On the π-Electron Distribution in Biphenylene Analogues

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Dedicated to Professor *Edgar Heilbronner* on the occasion of his 80th birthday

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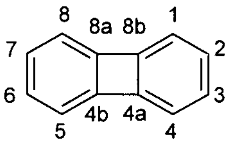
The bonding situation in a series of biphenylene analogues – benzo[*b*]biphenylene and its dication, 4,10-dibromobenzo[*b*]biphenylene, naphtho[2,3-*b*]biphenylene and its dianion, benzo[*a*]biphenylene, (biphenylene)tricarbonylchromium, benzo[3,4]cyclobuta[1,2-*c*]thiophene, benzo[3,4]cyclobuta[1,2-*c*]thiophene 2-oxide, benzo[3,4]cyclobuta[1,2-*c*]thiophene 2,2-dioxide, 4,10-diazabenzo[*b*]biphenylene, biphenylene-2,3-dione, benzo[3,4]cyclobuta[1,2-*b*]anthracene-6,11-dione, and 3,4-dihydro-2*H*-benzo[3,4]cyclobuta[1,2]cycloheptene – where one of the two benzo rings of biphenylene is replaced by a different π-system (B) was investigated on the basis of the NMR parameters of these systems. From the vicinal ^{1}H,^{1}H spin-spin coupling constants, the electronic structure of the remaining benzo ring (A) is derived *via* the *Q*-value method. It is found that increasing tendency of B to tolerate exocyclic double bonds at the central four-membered ring of these systems favors increased π-electron delocalization in the A ring. The analysis of the chemical shifts supports this conclusion. NICS (nucleus-independent chemical shift) values as well as C,C bond lengths derived from *ab initio* calculations are in excellent agreement with the experimental data. The charged systems benzo[*b*]biphenylene dication and naphtho[2,3-*b*]biphenylene dianion (**7**$^{2-}$) are also studied by ^{13}C NMR measurements. The charge distribution found closely resembles the predictions of the simple HMO model and reveals that **7**$^{2-}$ can be regarded as a benzo[3,4]cyclobuta[1,2-*b*]-substituted anthracene dianion. It is shown that the orientation of the tricarbonylchromium group in complexes of benzenoid aromatics can be derived from the vicinal ^{1}H,^{1}H coupling constants.

Introduction. – Since its successful synthesis [1], biphenylene (**1**), the first stable derivative of cyclobutadiene, has found considerable interest (for reviews, see [2]). Structural investigations by X-ray [3] and electron diffraction [4], as well as the determination of ^{1}H,^{1}H spin-spin coupling constants [5], soon showed that, despite overall π-electron delocalization, the benzo part of **1** displays a significant alternation of C,C bond lengths ($R(1,8b) = 137.2$, $R(1,2) = 142.8$, $R(2,3) = 137.0$ pm [4]). From the various resonance structures, those with exocyclic C=C bonds at the central four-membered ring are thus dominating [6], a conclusion supported also by the results of recent measurements of the ^{13}C chemical-shift tensor [7].



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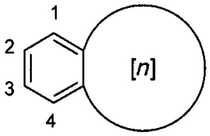
With respect to the NMR properties, it was of interest that the protons of **1** are more shielded by *ca.* 0.5 ppm than those of benzene despite the presence of two benzo units. Two alternative explanations were considered: *1*) a reduction of the diatropicity of the benzo units in **1** due to partial bond fixation, or *2*) the presence of a paramagnetic ring current in the central four-membered ring that partially quenches the diamagnetic currents in the outer rings [8]. Experimental results and theoretical investigations of the ^{1}H chemical shifts [9] led to the conclusion, that **1** sustains a paramagnetic ring current in the central four-membered ring, affecting the $\delta(^1\mathrm{H})$ values in the manner typical for [4*n*]-π-systems [10] with shielding for δ(1,4-H) and δ(2,3-H). Notwithstanding bond alternation (R(4a,4b) = 152.4, R(4a,8b) = 143.2 pm [4]), the high intensity expected for an unperturbed cyclic [4*n*]-π-system with equal bond lengths [10a] thus leads to a measurable effect on the ^{1}H resonances. Furthermore, the shielding is larger for 1,4-H than for 2,3-H, while, for a purely diatropic molecule, the second benzo ring should induce the reverse order, an argument which, however, is not unambiguous, as we show later. In line with the NMR observations is the fact that the diamagnetic susceptibility exaltation of **1** is not larger than that of benzene and only half as large as that of naphthalene or diphenyl [11]. In addition, the calculation of NICS (nucleus-independent chemical shift) values yields paratropism and reduced diatropism for the four- and six-membered rings of **1**, respectively [12].

Apart from the $\delta(^1\mathrm{H})$ values, vicinal ^{1}H,^{1}H spin-spin coupling constants are important indicators for the electronic structure of cyclic π-systems. They correlate, as was shown by *Karplus* [13], with the C,C bond length and, therefore, also with the π-bond order [14]. Empirical investigations have established this relation for unsaturated five-, six-, and seven-membered ring systems (for a review, see [15]). On this basis, we introduced the *Q*-value method for benzo[*n*]annulenes (**2**) [16] (for applications of the *Q*-value method, see [17]), which allows characterization an annulene *via* the ratio of the PPP SCF [18] π-bond orders, $P(\mu,\nu)$(PPP), of its benzo derivative **2**, where the $P(\mu,\nu)$(PPP) data are determined empirically from the vicinal ^{1}H,^{1}H coupling constants using the relation

$$P(\mu,\nu)(\mathrm{PPP}) = 0.104\ ^3J(^1\mathrm{H},^1\mathrm{H}) - 0.120 \qquad (1)$$

With *Eqn. 1*, one calculates $P(1,2)$ and $P(2,3)$ and $Q = P(1,2)/P(2,3)$, which now characterizes the free annulene: $Q < 1.0$ for delocalized [4*n*]-π-systems, which induce a bond alternation of $R(1,2) < R(2,3)$ in the benzoring, $Q > 1.1$ for delocalized [4*n* + 2]-π-systems which induce $R(1,2) > R(2,3)$, and $1.0 < Q > 1.1$ for localized (olefinic) π-systems with $R(1,2) \approx R(2,3)$. For **1**, this approach leads to a *Q* value of 0.849 [17f], which characterizes benzocyclobutadiene as a delocalized [4*n*]-π-system.



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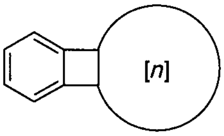

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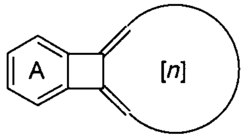

