and William C. Fultz for the X-ray structure determinations, to Frederic Davidson for analysis of the NMR spectra of **18** and **19**, and to Dr. D. A. Dixon for the PRDDO calculations. We thank Edward R. Holler, Jr., and Carlos Vazquez for their expert technical assistance.

Supplementary Material Available: Crystal structure analysis and tables of atomic coordinates, bond distances and bond angles, thermal parameters, and structure amplitudes for compounds **12b**, **17**, **26**, and **27** (25 pages). Ordering information is given on any current masthead page.

Dianions and Dications Derived from Bridged [4*n* + 2]Annulenes. Paratropism as a Function of Ring Size, Conformation, and Configuration

Klaus Müllen,* Thomas Meul, Peter Schade, Hans Schmickler, and Emanuel Vogel

Contribution from the Department of Organic Chemistry, University of Mainz, D-6500 Mainz, FRG, and the Department of Organic Chemistry, University of Köln, D-5000 Köln, FRG.

Received January 23, 1987

Abstract: Reduction and oxidation of bridged annulenes afford dianion and dication salts which are characterized by spectroscopic and chemical means. A broad series of title compounds is included in order to systematically vary the size, conformation, and configuration of the perimeters. These structural features markedly affect the observed paratropism of the $(4n)\pi$-ions, which is discussed in terms of the HOMO/LUMO gap and the degree of π-bond fixation. Paratropic annulene ions thus appear as most sensitive probes of bond theory. Information on the π-charge distribution in the dianions and dications comes from ^{13}C NMR studies and quenching experiments, the latter leading to useful synthetic applications.

1. Introduction

The bridging of annulenes[1-8] causes a perturbation of the π-bonding and gives rise to deviations from the expected properties of an ideal D_{nh} perimeter. For the purpose of chemical and spectroscopic considerations the inductive, hyperconjugative, and homoconjugative effects of the bridging must be worked out separately.[9-20] On the other hand, the introduction of saturated bridging groups offers the advantage that the π-perimeters are fixed within a particular ring configuration and ring conformation[21] and that one can construct homologous series of increasing ring size. These structural features allow one to assess electronic effects in a clear-cut way.

Knowledge of the frontier orbitals of a π-system is essential for an understanding of the prevailing bonding situation.[22] The creation of new frontier orbitals in annulenes upon going to the corresponding radical anions and radical cations has therefore proven a useful technique.[23,24] The spin density distribution which is inferred from ESR hyperfine coupling constants sensitively reflects the electronic effects of the bridging groups and the deviation of the perimeter from planarity.[18]

Further reduction (oxidation) toward the corresponding dianions (dications), although raising serious experimental difficulties, constitutes another promising approach:[25] (i) the creation of diamagnetic species brings into play NMR spectroscopy, which has proven the most significant method in the annulene field[26-28] (this is because the fundamental alternative of π-bond delocalization vs. π-bond localization[29-34] can be described via a number

---

(1) Boekelheide, V. In *Topics in Nonbenzenoid Aromatic Chemistry*; Nozoe, T., Ed.; Hirokawa: Tokyo, 1973. Boekelheide, V. *Pure Appl. Chem.* **1975**, *44*, 751.

(2) Vogel, E. *Spec. Publ. Chem. Soc.* **1967**, *21*, 113. Vogel, E. *Pure Appl. Chem.* **1971**, *28*, 355.

(3) Vogel, E. *Isr. J. Chem.* **1980**, *20*, 215.

(4) Gilchrist, T. L.; Tuddenham, D.; MaCague, R.; Moddy, C. J.; Rees, C. W. *J. Chem. Soc., Chem. Commun.* **1981**, 657.

(5) Lidert, Z.; Rees, C. W. *J. Chem. Soc., Chem. Commun.* **1982**, 499.

(6) Huber, W.; Lex, J.; Meul, T.; Müllen, K. *Angew. Chem.* **1981**, *93*, 401; *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 391.

(7) Huber, W.; Irmen, W.; Lex, J.; Müllen, K. *Tetrahedron Lett.* **1982**, 3889.

(8) Hafner, K.; Stowasser, B.; Krimmer, H.-P.; Fischer, S.; Böhm, M. C.; Lindner, H. J. *Angew. Chem.* **1986**, *98*, 646; *Angew. Chem., Int. Ed. Engl.* **1986**, *25*.

(9) Dewey, H. J.; Deger, H.; Frölich, W.; Dick, B.; Klingensmith, K. A.; Hohlneicher, G.; Vogel, E.; Michl, J. *J. Am. Chem. Soc.* **1980**, *102*, 6412.

(10) Blattmann, H.-R.; Boekelheide, V.; Heilbronner, E.; Weber, J.-P. *Helv. Chim. Acta* **1967**, *50*, 68. Blattmann, H.-R.; Heilbronner, E.; Wagnière, G. *J. Am. Chem. Soc.* **1968**, *90*, 4786.

(11) Kolc, J.; Michl, J.; Vogel, E. *J. Am. Chem. Soc.* **1976**, *98*, 3935. Michl, J. *J. Am. Chem. Soc.* **1978**, *100*, 6801.

(12) Spanget-Larsen, J.; Gleiter, R. *Helv. Chim. Acta* **1978**, *61*, 2999.

(13) Tanaka, J.; Tanaka, M.; Morita, M.; Nakagawa, M.; Iyoda, M. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 3458.

(14) Boschi, R.; Schmidt, W.; Gfeller, J.-C. *Tetrahedron Lett.* **1972**, 4107.

(15) Batich, C.; Heilbronner, E.; Vogel, E. *Helv. Chim. Acta* **1974**, *57*, 2288.

(16) Blattmann, H.-R.; Böll, W. A.; Heilbronner, E.; Hohlneicher, G.; Vogel, E.; Weber, J.-P. *Helv. Chim. Acta* **1966**, *49*, 2017.

(17) Paquette, L. A. *Angew. Chem.* **1978**, *90*, 114; *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 106.

(18) Gerson, F.; Müllen, K.; Vogel, E. *J. Am. Chem. Soc.* **1972**, *94*, 2924.

(19) Gerson, F.; Heilbronner, E.; Boekelheide, V. *Helv. Chim. Acta* **1964**, *47*, 1123. Mitchell, R. H.; Calder, I.; Huisman, H.; Boekelheide, V. *Tetrahedron* **1975**, *31*, 1109.

(20) Huber, W. *Helv. Chim. Acta* **1984**, *67*, 1368.

(21) Oth, J. F. M. *Pure Appl. Chem.* **1971**, *25*, 573.

(22) Garratt, P. In *Comprehensive Organic Chemistry*; Barton, D., Ollis, W. D., Eds.; Vol. 1, p 361.

(23) Gerson, F. *High Resolution ESR Spectroscopy*; Verlag Chemie: Weinheim, Federal Republic of Germany, 1970. Gerson, F.; Hammons, J. H. In *Nonbenzenoid Aromatics*; Synder, J. P., Ed.; Academic: New York, 1971; Vol. 2.

(24) Gerson, F.; Jachimowicz, J.; Nakagawa, M.; Iyoda, M. *Helv. Chim. Acta* **1974**, *57*, 2141.

(25) Müllen, K. *Chem. Rev.* **1984**, *84*, 603.

(26) Günter, H. *NMR Spektroskopie*; George Thieme: Stuttgart, West Germany, 1973.

(27) Haddon, R. C.; Haddon, V. R.; Jackman, L. M. *Fortschr. Chem. Forsch.* **1970**, *16*, 103.

(28) Jackman, L. M.; Sondheimer, F.; Amiel, Y.; Ben Efraim, D. A.; Gaoni, Y.; Wolovsky, R.; Bothner-By, A. A. *J. Am. Chem. Soc.* **1962**, *84*, 4307.

(29) Binsch, G.; Tamir, I.; Hill, R. D. *J. Am. Chem. Soc.* **1969**, *91*, 2446. Binsch, G.; Tamir, I. *J. Am. Chem. Soc.* **1969**, *91*, 2450.

(30) Nakajima, T. *Pure Appl. Chem.* **1971**, *28*, 219. Nakajima, T.; Toyota, A.; Fujii, S. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 1022.

(31) Longuet-Higgins, H. C.; Salem, L. *Proc. R. Soc. London, Ser. A* **1959**, *251*, 172; **1960**, *257*, 445.

(32) Coulson, C. A.; Dixon, W. T. *Tetrahedron* **1962**, *17*, 215.

of different experimental criteria);[26,27] (ii) dianion (dication) formation interconverts monocyclic $(4n + 2)\pi$- and $(4n)\pi$-systems and thus constitutes a simple test of Hückel's rule.[25,35]

Having succeeded in preparing dianions and dications of various bridged annulenes with acene perimeter, we can systematically evaluate (i) the influence of different electronic configurations within one and the same rigid framework or within varying ring sizes of identical molecular architecture and (ii) the influence of different ring conformations and ring configurations within isoelectronic $(4n)\pi$-systems.

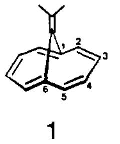
The dianions and dications of the title $[4n + 2]$annulenes are shown to possess a pronounced paratropic[36-39] character. More importantly, the NMR spectroscopic properties of the ionic $(4n)\pi$-systems turn out to reflect the above mentioned electronic and geometric effects in a much more sensitive way than do those of the corresponding neutral compounds. This sensitivity can be ascribed to the crucial importance of the HOMO/LUMO gap and of the degree of π-bond fixation for the paratropism of the ions.

Dianions and dications are expected to readily react with electrophiles or nucleophiles, respectively, whereby the point of the kinetically controlled attack should depend on the π-charge distribution in the ionic substrate.[40,41] The quenching process may lead to chemical reactions not feasible in the neutral compound. A related aspect is well documented for reductive alkylations of acenes.[42-47] Knowledge of the ground-state properties of annulene dianions thus turns out to be significant not only for bonding considerations but also for the design of useful chemical transformations.

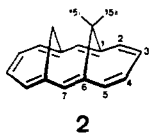
2. Results

The bridged annulenes **1**–**9** were prepared according to procedures published by us earlier.[48-56] All compounds were purified by repeated recrystallization prior to use.

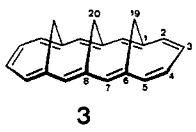
The reduction of the annulenes **1**–**9** was performed with lithium in THF-d_8 at −78 °C. Compound **8** was also reduced with potassium. The reaction times were quite different: while dianion formation was complete within a few hours for $\mathbf{7}^{2-}$ and $\mathbf{8}^{2-}$ and within 1 day for $\mathbf{1}^{2-}$, $\mathbf{3}^{2-}$, and $\mathbf{4}^{2-}$, it took about 2 weeks for $\mathbf{2}^{2-}$ and $\mathbf{5}^{2-}$ (lithium salts). This must be ascribed to the low solubility of the intermediate radical anions $\mathbf{2}^{\bullet-}$ and $\mathbf{5}^{\bullet-}$, whose reduction to the dianions is thus slow. While solutions of $\mathbf{1}^{2-}$ and $\mathbf{2}^{2-}$ as well as of $\mathbf{4}^{2-}$–$\mathbf{9}^{2-}$ could be kept in metal contact without a change of the NMR spectra, the NMR signals of $\mathbf{3}^{2-}$ broadened upon further reduction. ESR measurements demonstrated that $\mathbf{3}^{2-}$ underwent further reduction to a radical trianion $\mathbf{3}^{3\bullet-}$. The dianion $\mathbf{3}^{2-}$ could therefore only be detected by its NMR spectra if the progress of the reduction was carefully monitored. Even very long contact times did not give the tetraanion. The [18]annulene **3** thus differs from the didehydro[18]annulene **13** where we could obtain the complex redox sequence ranging from the radical monoanion up to a diamagnetic tetraanion.[57]



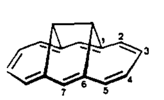
1



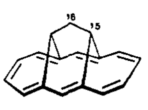
2



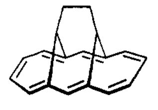
3



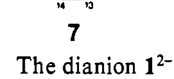
4



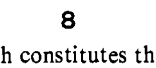
5



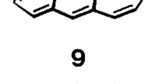
6



7



8



9

The dianion $\mathbf{1}^{2-}$, which constitutes the first example of a monocyclic 12π-dianion, exhibited an astonishing thermal stability; its THF solution could be warmed to +60 °C without a change of its ^{1}H NMR spectrum. The reduction of other bridged [10]annulenes was shown to be accompanied by various side reactions such as valence isomerizations[58] or cleavage of the bridging group to yield the naphthalene radical anion.[59] When solutions of **5** were placed in metal contact at 0 °C for several weeks the dianion spectra, finally obtained, failed to indicate any decomposition. The dications $\mathbf{2}^{2+}$, $\mathbf{3}^{2+}$, and $\mathbf{5}^{2+}$ were prepared by oxidation of the neutral annulenes with antimony pentafluoride in fluorosulfuryl chloride (1:2) at −25 °C.[60,61]

The structure proof of the novel dianions and dications rests upon NMR spectroscopic and chemical evidence. The symmetry

---

(33) Dewar, M. J. S.; Gleicher, G. J. *J. Am. Chem. Soc.* **1965**, *87*, 685.

(34) Dewar, M. J. S.; Haddon, R. C.; Student, P. J. *J. Chem. Soc., Chem. Commun.* **1974**, 569.

