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Solvent-Shared and Solvent-Separated Ion Multiples of Perylene Radical Anions and Dianions: An Exemplary Case of Alkali Metal Cation Solvation

Christian Näther, Hans Bock,* Zdenek Havlas,[†] and Tim Hauck

Department of Chemistry, University Frankfurt, Marie-Curie-Strasse 11,
D-60439 Frankfurt am Main, Germany

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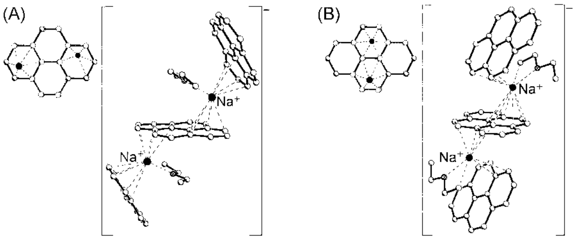
The hydrocarbon perylene ($C_{20}H_{12}$) has been crystallized, and several of its radical anions and dianion salts have been prepared by reduction with various alkali metal mirrors under argon and aprotic conditions in different ether solvents. The single-crystal structures determined at low temperature are discussed in terms of single and double negative charge perturbation based on geometry-optimized density functional calculations at the B3LYP level with 6-31G* basis sets. All perylene radical anion salts $[C_{20}H_{12}^{\bullet -}][M^{+}_{solv}]$ and $[C_{20}H_{12}^{\bullet -}\cdots C_{20}H_{12}][M^{+}_{solv}]$ crystallize as solvent-separated ion pairs, whereas the structures of the perylene dianion salts $[C_{20}H_{12}^{2-}(M^{+}_{solv})_2]$ or $[C_{20}H_{12}^{2-}][M^{+}_{solv}]_2$ strongly depend on the optimum solvation of the alkali metal countercations. The experimental results allow the rationalization of essential facets of the network of redox equilibria in solution.

Introduction

Multiple reductions of unsaturated hydrocarbons in aprotic solution proceed via a multidimensional network of electron transfer contact ion formation and cation solvation equilibria.[1] By comparison of single-crystal structural data with results from NMR, ESR, or UV/vis measurements, it often becomes obvious that solid-state structures of organometallic complexes largely represent the species in solution.[2,3] Single crystals grown from aprotic solutions, therefore, yield not only anionic intermediates exhibiting distorted molecular skeletons but also information on cation solvation or aggregation phenomena and, therefore, provide insight into ion pairing in solution.[2,3]

For instance, after reduction of pyrene in diethyl ether solution at a sodium metal mirror, a second polymorphic modification of the contact ion pair pyrene sodium diethyl ether can be crystallized at higher temperature (A, below):[3a]



(1)

Compared to the already known structure (B in (1)) crystallized at lower temperature,[4] the sodium countercations coordinate to two different positions of the pyrene ring. The information from temperature-dependent ESR studies of the pyrene radical anion in diethyl ether alkali metal countercation systems[5] are in full accord with the results from the single-crystal structure analysis.

Another solvation segment of these equilibria networks,[2,3] from which both the solvent-shared and the solvent-separated ion multiples crystallize simultaneously in a 1:1 stoichiometric ratio, becomes structurally visible on reduction of 1,1,4,4-tetraphenylbutadiene

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* To whom correspondence should be addressed.

[†] Permanent address: Institute of Organic Chemistry and Biochemistry of the Czech Academy of Sciences, Flemingova Nam 2, CS-11610 Prague 6, Czech Republic.

(1) General reviews: (a) Marcus, Y. *Ion Solvation*; Wiley: Chichester, 1985. (b) Swarc, M., Ed. *Ions and Ion Pairs in Organic Reactions*; Wiley-Interscience: New York, 1972 and 1974; Vols. 1 and 2. (c) Inoue, Y., Gokel, G. W., Eds. *Cation Binding by Macrocyles*; Marcel Dekker: New York, 1990. (d) Lubitz, W.; Plato, M.; Möbius, K.; Biehl, T. *J. Chem. Phys.* **1979**, *83*, 3402. (e) Bock, H.; Herrmann, W.-F.; Fenske, D.; Goesmann, H. *Angew. Chem.* **1988**, *100*, 1125; *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1067. (f) Bock, H.; Herrmann, H.-F. *J. Am. Chem. Soc.* **1989**, *111*, 7622. (g) Smid, J.; Hogen-Esch, T. E. *J. Am. Chem. Soc.* **1966**, *88*, 307.

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(4) Jost, W.; Adam, M.; Enkelmann, V.; Müllen, K. *Angew. Chem.* **1992**, *104*, 883; *Angew. Chem., Int. Ed. Engl.* **1992**, *104*, 883.

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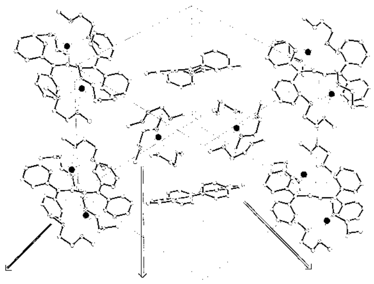
in aprotic dimethoxyethane solution at a sodium metal mirror (A, below):[3b]

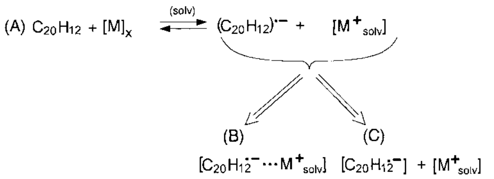
(A)



$$\underset{(B)}{[C_{28}H_{22}\,Na_2(C_4H_{10}O)_4]} \rightleftarrows \underset{(C)}{[[Na(C_4H_{10}O)_3]_2]^{+}} + \underset{(D)}{[C_{28}H_{22}]^{--}} \qquad (2)$$

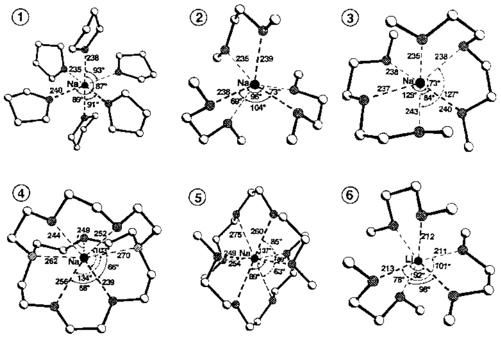
All components of the aprotic equilibrium network, the solvent-shared disodium 1,1,4,4-tetraphenylbutadiene dimethoxyethane (B in (2)) and the tris(dimethoxyethane) sodium (C in (2)) as well as "naked" 1,1,4,4-tetraphenylbutadiene dianion (D in (2)) are clearly recognizable in the 1:1 stoichiometric, densly packed crystal (A in (2)).[3b]

Cation solvation phenomena can be advantageous in the crystallization of specific contact ion multiples:[3c]



(3)