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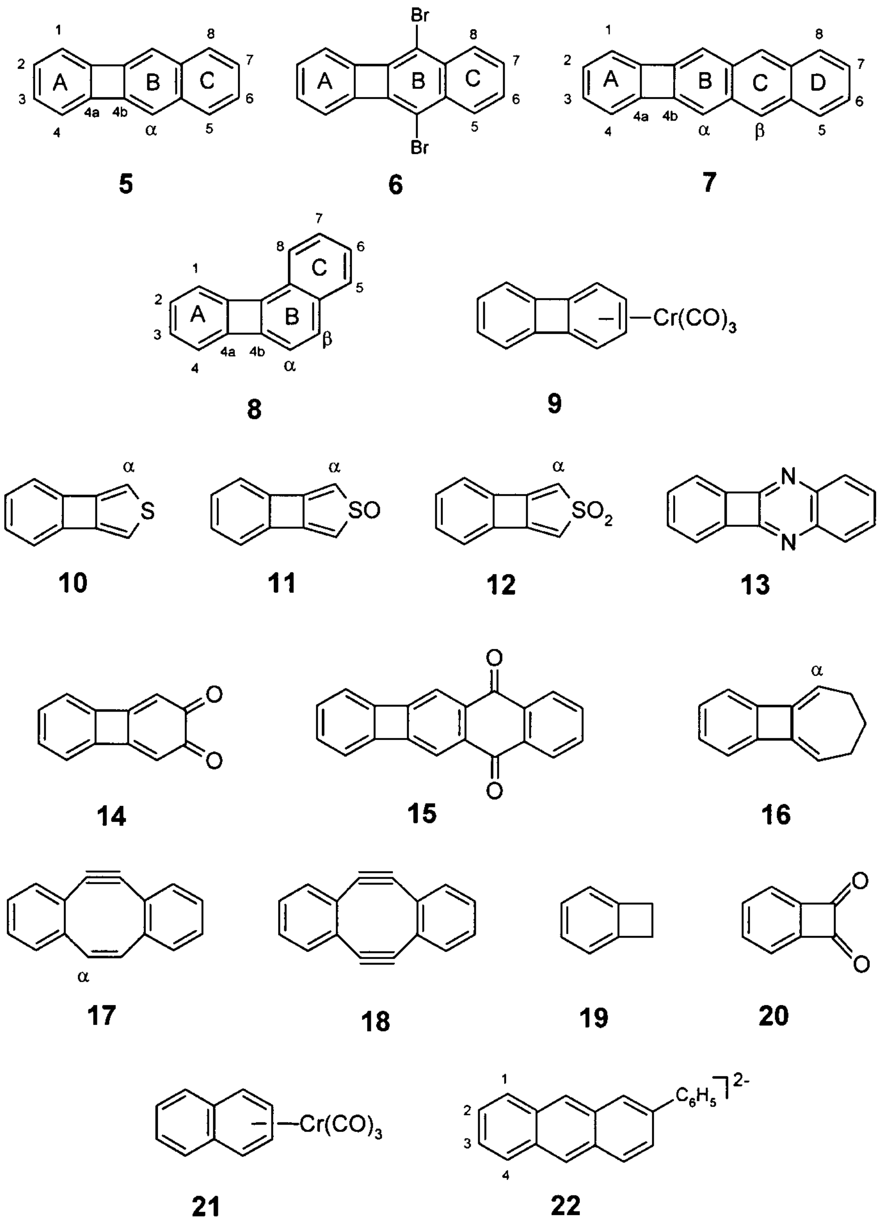
For biphenylene analogues such as **3**, in which one benzo ring in **1** is replaced by a π-system, which tolerates exocyclic C=C bonds at the central four-membered ring more readily then benzene, (**4**), we expect increasing *Q*-values for the remaining benzo ring because of increasing $[4n+2]$-π-delocalization. With this aspect in mind, we investigated, on the basis of complete spectral analyses and chemical-shift assignments, the ^{1}H-NMR spectra of benzo[*b*]biphenylene (**5**), 4,10-dibromobenzo[*b*]biphenylene (**6**), naphtho[2,3-*b*]biphenylene (**7**), benzo[*a*]biphenylene (**8**), (biphenylene)tricarbonylchromium (**9**), benzo[3,4]cyclobuta[1,2-*c*]thiophene (**10**), benzo[3,4]cyclobuta-[1,2-*c*]thiophene 2-oxide (**11**), benzo[3,4]cyclobuta[1,2-*c*]thiophene 2,2-dioxide (**12**), benzo[3,4]cyclobuta[1,2-*b*]quinoxaline (**13**), biphenylene-2,3-dione (**14**), benzo[3,4]-cyclobuta[1,2-*b*]anthracene-6,11-dione (**15**), and 3,4-dihydro-2*H*-benzo[3,4]cyclobuta[1,2]cycloheptene (**16**) (*Scheme*) and the charged systems $\mathbf{5}^{2+}$ and $\mathbf{7}^{2-}$, obtained from the parent hydrocarbon by oxidation with SO_2ClF/SbF_5 and reduction with Li, respectively. 1,2,5,6-Dibenzocyclooct-3-en-7-yne (**17**), a homologue of **1**, was also included in connection with earlier studies of 1,2,5,6-dibenzocyclooctadiyne (**18**) [17d]. The results are also of interest with respect to the electronic structure of the recently described phenylenes (for a review, see [19]).

Results. – The data obtained by spectral analysis are collected in *Table 1*, where the atom numbering is according to the *Scheme. Table 2* contains data of the reference systems used in the *Discussion*: **1**, cyclobutabenzene (**19**), cyclobutabenzene-1,2-dione (**20**), (naphthalene)tricarbonylchromium (**21**), and 2-phenylanthracene dianion (**22**; see *Scheme*). Details of the spectral analyses are given in the *Exper. Part*. We mention here, however, that unambiguous experimental assignment of the resonance frequencies was achieved in nearly all cases. In addition to the analysis of ^{13}C satellite spectra [17b], most easily done *via* inverse 2D-^{13}C,^{1}H shift-correlation experiments of the HMQC-type [20] (for reviews, see [20d]) (*cf. Exper. Part*), the magnitude of the one-bond ^{13}C,^{1}H coupling constants is a useful parameter in the present case because strain effects introduced by the central four-membered ring yield $^1J(1,^1\mathrm{H}) > {}^1J(2,^1\mathrm{H})$. This is the consequence of hybridization changes and is most clearly seen from the results obtained for cyclopropabenzene ($^1J(1,^1\mathrm{H}) = 168.5$ Hz, $^1J(2,^1\mathrm{H}) = 159.0$ Hz [21]). The reference values for the parent system **1** are $^1J(1,^1\mathrm{H}) = 163.3$ Hz and $^1J(2,^1\mathrm{H}) = 159.7$ Hz [22]. The determination of these data was based in most cases on inverse ^{13}C,^{1}H shift correlations as exemplified in *Fig. 1*. In addition, NOESY spectra [23] proved useful to establish the $\delta(^1\mathrm{H})$ assignment.

Discussion. – 1. *The* Q *Values.* For the determination of the *Q* values, the coupling constants ^3J(1-H,2-H) and ^3J(2-H,3-H) in the benzo part of **5**–**21** were corrected for strain effects introduced by the four-membered ring, which are also documented by the ^{13}C shielding-tensor measurements [7]. Comparison of the data for **19** [24] and benzene ($^3J = 7.54$ Hz [26]) yields increments of -0.18 Hz for ^3J(1-H,2-H) and $+0.24$ Hz for ^3J(2-H,3-H), which are entirely due to the strain effect. The empirical bond-order data derived from the corrected ^3J values and the *Q* values are shown in *Table 3*. Included are theoretical *Q* values from the *ab initio* calculations (see below).

Starting with the homologues **1**, **5**, and **7**, the series of the *Q* values 0.894, 0.914, 0.975 (calc. 0.84, 0.88, 0.92) documents the increasing tendency to integrate exocyclic C=C

Scheme



bonds at the central four-membered ring into the B Ring of the annelated acene. This is in complete agreement with the known bond alternation in naphthalene and anthracene [27]. For the Br derivative **6**, this tendency is even somewhat stronger than for the hydrocarbon, possibly as a result of an inductive effect of the halogen atoms.

Table 1. *^{1}H Chemical Shifts δ* (ppm, rel. to TMS) *and ^{1}H,^{1}H coupling constants* (Hz) *of* **1**, **5**–**17**, $\mathbf{5}^{2+}$, *and* $\mathbf{7}^{2-}$/2 Li$^+$

