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2,6-Bis[(dimethylamino)methyl]phenylsodium: the first trimeric organosodium compound

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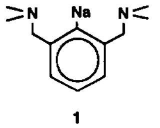
Abstract

The structural properties of 2,6-bis[(dimethylamino)methyl]phenylsodium (**1**) and its crystal structure are reported. Compound **1** is the first organosodium trimer, and the first example of a totally intramolecularly solvated organosodium compound.

Keywords: Sodium; Crystal structure

1. Introduction

Trimeric organoalkali compounds are relatively rare. Five years ago we described the first trimeric organolithium compound: 2,6-bis(dimethylamino)phenyllithium (**2**) [1]. Subsequent examples, in which one [2] or both [3] dimethylamino groups were replaced by tertiary butoxy groups, showed that under certain steric and coordinative restraints trimeric organolithium compounds can be isolated. The only unsolvated example of a trimeric species is a vinyllithium derivative [4]. Here we report the first trimeric organic derivative of a heavier alkali metal, viz. 2,6-bis[(dimethylamino)methyl]phenylsodium (**1**).



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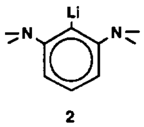

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To our knowledge **1** is also the first isolated organic derivative of a heavier alkali metal that is completely intramolecularly solvated. Compound **1** is of limited stability in both the solid state and in solution. Even in apolar solvents such as hexane, **1** decomposes and rearranges below −15°C to give the product with the metal attached to benzylic carbon. Dry crystals of **1** slowly turn orange above 0°C, indicating the occurrence of the benzylic rearrangement to the benzylic derivative. The X-ray structure of **1** shows it to be a chiral screw or propeller-like aggregate, with a structure resembling that of **2** (see Fig. 1).

The propeller has a pseudo three-fold rotation axis perpendicular to the Na–Na′–Na″ plane. The six membered CNaC′Na′C″Na″ ring is not flat. When the least squares plane (lsp) through this ring is defined it shows that the sodium atoms deviate from this plane on average by 0.115(1) Å and the metallated carbons by −0.114(4) Å. The aryl rings make angles of 66.2° (mean) with the lsp of the six membered Na–C ring. As can be seen in the X-ray structure (Fig. 1), approximately half of the sodium sphere seems to be empty and the coordination number of sodium is four. The Na–Na distances range from 3.460(2) Å to 3.477(2) Å. The metallated carbon (Cipso)–sodium distances range from 2.495(5) Å to 2.554(5) Å and are relatively short. Similar shortening of the C–Li bonds is also observed in **2**. The N–Na distances are normal: 2.405(4) Å to 2.434(4) Å. The fact that sodium deviates from its favoured coordination number (five) may be accounted for by the steric demands of the CH_2NMe_2-arms and the consequent position of the aryl rings. It is almost

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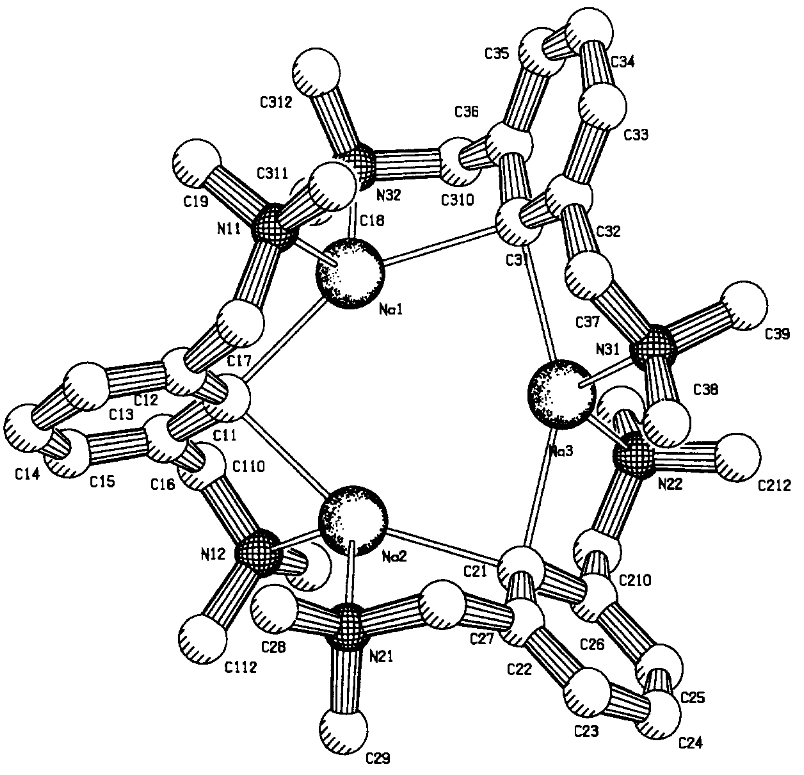

Fig. 1.

impossible to form a hexamer that consists of two stacked and rotated trimers, even if the aryl rings could make an angle of 90° with a (distorted) six membered C–Na ring. From a van der Waals plot of trimeric **1** (Fig. 2) it can clearly be seen that the sodium atoms are completely shielded by the CH$_2$NMe$_2$-arms.

