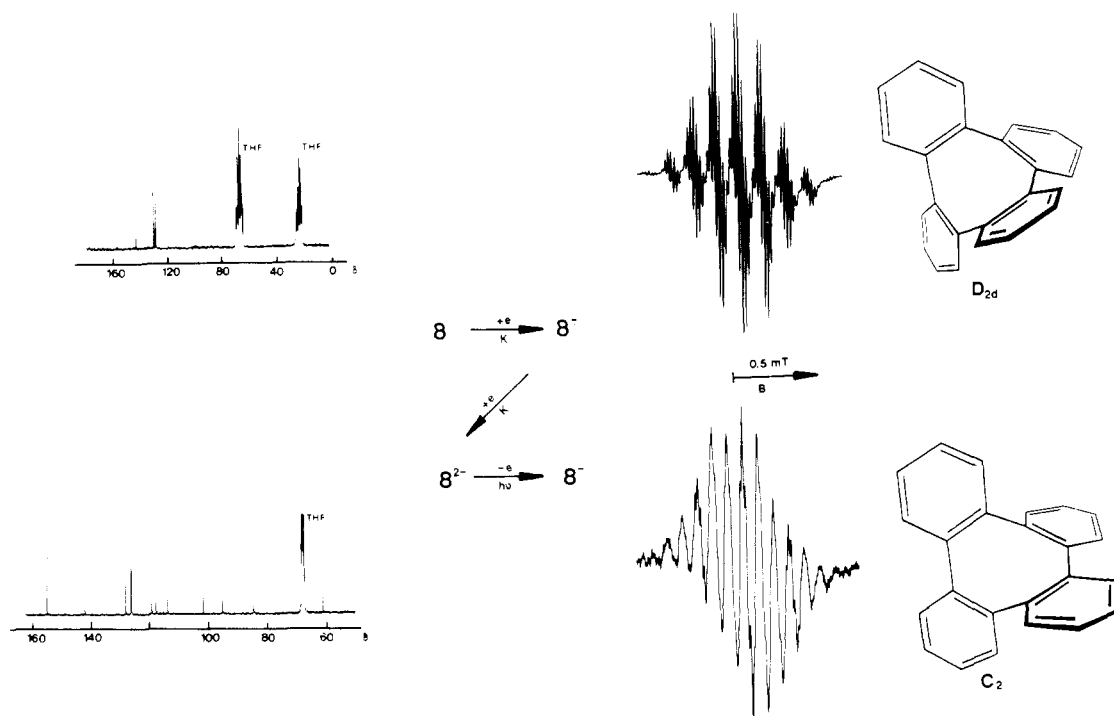(35) Heinz, W. Diplomarbeit, University of Mainz, 1985.

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Figure 1. Reduction of tetraphenylene (8) into its radical anion (8•⁻) and dianion (8²⁻) as well as photooxidation of 8²⁻ into 8•⁻. 8 and 8²⁻ are characterized by the ^{13}C NMR spectra and 8•⁻ by the ESR spectra.

and for the ring inversion, since the former process proceeds via a transition state *without* cyclic conjugation and the latter via a transition state *with* cyclic conjugation.[41]

We conclude from a consideration of the annulene field that ion formation can, but need not, create π-bond delocalized, rigid species. The ions can still be conformationally mobile if they possess a strong tendency toward π-bond fixation. Can ion formation via an electron-transfer process lower the symmetry of the substrate and afford distorted structures instead of creating highly symmetric structures with uniform charge distribution?

Consider the fascinating example of tetraphenylene (8) and its dianion 8²⁻.[14,44] There is no doubt from the ^{1}H NMR spectra of 8²⁻⁻⁸—just from counting the number of resonances—that the D_{2d} symmetry of the tub-shaped neutral system is not preserved. Instead, the molecule has only C_2 symmetry. This surprising deformation of the dianion is not due to side reactions, since reoxidation of the dianion quantitatively yields back the starting compound, and the dianion can be quenched with electrophiles to a diadduct. So, the constitution must remain intact upon reduction. The ^{13}C NMR spectrum of the neutral compound shows only three resonances; this finding supports a D_{2d} symmetry. In contrast, we observe 12 signals for the ion, indicating a deformation into two different biphenyl subunits. The proton signals of one subunit, as well as the related ^{13}C signals, are at much higher field than those of the other biphenyl moiety. Accordingly, we reach the conclusion that the deformation of the molecule into two different halves goes along with the localization of the excess charge in one entity.

