The remarkable electron impact mass spectrum of (2-benzyl-1,3-xylylene)-15-crown-4: expulsion of triethylene glycol by double hydrogen transfer

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During our investigations of the synthesis of magnesium-containing crown ethers, the mass spectral characterisation of a precursor, (2-benzyl-1,3-xylylene)-15-crown-4 ($C_{21}H_{26}O_4$), leads to a surprising result: its electron-impact mass spectrum was nearly identical with that of 1-methylanthracene, $C_{15}H_{12}$. Several deuteriated analogues and other model compounds were synthesised and investigated with respect to their ionisation-induced and collision-induced mass spectroscopic behaviour. A mechanism for the fragmentation of the ions of [2-benzyl-1,3-xylylene]-15-crown-4 to a $[C_{15}H_{12}]^{\bullet+}$ species is proposed. It involves consecutive 1,5-H transfer, to generate an open-chain polyether group, cyclisation of the two aromatic moieties, to give an anthracene-type intermediate, and remote hydrogen transfer, to release the triethylene glycol neutral.

Introduction

Previously, we reported surprising ligand-exchange reactions between the (2-functionalised) 1,3-xylylene-15-crown-4 ethers **1**–**3**† (Fig. 1) and diphenylmagnesium or phenylmagnesium bromide.[1] The crown ether ring can obviously direct the magnesium either to the aromatic carbon atom C2 (in halogen–metal exchange and metallation reactions) or to the oxygen atom bonded to C2 (in ether cleavage reactions). Therefore, it appeared interesting to investigate whether metallation might occur at a carbon atom bonded to the aromatic C2. The reaction of (2-methyl-1,3-xylylene)-15-crown-4 (**4**)[1e] with diphenylmagnesium did not result in any conversion, as shown by ^{1}H NMR spectroscopy and by D_2O quenching with subsequent GC–MS analysis. Obviously, the activation of the organomagnesium reagent by the crown ether ring is not sufficient for (an easy) metallation of these benzylic hydrogens to occur. Therefore, we synthesised the 2-benzyl analogue (2-benzyl-1,3-xylylene)-15-crown-4 (**5**), in which the *intra*-annular hydrogen atoms were expected to be more acidic than in **4**. Compound **5** was easily obtained by benzylation of **2**; nevertheless, the reaction of **5** with diphenylmagnesium did not lead to metallated products either.

Much to our surprise, however, the mass spectroscopic identification of **5** yielded the spectrum shown in Fig. 2; this spectrum is nearly identical with that of 1-methylanthracene ($C_{15}H_{12}$ at m/z = 192). Only a very weak molecular ion signal, [**5**$^{\bullet+}$], <1% of base peak m/z 192, is discernible, and there are few low-abundance signals at masses above 192 amu. This intriguing mass spectrum made us wonder about the mechanism of fragmentation, and in order to obtain additional information, we synthesised a number of deuterium-labelled derivatives of **5** and some related compounds and studied their fragmentation in detail by using metastable and stable ion analysis.

† IUPAC-recommended names: **1**, 3,6,9,12-tetraoxa-1(1,3)-benzenacyclotridecaphane; **2**, 1^2-bromo-; **3**, 1^2-methoxy-; **4**, 1^2-methyl-; **5**, 1^2-benzyl-; **6**, 1^5-benzyl-3,6,9,12-tetraoxa-1(1,3)-benzenacyclotridecaphane; **7**, 1^2-benzyl-2,5,8,11,14-pentaoxa-1(1,3)-benzenacyclotetradecaphane.

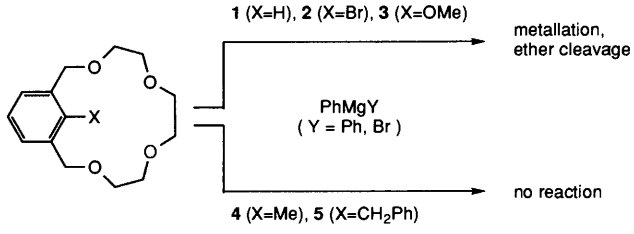


Fig. 1 Interactions between crown ethers and organometallic reagents

Results and discussion

Synthesis

A variety of labelled and unlabelled compounds were synthesised to clarify the fragmentation mechanism. In some cases alternative methods of synthesis were employed; details of synthetic procedures are given in the Experimental section.

Compounds **4** and **5** are not accessible *via* the usual route, *viz.*, *N*-bromosuccinimide (NBS) bromination of the corresponding 2-functionalised *m*-xylene and subsequent reaction with triethylene glycol. Therefore, the methyl or benzyl group was introduced by lithiation of **2** and subsequent reaction with an excess of methyl iodide or benzyl bromide, respectively.

Four deuterium-labelled derivatives of **5** were synthesised (Fig. 3), in which the deuterium labelling concerned the *intra*-annular benzyl group. The synthesis of these compounds was analogous to that of the parent compound **5**, the reaction this time being carried out with the appropriately deuterium-labelled benzyl bromides.

For the purpose of comparison, (5-benzyl-1,3-xylylene)-15-crown-4 (**6**), (2-benzyl-1,3-phenylene)-16-crown-5 (**7**) and the 'open' polyether-substituted diphenylmethanes 2-benzyl-(2,5-dioxahexyl)benzene (**8**), 2-benzyl-1,3-bis(2,5-dioxahexyl)benzene (**9**) and the corresponding dideuteriated analogues **8**-d_2 and **9**-d_2 (Fig. 4) were synthesised.

Compounds **6**, **8** and **9** could not be synthesised by routes analogous to those for the crowns **5** and **7**, because complete halogen–metal exchange occurred between the corresponding lithium compound and benzyl bromide, giving the starting

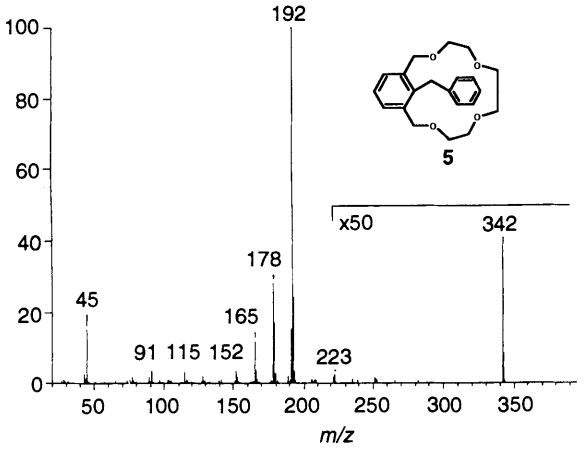


Fig. 2 70 eV EI mass spectrum of (2-benzyl-1,3-xylylene)-15-crown-4, **5**

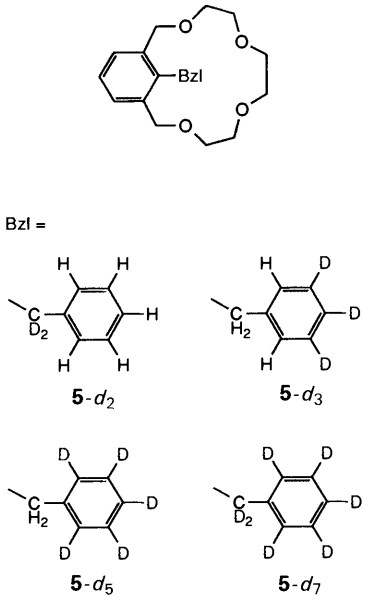


Fig. 3 Deuterium labelling of the intra-annular benzyl group of **5**

bromide and benzyllithium. Therefore, **6**, **8**, **8**-d_2, **9** and **9**-d_2 were obtained by the $CoCl_2$-catalysed coupling reaction of the corresponding Grignard reagents with (labelled) benzyl bromide.