(35) Hückel, E. Z. *Physik* **1931**, *70*, 204; **1931**, *72*, 310; **1932**, *76*, 628; **1933**, *83*, 632. Hückel, E. *Grundzüge der Theorie ungesättigter und aromatischer Verbindungen*; Verlag Chemie: Berlin, 1938.

(36) McQuilkin, R. M.; Garratt, P. J.; Sondheimer, F. *J. Am. Chem. Soc.* **1970**, *92*, 6682.

(37) Garratt, P. J.; Rowland, N. E.; Sondheimer, F. *Tetrahedron* **1971**, *27*, 3157.

(38) Paquette, L. A.; Hansen, J. F.; Kakihana, T. *J. Am. Chem. Soc.* **1971**, *93*, 168. Paquette, L. A.; Ley, S. V.; Meisinger, R. H.; Russell, R. K.; Oku, M. *Ibid.* **1974**, *96*, 5806.

(39) Huber, W.; Müllen, K.; Wennerström, O. *Angew. Chem.* **1980**, *92*, 636; *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 624.

(40) Müllen, K. *Angew. Chem.* **1987**, *99*, *192*; *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 204.

(41) Müllen, K. *Pure Appl. Chem.* **1986**, *58*, 177.

(42) Birch, A. J.; Subba Rao, G. In *Advances in Organic Chemistry, Methods and Results*; Taylor, E. C., Ed.; Wiley-Interscience: New York, 1972.

(43) Harvey, R. G. *Synthesis* **1970**, 161.

(44) Smith, H. *Organic Reactions in Liquid Ammonia, Chemistry in Non-aqueous Ionizing Solvents*; Wiley: New York, 1963.

(45) Rabideau, P. W.; Wetzel, D. M.; Husted, C. A.; Lawrence, J. R. *Tetrahedron Lett.* **1984**, *25*, 31.

(46) Lindow, D. F.; Cortez, C. N.; Harvey, R. G. *J. Am. Chem. Soc.* **1972**, *94*, 5406. Harvey, R. G.; Arzadon, L. *Tetrahedron* **1969**, *25*, 4887. Harvey, R. G.; Davis, C. C. *J. Org. Chem.* **1969**, *34*, 3607.

(47) Rabideau, P. W.; Burkholder, E. G. *J. Org. Chem.* **1978**, *43*, 4283. Rabideau, P. W.; Burkholder, E. G. *J. Org. Chem.* **1979**, *44*, 2354.

(48) Lindner, W. Ph.D. Thesis, University of Cologne, Federal Republic of Germany, 1984.

(49) Vogel, E.; Sombroek, J.; Wagemann, W. *Angew. Chem.* **1975**, *87*, 591; *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 564.

(50) Wagemann, W.% Iuoda, M.; Deger, H. M.; Sombroek, J.; Vogel, E. *Angew. Chem.* **1978**, *90*, 988; *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 956.

(51) Vogel, E.; Deger, H. M.; Hebel, P.; Lex, J. *Angew. Chem.* **1980**, *92*, 943; *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 913. Günther, H.; von Puttkamer, H.; Deger, H. M.; Hebel, P.; Vogel, E. *Ibid.* **1980**, *92*, 944 bzw; **1980**, *19*, 921.

(52) Vogel, E.; Vogel, A.; Kübbeler, H.-K.; Sturm, W. *Angew.* Chem. **1970**, *82*, 512; *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 514.

(53) Vogel, E.; Sturm, W.; Cremer, H.-D. *Angew. Chem.* **1970**, *82*, 513; *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 516.

(54) Vogel, E.; Püttmann, W.; Duchatsch, W.; Schieb, T.; Schmickler, H.; Lex, J. *Angew. Chem.* **1986**, *98*, 727.

(55) Vogel, E.; Schieb, T.; Schulz, W. H.; Schmidt, K.; Schmickler, H.; Lex, J. *Angew. Chem.* **1986**, *98*, 729.

(56) Vogel, E.; Reel, H. *J. Am. Chem. Soc.* **1972**, *94*, 4388.

(57) Müllen, K.; Huber, W.; Meul, T.; Nakagawa, M.; Iyoda, M. *J. Am. Chem. Soc.* **1982**, *104*, 5403.

(58) Gerson, F.; Huber, W.; Müllen, K. *Angew. Chem.* **1978**, *90*, 216; *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 208.

(59) Gerson, F.; Heilbronner, E.; Böll, W. A.; Vogel, E. *Helv. Chim. Acta* **1965**, *48*, 1494. Gerson, F.; Heinzer, J.; Vogel, E. *Helv. Chim. Acta* **1970**, *53*, 95.

(60) Brouwer, D. M.; Van Doorn, J. A. *Recl. Trav. Chim. Pays-Bas* **1972**, *91*, 1110.

(61) Olah, G. A.; Olah, J. A. In *Carbonium Ions*; Olah, G. A., Schleyer, P. v. R., Eds.; Wiley-Interscience: New York, 1970; Vol. 2. Olah, G. A.; Clifford, P. R.; Halpern, Y.; Johanson, R. G. *J. Am. Chem. Soc.* **1971**, *93*, 4219. Olah, G. A.; Halpern, Y.; Shen, J.; Mo, Y. K. *J. Am. Chem. Soc.* **1973**, *95*, 4960.

Table I. ^{1}H NMR Chemical Shifts of Neutral, Dianionic, and Dicationic Annulenes[a]

	color	H-2	H-3	H-7	H-bridge		
δ_H (**1**)	colorless	7.45	7.05		0.96 (H-12a)		
δ_H (**1**$^{2-}$/2Li$^+$)	violet	4.43[b]	4.66[b]		1.55		
δ_H (**2**)	orange	7.72	7.28	7.89	0.95 (H-15i)	−1.13 (H-15a)	
δ_H (**2**$^{2-}$/2Li$^+$)	black	2.83	3.56	2.70	11.95	8.50	
δ_H (**2**$^{2+}$/2SbF$_6^-$)	violet	7.72	7.15	6.13	9.27	6.83	
δ_H (**3**)	brown	7.55	6.95	7.62	1.32 (H-19i)	−0.45 (H-19a)	0.53 (H-20)
δ_H (**3**$^{2-}$/2Li$^+$)	brown	2.80	2.70[b]	2.81	12.99	8.38	14.21
δ_H (**3**$^{2+}$/2SbF$_6^-$)	green	7.07	7.27	6.07	7.58	4.35	8.25
δ_H (**4**)	red	8.17	7.82	8.00	−1.82 (H-15)		
δ_H (**4**$^{2-}$/2Li$^+$)	red-green	2.94[b]	1.72[b]	2.08	13.01		
δ_H (**5**)	orange	7.74	7.55	7.88	−1.16 (H-15)	−0.61 (H-16)	
δ_H (**5**$^{2-}$/2Li$^+$)	red-brown	2.19	3.20	2.72	10.37	7.11	
δ_H (**6**)	yellow	7.57	7.12	7.86	−0.96 (H-15)	0.52 (H-16)	
δ_H (**6**$^{2-}$/2Li$^+$)	brown-green	3.26[b]	2.47[b]	2.60	9.89	5.54	

	color	H-2	H-3	H-4	H-5	H-7	H-bridge	
δ_H (**7**)	yellow	7.52	7.28	7.06	6.92	7.19	2.36 (H-15i)	−0.36 (H-15a)
δ_H (**7**$^{2-}$/2Li$^+$)	violet	4.16[b]	5.27[b]	3.68[b]	5.28[b]	5.30	5.23	2.92
δ_H (**8**)	yellow	6.68	6.68	6.24	6.24	6.43	2.59	1.68
δ_H (**8**$^{2-}$/2Li$^+$)	violet-brown	4.70[b]	5.58[b]	3.95[b]	5.46[b]	4.75	2.32	1.28
δ_H (**8**$^{2-}$/2K$^+$)	violet-red	4.78[b]	5.65[b]	4.22[b]	5.50[b]	4.89	2.31	1.96

[a] δ_H values of dianions were measured with respect to the solvent signals (THF-d_8) and then referred to Me$_4$Si. δ_H values of dications (SO$_2$ClF) were measured with respect to acetone-d_6 as external standard and then referred to Me$_4$Si. Neutral compounds were measured at +25 °C, ions at −25 °C. [b] Assignments uncertain.

Table II. ^{13}C NMR Chemical Shifts of Neutral, Dianionic, and Dicationic Annulenes as well as of Ions Derived from Anthracene and Phenanthrene[a]

	C-1	C-2	C-3	C-7	C-8	C-bridge	
δ_c (**2**)	104.7	136.8	126.	133.3		25.2 (C-15)	
δ_c (**2**$^{2+}$/2SbF$_6^-$)	139.9	167.9	147.3	161.2		33.0	
δ_c (**2**$^{2-}$/2Li$^+$)	136.5	97.2	118.3	81.7		49.3	
δ_c (**3**)	107.0	138.4	126.5	137.0	96.6	26.7 (C-19)	14.1 (C-20)
δ_c (**3**$^{2+}$/2SbF$_6^-$)	133.9	151.6	144.6	164.8	127.4	32.8	24.7
δ_c (**3**$^{2-}$/2Li$^+$)	148.4	100.9	108.8	99.9	130.0	48.4	47.2
δ_c (**5**)	111.9	127.7	130.0	127.0		28.8 (C-15)	18.7 (C-16)
δ_c (**5**$^{2+}$/2SbF$_6^-$)	139.5	170.1	150.2	153.0		40.1	30.4
δ_c (**9**)	133.1	123.4	125.8	131.4		48.6 (C-15)	12.5 (C-17)
δ_c (**9**$^{2-}$/2Li$^+$)	173.4	91.7	123.3	96.4		14.4	30.8
δ_c (**18**$^{2-}$/2Li$^+$)	150.0	101.1	114.2	75.1			
δ_c (**18**$^{2+}$/2SbF$_6^-$)	139.4	165.1	153.5	187.1			
δ_c (**19**$^{2-}$/2Li$^+$)	139.7	118.2	104.8[f]				
$\Delta q_\pi'$ (**2**$^{2-}$–**2**)[c]	−0.013	−0.242	−0.114	−0.259			
$\Delta q_\pi''$ (**2**$^{2-}$–**2**)[d]	0.37	−0.47	−0.10	−0.61			
$\Delta q_\pi'''$ (**2**$^{2-}$–**2**)[e]	0.21	−0.32	−0.08	−0.41			

	C-1	C-bridge
δ_c (**8**)	135.1 (132.2, 131.8, 130.0, 129.4, 122.9, 117.7)[b]	43.3 (C-15)
δ_c (**8**$^{2-}$/2K$^+$)	142.6 (97.1, 130.1, 89.3, 121.1, 120.0, 100.5)[b]	42.8 (C-15)

[a] δ_c values of dianions were taken with respect to the solvent signals (THF-d_8) and then referred to Me$_4$Si. δ_c values of dications (SO$_2$ClF) were measured with respect to acetone-d_6 as external standard and then referred to Me$_4$Si. Neutral compounds were measured at +25 °C, ions at −25 °C. [b] Assignments uncertain. [c] Changes of local π-charge densities that result from ion formation; HMO model. [d] Changes of local π-charge densities that result from ion formation, values have been calculated from the ratio $\Delta\delta_c/K_c$, whereby $\Delta\delta_c$ is the experimental signal shift and K_c is the compound-specific proportionality constant. [e] Changes of local π-charge densities that result from ion formation, values have been calculated from the experimental signal shifts $\Delta\delta_c$ according to ref 82. [f] C-4, 137.6; C-5, 110.7; C-6, 163.6; C-7, 70.7.

Table III. Ring-Current-Induced Shielding Effects ($\Delta\delta_H^{RC}$) for Perimeter and Bridge Protons

	ring		bridge		
	$\Delta\delta_H^{RC}$[a]	$\Delta\delta_H^{RC}/S$[b]	$\Delta\delta_H^{exp}$[c]	$\Delta\delta_H$[d]	$\Delta\delta_H^{RC}$[e]
1^{2-}	−0.05	−0.03			
2^{2+}	−1.17	−0.57	7.96 (H-15a)	2.18	5.78
2^{2-}	−2.39	−0.80	9.63 (H-15a)	−0.58	10.21
3^{2+}	−3.06	−0.77	4.80 (H-19a)	+1.61	3.19
3^{2-}	−2.83	−0.71	8.83 (H-19a)	−0.64	9.47

[a] Charge-correction has been made according to method A assuming a uniform charge distribution; see text. [b] S is the relative ring area; see ref 57. [c] Signal shifts observed upon ion formation. [d] Charge correction has been made by calculating the electric field effect of the charged ring carbons upon the bridge protons (assuming a uniform charge distribution). This effect does not differ significantly when accepting a uniform or nonuniform (according to $\Delta q_\pi''$) charge distribution. [e] Ring-current-induced signal shift after correcting for the charge effect.

inherent in the ^{1}H and ^{13}C NMR spectra indicated the intact molecular framework of the ions and the existence of a cyclic π-conjugation. Reoxidation of the dianion salts with dry oxygen always yielded the starting materials as only identifiable products (together with varying amounts of polymer). For the representative example of **5**$^{2-}$/2Li$^+$ we performed extensive quenching experiments. The crucial outcome is the incorporation of two electrophiles upon protonation, alkylation, and acylation. The regioselectivity of the quenching process will be discussed in section 3.5.

