5. Single-Crystal Structure of the Solvent-Separated Radical Ion Pair [9,10-Diphenylanthracene$^{\cdot\ominus}$][Na$^{\oplus}$(THF)$_6$] and Its Implication for Cation Solvation[1])

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Dedicated to *Peter Weyerstahl* on the occasion of his 60th birthday

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The one-electron transfer to large π-delocalized hydrocarbons provides an interesting possibility to crystallize solvent-separated ion-pair salts containing optimally solvated cations. Accordingly, the reduction of 9,10-diphenylanthracene in aprotic THF solution at a sodium metal mirror allows to grow dark-blue prismatic crystals of its radical anion and sixfold THF-solvated sodium cation. The structure of the radical anion is very similar to that recently published for the neutral molecule. According to AM1 hypersurface calculations based on the structural data, the phenyl twist angles obviously must be determined by lattice packing, and the negative charge is delocalized predominantly within the anthracene π system. The counter cation [Na$^{\oplus}$(THF)$_6$], reported ordered for the first time, shows nearly octahedral coordination within a rather densily packed solvent shell. Due to the strong repulsions between the solvent molecules, its isodesmically calculated solvation enthalpy is smaller than that of the analogous dimethoxyethane complex [Na$^{\oplus}$(DME)$_3$].

Introduction. – 9,10-Diphenylanthracene, its radical anion, and its dianion frequently serve as prototype compounds for cyclovoltammetric [2] [3], UV/VIS- [2], NMR- [4–6], and ESR/ENDOR-spectroscopic [2] [4] [6] studies to determine the substituent effects of twisted Ph rings. In Me_2NH solution at 223 K, two reversible half-wave reduction potentials, $E_{1/2}^{\text{Red I}} = -1.98$ and $E_{1/2}^{\text{Red II}} = -2.50$ V, are recorded [3]. In imperfectly dried solvents, the second reduction becomes irreversible [3] due to monoprotonation of the 9,10-positions of the strong dianionic base as has been proven by ^{1}H- and ^{13}C-NMR studies in NH_3/THF mixtures [5]. Both the reversibility of the two reduction steps and the difference of 0.52 V between them suggest the existence of a stable radical anion [7]. Its ESR/ENDOR spectra in DME at 200 K [4] prove a spin population predominantly within the anthracene π system [4] and, according to HMO/*McLachlan* calculations, especially at C(9) and C(10) [2]. From the unusual sequence of ^{1}H coupling constants measured for the Ph rings, $|a_H^{ortho}| > |a_H^{meta}| \approx |a_H^{para}|$, twist angles between 60 and 65° are deduced [2] [4]. For the neutral molecule, dihedral angles between the anthracene and Ph

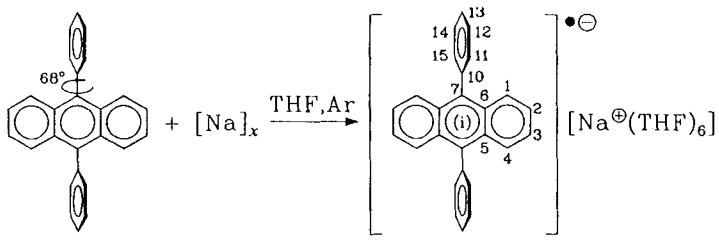
[1]) Part 26 of 'Structures of Charge-Perturbed or Sterically Overcrowded Molecules'; Part 25: [1].

[2]) Part of Ph. D. Thesis of *A. John*, University of Frankfurt, 1993.

planes of *ca.* 62° and of *ca.* 60° are estimated from ^{1}H-NMR [4] and UV/VIS [2] correlations and are found to be 68° by a recent ([8]: $R = 0.059$) and considerably improved ([9]: $R = 0.158$) single-crystal structure determination.

These findings and other results concerning solvent-shared and solvent-separated radical ion pairs, $[M^{\cdot\ominus}Me^{\oplus}]_{solv.}$ and $[M^{\cdot\ominus}][Me^{\oplus}_{solv.}]$, [10] as well as triple ion radical cations, $[M^{\cdot\ominus}Me^{\oplus}_1Me^{\oplus}_2]_{solv.}$, [11] have led us to reduce 9,10-diphenylanthracene in aprotic THF solution under Ar at a Na metal mirror (*Scheme 1*). We have succeeded in growing dark-blue prismatic crystals and in determining their structure (*cf. Experimental*).