For the attempted identification of the product ions, *m/z* 192, 1-methylanthracene (**10**) and 1-(hydroxymethyl)-9,10-dihydroanthracene (**11**) were synthesised (see the Experimental section).

Mass spectrometry

The EI mass spectrum of crown ether **5** (see Fig. 2) is nearly identical with that of 1-methylanthracene (**10**); the molecular ion peak of $\mathbf{5}^{\bullet+}$ at *m/z* 342 is very weak (< 1%) with respect to the *m/z* 192 base peak, and the intensity of other fragment ion signals at intermediate masses is low (< 5%). Both the second field free region parent ion spectrum (B^2/E) of *m/z* 192 and the metastable ion spectrum of *m/z* 342 show that ions *m/z* 192 are formed directly from the molecular ions $\mathbf{5}^{\bullet+}$. Moreover, an accurate mass measurement of *m/z* 192 indicated that these radical cations have the same elemental composition as the methylanthracenes, *viz.* $C_{15}H_{12}$. Obviously, the entire tetraoxadecane (or 'polyoxyethylene') unit of the crown ether is expelled! As the elimination of the elements of triethylene glycol, $HO(CH_2CH_2O)_3H$, in the form of two or more neutral fragments is energetically unfavourable, the product ions *m/z* 192 ($C_{15}H_{12}^{\bullet+}$) must be formed by loss of an intact molecule of triethylene glycol.

The loss of the polyoxyethylene ring as polyethylene glycol

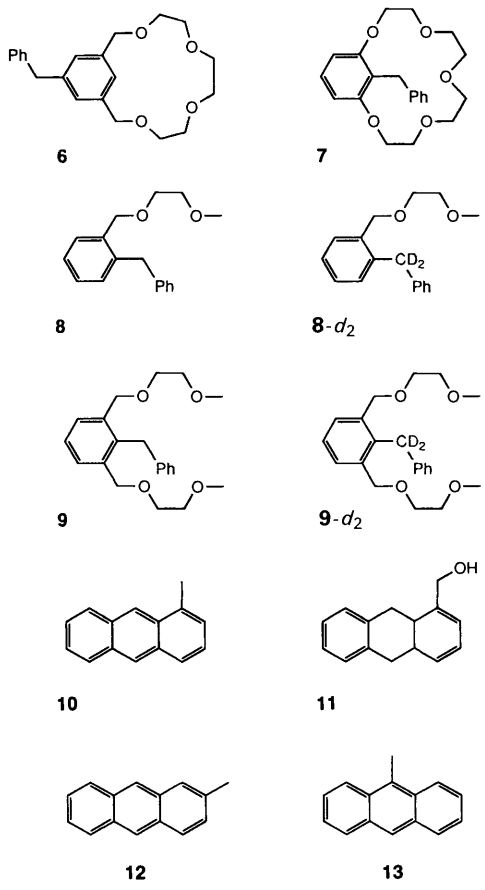


Fig. 4

is not a common fragmentation for (aryl) crown ethers. Reinhoudt *et al.*[2] observed that 1,2- and 1,3-xylylene crown ethers, with various polyoxyethylene chain lengths up to 1,3-xylylene-30-crown-9, fragment mainly *via* a ring-opening reaction to give either protonated crown ether ions (of general mass *m/z* [45 + (*n* − 1) × 44], with *n* ⩽ the number of oxyethylene units) or ions from the xylylene group, particularly *m/z* 104, [$C_8H_8^{\bullet+}$].

Similar fragmentations have been reported for aliphatic crown ethers,[3] 1,2-benzo crown ethers[4] and 2,6-pyridyl crown ethers.[5] The dissociative ionisation of 2-substituted 1,3-xylylene crown ethers has not been extensively investigated; several spectra from the Amsterdam laboratory (presented in Table 1) show that they behave generally like unsubstituted 1,3-xylylene crown ethers.[2] Thus, the mass spectral behaviour of the 2-benzyl substituted 1,3-xylylene crown ether **5** is unique.

Several mechanisms can be envisaged for the loss of triethylene glycol from ionised **5**, but crucial information to establish one exclusive mechanism required further experimental evidence. To this end, the fragmentation of $\mathbf{5}^{\bullet+}$ was studied by appropriate deuterium-labelling experiments, by experiments with structurally similar (labelled) compounds, by MS/MS experiments with $C_{15}H_{12}^{\bullet+}$ ions from various sources and by semiempirical MNDO/PM3 calculations.[6]

The EI mass spectra of the labelled analogues. **5**-d_2, **5**-d_3, **5**-d_5 and **5**-d_7, show that hardly any scrambling occurs among the hydrogen atoms of the benzylic ring, of the benzylic methylene group and of the rest of the molecule; partial mass spectra of **5**-d_2, **5**-d_3, **5**-d_5 and **5**-d_7 are given in Table 2. The EI spectrum of **5**-d_2 shows an exclusive shift of *m/z* 192 to *m/z* 193, $C_{15}H_{11}D^{\bullet+}$, thus indicating that one benzylic methylene hydrogen is involved in the loss of neutral triethylene glycol. The EI spectrum of **5**-d_5 shows an exclusive shift of *m/z* 192 to *m/z* 196, $C_{15}H_8D_4^{\bullet+}$, proving that loss of triethylene glycol also involves one hydrogen atom of the benzylic ring. The EI