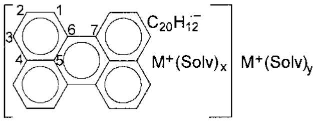
One-electron reduction of unsaturated π-hydrocarbons, for example $C_{20}H_{12}$, in aprotic solution (solv) at an alkali metal mirror $[M]_x$ will produce the corresponding π-hydrocarbon radical anion ($C_{20}H_{12}^{\bullet-}$) in a solvent-separated ion pair (C in (3)), if an extensive delocalization of the negative charge prevents contact ion formation at a preferred, negatively charged center.[2,3] In suitable and preferentially multidendate ether solvents, optimally ether-solvated metal cations (4) are formed in salts with several π-hydrocarbon anions:[3c]



(4)

The solvent-separated, "naked" π-hydrocarbon radical anions can be studied without any disturbing influence of the countercations.[3c] In contrast, with less effective solvents, such as spatially demanding THF, solvent-shared contact multiples result, as exemplified by the contact ion quintuplet of rubrene tetraanion $[C_{40}H_{28}^{4-}(Na^{+}(THF)_2)_4]$.[3k] These and numerous other results demonstrate that, in systematic, solvent-dependent studies, conditions can be optimized for the specific crystallization of π-hydrocarbon radical anion or dianion salts, either as solvent-separated or solvent-shared contact ion multiples.[2,3]

Here we report the structures of several alkali metal cation salts of the perylene radical anion and dianion, prepared by reduction of the π-hydrocarbon with various alkali metals in aprotic ether solvents (5):



Solvent	$M^{+}(C_{20}H_{12}^{\cdot-})_x$		$M_2^{+}C_{20}H_{12}^{--}$	x	y
DME	Li^{+}	3	Na^{+}	2	
			K^{+}	2	
Diglyme			Na^{+}		2
Triglyme	Na^{+}	2			
	K^{+}	2			
Tetraglyme	Cs^{+}	2	Na^{+}	2	

(5)

For comparison, the structure of the π-hydrocarbon perylene has been redetermined. In addition, the structures of the different metal perylene anion salts are discussed, along with the structural changes of perylene on its reduction based on the results of density functional calculations.

Experimental Section

Methods and Materials. All operations were performed under argon using Schlenk techniques. The solvents dimethoxyethane and *n*-hexane were redistilled from Na/K alloy; diglyme, triglyme, and tetraglyme were of commercial purity. For sodium or potassium reductions, the metals were carefully cleaned, and a reactive metal mirror was generated by distillation in a Schlenk tube at 10^{-6} mbar. Lithium was activated by additional ultrasonication, and cesium metal was of CHEMETALL purity grade.

Perylene Crystallization. Perylene (500 mg, Aldrich) was sealed in an evacuated glass tube, heated for 3 d above its melting point, and cooled slowly. The resulting yellow-orange crystals exhibited satisfactory diffraction properties.

Perylene Lithium Tris(dimethoxyethane). Perylene (300 mg), 10 mL of dry dimethoxyethane, and an excess of lithium were placed into a Schlenk tube. After short ultrasonic activation, the solution turned blue, and within 1 d blue crystals formed.

Perylene Potassium Bis(triglyme). A potassium metal mirror was generated from 300 mg of K in a Schlenk tube. On addition of 280 mg of perylene and 15 mL of triglyme, a blue reaction mixture formed. After all potassium metal had been consumed, the solution was covered with an *n*-hexane layer, and within 1 h green-blue crystals formed.

Perylene Cesium Bis(tetraglyme). Cesium metal (300 mg), 260 mg of perylene, and 17 mL of tetraglyme were allowed to react in a Schlenk tube under argon for several days. After complete reaction of the cesium metal, the resulting solution was covered three times with a layer of *n*-hexane, and within 8 h dark blue crystals formed.

Bis(perylene) Sodium Bis(triglyme). A sodium metal mirror was generated from 200 mg of Na in a Schlenk tube. After addition of 300 mg of perylene and 10 mL of triglyme, the reaction mixture was activated by ultrasonication, and the solution was covered several times with a layer of *n*-hexane. Within 3 d, yellow crystals formed.

Perylene Dipotassium Tetrakis(dimethoxymethane). A potassium metal mirror was generated in a Schlenk tube from 300 mg of K. After addition of 300 mg of perylene and 10 mL of dimethoxyethane, the reaction mixture turned first

Table 1. Crystal Data and Structure Refinement for Perylene and Some of Its Ion Pairs

	$C_{20}H_{12}$	$LiC_{20}H_{12}$ $(C_4H_{10}O_2)_3$	$KC_{20}H_{12}$ $(C_8H_{18}O_4)_2$	$CsC_{20}H_{12}$ $(C_{10}H_{22}O_5)_2$	$Na(C_{20}H_{12})_2$ $(C_8H_{18}O_4)_2$	$K_2C_{20}H_{12}$ $(C_4H_{10}O_2)_4$
MW (g cm^{-3})	252.3	545.7	647.8	829.8	884.1	691.0
a (Å)	10.270 (1)	17.584 (3)	13.734 (1)	20.600 (2)	12.001 (1)	9.140 (3)
b (Å)	10.839 (1)	13.031 (3)	12.237 (6)	30.752 (2)	16.870 (1)	17.047 (6)
c (Å)	11.278 (1)	14.972 (3)	20.259 (2)	12.729 (1)	23.201 (1)	11.449 (4)
β (°)	100.53 (1)	121.72 (1)	93.19 (4)	-	-	-
V (Å)^3	1234.4	2918.1	3399.5	8064.0	4697.4	1783.2
T (K)	293	120	130	130	150	90
Z	4	4	4	8	2	2
σ_{ber}	1.353	1.401	1.266	1.367	1.250	1.287
μ (mm^{-1})	0.07	0.08	0.21	0.97	0.09	0.31
crystal system	monoclinic	monoclinic	monoclinic	orthorhombic	orthorhombic	monoclinic
space group	$P2_1/c$	$C2/c$	$P2_1/c$	$Fdd2$	$Pccn$	$P2_1/n$
diffractometer	STOE	STOE	Siemens	Siemens	STOE	STOE
2θ range (deg)	$3 \le 2\theta \le 55$	$3 \le 2\theta \le 50$	$3 \le 2\theta \le 48$	$3 \le 2\theta \le 58$	$3 \le 2\theta \le 52$	$3 \le 2\theta \le 50$
measured reflns	4144	3618	5825	7582	8387	4353
R_{int}	0.0173	0.0174	0.0318	0.0273	0.0165	0.0231
independent reflns	2841	2574	5278	5358	4645	3148
reflns used	2841	2574	5277	5358	4645	$3071 > 5\sigma$
reflns $I < 4\sigma(I)$	1178	1953	3668	4577	2685	
parameters	182	232	797	231	297	313
wR_2 for all data	0.1287	0.1254	0.1052	0.1051	0.1153	
R for $F_o < 4\sigma(F_o)$	0.0422	0.0439	0.0428	0.0413	0.0403	$0.0467 > 5\sigma$
GOF	0.915	1.065	1.032	1.052	0.980	1.198
res elect dens	0.15/−0.12	0.38/−0.33	0.23/−0.21	0.94/−0.49	0.25/−0.20	0.31/−0.28

blue and then dark violet. After all potassium metal had reacted, the solution was covered with a layer of n-hexane, and within 1 d blue-violet crystals formed.

