The Structures of Solvent-separated Naphthalene and Anthracene Radical Anions

Hans Bock,* Claudia Arad, Christian Näther and Zdenek Havlas

Department of Chemistry, University of Frankfurt, Marie-Curie-Str. 11, D-60439 Frankfurt/Main, Germany

Reduction of naphthalene and anthracene in diglyme, a thermodynamically favourable chelate ether for Na^+ solvation, with sodium metal gave the crystalline solvent-separated radical anion salts, $[C_{10}H_8^{\cdot -}][Na^+(diglyme)_2]$ and $[C_{14}H_{10}^{\cdot -}][Na^+(diglyme)_2]$ whose structures were determined.

In the past we have studied methods to crystallize solvent-separated ion pairs or ion multiples from solution.[1] Especially in aprotic solvents, a multidimensional network of interrelated equilibria such as electron transfer, ion pair formation, ion solvation as well as ion aggregation is activated.[1,2] The dominant driving force for crystallization is frequently the thermodynamically favourable solvent complexation of the counter cations [eqn. (1)].[3]

$$C_nH_m + [Me]_\infty + x\ \text{Solvent} \rightleftarrows [C_nH_m^{\cdot -}][Me^+(\text{Solvent})_x] \qquad (1)$$

If the target in eqn. (1) is a crystal stabilized by an optimally solvated cation $[Me^+\ (\text{solvent})_x]$, radical counter anions $[C_nH_m^{\cdot -}]$ with extended π systems are preferred because they lack extensively charged centres which favour contact ion formation. To date crystalline salts of the radical anions of 9,10-diphenylanthracene,[3a,b] bianthryl[3a,c] 1,1,4,4-tetraphenylbuta-1,3-diene,[1,3d] 1,1,4,4-tetraphenylbutatriene[1] or perylene[3e] have been reported.

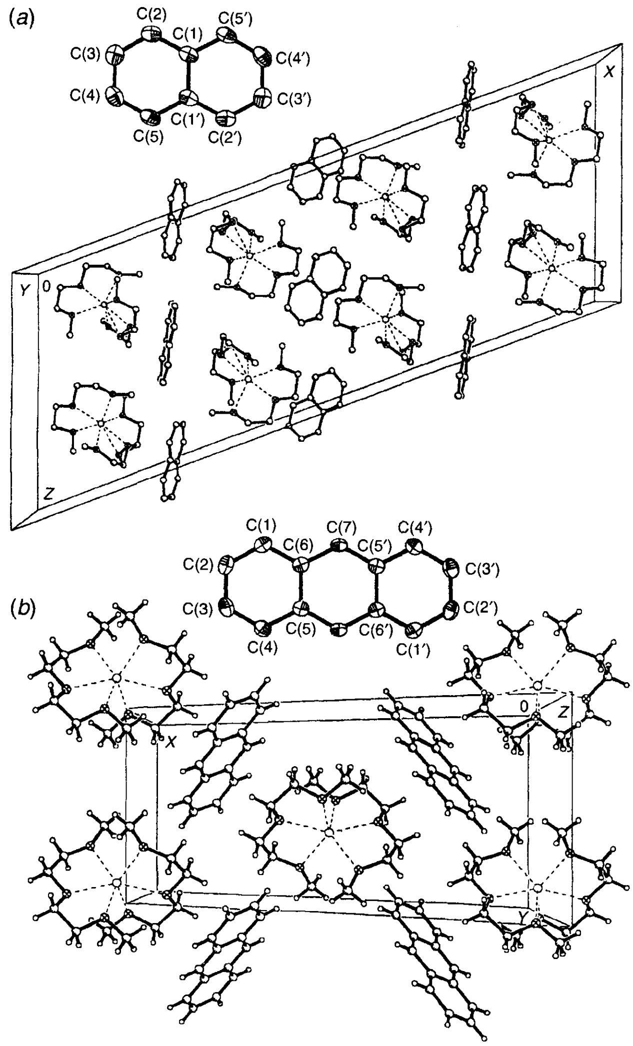

Fig. 1 Single crystal structures of (*a*) naphthalene–bis(diglyme)sodium†,‡ and (*b*) anthracene–bis(diglyme)sodium†