Table 1 Partial mass spectra[a] of some 2-substituted 1,3-xylylene crown ethers

	Number of oxygen atoms in crown, n[b]						
	4	4	4	4	4	4	5
	Intraannular substituent, X, at C2						
	I	Cl	OEt	OiPr	SEt	ZnBr	Me
Ion							
m/z 45	40	35	37	100	40	7	60
m/z 89	50	37	28	67	22	10	45
m/z 133	100	54	98	45	13	10	18
m/z 177	—	—	—	5	—	—	19
$\{M - [HO(CH_2CH_2O)_{n-1}H]\}^{\bullet+}$	—	—	37	—	100	—	—
$\{M - [O(CH_2CH_2O)_{n-1}H]\}^{+}$	—	—	100	10	84	—	—
$[M - (HO(CH_2CH_2O)_{n-2}CH_2CHO)]^{\bullet+}$	92	100	29	6	16	1	100
$[M - X]^{+}$	89	—	—	—	12	—	—
$M^{\bullet+}$	36	18	14	11	15	2	33
$C_8H_7S^{+}$ (m/z 135)	—	—	—	—	47	—	—
$[M - C_3H_6]^{\bullet+}$	—	—	—	—	65	—	—
$\{M - C_3H_6 - [O(CH_2CH_2O)_{n-1}H]\}^{+}$	—	—	—	51	—	—	—
$\{M - C_3H_6 - [HO(CH_2CH_2O)_{n-2}CH_2CHO]\}^{+}$	—	—	—	55	—	—	—
$[M - Br]^{+}$	—	—	—	—	—	100	—

[a] Not corrected for naturally occurring isotopic contributions. [b] n = 4: 1,3-xylylene-15-crown-4; n = 5: 1,3-xylylene-18-crown-5.

Table 2 Partial EI mass spectra and EI-MIKE spectra (in parentheses) of crown ethers **5**, **5**-d_2, **5**-d_3, **5**-d_5 and **5**-d_7

	Intensity[a,b] *vs.* mass (amu) of fragment ion [M − triethylene glycol]$^{\bullet+}$								
Crown[c,d]	191	192	193	194	195	196	197	198	199
5	15	100 (100)	7	2	—	—	—	—	—
5-d_2	2	12	100 (100)	1	3	—	—	—	—
5-d_3	1	1	7	35	100 (100)	1	—	—	—
5-d_5	—	—	—	4	18	100 (100)	2	9	3
5-d_7	—	—	—	—	2	8	100 (100)	8	6

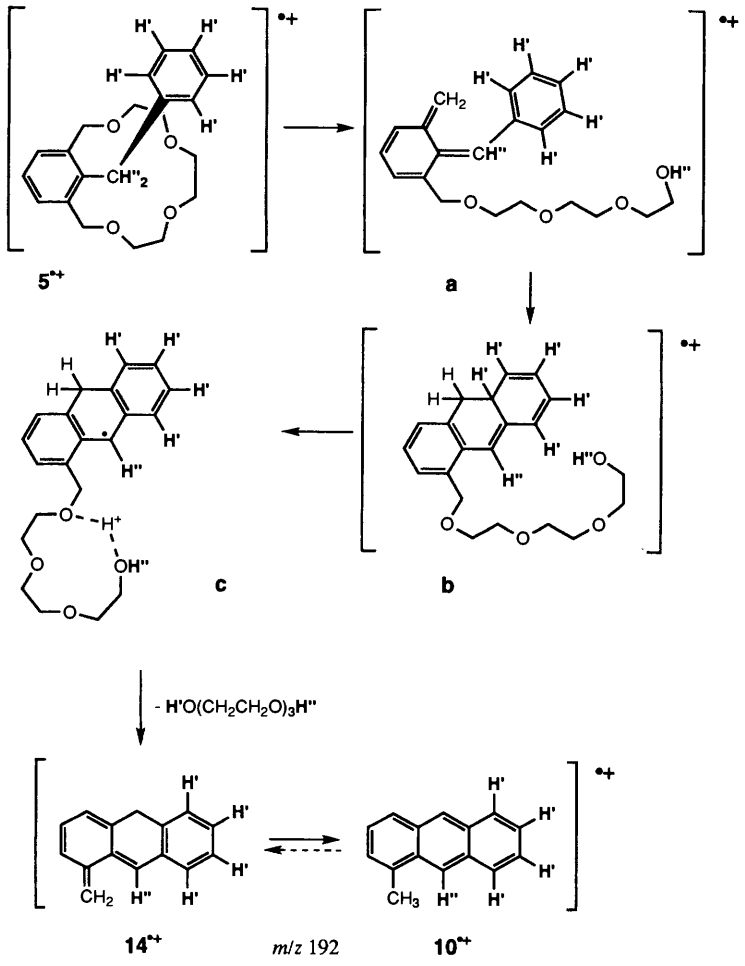
[a] In % of basepeak intensity. [b] EI Intensities corrected for naturally occurring ^{13}C isotopomers. [c] See Fig. 3 for labelling positions. [d] Isotopic purity (determined by ^1H NMR): **5**-d_2, **5**-d_5 and **5**-d_7 > 95%, **5**-d_3 > 85%.

spectrum of **5**-d_3 shows an exclusive shift of m/z 192 to m/z 195, which, together with the latter data, gives evidence that one of the *ortho*-hydrogen atoms of the benzylic ring is lost in the neutral triethylene glycol. Finally, the EI spectrum of **5**-d_7 is in line with these results; it shows m/z 197, $C_{15}H_7D_5^{\bullet+}$, as the base peak. The metastable ion kinetic energy (MIKE) and collision-induced dissociation (CID) spectra of the four isotopomers of **5** confirm the observations of the EI spectra and show that even long-lived (mean lifetime ~ 10^{-5} s) molecular ions **5**$^{\bullet+}$ do not scramble hydrogen atoms of the arene and benzylic positions; the partial MIKE spectra of **5**-d_2, **5**-d_3, **5**-d_5 and **5**-d_7 are included in Table 2. Because all atoms of the polyoxyethylene chain are saturated, it may safely be assumed that the H and D atoms transferred from the methylene and from one of the *ortho* positions of the benzyl group become hydroxy-group atoms in the triethylene glycol neutral. Furthermore, the lack of hydrogen exchange in the d_2, d_3, d_5 and d_7 isotopomers, as shown by the MIKE and CID spectra of [**5**-d_2]$^{\bullet+}$, [**5**-d_3]$^{\bullet+}$, [**5**-d_5]$^{\bullet+}$ and [**5**-d_7]$^{\bullet+}$, provides no evidence for the involvement of ion–molecule complexes in the fragmentation of **5**$^{\bullet+}$. Such complexes are generally characterised by efficient exchange of chemically equivalent hydrogens, at least at longer ion lifetimes, and especially for hydroxy hydrogens.[7] Therefore, a mechanism involving ion–molecule complexes is unlikely in the present case.