A Ring	δ(1,4)	δ(2,3)	*J*(1,2)	*J*(1,3)	*J*(1,4)	*J*(2,3)	RMS a)	MHz b)	Solvent/conc. [M]							
5	6.937	6.960	7.13	0.81	1.09	8.12	0.05	400	$CDCl_3$/0.03							
6 c)	6.900	6.807	7.16	0.84	0.99	8.01	0.04	100	C_6D_6/CS_2 1 : 1/0.16							
7	7.075	7.104	7.36	0.78	1.16	7.94	0.06	400	CD_2Cl_2/0.04							
9	6.348	6.547	7.16	0.83	1.02	8.18	0.05	100	C_6D_6/0.25							
10	6.643	6.703	7.08	0.84	1.02	8.14	0.04	100	C_6D_6/CS_2 3 : 1/0.33							
	6.862	6.920						400	$CDCl_3$/0.12							
11	7.528	7.558	7.66	0.82	1.14	7.73	0.03	400	$CDCl_3$/0.04							
12	7.663	7.690	7.79	0.82	1.16	7.70	0.04	400	$CDCl_3$/0.09							
13	7.428	7.295	7.41	0.80	1.11	7.84	0.06	100	$CDCl_3$/0.04							
14	7.640 d)	7.640 d)	7.45	0.81	1.24	7.65	0.06	400	$CDCl_3$/0.02 + Eu(fod)$_3$/0.004							
15	6.923	6.982	6.67	0.86	0.99	8.34	0.08	400	$CDCl_3$/0.014							
16	7.137	7.115	7.40	0.79	1.25	7.69	0.04	400	$CDCl_3$/0.01							
$\mathbf{5}^{2+}$	9.55	9.78	8.14	0.90	1.39	6.91	0.03	400	SbF_5/SO_2ClF 1 : 1/0.15							
$\mathbf{7}^{2-}$/2 Li$^+$	5.014	5.103	5.88	0.90	1.40	6.39		400	Et_2O/0.04							
B,C,D Ring	δ(α)	δ(β)	δ(5,8)	δ(6,7)	*J*(5,6)	*J*(5,7)	*J*(5,8)	*J*(6,7)	RMS a)							
5	6.95		7.477	7.264	7.95	1.38	0.57	7.12	0.07							
6			7.792	7.329	8.23	1.26	0.54	7.16	0.02							
7	7.106	7.969	7.839	7.414	8.33	1.32	0.72	6.72	0.10							
9			4.672	4.345	5.90	0.72	0.99	6.54	0.05							
10	6.22															
11	6.69															
12	6.45															
13			7.657	7.396	8.03	1.49	0.46	7.24	0.04							
14	6.55															
15	7.486		8.243	7.773	7.89	1.19	0.58	7.31	0.05							
16	5.90															
$\mathbf{5}^{2+}$	9.86		9.55	9.78	8.65	0.77	1.15	7.73	0.07							
$\mathbf{7}^{2-}$/2 Li$^+$	3.425	2.404	3.969	4.746	6.76	1.54	0.86	6.80								
	δ(1)	δ(2)	δ(3)	δ(4)	*J*(1,2)	*J*(1,3)	*J*(1,4)	*J*(2,3)	*J*(2,4)	*J*(3,4)				RMS a)	MHz b)	Solvent/conc. [M]
8	6.542	6.596	6.570	6.429	6.60	0.77	0.95	8.39	0.83	6.62				0.03	400	$CDCl_3$/0.3
17	6.517	6.837	6.883	6.667	7.50	1.42	0.42	7.59	1.20	7.73				0.05	400	(D_6)Acetone/0.1
	δ(α)	δ(β)	δ(5)	δ(6)	δ(7)	δ(8)	*J*(α,β)	*J*(5,6)	*J*(5,7)	*J*(5,8)	*J*(6,7)	*J*(6,8)	*J*(7,8)			
8	6.950	7.350	7.418	7.261	7.173	7.538	7.81	8.39	1.75	0.80	6.88	1.21	8.43	0.12	400	
17	5.449	5.449														

a) Root-mean-square error between calculated and observed transitions. b) NMR Frequency used. c) δ(^{1}H) Assignment may be interchanged. d) Degenerate in CS_2 at δ = 7.64 ppm; spectral analysis was performed after addition of Eu(fod)$_3$; the induced shift difference was 74.2 Hz.

Noteworthy is the low *Q* value for the angular annelated system **8**, which is even smaller than the *Q* value for **1**. The resonance structure given for **8** (see *Scheme*) is thus less favorable then the corresponding structure for **1**. This is reasonable when one realizes that the C,C bond-length change involved is larger for **8** then for **1** because *R*(1,2) in naphthalene is shorter then the benzene C,C bond. Similarly, according to a different view, in **1** the resonance energy of benzene is lost, while in **8** the larger resonance energy of naphthalene is involved (150 *vs.* 259 kJ/mol [28] or 0.39 *vs.* 0.55 *β*-units [29]). The *π*-electron delocalization in the A ring of **8** is thus more strongly perturbed than in all other systems, including **1**.

The *Q* values of the C and D rings of **5**, **6**, and **7** (*Table 3*) are somewhat smaller than the *Q* values of naphthalene (1.252 [17g]) and anthracene (1.361 based on 8.55 and 6.59 Hz for ^3J(1,2) and ^3J(2,3), resp. [30]). This confirms the partial bond fixation in the

Table 2. *^{1}H-NMR Data: δ(^{1}H)/ppm and J(^{1}H,^{1}H)/Hz of Model Compounds* **1** *and* **18**–**22**

	$\delta(1,4)$	$\delta(2,3)$	$J(1,2)$	$J(1,3)$	$J(1,4)$	$J(2,3)$		Ref.
1	6.59	6.69	6.87	0.82	1.04	8.34		[21]
18	6.664	6.848	7.61	1.28	0.54	7.87		[17d]
19	6.764	6.907	7.36	0.98	1.06	7.78		[24]
20	8.080	7.856	7.71	0.77	1.24	7.15		[24]
21[a])	6.901	6.765	8.62	1.20	0.62	6.73		this work
	$\delta(5,8)$	$\delta(6,7)$	$J(5,6)$	$J(5,7)$	$J(5,8)$	$J(6,7)$		
21	5.309	4.674	6.73	1.11	0.28	6.07		this work
	$\delta(1)$	$\delta(2)$	$\delta(3)$	$\delta(4)$	$J(1,2)$	$J(2,3)$	$J(3,4)$	
22[b])	4.13	4.77	4.86	4.16	7.17	6.98	7.27	[25]

[a]) $J(5,6) = 8.28$, $J(6,7) = 6.85$ Hz for naphthalene [30]. [b]) Long-range couplings were not resolved.

B ring of these systems which leads to more equal bond lengths in the C and D ring, respectively. In other words, resonance structures such as **5a** and **7a** gain more weight. The angular annelated system **8**, on the other hand, does not show a significant *Q* value

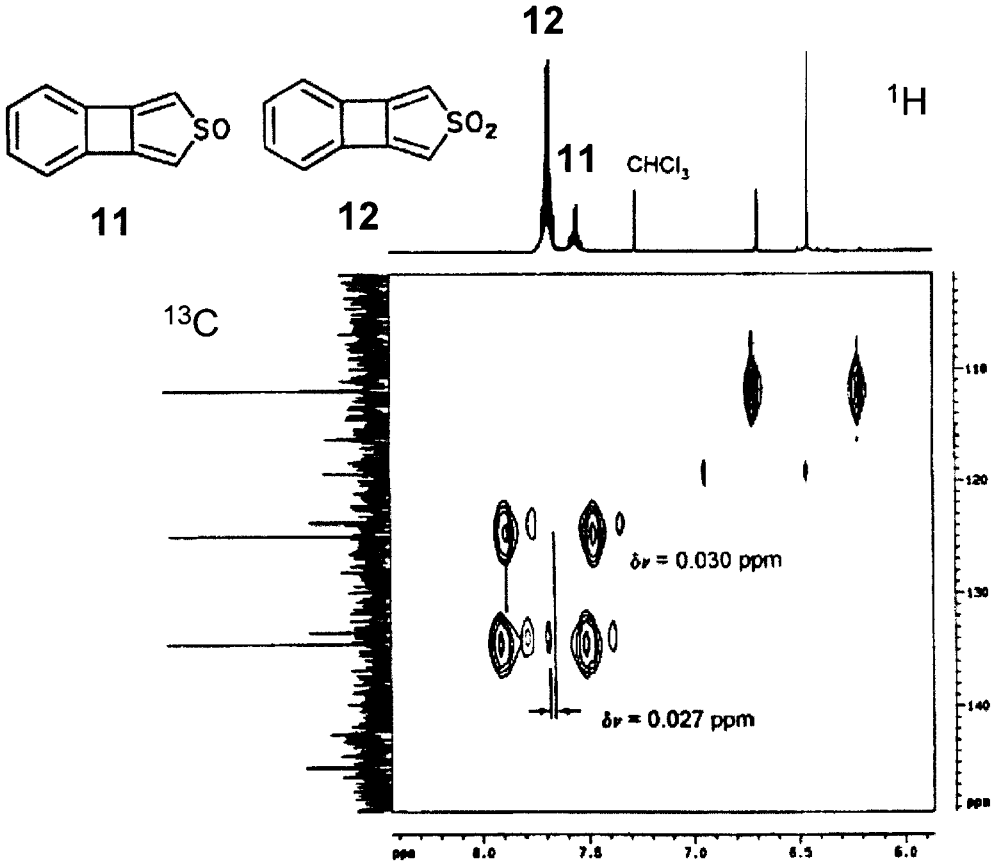


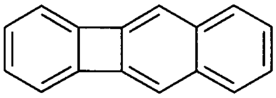
Fig. 1. *100/400-MHz Inverse ^{13}C,^{1}H shift correlation for* **11** *and* **12** (for data, see *Table 1* and *Exper. Part*)

Table 3. *Empirical PPP-SCF* π*-Bond Orders Calculated from the Vicinal* $^1H,^1H$ *Coupling Constants of* **1**, **5**–**17**, $\mathbf{5}^{2+}$ *and* $\mathbf{7}^{2-}$ *after Correction of* $^3J(1,2)$ *and* $^3J(2,3)$ *for Strain Effects and Resulting* Q *Values as well as* Q′ *Values from* ab initio *Calculations* (see text)