If the aim is to crystallize novel radical anions, then the choice of solvent becomes decisive. For the Na^+ cation,[4] the following increasing enthalpies (kJ mol^{-1}) for six coordinate ether solvation have been calculated based on structural data: $[Na^+(THF)_6]$ −587 < $[Na^+(DME)_3]$ −671 < $[Na^+(diglyme)_2]$ −677.[3a] Using this information, we grew black crystals of the naphthalene and anthracene radical salts, $[C_{10}H_8^{\cdot -}][Na^+(diglyme)_2]$ and $[C_{14}H_{12}^{\cdot -}][Na^+(diglyme)_2]$,† from diglyme after sodium reduction according to eqn. (1).[5]

The unit cells of both crystals belong to the same monoclinic symmetry group (Fig. 1), but contain either $Z = 8$ or 4 contact ion pairs. In both radical anion salts (Fig. 1) nearly complete solvent separation was observed with the shortest nonbonded C···C distances between the anions of 397 (*a*) and 393 pm (*b*) and between the anions and the diglyme solvated cations of 358 (*a*) and 349 pm (*b*). The naphthalene radical anions occupy two different positions.[5] The Na^+ counter cations are six-coordinated by two diglyme ligands and form a distorted octahedron $[Na^+O_6]$.

Relative to the neutral hydrocarbons naphthalene and anthracene,[6] the planar radical anions show significant structural changes Δd_{CC} (pm) and ΔCCC angle (°) (Fig. 2).

The negative charge causes contraction of the outer ring CC bonds by about −4 pm and lengthening of the inner bonds by up to +3 pm. The accompanying CCC angle changes can be rationalized in terms of CC bond lengthening and shortening.

The observed geometry changes are reproduced by *ab initio* UHF calculations using a double zeta basis set [d_{CC} (pm) and < CCC (°)], Fig. 3.

The Mulliken charge population shows that negative charge is preferentially driven to the long-axis periphery. The largest π spin densities are predicted and observed by ESR for the centre of the molecule,[8] Fig. 4 [○: calculated π spin population, □ ESR coupling constants (mT)[9]].

The uncorrelated *ab initio* spin populations approximately reproduce the overall trends.

In summary, sodium metal reduction in diglyme solutions and under aprotic conditions following the general approach [eqn. (1)] yields the two prototype solvent-separated π hydrocarbon radical anions presented. Their structure determination[5,6] reveals significant peripheral bond lengthening [Fig. (2)], which can be rationalized quantum chemically [Fig. (3)] based on the experimental structural data and further

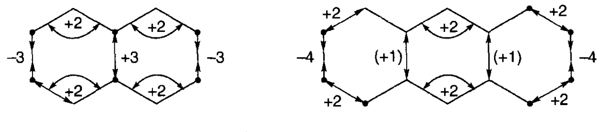

Fig. 2 Structural changes on single electron reduction of naphthalene and anthracene

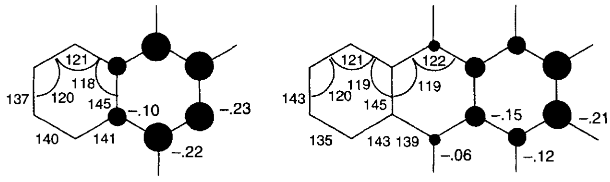

Fig. 3 *Ab initio* SCF structures and charge distributions

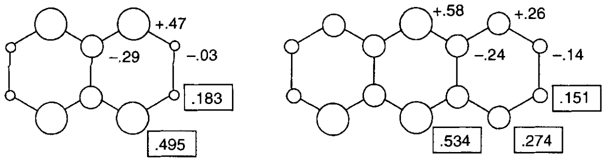

Fig. 4 *Ab initio* SCF spin populations and ESR ^1H coupling constants (bordered)

molecular properties such as the δ spin population discussed qualitatively (Fig. (4)]. This study adds to an improved understanding of π hydrocarbon radical anion ground states, and in perspective, many more may be crystallized using analogous reduction conditions.

