0.0057(3); (twin: $\bar{1}00$, $0\bar{1}0$, 001). $R_1 = 0.029$, $wR_2 = 0.071$ (all 325 independent reflections). Isotypic LaISi: $a = 421.9(2)$, $c = 1179.4(1)$ pm, PrISi: $a = 416.4(1)$, $c = 1161.9(1)$ pm. $La_5I_3Si_5$: $C2/m$; $a = 2401.9(1)$, $b = 425.34(2)$, $c = 1571.61(7)$ pm, $\beta = 119.38(1)^\circ$. La(1): 0.0856(1), 0, 0.5629(1); La(2): 0.3390(1), 0, 0.9422(1); La(3): 0.2622(1), 0, 0.6693(1); La(4): 0.1638(1), 0, 0.8339(1); La(5): 0.4826(1), 1/2, 0.7100(1); I(1): 0.3274(1), 1/2, 0.5627(1); I(2): 0.4091(1), 0, 0.7956(1); I(3): 0.0597(1), 1/2, 0.9334(1); Si(1): 0.0759(1), 1/2, 0.7076(1); Si(2): 0.2499(1), 1/2, 0.9599(1); Si(3): 0.9912(1), 1/2, 0.5731(1); Si(4): 0.2601(1), 1/2, 0.8098(1); Si(5): 0.1719(1), 1/2, 0.6806(1); $R_1 = 0.024$, $wR_2 = 0.051$ (all 3000 independent reflections). b) Image plate (IPDS, Stoe); $Mo_{K\alpha}$ radiation. $La_4I_3Si_4$: $C2/m$; $a = 2436.0(5)$, $b = 424.0(1)$, $c = 1257.0(3)$ pm, $\beta = 97.59(3)^\circ$. La(1): 0.5036(1), 0, 0.1653(1); La(2): 0.5747(1), 1/2, 0.4456(1); La(3): 0.3613(1), 0, 0.2918(1); La(4): 0.3548(1), 0, 0.9760(1); I(1): 0.6328(1), 0, 0.2889(1); I(2): 0.2014(1), 0, 0.5729(1); I(3): 0.2435(1), 0, 0.1311(1); Si(1): 0.5230(3), 0, 0.5902(2); Si(2): 0.5428(3), 1/2, 0.6828(2); Si(3): 0.5510(3), 1/2, 0.0168(2); S(4): 0.5967(3), 1/2, 0.8600(2); $R_1 = 0.044$, $wR_2 = 0.081$ (all 1952 independent reflections). Further details on the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666 (Frau S. Höhler-Schlimm); e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository numbers CSD-407246 (CeISi), CSD-407247 ($La_4I_3Si_4$), and CSD-407248 ($La_5I_3Si_5$).

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Tris(tetramethylethylenediamine-sodium)-9,9-bianthryl—The Salt of a π Hydrocarbon Radical Trianion with Three $Na^+ - C_\pi$ Contacts to One Molecular Half

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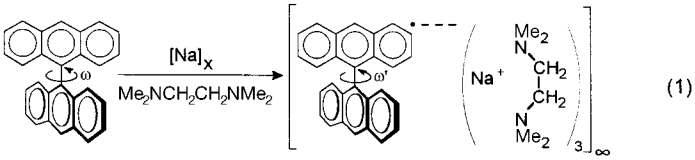
Dedicated to Professor Dieter Seebach on the occasion of his 60th birthday

Reductions of π hydrocarbons by sodium metal in aprotic solutions[1] of efficient cation-solvating ethers[2] facilitate the growth of single crystals (and thus the determination of the structures) of a wide variety of solvent-separated or solvent-shared contact-ion multiples containing radical ions, dianions, or even tetraanions.[1–3] Representative examples are the bare naphthalene radical anion that can be isolated from diglyme solution as a salt with an advantageously solvated sodium cation,[3a] the tetraphenylbutadiene dianion that crystallizes in stoichiometrically 1:1 solvent-separated and solvent-shared ion triples,[3b] or the rubrene tetraanion that has been structurally characterized as contact-ion quintuple with four THF-coordinated Na^+ countercations.[3c]

Still missing is a salt of a radical trianion. By reduction of 9,9′-bianthryl with sodium in a solution containing a mixture of tetramethylethylenediamine and benzene [Eq. (1)], the sodium salt of a π hydrocarbon radical trianion has been isolated as black blocks.[4a]



(1)