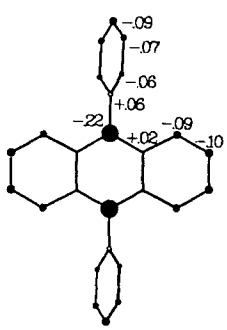
Scheme 1



Structure of 9,10-Diphenylanthracene Radical Anion. – In the relatively dense ($d_{calc.} = 1.210$ g cm^{-3}) crystals, the radical anions with twisted Ph substituents and the six-fold THF solvated $Na^{\oplus}$ counter cations (*Fig. 1, a*) form separate layers (*Fig. 1, b*).

The 9,10-diphenylanthracene radical anion $M^{\cdot\ominus}$ and the neutral molecule are both centrosymmetric with Ph twist angles of 67° (*Fig. 1, a*) and 68° (*Scheme 1*), respectively. The significant differences between the two species are: *1*) strongly alternating peripheral bonds between centers C(1) and C(4) of 135, 141, and 135 pm in M [8] *vs.* equalized bonds of 139 pm in $M^{\cdot\ominus}$ (*Tables 1* and *2*) a slight lengthening of the ring bonds involving the substitution center C(7) from 141 pm in M [8] to 143 pm in $M^{\cdot\ominus}$ (*Table 1*). Both changes are due to the additional negative charge and are readily explained by an AM1 charge distribution for the C-centres (*Scheme 2*) calculated from the structural data of the

Scheme 2



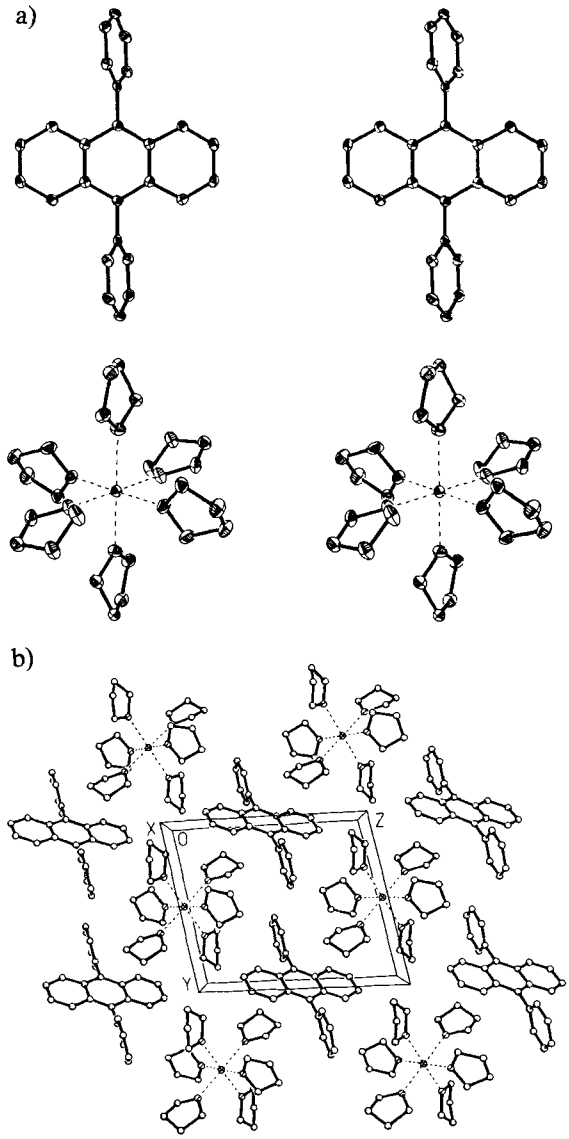


Fig. 1. *Single-crystal structure of the solvent-separated radical ion pair [9,10-diphenylanthracene$^{\cdot\ominus}$][Na$^{\oplus}$(THF)$_6$].* *a*) Stereoview of the six-fold THF solvated $Na^{\oplus}$ ion and the radical ion (50% thermal ellipsoids; for structural data, see *Table 1*; for numbering, see *Scheme 1*) and *b*) crystal packing (unit cell with $Z = 1$ in x-direction).

radical anion (*Table 1*), which reflects for the central anthracene system the squared HMO coefficients $(c^{\pi}_{-1})^2$ of its lowest unoccupied π molecular orbital [12].

