101. Perimeter-Type Structures in Charged [4n + 2]Annuleno[4n + 2]annulenes. The Importance of the Frontier-Orbitals

by Walter Huber*

Institut für Physikalische Chemie der Universität, Klingelbergstrasse 80, CH 4056 Basel

and Klaus Müllen* and Christoph Schnieders

Institut für Organische Chemie der Universität, J.-J.-Becher-Weg 18 20, D 6500 Mainz

and Masahiko Iyoda and Masazumi Nakagawa

Department of Chemistry, Faculty of Science, Osaka University, Toyonaka, Osaka, 520 Japan

The tetra(*tert*-butyl)[14]annuleno[14]annulene 1 is transformed, *via* alkali metal reduction, into its radical monoanion, dianion, radical trianion, and tetraanion. The paramagnetic species are characterized by ESR and ENDOR spectroscopy and the diamagnetic species by ^{1}H- and ^{13}C-NMR spectroscopy. Well–resolved ESR and NMR spectra can only be obtained, if the reduction is carefully monitored. For the interpretation of the data, the ions derived from the structurally related [14]- and [22]annulenes 3 and 5 as well from the tetra(*tert*-butyl)[14]annuleno[18]annulene 2 serve as suitable model compounds. While the behavior of the neutral annulenoannulene 1 is governed by that of the [14]annulene-subunit, the corresponding ionic systems can best be described as macrocyclic perimeters. This outcome can be rationalized by the nodal properties of the frontier MO's.

Introduction. – When characterizing the [4n + 2]annuleno[4n + 2]annulenes one is concerned with a fascinating question: is the π-structure of the bicyclic molecules determined by the conjugation within the 'overall' periphery or within the single monocyclic subunits [1] [2]? This problem was carefully investigated for the dehydroannulenoannulenes 1 and 2 [3], which offer the advantage of a rigid and planar molecular framework. Moreover, a homologous series of monocyclic compounds (3–6) with identical ring configuration and ring conformation was available allowing for a systematic study of chemical and spectroscopic properties as a function of ring size [4].
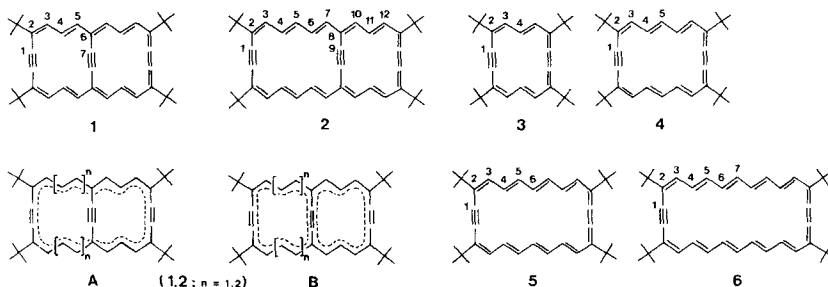
There is firm evidence from NMR and X-ray investigations that the bicyclic compounds cannot adequately be represented by the perimeter-type structure **A** [1]. The most convincing arguments in favor of this conclusion are the ^{13}C-NMR chemical shifts of the central sp-hybridized C-atoms, the length of the corresponding formal triple bond, and the ring current effects measured by the chemical shift difference of 'inner' and 'outer' protons.

It has been well-established that the electronic structure of conjugated hydrocarbons can be affected deeply by successive electron-transfer processes leading to mono- and multiply-charged species [5–7]. Here, we report the preparation and spectroscopic detection of ionic species derived from the bicyclic compounds **1** and **2**. The comparison of the spectroscopic data with those of the monocyclic annulene counterparts **3–6** provides insight into the π-bonding of charged [4n + 2]annuleno[4n + 2]annulenes.

Experimental. – The synthesis of the neutral compounds **1–6** was described by *Nakagawa* and coworkers [3] [4]. The corresponding negatively charged ions were prepared by reaction of the neutral compounds with alkali metals (Li, K) in THF. To obtain well-resolved ESR, ENDOR and NMR spectra, it was necessary to carefully monitor the electron transfer by spectroscopic means. Such problems were particularly acute in the case of the diamagnetic dianions and tetraanions for which NMR signals were only detectable if precisely two and four *Faraday*, respectively, had been transferred. The intact molecular frameworks of the charged species were proven spectroscopically by the symmetry inherent in the respective ESR, ENDOR, and NMR spectra, and chemically by the reoxidation of the samples with dry oxygen, which yielded the parent compounds as sole products.