The fact that one of the benzylic methylene hydrogen atoms is incorporated into the triethylene glycol molecule lost from **5**$^{\bullet+}$ may arise from an '*ortho* effect'.[8] The *ortho* effect could give rise to a first step (**5**$^{\bullet+}$ ⟶ **a**) in the loss of triethylene glycol, as is depicted in Scheme 1. This corresponds to the loss of water from the molecular ions of 2-methylbenzyl alcohol,[8a] 2-methylbenzhydrols[9] and *o*-(hydroxymethyl)diphenylmethanes.[10]

That the *ortho* effect is operative is corroborated by the spectra of **8** and **9** and their isotopomers **8**-d_2 and **9**-d_2, respectively, and by the spectra of **6** and **7** (Fig. 4). The EI mass spectrum of **6** (see the Experimental section) shows the behaviour of a common 1,3-xylylene crown.[2] Also, the EI mass spectrum of the 2-benzylphenylene crown, **7** (also given in the Experimental section), shows no unexpected fragmentation pattern. Thus, compounds similar to **5** behave like common aryl crown ethers in the absence of substituents that would allow the *ortho* effect. It may be noted that ions **7**$^{\bullet+}$ may undergo a shift of a benzylic methylene H atom to one of the oxygen atoms, but that this would not lead to facile fragmentation.

The mass spectra of **8** and **9** show a loss of 76 amu, *viz.*



Scheme 1

$CH_3OCH_2CH_2OH$, from the molecular ion, to give *m/z* 180 and *m/z* 268, respectively. In both cases, the *ortho* effect leads to immediate separation of the neutral and the ion, in contrast with the process in $\mathbf{5}^{\bullet+}$. It should be noted that the intensity of the molecular ions, $\mathbf{8}^{\bullet+}$ and $\mathbf{9}^{\bullet+}$, is too low to allow any MS/MS experiments. The EI mass spectra of the isotopomers, **8**-d_2 and **9**-d_2, exclusively show the loss of 77 amu, $CH_3OCH_2CH_2OD$, to give *m/z* 181 and *m/z* 269, respectively. Interestingly, the relative abundance of ions $[\mathbf{9} - CH_3OCH_2CH_2OH]^{\bullet+}$ (*m/z* 268) and $[\mathbf{9}\text{-}d_2 - CH_3OCH_2CH_2OD]^{\bullet+}$ (*m/z* 269) is only about 1% of the base peak and the elimination of the second molecule of unlabelled $CH_3OCH_2CH_2OH$ from this fragment, giving ions *m/z* 192, seems to be favourable. This is a remarkable parallel in the mass spectra of the 'open' crown-ether **9** and the 'closed' one **5** (see below).

The fragmentation of $\mathbf{8}^{\bullet+}$ is comparable to that of *o*-hydroxymethyldiphenylmethane:[10] it has been reported that this compound loses H_2O upon ionisation and labelling experiments proved that the second hydrogen does not originate from the hydroxymethyl group (but rather from the diaryl-substituted CH_2 group). This proves that a cleavage reaction based on the *ortho* effect occurs as the first step in the fragmentation of $\mathbf{8}^{\bullet+}$ and $\mathbf{9}^{\bullet+}$ and, by analogy, of $\mathbf{5}^{\bullet+}$. Thus, the *o*-quinodimethane ion **a**, bearing an open-chain triethylene glycol ether group, may be assumed to be the first intermediate in the fragmentation of ions $\mathbf{5}^{\bullet+}$.

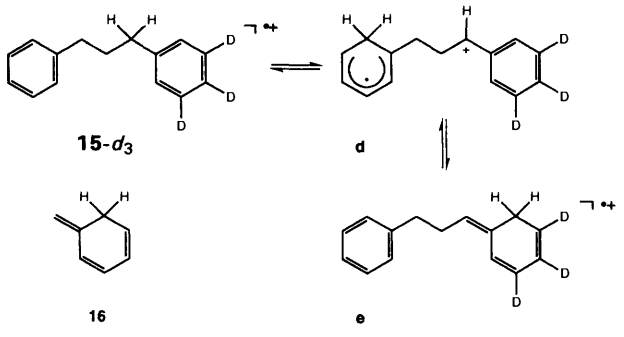
Further support is derived from semiempirical MNDO/PM3 calculations;[6] the heats of formation, at 298 K, of ion structures involved in the *ortho*-effect reaction were calculated using full geometry optimisation. The ions $\mathbf{5}^{\bullet+}$ have a ΔH_f^{298} of 456 kJ mol^{-1}, whereas the *ortho*-hydrogen transfer step (not shown in Scheme 1) is calculated to require at least an additional 43 kJ mol^{-1} to generate the distonic ion intermediate with its ΔH_f^{298} of 499 kJ mol^{-1}. With additional opening of the crown, however, the resulting intermediate, **a**, has a ΔH_f^{298} of 472 kJ mol^{-1}. Thus, the (approximate) barrier for the *ortho* effect is sufficiently low for the reaction to proceed. As will be shown in the next paragraphs, the initial hydrogen transfer represents the energy-determining step of the overall fragmentation reaction of ions $\mathbf{5}^{\bullet+}$.

The second step in the fragmentation of $\mathbf{5}^{\bullet+}$, which apparently leads to expulsion of triethylene glycol, proved less straightforward to rationalise. We attempted to identify structurally the *m/z* 192 product ions, by comparison of MS/MS spectra of $C_{15}H_{12}^{\bullet+}$ radical cations from several other sources. However, the molecular ions from 1-, 2- and 9-methylanthracene ($\mathbf{10}^{\bullet+}$, $\mathbf{12}^{\bullet+}$ and $\mathbf{13}^{\bullet+}$, respectively) and the $C_{15}H_{12}^{\bullet+}$ fragment ions generated from $\mathbf{5}^{\bullet+}$ and from $\mathbf{11}^{\bullet+}$ (by loss of water) yielded identical MIKE and CID spectra. Moreover, these identical spectra did not yield any structure-specific information, although the presence of a fused ring aromatic system could be deduced from the fragmentation pattern. The charge stripping (CS) region of the CID spectra, which is known to provide information for the distinction of isomers (*e.g.* for the radical ions of propene and cyclopropane[11]), was obscured by common CID signals; the overall abundance of peaks in the CID mass spectrum prevented successful application of a floating collision cell voltage to offset the CS spectrum. Thus, from the MIKE and CID spectra, it is clear only that all $C_{15}H_{12}^{\bullet+}$ ions investigated rearrange to a similar structure, or to a similar mixture of structures, below their dissociation threshold. Moreover, the MIKE and CID spectra do not allow structural distinction of the $C_{15}H_{12}^{\bullet+}$ product ions from the fragmentation of $\mathbf{5}^{\bullet+}$ and $\mathbf{9}^{\bullet+}$ (*i.e.* [**9** − 2

$CH_3OCH_2CH_2OH]^{\bullet+}$), nor do the MS/MS spectra of the fragment ions from **5**-d_2, **5**-d_3, **5**-d_5, **5**-d_7 and **9**-d_2 allow any conclusion with respect to the position of deuterium within the fragment ions.