Crystal Structure Analysis. All crystal structures were determined using a four-circle diffractometer, STOE AED-II or Siemens P4, with Kα radiation. Structures were solved using direct methods (SHELXS-86), and refinement was acomplished against F^2 using SHELXL-93, except for perylene dipotassium tetrakis(dimethoxyethane), for which SHELXTL-PC was used. All heavy atoms were refined anisotropically. The hydrogen centers were placed in ideal positions and refined isotropically using the riding model (Table 1).

For perylene cesium bis(tetraglyme), the absolute structure cannot be determined: the Flack parameter refined to a value of 0.52(3). The pseudocentrosymmetric structure can be solved in the centrosymmetric space group $Fddd$, but the radical anion is disordered in two different orientations. In addition, the extinction conditions for $Fddd$ are not completely fulfillled.

Density Functional Calculations. All calculations were performed using the program GAUSSIAN 94 at the B3LYP level with a 6-31 G* basis set on the NEC SX-4 computer of the high-performance computing center in Stuttgart.

Crystal Structures

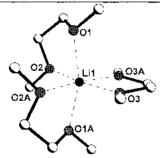
Perylene. The β-form is the thermodynamically more stable of the known dimorphic modifications at room temperature.[6] Its diffraction data, however, have been recorded only at relatively low resolution. For a more detailed structural comparison with both its radical anion and its dianion, therefore, the structure of the α-form of perylene has been redetermined using crystals obtained by sublimation.

Bond lengths and angles of perylene (Table 4) are comparable to those obtained by electron[6] diffraction. It exhibits a planar molecular skeleton, with the largest deviations of the individual centers amounting to ±0.39 Å. Both naphthalene subunits are only negligibly twisted by 0.80(5)°, although their C−C distance of 1.48 Å corresponds almost to a single bond (Table 4).

Radical Anion Salts. Structures of four perylene radical anion ($C_{20}H_{12}^{\bullet -}$) salts listed in (5) will be presented, all of which are solvent-separated ion pairs (Figure 1 and Table 2).

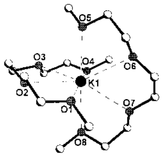
Table 2. Distances M$^+ \cdots$O (Å) in Solvent-Separated Ion Pairs of Perylene Radical Anions

(A)



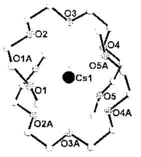
Li(1) - O(3)	2.105 (3)
Li(1) - O(3A)	2.105 (3)
Li(1) - O(1)	2.124 (1)
Li(1) - O(1A)	2.124 (1)
Li(1) - O(2)	2.136 (3)
Li(1) - O(2A)	2.136 (3)

(B)



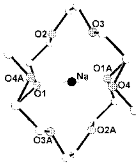
K(1) - O(4)	2.699 (2)
K(1) - O(8)	2.706 (2)
K(1) - O(5)	2.719 (2)
K(1) - O(1)	2.725 (2)
K(1) - O(3)	2.806 (2)
K(1) - O(7)	2.813 (2)
K(1) - O(2)	2.845 (2)
K(1) - O(6)	2.864 (2)

(C)



Cs(1) - O(1A)	3.044 (6)
Cs(1) - O(1)	3.044 (6)
Cs(1) - O(3)	3.058 (2)
Cs(1) - O(3A)	3.058 (2)
Cs(1) - O(5)	3.076 (6)
Cs(1) - O(5A)	3.076 (6)
Cs(1) - O(4A)	3.257 (5)
Cs(1) - O(4)	3.257 (5)
Cs(1) - O(2A)	3.268 (5)
Cs(1) - O(2)	3.268 (5)

(D)



Na - O(1)	2.539 (2)
Na - O(2)	2.746 (2)
Na - O(3)	2.603 (1)
Na - O(4)	2.494 (2)
Na - O(1A)	2.539 (2)
Na - O(2A)	2.746 (2)
Na - O(3A)	2.603 (1)
Na - O(4A)	2.494 (2)

Special facets of the individual derivatives (Experimental Section) are as follows:

Perylene Lithium Tris(dimethoxyethane). The air- and moisture-sensitive crystals of the solvent-separated ion pair crystallize in the monoclinic space group $C2/c$ with four formula units in the cell. In the crystal structure, the solvent-wrapped cations are located in channels parallel to the c-axis, built up of radical anions (Figure 1A). Each metal complex is surrounded by four radical anions and every Li$^+$ countercation within an distorted octahedron by six oxygen centers of three DME solvent molecules with Li$^+\cdots$O distances between 2.105(3) and 2.136(3) Å (Table 2A). The structure of the perylene radical anion exhibits small but significant differences relative to the perylene molecule: The central C−C bond between the naphthalene subunits is shortened by 0.029 Å to 1.447(3) Å,

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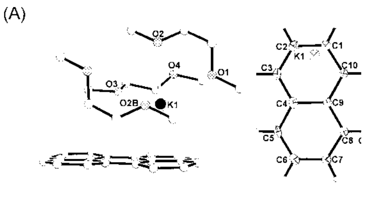
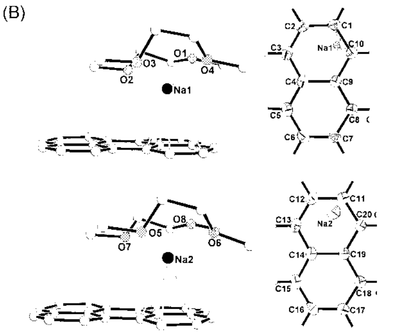
(6) (a) Tanaka, J. *Bull. Chem. Soc. Jpn.* **1963**, *36*, 1237. (b) Cameraman, A.; Trotter, J. *Proc. R. Soc. London, Ser. A* **1964**, *279*, 129. (c) Kerr, A. K. *Acta Crystallogr.* **1966**, *A21*, 119.