A possible explanation for the formation of a trimer instead of the more obvious dimer relates to the length of the CH$_2$NMe$_2$-arms relative to the atomic radius of sodium which results in a longer Cipso–metal bond, see Fig. 3. The arms are too short to allow complete chelation of the nitrogens with sodium (**a**). Complete chelation pulls the dimer together, resulting in a normal Na–N distance and a Na–Cipso–Na′ angle as observed in the X-ray structure. However, this geometry results in a repulsion between the Cipso lone pairs (**b**) that may cause opening of the dimer (**c**), addition of a monomer then yielding the trimer (**d**).

Another possibility is that three 'activated' dimers form two trimers. The lithium analogue of **1** is dimeric [5] but the lithium phenolate analogue, in which the

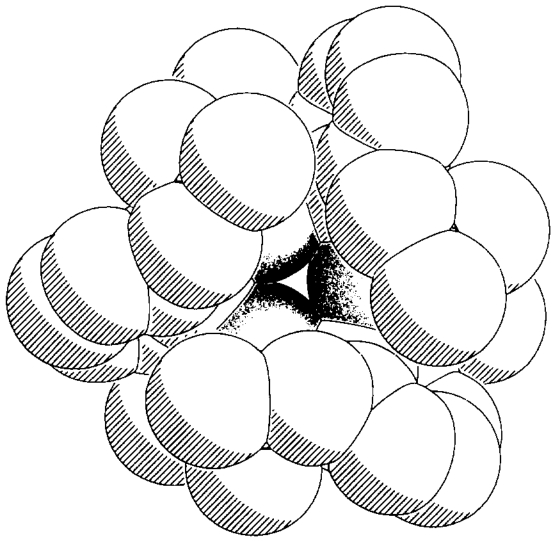

Fig. 2.

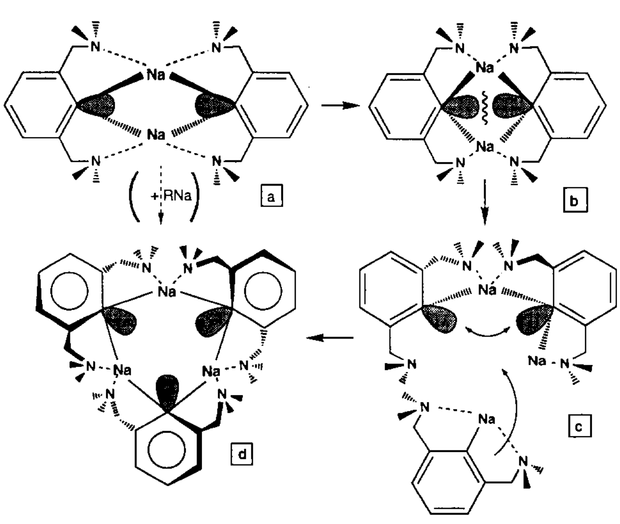

Fig. 3.

'Cipso'–lithium distance is artificially elongated by an oxygen atom, is also trimeric [6]. The trimeric structure of **2** is the result of shortening the chelating arms to NMe_2-s; these arms are too short for bonding to lithium. Unfortunately the potassium derivative of **1** appeared to be unstable above −65°C (even in apolar solvents such as hexane) and could therefore not be isolated. Above this temperature a dark-red insoluble and apparently polymeric benzyl-metallated compound is obtained [7].

Crystals of **1** are slightly soluble in toluene-d_8 and NMR [8] can be performed only below −50°C. Above this temperature **1** decomposes, giving a tarry brown product in the NMR tube presumably due to solvent attack combined with the rearrangement to a benzylic species. As can be seen in the X-ray structure (Fig. 1), the two CH_2NMe_2-arms are diastereotopic. In the ^1H-spectrum an AB-pattern for the benzylic protons and two distinct NMe_2-signals are observed at −50°C. The ^{13}C-spectrum also contains two NMe_2-signals. The process responsible for the coalescence of the signals from the CH_2NMe_2-arms may initiate the decomposition of **1**. The metallated carbon of the ^6Li-analogue of **1** resonates at 188.5 ppm [9]. The metallated carbon of **1** gives a sharp resonance at 196.6 ppm which is in accordance with increasing polarity of the carbon–metal bond [10] going from lithium to the heavier alkali metals.