As mentioned above, the second proton transfer involves specifically one of the *ortho*-hydrogen atoms of the benzyl group. This specificity can be maintained only if the bond of this particular hydrogen atom is activated by ring closure, leading to the anthracene-type intermediate **b**.[9] The transfer of the *ortho*-hydrogen, as a proton, from the weakened doubly allylic C–H bond of **b** to the remote part of the triethylene glycol unit may be facilitated by the high flexibility of the polyether group, as depicted in Scheme 1 (**b** ⟶ **c**). It should be noted that this hydrogen-transfer step should be highly exothermic because of the high proton affinity (PA) of polyethers, as compared with that of olefins and arenes.[12] For example, the PA of diethylene glycol dimethyl ether, $(MeOCH_2CH_2)_2O$, is 916 kJ mol^{-1}, similar to that of α,ω-dimethoxyalkanes, *e.g.* $MeO(CH_2)_5OMe$ (929 kJ mol^{-1},[12,13] thus exceeding the PAs of simple methyl alkyl ethers by over 80 kJ mol^{-1}.[14]

The fact that protons in protonated aromatic ring systems (arenium ions) tend to interchange very quickly[15a] is not in contradiction to the specificity of the hydrogen transfer observed, and assumed for the mechanism suggested in Scheme 1. Much in contrast with even-electron arenium ions,[15a] it was found that *radical cationic* species derived from alkylbenzenes,[15b] and from the isotoluenes[16,17] (*cf.* **16**; Scheme 2) do



Scheme 2

not undergo proton (or hydrogen atom) ring walk isomerisation. As a particularly relevant example,[18] 1,3-diphenylpropane radical cations (*e.g.*, **15**-d_3) undergo a highly regiospecific interchange of all hydrogen atoms at the benzylic and at the *ortho* positions, probably involving the distonic ion **d** (Scheme 2) and the isotoluene-type ion **e**. The latter species corresponds strictly to the intermediate **b** postulated for the fragmentation of the crown ether ions **5**$^{\bullet+}$ (Scheme 1). In both these species hydrogen exchange within the isotoluene ring does not occur.

The exothermicity is confirmed by the results of MNDO/PM3 calculations. The ΔH_f^{298} of the intermediate ring-closed ion, **b**, lies at 304 kJ mol^{-1}, leading to an exothermicity of 152 kJ mol^{-1} on going from **5**$^{\bullet+}$ to **b** and providing a suitable driving force for the reaction. With the ring proton placed on the terminal hydroxy group of the open crown, **b**, a ΔH_f^{298} of 316 kJ mol^{-1} is found. Coordination of one proton to more than one oxygen atom in a polyether system is known to be thermodynamically favourable when the oxygen atoms are separated by a sufficiently long chain; two or more oxyethylene units are required to achieve multiple coordination in polyethers.[19] Therefore, initial protonation of the terminal hydroxy group would lead to ions **c**, which involve coordination of the proton to the hydroxy oxygen and the benzylic oxygen atom of the crown. MNDO/PM3 calculations put ΔH_f^{298} **(c)** at 332 kJ mol^{-1}, close to ΔH_f^{298} **(b)**. The calculated minima for **b** and **c** may well be local, because the polyoxyethylene unit can assume many different conformations. However, with the calculations reflecting even the worst case, the intermediacy of **b** and **c** is probable, because the excess energy of **5**$^{\bullet+}$ with respect to **c** is large, *i.e.*, > 130 kJ mol^{-1} according to MNDO/PM3. The combined product ΔH_f^{298} lies at 263 kJ mol^{-1}, the overall exothermicity of the fragmentation reaction of **5**$^{\bullet+}$ then being 193 kJ mol^{-1} according to MNDO/PM3. Remarkably, the twofold elimination of $CH_3OCH_2CH_2OH$ from the 'open' crown-ether ions **9**$^{\bullet+}$ should be similarly exoergic and is, in fact, also highly efficient, as mentioned above.

Table 3 MNDO/PM3 calculated heats of formation of $C_{15}H_{12}^{\bullet+}$ ions

Compound[a]	ΔH_f^{298}[ion]/kJ mol^{-1}
1-Methylanthracene (**10**)	980
2-Methylanthracene (**12**)	975
9-Methylanthracene (**13**)	978
1-Methylene-1,10-dihydroanthracene (**14**)	1069
3*H*-dibenzo[*a*,*d*]cycloheptene	1051
8*H*-cyclohepta[*b*]naphthalene	1103

[a] Structures of the ions were fully optimized.

The proposed *m*/*z* 192 product ion, ionised 1-methylene-1,10-dihydroanthracene (**14**$^{\bullet+}$), may subsequently rearrange to other isomeric structures which are thermodynamically more favourable. This is corroborated by the fact that the MIKE and CID spectra of all $C_{15}H_{12}^{\bullet+}$ ions are similar. Further support for such rearrangements of **14**$^{\bullet+}$ comes from thermodynamic considerations. Experimental heats of formation are not available for $C_{15}H_{12}^{\bullet+}$ ions, although experimental ionisation energies have been reported for some of the isomers and ΔH_f[**12**] and ΔH_f[**13**] have been estimated.[12] In order to obtain a set of comparable values, the ΔH_f values of some $C_{15}H_{12}^{\bullet+}$ isomers, which may conceivably be involved in the above fragmentation, were also approximated by MNDO/PM3 calculations. The results of these calculations are summarised in Table 3.

The heat of formation of **14**$^{\bullet+}$ lies about 90 kJ mol^{-1} above that of the methylanthracene-type and between those of the cycloheptatriene-type radical cations. Therefore, a rearrangement of **14**$^{\bullet+}$ to any of the ionised methylanthracene isomers is thermodynamically favourable, consistent with the fact that aromatic compounds, in general, may scramble all or a large part of their constituent atoms.[15,20] Given the high exothermicity of the overall fragmentation process, consecutive H-atom shifts to generate 1-methylanthracene radical cations **10**$^{\bullet+}$ as the final fragment ions appears to be most probable.

Experimental

Instrumentation

NMR spectra were obtained on a Bruker AC 200 spectrometer (^{1}H NMR: 200 MHz; Bruker, Rheinstetten, Germany). GC–MS analyses were performed on an HP 5890 II GC coupled to a 5971 mass selective detector (Hewlett Packard, Palo Alto, CA) and equipped with a 50 m/0.25 mm id HP1 column. EI and MIKE spectra were obtained on a Finnigan MAT 90 mass spectrometer of *BE* geometry (Finnigan MAT, Bremen, Germany), using a direct inlet probe, and operating with a source temperature of 200 °C and at 70 eV. Accurate mass measurement was performed by peak-matching at a resolution of ~10 000. CID mass spectra were obtained on a Fisons Autospec of EBE geometry (Fisons, Manchester, UK), using the third field-free region collision gas cell with helium as the collision gas (at a pressure equivalent of ~33% main beam intensity reduction). The Autospec was operated at a source temperature of 200 °C, with 70 eV ionisation, 8 kV acceleration voltage, and using an unheated direct inlet probe (EI and

MIKE spectra from the Autospec were identical with those obtained on the MAT 90).