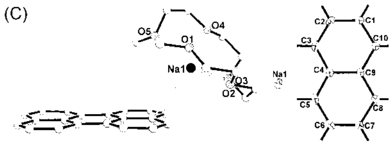
Table 3. $M^+\cdots O$ and $M^+\cdots C$ Distances (Å) in Contact and Solvent-Separated Ion Pairs of Perylene Dianions



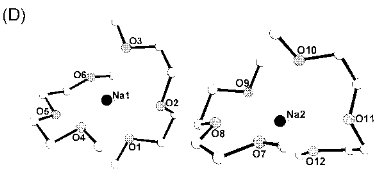
K(1) - C(1)	2.994 (2)
K(1) - C(2)	3.118 (2)
K(1) - C(3)	3.336 (2)
K(1) - C(4)	3.521 (2)
K(1) - C(9)	3.380 (2)
K(1) - C(10)	3.090 (2)
K(1) - O(1)	2.714 (2)
K(1) - O(2)	2.884 (2)
K(1) - O(3)	2.678 (2)
K(1) - O(4)	2.908 (2)
O(2) - K(1A)	2.956 (2)



Na(1) - C(1)	2.681 (2)
Na(1) - C(2)	3.006 (3)
Na(1) - C(9)	3.105 (2)
Na(1) - C(10)	2.703 (2)
Na(1) - O(1)	2.447 (2)
Na(1) - O(2)	2.343 (2)
Na(1) - O(3)	2.439 (2)
Na(1) - O(4)	2.373 (2)
Na(2) - C(11)	2.705 (2)
Na(2) - C(12)	2.871 (2)
Na(1) - C(13)	3.079 (3)
Na(2) - C(19)	3.003 (2)
Na(2) - C(20)	2.734 (2)
Na(2) - O(5)	2.374 (2)
Na(2) - O(6)	2.426 (2)
Na(2) - O(7)	2.408 (2)
Na(2) - O(8)	2.408 (2)



Na(1) - C(4)	3.087 (1)
Na(1) - C(5)	2.382 (1)
Na(1) - O(1)	2.520 (1)
Na(1) - O(2)	2.382 (1)
Na(1) - O(3)	2.497 (1)
Na(1) - C(4)	2.487 (1)
Na(1) - C(5)	2.395 (1)



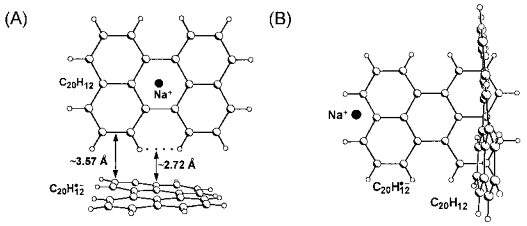
Na(1) - O(1)	2.353 (4)
Na(1) - O(2)	2.378 (3)
Na(1) - O(3)	2.395 (3)
Na(1) - O(4)	2.384 (3)
Na(1) - O(5)	2.370 (3)
Na(1) - O(6)	2.429 (3)
Na(2) - O(7)	2.349 (4)
Na(2) - O(8)	2.470 (4)
Na(2) - O(9)	2.460 (3)
Na(2) - O(10)	2.353 (4)
Na(2) - O(11)	2.505 (3)
Na(2) - O(12)	2.353 (3)

and the adjacent bond C1−C10 (5) is elongated by 0.033 Å to 1.413(3) Å (Table 4). The molecular skeleton remains planar within experimental error, and the largest deviation of individual centers from the mean plane amounts to 0.02 Å.

Perylene Potassium Bis(triglyme). In the solvent-separated perylene radical ion salt, the potassium countercation is surrounded by two triglyme molecules. In its crystal structure (monoclinic, $P2_1/c$, $Z = 4$), the radical anions as well as the solvent-wrapped K^+ countercations alternate along the *b*-axis perpendicular to the radical anion layers (Figure 1B). The 8-fold O-coordinated K^+ countercations exhibit $K^+\cdots O$ distances between 2.699(2) and 2.864(2) Å (Table 2B). The perylene radical anion (Table 4) is twisted by an interplanar angle of about 7° between the naphthalene subunits.

Perylene Cesium Bis(tetraglyme). In the crystal structure (orthorhombic, $Fdd2$, $Z = 8$), the radical anions as well as the solvent-wrapped cations are alternatingly stacked along the *b*-axis (Figure 1C). The bis(tetraglyme)-solvated cesium countercation is 10-fold O-coordinated, with $Cs^+\cdots O$ distances between 3.044(6) and 3.268(5) Å (Table 2C). The interplanar angle of about 13° between the naphthalene subunits of the perylene radical anion is significantly increased.

Bis(perylene) Sodium Bis(triglyme). From a triglyme solution of perylene in contact with a sodium mirror, green crystals formed. These contain one triglyme-solvated Na^+ countercation and two crystallographically independent perylene molecules. In the crystal (orthorhombic, $Pccn$, $Z = 2$), stacks of perylene molecules and triglyme-separated sodium cations alternate along the *c*-axis (Figure 1D and Table 2D). In the channels between these stacks, a second perylene molecule is located. Both perylene molecules are oriented nearly perpendicular to each other with an intermolecular distance between a C−H hydrogen from one perylene molecule to the mean plane of the second perylene molecule of 2.72 Å (A in (6)), which bisects one hydrocarbon (B in (6)) close to the countercation (Figure 1D).



(6)

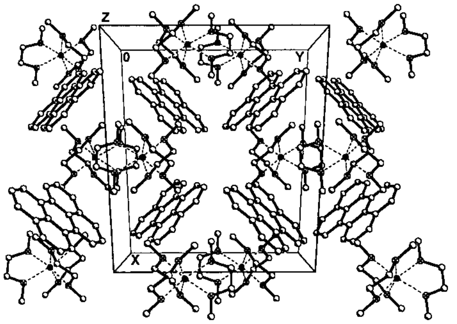
Bond distances and angles in the two crystallographically independent perylene molecules differ significantly (Table 4) and, according to the density functional calculations performed (cf. Experimental Section), exhibit deviating charge distributions. The perylene radical anions form the stacks, and the neutral perylene

Table 4. Selected Bond Lengths (Å) and Angles (deg) for Perylene, Its Radical Anion, and Its Dianion Salts (All Structural Parameters Averaged Assuming 2/*m* Symmetry)[a]