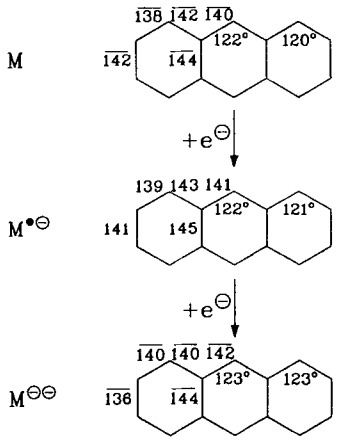
According to the calculated carbon charges, which are partly compensated by adjacent polarized $H^{\delta\oplus}$ centers, *ca.* $^4/_5$ of the negative charge is predicted at the Ph substitution centers C(7) and C(7′) as well as at the peripheral ring C-atoms C(1)···C(4) and

Table 1. *Selected Structural Data for the 9,10-Diphenylanthracene Radical Anion* (for arbitrary numbering, *cf. Scheme 1*) *and for the Six-fold THF-Solvated Sodium Counter Cation*

9,10-Diphenylanthracene			
Distances [pm]			
C(1)–C(2)	138.5(3)	C(1)–C(6)	142.2(3)
C(2)–C(3)	139.5(3)	C(3)–C(4)	138.4(3)
C(4)–C(5)	142.2(2)	C(5)–C(6)	143.9(3)
C(5)–C(7A)	143.0(3)	C(6)–C(7)	142.9(3)
C(7)–C(10)	149.1(3)	C(7)–C(5A)	143.0(3)
C(10)–C(11)	140.1(3)	C(10)–C(15)	139.6(3)
C(11)–C(12)	138.9(3)	C(12)–C(13)	138.8(3)
C(13)–C(14)	138.6(3)	C(14)–C(15)	138.9(3)
Angles [°]			
C(2)–C(1)–C(6)	122.0(2)	C(1)–C(2)–C(3)	120.0(2)
C(2)–C(3)–C(4)	119.7(2)	C(3)–C(4)–C(5)	122.2(2)
C(4)–C(5)–C(6)	118.0(2)	C(4)–C(5)–C(7A)	122.3(2)
C(6)–C(5)–C(7A)	119.7(2)	C(1)–C(6)–C(5)	118.1(2)
C(1)–C(6)–C(7)	122.2(2)	C(5)–C(6)–C(7)	119.7(2)
C(6)–C(7)–C(10)	119.8(2)	C(6)–C(7)–C(5A)	120.6(2)
C(10)–C(7)–C(5A)	119.6(2)	C(7)–C(10)–C(11)	121.6(2)
C(7)–C(10)–C(15)	120.8(2)	C(11)–C(10)–C(15)	117.6(2)
C(10)–C(11)–C(12)	121.4(2)	C(11)–C(12)–C(13)	119.9(2)
C(12)–C(13)–C(14)	119.5(2)	C(13)–C(14)–C(15)	120.4(2)
C(10)–C(15)–C(14)	121.1(2)		
THF-Solvation of Na			
Distances [pm]			
Na–O(1)	238.3(2)	Na–O(2)	234.6(2)
Na–O(3)	240.2(1)	Na–O(1A)	238.3(2)
Na–O(2A)	234.6(2)	Na–O(3A)	240.2(1)
Angles [°]			
O(1)–Na–O(2)	88.6(1)	O(1)–Na–O(3)	92.8(1)
O(2)–Na–O(3)	90.4(1)	O(1)–Na–O(1A)	180.0(1)
O(2)–Na–O(1A)	91.4(1)	O(3)–Na–O(1A)	87.2(1)
O(1)–Na–O(2A)	91.4(1)	O(2)–Na–O(2A)	180.0(1)
O(3)–Na–O(2A)	89.6(1)	O(1A)–Na–O(2A)	88.6(1)
O(1)–Na–O(3A)	87.2(1)	O(2)–Na–O(3A)	89.6(1)
O(3)–Na–O(3A)	180.0(1)	O(1A)–Na–O(3A)	92.8(1)
O(2A)–Na–O(3A)	90.4(1)	Na–O(1)–C(31)	132.4(1)
Na–O(1)–C(34)	116.1(1)	Na–O(2)–C(41)	120.8(1)
Na–O(2)–C(44)	130.9(1)	Na–O(3)–C(51)	127.0(1)
Na–O(3)–C(54)	124.2(1)		