	P(1,2)	*P*(2,3)	*Q* A-Ring	*Q′* A-Ring	*P*(5,6)	*P*(6,7)	*Q* C or D Ring	*Q′* C or D Ring
1	0.613	0.722	0.849	0.84				
5	0.640	0.700	0.914	0.88	0.707	0.620	1.140	1.11
6	0.634	0.688	0.922		0.736	0.625	1.178	
7	0.664	0.681	0.975	0.92	0.746	0.579	1.288	1.21
8	0.585	0.728	0.804	0.81	0.753	0.596	1.263	1.23
	0.587[a])		0.806		0.757[b])		1.270	1.21
9	0.643	0.706	0.911					
10	0.635	0.702	0.905	0.88				
11	0.695	0.659	1.054	0.95				
12	0.709	0.656	1.081	0.96				
13	0.669	0.670	0.999		0.715	0.633	1.129	
14	0.674	0.651	1.035					
15	0.592	0.722	0.820		0.701	0.640	1.095	
16	0.668	0.655	1.020					
17	0.660	0.669	0.987					
	0.684[a])		1.022					
$\mathbf{5}^{2+}$	0.745	0.574	1.298		0.780	0.684	1.140	
$\mathbf{7}^{2-}$	0.510	0.520	0.981		0.583	0.587	0.993	

[a]) $P_{3,4}$. [b]) $P_{7,8}$.

change in the C ring in comparison to naphthalene. This supports the conclusion from above that strong bond fixation in the sense of **8**, which would relieve the 'stress' on the A-ring π-system, is less important then one might expect.



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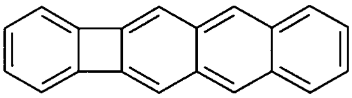

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It was of interest to calculate NICS values for **1**, **5**, **7**, and **8**, since these parameters had been introduced in 1996 by *Schleyer et al.* [12] to characterize the shielding properties of cyclic π-systems. Typical NICS values are *ca.* -12 to -10 ppm for benzene, and *ca.* $+25$ ppm for (rectangular) cyclobutadiene. We have applied the GAUSSIAN program system [31] with GIAO (magnetically gauge-independent) G6-311** (Gaussian triple valence polarized) basis sets. Concerning negative ions, additional diffuse basis functions are definitely necessary in the gas phase; however, since we want to compare the calculated values with solution measurements, it seems recommendable not extend the basis sets. Both the *Hartree-Fock* (HF) and the B3LYP (hybrid *Hartree-Fock* and density functional) approximations were used [32]. The geometric structures of the molecules were optimized at first, and then the NICS values were determined at the geometric centers of the rings. Typically, the B3LYP values are by *ca.* 1 to 2 units larger than the HF values. Therefore, we give only the mean HF/B3LYP values in *Table 4*.

Table 4. *NICS Values* [ppm] *for* **1**, **5**, **7**, **8**, **10**–**12**, $\mathbf{1}^{2+}$, *and* $\mathbf{1}^{2-}$. Positive values represent paratropic ('antiaromatic') units, negative values diatropic ('aromatic') units.

	A Ring	Four-membered ring	B Ring	C Ring	D Ring
1	−4	+18	−4		
5	−9	+15	−5	−3	
7	−7	+13	−1	−10	−8
8	−2	+21	−7	−7	
10	−7	+13	−9		
11	−8	+6	−5		
12	−7	+5	−5		
$\mathbf{1}^{2+}$	−4	−2	−4		
$\mathbf{1}^{2-}$	−11	−20	−11		

Those values differ by *ca.* 1 to 2 units from the values obtained by *Schleyer et al.* [12] with smaller basis sets at the HF level. According to the respective accuracy and validity of the theoretical data, we do not present digits after the decimal point.

The results for **1** agree with those already obtained [12] and show the strong paratropism in the central four-membered ring as well as the reduced diatropism in the outer six-membered rings. Weak and strong diatropism is calculated for the dication, $\mathbf{1}^{2+}$, and the dianion, $\mathbf{1}^{2-}$, respectively, in agreement with our NMR results [17f]. Of special interest is the trend observed for the NICS values of the four-membered ring in the hydrocarbons **1**, **5**, **7**, and **8**. In line with the conclusions drawn above from the Q values the paratropic properties are reduced in the series **1**–**5**–**7**, but increase again for the angular system **8**, which has the largest positive NICS value. This confirms earlier results based on LCAO calculations [8][9]. The different effect of linear and angular benzo annelation has also been deduced by *Barton* and *Rowe* [33] for **8** and a number of related systems from chemical-shift measurements and the consideration of $^3J(\alpha,\beta)$.

It was also of interest to calculate bond lengths on the basis of the empirical relationship between C,C bond lengths and vicinal ^{1}H,^{1}H coupling constants in six-membered rings [30],

$$R(\mu,\nu) = [56.65 - {}^3J(^1\mathrm{H},^1\mathrm{H})]/35.10 \qquad (2)$$

The C,C bond length $R(1,2)$ and $R(2,3)$ for **1**, **5**, **7**, and **8** given in *Table 5* are in good agreement with the data available from electron diffraction, X-ray results, and *ab initio* calculations. The shortening of $R(1,2)$ and the lengthening of $R(2,3)$ as a consequence of the change in electronic structure is thus well established. The average values (pm) calculated by the *ab initio* methods are 142.5, 141.8, 141.0, 140.5 for $R(1,2)$ and 137.4, 137.9, 138.6, 139.0 for $R(2,3)$ for **8**, **1**, **5**, and **7**, respectively, in excellent agreement with the NMR results.

As compared to **1**, we find a significant increase of the Q value for the tricarbonylchromium complex **9**. The question of whether (benzene)tricarbonylchromium has alternating C,C bond lengths has been frequently discussed [35] and experimental findings support a small alternation [36]. The present observation points in the same direction because the larger Q value means more bond alternation in the coordinated ring than in the remaining benzo ring of **9**. The Q value of the B ring cannot be used as an argument because complexation affects the coupling constants, and quantitative data for a correction of this influence are not available. The strong

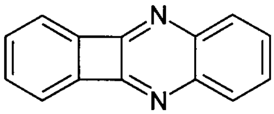
Table 5. *C,C Bond Lengths* [pm] *of* **8**, **1**, **5**, *and* **7** *in the A Ring Calculated from the* $^3J(^1H,^1H)$ *Data in* Table 1 (*A*), *from Electron Diffraction* [4] *and X-Ray* [3][34] *Data* (B, available for **1** and **5** only), *and from the* ab initio G6-311** *Calculations* (*C*, upper/lower entry: HF/B3LYP)

	A				*B*		*C*			
	8	**1**	**5**	**7**	**1**	**5**	**8**	**1**	**5**	**7**
R(1,2)	142.5	141.8	141.1	140.4	142.2	138.7	142.8	141.8	140.7	140.1
					142.8		142.3	141.9	141.2	140.9
R(2,3)	137.5	137.6	138.3	138.8	138.2	138.5	136.4	137.1	138.0	138.5
					137.0		138.3	138.7	139.2	139.5
Ref.					[3][4]	[34]				

difference between the π-electron structures of the (benzocyclobutene)tricarbonylchromium 8π partial structure of **9** and the (benzene)tricarbonylchromium 6π partial structure of the tricarbonyl(naphthalene)chromium complex **21** is, however, apparent from the Q values found in the unsubstituted rings, where we find, on the basis of the data for $^3J(1,2)$ and $^3J(2,3)$ (*Table 2*), a value of 1.338 for **21**. In **9**, the A ring is associated with a $[4n]$-π-system, in **21**, however, with a $[4n+2]$-π-system.

Another series of interest are the heterocycles **10**–**12**. With $Q = 0.905$, **10** clearly shows $[4n]$-π-character for the thiophene-annelated cyclobutadiene partial structure. This means, on the other hand, that the C=C bonds in the thiophene ring are delocalized, and that thiophene has benzene-like properties, a fact long known indeed [37]. Sulfur oxidation considerably quenches delocalization in the heterocyclic 6π-system, and the Q values of 1.054 and 1.081 indicate a stabilization of olefinic *exo*-dimethylidene structures **11** and **12** for the oxide and the dioxide, respectively. This is also reflected in the well-known *Diels-Alder* reactivity of both systems [37]. The NICS values calculated for these systems (*Table 4*) as well as the calculated Q values (*Table 3*) fully support our interpretation. They show a drastic reduction of the paramagnetic properties of the central four-membered ring in going from **10** to the oxidized systems **11** and **12**, which are closely related.