Compounds

Reactions involving organomagnesium compounds were carried out in fully sealed glassware using standard high vacuum techniques. Solvents were dried by distillation from liquid Na/K alloy after predrying on NaOH. The THF needed for the synthesis of crown ethers and related compounds was dried by distillation from $LiAlH_4$ before use. All melting points are uncorrected.

The starting materials benzyl bromide (Merck), sodium hydride (Janssen), 1-bromo-2,6-dimethylbenzene (Janssen), 1-bromo-3,5-dimethylbenzene (Aldrich), 2-methylanthracene (Aldrich) and 9-methylanthracene (Aldrich) were commercially available.

Synthesis of starting materials

The crown ethers (2-bromo-1,3-xylylene)-15-crown-4 (**2**)[21] and (5-bromo-1,3-xylylene)-15-crown-4[1b] are known; they were synthesised from triethylene glycol and 1-bromo-2,6- or 1-bromo-3,5-bis(bromomethyl)benzene, respectively. [*ring*-$^2H_5$]Toluene was obtained after bromination of [$^2H_6$]benzene (with Br_2 and $AlCl_3$) and subsequent quenching of the Grignard reagent of [$^2H_5$]bromobenzene (in THF) with methyl iodide. Similarly, [*methyl*-$^2H_3$]toluene was obtained from bromobenzene and [$^2H_3$]methyl iodide. [α,α-$^2H_2$]Benzyl bromide, [*ring*-$^2H_5$]benzyl bromide and [$^2H_7$]benzyl bromide were then prepared from the appropriately labelled toluene by NBS bromination in CCl_4. [3,4,5-$^2H_3$]Benzyl bromide was prepared from 4-methylanilinium chloride by adapting a labelling sequence used previously for the preparation of [3,4,5-$^2H_3$]bromobenzene.[14,18] 1,3-Phenylene-16-crown-5 was kindly donated by Dr. David. B. Amabilino and Professor J. F. Stoddart, University of Birmingham (UK).

Synthesis of [3,4,5-$^2H_3$]benzyl bromide

4-Methylanilinium chloride was converted into [2,6,*N*,*N*,*N*-$^2H_5$]-4-methylanilinium chloride by repeated H/D exchange with D_2O.[22] [$^2H_3$]Hypophosphoric acid was prepared by careful concentration of commercial H_3PO_2 (50%, Aldrich) *in vacuo* (0.1 mbar, 60–70 °C) followed by H/D exchange with the same volume of D_2O (99.75% D, Merck). After a total of six exchange cycles, D_2O was added to the concentrated D_3PO_2 to give a *ca.* 50% solution.

[2,6,*N*,*N*,*N*-$^2H_5$]-4-Methylanilinium chloride (14.8 g, 0.10 mol) was dissolved in D_3PO_2 (80 ml, 50% v:v in D_2O) under nitrogen and with gentle heating. The solution was then cooled to −15 °C and predried sodium nitrite (7.6 g, 0.11 mol) was added in small portions with stirring. Desazotisation started while the temperature of the reaction mixture was kept at −5 to 0 °C. When the reaction had ceased, water was added and the product was extracted with diethyl ether, dried with sodium sulfate, and purified by distillation through a short column to give [3,4,5-$^2H_3$]toluene (4.9 g, 53%), bp 109–110 °C, δ(60 MHz; $CDCl_3$) 2.40 (s, 3.0 H), 7.20 (s, 2.1 H).

[3,4,5-$^2H_3$]Toluene (3.0 g, 32 mmol) was dissolved in dry tetrachloromethane (30 ml), *N*-bromosuccinimide (5.7 g, 32 mmol) and azoisobutyronitrile (0.1 g) were added and the mixture was heated to reflux temperature for 3 h. Work-up and double distillation of the crude product gave [3,4,5-$^2H_3$]benzyl bromide (3.5 g, 63%), bp 84–86 °C (20 mbar), δ(300 MHz; $CDCl_3$) 4.50 (s, 2.00 H), 7.39 (s, 1.89 H, corresponding to *ca.* 95% arene H); *m*/*z* (EI, 70 eV) 172 (2.0), 173 (6.0, [D_3, ^{79}Br]-$M^{\bullet+}$), 174 (2.5), 175 (6.0), 95 (12), 94 (100), 93 (22), 92 (6), 91 (5). Isotope purity: *ca.* 10% $^2H_2$, 85% $^2H_3$, 5% $^2H_4$.

Synthesis of benzyl substituted 1,3-xylylene crown ethers 5 and 6

The 2- and 5-benzyl-1,3-xylylene crown ethers (**5** and **6**, respectively) could not be synthesised from the appropriate oligo ethylene glycol and 2-benzyl-1,3-dimethylbenzenes, but instead were synthesised from (2-bromo-1,3-xylylene)-15-crown-4 and from (5-bromo-1,3-xylylene)-15-crown-4.

Synthesis of (2-benzyl-1,3-xylylene)-15-crown-4 (5,5-d_2, 5-d_3, 5-d_5 and 5-d_7)

Synthesis of 5. A solution of **2** (2.1 mmol, 0.70 g) in THF (10 ml) was prepared under argon. After cooling to −60 °C, 1 equiv. of *n*-butyllithium (2.1 mmol, in *n*-hexane, 1.31 ml) was added within 1 min, yielding 2-lithio-1,3-xylylene-15-crown-4. Introduction of the benzyl group was achieved by the addition of benzyl bromide (2.5 mmol, 0.6 g) to the dark-yellow solution of this lithio compound. The solution was slowly warmed to room temperature, after which it was stirred for an additional 2 h. The reaction mixture was evaporated to dryness, water was added and the organic material isolated by extraction with diethyl ether. The organic phase was dried ($MgSO_4$), filtered and evaporated to dryness to yield a yellow oil (1.02 g), which was analysed by GC–MS. Apart from benzyl bromide, pentylbenzene and 1,2-diphenylethane the oil contained the crown ethers: **1** (30%), (2-butyl-1,3-xylylene)-15-crown-4 (17%) and **5** (53%). Compound **5** was obtained in pure form by preparative GC, using a 2 m 10% OV 101 column (id 4 mm). The compound solidified as a pale yellow solid upon standing (mp 110–111 °C).

5: δ[$CDCl_3$; 200 MHz; δ($CHCl_3$) = 7.27 ppm] 3.32–3.69 (m, 12 H, C_2H_4), 4.02, 4.84 (dd, AB, ^2J = 12.6 Hz, 4 H, xylylene-CH_2) 4.64 (s, 2 H, benzyl-CH_2), 6.96–7.19 (m, 3 H, aryl-H); *m*/*z* 342 ($M^{\bullet+}$, $C_{21}H_{26}O_4$, 0.7%), 192 (100), 191 (15), 179 (17), 178 (28), 165 (11), 152 (3), 115 (3), 103 (1), 91 (4), 89 (1), 77 (1), 75 (1), 45 (15), 43 (2) (Calc. for $C_{21}H_{26}O_4$: 342.1831. Found: 342.184 ± 0.002; Calc. for $C_{15}H_{12}$: 192.0939. Found 192.094 ± 0.001).