C(1′)···C(4′), the rest being located in the two twisted Ph rings. Altogether, the AM1 charge distribution for 9,10-diphenylanthracene radical anion suggests a considerable delocalization of the additional electron, which avoids accumulation of the negative charge at preferred centers and, therefore, potential contact-ion pair formation. In the parent molecule anthracene, the structural effects of additional negative charges in its 14-center π system are only small as is revealed by a comparison of the averaged gas phase [13] and solid-state [14] structures of the neutral molecule M with those determined for its radical anion $M^{\cdot\ominus}$ in the strongly solvated $[Mg_2Cl_3(THF)_6]^{\oplus}$ salt [15] and for its dianion

Scheme 3



$M^{\ominus\ominus}$ in a dilithium contact-ion triple [16] (*Scheme 3*). Except for the bond distances C(2)–C(3) and C(2′)–C(3′) in the dilithium complex, all structural parameters are equal within the error limits of the structure determinations.

Surprisingly [17], on one-electron reduction of 9,10-diphenylanthracene M to its radical anion $M^{\cdot\ominus}$ the dihedral angles between the anthracene and Ph planes remain the same (M [8]: 68°; $M^{\cdot\ominus}$ (*Table 1*): 67°). For rationalization, a two-dimensional AM1 enthalpy-of-formation hypersurface was calculated based on the structural parameters determined (*Fig. 1, a*, and *Table 1*) and the dihedral angles ω_1 and ω_2 were varied independently. The potential trough is rather shallow (*Fig. 2*), its walls become steep only at dihedral angles $\omega < 40°$, when steric repulsions between the hydrogens at centers C(1)/C(15), C(4)/C(11′), C(1′)/C(15′), and C(4′)/C(11) become increasingly important. From the contour plot (*Fig. 2*), an enthalpy difference between the minimum at $\omega_1 = 92°$ and $\omega_2 = 88°$ and the crystal structure with $\omega_1 = \omega_2 = 67°$ of 21 kJ mol^{-1} can be estimated.

Although the Ph twisting costs little energy at dihedral angles of $\sim 90°$, the ones found in the crystal, $\omega_1 = \omega_2 = 67°$, deviate by *ca.* 20° from those of the calculated enthalpy minimum (*Fig. 2*) and must, therefore, be determined to a large extent by the dense and energetically favorable crystal packing (*Fig. 1, b*) [17]. Viewed in x-direction, the y,z-layer consists of alternate strings of radical anions and the solvated cations $[Na^{\oplus}(THF)_6]$, which fill the space between the anthracene subunits enlarged by the twisting of the Ph rings. The crystal packing of neutral 9,10-diphenylanthracene, which exhibits identical dihedral angles of 68° [8], is also rather dense ($d_{calc.} = 1.237$ g cm^{-3}) and shows in the y,z-layers analogous strings of the anthracene subunits with the planes of the twisted Ph rings arranged almost parallel to each other. An additional AM1 enthalpy hypersurface calculated from the structural data (*Scheme 4*) supports the assumption of a conformer enforced by crystal-packing effects. The resulting potential is rather shallow for dihedral angles around 90°, and only a negligibly small enthalpy difference is predicted between its minima $\omega_1 = \omega_2 = 70°$ and the experimentally determined value $\omega = 68°$ [8].

