

Communications to the Editor

Competing Na⁺ Solvation: Ether-Shared and Ether-Separated Triple Ions of Perylene Dianion^{1a}Hans Bock,* Christian Näther,^{1b} and Zdenek Havlas^{1c}

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Received August 2, 1994

The thermodynamically favorable solvation especially of cations affects the multidimensional networks of interrelated equilibria^{1a,2,3} such as electron transfer and contact ion pair formation as well as aggregation in various ways and, therefore, controls many geochemical to biological processes.⁴ For a more detailed study of the interdependencies, Na⁺ was selected because of its small ionic radius, its high solvation enthalpy,^{1a,4a} and the moderately low reduction potential of sodium metal.^{4a} Na⁺ forms countless salts, complexes, and organometallic compounds of impressive structural diversity.^{4a,c} These include (i) dibenzene sandwiches,⁵ (ii) the surprising 1:1 stoichiometric cocrystallization of solvent-shared [Na⁺(DME)₂]₂M²⁻ plus solvent-separated [Na⁺(DME)₃]₂[M²⁻] triple ions of tetraphenylbutadiene dianion,^{3c} and (iii) the ether solvates of radical anion salts [Na⁺(RO(CH₂CH₂O)_{m-1}R)_n][M^{•-}] stretching from almost octahedral [Na⁺(THF)₆] (*m* = 1, *n* = 6) to 8-fold-

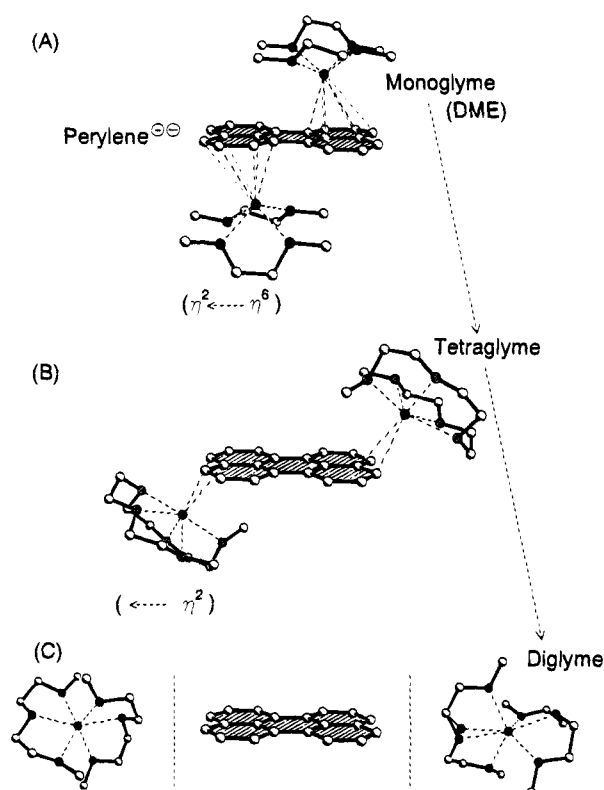


Figure 1. Single crystal structures of (A) disodium perylene tetrakis(dimethoxyethane) [C₂₀H₁₂²⁻{Na⁺(H₃COCH₂H₂COCH₃)₂}]₂, a solvent-shared triple ion with an η⁶-half-sandwich sodium π coordination to the perylene dianion; (B) disodium perylene bis(tetraglyme) [C₂₀H₁₂²⁻{Na⁺(H₃CO(CH₂H₂CO)₄CH₃)₂}]₂, another solvent-shared triple ion but with η² sodium (π/σ) coordination to the perylene dianion rim; and (C) disodium perylene tetrakis(triglyme) [C₂₀H₁₂²⁻{Na⁺(H₃CO(CH₂H₂CO)₂CH₃)₂}]₂, a solvent-separated triple ion of perylene dianion and two sodium bis(triglyme) counteranions (see text).

coordinated [Na⁺(triglyme)₂] (*m* = 4, *n* = 2).^{3a} Along these lines of incredibly fine-tuned cation complexation effects,^{3,5} we report here on an unprecedented case of Na⁺ solvation competition (Figure 1). On increasing contacts Na⁺•••O to polyethers, the sodium counteranions of the perylene dianion are visibly withdrawn from the surface of this planar electron-rich pentacyclic hydrocarbon, reducing their π hydrocarbon coordination from η⁶ via η² to zero (Figure 1).

