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MULTIPLY CHARGED ANIONS FROM MOLECULES WITH EXTENDED Π-SYSTEMS

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Abstract. Multiply charged anions have been prepared by alkali metal reduction of molecules built from benzene rings joined by vinylene groups. Thus, a tetra-(stilbenyl)ethylene can be reduced to an octaanion and a [2_8]paracyclophaneoctaene to three different anions, assigned as the tetra-, hexa-, and octaanion, respectively. The hexaanion, a cyclic 54 π-electron system, is diatropic.

Reduction of conjugated hydrocarbons by alkali metals often results in multiply charged anions regardless of the topology of the π-system[1]. Thus, annulenes and conjugated cyclophanes form diatropic or paratropic anions depending on the number of cyclically conjugated π-electrons in the product[1-4]. The linear analogues give anions which lack tropicity but, as in the case of polymers might show a dramatic increase in electron mobility i.e. electric conductivity[5]. By investigation of small model compounds, an upper limit for the doping level of the polymer should be detectable. Furthermore, by a comparison of linear and cyclic model compounds with similar structural elements, reduction experiments may provide information on the onset of tropicity and on the validity of Hückel's rule for macrocyclic π-systems. For this purpose we have considered extended π-systems with phenylene-vinylene repeating units.

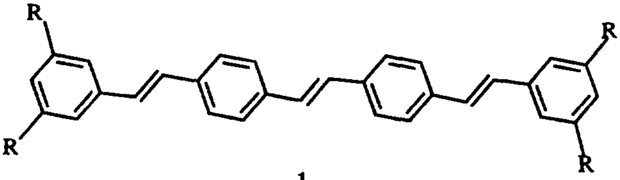
Our previous studies have shown that the bis-styrylstilbene 1 as well as the cyclophanetetraene 2 can be reduced both chemically and electrochemically in four successive electron-transfer steps to yield tetraanions as final products[4,6]. The dianion (tetraanion) of 2 is diatropic (paratropic) since it contains a cyclic 26 π- (28 π-) system. Deviation from planarity or the presence of local benzene rings does not affect the over-all tropicity.

Two molecules with considerably larger π-systems have now been prepared and reduced, *viz.* the tetrastilbenylethylene 3 and the [2_8]paracyclophaneoctaene 4[7]. The compounds can formally be regarded as "dimers" of 1 and 2, respectively.

The 1,1,2,2-tetra(3′,5′-di-tert.-butylstilbenyl)ethylene 3 was synthesized by standard reactions from tetraphenylethylene. Bromination of the parent compound gave tetra-(para-bromophenyl)ethylene. Treatment of this with butyllithium followed by dimethylformamide and then weak acid gave the tetraaldehyde which on reaction with base and four equivalents of the triphenylphosphonium salt from 3,5-di-tert.-butylbenzyl bromide afforded a mixture of 3 with different configurations at the double bonds. Refluxing the product in toluene in the presence of iodine finally gave the all-E-isomer of 3 [yield from aldehyde 55%; m.p. 282-284°C; ^{1}H NMR ($CDCl_3$): δ 1.34 (72H, s), 7.01 (4H, d, J=16.4Hz), 7.07 (8H, d, J=8.2Hz), 7.10 (4H, d, J=16.4Hz), 7.30

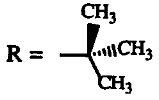
(8H, d, *J*=8.2Hz), 7.33 (8+4H, s)].

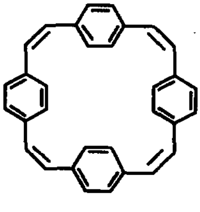
A low yield of the macrocycle 4 [m.p. 295°C (decomp.); M$^+$ 816(100%); ^{1}H NMR see Table 1] was obtained on reaction of Z-stilbene-4,4′-dialdehyde with the phosphonium salt from either the E- or Z-isomer of 4,4′-bis-(bromomethyl)stilbene with base in DMF at -40°C. On formation of the ylid the Z-isomer rapidly rearranges to the E-isomer. Since the bisphosphonium salt from the Z-isomer is more soluble than the E-isomer and the reaction has to be run at the lowest possible temperature to ensure high Z-selectivity in the Wittig reactions it is advantageous to use the Z-isomer. The configuration of the macrocycle 4 follows from its ^{1}H NMR spectrum. By comparison with the spectra of Z,Z,E,Z,Z,E-[2_6]paracyclophanehexaene and [2_8]paracyclophane with six Z-double bonds and two triple bonds instead of the E-double bonds of 4, it is clear that 4 has the assigned configuration[8].