The ESR spectra and the ENDOR spectra of the paramagnetic derivatives of **1–6** were taken on a *Varian E-9-ESR* spectrometer with an attached *Varian E-1700-ENDOR* unit. For the ^{1}H- and ^{13}C-NMR spectroscopic description of the diamagnetic ions, a *Bruker-WM 300* spectrometer was used.

Results. – The results of ESR and NMR spectroscopic investigations on the negatively charged ions of **3** (**3⁻**, **3²⁻**), **4** (**4⁻**, **4²⁻**, **4³⁻**, **4⁴⁻**), **5** (**5⁻**, **5²⁻**, **5³⁻**, **5⁴⁻**), and **6** (**6⁻**, **6²⁻**, **6⁴⁻**) have been explicitly given in [8–11]. Upon alkali metal reduction, **1** was transformed into the radical anion and, subsequently, into the dianion, the radical trianion, and the tetraanion. *Fig. 1* shows the ESR spectra of **1⁻** and **1³⁻** as well as the ^{1}H-NMR spectra of **1**, **1²⁻**, and **1⁴⁻**. The analysis of the ESR spectra was supported by the observation of the ENDOR spectra. The hyperfine coupling constants of the paramagnetic species **1⁻** and

Table 1. *ESR Hyperfine Coupling Constants* [mT] *of Radical Monoanions and Radical Trianions*

		2b(t-Bu)	3	4	5	6	7	10	11	12	Ref.
$a_H{}^{a)}$	**1⁻**	< 0.01$^{b)}$	0.069	0.345	0.115						This work
	1³⁻	< 0.01$^{b)}$	0.250	0.036	0.279						This work
	5⁻	< 0.01$^{b)}$	0.064	0.337	0.134	0.397					[8] [11]
	5³⁻	< 0.01$^{b)}$	0.250	0.057	0.287	0.093					[11]
$a_H{}^{a)}$	**3⁻**	< 0.01$^{b)}$	0.108	0.514							[8] [11]
$a_H{}^{a)}$	**2⁻**	< 0.01$^{b)}$	0.057	0.305	0.104	0.321	0.057	0.104	0.268	0.057	This work
	4⁻	< 0.01$^{b)}$	0.087	0.402	0.135						[8]
	6⁻	< 0.01$^{b)}$	0.061	0.285	0.114	0.310	0.122				[11]
$a_H{}^{c)}$	**1⁻**		+0.076	−0.322	+0.109						
	1³⁻		−0.215	+0.039	−0.334						
	2⁻		+0.059	−0.298	+0.101	−0.291	+0.087	+0.091	−0.243	+0.054	