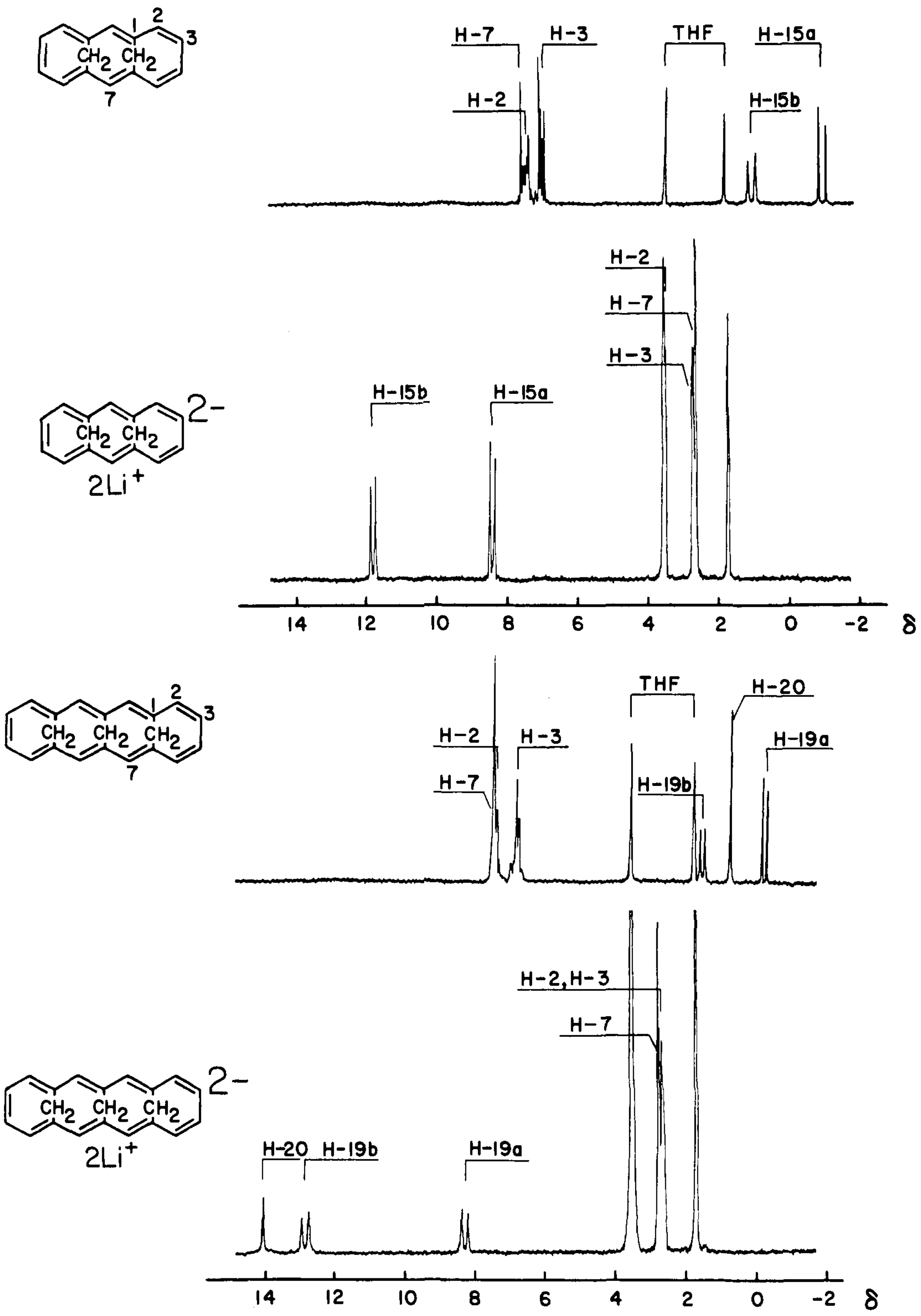


Figure 1. ^1H NMR spectra of **2** and $2^{2-}/2Li^+$ as well as **3** and $3^{2-}/2Li^+$ (60 MHz, THF-d_8).

The ^1H and ^{13}C NMR resonances of the title ions are given in Tables I–IV. Typical spectra are shown in Figures 1, 2, and 4. The assignments of the ^1H NMR resonances of the ionic species were achieved from the splitting patterns and the relative signal intensities. In the complete annulene series the protons H-2 through H-5 constitute an AA′BB′ spin system which could be identified by its typical absorptions. For 2^{2-} and 3^{2-} a differentiation between H-2 (H-5) and H-3 (H-4) was possible because of the line broadening of the signal of H-2 and H-5, which is due to a long-range coupling with the bridge protons H-15i or H-19i, respectively.[51] For the example of **2**, signal assignments were supported by the inclusion of a 2,5-dideuterio derivative. If no long-range coupling was detectable, the assignment of H-2 (H-5) and H-3 (H-4) was made by analogy with the ions of **2** and **3**.

Table IV. Centers of Gravity ($\langle\delta\rangle$) of Ring and Bridge Proton Signals in Neutral and Dianionic [14]Annulenes

	$\langle\delta_{\text{ring}}\rangle$	$\langle\delta_{\text{bridge}}\rangle$
9	7.99	-1.85
$\mathbf{9}^{2-}/2Li^+$	1.48	7.70
10	8.61	-4.53
$\mathbf{10}^{2-}/2K^+$	-0.14	11.96
11	8.54	-4.25
$\mathbf{11}^{2-}/2K^+$	-3.60	21.00

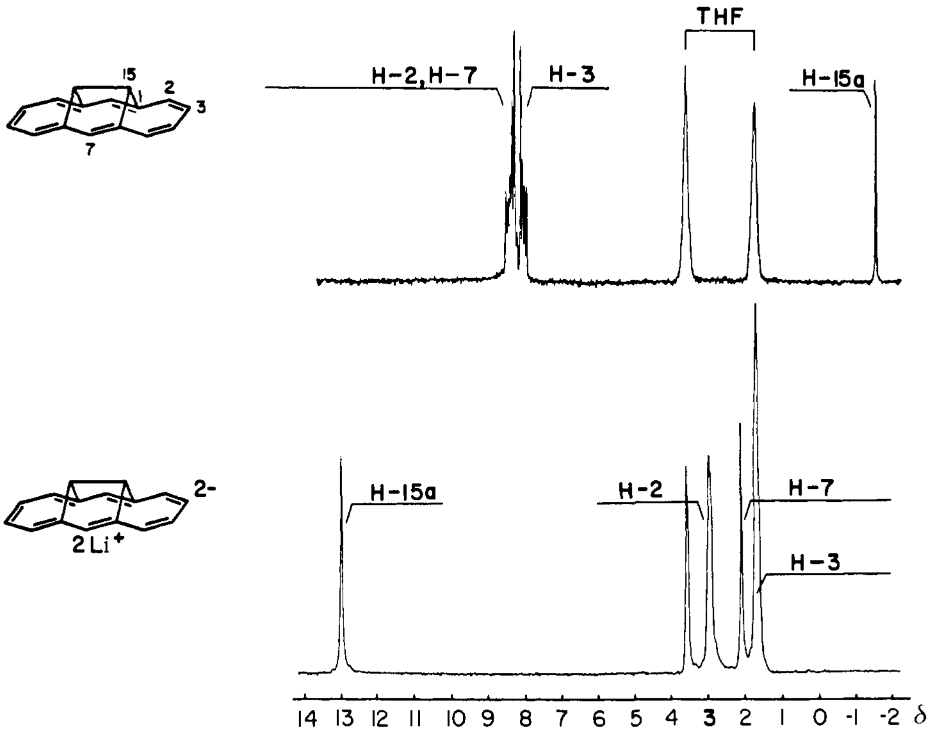


Figure 2. ^{1}H NMR spectra of **4** and $4^{2-}/2Li^+$ (60 MHz, THF-d_8).

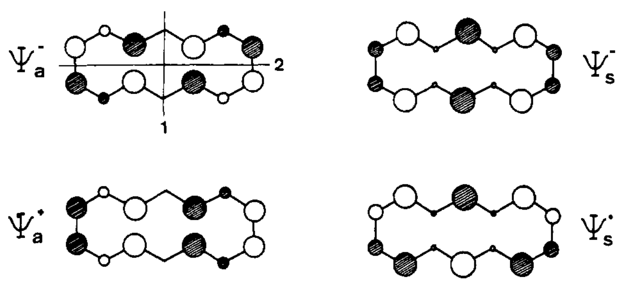


Figure 3. Schematic representation of the two highest occupied MOs and the two lowest unoccupied MOs of a [14]annulene. The perimeter is distorted to an acene configuration.

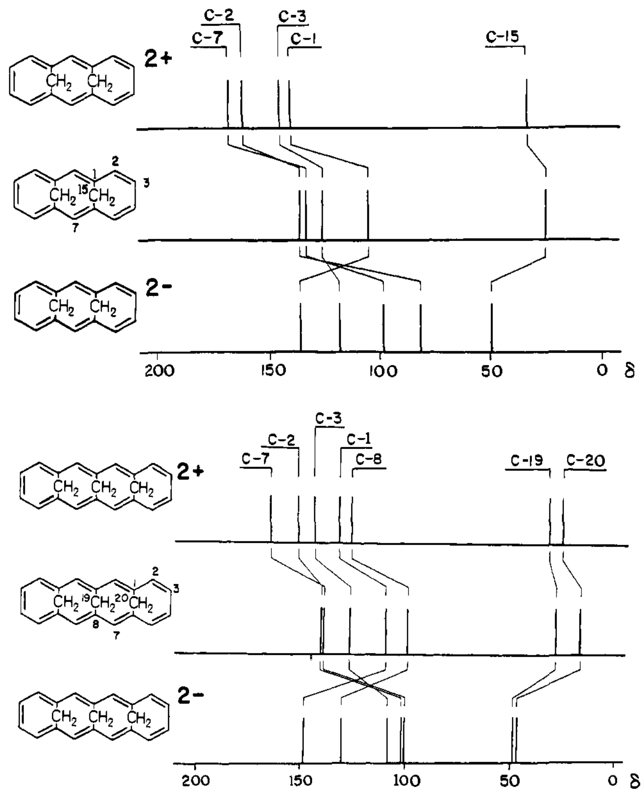


Figure 4. ^{13}C NMR spectra (22 MHz, schematic representation) of **2** (THF-d_8), $2^{2-}/2Li^+$ (THF-d_8), and $2^{2+}/2SbF_6^-$ (SO_2ClF) as well as of **3** (THF-d_8), $3^{2-}/2Li^+$ (THF-d_8), and $3^{2+}/2SbF_6^-$ (SO_2ClF).

The hydrogens H-7 and H-14 (H-7, H-9, H-16, and H-18 for the perimeter of **3**) could be identified by their singlet absorption. The bridge protons H-15i/H-15a of 2^{2-}, 2^{2+}, 7^{2-} and 8^{2-} as well as H-19i/H-19a of 3^{2-} and 3^{2+} gave rise to absorptions of AB systems. Their assignments were based on the assumption that the protons H-15i or H-19i which are closer to the center of the ring suffer from stronger ring current effects.[51,62] Support for this assumption comes from the relative chemical shifts of H-19 and H-20 in 3^{2-}. The assignments of the ^{13}C NMR resonances given in Table II came from the following pieces of evidence: (i) proton-bearing and quaternary (bridgehead) ring centers were distinguished via the off-resonance ^{1}H-decoupled spectra, (ii) C-2, C-3, and C-7 were differentiated via selective ^{1}H-decoupling experiments, and (iii) resonances of the bridges in the aliphatic domain were identified from relative intensities and the multiplicity observed in off-resonance decoupled ^{13}C NMR spectra.

Reductive methylation of **5** (liquid ammonia, lithium, methyl bromide) afforded a 3:1 mixture of the dimethyl derivatives **22b** and **23b** in a nearly quantitative yield. The reaction temperature (−78, −33 °C) and the mode of quenching (normal/inverse) were varied in order to detect an eventual protonation of the dianion $5^{2-}/2Li^+$. Monomethyl dihydro derivatives were only formed when dimethyl sulfate was applied as alkylating material. Compounds **22b** and **23b** could be separated by column chromatography (silica gel/hexane) and repeated recrystallizations from methanol. Their structural assignment will be discussed in section 3.5.

Compound **22b** could be dehydrogenated to the dimethyl annulene **24b** with dichlorodicyanobenzoquinone at room temperature. Attempted hydroxymethylation of 5^{2-} via quenching with formaldehyde only gave the neutral annulene **5**. Reaction of $5^{2-}/2Li^+$ (THF) with methyl chloroformate afforded a complex mixture of mono- and diadducts (different regioisomers) from which the diester **22c** could be isolated via crystallization. Upon aqueous workup under weakly basic conditions one obtained the isomeric dihydro adduct **26c**. Dehydrogenation of the crude reaction mixture and column chromatography provided the pure annulenes **24c**, **25c**, and **27c**. The diols **24d** and **25d** as well as the corresponding dibromides **24e** and **25e** could be prepared from the corresponding diesters via standard procedures. Generation of the dianion $\mathbf{5}^{2-}$ in liquid ammonia and reaction with methyl chloroformate provided a nearly quantitative yield of the dihydro derivative **22a**.

When the dianion salt $\mathbf{12}^{2-}/2Li^+$ was prepared in THF and quenched with dimethyl sulfate or methyl chloroformate one obtained the dihydroannulene systems **30b** and **30c**. Application of the bifunctional electrophile 1,3-dibromopropane did not allow the incorporation of a propylene bridge at C-4 and C-11 but gave the diadduct **30d**.