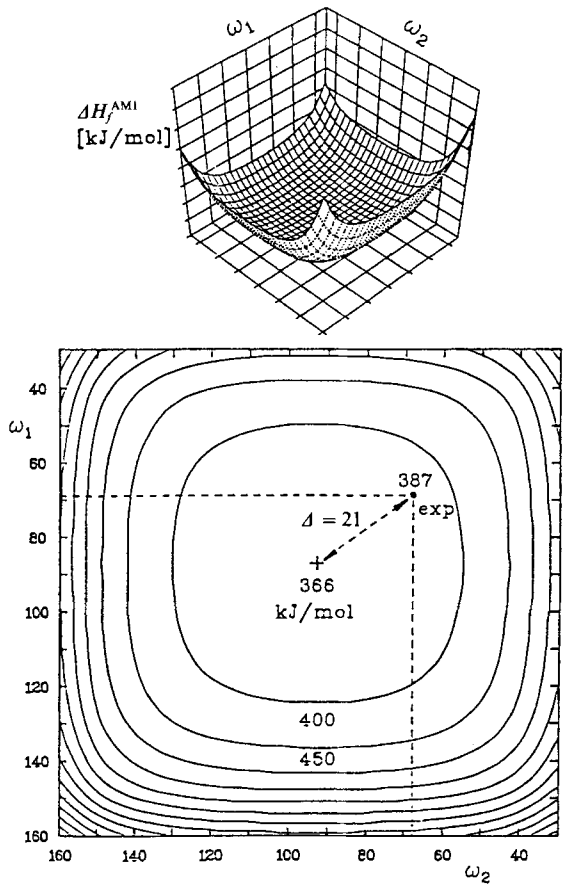
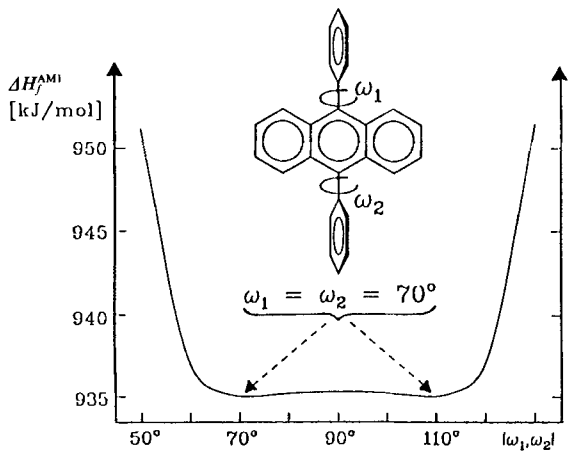


Fig. 2. *Contour plot from two-dimensional AM1 enthalpy-of-formation calculations for Ph twisting in 9,10-diphenylanthracene radical anion* (+: calculated minimum; ●: experimental dihedral angles) *with a graphical representation of the rather shallow potential trough*

Scheme 4



In summary, a comparison of the single-crystal structures of both 9,10-diphenylanthracene and its radical anion do not exhibit large specific differences characteristic for the insertion of an additional electron. Due to the delocalization of the negative charge over the 14-center π system, no preferential site for the formation of a contact radical ion pair [7] results, and, therefore, the sodium metal reduction product crystallizes with a solvent-separated counter cation.

Structure of the Counter Cation $[Na^{\oplus}(THF)_6]$. – The $Na^{\oplus}$ cation is solvated with six THF molecules (*Fig. 1, a*). This species has been first reported in a solvent separated salt of tris(η^5-cyclopentadienyl)lutetium-hydride dimer anion, but with one THF severely disordered ([19]: $R_w = 0.10$), and is the only occurrence of a $[Na^{\oplus}(THF)_6]$ ion in the *Cambridge Structural Data Base*.

The cation $[Na^{\oplus}(THF)_6]$ is located on a crystallographic center of inversion and contains an almost perfect $Na^{\oplus}O_6$ octahedron (*Fig. 1, a*) with angles O_xNaO_y between 89 and 93° and contact distances $Na^{\oplus}$–O between 235 and 240 pm (*Table 1*). It may be compared to the structures of related complexes, in which the $Na^{\oplus}$ is solvated by either three dimethoxyethane (DME) or two diglyme molecules, $[Na^{\oplus}(H_3CO-H_2CCH_2-OCH_3)_3]$ or $[Na^{\oplus}(H_3CO-H_2CCH_2-O-H_2CCH_2-OCH_3)_2]$, each with $Na^{\oplus}$ coordination number 6. The latter complexes are found in solvent-separated radical anion salts of tetraphenylbutadiene [10] [20], tetraphenylbutatriene [10] [21], bianthryl [22], or of perylene [23] (*Fig. 3*).