The structures of the ether-shared (Figure 1A,B) and ether-separated (Figure 1C) triple ions,^{3a,6,7} crystallized from the respective ether solution by adding an *n*-hexane layer, show the following regularities and peculiarities.

Perylene Dianions. On electron addition, M + e⁻ → M^{•-} + e⁻ → M²⁻, the 20 π-center molecule perylene M, as

(1) (a) Preliminary communication in the summary on charge perturbed and sterically overcrowded molecules: Bock, H.; Ruppert, K.; Näther, C.; Havlas, Z.; Herrmann, H.-F.; Arad, C.; Göbel, I.; John, A.; Meuret, J.; Nick, S.; Rauschenbach, A.; Seitz, W.; Vaupel, T.; Solouki, B. *Angew. Chem.* **1992**, *104*, 564; *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 550. (b) Part of Ph.D. Thesis: Näther, C. University of Frankfurt, 1994. (c) On leave from Czech Academy of Sciences, Flemingovo Nam, CZ 16610 Prague.

(2) Bock, H. *Mol. Liq. Cryst.* **1994**, *240*, 155; *Acta Nova Leopoldina* **1994**, *38*, 221.

(3) (a) Bock, H.; Näther, C.; Havlas, Z.; John, A.; Arad, C. *Angew. Chem.* **1993**, *105*, 931; *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 875 and references therein. (b) Bock, H.; John, A.; Näther, C.; Havlas, Z.; Mihokova, E. *Helv. Chim. Acta* **1994**, *77*, 41. (c) Bock, H.; Näther, C.; Ruppert, K.; Havlas, Z. *J. Am. Chem. Soc.* **1992**, *114*, 6907.

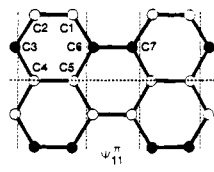
(4) (a) Cf., e.g.: Wiberg, N. *Hollemann/Wiberg: Lehrbuch der Anorganischen Chemie*; de Gruyter: Berlin, 1985. The first vertical ionization energy of Na, IE₁^v = 5.13 eV, and the hydration enthalpy of [Na⁺(H₂O)₁₇], ΔH_f = -390 kJ mol⁻¹, both contribute to the rather low first reduction potential, E_{1/2}^{red}(Na) = -2.71 V. The ionic radius *r* = 97 pm, increasing to 113 pm for 30% covalent contribution,^{1a} fits nicely into a benzene hexagon of 240 pm diameter and, therefore, supports the formation of (C₆H₆)₂Na sandwich subunits such as the one observed in the DME solvate (Figure 1A). (b) Kaim, W.; Schwederski, B. *Bioanorganische Chemie*; Teubner: Stuttgart, 1991. (c) Wells, A. F. *Structural Inorganic Chemistry*, 5th ed.; Oxford University Press: Oxford, 1987.

(5) (a) Bock, H.; Ruppert, K.; Fenske, D. *Angew. Chem.* **1989**, *101*, 1717; *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1685. (b) Bock, H.; Ruppert, K.; Havlas, Z.; Fenske, D. *Angew. Chem.* **1990**, *101*, 1095; *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1042.