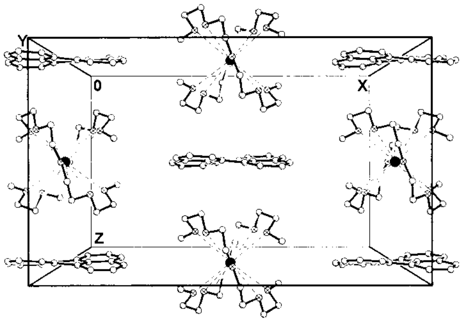
			$[C_{20}H_{12}^{\bullet-}]$			$[C_{20}H_{12}^{\bullet-}\cdots C_{20}H_{12}]$,	$[C_{20}H_{12}^{2-}]$			
		$C_{20}H_{12}$	$LiC_{20}H_{12}(C_4H_{10}O_2)_3$	$KC_{20}H_{12}(C_8H_{18}O_4)_2$	$Cs\ C_{20}H_{12}(C_{10}H_{22}O_5)_2$	$Na(C_{20}H_{12})_2(C_8H_{18}O_4)_2$	$Na_2C_{20}H_{12}(C_6H_{14}O_3)_4$	$Na_2C_{20}H_{12}(C_{10}H_{22}O_5)_2$	$K_2C_{20}H_{12}(C_4H_{10}O_2)_4$	$K_2C_{20}H_{12}(C_8H_{18}O_4)_2$
bond length (Å)	1−2	1.394	1.381	1.383	1.387	1.400, 1.387	1.376, 1.376	1.363	1.374	1.381
	2−3	1.355	1.378	1.370	1.370	1.363, 1.378	1.394, 1.396	1.390	1.397	1.394
	3−4	1.410	1.413	1.409	1.408	1.417, 1.412	1.418, 1.419	1.401	1.419	1.417
	4−5	1.426	1.443	1.439	1.445	1.430, 1.449	1.454, 1.452	1.465	1.457	1.456
	5−6	1.429	1.431	1.426	1.422	1.431, 1.430	1.436, 1.438	1.430	1.436	1.436
	1−6	1.380	1.413	1.407	1.419	1.386, 1.415	1.442, 1.440	1.447	1.439	1.435
	6−7	1.476	1.447	1.445	1.439	1.478, 1.448	1.432, 1.430	1.413	1.432	1.430
	esd	0.003	0.003	0.004	0.009	0.003, 0.002	0.003, 0.003	0.008	0.002	0.002
angle (deg)	1−2−3	120.6	121.1	121.0	121.4	120.6, 121.0	121.6, 121.5	121.7	121.9	121.4
	2−3−4	120.7	120.7	120.8	120.9	120.7, 121.1	120.8, 120.7	121.3	120.5	120.9
	3−4−5	119.1	119.0	119.0	118.7	119.1, 118.8	118.7, 118.8	118.6	118.6	118.6
	4−5−6	119.3	119.4	119.3	119.6	119.3, 119.2	119.7, 119.7	119.2	119.7	119.5
	5−6−1	118.5	118.4	118.7	118.7	118.7, 118.9	118.4, 118.4	118.5	118.5	118.6
	5−6−7	119.3	119.4	119.9	117.9	119.1, 119.3	119.7, 119.7	119.2	119.7	119.5
	esd	0.2	0.2	0.2	0.5	0.2, 0.2	0.2, 0.2	0.5	0.1	0.2

[a] For atom numbering, cf. Scheme 5.

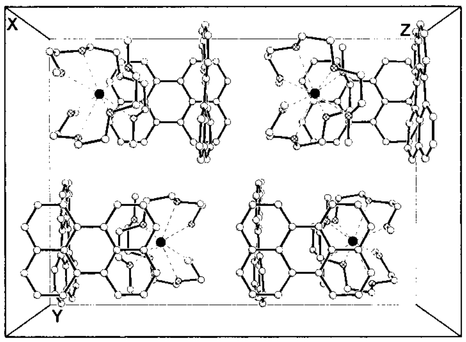
(A) $[\mathrm{Li^+(DME)_3}]\,[\mathrm{C_{20}H_{12}^{\bullet-}}]$:



(B) $[\mathrm{K^+(Triglyme)_2}]\,[\mathrm{C_{20}H_{12}^{\bullet-}}]$:



(C) $[\mathrm{Cs^+(Tetraglyme)_2}]\,[\mathrm{C_{20}H_{12}^{\bullet-}}]$:



(D) $[\mathrm{Na^+(Triglyme)_2}]\,[\mathrm{C_{20}H_{12}^{\bullet-}\cdots C_{20}H_{12}}]$:

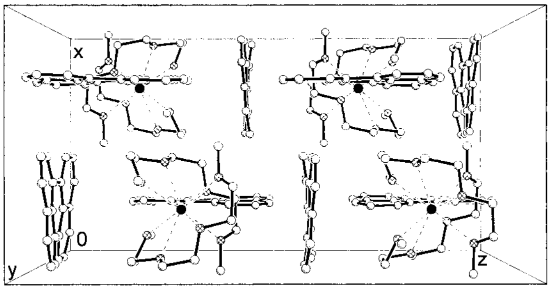
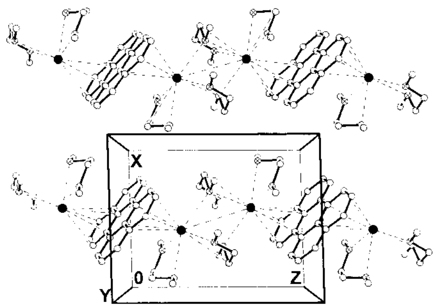
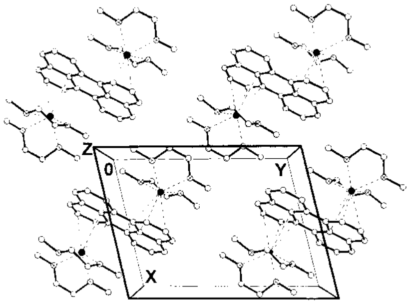


Figure 1. Crystal structures of perylene radical anion salts: (A) perylene lithium tris (dimethoxyethane), (B) perylene potassium bis(triglyme), (C) perylene cesium bis(tetraglyme), and (D) bis(perylene) sodium bis(triglyme) (cf. text).

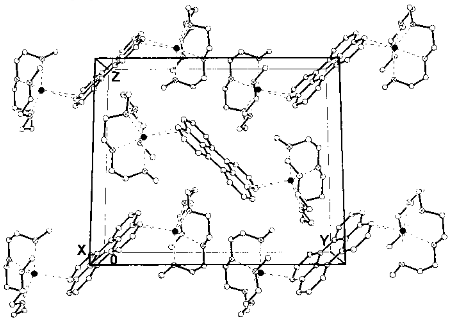
(A) $[\mathrm{(DME)_2K^+\cdots[C_{20}H_{12}^{--}]\cdots K^+(DME)_2}]_\infty$



(B) $[\mathrm{(DME)_2Na^+\cdots[C_{20}H_{12}^{--}]\cdots Na^+(DME)_2}]$



(C) $[\mathrm{(Tetraglyme)Na^+\cdots[C_{20}H_{12}^{--}]\cdots Na^+(Tetraglyme)}]$



(D) $[\mathrm{(Diglyme)_2Na^+\cdots[C_{20}H_{12}^{--}]\cdots Na^+(Diglyme)_2}]$

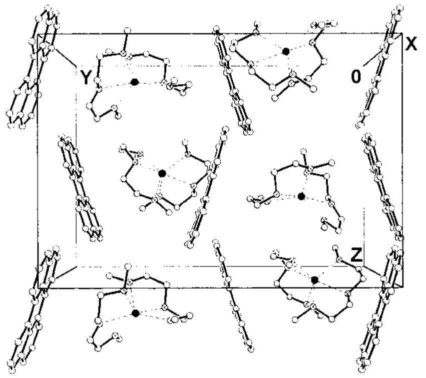


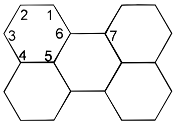
Figure 2. Crystal structures of perylene dianions: (A) perylene dipotassium tetrakis (dimethoxyethane), (B) perylene disodium tetrakis(dimethoxyethane), (C) perylene disodium bis(tetraglyme) and (D) perylene disodium tetrakis(diglyme).

molecules are located between them. In the triglyme-solvated countercations, distances $\mathrm{Na^+\cdots O}$ between 2.494(2) and 2.746(2) Å (Table 2D) are found.