^{a})   Solvent: 1,2-dimethoxyethane; counterion: K^+; T = −80°.
^{b})   Values estimated from the ENDOR line width.
^{c})   Coupling constants calculated by the HMO-*McLachlan* procedure ($\alpha_\mu = \alpha$; $\beta_{\mu\nu} = 1.5\beta$ (for formal triple bonds); $\beta_{\mu\nu} = \beta$ (for the remaining bonds); $\lambda = 1.2$) and the *McConnell* relationship ($Q = -2.5$ mT).
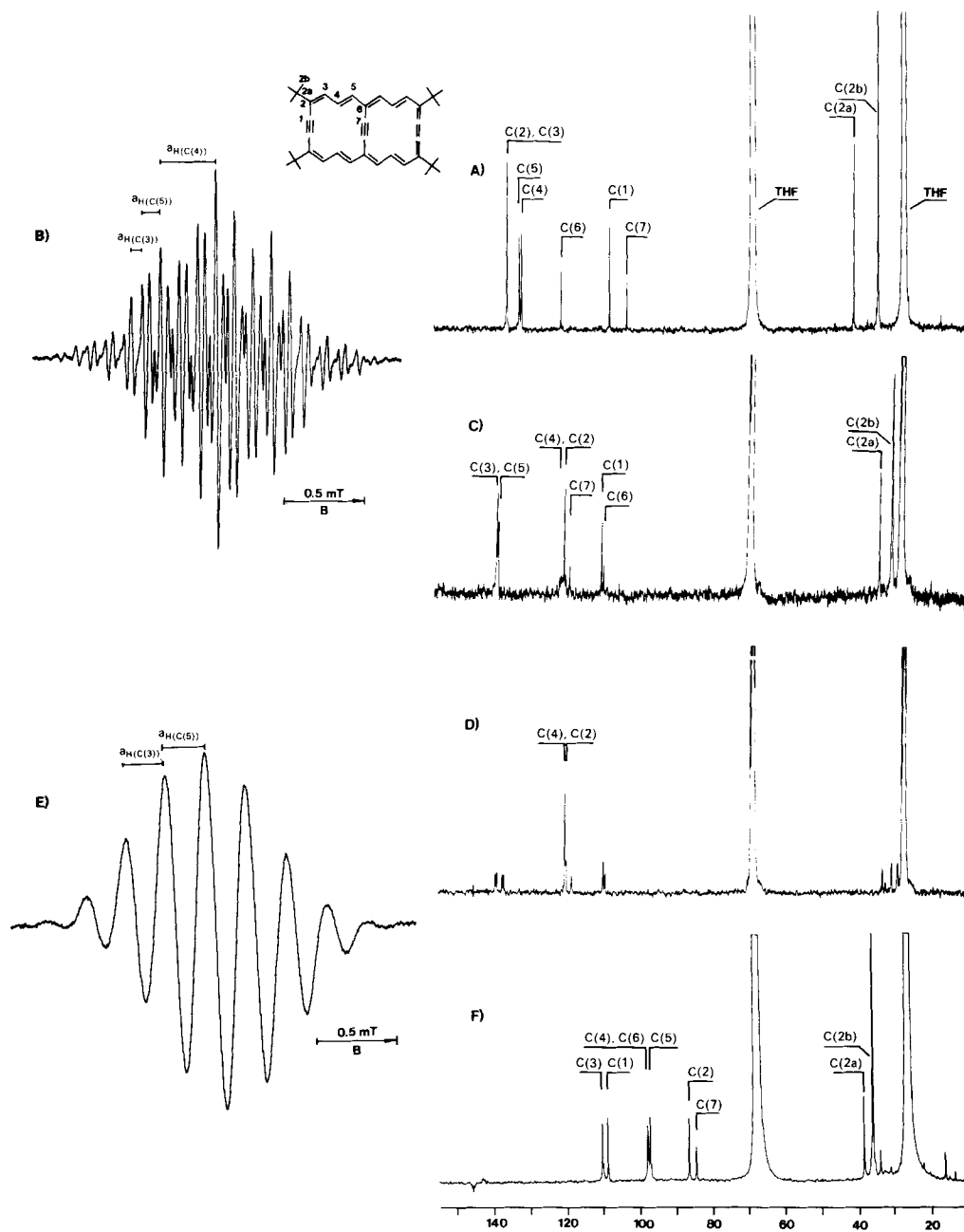
Fig. 1. *Reduction of* **1** *as controlled by NMR and ESR spectroscopy*. The diamagnetic species **1** (*A*), **1**$^{2-}$/2Li$^+$ (*C,D*) and **1**$^{4-}$/4Li$^+$ (*F*) are characterized by their ^{13}C-NMR spectra ((D$_8$)THF, −30°), the paramagnetic species **1**$^{\cdot-}$/K$^+$ (*B*) and **1**$^{3\cdot-}$/3K$^+$ (*E*) by their ESR spectra (1,2-dimethoxyethane, −80°). The ^{13}C-NMR spectra in *A*, *C* and *F* have been taken under ^{1}H-noise decoupling, *D* depicts the ^{13}C-NMR spectrum of **1**$^{2-}$/2Li$^+$ recorded under selective decoupling of H–C(4).

$1^{3\cdot}$ as well as those of the homologous radical anions $2^{\cdot}$ are given in *Table 1*. The ¹H- and ¹³C-NMR chemical shifts of 1^{2-} and 1^{4-} are summarized in *Tables 2* and *3*, respectively.