$\xrightarrow{e^-}\ \xrightarrow{e^-}\ 1^{4-}/4Li^+$

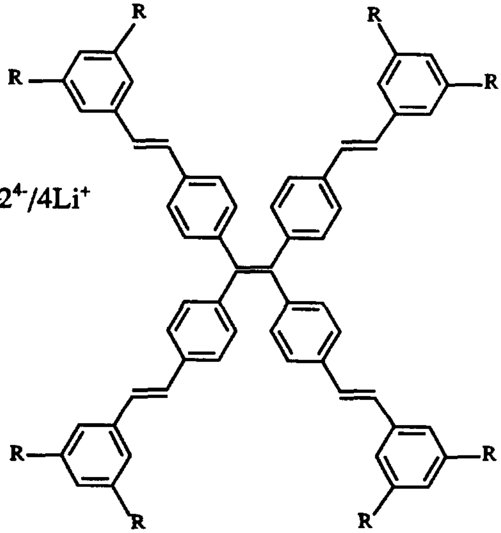
1



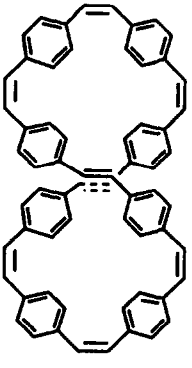


$\xrightarrow{e^-} 2^{2-}/2Li^+ \xrightarrow{e^-} 2^{4-}/4Li^+$

2



3



$\xrightarrow{e^-}$ 4a $\xrightarrow{e^-}$ 4b $\xrightarrow{e^-}$ 4c

4

On treatment with alkali metals in [D_8]-tetrahydrofuran (THF) both 3 and 4 afford deeply coloured diamagnetic anions which can be characterized by their ^1H NMR spectra. The structural assignment is severely inhibited by (i) the low solubility of both neutral and ionic species, (ii) the formation of reduction products with different charges and (iii) the possibility of more than one stereoisomer.

While treatment of 3 with potassium at -78°C produces a dianion, the corresponding reaction with lithium at -20°C results in a species which, based on NMR evidence and quenching experiments, can be identified as the octaanion. The ^1H NMR spectrum of $3^{8-}/8Li^+$ consists of broad resonances for the aromatic (δ_H 4.7-6.5) and olefinic protons (δ_H 2.7-3.3) and two singlets for the tert.-butyl protons (δ_H 1.05, 1.12). These chemical shifts closely correspond to those of the tetraanion salt $1^{4-}/4Li^+$. It is known from $1^{4-}/4Li^+$ that the increasing charge significantly raises the barrier for the rotation about the formal single bonds so that $3^{8-}/8Li^+$ may well exist as several conformational isomers.

Reduction experiments on 4 revealed even more complex processes than observed for 3. Three different species which can be observed by ^1H NMR spectroscopy appear successively on exposure of 4 to lithium. The resulting anions are called 4a, 4b, and 4c, respectively. Anions 4a and 4b can be observed at the same time, and so can 4b and 4c. The final product is 4c which can be detected without 4a or 4b being present in the solution. Quenching of 4c by dimethyl sulphate results in a mixture of methylated species containing two, four, six or eight methyl groups according to their MS. The oxidation of 4c with air indicates that the ring system remains intact upon the electron transfer.

Table1. ^1H NMR data of macrocycle 4 and its lithium salts 4a, 4b and 4c. The chemical shifts δ_H and shift differences $\Delta\delta_H$(in parenthesis) for the adjacent protons on the benzene rings or vinylene bridges are given.

compound	4	4a	4b	4c
	7.28-7.24(0.04)	6.9-4.3(2.6)	-3.5- -4.8(1.3)	7.8-4.1(3.7)
aromatic	7.18	7.2-5.9(1.3)	-5.1- -6.0(0.9)	6.8-4.2(2.6)
protons		6.9-6.1(0.8)	9.4- 8.7 (0.7)	6.6-5.7(0.9)
		5.9-5.8(0.1)	8.6	5.85
olefinic	6.92	5.3-4.8(0.5)	8.6	3.6-3.4(0.2)
protons	6.55-6.53(0.02)	4.2	8.3	4.95
	6.53	?[a]	8.3?[a]	?[a]