3. Discussion

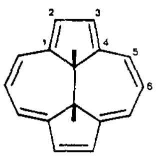
In the neutral [4*n* + 2]annulenes **1–3** the deshielding of the ring protons (outside the ring) and the shielding of the bridge protons (inside the ring) indicate a pronounced diatropism.[51,62,63] The situation is totally reversed, however, in the corresponding $(4n)\pi$-dianions and dications (see Tables I, III, and IV as well as Figures 1 and 2): there is no doubt from the extreme shielding effects, in particular from the lowfield resonances of the aliphatic bridge protons, that the ions exist as paratropic species. If not mentioned otherwise, dianions exist as Li^+ and dications as SbF_6^- salts.

3.1. π-Charge Distribution. In the present section we shall determine local π-charge densities "theoretically" via a simple MO model and "experimentally" via the ^{13}C NMR spectra.

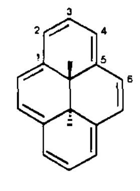
An ideal [14]annulene possesses two pairs of degenerate HOMOs and LUMOs. These are schematically depicted in Figure 3. The perimeter has been deformed from D_{14h} to D_{2h} (acene) symmetry. Restricting ourselves to the HMO model, this process does not affect the orbital energies. When attempting to simulate the electronic effects of the bridging one encounters a superposition of inductive, homoconjugative, and hyperconjugative phenomena. These effects remove the degeneracy within the HOMO and LUMO pair and control the energetic sequence of the annulene orbitals. From the latter it can be inferred which of the LUMOs accepts the additional charge upon formation of a radical anion or dianion. As a consequence, one obtains information regarding the distribution of the π-charge. The ESR hyperfine coupling constants of the radical anions $\mathbf{4}^{\bullet-}$–$\mathbf{6}^{\bullet-}$ indicate that the unpaired electron occupies the molecular orbital Ψ_s^-. This finding can be rationalized by simply accounting for the inductive effect of the saturated bridging group. The latter perturbation destabilizes Ψ_a^- to a larger extent than Ψ_s^-. The assumption of a homoconjugative interaction between the bridgehead positions would lead to the same level ordering.

A discussion of the corresponding radical cations is more complicated since an inductive effect tends to destabilize and a homoconjugative effect (depending on the degree of planarity) tends to stabilize Ψ_a^+ with respect to Ψ_s^+.[64] Furthermore, a hyperconjugative effect is operative. As a consequence of this interplay, the energetic sequence of Ψ_s^+ and Ψ_a^+ may vary depending on the particular annulene.

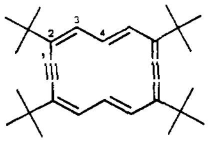
When one applies similar arguments to compound **10** and its radical anion, one would predict Ψ_a^- to be of lower energy than Ψ_s^-, yet, the spin density in $\mathbf{10}^{\bullet-}$[65] appears to be distributed according to Ψ_s^-; this finding also holds for $\mathbf{11}^{\bullet-}$. Clearly, a hyperconjugative interaction between the bridge and the perimeter orbitals of $\mathbf{10}^{\bullet-}$ and $\mathbf{11}^{\bullet-}$ has to be invoked. This effect contributes to a stabilization of Ψ_s^- with respect to Ψ_a^-. Not surprisingly, a quantitative description of the complex situation has not yet been achieved although various spectroscopic techniques have been applied.[9-20] While we shall not touch upon these perturbational models in detail, we emphasize that under the influence of the various perturbations the HOMO/LUMO gap for the ions may become rather small (see below).



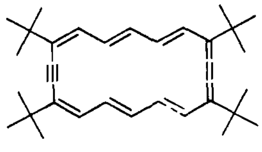
10



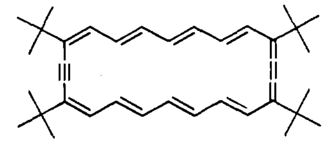
11



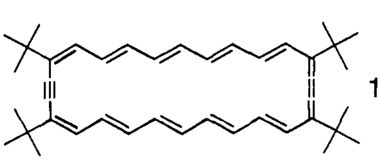
12



13



14



15

Assuming Ψ_s^- as the doubly occupied MO of a [14]annulene dianion, e.g., of $\mathbf{2}^{2-}$, one can calculate the local π-charges q_π within a simple HMO treatment and arrive at theoretical $\Delta q_\pi'$ values (changes of q_π upon ion formation), which are given in Table II. In view of the underlying simplifications—unknown geometry and neglect of the influence of the counterions[66-71]—a more sophisticated MO treatment does not appear significant.

There is evidence that ^{13}C chemical shifts of carbons in the π-pheriphery provide a measure of the π-charge distribution.[72-76] Within a rough approximation the increase in the local π-charge density Δq_π is proportional to the upfield shift Δq_π of the corresponding ^{13}C NMR signal according to $K_c = \Delta\delta_c/\Delta q_\pi$.

Particularly striking features of the ^{13}C NMR spectrum of $\mathbf{2}^{2-}$ (see Figure 4) are the large shift range of signals from ring carbons, the *downfield*[57] (!) shift of the resonance of C-1 (C-6, C-8, C-13), and the extreme highfield position of the resonance of C-7 (C-14). One concludes from a qualitative correlation of $\Delta\delta_c$ and Δq_π values that (i) the π-charge distribution is largely nonuniform and (ii) the MO Ψ_s^- has accepted the excess charge. Similar findings are made for the dianion $\mathbf{9}^{2-}$ where the deshielding of C-1 upon dianion formation ($\Delta\delta_c = 40$) is even more pronounced.

The low solubility of $\mathbf{5}^{2-}$ did not allow a determination of its ^{13}C NMR resonances. From the above MO model it is clear, however, that the charge is again distributed according to Ψ_s^-.[18]

---

[62] Günther, M. E.; Schmitt, P.; Moskau, D.; Günther, H.; Scott, L.; Kirms, M. A. *Chem. Ber.* **1986**, *119*, 2942.

[63] Sondheimer, F. *Acc. Chem. Res.* **1972**, *5*, 81.

[64] Gerson, F.; Huber, W.; Lopez, J. *J. Am. Chem. Soc.* **1984**, *106*, 5808.

[65] Huber, W. *Helv. Chim. Acta* **1984**, *67*, 625.

[66] Müllen, K.; Huber, W.; Meul, T.; Nakagawa, M.; Iyoda, M. *Tetrahedron* **1983**, *39*, 1575.

[67] Vogler, H. *Croat. Chem. Acta* **1984**, *57*, 1177.

[68] Vogler, H. *J. Chem. Soc., Perkin Trans. 2* **1985**, 2033.

[69] Edlund, U. *Org. Magn. Reson.* **1979**, *12*, 661. Edlund, U.; Eliasson, B.; Kowalewski, J.; Trogen, L. *J. Chem. Soc., Perkin Trans. 2* **1981**, 1260.

[70] Jemmis, E. D.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1982**, *104*, 4781.

[71] Edlund, U.; Eliasson, B. *J. Chem. Soc., Chem. Commun.* **1982**, 950.

[72] O'Brien, D. H.; Hart, A. J.; Russell, C. R. *J. Am. Chem. Soc.* **1975**, *97*, 4410.

[73] Becker, B. C.; Huber, W.; Müllen, K. *J. Am. Chem. Soc.* **1980**, *102*, 7803.

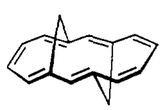
[74] Olah, G. A.; Mateescu, G. D. *J. Am. Chem. Soc.* **1970**, *92*, 1430.

[75] Lauterbur, P. C. *Tetrahedron Lett.* **1961**, 274. Spiesecke, H.; Schneider, W. G. *Tetrahedron Lett.* **1961**, 468.

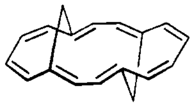
[76] Müllen, K. *Helv. Chim. Acta* **1976**, *59*, 1357.

We note that the spin density distribution in the radical anions of mono- and polycyclic π-systems is usually analogous to the charge distribution in the corresponding dianions. The ESR hyperfine coupling constants of $\mathbf{5}^{\cdot-}$ are a_H(H-7) = 0.344 and a_H(H-2) = 0.278 mT thus pointing toward the participation of Φ_s^-.

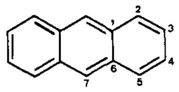
Reference to the isoelectronic anthracene dianion $\mathbf{18}^{2-}$ is revealing.[76] It is readily deduced from the shift data (see Table II) that here again the carbons C-7 (C-14) suffer from the highest charge-induced upfield shift while C-1 (C-6, C-8, C-13) are *deshielded.* A difference between the anthracene and annulene dianions can be seen from the shielding of C-2 (C-4, C-9, C-12): in the annulene dianions the latter carbons adopt a charge density similar to the one in C-7 (C-14).



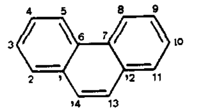
16



17



18



19

We have shown from convincing ^{1}H and ^{13}C NMR spectroscopic evidence that the highest π-charge density within the phenanthrene dianion $\mathbf{19}^{2-}$ is localized at the central positions C-13 (C-14).[77] While in $\mathbf{19}^{2-}$ the protons H-13 (H-14) absorb at highest field, they appear at lowest field in the annulene dianion $\mathbf{7}^{2-}$. This outcome reveals that $\mathbf{7}^{2-}$ and $\mathbf{19}^{2-}$ do not possess the close relationship observed for $\mathbf{18}^{2-}$ and the related annulene dianions.

Problems are encountered for the dications $\mathbf{2}^{2+}$ and $\mathbf{3}^{2+}$ (see Table II and Figure 4). From the pairing properties of alternating annulene π-systems one might expect a close analogy of the π-charge distributions within dianions and dications. Indeed, the reaction of $\mathbf{2}^{2+}$ with methanol to yield the quenching product **20** seems to support such an assumption. A decision as to the frontier orbital in $\mathbf{2}^{2+}$ is not straightforward, however, since the downfield shifts $\Delta\delta_C$ observed upon cation formation are similar for each π-center. The same characteristics hold for $\mathbf{9}^{2+}$ but not for the anthracene dication. In the latter the sequence of the ^{13}C NMR resonances can correctly be predicted from the AO coefficients of the (empty) bonding orbital Ψ_a^+; i.e., the carbon centers bearing the highest negative charge in $\mathbf{18}^{2-}$ accept the highest positive charge in $\mathbf{18}^{2+}$.

It is known from related cases of hydrocarbons that the π-charge distribution in their dications appears more "homogeneous" than that in the corresponding dianions.[78] This can be explained by the fact that in the alkali metal salt of a dianion the counterion exerts a polarizing effect. Stronger ion pairing can therefore lead to a further increase of the π-charge at positions with a high AO coefficient of the frontier orbital and contribute to a nonuniform charge distribution. The related effect in the dication should be much smaller as a result of the weaker polarizing effect of the (large) counterion. Nevertheless, the π-charge distribution in the anthracene dication, the analogue of $\mathbf{2}^{2+}$, is nonuniform, and so is the one in related $(4n + 2)\pi$-dications. In dealing with the *uniform* charge distribution of $\mathbf{2}^{2+}$, it appears more appropriate to refer to the possibility of a small HOMO/LUMO gap.[79]

This fact implies the existence of excited configurations which are similar in energy to that of the Hartree–Fock wave function Ψ_0 with a nonuniform π-charge distribution determined by Ψ_a^+. Consequently, a Hartree–Fock instability of Ψ_0 might occur.[80,81] This could demand an approach beyond the mean-field approximation for a sufficiently accurate description of the ground state or lead to a symmetry reduction. In both cases the π-charge distribution would no longer be governed simly by Ψ_a^+.

An interpretation of the ^{13}C NMR spectra of $\mathbf{3}^{2-}$ and $\mathbf{3}^{2+}$ (see Figure 4) is similar to the one of $\mathbf{2}^{2-}$ and $\mathbf{2}^{2+}$ and need not be discussed in detail.

We have so far used the charge density/^{13}C shift correlation in a qualitative sense.[72-74] A quantitative application of $K_c = \Delta\delta_c/\Delta q_\pi$ and the determination of experimental charge densities requires a consideration of the proportionality constant K_c. From the upfield shift of the center of gravity of the ring signals $[\Delta\langle\delta_c\rangle]$ and the change of the average π-charge density $\Delta\langle q_\pi\rangle$, one calculates the proportionality constant $K_c = \Delta\langle\delta_c\rangle/\Delta\langle q_\pi\rangle$ for $\mathbf{2}^{2-}$, $\mathbf{3}^{2-}$, and $\mathbf{9}^{2-}$ as 84.0, 101.7, and 23.1 ppm/unit charge. The deviation from the "normal" value of 160 ppm/unit charge is striking. We have documented for various cases of mono- and polycyclic π-systems, however, that normal K_c values are only observed for diatropic species, and this finding is valid for doubly as well as quadruply charged anions.[57,73,82-84]

A detailed discussion of K_c values for paratropic ions has been published by us elsewhere.[82] For a great number of anions derived from mono- and polycyclic π-systems the abnormal K_c values turn out to correlate with the degree of paratropism as measured by the ^{1}H NMR chemical shifts. The average energy for mixing of electrons from the ground state to various low lying excited states (ΔE) forms a reasonable basis for rationalizing the low K_c values of paratropic anions. The ΔE factor enters the denominator in the Karplus–Pople equation for nuclear paramagnetic shielding, which is thought to dominate ^{13}C screening.[85] ΔE also enters the denominator of some terms in the theoretical models of paramagnetic ring currents.[99] (The title dianions seem to play a special role since, e.g., $\mathbf{7}^{2-}$ exhibits a largely diminished K_c value [59.5 ppm/unit charge] although it is characterized as possessing only a weak paratropism.)