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Footnotes

† *Crystal data* for $C_{10}H_8Na \cdot 2\ C_6H_{14}O_3$, (dimensions: 0.5 × 0.4 × 0.4 mm^3), $M = 419.5$, $a = 4019.8$ (2), $b = 785.2$ (1), $c = 1595.8$ (1) Å, $\beta = 111.31$ (1)°, $V = 4692.5 \times 10^6$ pm^3, ($T = 130$ K), $\rho_{calc.} = 1.188$, monoclinic $C2/c$ (No. 15), $Z = 8$, Mo-Kα radiation, $\mu = 0.10$ mm^{-1}. Siemens P4 four-circle diffractometer, 7315 reflections within $3° \leqslant 2\theta \leqslant 55°$, of which 5005 independent and 3947 with $I > 2\sigma(I)$. Structure solution by direct methods and difference Fourier technique (SHELXS-86). Refinement with full-matrix least-squares (SHELXL-93). $R1 = 0.0499$, $wR2 = 0.1167$ for 281 parameters and 3947 reflections, $R_{int} = 0.0272$. $w = 1/[\sigma^2(F_0{}^2) + (0.0443\ P)^2 + 5.53\ P]$, shift/error < 0.001, residual electron density 0.57/−0.35 e Å^{-3}. C, O, Na refined anisotropically. H geometrically ideally positioned and refined according to the riding model using isotropic displacement parameters. There are two independent naphthalene radical anions in the asymmetric unit, each located around a centre of inversion, of which one is slightly disordered in two orientations, and refined using a split model. For $C_{14}H_{10}Na \cdot 2\ C_6H_{14}O_3$, (dimensions: 0.7 × 0.5 × 0.3 mm^3), $M = 469.6$, $a = 2344.4$ (2), $b = 944.7$ (1), $c = 1427.1$ (1), $\beta = 124.42$ (1)°, $V = 2607$ (5) × 10^6 pm^3, ($T = 130$ K), $\rho_{calc.} = 1.196$, monoclinic $C2/c$ (No. 15), $Z = 4$, Mo-Kα radiation, $\mu = 0.10$ mm^{-1}. Siemens P4 four-circle diffractometer, 2990 reflections within $3° \leqslant 2\theta \leqslant 55°$, of which 2511 independent and 2022 with $I > 2\sigma(I)$. Structure solution by direct methods and difference Fourier technique (SHELXS-86). Refinement with full-matrix least-squares (SHELXL-93). $R1 = 0.0362$, $wR2 = 0.0896$ for 150 parameters and 2022 reflections, $R_{int} = 0.0210$. $w = 1/[\sigma^2(F_0{}^2) + (0.0402P)^2 + 1.59P]$, shift/error < 0.001, residual electron density 0.19/−0.15 e Å^{-3}. C, O, Na are refined anisotropically. H geometrically ideally positioned and refined according to the riding model using fixed isotropic displacement parameters.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

‡ *Selected bond lengths (Å) and angles (°)* For naphthalene–bis(diglyme) sodium: C(1)–C(1′) 145, C(1)–C(2) 141, C(2)–C(3) 140, C(3)–C(4) 138, Na–0236; C(1′)–C(1)–C(2) 119, C(1)–C(2)–C(3) 121, O(1)–Na(1)–O(2) 70, O(1)–Na(1)–O(3) 136. For anthracene–bis(diglyme) solution: C(1)–C(2) 139, C(2)–C(3) 139, C(4)–C(5) 142, C(5)–C(6) 145, C(6)–C(7) 142, Na–0237; C(1)–C(2)–C(3) 120, C(3)–C(4)–C(15) 122, C(4)–C(5)–C(6) 118, C(5)–C(6)–C(7) 118, C(6)–C(7)–C(5′) 123, O(1)–Na(1)–O(2) 70, O(1)–Na(1)–O(3) 135.

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9 See, *e.g.* E. Heilbronner and H. Bock, *The HMO Model and its Application*, Wiley, London, 1976, Vol. 1, p. 313 and Vol. 2, p. 265.