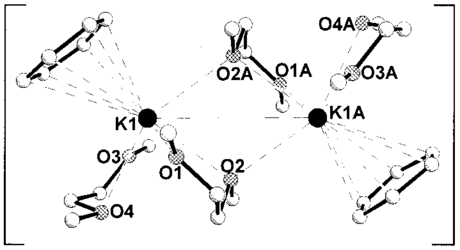
Perylene Dianion Salts. Four perylene dianion salts have been crystallized and structurally characterized ((5) and Experimental Section); all represent solvent-shared contact ion triplets (Figure 2 and Table 3).

Perylene Dipotassium Tetrakis(dimethoxyethane). In the crystal structure (Figure 2A), the potassium cations of the contact ion pairs are solvated by three different dimethoxyethane molecules and form a one-dimensional solvate structure in the direction of the *c*-axis. Each $\mathrm{K^+}$ countercation (7) is connected to one perylene dianion molecule and to five oxygen centers of three DME molecules (Table 3A): one of them coordi-

Table 5. Measured and Calculated Bond Lengths (Å) for Perylene, Its Radical Anion, and Its Dianion (Experimental Values Averaged for All Structures Determined)

		$C_{20}H_{12}$		$[C_{20}H_{12}^{\bullet-}]$		$[C_{20}H_{12}^{2-}]$	
		exp	calc	exp	calc	exp	calc
	1−2	1.39	1.40	1.38	1.39	1.37	1.38
	2−3	1.36	1.37	1.37	1.39	1.37	1.38
	3−4	1.41	1.42	1.41	1.42	1.41	1.42
	4−5	1.43	1.43	1.44	1.45	1.46	1.46
	5−6	1.43	1.43	1.43	1.43	1.44	1.44
	1−6	1.38	1.39	1.41	1.42	1.44	1.44
	6−7	1.48	1.48	1.44	1.45	1.43	1.44

nates to only one K^+, whereas the two other DME ligands bridge two symmetry-equivalent countercations with distances $K^+\cdots O$ between 2.678(2) and 2.956(2) Å.



(7)

The η^6-coordinated K^+ countercations are located unsymmetrically about 2.83 Å above the ring center with contact distances $K^+\cdots C$ varying between 2.994(2) and 3.521(2) Å (Table 3A).

Perylene Disodium Tetrakis(dimethoxyethane). The crystal contains two crystallographically independent sodium complexes in the asymmetric unit (Figure 2B), which differ significantly in their oxygen coordination spheres: the $Na^+\cdots O$ distances are between 2.343(2) and 2.447(2) Å for Na1, which is only η^4-coordinated to one phenyl ring, and between 2.374(2) and 2.426(2) Å for Na2 (Table 3B), which exhibits five $Na^+\cdots C$ contacts to the perylene dianion. Both six-membered rings are unsymmetrically coordinated with Na1⋯C distances between 2.681(2) and 3.105(2) Å and Na2⋯C between 2.705(2) and 3.079(3) Å (Table 3B). The structural parameters for the two crystallographically independent perylene dianions are identical within experimental error (Table 4). Expectedly, the perylene dianion structure deviates significantly from that of the neutral perylene molecule: the central C−C bond between the naphthalene subunits is shortened by 0.046(3) to 1.432(3) Å and the adjacent bond C1−C6 elongated by 0.060(3) to 1.440(3) Å (Table 3B and Table 4). The perylene dianion is planar within experimental error, and the largest deviation of a center from the molecular mean plane amounts to about 0.08 Å.

Perylene Disodium Bis(tetraglyme). In the presence of the pentadentate oxygen ligand tetraglyme, the perylene disodium salt crystallizes as a contact ion triple (Figure 2C). The Na^+ countercations are coordinated to all five oxygen centers of each solvent molecule with $Na^+\cdots O$ distances between 2.382(1) and 2.520(1) Å (Table 3C) and, therefore, shifted to the peripheral centers of the perylene dianion, exhibiting two different $Na^+\cdots C$ contacts of 2.793(1) and 3.087(1) Å.

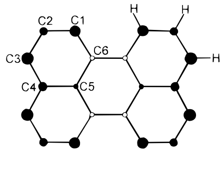
Perylene Disodium Tetrakis(diglyme). The crystal structure (Figure 3D) shows two independent Na^+ countercations in the asymmetric unit, each surrounded by three oxygen centers of two diglyme molecules with $Na^+1\cdots O$ distances between 2.353(4) and 2.429(3) Å and $Na^+2\cdots O$ between 2.349(4) and 2.505(3) Å (Table 3D).

Discussion

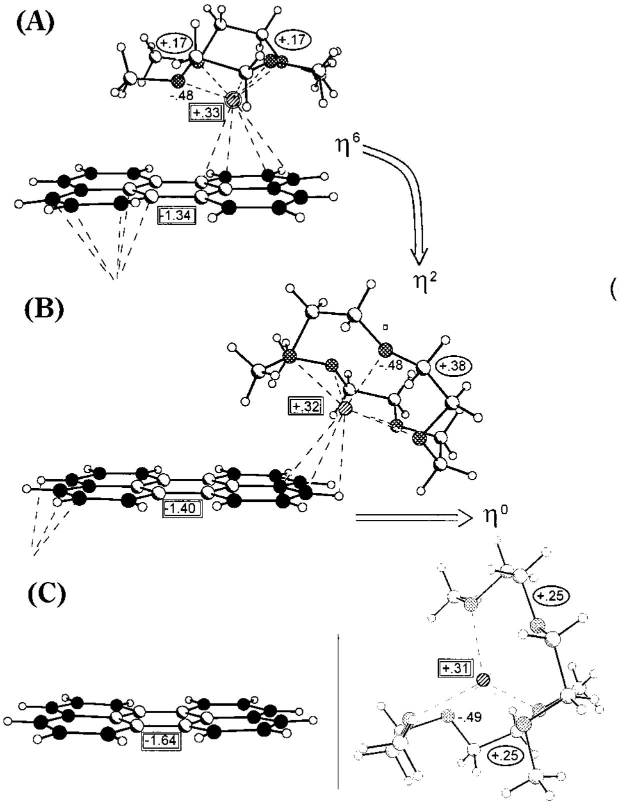
Charge Perturbation in Perylene Radical Anion and Dianion. Comparison of the nine structures determined at low temperature (Experimental Section, Table 1), which includes the improved one of the neutral perylene molecule, reveals significant changes of the geometry from the neutral molecule on going from the radical anion to the dianion. The charge perturbation affects especially the bond lengths, whereas the bond angles remain largely constant: the C−C bond between the naphthalene subunits is shortened from 1.48 Å in perylene to 1.45 Å in the radical anion and to 1.43 Å in the dianion (Table 4). The outside ring bonds, such as 2−3 to 1−6, are elongated by up to 0.03 Å in the radical anion and by up to 0.06 Å in the dianion (Table 4). Expectedly, the overall changes are relatively small on one-electron reduction but, in general, are substantial on two-electron insertion.