To rationalize this result we refer to the previous cyclooctatetraene examples where an effective delo-

Chart I.
The Possible Structures of the Dianion of Tetraphenylene
(8²⁻)
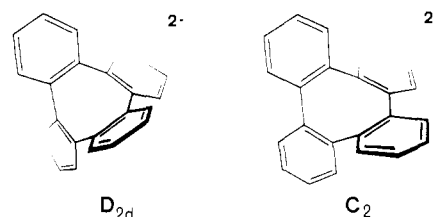
calization of the π-charge requires some flattening of the π-system. In compound 8 this conformational change is hindered by the nonbonding interactions of all the ortho protons and the increase of the bond angles. As a consequence, the barrier to ring inversion in 8 is extremely high, at least 40 kcal/mol.[44] As a result of this steric hindrance, the dianion does not adopt a structure with four twisted benzene rings; instead it adopts (as depicted in Chart I) a structure with two different biphenyl units, each with strongly interacting benzene rings. The biphenyl moieties are orthogonal or at least strongly twisted with respect to each other. Another surprising outcome is that even at +150 °C (where the potassium salt of the dianion is still stable) the NMR spectra remain unaffected. It follows that there is no intramolecular charge transfer between the two subunits, and this result is true irrespective of the mode of ion pairing.

The corresponding radical anion[45] possesses D_{2d} symmetry and is thus similar to the neutral compound: There are only two independent ESR hyperfine coupling constants. We must therefore describe the above deformation process as a specific property of the dianion. However, when the tetraphenylene dianion is irradiated by UV light, it is oxidized to a radical anion

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owing to a photoejection process. The ESR spectrum recorded under these conditions differs from the one obtained upon normal reduction of the neutral compound (see Figure 1).

The hyperfine coupling constants exclude the occurrence of a side reaction of the ions; they reveal, however, that the spin density is again localized in one biphenyl moiety. We conclude that the radical anion, existing under these nonequilibrium conditions, possesses the distorted dianion structure.

Through-Space Interaction of π-Systems

The delocalization of π-charge in an ionic species can proceed not only via a conventional π,π-conjugation but also via a through-space interaction of separate electroactive π-systems. The basic question within this context is how an electron transfer can affect the relevant orbital overlap.

The formation of cyclic conjugation via such a homoconjugation is a favorite subject since a homoaromatic structure can be detected spectroscopically. The formation of a structure with cyclic conjugation in the bicyclo[3.2.1]octadienyl anion 19 and the role of the counterion are still a matter of dispute.[46–49,58] One argument against homoaromaticity in 19 is that the

19   20
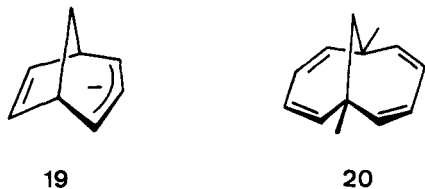
energy difference and the separation of the basis orbitals, an allyl and π*-unit, are too large. The norbornadiene vinylogue 20,[50] which is composed of two identical butadiene subunits, seems to constitute a more favorable case. If both π-moieties accept an extra electron and if there is an interaction (which can also involve Li bridging), the resulting ion pair might exist as an example of the long-elusive bishomocyclooctatetraene dianion.