The assignment of the ¹H-NMR chemical shifts in 1^{2-} and 1^{4-} was based on the observed intensities and multiplicities (*s:* t-C₄H₉; *d:* H—C(3) and H—C(5); *t:* H—C(4)). The ¹³C-NMR chemical shifts of proton-bearing centers were then assigned by selective decoupling experiments. The quarternary ¹³C-NMR absorptions were assigned *via* the splitting patterns in the 'coupled' ¹³C-NMR spectra and *via* the relative signal intensities (see *Discussion* and *Table 3*). The assignment of the hyperfine coupling constants in the paramagnetic derivatives is only unambiguous for the protons of the t-Bu groups. The assignment of the remaining coupling constants does not follow from experiment, and is based on a HMO-*McLachlan* calculation of the spin density distribution (see *Table 1*).

Discussion. – It has been demonstrated recently that successive electron transfers to polycyclic π-systems can lead to ionic products having completely different structures [12–14]. The basic question in a discussion of the title compounds is whether or not a 'peripheral' conjugation is of higher importance in the ions than in the neutral compounds (structure **A** *vs.* structure **B**). One can expect that the mode of π-bonding in the ionic species is highly dependent on the character of the highest occupied molecular orbital. *Fig. 2* schematically depicts the LUMO and the NLUMO of the
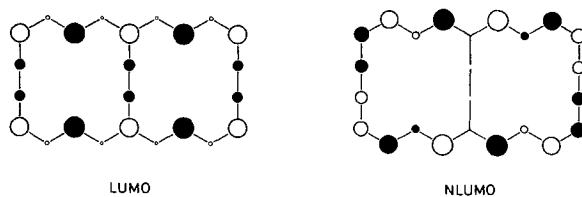

LUMO   NLUMO

Fig. 2. *Schematic representation of the LUMO and NLUMO of* **1** (see text)

[14]annuleno[14]annulene. It is obvious from this representation that the MO coefficients at the central sp-hybridized C-atoms are rather small for the LUMO and vanish in the case of the NLUMO. These two orbitals thus constitute perimeter-type orbitals. On going from the neutral compound to the tetraanion of **1**, one expects a successive filling of the LUMO and the NLUMO by the extra electrons. This expectation is fully born out by experiment. The observed coupling constants of $1^{\cdot}$ and $1^{3\cdot}$ correlate well with those calculated for the single occupancy of the LUMO and the NLUMO, respectively. Moreover, the coupling constants of $1^{\cdot}$ and $1^{3\cdot}$ match those observed for the corresponding ions of the didehydro[22]annulene ($5^{\cdot}$ and $5^{3\cdot}$) [11] (see *Table 1*). The hyperfine data of $2^{\cdot}$ are fully comparable with those of the radical anion of the didehydro[26]annulene **6** [8] (see *Table 1*). In close analogy to the case of $1^{\cdot}$, the singly occupied molecular orbital again constitutes a perimeter orbital.

Turning now to the diamagnetic derivatives of **1**, the ring-current effects as well as the charge distribution are the most significant criteria for determining the π-bonding. The existence of large ring-current effects within the dianion 1^{2-} and the tetraanion 1^{4-} is obvious from the extreme shift differences of inner and outer ring protons (see *Table 2*). These $\Delta(\delta_{H_i} - \delta_{H_a})$ values are of the same magnitude as those of the dianion and the tetraanion of **5** [9]. It is thus straightforward to characterize 1^{2-} and 1^{4-} as strongly

Table 2. ^1H-NMR Chemical Shifts (δ_H) of **1**, **1**$^{2-}$, and **1**$^{4-}$ as Compared with those of **5**, **5**$^{2-}$, and **5**$^{4-}$ (ions as Li salts in $(D_8)THF$)[a]

		3	4	5	6	2b
δ_H	**1**	10.36	–2.96	9.72		2.04
	1^{2-}	0.44	26.97	–1.10		–0.43
	1^{4-}	10.27	–8.60	8.79		2.21
	5	8.76	–0.82	9.21	–0.82	1.28
	5^{2-}	1.15	24.80	–0.29	23.23	–0.29
	5^{4-}	9.03	–10.67	+10.61	–9.50	2.29
$\Delta\delta_H$	**1**$^{2-}$/**1**	–9.92	+29.93	–10.82		–2.47
	1^{4-}/**1**	–0.09	–5.64	–0.93		0.17
	5^{2-}/**5**	–7.61	25.62	–9.5	+24.05	–1.57
	5^{4-}/**5**	+0.27	–9.85	1.4	–8.68	1.01
$\Delta(\delta_{H_i} - \delta_{H_a})$	**1**		–13.32	–12.68		
	1^{2-}		+26.53	+28.07		
	1^{4-}		–18.87	–17.39		
	5		–9.58	–10.09	–10.03	
	5^{2-}		+23.65	+25.09	+23.52	
	5^{4-}	–	19.7	–21.28	–20.11	