The structure determination of the radical trianion salt[4b] (Figure 1) reveals a surprise: In the solvent-shared contact ion quadruple, all three TMEDA-solvated sodium ions are η^6-coordinated to the same anthryl moiety of the 9,9′-bianthryl radical trianion (Figure 1B), whereas the perpendicular hydrocarbon residue forms only two η^1 and η^2 contacts to the centers Na1 and Na3 of an adjacent contact-ion aggregate in the *y* direction of the polymer string (Figure 1A, B). The shortest $Na^+ - C$ η^6 contacts are found for Na2 (average 269 pm); the ones for Na3 and Na1 of 285 and 289 pm are longer because of the additional relatively short contacts of

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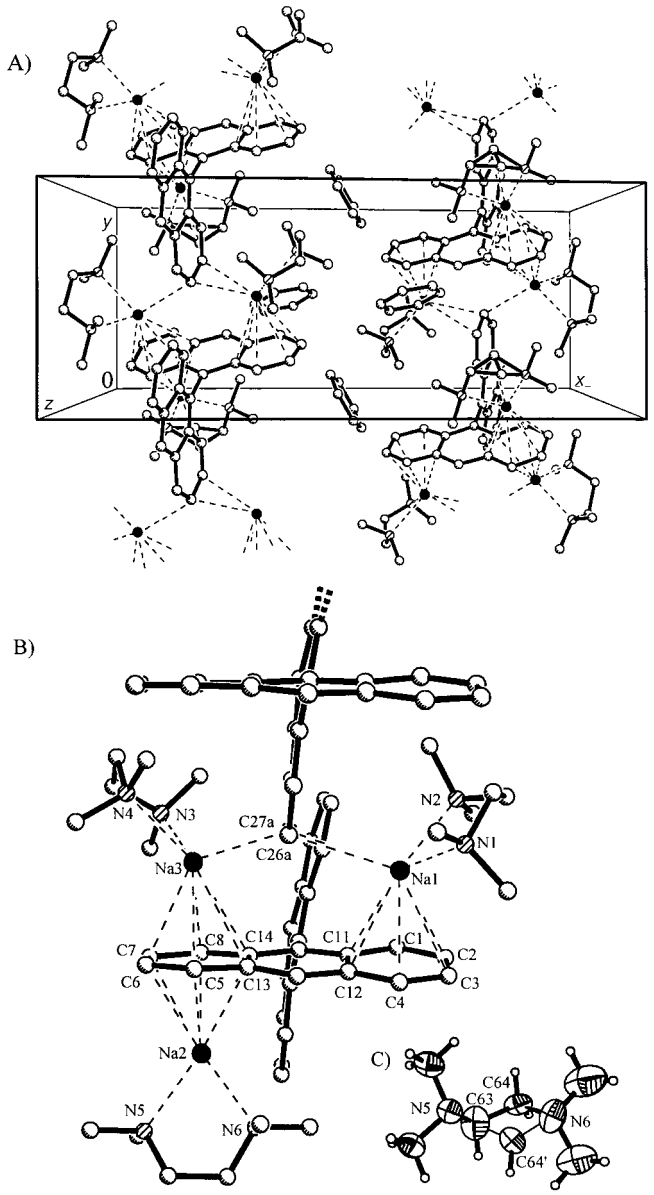

Figure 1. Single-crystal X-ray structure of tris(tetramethylethylenediamine-sodium)-9,9-bianthryl) · 1.5 benzene at 130 K. A) Unit cell (monoclinic, $P2_1/c$, $Z = 4$) along the crystallographic b axis, B) coordination sphere of the Na ions, and C) molecular structure of the disordered[4b] TMEDA ligand (thermal ellipsoids at 50% probability). Selected bond lengths [pm] and angles [°]: Na1 – C1/C12 272 – 302, Na3 – C5/C14 266 – 303, Na1 – C26a 283, Na1 – C27a 311, Na3 – C27a 274, Na2 – C5/C14 265 – 273, Na – N 240 – 251; ω(CC-CC) = 77.