In case of **13** and **14**, the heteroatoms favor bond fixation in the B ring in the sense of structure **4** and the Q values are in the region typical for olefinic systems like **16** that serves here as a model for structure **4**. The Q value for the C ring of **13** is lower than that obtained for phenazine (1.343) from the reported coupling constants of $^3J(1,2) = 8.61$ and $^3J(2,3)$ of 6.70 Hz [38]. This points again to the relative importance of resonance structure **13a** analogous to **5a** and **7a** above. The structure **15**, on the other hand, is characterized by its Q value as a 2,3-disubstituted biphenylene, the C=O groups effectively seperating the biphenylene partial structure from the C ring.



13a

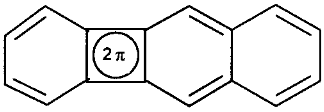
From the charged species obtained by reduction of the hydrocarbons with Li, the dianions $\mathbf{5}^{2-}$ and $\mathbf{7}^{2-}$ show, as the parent system $\mathbf{1}^{2-}$, four-membered ring-opening reactions [17f][39] to the corresponding 2-lithioarene-2′-lithiophenyl compounds. However, as in the case of $\mathbf{1}^{2-}$ and contrary to the situation found for $\mathbf{5}^{2-}$, the half-life of $\mathbf{7}^{2-}$ is sufficient to investigate its NMR spectrum.

In the case of **5**, we thus investigated the stable dication $\mathbf{5}^{2+}$, a 14π electron system, which yields Q values of 1.298 and 1.140 in the benzo and the naphthalene partial structure, respectively. This indicates stronger bond fixation in the A ring than in the hydrocarbon, which, in addition, is reversed ($R(1,2) < R(2,3)$). The central four-membered ring of $\mathbf{5}^{2+}$ thus sustains a diatropic dication as in **23**. An analogous electronic structure was suggested for $\mathbf{1}^{2+}$ where the Q value amounts to 1.431 [17f].

The dianion $\mathbf{7}^{2-}$ yields Q values of 0.981 and 0.993 in the A and D ring, respectively, which characterize the annelated rings as $[4n]$-π-systems. This is surprising, since we deal with a system of 22π electrons that should show diatropic $[4n+2]$ properties. The dianion $\mathbf{7}^{2-}$ apparently does not sustain a diatropic dianion in the four-membered ring as in **24**, but must be described as a 3,4-benzocyclobuta[1,2-*b*]-annelated anthracene dianion **25**. The A ring is thus connected to a paratropic 16π electron system. This interpretation is strongly supported by the chemical shifts, as we show later. For 2-phenylanthracene dianion (*Table 2*), we find $Q = 1.033$ and 1.050 in the A ring. Both results support the $C_{14}H_8^{2-}$ partial structure for $\mathbf{7}^{2-}$.

2. *Chemical Shifts.* We now turn to the ^{1}H chemical shifts as a second indicator of π-electron structure, which formed the basis of most of the earlier investigations of the bonding situation in **1** and related systems [8][9][33]. In this context, two aspects are of importance: *1*) the shielding in comparison to $\delta(^1H)$ in benzene as a diatropic 6π-electron system, and *2*) the relative position of the 1,4-H and 2,3-H resonance in the A ring.

Fig. 2 shows the chemical-shift data for the A ring of **1**, **5**, and **7**–**16** in the order of increasing Q values. The data for **6** and **9**, where C_6D_6 was used as co-solvent or solvent, and where the assignment is uncertain, are not included because of the possibility of solvent shifts. An independent ^{1}H-NMR study, however, exists for **9** [40], in which the more inert solvent acetone was used. These results (δ(1,4-H) = 6.936 ppm, δ(2,3-H) = 6.985 ppm), which were confirmed by specific deuteration, are thus included in *Fig. 2*. For **10**, we used the data measured in $CDCl_3$, for **8** δ(4-H) was used because 1-H is deshielded by ring C.



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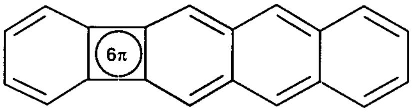

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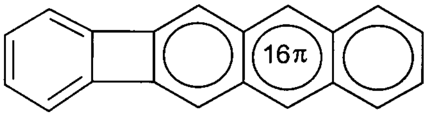

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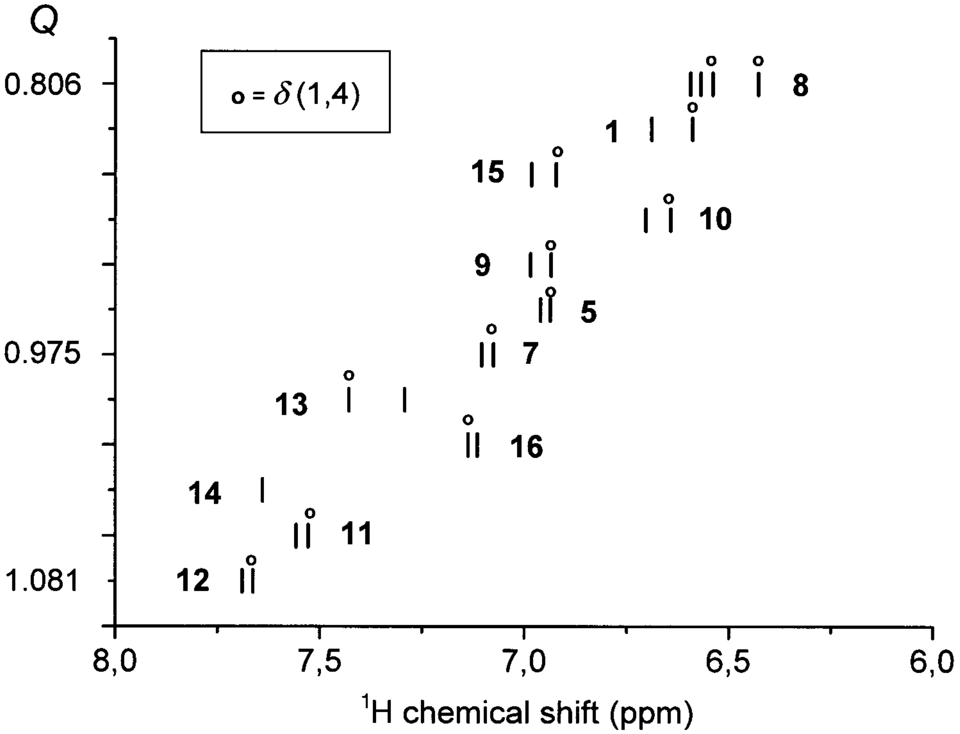


Fig. 2. *Graphical representation of the* ^1H *chemical shifts of* **1**, **5**, **7**–**16**, *and* **19** (note that the *Q* scale is not linear)

As expected, a general low-field shift is observed with increasing stabilization of structure **4**. Less bond fixation in the A ring thus increases its diatropic character, and the exocyclic bonds quench the paratropism of the central four-membered ring.

In the series of the hydrocarbons **1**, **5**, **7**, and **8**, the angular system **8** displays the highest shielding. This confirms our conclusion drawn above from the *Q* value of **8** that angular annelation of naphthalene perturbs the A ring more strongly than the annelation of a benzo ring in **1**. It is of interest in this context that a strong paramagnetic ring current has been calculated for the four-membered ring in **8** [8][9], and our calculations showed the highest positive NICS value for this compound (*Table 4*). Increasing low-field shifts for **5** and **7** are in accord with the known bond-fixation tendency in the acenes; however, unambiguous assignment of the $\delta(^1H)$ values now shows that this trend is not accompanied by a reversal of the order $\delta(1,4\text{-H}) < \delta(2,3\text{-H})$. As the data of the model system **19** (*Table 2*) clearly show, the shielding of the 1,4-protons seems to be an inherent property of the cyclobutabenzene system and can be related to the strain effect introduced by the four-membered ring. On the other hand, for **13** and **16** we find as an exception the reverse order: $\delta(1,4\text{-H}) > \delta(2,3\text{-H})$, possibly an effect of the nitrogen and the diamagnetic anisotropy of the C=C bonds in the seven-membered ring, respectively. Thus, the shift order $\delta(1,4\text{-H}) < \delta(2,3\text{-H})$ is *not* an unambiguous argument in favor of a paratropic ring current effect in the four-membered ring of **1** and its analogues. Chemical-shift changes are thus a subtle consequence of structural variations, and their interpretation needs caution. Furthermore, in cases of small relative chemical shifts a cross-over of the resonances may already be induced by a solvent or substituent effect. These observations confirm that, in many cases, more reliable information about π-bond structure comes from the coupling constants that are less prone to solvent and long range substituent effects.