The experimental changes of local π-charge densities, $\Delta q_\pi''$, which have been determined from the $\Delta\delta_C$ values of individual carbon signals and the "compound-specific" K_c values, are given in Table II for the example of $\mathbf{2}^{2-}$. This treatment is, certainly, inadequate for anions with extremely low K_c values,[82] and one expects from the applied sensitivity factor that the nonuniform character of the π-charge distribution is overestimated.

In another method of experimentally determining the charge density pattern within paratropic dianions[82] we have described their ^{13}C NMR chemical shifts as a sum of a "pure" charge term and a variable anisotropy term. The latter is thereby derived from the ring-current-induced shifts of the corresponding proton signals. The resulting $\Delta q_\pi'''$ values for $\mathbf{2}^{2-}$ are also included in Table II.

3.2. Paratropism of a Homologous Series of Dianions. Prior to a discussion of ring-current effects upon proton resonances, one must consider the pure charge effect $\Delta\delta_H$.[86] Application of eq 1 will subsequently provide the "charge-corrected" signal shifts

$$\Delta\delta_H{}^{RC} = \Delta\delta_H{}^{exp} - \Delta\delta_H \qquad (1)$$

$\Delta\delta_H{}^{RC}$ being induced by the anisotropic ring-current effects.

---

(77) Müllen, K. *Helv. Chim. Acta* **1978**, *61*, 1296.

(78) Benken, R.; Finneiser, K.; von Puttkamer, H.; Günther, H.; Eliasson, B.; Edlund, U. *Helv. Chim. Acta* **1986**, *69*, 955.

(79) Cohen, Y.; Meyer, A. Y.; Rabinovitz, M. *J. Am. Chem. Soc.* **1986**, *108*, 7039. Minsky, A.; Meyer, A. Y.; Rabinovitz, M. *Tetrahedron* **1985**, *41*, 785.

(80) Thouless, D. J. *The Quantum Mechanics of Many-Body Systems*; Academic: New York, 1961.

(81) Cizek, J.; Paldus, J. *J. Chem. Phys.* **1967**, *47*, 3976.

(82) Eliasson, B.; Edlund, U.; Müllen, K. *J. Chem. Soc., Perkin Trans. 2* **1986**, 937.

(83) Eliasson, B.; Edlund, U. *J. Chem. Soc., Perkin Trans. 2* **1983**, 1837. Eliasson, B.; Lejon, T.; Edlund, U. *J. Chem. Soc., Chem. Commun.* **1984**, 591.

(84) Minsky, A.; Meyer, A. Y.; Rabinovitz, M. *J. Am. Chem. Soc.* **1982**, *104*, 2475. Minsky, A.; Klein, J.; Rabinovitz, M. *J. Am. Chem. Soc.* **1981**, *103*, 4586.

(85) Karplus, M.; Pople, J. A. *J. Chem. Phys.* **1963**, *38*, 2803.

(86) Fraenkel, G.; Carter, R. E.; McLachlan, A.; Richards, J. H. *J. Am. Chem. Soc.* **1960**, *82*, 5846. Spiesecke, H.; Schneider, W. G. *Tetrahedron Lett.* **1961**, 468. Colpa, J. P.; MacLean, C.; Mackor, E. L. *Tetrahedron* **1963**, *19*, suppl. 2, 65. Schaefer, T.; Schneider, W. G. *Can. J. Chem.* **1963**, *41*, 966. Black, P. J.; Brown, R. D.; Heffernan, M. L. *Aust. J. Chem.* **1967**, *20*, 1305.

A commonly applied method for determining $\Delta\delta_{\mathrm{H}}$ values is based on eq 2. Thereby, the signal shift $\Delta\delta_{\mathrm{H}}$ is determined from

$$K_{\mathrm{H}} = \Delta\delta_{\mathrm{H}}/\Delta q_{\pi} \qquad (K_{\mathrm{H}} = 10.6\ \mathrm{ppm}/e) \qquad (2)$$

the charge on the carbon to which the proton is attached. In a simple treatment (method A, see ref 87), we ignore differences of the particular ring positions by considering the average (ring) proton signal of neutral and charged species, and we assume a uniform π-charge distribution. Application of eq 1 and 2 then provides the $\Delta\delta^{\mathrm{RC}}$ values for the perimeter protons, which are given in Table III.[87] Also reported in Table III are the downfield shifts $\Delta\delta_{\mathrm{H}}^{\mathrm{exp}}$ observed for the signals of bridge protons upon ion formation. Furthermore, these values have been corrected for the influence of charge by calculation of the linear and quadratic electric field effects exerted by the charge at the ring carbons.[26,78]

Since dianions and dications with identical perimeter (e.g., **2**$^{2+}$/**2**$^{2-}$ or **3**$^{2+}$/**3**$^{2-}$) are truly homologous $(4n)\pi$-systems with the number of π-electrons differing by 4, a comparison of their paratropism is tempting.[88] It appears from Table III that $\Delta\delta_{\mathrm{H}}^{\mathrm{RC}}$ values of ring protons are rather small and that their interpretation is not straightforward. On the other hand, the $\Delta\delta_{\mathrm{H}}^{\mathrm{exp}}$ and $\Delta\delta_{\mathrm{H}}^{\mathrm{RC}}$ values of bridge protons indicate that the paratropism of the dianions is more pronounced than that of the dications with the same ring size. This is in accord with related findings in the literature;[89,90] however, the validity of such a conclusion is limited by the problems associated with a differentiation of charge and ring-current effects upon ^{1}H and ^{13}C chemical shifts.

When comparing the paratropism of ions with *different* ring size, one has to account for geometric effects.[91-99] It appears adequate in view of the structural analogy of the present ions to consider the term $\Delta\delta_{\mathrm{H}}^{\mathrm{RC}}/S$ as a rough measure of the ring-current effect where S is the ring area.[98-100] Assuming the relative ring areas S of **1**$^{2-}$, **2**$^{2-}$/**2**$^{2+}$, and **3**$^{2-}$/**3**$^{2+}$ to be 2, 3, and 4, respectively, one obtains the $\Delta\delta^{\mathrm{RC}}/S$ values that are given in Table III. Within the homologous series **1**$^{2-}$, **2**$^{2-}$, and **3**$^{2-}$ the paratropic ring-current effect decays according to the sequence **2**$^{2-}$ > **3**$^{2-}$ ≫ **1**$^{2-}$. This result, which is true regardless of the method of "charge correction", is in sharp contrast to the related series of $(4n)\pi$-dianions **12**$^{2-}$–**15**$^{2-}$, which we described recently.[57] In the latter case with *planar* rings a plot of the paratropism vs. ring size gave a smoothly decaying curve. Furthermore, within the isoelectronic 12π-systems **1**$^{2-}$/**2**$^{2+}$ and the isoelectronic 16π-systems **2**$^{2-}$/**3**$^{2+}$ the relative magnitude of paratropic effects is **2**$^{2-}$ > **3**$^{2+}$ and **2**$^{2+}$ ≫ **1**$^{2-}$. Without going into further details we mention that a similar discussion of isoelectronic *diatropic* species is possible when contrasting **2** and **3** with the dication and dianion derived from the [16]annulene **17**.[90]

The obvious explanation for the above results is the nonplanarity of the π-system **1**$^{2-}$. Various 1,6-bridged [10]annulenes are known from X-ray investigations[101] to adopt π-perimeters which severely deviate from coplanarity. The twisting of the π-orbitals, on the other hand, does not suffice to significantly quench the diatropism of the systems. The paratropism of the corresponding dianion, however, is largely supressed.

Encountering the problems that are created by the different ring conformations in the bridged annulenes, one must search for a group of paratropic dianions with identical ring configuration but different ring conformation.

3.3. Paratropism and Ring Conformation.

Compounds **4**, **5**, and **6** constitute a series of [14]annulenes whose perimeters increasingly deviate from a coplanar arrangement. This feature is due to the size of the bridging alkanediylidene group and thus the distance of the centers 15 and 16.[102-104] Various spectroscopic properties have been shown to sensitively reflect the above conformational effect and to reveal the subtle interdependence of steric and conjugational phenomena.[9-20]

^{1}H NMR spectroscopy proves to be of special value since the chemical shifts of both ring and bridge protons depict the decreasing diatropism within the less planar analogue.

Upon dianion formation the downfield shifts of the signals of H-15 in **4**$^{2-}$, **5**$^{2-}$, and **6**$^{2-}$ are 14.8, 11.5, and 10.9 ppm, respectively. Obviously, the higher degree of bending within the dianion causes, again, a decrease of the paratropism. As in the case of **1**, **2**, and **3**, the paratropic effects of the dianions reflect the bending of the perimeter and the resulting π-bond fixation in a much more sensitive way than do the diatropic ones in the neutral compounds.

Further support in favor of this finding is obtained from the pairs of compounds **7**/**7**$^{2-}$ and **8**/**8**$^{2-}$, which constitute the borderline cases within the present evaluation of ring-current effects. Clearly, the situation is complicated due to the fact that **7** and **8** possess another ring configuration, namely, a phenanthrene-type perimeter.[54,55] While we will touch upon the influence of the ring configuration in section 3.4 we mention that according to an X-ray analysis compound **7** has a higher degree of bending than the foregoing [14]annulenes, the maximum angle of torsion being 45° for **7** compared to 34° for **2**.[105] It is the outstanding feature of compound **8** that the strongest twisting of the π-orbitals is "localized" within the central moiety (e.g., φ_{67} = 84°). In that respect **8** is closely related to the acene perimeter **16**.[106,107]

While the ^{1}H NMR chemical shifts of **7** indicate a small, but significant, diatropism, no such effect is detectable for **8** (and **16**) [δ_{H} (bridge) 2.36, −0.36 (**7**); 2.59, 1.68 (**8**)]. We deduce that **8**, although possessing a $(4n + 2)\pi$-perimeter, is of olefinic character. It is an open question as to which degree of bending a neutral [4*n* + 2]annulene can tolerate without suffering from a total quench

---

(87) Toward a refined treatment one could calculate $\Delta\delta^{\mathrm{RC}}$ increments for particular ring protons. This can simply be done (method B) by introducing the known $\Delta\delta_{\mathrm{c}}''$ or $\Delta\delta_{\mathrm{c}}'''$ values from Table II into eq 3. Another approach of deriving individual $\Delta\delta^{\mathrm{RC}}$ increments (method C) can calculate ring proton chemical shifts from linear and quadratic electric field effects originating from charges on surrounding carbon centers. The $\Delta\delta^{\mathrm{RC}}$ values obtained from methods B and C turn out to differ significantly. Particularly striking are the results for **3**$^{2-}$. The observed discrepancies and the drawbacks of method C which have been reported in the literature[78] prompted us to consider only average signals of ring protons according to the crude method A (see text).

(88) The paratropism of the $(4n)\pi$-systems sensitively depends upon the degree of π-bond fixation and the HOMO/LUMO gap (see section 3.3). According to the pairing properties of alternating π-systems, the dianion and dication should possess the same HOMO/LUMO gap (even within a PPP treatment). However, the pairing theorem does only hold for neutral systems so that dianions and dications might well exhibit different RC effects.

(89) Meul, T., Ph.D. Thesis, University of Cologne, Federal Republic of Germany, 1982.

(90) Müllen, K.; Meul, T.; Vogel, E.; Kürschner, U.; Schmickler, H.; Wennerström, O. *Tetrahedron Lett.* **1985**, *26*, 3091.

(91) Haigh, C. W.; Mallion, R. B. *Prog. Nucl. Magn. Reson. Spectrosc.* **1980**, *13*, 303.

(92) Pople, J. A. *J. Chem. Phys.* **1956**, *24*, 1111.

(93) Waugh, J. S.; Fessenden, R. W. *J. Am. Chem. Soc.* **1957**, *79*, 846.

(94) Johnson, C. E.; Bovey, F. A. *J. Chem. Phys.* **1958**, *29*, 1012.

(95) Haddon, R. C. *Tetrahedron* **1972**, *28*, 3613, 3635.

(96) London, F. *J. Chem. Phys.* **1937**, *5*, 837.

(97) Pople, J. A. *Mol. Phys.* **1958**, *1*, 175.

(98) McWeeny, R. *Mol. Phys.* **1958**, *1*, 311.

(99) Ramsey, N. F. *Phys. Rev.* **1952**, *86*, 243. Salem, L. *The Molecular Orbital Theory of Conjugated Systems*; W. A. Benjamin: New York, 1966; p 209.

(100) The ring-current-induced shielding of a particular proton depends on the size of the secondary magnetic field and thus on geometric factors such as the shape of the perimeter and the location of the proton with respect to the ring. In an approximate approach $\Delta\delta_{\mathrm{H}}^{\mathrm{RC}}$ is proportional to the ring-current intensity, the ring area S, and the inverse cube distance of the nucleus from the ring center (see ref 98 and 99).

(101) Bianchi, R.; Pilati, T.; Simonetta, M. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1980**, *B36*, 3146. Biancihi, R.; Morosi, G.; Mugnoli, A.; Simonetta, M. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1973**, *B29*, 1196.