Our NMR data for $20^{2-}/2Li^{+}$[51] support its description as a symmetric, π-bond-delocalized, diatropic species. Examination of the two-electron reduction of 20 by cyclic voltammetry is even more significant. Simulation of the current-potential curves provides evidence for an ECE mechanism. The first reversible electron transfer (e) is followed by a rapid irreversible "chemical" step (c). One can look at this process as a conformational change improving the interaction of the basis orbitals, and thereby explain why the second electron transfer occurs at a more positive potential than the first one. There is a conjugational stabilization as a result of the conformational change in the radical anion, and the second electron is transferred with greater ease than the first one in spite of the inherent Coulomb effect.

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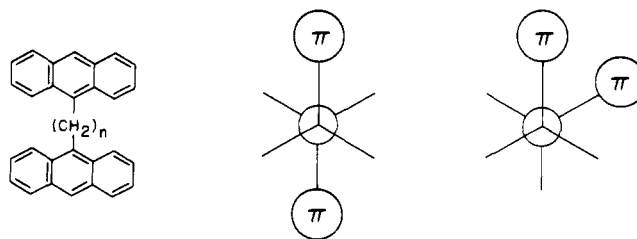
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(49) Christl, M.; Leininger, H.; Brückner, D. J. Am. Chem. Soc. 1983, 105, 4843.

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Chart II.
Conformations of the Dianthrylethane 21a

A different type of through-space interactions occurs in ions derived from dianthrylalkanes (21)[16] and anthracenophane (22).[52] It is clear that the face-to-face
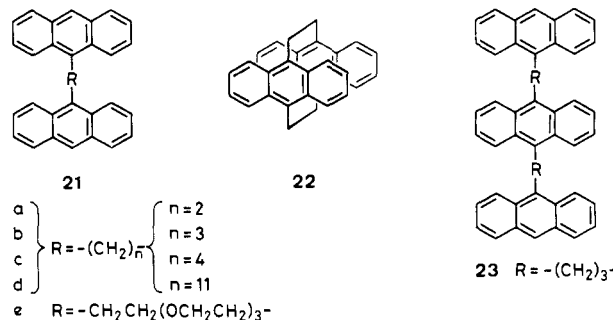
arrangement of the anthracenes in 22 enforces their intramolecular through-space interaction. In the dianthrylalkanes 21 we modify not only the chain length and the distance between the electrophores but also the conformation of the flexible chain (see Chart II). We anticipate that the syn arrangement of the π-moieties is more favorable for a through-space interaction than the anti conformation.[53] However, before considering the geometry of the ionic species, we must focus on two important structural properties of the ions: (i) the distribution of the excess charge and spin density among the separate moieties and (ii) the spin multiplicity of the highly charged species. One problem is that the radical monoanion can have its spin density localized in one subunit or delocalized over both units. A related question of charge localization or delocalization arises for the dianion. An additional problem is that it can exist a paramagnetic biradical or as a diamagnetic system with a singlet ground state.
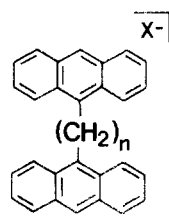
Let us take dianthrylethane 21a as a representative example and consider the spin density distribution in its radical anion (with potassium as counterion).[16] In a mixture of dimethoxyethane (DME) and hexamethylphosphorotriamide (HMPT), we detect five sets of ESR hyperfine coupling constants for four protons each, and one set for two equivalent protons. These findings point toward a structure having the unpaired electron delocalized over both units within the time scale of the experiment. Similar measurements show that in methyltetrahydrofuran (MTHF), which favors a tight interaction of organic ion and counterion, the radical anion has its spin density localized within one anthracene subunit.

The ESR and ENDOR spectra of the radical trianion are very similar to those of the radical monoanion in MTHF. It follows that even in solvents with high

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X^-					

n =	2	3	4	6	11
1	d+−	d+−	d+−	d−	d−
2	s+ t	s+ t	s+ t	t	d−
3	d−	d−	d−	d−	d−
4	s−	s−	s−	s−	s−

s: singlet   + : delocalized
d: doublet   − : localized
t: triplet

cation-coordinating ability the more highly charged species, the trianion, favors a spin-localized structure.