[a] assignment uncertain

An analysis of the ^1H NMR spectra of the three different anions 4a-c reveals the presence of eight different types of aromatic protons in each anion. Decoupling experiments show which protons are adjacent (ortho-protons) on the benzene rings. Assuming that the rotation of the benzene rings and the E-vinylene groups is slow on the NMR time scale in the anions, one must conclude that there are only two types of benzene rings in each anion, which also holds for the parent compound. Thus, no configurational change seems to occur on reduction of the Z,Z,Z,E,Z,Z,Z,E-[2_8]paracyclophaneoctaene. The two most striking features of the NMR spectra of 4a-c are (i) the large shift difference for some of the ortho-protons (see Table 1) and (ii) the large ring current effect in 4b. In contrast, there is little or no indication of ring current effects in the spectra of 4a and 4c. The high field signals ($\delta<0$) in spectrum of 4b are due to aromatic protons only. Thus, 4b must exist as a diatropic anion and contain a π-perimeter of 4n+2 electrons. A dianion from 4 has 50 π-electrons cyclically conjugated and a hexaanion has 54 π-electrons. Since 4b seems to be formed from reduction of 4a we prefer the latter possibility and therefore suggest that 4a and 4c are 52- and 56 π-perimeter compounds, respectively.

The large shift difference between certain ortho-protons in 4c and to some extent also 4a (see Table 1) cannot arise from ring current effects of the whole macrocycle, but is caused by the anisotropic ring current in closely located benzene rings. Thus anions 4c and 4a cannot be planar. Inspection of molecular models (CPK) shows the relatively strain free conformation of 4 and its derivatives which resembles the figure eight (D_2-symmetry). In such a conformation the four central benzene rings are close to each other and induce large chemical shifts on protons in the neighboring rings. This effect is largest in 4c and 4a, but is also present in 4b. The importance of overlap between adjacent rings should increase with charge and reduce the flexibility of the anions.

The available spectroscopical data are not sufficient to fully prove the suggestions presented here. The ^{1}H NMR spectrum of 4a has some rather broad peaks indicative of the presence of more than one conformer (with respect to the central E-vinylene groups) rather than rapid electron transfer reactions or the presence of paramagnetic species. As mentioned the spectra of 4a and 4b were observed simultaneously as were the spectra of 4b and 4c. This can be rationalized by assuming different geometries of the anions and thus slow intermolecular electron transfer reactions.

In conclusion, all available data point towards the formation of multiply charged anions from reduction of 4 with alkali metals. The charge of the anions ranges from four to eight. Two atropic non-planar, anionic π-perimeter species with 52 and 56 π-electrons are formed as well as one diatropic, planar, 54 π-perimeter hexaanion. These anions constitute the largest cyclically conjugated π-systems known.

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References and notes

1. K. Müllen, *Chem. Rev.* **84** (1984) 603.
2. K. Müllen, T. Meul, P. Schade, H. Schmickler, E. Vogel, *J. Am. Chem. Soc.* **109** (1987) 4992.
3. a) K. Müllen, H. Unterberg, W. Huber, O. Wennerström, U. Norinder, D. Tanner, B. Thulin *J. Am.Chem. Soc.* **106** (1984) 7514. b) D. Tanner, O. Wennerström, U. Norinder, K. Müllen, R. Trinks, *Tetrahedron* **42** (1986) 4499.
4. W. Huber, K. Müllen, O. Wennerström, *Angew. Chem.* **92** (1980) 636; *Angew. Chem. Int. Ed. Engl.* **19** (1980) 624.
5. a) C. K. Chiang, C. R. Fincher, Y. W. Park, A. J. Heeger, H. Shirakawa, E. J. Lewis, S. C. Gau, A. G. MacDiarmid, *Phys. Rev. Lett.* **39** (1977) 1098. b) R. H. Baughman, J. L. Bredas, R. R. Chance, R. L. Elsenbaumer, L. W. Shacklette, *Chem. Rev.* **82** (1982) 209.
6. a) J. Heinze, J. Mortensen, K. Müllen, R. Schenk. *J. Chem. Soc. Chem. Commun.* **1987.** 701. b) R. Schenk, K. Müllen, *to be published.*
7. According to IUPAC Organic Chemistry Division, provisional Phane nomenclature draft 23. April 1990, cyclophane **4** can be named Z(2,3)Z(5,6)Z(8,9)E(11,12)-Z(14,15)Z(17,18)Z(20,21E(23,24) 1.4.7.10.13.16.19.22(1,4)octabenzocyclotetracosaphaneoctaene.
8. a) U. Norinder, D. Tanner, O. Wennerström, *Tetrahedron Lett.* **1983** 5411. b) O. Wennerström, I. Raston, M. Sundahl, D. Tanner, *Chemica Scripta* **27** (1987) 567.

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