Density Functional Calculations. Additional information on the structural perturbation due to radical anion and dianion formation as well as on the density distribution of individual perylene salts, especially concerning the solvate $[(\text{triglyme})_2Na^+][C_{20}H_{12}^{\bullet-}\cdots C_{20}H_{12}]$, is provided by DFT calculations at the B3LYP level starting from the single-crystal structural data (Experimental Section). In general, the geometry changes observed on electron insertion into the perylene π-hydrocarbon are reproduced. The experimentally determined and the calculated bond lengths agree within 0.01 Å (Table 5). The gas- phase electron affinities $C_{20}H_{12} + e^- \rightleftarrows C_{20}H_{12}^{\bullet-} + e^- \ C_{20}H_{12}^{2-}$ are approximated by DFT total energy differences for additionally geometry-optimized structures $C_{20}H_{12}$, $C_{20}H_{12}^{\bullet-}$, and $C_{20}H_{12}^{2-}$ to about −51 and −243 kJ mol^{-1}. For increasing electron insertion, however, only small changes in the DFT charge populations are predicted (Table 6), which, on the other hand, parallel to the small structural distortions observed (Table 5) between perylene, its radical anion, and its dianion. Unexpectedly small differences are also calculated for the tremendous changes in cation solvation, as shown by the structures determined for the individual contact ion pairs with sodium counter-

Table 6. Charge Distribution in Perylene, Its Radical Anion, and Its Dianion Bond

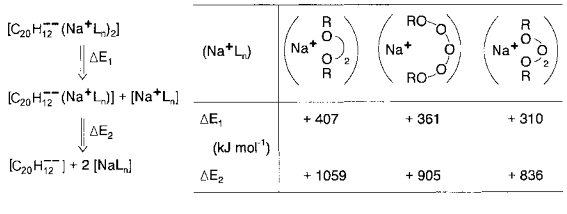
	q_u	C1	C2	C3	C4	C5	C6	H
	$C_{20}H_{12}$	−0.23	−0.13	−0.20	+0.13	+0.02	+0.09	+0.13
	$C_{20}H_{12}^{2-}$	−0.23	−0.13	−0.24	+0.15	0	+0.05	+0.08
	$C_{20}H_{12}^{2}$	−0.24	−0.13	−0.28	−0.17	−0.2	+0.02	+0.02

cations (Figure 2 and Table 3B, C, and D):[2f] the Na$^+$ contact to the perylene dianion surface is reduced from η^6 in the 4-fold O-coordinated $[\cdots^+(\mathrm{DME})_2]$ (A in (8)), to η^2 in the O-pentacoordinated $[\cdots\mathrm{Na}^+(\text{tetraglyme})]$ (B in (8)), to zero in the solvent-separated ion pair with the countercation $[\mathrm{Na}^+(\text{triglyme})_2]$ (C in (8)).



(8)

For both solvent-shared contact ion triples of different Na$^+$ → C$_\pi$ hapticity, almost identical perylene dianion charges of −1.34 and −1.40 (A and B in (8), □) are calculated; a considerable increase to −1.64 results only on dianion/cation separation (C in (8)). The Na$^+$ charges remain constant between 0.31 and 0.33, whereas the ether ligand charges increase from 2 × (+0.17) for DME solvation via +0.38 for tetraglyme to 2 × (+0.25) for diglyme (○ in (8)). Summarizing, there is only a fine-tailored difference between $[\mathrm{Na}^+(\mathrm{C}\eta^6 + 4\ 0)]$ and $[\mathrm{Na}^+(\mathrm{C}\eta^2 + 5\ 0)]$ coordination, in contrast to the larger one on solvent ion separation (C in (8)). To gain further insight, interaction energies ΔE_1 and ΔE_2 have been approximated for the stepwise dissociation of the differently solvated perylene dianion M^{2-} contact ion triples by combining the DFT enthalpies of formation calculated for them and for their fragments (9).

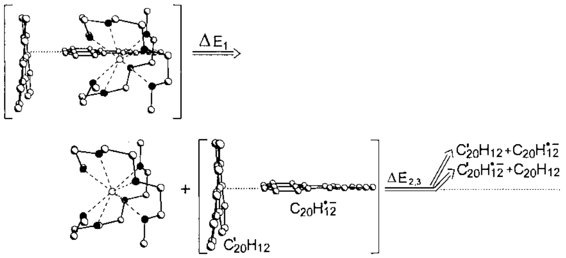


(Na$^+$L$_n$)			
ΔE_1 (kJ mol^{-1})	+ 407	+ 361	+ 310
ΔE_2	+ 1059	+ 905	+ 836

(9)

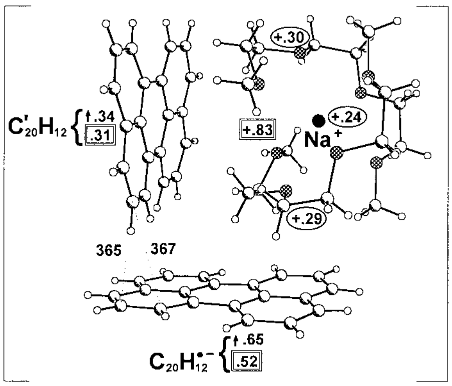
Accordingly, the formation of perylene dianion contact dianion triples is a cooperative process, with the attachment of a second cationic fragment being energetically more favorable ((9), $\Delta E_2 > \Delta E_1$). The Na$^+$ solvation effects by the multidenate polyether ligands are again in the sequence 2 DME (→ η^6) > 1 tetraglyme (→ η^2) > 2 diglyme (→ η^0), as already indicated both by the experimental structural results (Figure 2 and Table 3) and by the calculated charge densities (8).

Perylene Solvate of Perylene Radical Anion in Sodium Bis(triglyme). $[\mathbf{P}^{\bullet-}\cdots\mathbf{P}][\mathbf{Na}^+(\mathbf{RO(CH_2CH_2O)_2R_2})]$. In addition to the experimental structure already presented (Figure 1 and (6); Table 2D), the results of density functional calculations for this rather unusual and rare π-hydrocarbon dimer radical anion (10,11) will be discussed in detail. To continue with an approximate interaction energy (10), the dissociation of the bis(triglyme)-solvated Na$^+$ countercation should require about +230 kJ mol^{-1}, a surprisingly high energy although less than needed for the contact triples of perylene dianion (9).



(10)

The remaining fictive hydrocarbon dimer radical anion $\mathrm{C_{20}H_{12}}^{\bullet-}\cdots\mathrm{C'_{20}H_{12}}$ is calculated to split preferentially into $\mathrm{C_{20}H_{12}}^{\bullet-} + \mathrm{C'_{20}H_{12}}$ ((10), ΔE_2 = 25 kJ mol^{-1}), whereas, according to the DFT fragment energies, the second pathway into $\mathrm{C_{20}H_{12}} + \mathrm{C'_{20}H_{12}}^{\bullet-}$ under additional spin transfer (11) can only be enforced at higher energy ((10), ΔE_3 = 45 kJ mol^{-1}). This quantum chemical result, which suggests some spin delocalization over the dimer radical contact ion pair, can be specified by the charge ((11), □, ○)and spin densities (11, ↑).