The dianion salt, which we detect as an intermediate between the mono- and trianion stages, gives rise to highly resolved ^1H and ^{13}C NMR spectra (as the lithium or potassium salt). This result provides evidence for a singlet ground state. From the number of independent NMR signals, only nine ^{13}C resonances, it is clear that the excess π-charge is uniformly distributed over both anthracene moieties. Quite a surprising result is obtained from the ESR spectra taken at the same stage of the reduction. Under appropriate experimental conditions, i.e., in the glass at −170 °C, we can also detect a triplet state of the dianion.

Let us now turn to the conformation of the bridging group. The hyperfine coupling constants for the spin-delocalized radical anions of the dianthrylalkanes with ethylene, trimethylene, and tetramethylene linkages are quite similar to the corresponding data in anthracenophane. We deduce from these data that the radical anions with uniform spin density distribution possess conformations with an eclipsed or partially eclipsed arrangement of the π-systems. The same argument is valid for the singlet dianion of dianthrylethane whose chemical shifts show a striking similarity with those of the anthracenophane dianion. However, the triplet biradicals adopt a different geometry. From the zero-field parameters we can estimate the mean distances of the unpaired electrons within these species. These data reflect the increasing chain length, but are only compatible with anti arrangements of the anthracene units.

Chart III summarizes the results from increasing the charge (*X*) of the ions (mono- to tetraanions) and increasing the chain length (*n*). Both features appear to favor a localization of the spin or charge density in one π-moiety.

It is clear that the structures of the ions result from a subtle balance of competing energy terms. Among those are the stabilization energy due to the interaction of the π-systems, the electron–electron repulsion energy of two charged anthracene units, and the ion-pairing energy. Within a simple π-MO model the stabilization energy due to the interaction increases when going from the neutral to the mono- and dianionic compound, but decreases upon the injection of further electrons. In contrast, the "Coulomb" energy increases with any extra charge. It appears quite reasonable, therefore, that the mono- and dianion can adopt conformations with interacting π-systems and the tri- and tetraanions cannot.

As anticipated from the chain length of dianthryl-undecane (**21d**), the corresponding radical anion has its spin density localized in one anthracene unit. From the conformational behavior of poly(oxyethylenes) one might expect that they are more suitable for bringing the electroactive end groups into tighter contact than are poly(methylene) bridging units. Indeed, the radical anion of the dianthryl compound **21e** (Li, MTHF), with an oxygen-containing 11-membered linkage,[54,55] undergoes an intramolecular electron-transfer process which causes a line broadening of the ESR signals (the free energy of activation is about 3.5 kcal/mol). In contrast, the radical anion of the hydrocarbon **21d** is spin-localized under all experimental conditions. We ascribe this outcome to the more favorable conformation—the poly(oxyethylene) chain can avoid an all-trans conformation—and, probably, to the cation-coordinating ability of the oxygens which supports a sandwich arrangement of the counterion between the π-systems.

The behavior of compound **23**,[55] which contains three anthracene units, is similar to that of the dianthryl-propane (**21b**): depending on the ion pairing, the corresponding radical anion exists as a spin-localized or spin-delocalized species. Moreover, **23** forms a stable hexaanion whose conformations can be shown from cyclovoltammetric evidence to depend on the size of the counterion.[56]

Concluding Remarks

The above results demonstrate that electron-transfer processes can markedly affect the π-bonding structure of electroactive substrates. Obviously affected by the redox reactions are conformational interconversions. These conformational changes can be described spectroscopically and interpreted MO theoretically in a straightforward manner. The most significant experimental criteria concern the symmetry inherent in NMR and ESR spectra and the occurrence of dynamic line-broadening effects which also allow for kinetic analysis. We can thus compare the energy profiles of conformational processes for different redox states. The significance of our approach in the study of unsaturated mono- and polycycles is obvious: having developed a technique for systematically monitoring the structural and energetic effects of electron transfer reactions, we can detect novel and quite unexpected modes of π-conjugation.

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