(102) Bianchi, R.; Casalone, G.; Simonetta, M. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1975**, *B31*, 1207.

(103) Casalone, G.; Gavezzotti, A.; Mugnoli, A.; Simonetta, M. *Angew. Chem.* **1970**, *82*, 516; *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 519. Gavezzotti, A.; Mugnoli, A.; Raimondi, M.; Simonetta, M. *J. Chem. Soc., Perkin Trans. 2* **1972**, 425.

(104) Gramaccioli, C. M.; Mugnoli, A.; Pilati, T.; Raimondi, M.; Simonetta, M. *J. Chem. Soc., Chem. Commun.* **1971**, 973. Gramaccioli, C. M.; Mugnoli, A.; Pilati, T.; Raimondi, M.; Simonetta, M. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1972**, *B28*, 2365.

(105) Destro, R.; Pilati, T.; Simonetta, M. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1977**, *B33*, 940.

(106) Vogel, E.; Haberland, U.; Günther, H. *Angew. Chem.* **1970**, *82*, 510; *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 513.

(107) Gramaccioli, C. M.; Mimun, A. S.; Mugnoli, A.; Simonetta, M. *J. Am. Chem. Soc.* **1973**, *95*, 3149. Simonetta, M. *Pure Appl. Chem.* **1980**, *52*, 1597.

of its diatropism.[3,108] However, the known dependence of the resonance integrals of peripheral bonds upon the cosine of the corresponding angles of torsion[109] readily explains why the prevailing degree of π-bond fixation does not fully quench the diatropism.

Although the geometry of the dianions is unknown, one can reasonably assume in view of the rigid perimeters that the arguments concerning the bending of the neutral π-systems also hold for the corresponding ions. In **7**$^{2-}$ the resonances of both ring and bridge protons appear in the same shift range (two signals of perimeter protons [2 H each] are at δ 3.68 and 4.16 while the bridge protons H-15i and H-15a appear at δ 2.92 and 5.23). Obviously, the indications for a paratropic character of the π-system are much less pronounced than those in the related species **2**$^{2-}$ as well as in **4**$^{2-}$–**6**$^{2-}$.

While the average signal of the bridge protons is slightly shifted downfield upon going from **7** to **7**$^{2-}$, it is essentially unaffected upon transition from **8** to **8**$^{2-}$: the ring-current effect is totally quenched for the nonplanar dianion **8**$^{2-}$.

The upfield shifts of the ^{1}H NMR signals of the anthracene and phenanthrene dianions, **18**$^{2-}$ and **19**$^{2-}$, are much larger than expected from pure charge effects.[76,77] By application of the same criteria as above, this points toward the formation of essentially paratropic ($4n = 16$)π-systems. Comparing the benzenoid species with the closely related annulenes, e.g., with **2**$^{2-}$ and **7**$^{2-}$, one would even conclude that the former exhibit a larger paratropic effect. It should be noted, however, that the treatment of ring-current effects in polycyclic benzenoid compounds differs from that of the related annulenes.[110]

3.4. Paratropism and Ring Configuration. In the above discussion we have investigated the dia- and paratropism within perimeters of varying conformation but fixed configuration. A complementary approach is possible when considering annulenes which are more or less planar but have different sequences of double bond configuration. Compounds **9**,[56] **10**,[6,7] and **11**[111-115] as well as their dianions **9**$^{2-}$, **10**$^{2-}$,[116] and **11**$^{2-}$[117] provide most suitable subjects. These [14]annulenes have in common a dimethylethanediylidene moiety as a bridge; **9** possesses an anthracene, **10** and **11** a pyrene perimeter. While the perimeter of **9** deviates only slightly from a coplanar geometry, those of **10** and **11** are essentially planar.

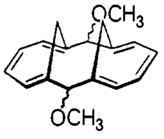
Let us consider the average signal of the perimeter protons $\langle\delta_{\text{ring}}\rangle$ and that of the bridge (methyl) protons $\langle\delta_{\text{bridge}}\rangle$ for the neutral and dianionic systems (see Table IV). Not unexpectedly, from what has been said above, **10** and **11** appear to be very similar while the diatropism of **9** is less pronounced. The spectacular low-field resonances of the methyl protons in **9**$^{2-}$–**11**$^{2-}$ leave no doubt as to the paratropism of the dianions. Surprisingly enough, however, the corresponding signal shifts $\Delta\langle\delta_{\text{bridge}}\rangle$ are +9.6, +16.5, and +25.3 ppm and reveal appreciable differences of the dianions, differences which cannot simply be explained by a bending of the perimeter and the resulting tendency toward π-bond fixation.

We recall that within the perturbational approach of Ramsey paratropic effects originate from the admixture of electronically excited states to the zero-field ground state.[99] Thus within the limits of a simple MO model an increasing HOMO/LUMO gap of the dianions is expected to decrease the paratropic effects. This trend can result from a double bond fixation, which is more important for the detection of a paratropic than of a diatropic behavior. As a consequence, slight structural changes (e.g., configuration, conformation, or ion pairing) of ($4n$)π-systems may deeply affect the prevailing paratropism although its quantitative assessment is hard to achieve.

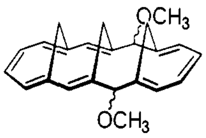
The crucial role of double bond fixation and of the HOMO/LUMO gap has been pointed out by Pople and Untch in their treatment of [$4n$]annulenes.[118] It should be noted, however, that their approach is inadequate for the dianions and dications of [$4n$ + 2]annulenes.

We have shown for a number of examples that the transition from neutral to charged π-systems is accompanied by an increased tendency toward π-bond delocalization.[119] Having succeeded in obtaining highly resolved ^{1}H NMR spectra of **2**$^{2-}$ we were able to exactly analyze the AA′BB′ spin system of H-1/H-4. The vicinal coupling constants are ^3J (H-2, H-3) = 5.83 and ^3J (H-3, H-4) = 10.04 Hz. A correlation of ^3J with the corresponding π-bond orders[120] indicates a pronounced tendency toward a (first-order) π-bond fixation in the dianions. The corresponding values for the neutral compound are 9.24 and 9.29 Hz, respectively, pointing toward a π-bond delocalization. A second-order π-bond fixation[121-123] with a concomitant symmetry deformation of the present ($4n$)π-systems is not observed as witnessed by the sharp signals of *one* AB system (H-15a, H-15i) in **2**$^{2-}$ or by the number of signals in the ^{13}C NMR spectra. It cannot be excluded, however, that a rapid π-bond shift occurs, e.g., in **2**$^{2-}$, which even at −80 °C gives rise to an effective C_{2v} symmetry of the perimeter. The dianions **7**$^{2-}$ and **8**$^{2-}$ (with phenanthrene perimeter) also exhibit a strong π-bond alternation. This can be deduced from the fact that the vicinal coupling constants in the spin system H-2/H-5 of **8**$^{2-}$ vary between 5.6 and 8.9 Hz, while the values of the neutral compound are between 5.3 and 11.0 Hz.

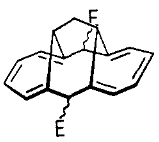
3.5. Reaction of the Dianions with Electrophiles. The kinetically controlled reaction of the title dianions with electrophilic agents is expected to proceed at the position of the highest π-charge density.[40,41] From the discussion of the π-charge distribution in **2**$^{2-}$ and **5**$^{2-}$ (see section 3.1) one predicts such an attack to occur at the ring positions 7 (14) and/or 2 (5). This quenching reaction will now be worked out for the representative case of the (most easily accessible) dianion **5**$^{2-}$.



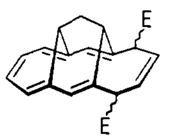
20



21



22



23

a, E = H
b, E = CH_3
c, E = $COOCH_3$
d, E = CH_2OH
e, E = CH_2Br

---

(108) Haddon, R. C.; Scott, L. T. *Pure Appl. Chem.* **1986**, *58*, 137.

(109) Heilbronner, E.; Bock, H. *Das HMO-Modell und seine Anwendung*; Verlag Chemie: Weinheim, 1968; p 135.

(110) Barfield, M.; Grant, D. M.; Ikenberry, D. *J. Am. Chem. Soc.* **1975**, *97*, 6956.

(111) Boekelheide, V.; Philips, J. B. *J. Am. Chem. Soc.* **1967**, *89*, 1695.

(112) Du Vernet, R.; Boekelheide, V. *Proc. Natl. Acad. Sci. U.S.A.* **1974**, *71*, 2961.

(113) Mitchell, R. H.; Boekelheide, V. *J. Am. Chem. Soc.* **1974**, *96*, 1547.

(114) Mitchell, R. H.; Anker, W. *Tetrahedron Lett.* **1981**, 5139.

(115) Mitchell, R. H. *Isr. J. Chem.* **1980**, *20*, 594. Mitchell, R. H.; Carruthers, R. J.; Mazuch, L.; Dingle, T. W. *J. Am. Chem. Soc.* **1982**, *104*, 2544. Mitchell, R. H.; Yan, J. S. H.; Dingle, T. W. *Ibid.* **1982**, *104*, 2551. Mitchell, R. H.; Williams, R. V.; Dingle, T. W. *Ibid.* **1982**, *104*, 2560.

(116) Klabunde, K.-U.; Müllen, K.; Vogler, H. *Tetrahedron* **1987**, *43*, 1183.

(117) Mitchell, R. H.; Klopfenstein, C. E.; Boekelheide, V. *J. Am. Chem. Soc.* **1969**, *91*, 4931.

(118) Pople, J. A.; Untch, K. G. *J. Am. Chem. Soc.* **1966**, *88*, 4811.

(119) Müllen, K.; Unterberg, H.; Huber, W.; Wennerström, O.; Norinder, U.; Tanner, D. *J. Am. Chem. Soc.* **1984**, *106*, 7514. Tanner, D.; Wennerström, O.; Norinder, U.; Müllen, K.; Trinks, R. *Tetrahedron* **1986**, *42*, 4499.

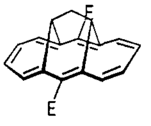
(120) Günther, H.; Schmickler, H.; Günther, M.-E.; Cremer, D. *Org. Magn. Reson.* **1977**, *9*, 420.

(121) Binsch, G. In *Aromaticity, Pseudo-Aromaticity, Anti-Aromaticity*; Bergmann, E. D., Pullman, B., Eds.; Jerusalem, 1971; p 25.

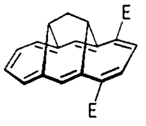
(122) Binsch, G.; Tamir, I.; Hill, R. D. *J. Am. Chem. Soc.* **1969**, *91*, 2446.

(123) Haddon, R. C. *J. Am. Chem. Soc.* **1979**, *101*, 1722.

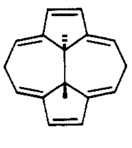
Let us compare the regio- and stereoselectivity of the reductive annulene transformation with the one of the isoelectronic anthracene (**18**). The latter reaction performed in liquid ammonia as solvent has been extensively studied.[42-47] It was concluded from preparative and spectroscopic evidence that the anthracene dianion ($\mathbf{18}^{2-}$) formed via reduction of **18** in liquid ammonia is rapidly protonated by the solvent at C-7, thus giving rise to a monoanion.[124] The addition of an ammonia solution of the latter to an excess of an alkylating agent (inverse quench) provides the monoalkyldihydroanthracenes as main product. Experimental conditions allowing for the deprotonation of the monoalkyl dihydro derivative (e.g., by the amide ion formed upon protonation of the dianion) and subsequent alkylation also provide the dialkyl dihydro product.[43] The latter process might appear rather similar to the direct dialkylation of $\mathbf{18}^{2-}$ in ethereal solvents. It has been found, however, that the regioselectivity of the reductive alkylation, i.e., the dominance of attack at centers 7 and 14, is higher in liquid ammonia.[125]



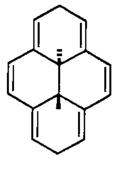
24



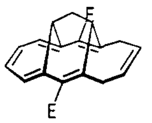
25



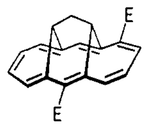
28



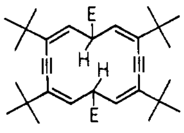
29



26



27



30

a, E = H
b, E = CH_3
c, E = $COOCH_3$
d, E = CH_2OH
e, E = CH_2Br

a, E = H
b, E = CH_3
c, E = $COOCH_3$
d, E = $(CH_2)_3Br$

When **5** is reductively methylated (liquid ammonia, lithium, methyl bromide) one observes a 3:1 mixture of the dimethyl derivatives **22b** and **23b**. The outcome of the methylation does not vary with the reaction temperature (−78, −33 °C) and the mode of quenching (normal/inverse). One concludes that the dianion $\mathbf{5}^{2-}$ (as dilithium salt) is not protonated by the solvent. Monomethyl derivatives are only observed when dimethyl sulfate is applied as alkylating material. This finding appears reasonable, however, from the concomitant formation of ammonium salts upon reaction of ammonia and dimethyl sulfate. Thereby, the initially formed monoalkylated anion undergoes rapid protonation.[126]

The spectral data of compounds **22b** and **23b** support the given structural assignment. Particularly important in view of the stereochemical course of the quenching reaction is the relative position of the incorporated methyl groups. The fact that the methyl and allylic protons of **22b** absorb as a single doublet and quartet, respectively, indicates the cis arrangement of the substituents. A tentative decision as to the cis or trans position with respect to the bridge can be made from the long-range coupling ^4J (H-15, H-7). The latter is known from related experience to be particularly large for a W arrangement of the relevant C–H and C–C bonds. The small unresolved coupling ^4J (H-15, H-7) in **22b** provides evidence that the electrophilic agent comes in from a direction "opposite" to the bridge.