For the trio **10**–**12**, the shielding of the resonance frequencies confirms the special nature of **10**, already discussed on this basis by *Garratt* and *Vollhardt* [41] and derived above from the *Q* value analysis. The B-ring resonance, which is shielded by nearly 1 ppm if compared to δ(2,5-H) in thiophene (7.19 ppm [42]), also fits into this picture. Again, the order δ(1,4-H) < δ(2,3-H) holds for all systems. Of special interest are the calculated NICS values (*Table 4*), which show that the downfield shift observed for the 2-oxide and 2,2-dioxide are not due to increasing diamagnetism in the A or B ring but are rather a consequence of the quenched paramagnetism in the central four-membered ring.

Notwithstanding the additional effects that may influence chemical shifts discussed above, there is in general a parallel behavior between the chemical-shift data for the compounds studied and the results of the *Q* value analysis. Plotting δ(1,4-H) for **1**, **5**, and **7**–**16** *vs.* the corresponding *Q* value, we find a good linear correlation between both quantities (*Fig. 3*).

The ^{1}H chemical shifts in the charged systems $\mathbf{5}^{2+}$ and $\mathbf{7}^{2-}$ are strongly determined by the charge distribution that can be best estimated from ^{13}C-NMR data. Therefore,

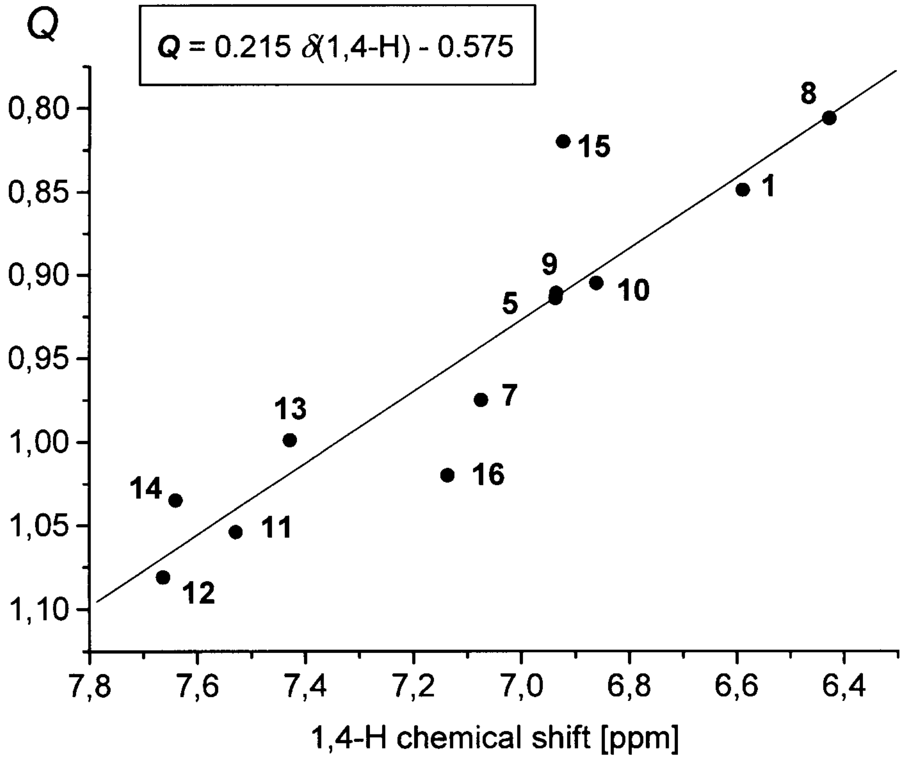


Fig. 3. *Plot of* δ*(1,4-H)* [ppm] vs. *the* Q *value for* **1**, **5**, *and* **7**–**16**

^{13}C-NMR spectra were analyzed for both the neutral and the charged systems, and these data are collected in *Table 6*. Due to low solubility, we were not able to measure and assign the quaternary ^{13}C resonances of **7**, and these data have been derived by shift-increment calculations from the data of **5**, naphthalene, and anthracene as described in the *Exper. Part*. The differences of the $\delta(^{13}\mathrm{C})$ data for neutral and charged systems, $\Delta\delta(^{13}\mathrm{C})$, which are, on the basis of the well-known equation [43]

$$\Delta\rho = 160\,\Delta\delta(^{13}\mathrm{C}) \qquad [3],$$

proportional to the π-charge density changes $\Delta\rho$, are depicted in *Fig. 4*. The sum of the $\Delta\delta(^{13}\mathrm{C})$ values for **5**$^{2+}$ and **7**$^{2-}$ amounts to 322 and 320 ppm, respectively, which is in excellent agreement with the expectations based on *Eqn. 3* and the total charge difference $\Delta\rho = 2$. For **5**$^{2+}$, a nearly equal charge-density distribution is found, while, for **7**$^{2-}$, the negative charge is concentrated in the anthracene partial structure. This observation is in line with our discussion of the Q value and the prediction of simple HMO theory, which yields the orbital coefficients given graphically in *Fig. 4* for the HOMO of **5**$^{2+}$ and the LUMO of **7**$^{2-}$. Similar charge concentrations have been found before for dibenzo[*b,d*]tetracene dianion [44] and tribenzo[*a,c,i*]phenazine dianion [45]. The ^{1}H chemical shifts (*Table 1*) also reflect the high charge density and, in addition, the paratropic nature of rings B, C, and D with highly shielded resonances for α-H, β-H, and 5-H, 6-H close to the values found for naphthalene and anthracene dianion [17g] [46]. We also note that the $\Delta\delta(^{13}\mathrm{C})$ values for **7**$^{2-}$ indicate partial positive charges at the quaternary positions, C(4a) and C(12b), a charge polarization, which is in line with observations made for the dianions of other benzenoid hydrocarbons [17g] [46b].

3. *The Structure of the Dibenzo-dehydro[8]annulene* **17**. For **17**, we find Q values of 0.978 and 1.022, which signal weak paratropic properties for the annelated benzo-dehydro[8]annulene (**26**). For the related **18**, we had found $Q = 0.961$ [17d], indicating a significant paramagnetism for the annelated benzo-didehydro[8]annulene (**27**). Apparently, **17** lacks the planarity found for **18**. In addition, the C=C bond of **17** destroys the symmetry present in **18**, which may quench the paramagnetic ring current. We note that the closely related ESR data [47] for the radical anions of **17**, **18**, and **28** suggest similar molecular geometry and planarity. Differences in the ^{1}H resonances for **17** and **18** are small and again the order $\delta(1,4\text{-H}) < \delta(2,3\text{-H})$ holds.

Table 6. *^{13}C-NMR Data* ($\delta(^{13}\mathrm{C})$ in ppm, rel. to TMS) *for the Charged Systems* **5**$^{2+}$ *and* **7**$^{2-}$, *their Parent Systems* **5**, *and* **7**, *and the $\Delta\delta(^{13}C)$ values*a))

	$\delta(1)$	$\delta(2)$	$\delta(4a)$	$\delta(4b)$	$\delta(5)$	$\delta(5a)$	$\delta(6)$	$\delta(7)$
5^{2+}	132.28	163.13	174.57	161.27	135.21	157.15	149.42	136.91
5	119.23	129.27	150.27	147.21	115.14	133.05	128.57	126.15
$\Delta\delta$	13.1	33.9	24.3	14.1	20.1	24.1	20.9	10.8

	$\delta(1)$	$\delta(2)$	$\delta(4a)$	$\delta(4b)$	$\delta(5)$	$\delta(5a)$	$\delta(6)$	$\delta(6a)$	$\delta(7)$	$\delta(8)$
7^{2-}	121.40	101.90	152.44	137.34	92.85	147.31	84.52	147.88	107.21	118.26
7b))	130.1	120.4	*150.3*	*147.2*	114.7	*131.6*	127.2	*131.8*	128.1	126.1
$\Delta\delta$	– 8.7	– 18.5	+ 2.1	– 9.9	– 21.8	– 15.7	– 42.7	– 16.1	– 20.9	– 7.8

a) The C-atom numbering follows that given in *Fig. 4*. b) The δ values for the quarternary C-atoms were derived from shift increments (*cf. Exper. Part*) and are given in *italics*.