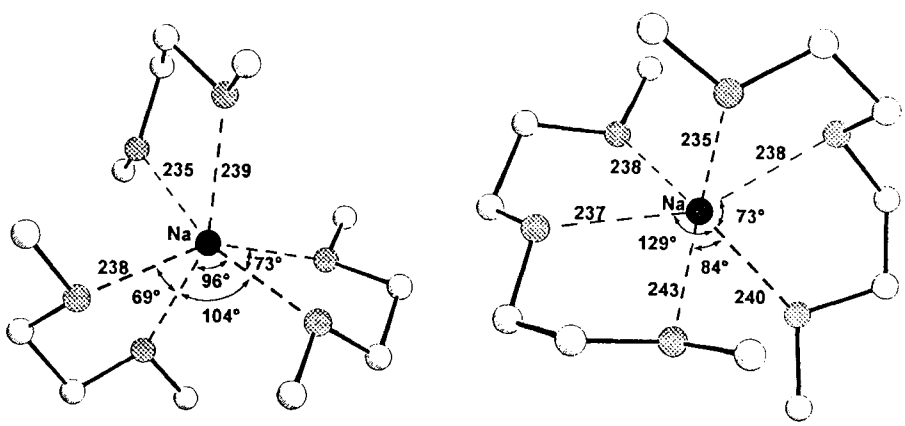
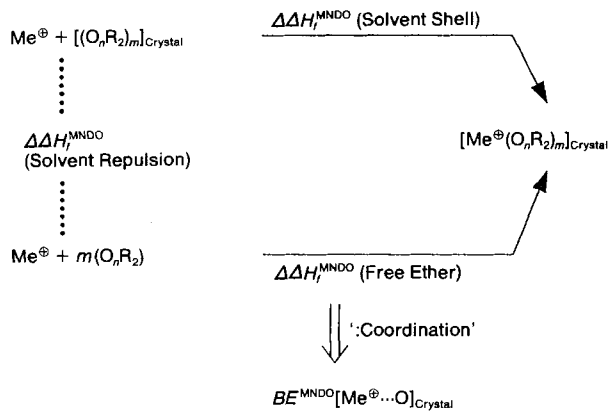


Fig. 3. *Structures of solvent-separated, optimum-solvated sodium counter cations $[Na^{\oplus}(DME)_3]$ and $[Na^{\oplus}(diglyme)_2]$ in crystallized salts of large π hydrocarbon radical anions*

In the DME- or diglyme-solvated, sixfold-coordinated $Na^{\oplus}$ complexes (*Fig. 3*), contact distances between 235 and 243 pm result, which are comparable to the ones observed in $[Na^{\oplus}(THF)_6]$ (*Fig. 1, a*, and *Table 1*), whereas the angles O_xNaO_y vary between 69° and 129° and indicate severely distorted NaO_6 octahedra [10] [21–23].

The comparison between the three different $Na^{\oplus}$ solvates each of coordination number 6 is based on MNDO evaluation of isodesmic-type interactions between $Na^{\oplus}$ and the oxohydrocarbon ligands and of the repulsions between the ligand themselves within the solvent shell (*Scheme 5*).

Scheme 5



The MNDO calculations are based on the experimental structural data determined (*Fig. 1, a* and *3*). Removal of the cation $M^{\oplus} = Na^{\oplus}$ from its respective ether solvate $[M^{\oplus}(O_nR_2)_m]$ yields the enthalpy of formation difference $\Delta\Delta H_f^{MNDO}$(solvent shell); disassembling the cage into the ether components yields $\Delta\Delta H_f^{MNDO}$(solvent repulsion). The average bond energy BE^{MNDO} $[Na^{\oplus}\cdots O]$ is $^1/_6$ of the difference $\Delta\Delta H_f$(solvent shell) – $\Delta\Delta H_f^{MNDO}$(solvent repulsion) (*Table 2*: $\Delta\Delta H_f^{MNDO}$(free ethers)).