Compound **22b** smoothly transforms into the dimethylannulene **24b** if reacted with dichlorodicyanobenzoquinone at room temperature. Attempted hydroxymethylation via quenching of $\mathbf{5}^{2-}/2Li^+$ (THF) with formaldehyde fails. The only product recovered is the neutral annulene **5**, which must have been formed via an electron-transfer process. Reaction of $\mathbf{5}^{2-}/2Li^+$ (THF) with methyl chloroformate affords a complex mixture of mono- and diadducts (different regioisomers), the relative yields (e.g., of **22c** and **26c**) depending on the reaction conditions. The formation of **26c** can be ascribed to a base-induced proton migration whose driving force is the formation of a conjugated pentaene system. Dehydrogenation of the crude reaction mixture and column chromatography provide the pure annulenes **24c**, **25c**, and **27c**. The diols **24d** and **25d** as well as the corresponding dibromides **24e** and **25e** are then accessible via standard procedures. Finally, when the dianion $\mathbf{5}^{2-}$ is generated in liquid ammonia and reacted with methyl chloroformate one obtains a nearly quantitative yield of the dihydro derivative **22a**. Obviously, the ammonium salt resulting from the reaction between the quenching reagent and the solvent acts as proton source.[126]

The reduction and reductive alkylation of the [14]annulene is of both mechanistic and preparative significance. The resulting adducts **22** and **23**, constituting dihydro derivatives of the parent annulene **5**, serve as suitable reference compounds for evaluating the diatropism of the conjugated species **5**. The easy rearomatization of the disubstituted species **22** and **23** is noteworthy since the alkyl derivatives of the annulene have not yet been available via direct Friedel–Crafts alkylation. With a suitable choice of the electrophile or its modification after the quenching process the reductive alkylation of the annulene provides useful intermediates for further synthetic transformations. Thus, the annulene derivatives **24** and **25** may serve as starting compounds for a subsequent annulenophane formation.

It has been pointed out above that the paratropism of the various [14]annulenes differs markedly with the structure of the π-perimeter. On the other hand, the [14]annulene dianions with anthracene, phenanthrene, and pyrene perimeter as well as the dianion of the didehydro[14]annulene **12** show a close analogy with respect to their π-charge distribution. It follows from the NMR analysis that the highest π-charge density within the dianions $\mathbf{5}^{2-}$, $\mathbf{10}^{2-}$, $\mathbf{11}^{2-}$, and $\mathbf{12}^{2-}$ is established at the carbon centers C-7 (C-14), C-6 (C-13), C-3 (C-8), and C-4 (C-11), respectively. These spectroscopic findings, which can be rationalized by the involvement of Ψ_s^- as the HOMO of the dianions, are nicely supported by the results of quenching experiments. It has been reported that upon reduction the [14]annulenes **10** and **11** transform into the dihydro derivatives **28** and **29**.[116,117] In order to complete this picture we have submitted the didehydroannulene **12**[127] to reductive alkylation and acylation. Thereby the dianion salt $\mathbf{12}^{2-}/2Li^+$ is created in THF and quenched with dimethyl sulfate or methyl chloroformate to regioselectively yield the dihydroannulene systems **30b** and **30c**. Application of the bifunctional electrophile 1,3-dibromopropane does not lead to the incorporation of a propylene bridge at C-4 and C-11 but gives the diadduct **30d**.

4. Conclusion

Neutral annulenes have for long served as useful model compounds for theoretical and spectroscopic studies. In contrast, bond theory has not recognized the importance of paratropic ionic π-systems as a most sensitive probe of cyclic conjugation. This shortcoming is due to the fact that quantum mechanical approaches toward the calculation of ring-current effects are rare and that the treatment of charged species must account for the actual ion pair structure and thus the role of counterion and solvent. It is hoped that the surprising spectroscopic results of this paper and the inclusion of a broad series of different annulenes will stimulate further theoretical considerations.

5. Experimental Section

A typical procedure for the preparation and NMR spectroscopic detection of the dianions is as follows.

The reactions were performed in sealed NMR tubes containing the alkali metal in a concentric compartment at the top of the tube. Po-

---

[124] Müllen, K.; Huber, W.; Neumann, G.; Schnieders, C.; Unterberg, H. *J. Am. Chem. Soc.* **1985**, *107*, 801.

[125] Bender, D.; Unterberg, H.; Müllen, K. *Angew. Chem.* **1986**, *98*, 446; *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 444.

[126] Neumann, G.; Müllen, K. *J. Am. Chem. Soc.* **1986**, *108*, 4105.

[127] Nakagawa, M. *Pure Appl. Chem.* **1975**, *44*, 885.

tassium was deposited as a mirror; lithium was introduced as active wires which were kept in the upper part of the tube by a small constriction in the glass. The starting compound (5 mg) had been placed at the bottom of the tube, dry THF-d_8 was distilled in from a storage vessel, and the solution was degassed by repeated freeze–pump cycles. The alkali metal was then inserted and the tube sealed. After the ^{1}H NMR spectrum of the neutral compound was recorded, the reduction was initiated by turning the tube and contacting the solution with the metal. The formation of the radical anion, which was accompanied by a deep color of the solution, broadened the NMR signals into the noise. Prolonged metal contact led to the appearance of the NMR signals of the diamagnetic dianion whose color is reported in Table I.

The oxidation experiments with antimony pentafluoride were performed according to techniques described in the literature.

7,14-Dimethyl-7,14-dihydro-1,6;8,13-propanediylidene[14]annulene (22b). A three-necked 100-mL round-bottomed flask equipped with magnetic stirring, a gas-inlet tube, a dry ice condenser, and a serum cap was dried with a flame in an argon stream and then allowed to cool to room temperature. A thin-walled glass ampule containing lithium wire (24 mg, 3.4 mmol; pressed and sealed under vacuum) was introduced, and 50 mL of dry ammonia was distilled in from a storage vessel containing alkali metal. The ammonia was maintained at its boiling temperature (−33 °C). The ampule was broken to yield the deep-blue solution of Li in NH_3. Annulene **5** (300 mg, 1.38 mmol) was solved in 20 mL of dry, degassed THF and added dropwise to the ammonia. Complete addition and formation of the dianion was indicated by the appearance of a deep red-brown color. After 5 min of additional stirring at −33 °C, 5 mL of freshly distilled methyl bromide was injected with a syringe. After the solution, which became colorless within a few seconds, was stirred for 30 min, the ammonia was allowed to evaporate. Water (30 mL) was added and the mixture extracted with hexane. The combined organic layers were washed with water and dried over magnesium sulfate. The residue which remained after evaporation of the solvent was chromatographed over silica gel (1.5 m, $\phi = 2$ cm). Hexane eluted two colorless fractions. From the first fraction, which contained **22b** as main component, 180 mg of pure **22b** (53%) could be obtained after repeated crystallizations from methanol. **22b**: mp 148 °C (colorless needles); ^{1}H NMR (60 MHz, C_6D_6) δ 6.48 (m, 4 H), 5.91 (m, 4 H), 3.26 (quart, 2 H), 2.43 (t, 2 H), 1.89 (t, 2 H), 1.65 (d, 6 H); UV (CH_2Cl_2) 260 (8218) nm; MS (70 eV), *m/e* (rel intensity) 248 ($M^{\bullet+}$, 100), 233 ($M^{\bullet+} - CH_3$, 73), 218 ($M^{\bullet+} - 2CH_3$, 36), 202 (42); exact mass calcd for $C_{19}H_{20}$ 248.1591, found 248.1597.

7,14-Dicarbomethoxy-7,14-dihydro-1,6;8,13-propanediylidene[14]annulene (22c). The annulene **5** (218 mg, 1 mmol) was solved in dry, degassed THF and reduced at −78 °C with lithium wire in a sealed glass ampule. When the dianion formation was complete the red-brown solution was separated from the metal and the ampule opened under argon. An excess of freshly distilled methyl chloroformate was rapidly added with a syringe at −10 °C. After evaporation of the solvent and of the reagent under vacuum, the residue was solved in ether. Addition of hexane gave 100 mg (29%) of the colorless, microcrystalline diester **22c**: ^{1}H NMR (60 MHz, $CDCl_3$) δ 6.61 (m, 4 H), 6.17 (m, 4 H), 4.15 (s, 2 H), 3.84 (s, 6 H), 2.57 (t, 2 H), 2.22 (t, 2 H); MS (70 eV), *m/e* (rel intensity) 336 ($M^{\bullet+}$, 8), 304 (32), 202 (100).

7,14-Dicarbomethoxy-2,5-dihydro-1,6;8,13-propanediylidene[14]annulene (23c). The dianion $\mathbf{5}^{2-}/2Li^+$ was prepared in THF as described above. Quenching was performed by *slow* addition of methyl chloroformate with a syringe. The resulting isomer **23c** was recrystallized from methanol. **23c**: mp 168–169 °C (yellow needles); ^{1}H NMR (60 MHz, $CDCl_3$) δ 7.09 (m, 2 H), 6.62 (m, 2 H), 5.60 (t, 2 H), 3.81 s, 6 H), 3.59 (quart, 1 H), 3.33 (d, 2 H), 1.30 (t, 2 H), 0.25 (quart, 1 H).

7,14- (24c), 2,5- (25c), and 2,7-Dicarbomethoxy-1,6;8,13-propanediylidene[14]annulene (27c). Annulene **5** (436 mg, 2 mmol) was dissolved in THF and reduced with lithium as described above. The resulting dianion solution was quenched with methyl chloroformate. The residue which remained after evaporation of the solvent and of the reagent was filtered over silica gel (10 cm, $\phi = 2$ cm) with ether/hexane 3:1. After removal of the solvent the crude product was solved in benzene (200 mL), DDQ (454 mg, 2 mmol) was added, and the mixture was boiled for 6 h. After the mixture cooled to room temperature, 2 mL of cyclohexa-1,4-diene were added in order to remove the residual quinone. The hydroquinone was separated by filtration and washed with methylene chloride. The residue which remained after removal of the solvent was chromatographed over silica gel (1.5 m, $\phi = 2$ cm). Ether/hexane (1:2) eluted a yellow fraction containing a small amount of starting material. The following orange fractions were pure 2,5-dicarbomethoxyannulene **25c** (222 mg, 33%), 2,7-dicarbomethoxyannulene **27c** (26 mg, 4%), and 7,14-dicarbomethoxyannulene **24c** (166 mg, 25%). Compounds **25c**, **27c** and **24c** were recrystallized from methanol. **24c**: mp 156–157 °C (orange needles); ^{1}H NMR (60 MHz, $CDCl_3$) δ 8.03 (m, 4 H), 7.67 (m, 4 H), 3.94 (s, 6 H), −0.55 (t, 2 H), −1.14 (t, 2 H); UV (CH_2Cl_2) 515 (933), 392 (6311), 307 (102454) nm; MS (70 eV), *m/e* (rel intensity) 334 ($M^{\bullet+}$, 30), 215 ($M^{\bullet+} - 2CO_2CH_3 - H$, 100). **25c**: mp 131–132 °C (orange needles); ^{1}H NMR (60 MHz) δ 8.65 (s, 1 H), 8.52 (s, 1 H), 7.79 (m, 4 H), 4.09 (s, 6 H), −0.40 (t, 2 H), −0.99 (quart, 1 H), −1.38 (quart, 1 H); UV (CH_2Cl_2) 520 (3214), 417 (7127), 327 (71272) nm; the MS spectrum is identical with that of **24c**; exact mass calcd for $C_{21}H_{18}O_4$ 334.1213, found 334.1211. **27c**: ^{1}H NMR (60 MHz, $CDCl_3$) δ 8.73 (s, 1 H), 8.64–7.57 (m, 7 H), 4.07 (s, 3 H), 3.93 (s, 3 H), −0.46 (t, 2 H), −1.08 (quart, 1 H), −1.21 (quart, 1 H).

2,5-Bis(hydroxymethyl)-1,6;8,13-propanediylidene[14]annulene (25d). To a magnetically stirred solution of the diester **25c** (334 mg, 1 mmol) in 30 mL of dry toluene at −10 °C was added dropwise 3.7 mL of a 1.2 M solution of diisobutylaluminum hydride in toluene (4.4 mmol). After the mixture stirred for 1 h at room temperature, 30 mL of ether, 1 mL of H_2O, 1 mL of $NaOH/H_2O$ (10 vol %), and 1 g of sodium sulfate were added. Solid material was removed by filtration and washed with ether. The combined organic layers were dried over $MgSO_4$, and the solvent was evaporated. One obtained 236 mg (85%) of the diol **25d**, which was recrystallized from methyl acetate/hexane. **25d**: mp 142–143 °C (orange needles); ^{1}H NMR (60 MHz, $CDCl_3/CD_2Cl_2$, 1:1) δ 8.05 (s, 2 H), 7.70 (m, 4 H), 7.51 (s, 2 H), 5.12 (d, 4 H), 1.97 (t, 2 H), −0.50 (t, 2 H), −0.99 (quart, 1 H), −1.25 (quartz, 1 H); MS (70 eV), *m/e* (rel intensity) 278 ($M^{\bullet+}$, 90), 215 ($M^{\bullet+} - 2CH_2OH - H$, 100); exact mass calcd for $C_{19}H_{18}O_2$ 278.1310, found 278.1309.