[a] $\Delta\delta_H$: Signal shifts observed upon going from the neutral (**1**, **5**) to the charged species (**1**$^{2-}$, **5**$^{2-}$, **1**$^{4-}$, **5**$^{4-}$); $\Delta(\delta_{H_i} - \delta_{H_a})$: shift difference of protons inside (H_i) or outside (H_o) the π-system.

paratropic and diatropic species with a 24π- = $(4n)\pi$- and a 26π- = $(4n + 2)\pi$-perimeter conjugation, respectively.

An inspection of the charge distribution in **1**$^{2-}$ and **1**$^{4-}$ supports the assumption of an 'acetylene'-bridged annulene. In quantitatively describing the charge distribution, one can make use of the well-established proportionality between the charge-induced shifts of individual ^{13}C-NMR signals (Table 3) and the changes of local π-charge densities ($\Delta q_\pi = \Delta\delta_C/K_C$) [9]. The basic problem with such an approach is the choice of a suitable constant K_C [9] [15]. In dealing with the charge distribution of ions derived from various mono- and polycyclic π-systems it was found that 'compound-specific' K_C values must be determined by dividing the charge-induced shift of the center of gravity of the ^{13}C-NMR

Table 3. ^{13}C-NMR Chemical Shifts (δ_C) of **1**, **1**$^{2-}$, and **1**$^{4-}$ (ions as Li salts in $(D_8)THF$)[a]

		1	2	3	4	5	6	7	
δ_C	**1**	106.9	135.2	135.2	131.2	131.8	120.3	102.1	$\langle\delta_C\rangle = 125.3$
δ_C	**1**$^{2-}$	108.7	119.1	137.8	119.4	137.4	108.1	117.5	$\langle\delta_C\rangle = 122.5$
δ_C	**1**$^{4-}$	108.6	86.2	110.2	97.6	96.8	97.6	84.1	$\langle\delta_C\rangle = 98.4$
$\Delta\delta_C$	(**1**/**1**$^{2-}$)	–1.8	16.1	–2.6	11.8	–5.6	12.2	–15.4	$\Delta\langle\delta_C\rangle = 2.8$ ($K_C = 33.6$)
$\Delta\delta_C$	(**1**/**1**$^{4-}$)	–1.7	49.0	25.0	33.4	35.0	22.7	18.0	$\Delta\langle\delta_C\rangle = 26.9$ ($K_C = 161.4$)
$\Delta q'_\pi$	(**1**/**1**$^{2-}$)	0.05	0.16	0.01	0.18	0.01	0.17	0.05	
$\Delta q'_\pi$	(**1**/**1**$^{4-}$)	0.11	0.24	0.14	0.20	0.18	0.17	0.05	
$\Delta q''_\pi$	(**1**/**1**$^{2-}$)	–0.01	0.48	–0.08	0.35	–0.17	0.36	–0.46	
$\Delta q''_\pi$	(**1**/**1**$^{4-}$)	–0.01	0.30	0.15	0.21	0.22	0.14	0.11	

[a] $\langle\delta_C\rangle$ = Average signal; $\Delta\delta_C$ = signal shift observed upon ion formation; $\Delta\langle\delta_C\rangle$ = shift for the average signal; $\Delta q'_\pi$ = calculated π-charge densities (HMO: $\alpha_\mu = \alpha$; $_{\mu\nu} = 1.5\,\beta$ (for the formal triple bonds), $\beta_{\mu\nu} = \beta$ (for the remaining bonds)); $\Delta q''_\pi = \pi$-charge densities which have been calculated from the individual $\Delta\delta_C$-values ($\Delta q''_\pi = \Delta\delta_C/K_C$).

signals ($\Delta \langle \delta_C \rangle$) by the average change of the π-charge density (*e.g.* 2/14 in the case of a [14]annulene dianion). When calculating such values, it appeared as a most significant finding that charged paratropic perimeter systems possess low K_C values (< 115 ppm/ unit charge), whereas those of the diatropic counterparts (> 150 ppm/unit charge) are close to the ones given in the literature for various monoanions. It is interesting to note that the K_C values of the dianion 1^{2-} ($K_C = 34$ ppm/e) and the tetraanion ($K_C = 161$ ppm/e) support their description as paratropic and diatropic species, respectively.