2. Experimental methods

2.1. Synthesis of 1

To a stirred solution of 0.9 g (4.6 mmol) of 2,6-bis[(dimethylamino)methyl]phenyllithium (^6Li) in 10 ml of hexane was added dropwise a solution of 0.6 g (5.5 mmol) sodium *tert*-amylate in 10 ml of hexane at −50°C. The clear yellowish reaction mixture was stirred for 30 min. During this period the temperature was gradually raised to −20°C. Subsequently the reaction mixture was concentrated in vacuo until a white solid precipitated. Warming up the mixture to −10°C gave a clear, slightly red, solution. The solution was cooled slowly to −33°C in a refrigerator using a Dewar vessel. After a few hours colourless crystals of **1**, suitable for X-ray diffraction, precipitated. The supernatant was decanted and cold (−30°C) paraffin oil was poured onto the crystals. As quickly as possible a crystal was selected and mounted on the X-ray diffractometer. Working up the crystals used for NMR was carried out below − 30°C: the crystals were washed twice with cold hexane (−30°C) and dried in vacuo. Dry crystals of **1** remain colourless and stable for weeks when stored under −30°C and are very air sensitive but not pyrophoric. Preparation of the NMR-samples occurred by systematically cooling all glasswork with liquid nitrogen. All procedures were carried out in a nitrogen atmosphere using freshly distilled and dried solvents.

2.2. X-ray analysis

Crystal data for **1**: $Na_3C_{36}H_{57}N_6$, $M_r = 642.86$, clear transparent, rhombus shape ($0.15 \times 0.30 \times 0.38$ mm), triclinic, spacegroup $P\text{-}\bar{1}$ (no. 2), $a = 11.3600(15)$, $b = 11.3838(11)$, $c = 17.364(3)$ Å, $\alpha = 97.979(11)$, $\beta = 100.863(12)$, $\gamma = 111.655(10)°$, $V = 1995.5(5)$ Å^3, $Z = 2$, $\rho_{calc} = 1.070$ g cm^{-3}, $F(000) = 696$, $\mu(\mathrm{Mo}\ K\alpha) = 0.9$ cm^{-1}, 6816 reflections measured, 6578 independent ($1.2° < \theta < 25.4°$, $\omega/2\theta$ scan, $\Delta\omega = 0.73 + 0.35 \tan\theta°$, $T = 150$ K, Mo $K\alpha$ radiation, graphite monochromator, $\lambda = 0.71073$ Å) on an Enraf Nonius CAD4-T diffractometer on rotating anode. Data were corrected for *Lp* and for linear decay of 1.5% of the reference reflections ($-2\,0\,3$, $-1\,-2\,4$, $-1\,-4\,2$) during 16 h of X-ray exposure time. Empirical absorption correction applied as implemented in PLATON (DIFABS, correction range 0.918–1.122). The structure was solved by automated direct methods (SHELXS-86). Refinement on F^2 was carried out by full-matrix least-squares techniques (SHELXL-93); no observance criterion was applied during the refinement. Final $R1$ value 0.0706, for 3120 reflections with $I > 2.0\sigma(I)$, $wR2 = 0.1290$ for all 6578 data, $w = 1/[\sigma^2(F_o^2) + (0.0416 * P)^2]$, with $P = [\max(F_o^2, 0) + 2 * F_c^2]/3$, $S = 0.930$, for 418 parameters. All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were refined with a fixed isotropic thermal parameter related to the value of the equivalent isotropic thermal parameter of their carrier atoms by a factor of 1.5 for the methyl and 1.2 for the aromatic hydrogens respectively. Weights were refined in the final refinement cycles. Further details of the structure determination, including atomic coordinates, bond lengths and angles, thermal parameters are available on request from the director of the Cambridge Crystallographical Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW (UK), on quoting the full journal citation.

Acknowledgements

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[7] Quenching with dimethyldisulfide proves the benzylic rearrangement.

[8] NMR data of **1** in [D_8]toluene, −50°C; ^{1}H (300 MHz): $\delta = 1.68$, 2.06 (s, 6H, $N(CH_3)_2$, two signals), 3.01, 3.88 (both d (AB pattern), 2H, $^2J(HH) = 10.4$ Hz, NCH_2), 7.06 (d, 2H, $^3J(HH) = 7.3$ Hz), 7.23 (dd, 1H, $^3J(HH) = 7.12, 7.45$ Hz). ^{13}C (75 MHz): $\delta = 42.2$, 47.9 ($N(CH_3)_2$, two signals), 74.2 (NCH_2), 123.9, 126.3, 150.8 (arom) 196.6 (metallated carbon).

[9] The signal of the lithiated carbon splits into five signals with an intensity ratio of 1:2:3:2:1 ($^1J(^{13}C, ^6Li) = 7.5$ Hz) which is idendicative for a carbon bonded to two ^{6}Li nuclei.

[10] For phenyllithium: W. Bauer, W. Winchester and P.v.R. Schleyer, *Organometallics, 6* (1987) 2371.