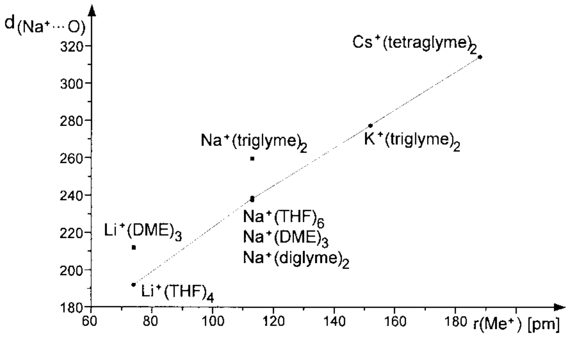


(11)

With 0.65 of the spin in one perylene molecule, $\mathrm{C_{20}H_{12}}^{\bullet-}$ can be assigned to be the dominant radical anion, with a negative charge of −0.52 calculated versus $\mathrm{C'_{20}H_{12}}$, with a spin population of 0.34 and a negative charge of −0.31. For the 2-fold triglyme-solvated countercation, the compensating positive charge of +0.83 is correctly calculated from the experimental structural data ((11), ligands +0.30 and +0.29, Na$^+$ +0.24).

Cation Solvation in Solvent-Separated Perylene Radical Anion Salts. Independent of their countercation as well as of their ether solvent ligand, all structurally characterized perylene radical anion salts crystallize as solvent-separated ion pairs, because the extensive charge delocalization in large π-hydrocarbon radical anions such as the one of perylene prevents preferred centers for contact ion formation.[3c] The perylene radical anion salt dissociation also in different solvents is confirmed by ESR studies.[7] Solvent-separated ion multiples, however, can only be generated in weakly solvating reagents such as diethyl ether or methyltetrahydrofuran and especially at lower temperatures. In contrast, aprotic ether solutions[3b] can contain sodium salts of smaller hydrocarbon radical anions, such as those of naphthalene or the biphenyl as solvent-shared contact ion pairs, even at room temperature.[8]

In most of the structures presented here (Figures 1 and 2), optimally solvated countercations result, which are energetically favored.[3c] In perylene lithium (Figure 1A), the countercation is surrounded by three DME molecules, acting as bidentate solvation ligands and helping to exceed the preferential Li^+ coordination number of four. Therefore, the average $Li^+\cdots O$ distances of 2.12 Å are 0.16 Å longer than those in four-coordinated Li^+ complexes with monodentate ligands such as THF[9] (12). In the sodium complexes (Figures 1D and 2D), each Na^+ countercation is coordinated by two diglyme or two triglyme ligands. With Na^+ cations often favoring the coordination number 6, in 8-fold coordinated ones, the average $Na\cdots O$ distance is about 0.2 Å longer than that in the 6-fold coordinated complex (12). For the K^+ countercation in perylene bis(triglyme) potassium (Figure 1B), the optimum solvent triglyme provides 8-fold coordination. The largest alkali metal cation, Cs^+, is well coordinated by two tetraglyme ligands (Figure 1C). For all these perylene radical anion salts with solvated countercations of preferred coordination number, an approximately linear correlation between the radius r_{M^+} and the average distance $d_{M^+\cdots O}$ results (12):

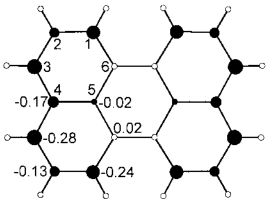


(12)

For solvate complexes with higher than ususal coordination number of the metal countercation, such as in 6-fold O-coordinated lithium tris(dimethoxyethane) or in 8-fold O-coordinated sodium bis(triglyme), deviation from linear behavior is observed.

Cation Solvation in Solvent-Shared Perylene Dianion Salts. The effects of both countercation and solvent ligand are clearly visible in the structures of the different perylene dianion salts presented (Figure 2A–D). The potassium and sodium countercations are located each close above or below the centroid of two diagonally opposite rings. The larger potassium cation exhibits contacts to six perylene π centers (Figure 2A), whereas the smaller sodium cation coordinates only η^5 or η^4 to the perylene dianion and, in addition, to two DME ligands (Figure 2B). For the same reason, the K^+ cation, which would not be effectively solvated by only four oxygens of two dimethoxyethane molecules, adds to one O center of an additional DME molecule, forming a polymeric structure (Figure 2A). Crystallization of the disodium salt from diglyme results in a solvent-separated ion pair, in which the sodium countercation is coordinated to six oxygen centers of two diglyme ethers. The Na^+ solvation by two tetraglyme molecules is prevented by steric overcrowding, and, because the five oxygen centers of one tetraglyme (Figure 2C) cannot sufficiently solvate one Na^+ cation, its coordination sphere is completed by withdrawal to the perylene dianion periphery, providing two additional $Na+\cdots C$ contacts.

In the perylene dianion salts which crystallize as contact ion pairs (Figure 2A–C), the cation is connected to the C-centers of highest negative charge. The calculated charge distribution shows the highest charges at the outer C-centers 1, 2, and 3, which is confirmed by NMR measurements (13).[10]



(13)

The charges correlate with the structural parameters (Table 3): in both the perylene dipotassium and the disodium (bis(dimethoxyethane) salts, the shortest distances observed are $M+\cdots C1$ and, in perylene disodium bis(tetraglyme), $Na^+\cdots C3$. Nevertheless, the potential energy hypersurface above such a hydrocarbon dianion is supposedly rather flat; therefore, several different countercation locations should be feasible.

Conclusions

Summarizing, the structural and quantum chemical investigations of perylene radical anion and dianion salts demonstrate an exemplary case of varying countercation solvation. In addition, they illustrate how the network of equilibria in aprotic solution between different ion pairs[2a] can be influenced by changing either the countercation or the ether solvent and how solvent-separated or solvent-shared contact ion multiples of a given salt can be crystallized selectively. The knowledge gathered helps to navigate the reactivity of such compounds in solution by effective solvation of their countercations to the crystallization of salts containing “naked anions”, in which radical anions or dianions can be studied without the disturbing influence of a given

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countercation. In addition, changes of the countercation or the solvent influence the disproportionation equilibrium of radical anions to the dianion and the neutral molecule[11] and, therefore, help to selectively prepare and crystallize radical anion or dianion salts. The network of equilibria involved is rather complex, and continuing investigations of cation solvation phenomena[2,3] are needed to improve the understanding of them.

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Supporting Information Available: Tables of atomic coordinates, isotropic and anisotropic displacement parameters, and bond lengths, angles, and torsion angles for the compounds described herein (32 pages). Ordering information is given on any current masthead page.

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