(6) Crystal structure of disodium perylene tetrakis(dimethoxyethane) [C₂₀H₁₂²⁻(Na⁺(CH₃O(CH₂)₂OCH₃)₂)₂]: blue-violet prisms from perylene reduction in DME with 1.5-fold stoichiometric sodium metal mirror, generated at 10⁻⁶ mbar, and covering the deep-blue ether solution with an *n*-hexane layer; crystal size, 0.5 × 0.4 × 0.4 mm, MW = 658.78 g/mol; *a* = 953.0(2), *b* = 1266.1(2), and *c* = 1528.2(3) pm, α = 86.22(2)°, β = 85.36(2)°, γ = 76.31(2)°, *V* = 1783.5 × 10⁶ pm³ (*T* = 150 K), *ρ*_{calc} = 1.227 g/cm³, triclinic *P*1 (No. 2), *Z* = 2; Mo Kα radiation, μ = 0.10 cm⁻¹; four-cycle diffractometer STOE-AED-II, 6966 reflections measured within 3° ≤ 2θ ≤ 51°, of which 6535 were independent and used for refinement; structure solution by direct methods and difference Fourier technique (SHELX-86); refinement against *F*² (SHELXL-93); *R*1 = 0.0460 for 5284*F*_o > 4σ(*F*_o); *wR*2 = 0.1379 for 445 parameters and 6535 reflections; *W* = 1/[(σ²(*F*_o)² + 0.0848*P*)² + 0.50*P*]; *G*OF = 1.068, shift/error ≤ 0.001, extinction correction, residual electron density 0.53/-0.30 e/Å³. C, O, and Na atoms have been refined anisotropically, the H atoms (after being geometrically ideally positioned) isotropically using the riding model; there are two independent molecules in the asymmetric unit.

(7) Crystal structure of disodium perylene bis(tetraglyme) [C₂₀H₁₂²⁻(Na⁺(CH₃O(CH₂CH₂O)₄CH₃)₂)₂]: for the growth of the blue-violet prisms see ref 6; crystal size, 0.5 × 0.4 × 0.2 mm; MW = 742.83 g/mol; *a* = 837.6(1), *b* = 1639.5(2), and *c* = 1393.3(1) pm, β = 103.01(1)°, *V* = 1864.2 × 10⁶ pm³ (*T* = 100 K), *ρ*_{calc} = 1.323 g/cm³, monoclinic *P*2₁/*n* (No. 14), *Z* = 2, Mo Kα radiation, μ = 0.11 cm⁻¹; four-cycle diffractometer STOE-AED-II, 4918 reflections measured within 3° ≤ 2θ ≤ 53°, of which 3878 were independent and used for refinement; structure solution by direct methods and difference Fourier technique (SHELXS-86); refinement against *F*² (SHELXL-93); *R*1 = 0.0325 for 3290*F*_o > 4σ(*F*_o); *wR*2 = 0.0899 for 252 parameters and 3878 reflections; *W* = 1/[(σ²(*F*_o)² + 0.7448*P*)² + 0.77*P*]; *G*OF = 1.05, shift/error ≤ 0.001, extinction correction, residual electron density 0.32/-0.21 e/Å³. C, O, and Na atoms have been refined anisotropically, the H atoms (after being geometrically ideally positioned) isotropically using the riding model.

expected,^{1a} is only slightly⁵ distorted. In accord with the qualitative HMO eigenfunction Ψ_{11}^{π} for the consecutively populated lowest unoccupied molecular orbital (1),^{8a} which exhibits five nodal planes, all bonds with a π bonding contribution (O—O or ●—●), such as 1–2 or 6–7, are shortened and all those with an antibonding one (O—●), such as 2–3 or 1–6, are elongated (values in pm):^{8b–d}



C–C	M ^{8b}	M ^{8c}	M ^{2– 8d}
1–2	140	138	137
2–3	136	138	140
3–4	141	141	141
4–5	143	144	145
1–6	138	141	144
6–7	148	145	143

The different η^6 , η^2 , or zero coordinations of the Na⁺ counterions to perylene dianion (Figure 1) do not cause significant changes in its C–C bond lengths.^{8d} An MNDO calculation based on the structural data for the ether-separated dianion salt (Figure 1C) predicts the negative charges to be localized predominantly at center C3 (–0.30) and C1 (–0.20).

Na⁺ Coordination. The contact distances Na⁺···C _{π} between the counterions and the perylene dianion surface as well as Na⁺···O to the ether oxygens reveal interesting facets (values in pm):

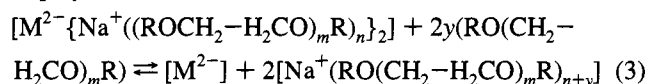
Na ⁺ counterion	Na ⁺ ···C ^{δ^-}	Na ⁺ ···C ^{δ^-}	Na ⁺ ···O	Na ⁺ ···O
[Na ⁺ (Monoglyme) ₂]	268–311	289	234–245	240
[Na ⁺ (Tetraglyme)]	279–309	294	238–252	246
[Na ⁺ (Diglyme) ₃]			233–251	239