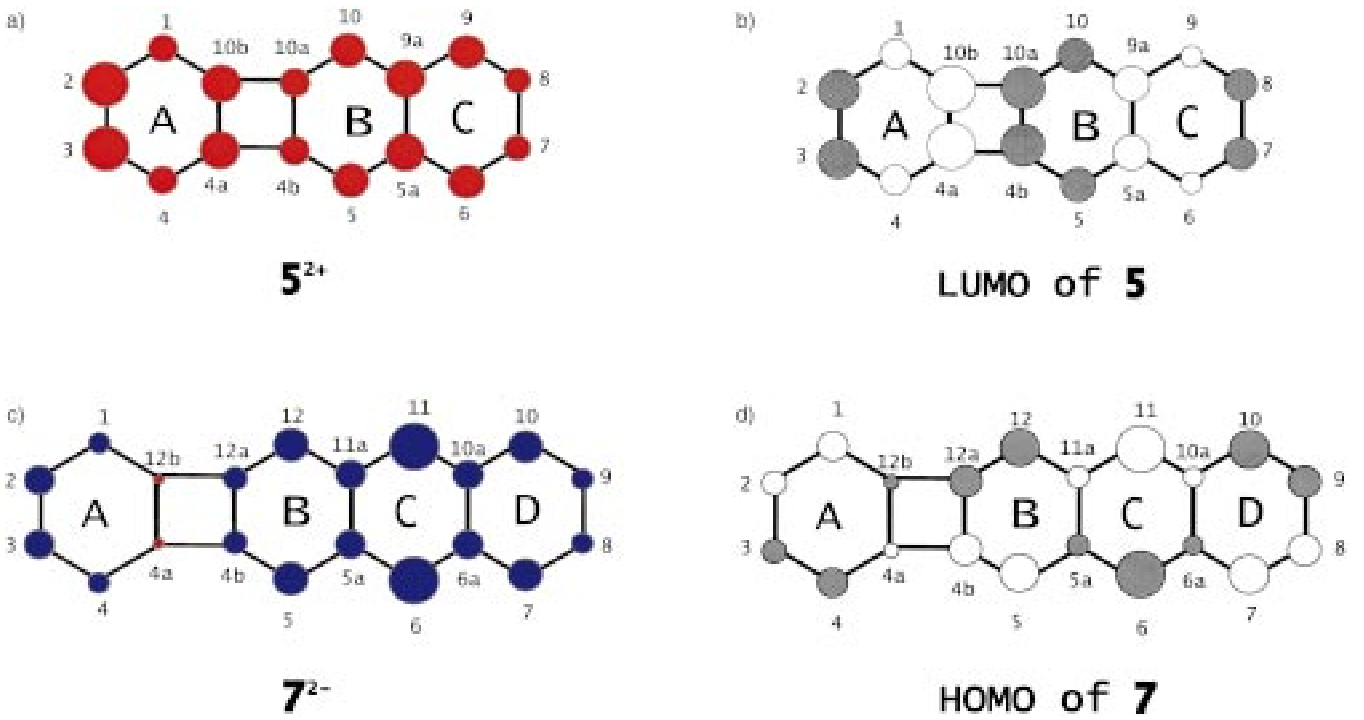
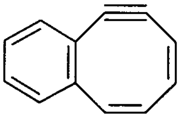


Fig. 4. *Graphical representation of the Δδ(^{13}C) values for the pairs* **5**/**5**$^{2+}$ (*a*) and **7**/**7**$^{2-}$ (*b*) (down-field shifts in red, high-field shifts in blue), and Hückel *LUMO of* **5** (*c*) *and* Hückel *HOMO of* **7** (*d*). The numbering does not correspond to that used in *Table 1* for the protons.



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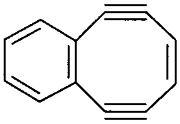

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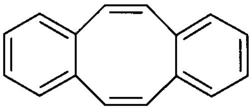

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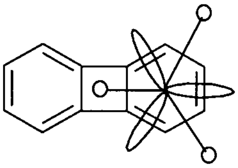
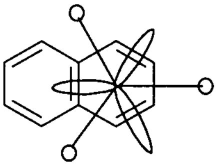
4. *The Orientation of the $Cr(CO)_3$ Group in* **9** *and* **21**. From X-ray analysis, it is known that the orientations of the $Cr(CO)_3$ in **9** and **21** are different. While for **21** the orientation **21a** is found [48], which is present also in other acene complexes [49], **9** has orientation **9a** (O = CO) [35]. This difference has been explained on the basis of MO arguments and can be derived in a straightforward manner from the different type of π-bond fixation in both systems: bonding to Cr occurs where the higher π-electron density is found. Due to the octahedral arrangement of the metal orbitals, the *endo*- or *exo*-orientation of the CO groups results for **9** and **21**, respectively, and the largest changes for the vicinal $^1H,^1H$ coupling constants are found for the C,C bond coordinated to the metal: $\Delta J(5,6) = 0.97$, $\Delta J(6,7) = 1.80$ Hz for **9** and $\Delta J(5,6) = 1.55$, $\Delta J(6,7) = 0.78$ Hz for **21** (*Tables 1* and *2*). The $^3J(^1H,^1H)$ data, therefore, allow conclusions as to the preferred orientation of the $Cr(CO)_3$ groups.



9a



21a

Conclusions. – We have shown that vicinal $^1H,^1H$ coupling constants allow detailed insights into the structure and bonding situation in cyclic π-systems. Contrary to ^1H chemical shifts, they are less sensitive to substituent effects and practically insensitive to solvent effects. The *Q*-value method thus successfully describes the electronic structure of π-systems that are annelated to a benzo ring. Our results show that the cyclobutabenzene unit stabilizes exocyclic C=C bonds at the four-membered ring and can thus be used as a synthetic tool to prepare certain, otherwise unstable diene structures. This was shown by the successful synthesis of biphenylene-2,3-oxide, which sustains a partial benzene-oxide structure stable against electrocyclic ring opening to the corresponding oxepine [50]. Other examples are the synthesis of a norcaradiene [51] and the double-bond localization found for angular phenylenes [19][52].

We are indebted to the *Deutsche Forschungsgemeinschaft* and the *Fonds der Chemischen Industrie*, Frankfurt/M., for continued support.

Experimental Part

Synthesis. The compounds studied were prepared according to known procedures: **5**, **6** [53] [54], **7**, **15** [55], **8** [56], **10**–**12** [41], **13** [57], **14** [58], **16** [59], **17** [60]; **9** was available from earlier work. The charged systems $\mathbf{5}^{2+}$and $\mathbf{7}^{2-}$ were prepared under Ar directly in the NMR tube from the hydrocarbons by treatment with SO_2ClF/SbF_5 ($\mathbf{5}^{2+}$) and reduction with lithium in THF ($\mathbf{7}^{2-}$).

Spectra. Samples were dissolved, the solns. degassed with the pump-freeze technique, and sealed in NMR tubes. Concentrations are given in *Table 1*. Measurements were performed at r.t. with *a Varian HA-100*, a *Bruker WH-400*, and a *Bruker AMX-400* spectrometer. With the exception of **8**, all systems possess C_{2v} symmetry and provide consequently *AA′BB′*- or *AA′XX′*-type spectra for the protons of ring A, B, or C. Since these spectra do not allow us to distinguish the *A* from the *B* or *X* resonances [61], independent methods had to be used for an unambiguous $\delta(^1H)$ assignment. These were

– the measurement of the ^{13}C satellites [17f] [62] (*Method A*),

– the different magnitude of the $^1J(^{13}C,^1H)$ coupling constants determined from the ^1H spectrum or directly by an inverse $^{13}C,^1H$-shift correlation [20] (*Method B1* and *B2*, respectively, see *Introduction*),

–in addition, 2D-NOESY [23], NOE difference spectra [63]), and long-range (< 1 Hz) optimized COSY spectra [20d] were used. Specific deuteration served for an unambiguous assignment in some cases (*Method C*).

Method A is based on the fact that the widths of the ^{13}C satellites for 1,4-H and 2,3-H differ significantly, because, in the first case, *ortho*-, *meta*-, and *para*-$^1H,^1H$ couplings are involved, while, for 2,3-H, we have two *ortho*- and one *meta*-coupling. This results in a width *w* of *ca.* 9 Hz in the first and of *ca.* 16 Hz in the second case. The satellites are also recorded as F_2 traces of inverse $^{13}C,^1H$ correlations and show, as a consequence of the $^1H,^1H$ coupling discussed above, a *doublet* structure of *ca.* 9 Hz width and a *triplet* structure of *ca.* 16 Hz width for 1,4-H (5,8-H) and 2,3-H (6,7-H), resp. (*Fig. 5*).