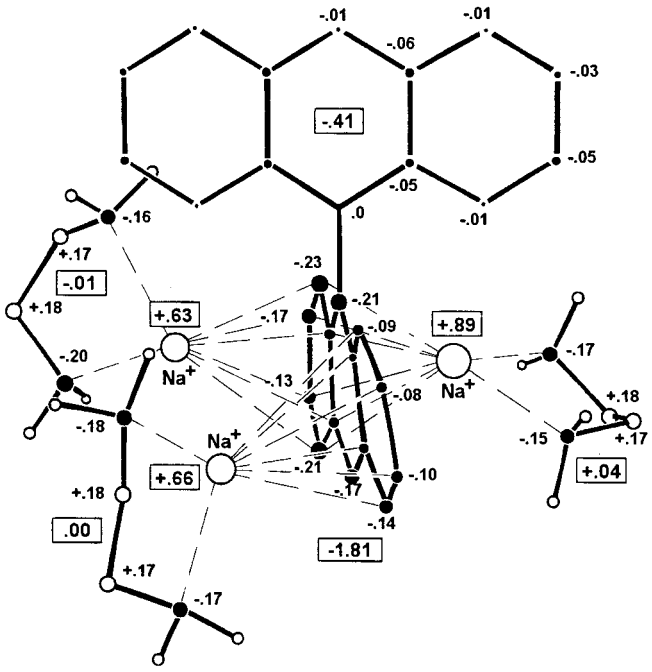

Figure 2. Charge distribution in the title compound determined by density functional calculations.[5] For reasons of space the zero before the comma has been omitted.

274 pm (Na3) and 283 pm (Na1) to the center C26a of the adjacent radical trianion in the polymer chain (Figure 1B).

The coordination of all three Na^+ ions to only one anthryl residue suggests a predominant delocalization of the negative charge within this half of the hydrocarbon, an assumption that is supported by density functional calculations with natural population analysis[5] based on the structural data (Figure 2).[4b] The largely contact-free bianthryl half holds only $\Sigma q^{\mu}_{DFT} = -0.41$ negative charge, in contrast to the threefold Na^+ complexed half with $\Sigma q^{\mu}_{DFT} = -1.91$. Values between $q^{\mu}_{DFT} = +0.63$ and $+0.66$ are predicted for the Na^+ centers at the six-membered ring substituted on both sides and $+0.89$ for that at the singly complexed one. Their reduced positive charges suggest small covalent bonding contributions to both the trianion and the TMEDA ligands. For the N centers of the amino groups coordinated within five-membered chelate rings to the Na^+ cations, charges q^{μ}_{DFT} between -0.15 and -0.20 result;[5] however, due to ($N^{\delta-} \leftarrow C^{\delta+}$) polarization the ethylenediamine ligands remain overall nearly neutral. The calculated polarity of $q^{\mu}_{DFT}(Na^+) \approx 0.7$ and $\Sigma q^{\mu}_{DFT}(2\,N) \approx -0.3$ illustrates the efficient TMEDA solvation of the Na^+ ions, essential for the formation of the radical trianion.[6]

Which consecutive steps within the network of equilibria[1] during the redox reaction (1) could lead to the formation of the contact ion quadruple with the unexpected threefold Na^+ coordination to only one bianthryl half (Figure 1)? On sodium metal reduction in dimethoxyethane (DME), an ether analogous to TMEDA, the solvent-separated salt of bianthryl radical monoanion, $[Na^+(dme)_3][9,9'\text{bianthryl}]$, crystallizes.[6] Cyclic voltammetry measurements[7] prove that bianthryl, twisted by about 80° due to H/H repulsion between the molecular halves,[6] represents an "electron storage" π system, which can be oxidized to its tetracation and reduced to its tetraanion.[7] According to ESR measurements, the twisted product of the two-electron reduction is a triplet diradical dianion.[7a] If the approach of a countercation is calculated on a MNDO/CI hypersurface,[8] configuration interaction predicts a biradical state with 10% admixture of a localized configuration corresponding to a dianion singlet state. The coordination of a second Na^+(TMEDA) lowers the negative charge in the contact-ion bianthryl residue into which the third electron must also be inserted.[8] Then the formation of a contact ion quadruple should result in a radical trianion doublet state. Even though other effects such as the stabiliza-

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tion by the dimer contact Na2-C26a-Na3 (Figure 1B) are neglected, the extensive approximative calculations suggest the following course for as the reduction of bianthryl in a TMEDA/benzene solution at a sodium metal mirror: Via the radical anion an ESR-spectroscopically proven diradical dianion should be formed, which on further electron insertion adds all three $[Na(tmeda)]^+$ ligands to only one half of the bianthryl moiety (Figure 1B). According to the calculations, each coordination step should increase the total negative charge, which is essential for the contact ion formation.[1]

Attempts to prepare the sodium salt of a 9,9′-bianthryl tetraanion[9] under changed reduction conditions[3c] likewise yielded black crystals of the $[Na(pmdta)]^+$ salt of 10,10′-dihydro-9,9′-bianthryl dianion,[9] in which the two Na^+ counterions are coordinated between the mutually perpendicular molecular halves analogous to the tetraphenylethylene dianion.[1] This result is in accord with the cyclic voltammetrically irreversible third and fourth reduction potentials in solution,[7] but stimulates a search for Na^+ solvate ligands that stabilize the counterions better than the advantageous ether→amine exchange in the radical trianion salt reported here.

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