The deuterium-labelled compounds **5**-d_2, **5**-d_3, **5**-d_5 and **5**-d_7 were prepared analogously to **5** by reacting 2-lithio-1,3-xylylene-15-crown-4 with benzyl bromide-d_2, -d_3, -d_5 and -d_7, respectively.

5-d_2: *m*/*z* 344 ($M^{\bullet+}$, $C_{21}H_{24}D_2O_4$, 1%), 194 (16), 193 (100), 192 (10), 180 (6), 179 (2), 178 (1), 167 (4), 166 (1) + impurities in low *m*/*z* region.

5-d_3: *m*/*z* 345 ($M^{\bullet+}$, $C_{21}H_{23}D_3O_4$, 0.01%), 195 (100), 194 (33), 181 (11), 180 (7).

5-d_5: *m*/*z* 347 ($M^{\bullet+}$, $C_{21}H_{21}D_5O_4$, 0.05%), 196 (100), 195 (12), 194 (3), 183 (10), 182 (12).

5-d_7: *m*/*z* 349 ($M^{\bullet+}$, $C_{21}H_{19}D_7O_4$, 0.8%), 198 (24), 197 (100), 196 (7), 195 (2), 186 (3), 185 (6), 184 (7), 183 (8), 182 (2), 171 (2), 170 (2), 169 (2), 119 (1), 105 (1), 98 (1), 97 (1), 46 (6), 45 (4).

The synthesis of compounds **6**, **8** and **9** from the reaction of their lithium precursors with benzyl bromide was not successful. In these cases, the corresponding lithium compounds reacted with benzyl bromide to form benzyllithium and the starting bromides. Therefore, these compounds were prepared by $CoCl_2$-catalysed coupling of the appropriate Grignard compounds with the (deuteriated) benzyl bromides. As in the case of **6**, where the starting bromide (5-bromo-1,3-xylylene)-15-crown-4 was unreactive in the reaction with magnesium, the Grignard reagent was prepared *in situ* by the metathesis between the organolithium analogue (5-lithio-1,3-xylylene)-15-crown-4 and magnesium bromide.

Synthesis of (5-benzyl-1,3-xylylene)-15-crown-4 (6)

A solution of (5-bromo-1,3-xylylene)-15-crown-4[23] (0.52 mmol, 0.171 g) in THF (25 ml) was prepared under argon. After cooling to −70 °C, 1 equiv. of *n*-butyllithium (0.5 mmol, in *n*-hexane, 0.31 ml) was added within 1 min. The resulting (5-lithio-1,3-xylylene)-15-crown-4 was converted into its bromomagnesium analogue by addition of $MgBr_2$ (10 ml, 0.2 M in THF). Introduction of the benzyl group was achieved by the subsequent addition of benzyl bromide (1.7 mmol, 0.29 g) and a catalytic amount of $CoCl_2$. The colour of the resulting reaction

mixture changed from purple *via* green to blue. The solution was slowly warmed to room temperature, after which it was stirred overnight. The reaction mixture was evaporated to dryness, water was added and the organic material isolated by extraction with diethyl ether. The organic phase was dried ($MgSO_4$), filtered and evaporated to dryness to yield a yellow oil (1.05 g), which was analysed with GC–MS and ^1H NMR spectroscopy. Apart from benzyl bromide and 1,2-diphenylethane, **1** and **6** (73% and 27% relative GC peak area, respectively) were present as major crown ether components. Compound **6** was obtained pure by preparative GC (*vide supra*).

6: δ[$CDCl_3$; 200 MHz; $\delta(CHCl_3)$ = 7.27] 3.71 [s, 4 H, O(2)CH_2CH_2O(3)], 3.71 [m, A_2B_2, 8 H, O(1)CH_2CH_2O(2)], 3.95 (s, 2 H, benzyl-CH_2) 4.60 (s, 4 H, xylylene-CH_2), 6.89 (s, 2 H, aryl-H4 and H6), 7.1–7.3 (m, 5 H, benzyl-H), 7.81 (s, 1 H, aryl-H2); *m/z* 342 ($M^{\bullet+}$, $C_{21}H_{26}O_4$, 54%), 194 (18), 193 (18), 179 (96), 165 (23), 133 (56), 89 (93), 45 (100) (Calc. for $C_{21}H_{26}O_4$: 342.1831. Found: 342.1831 ± 0.0004).

Synthesis of (2-benzyl-1,3-phenylene)-16-crown-5 (7)

Compound **7** was prepared *via* the direct lithiation of 1,3-phenylene-16-crown-5. A solution of 1,3-phenylene-16-crown-5 (0.32 mmol, 0.086 g) in THF (5 ml) was prepared under argon. After cooling to −30 °C, 1.5 equiv. of *n*-butyllithium (0.48 mmol, in *n*-hexane, 0.30 ml) was added within 1 min, after which the reaction mixture was stirred for 1 h. Introduction of the benzyl group was achieved by the addition of benzyl bromide (1.7 mmol, 0.29 g) to the white suspension of (2-lithio-1,3-phenylene)-16-crown-5. The solution was slowly warmed to room temperature, after which water was added. After evaporation of the THF, the organic material was isolated by extraction with diethyl ether. The organic phase was dried ($MgSO_4$), filtered and evaporated to dryness to yield a yellow oil (0.417 g), which was analysed by GC–MS. Apart from benzyl bromide and 1,2-diphenylethane, the oil contained 1,3-phenylene-16-crown-5 (37%) and **8** (63%). After evaporation under high vacuum (10^{-3} mbar) for 10 h at 55 °C, the residue was a white solid, containing 1,3-phenylene-16-crown-5 (34%) and **7** (66%). After crystallisation from acetone at −20 °C, compound **7** was obtained pure as white crystals (mp 93–95 °C; 0.017 g, 0.047 mmol, 15%).

7: δ[$CDCl_3$; 200 MHz; $\delta(CHCl_3)$ = 7.27] 3.34–3.80 (m, 12 H, 2 × A_2B_2 and 2 × B_2 part of A_2B_2, C_2H_4 + CH_2), 4.22 (s, 2 H, benzyl-CH_2) 4.22–4.49 (m, 4 H, 2 × A_2 part of A_2B_2, phenylene-OCH_2), 6.67 (d, ^3J = 8.2 Hz, 2 H, phenylene-H4 and H6), 7.07–7.35 (m, 6 H, phenylene-H5 and 5 × benzyl-H); *m/z* 358 ($M^{\bullet+}$, $C_{21}H_{26}O_5$, 100%), 267 (27), 226 (52), 209 (38), 197 (76), 153 (41), 91 (96), 45 (73) (Calc. for $C_{21}H_{26}O_5$: 358.1780. Found: 358.1784 ± 0.001).