Table 2. *MNDO Enthalpy-of-Formation Differences* (*cf. Scheme 5*) *for Hexacoordinated* $Na^{\oplus}$ *Cations Solvated by Different Ethers as well as Average Bond Energies* (all values in kJ mol^{-1}; calculations are based on the experimental structures (*Fig. 3*))

CN	Ether	$\Delta\Delta H_f$ (solvent shell)	$\Delta\Delta H_f$ (solvent repulsion)	$\Delta\Delta H_f$ (free ethers)	BE $[Na^{\oplus}\cdots O]$
6	6 THF	−830	−243	−587	−98
6	3 DME	−771	−100	−671	−112
6	2 Diglyme	−743	−66	−677	−113

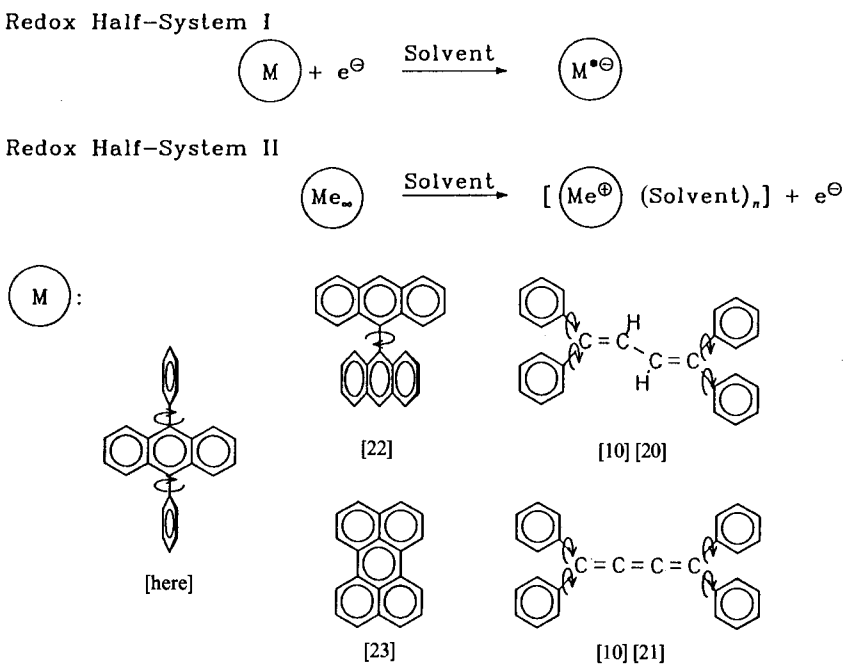
The repulsion between the individual ether molecules within the solvent shell can differ considerably (*Table 2*): the values $\Delta\Delta H_f^{MNDO}$(solvent repulsion) which are calculated based on the experimental structures (*Scheme 5*) range from −243 kJ mol^{-1} for the overcrowded THF complex (*Fig. 1, a*) to only −66 kJ mol^{-1} in the diglyme solvate (*Fig. 3*) and average $Na^{\oplus}\cdots O$ bond energies are only −98 kJ mol^{-1} for THF solvation compared to values *ca.* 15% larger in the DME and diglyme solvates. Entropy contributions $T\Delta S$ of 2 to 4 kJ mol^{-1} at 300 K, estimated from values for the crystallization of hydrocarbons [24], are considered to be small and are neglected. The bond energies seem to be much smaller than the enthalpies on cation kryptation [25], therefore, repulsion within the solvent shell around the cation seems to play an essential rôle [26]. Especially in $[Na^{\oplus}(THF)_6]$ the rather large enthalpy gain on inserting the $Na^{\oplus}$ cation into the preformed solvent-shell structure is reduced considerably, if the repulsion between the six THF molecules in their structurally determined arrangement is taken into account

(*Table 2:* $\Delta\Delta H_f^{MNDO}$(solvent shell) *vs.* $\Delta\Delta H_f^{MNDO}$(solvent repulsion)). THF is thus one of the less favorable ether solvents for $Na^{\oplus}$ solvation.