Based on such K_C values, we have determined 'experimental' changes in π-charge densities ($\Delta q_\pi''$) by dividing the individual changes in ^{13}C-NMR chemical shifts $\Delta \delta_C$ by the relevant K_C. Obviously, these $\Delta q_\pi''$-values are in reasonable agreement with those calculated from a simple HMO model. The correlation between experimental and theoretical Δq_π-values is relatively poor for C(7) of both 1^{2-} and 1^{4-}. It should be noted, however, that C(7) is not within the periphery of the diatropic/paratropic perimeter, and, therefore, suffers from ring-current-induced shielding/deshielding effects. The data also reveal, that for a given π-center the change in charge density on going from 1 to 1^{2-} and from 1^{2-} to 1^{4-} resembles the spin density in 1^{-} and 1^{3-}, respectively. The chemical shifts of C(1)–C(5) in the tetraanion are very similar to those in the tetraanion of the [22]annulene **5** [9]. This finding together with the localization of the excess charge in the periphery support perimeter structure of 1^{4-}.

Conclusion. – ESR and NMR spectroscopic arguments create a consistent view of the prevailing π-bonding in the ions derived from dehydro[4n + 2]annuleno[4n + 2]-annulenes. These ions, but not the neutral compounds, behave as perimeter systems and constitute novel examples of *Platt*'s perimeter rule [16]. Such a behavior could have been predicted simply by inspecting the nodal properties of the frontier orbitals involved in the radical anion or dianion, and the radical trianion or tetraanion.

REFERENCES

[1] M. Nakagawa, *Angew. Chem.* **1979**, *91*, 215; *ibid. Int. Ed.* **1979**, *18*, 202.
[2] T. M. Cresp, F. Sondheimer, *J. Am. Chem. Soc.* **1975**, *97*, 4412.
[3] S. Akiyama, M. Iyoda, M. Nakagawa, *J. Am. Chem. Soc.* **1976**, *98*, 6410.
[4] M. Nakagawa, *Pure Appl. Chem.* **1975**, *44*, 885.
[5] K. Müllen, *Chem. Rev.* **1984**, *84*, 603.
[6] J. F. M. Oth, K. Müllen, H. Königshofen, J. Wassen, E. Vogel, *Helv. Chim. Acta* **1974**, *57*, 2387.
[7] K. Müllen, J. F. M. Oth, H. W. Engels, E. Vogel, *Angew. Chem.* **1979**, *91*, 251; *ibid. Int. Ed.* **1979**, *18*, 229.
[8] F. Gerson, I. Jachimowicz, M. Nakagawa, M. Iyoda, *Helv. Chim. Acta* **1974**, *57*, 2141.
[9] K. Müllen, W. Huber, T. Meul, M. Nakagawa, M. Iyoda, *J. Am. Chem. Soc.* **1982**, *104*, 5403.
[10] K. Müllen, W. Huber, T. Meul, M. Nakagawa, M. Iyoda, *Tetrahedron* **1983**, *39*, 1575.
[11] W. Huber, *Helv. Chim. Acta* **1985**, *68*, 1140.
[12] B. C. Becker, W. Huber, C. Schnieders, K. Müllen, *Chem. Ber.* **1983**, *116*, 1573.
[13] W. Huber, A. May, K. Müllen, *Chem. Ber.* **1981**, *114*, 1318.
[14] A. Minsky, M. Rabinovitz, *J. Am. Chem. Soc.* **1984**, *106*, 6755.
[15] B. Eliasson, U. Edlund, K. Müllen, *J. Chem. Soc., Perkin Trans. 2*, in press.
[16] I. R. Platt, *J. Chem. Phys.* **1954**, *22*, 1448.