Synthesis of 2-benzyl-1-(2,5-dioxahexyl)benzene (8)

To a solution of 2-(bromomagnesio)-(2,5-dioxahexyl)benzene[24,25] (0.78 mmol) in 8 ml of THF, in a fully sealed glass system, were added 0.43 g (2.52 mmol) benzyl bromide and a catalytic amount of $CoCl_2$. After being stirred at 70 °C overnight, during which the colour changed from very dark blue to azure, the reaction mixture was quenched with D_2O. The organic material was isolated by extraction with diethyl ether. The organic phase was dried ($MgSO_4$), filtered and evaporated to dryness to yield a yellow oil (0.42 g), which was analysed by GC–MS. Apart from benzyl bromide and 1,2-diphenylethane, the oil contained **8** and 2,2′-bis(2,5-dioxahexyl)biphenyl. After evaporation under high vacuum (10^{-3} mbar) for 7 h at 50 °C, the residue was an oil (0.069 g), containing **8** (59%) and 2,2′-bis(2,5-dioxahexyl)biphenyl (41%). Both compounds were purified by preparative GC (*vide supra*).

8: δ[$CDCl_3$; 200 MHz; $\delta(CHCl_3)$ = 7.27] 3.38 (s, 3 H, OMe), 3.51–3.58 (m, 4 H, C_2H_4), 4.09 (s, 2 H, benzyl-CH_2), 4.54 (s, 2 H, aryl-CH_2O), 7.12–7.39 (m, 4 H, aryl-H); *m/z* 180 ([M − $HOC_2H_4OCH_3$]$^{\bullet+}$, 100%), 179 ([M − C_6H_5]$^+$, 89), 165 (40), 152 (4), 91 (4), 45 (5).

Synthesis of 2-benzyl-1,3-bis(2,5-dioxahexyl)benzene (9 and 9-d_2)

To a solution of 2-(bromomagnesio)-1,3-bis(2,5-dioxahexyl)-benzene[24,25] (2.5 mmol) in 22 ml of THF, in a fully sealed glass system, were added 0.72 g (4.2 mmol) benzyl bromide (or [$^2H_2$]benzyl bromide) and a catalytic amount of $CoCl_2$. The green solution was stirred for four days at room temperature after which the reaction mixture was quenched with D_2O. The organic material was isolated by extraction with diethyl ether. The organic phase was dried ($MgSO_4$), filtered and evaporated to dryness to yield a dark red oil (1.1 g), which was analysed by GC–MS. Apart from benzyl bromide and 1,2-diphenylethane, this oil contained two polyether compounds: 1,3-bis(2,5-dioxahexyl)benzene (26%; no deuterium incorporation) and **9** (74%). Compounds **9** and **9**-d_2 were obtained pure after preparative GC (*vide supra*).

9: δ[$CDCl_3$; 200 MHz; $\delta(CHCl_3)$ = 7.27], 3.30 (s, 6 H, 2 × OMe), 3.38–3.53 (m, A_2B_2 8 H, 2 × C_2H_4) 4.15 (s, 2 H, benzyl-CH_2), 4.45 (s, 4 H, aryl-CH_2O), 6.89–7.39 (m, 3 H, aryl-H); *m/z* 268 ([M − $HOC_2H_4OCH_3$]$^{\bullet+}$, 1.2%), 192 (100), 178 (23), 165 (5) (Calc. for $C_{21}H_{26}O_4$: 344.1988. Found: 344.199 ± 0.001).

9-d_2: *m/z* 269 ([M − $DOC_2H_4OCH_3$], 1%), 193 (100).

Synthesis of 1-methylanthracene (10)

10 was synthesised according to Scholl and Donat[26] by a slightly adapted procedure. The reaction of *o*-tolylmagnesium bromide with phthalic anhydride gave 2-(methylbenzoyl)benzoic acid.[27] Ring-closure with 10% fuming sulfuric acid yielded 1-methylanthraquinone. The product was reduced with HI–I_2–red phosphorus, under reflux, to yield—after work-up—1-methyl-9,10-dihydroanthracene (85%) and 1-methylanthracene (15 %). The former was converted into the latter by refluxing with triphenylmethanol and trifluoroacetic acid.[28]

1-(Hydroxymethyl)-9,10-dihydroanthracene (11)

Compound **11**[23] has previously been synthesised[29] but the procedure was not provided. We found a route *via* 1-anthraquinone carboxylic acid[23,30] for the synthesis of 9,10-dihydroanthracene-1-carboxylic acid[31] convenient. 3-Benzoylphthalic acid[32] (4.06 g, 15.0 mmol) was heated to 190 °C in the presence of 0.95 g red phosphorus and 4.0 g 50% HI. After 5 h, 1 g of HI was added and the mixture was heated for a further 3 h. After cooling to room temperature, water was added and the organic material was extracted with CH_2Cl_2 and Et_2O. The organic phase was dried ($MgSO_4$), filtered and evaporated to dryness to yield almost pure 9,10-dihydroanthracene-1-carboxylic acid as a yellow solid (0.78 g, 24%). The carboxylic acid was esterified by stirring with methanol and sulfuric acid and subsequently reduced by $LiAlH_4$ to yield **11**.

MNDO/PM3 calculations were performed using the MOPAC6.0 package, on the Convex computer of the CAOS/CAMM centre of Nijmegen University (the Netherlands); all ion structures were fully optimised.

Acknowledgements

The support of the CAOS/CAMM centre at Nijmegen University (the Netherlands) and of the *Fonds der Chemischen Industrie* (Germany) is gratefully acknowledged.

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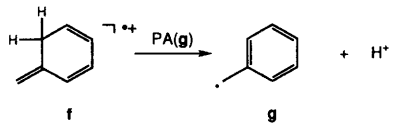
13 Removal of the 'angular' proton of the isodihydroanthracene radical cationic moiety of **c** (Scheme 1) may be considered to be analogous to deprotonation of the *ortho*-isotoluene ion **f** giving the benzyl radical **g** (Scheme 3). From known heats of formation,[12,17] PA(**g**) = ΔH_f(**g**) + $\Delta H_f(H^+)$ − ΔH_f(**f**) = 205 + 1530 − 933 = 802 kJ mol^{-1}. From this approximation, the intramolecular proton transfer step **b** ⟶ **c** (Scheme 1) is estimated to be exothermic by ΔH_r = PA(**g**) − PA(triethylene glycol) = 802 − 916 = −114 kJ mol^{-1}. Although this value may be slightly too high [use of PA(**g**) representing a lower limit], the exothermicity of the proton transfer **b** ⟶ **c** step is beyond doubt.



Scheme 3

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Paper 5/06228D
Received 20*th September* 1995
Accepted 16*th November* 1995