In the following, we briefly summarize the assignment strategy used for the individual systems:

5: *Method C*, deuteration in 5,10-position in order to suppress long-range coupling, *Method A* for the C ring with *w* = 9.2 Hz at low field (7.477 ppm) and 15.8 Hz (t) at high field (7.264 ppm), *Method B2* for the A ring with $^1J(1,^1H) = 163.7$ and $^1J(2,^1H) = 155.4$ Hz.

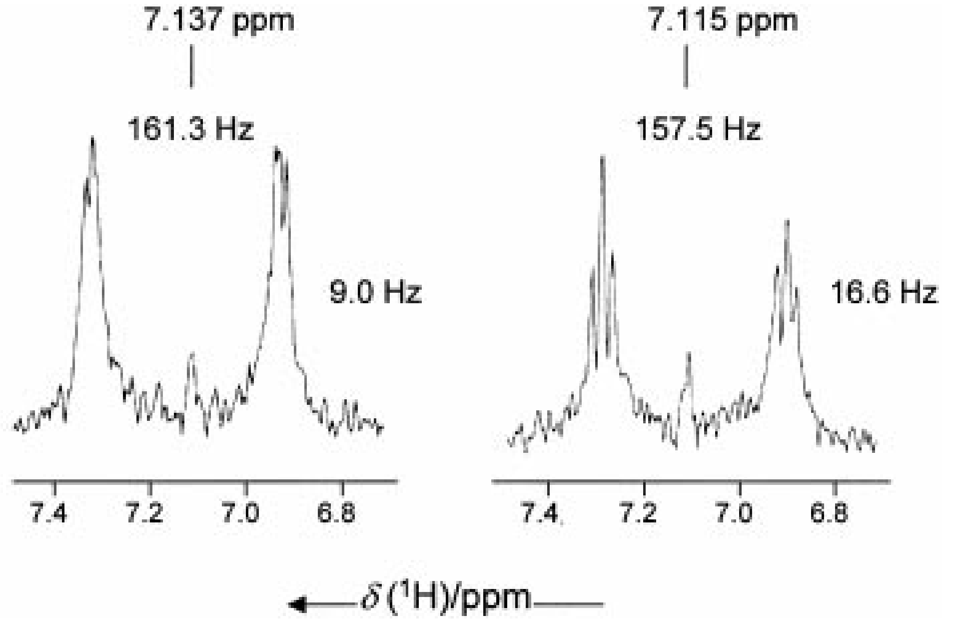


Fig. 5. F_2 *Traces of the* ^{13}C *resonances at 118.4* (left) *and 128.3 ppm* (right) *observed in an HMQC inverse* $^{13}C,^1H$ *shift correlation experiment for* **16**, *showing the different widths and structure of the* ^{13}C *satellites for 1,4-H* (left) *and 2,3-H* (right), *as well as the different* $^1J(^{13}C,^1H)$ *values for these positions*

6: The degeneracy of the A ring resonances was lifted by using C_6D_6 as co-solvent, assignment was not established. For the C ring, the deshielding effect of the Br substituents requires δ(5,8-H) > δ(6,7-H).

7: COSY LR Spectra with cross-peaks at 7.839/7.969 and 7.96/7.11 ppm for the B, C, and D ring; *Method B2* for the A ring with 129.7 ppm/161.9 Hz for the high-field and 120.1 ppm/159.1 Hz for the low-field ^{13}C,^{1}H correlation.

8: *Method C* with β-D-**8** (for numbering see Formulae); an isotope shift of 0.05 ppm for one ^{13}C,H-resonance in the C ring allowed to assign δ(5-H), vicinal ^{1}H,^{1}H connectivities were revealed by ^{1}H,^{1}H INADEQUATE spectra [64]; assignment for the A ring was achieved by a 2D NOESY spectrum, which showed an NOE between the *doublet* at 7.538 and the signal at 6.542 ppm.

9: The well-known complexation effects with high-field shifts for the B-ring protons and $\delta(5,8) < \delta(6,7)$ allowed assignment of these resonances and to distinguish them from the A-ring resonances; *Method A* for the relative assignment in the A ring with *w ca.* 9 and 13 Hz for δ(1,4-H) and δ(2,3-H), resp.; an independent analysis [40], which used specific deuteration for the assignment, agrees with our results.

10: *Method B1* with 163.6 Hz for the high-field and 160.5 Hz for the low-field resonance, and $w = 9$ Hz and 16 Hz at high and low field, resp.

11: *Method B2* with 123.7 ppm/167.3 Hz for the high-field and 133.4 ppm/163.3 Hz for the low-field ^{13}C,^{1}H correlation, which showed a *doublet* structure ($w = 8$ Hz) and a *triplet* structure ($w = 17.5$ Hz), respectively;

12: *Method B2* with 124.9 ppm/167.3 Hz for the high-field and 134.2 ppm/163.3 Hz for the low-field ^{13}C,^{1}H correlation, which showed a *doublet* structure ($w \approx 8$ Hz) and a *triplet* structure ($w \approx 17.5$ Hz), resp.

13: *Method A* for the A- and D-ring protons; the ^{1}H resonance at 7.65 yielded 9.8 Hz, that at 7.29 ppm 14.5 Hz; *Method B2* yielded 166.5 Hz at 122.6/7.428 ppm and 162.6 at 133.7/7.295 ppm.

14: Because of degeneracy, a shift difference had to be induced by [Eu^{III}(fod)$_3$] in order to allow spectral analysis.

15: *Method B2* with 165.8 and 161.2 Hz for 1,4-H and 2,3-H at 6.923 and 6.982 ppm, resp., in the A ring; in the D ring $^1J(^{13}C,^1H)$ data of 170.5 and 165.8 Hz are measured for the ^{13}C/^{1}H resonances at 126.9/8.24 and 133.8/7.77 ppm, resp. The former agrees with the coupling measured for α-H (170.4 Hz at 113.7/7.49 ppm) and was thus assigned to 5,8-H.

16: *Method B2* with 128.3 ppm/157.5 Hz for the high-field and 118.4 ppm/161.3 Hz for the low-field ^{13}C,^{1}H correlation; *Method A* yielded a *triplet* of $w \approx 18$ Hz and a *doublet* of $w \approx 9$ Hz for the high- and low-field part of the *AA′BB′* system; both methods thus indicate δ(1,4-H) > δ(2,3-H).

17: The high-field resonance of 1,4-H showed line broadening (^5J to the olefinic protons) and was assigned to 1-H, in agreement with the shielding expected from the C≡C bond.

19: *Method B2* with 122.2 ppm/161.7 Hz for the high-field and 126.5 ppm/158.5 Hz for the low-field ^{13}C,^{1}H correlation; *Method A* yielded a *doublet* of $w \approx 8$ Hz and a *triplet* of $w \approx 16.2$ Hz, resp., for the high- and low-field part of the *AA′BB′* system; both methods thus yield δ(1,4-H) < δ(2,3-H).

21: Line-broadening due to long-range inter-ring coupling [66] established the assignment of 1,4-H and 5,8-H.

The ^{13}C resonances for **5** and **7** were based on the ^{1}H assignments by ^{13}C,^{1}H shift correlations. Due to low solubility, the quarternary ^{13}C resonances of **7** could not be measured. They were estimated by the following arguments: annelation of ring D to **5** should not result in strain or charge-density effects at the four-membered ring, while the introduction of the benzo[3,4]cyclobuta[1,2] unit to anthracene should not affect ring C and D. For C(4a)/C(12b) (for numbering see *Fig. 3*) and C(4b)/C(12a), the data of **5** (*Table 6*) were used, while the anthracene value for C(4a) (131.8 ppm [65]) served for C(6a)/C(10a). For the remaining resonance C(5a)/C(11a), again the anthracene value served as a basis, the annelation increment of −0.2 ppm was obtained from the difference of the ^{13}C resonances 9,10 of naphthalene and δ(5a) in **5**. For **5**$^{2+}$ and **7**$^{2-}$, the ^{1}H resonances in the C and D rings were assigned by 2D-NOESY spectroscopy, and the ^{13}C assignment was based on these ^{1}H assignments by ^{13}C,^{1}H shift-correlation experiments. For the A-ring assignments, the data of **1**$^{2+}$ and **1**$^{2-}$ served as models.

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