Increased ether solvation (Figure 1, A → B) elongates the average contact distance Na⁺···C _{π} ^{δ^-} by 6 pm, and the increase in the Na⁺ coordination from four to five ether oxygen centers elongates the average distance Na⁺···O by 6 pm. In contrast, Na⁺ oxygen hexacoordination in the energetically favorable

(8) (a) Cf., e.g.: Heilbronner, E.; Bock, H. *The HMO Model and its Application*; (German Ed.); Verlag Chemie: Weinheim, 1968–1970; Vols. 1–3; (English Ed.) Wiley: New York, 1975/76; (Japanese Ed.) Hirokawa: Tokyo, 1973; (Chinese Translation) Kirin University Press: 1983. (b) Perylene crystals have been grown from the melt;^{1b} the structure is not yet published. (c) Reduction with lithium metal in DME yields crystals of a solvent-separated radical anion salt, [C₂₀H₁₂^{•-}][Li⁺(DME)₃]; Bock, H.; Näther, C., unpublished.^{1b} (d) Average values, which deviate from the individual values by about ± 1 pm).

triple diglyme solvate,^{3a} the average distance Na⁺···O decreases by 7 pm.

Estimates of Solvation Enthalpies. Starting from the crystal structure data,^{3a,6,7} differences in enthalpies of formation, ΔH_f^{MNDO} (kJ mol⁻¹), have been calculated⁹ (neglecting the presumably small^{3a} entropy contributions) for the hypothetical equilibria between ether-shared and ether-separated triple ions of perylene dianion M²⁻:



ether	Fig 1	ΔH_f^{MNDO} (kJ mol ⁻¹)	
		[M ²⁻ {Na ⁺ _{ether} }] ₂ ⇌ [M ²⁻] + 2[Na ⁺ _{ether}]	
H ₃ CO(CH ₂ -H ₂ CO) ₂ CH ₃ (A)		-2806	-2760
H ₃ CO(CH ₂ -H ₂ CO) ₄ CH ₃ (B)		-2236	-2094
H ₃ CO(CH ₂ -H ₂ CO) ₂ CH ₃ (C)		-2764	-2831

(4)

All experimentally determined structures are predicted to be more stable (4). Accordingly, diglyme is the most favorable Na⁺ solvating ether, and therefore the ether-separated triple ion (Figure 1C) is preferred. For the ether-shared triple ion, predicted as observed (cf. (4) and Figure 1), for monoglyme the η^6 (Na⁺···C) coordination wins over an additional ether solvation η^2 (Na⁺···O) (Figure 1A), and for tetraglyme, the additional η^2 (Na⁺···O) coordination prevents the separation of η^5 (Na⁺···O) solvates (Figure 1B).

Summarizing, the “stroboscopic” Na⁺ solvation triple ions of perylene dianion (Figure 1) are another example^{1a,3c,5b} for delicate solvation energy differences, which due to the optimum charge distribution at the total energy minimum, together with an advantageous lattice packing,^{3c} determine how crystals will grow from solutions with multidimensional networks of inter-related equilibria.^{1a,2–4}

Supplementary Material Available: Tables of atomic coordinates, isotropic and anisotropic parameters, bond distances, and bond and torsion angles; SHELXL-93 crystal structure refinement data for disodium perylene bis(tetraglyme) (16 pages); listing of observed and calculated structure factors (9 pages). This material is contained in many libraries on microfiche, immediately follows in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and internet access instructions.

JA9425445

(9) (a) Parameter optimization: Havlas, S.; Nick, S.; Bock, H. *Int. J. Quantum Chem.* **1992**, *4*, 449. (b) For the Na⁺ ether solvates [Na⁺(CH₃O-(CH₂-CH₂O)_mCH₃)_n], the following bond enthalpy contributions [Na⁺···O] (kJ mol⁻¹) are estimated by MNDO calculations on the basis of the structural data:^{3a,b} monoglyme ($m = 1$, $n = 3$) –112, diglyme ($m = 2$, $n = 2$) –113; triglyme ($m = 3$, $n = 2$), –89, and 2,2,1-cryptand –115 (including Na⁺···N).