Outlook: General Procedure to Crystallize Optimally Solvated Cations. – The structure determined for the radical anion salt [9,10-diphenylanthracene$^{\cdot\ominus}$][$Na^{\oplus}(THF)_6$] confirms solvent-separated ions (*Fig. 1*). The hydrocarbon shows no significant structural changes – not even in the Ph twist angles – on introducing an extra electron, $M + e^{\ominus} \rightarrow M^{\cdot\ominus}$, into the 14-center π anthracene subsystem. The radical anion is extensively delocalized (*Scheme 2*) and does not provide a strongly localized negative charge favoring contact-ion pair formation. Therefore, the $Na^{\oplus}$ counter cation is completely solvated by six THF ligands.

The tendency of relatively large, delocalized π-type radical anions to avoid contact-ion pair formation with metal cations at a preferred negatively charged center seems to be a general principle to crystallize solvent-separated and optimally solvated counter cations, if the corresponding metal can be used as the reducing agent (*Scheme 6*).

Scheme 6



According to the experience gathered so far, this trend holds for 9,10-diphenylanthracene and bianthryl [22], fluxional 1,1,4,4-tetraphenylbutadiene [10] [20] and -butatriene [10] [21], and for rather rigid perylene [23]. There are presumably many more unsaturated hydrocarbons, which under aprotic reduction conditions will take up only one electron and crystallize with solvent-separated counter cations. In addition to ethers, amines or phosphines might be considered as solvents. The resulting alkali-cation complexes would provide much interesting microscopic information on cation solvation.

The project is supported by the *Deutsche Forschungsgemeinschaft*, the State of Hessen, and the *Fonds der Chemischen Industrie*.

Experimental. – *9,10-Diphenylanthracene* (*Aldrich*) can be used without further purification. THF has been refluxed over Na/K alloy and, after distillation under Ar, repeatedly degassed at 10^{-4} mbar.

Crystal Growth of Radical-Anion Salt. 9,10-Diphenylanthracene (105 mg, 32 mmol) is dissolved in 23 ml of THF and reacted with a Na mirror, generated by heating 10 mg (0.43 mmol) of the metal at 10^{-4} mbar. After keeping the dark blue soln. for 2 d without shaking, dark-blue prisms of the air- and H_2O-sensitive title compound had grown.

Crystal-Structure Determination. Crystal shape 0.3 × 0.4 × 0.6 mm. $C_{26}H_{18}Na \times 6\ C_4H_8O$ (M.Wt. = 786.1 g mol^{-1}): $a = 862.0(3)$ pm, $b = 1039.7(3)$ pm, $c = 1244.1(3)$ pm, $\alpha = 78.62(2)°$, $\beta = 82.65(2)°$, $\gamma = 82.82(3)°$, $V = 1078.31 \cdot 10^6$ pm^3, $Z = 1$, $d_{calc.} = 1.210$ g cm^{-3} (100 K), $\mu(MoK_\alpha) = 0.08$ mm^{-1}, triclinic, space group $P\bar{1}$ (Int. Tab. Nr. 2), *Siemens-AED II* four-circle diffractometer, graphite monochromator, 4388 recorded reflexes within $3° < 2\Theta < 51°$, of which 2781 are independent with $I > 1.5\sigma(I)$, $N = 2781$, $NP = 275$, $R = 0.041$, $R_w = 0.042$, residual electron density +0.23/−0.23 $eÅ^{-3}$. Structure solution by direct methods (SHELXTL-PLUS), C, O, Na refined anisotropically, H isotropically. Further details of the crystal-structure determination can be obtained from the *Cambridge Crystallographic Data Centre*.

MNDO and AM1 Calculations. Performed using the program version SCAMP IV/1 (Author: Dr. *T. Clark*, University of Erlangen) on our work station *IBM RISC 6000/320*. For the sodium parameters, *cf.* [27]. The two-dimensional hypersurface (*Fig. 2*) has been calculated starting from the crystal structure twisting both dihedral angles in 10° steps.

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