7,14-Bis(hydroxymethyl)-1,6;8,13-propanediylidene[14]annulene (24d). The diester **24c** (334 mg, 1 mmol) was reduced as described above. One obtained 102 mg (73%) of the diol **24d**, which was recrystallized from chloroform/hexane. **24d**: mp 234 °C (orange needles); ^{1}H NMR (60 MHz, CD_2Cl_2) δ 8.26 (m, 4 H), 7.71 (m, 4 H), 5.15 (s, 4 H), 3.67 (s, 2 H), −0.58 (t, 2 H), −1.28 (t, 2 H); MS (70 eV), *m/e* (rel intensity) 278 ($M^{\bullet+}$, 100), 215 ($M^{\bullet+} - 2CH_2OH\text{-}H$, 80), 202 (68).

2,5-Bis(bromomethyl)-1,6;8,13-propanediylidene[14]annulene (25e). To a magnetically stirred solution of the diol **25d** (139 mg, 0.5 mmol) in 20 mL of dry ether (containing a few drops of pyridine) at 0 °C was added freshly distilled phosphorous tribromide (95 mg, 0.35 mmol in 5 mL of ether) under an argon atmosphere. The solution was stirred at 0 °C for 1 h and at room temperature for 3 h. Ice water (20 mL) was added, the layers were separated, and the aqueous layer was extracted with ether. The combined organic layers were washed 3 times with cold $NaHCO_3$ solution (5% in H_2O) and cold water. After the mixture was dried with $MgSO_4$, the ether was evaporated. One obtained 172 mg (86%) of dibromide **25d** as an orange solid which was used for further reactions without purification. **25e**: ^{1}H NMR (60 MHz, $CDCl_3$) δ 8.09 (s, 2 H), 7.77 (m, 4 H), 7.65 (s, 2 H), 5.28 (m, 4 H), −0.46 (t, 2 H), −0.97 (quart, 1 H), −1.10 (quart, 1 H); MS, see **24c**.

7,14-Bis(bromomethyl)-1,6;8,13-propanediylidene[14]annulene (24e). **24e** was prepared from **24d** according to the above procedure. The yield of the raw dibromide (orange solid) was 61%. **24e**: ^{1}H NMR (60 MHz, $CDCl_3$) δ 8.14 (m, 4 H), 7.72 (m, 4 H), 4.91 (s, 4 H), −0.47 (t, 2 H), −1.17 (t, 2 H); MS (70 eV), *m/e* (rel intensity) 406, 404, 402 ($M^{\bullet+}$, 12), 325, 323 ($M^{\bullet+} - Br$, 60), 244 ($M^{\bullet+} - 2Br$, 40), 218 ($M^+ - 2CHBr$, 100).

7,14-Dihydro-1,6;8,13-propanediylidene[14]annulene (22a). The annulene **5** (109 mg, 0.5 mmol) was solved in 10 mL of dry THF and 20 mL of liquid ammonia and reduced with 9 mg of lithium at −33 °C (see above). After addition of an excess of methyl chloroformate the red-brown color disappeared instantaneously. The ammonia was allowed to evaporate, 100 mL of hexane was added, and the organic solution was washed with water. After filtration over silica gel (hexane), removal of the solvent, and recrystallization from methanol, one obtained 100 mg (91%) of the dihydroannulene **22a**: mp 103–105 °C (colorless needles); ^{1}H NMR (60 MHz, $CDCl_3$) δ 6.45 (m, 4 H), 5.95 (m, 4 H), 3.52 (m, 4 H), 2.42 (t, 2 H), 2.24 (s, 2 H); UV (CH_2Cl_2) 295 (sh), 257 (8152); MS (70 eV), *m/e* (rel intensity) 220 ($M^{\bullet+}$, 25), 129 (100); exact mass calcd for $C_{17}H_{16}$ 220.1252, found 220.1252.

7,14-Dimethoxy-7,14-dihydro-1,6;8,13-bis(methano)[14]annulene (20) via Quenching of $\mathbf{2}^{2+}/2SbF_6^-$. Finely powdered annulene **2** (103 mg, 0.5 mmol) was added in small portions to a mixture of freshly distilled antimony pentafluoride (1 mL) and fluorosulfuryl chloride (2 mL) at −78 °C under a stream of argon. The red-violet solution of the dication was brought to −20 °C, and 5 mL of methanol was slowly added with stirring. The reaction mixture (whose color turned to brown upon quenching) was allowed to warm to room temperature and was poured into 20 mL of water saturated with $NaHCO_3$. The mixture was extracted 3 times with ether, and the organic layer was washed with water and dried. Evaporation of the solvent and sublimation (150 °C, 0.1 Torr) of the residue gave 30 mg (22%) of the dimethyl ether **20**: mp 79 °C; ^{1}H NMR (90 MHz, CD_3COCD_3) δ 6.37 (m, 4 H), 5.94 (m, 4 H), 4.60 (d, 2 H), 1.42 (d, 2 H), 4.13 (s, 2 H), 3.38 (s, 6 H); UV (dioxane) 233 (28 840), 255 (11 750), 312 (sh) nm; MS (80 eV), *m/e* (rel intensity) 268 ($M^{\bullet+}$, 62), 253 (5), 237 (11), 221 (18), 206 (18), 205 (38), 204 (22), 203 (34).

5,12-Dimethyl-5,12-dihydro-3,7,10,14-tetra-*tert*-butyl-1,8-didehydro-[14]annulene (30b). The annulene **12** (201 mg, 0.5 mmol) in 20 mL of dry THF was reduced with lithium at −78 °C in a sealed glass ampule. When the dianion formation was complete the color of the solution turned to dark red. The ampule was opened under an argon atmosphere, the solution was allowed to warm to −40 °C, and an excess of freshly distilled dimethyl sulfate was added. The solvent was removed under reduced pressure and the residue chromatographed over Alox (neutral, act. II–III, 60 cm, $\phi = 3$ cm). Hexane eluted a red fraction which gave 40 mg of the starting materials and a colorless fraction. After removal of the solvent and recrystallization from methanol one obtained 216 mg (50%) of **30b**: mp 243–244 °C (colorless needles); ^{1}H NMR (60 MHz, $CDCl_3$) δ 5.72 (d, 4 H), 4.67 (m, 2 H), 1.24 (s, 36 H), 1.17 (d, 6 H); ^{13}C NMR (20 MHz, $CDCl_3$) δ 136.6 (C-4, -6, -11, -13), 133.3 (C-3, -7, -10, -14), 94.1 (C-1, -2, -8, -9), 39.4 (C-5, -12), 35.9 (C-3a, -7a, -10a, -14a), 29.9 (CH_3, *tert*-butyl), 23.0 (C-3a, -12a); MS (70 eV), *m/e* (rel intensity) 432 ($M^{\bullet+}$, 8), 417 ($M^{\bullet+} - CH_3$, 4), 402 ($M^{\bullet+} - 2CH_3$, 9), 57 (*tert*-butyl, 100); exact mass calcd for $C_{32}H_{48}$ 432.3756, found 432.3750.

5,12-Dicarbomethoxy-5,12-dihydro-3,7,10,14-tetra-*tert*-butyl-1,8-didehydro[14]annulene (30c) and 5,12-Bis(bromopropyl)-5,12-dihydro-3,7,10,14-tetra-*tert*-butyl-1,8-didehydro[14]annulene (30d). The annulene **12** (201 mg, 0.5 mmol) was reduced and the resulting dianion quenched as described above. The quenching reagents were (a) methyl chloroformate and (b) 3-dibromopropane. (a) Chromatography over Alox (neutral, act. I–II) with hexane/ether (4:1) and recrystallization from methanol gave 145 mg (45%) of the diester **30c**. (b) Chromatography over Alox (neutral, act. III) and recrystallization from methanol gave 120 mg (37%) of the diadduct **30d**. The amount of recovered (reoxidized) starting material was 53 mg. **30c**: mp 227 °C (colorless needles); ^{1}H NMR (60 MHz, $CDCl_3$) δ 5.66 (s, 6 H), 3.72 (s, 6 H), 1.20 (s, 36 H); MS (70 eV), *m/e* (rel intensity) 520 ($M^{\bullet+}$, 13), 463 ($M^{\bullet+}$ − *tert*-butyl, 20), 57 (*tert*-butyl, 100); exact mass calcd for $C_{34}H_{48}O_4$ 520.3575, found 520.3567. **30d**: mp 144–146 °C (colorless needles); ^{1}H NMR (60 MHz, $CDCl_3$) δ 5.45 (d, 4 H), 4.90–4.37 (m, 2 H), 3.47 (t, 4 H), 2.27–1.44 (m, 8 H), 1.20 (s, 36 H); UV (CH_2Cl_2) 275 (12 709), 250 (27 980) nm; MS (70 eV), *m/e* (rel intensity) 648, 646, 644 ($M^{\bullet+}$, 22), 587, 589, 591 ($M^{\bullet+}$ − *tert*-butyl, 29), 531, 533, 535 ($M^{\bullet+}$ − 2*tert*-butyl, 50), 475, 477, 479 ($M^{\bullet+}$ − 3*tert*-butyl, 50); exact mass calcd for $C_{36}H_{54}Br_2$ 646.2572, found 646.2564.

Acknowledgment. We thank the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for financial support.

Investigation of the 2,7-Dihalofluorenylidenes: Search for Heavy Atom Effects in the Reactions of Triplet Carbenes

Stanton F. Rak, Stephen C. Lapin, Daniel E. Falvey, and Gary B. Schuster*

Contribution from the Department of Chemistry, Roger Adams Laboratory, University of Illinois, Urbana, Illinois 61801-3731.

Received March 4, 1987

Abstract: The properties of the 2,7-dihalofluorenylidenes (Cl, Br, I) were examined by laser and EPR spectroscopy and by conventional chemical analyses. Their reactions with alcohols and olefins were studied. No evidence was found for the operation of a heavy atom effect in their reaction with methyl alcohol. Analysis of the kinetic and product results indicates an energy gap between the triplet (ground state) and the singlet for the three dihalofluorenylidenes of 4.2 ± 0.5 kcal/mol, ca. twice the value of fluorenylidene itself.

The keystone of carbene chemistry is spin–specific reactivity. In this model, reactions are identified as originating from the singlet or triplet spin states of a carbene. For example, the well-known Skell–Woodworth hypothesis is used to classify stereospecific cyclopropanation as a reaction of the singlet state while the nonstereospecific outcome is assigned to reaction of the triplet state.[1] Similarly, in reactions with alcohols, singlet carbenes generally are thought to add across the oxygen–hydrogen bond to form ethers[2] (eq 1) and the triplets are believed to abstract hydrogen atoms to create radical pairs (eq 2).[3] This notion of spin-specificity has been challenged by the suggestion that triplet diphenylcarbene (DPC) can add to alcohols to form ethers in a concerted reaction.[4,5] This hypothesis may be tested by searching for an intramolecular heavy atom effect in a series of substituted fluorenylidenes. The results of this investigation are reported herein.

Table I. X-Band EPR Spectra of Carbenes in MTHF Glass at 8 K

carbene	transitions, G	$\lvert D\rvert$, cm^{-1}	$\lvert E\rvert$, cm^{-1}	g_{perp}	g_{par}
CFL	1038 z_1 2156 double quantum 4544 x_2 5685 y_2 7810 z_2	0.4158	0.0287	2.002	2.003
BFL	1014 z_1 2170 double quantum 4550 x_2 5668 y_2 7790 z_2	0.4134	0.0281	2.000	2.002
IFL	963 z_1 4543 x_2 5639 y_2 7747 z_2	0.4088	0.0277	2.000	2.003
DPC	997 z_1 4717 x_2 5491 y_2 7748 z_2	0.4101	0.0196	2.033	2.002

Results

1. EPR Spectroscopy. The most certain way to identify a triplet carbene is to observe its characteristic EPR spectrum. We ir-

---

(1) Skell, P. S.; Woodworth, R. C. *J. Am. Chem. Soc.* **1956**, *78*, 4496.

(2) Kirmse, W. *Liebigs Ann. Chem.* **1963**, *666*, 9. Bethell, D.; Stevens, G.; Tickle, P. *J. Chem. Soc. D* **1970**, 792. Tomioka, H.; Izawa, Y. *J. Am. Chem. Soc.* **1977**, *99*, 6128.

(3) Closs, G. L.; Trifunac, A. D. *J. Am. Chem. Soc.* **1970**, *92*, 2186. Moss, R. A.; Dolling, U.-H. *Ibid.* **1971**, *93*, 954. Baldwin, J. E.; Andrist, A. H. *J. Chem. Soc. D* **1971**, 1512. Roth, H. D. *Acc. Chem. Res.* **1977**, *10*, 85.

(4) Griller, D.; Nazran, A. S.; Scaiano, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 198. Griller, D.; Nazran, A. S.; Scaiano, J. C. *Acc. Chem. Res.* **1984**, *17*, 283. Nazran, A. S.; Griller, D. *J. Am. Chem. Soc.* **1985**, *107*, 4613. Griller, D.; Nazran, A. S.; Scaiano, J. C. *J. Phys. Chem.* **1986**, *90*, 24.

(5) The EPR spectrum of ^{3}BFL has been reported previously: Murahashi, S.-I.; Moritanai, I; Nagai, T. *Bull. Chem. Soc. Jpn.* **1967**, *40*, 1655.