A New Type of Structure in Sodium Amide Ring Chemistry: Crystal Structure of $[PhCH_2(Me)NNa(tmeda)]_2$ showing a Buckled, rather than the Normal Planar, $(NNa)_2$ Cyclic Ring, with a *cisoid*, rather than the Normal *transoid*, Arrangement of Amido-substituents (tmeda = tetramethylethylenediamine)

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The red crystalline complex $[PhCH_2(Me)NNa(tmeda)]_2$, synthesised from equimolar proportions of PhNa, the secondary amine $PhCH_2(Me)NH$ and the Lewis base tmeda (tetramethylethylenediamine, $Me_2NCH_2CH_2NMe_2$), has been structurally identified by X-ray diffraction studies, which reveals a new type of structure based on a buckled $(NNa)_2$ dimeric ring with a *cisoid* arrangement of amido-substituents.

Since the pioneering work on sodamide by Gay-Lussac and Thenard nearly two centuries ago[1] sodium amides have been much in demand as reagents in applications such as amide transfer, proton abstraction and anionic-polymerisation initiation.[2] Yet, in terms of structural knowledge, this area remains largely unexplored. Until recently, crystal structure reports were limited to those of the simple silylamide $[(Me_3Si)_2NNa]_\infty$,[3] the octamethyltrisiladiazane derivative $[(Me_3SiNNa)_2SiMe_2]_3$,[4] and two mixed-metal lanthanides $NaEu[N(SiMe_3)_2]_3$ and $NaYb[N(SiMe_3)_2]_3$.[5] However, during the past year, five more structures have been crystallographically characterised. A common structural type has emerged from this list: a planar $(NNa)_2$ ring arrangement exhibiting *transoid* orientations of the *N*-attached substituents, adopted by $[N\text{-sodioindole (tmeda)}]_2$,[6] $[N\text{-sodioindole(pmdeta)}]_2$ (pmdeta = pentamethyldiethylenetriamine),[6] $[\text{phenyl(2-pyridyl)amidosodium(pmdeta)}]_2$[7] and $[\textit{tert}\text{-butyl(di-}\textit{tert}\text{-butylfluorosilyl)amidosodium(thf)}]_2$ (thf = tetrahydrofuran).[8] In complete contrast to this trend, we now report the crystal and molecular structure of $[PhCH_2(Me)NNa(tmeda)]_2$, **1**, which opts for a non-planar, slightly-folded $(NNa)_2$ cyclic ring with a *cisoid* arrangement of benzyl-methyl amido-attached ligands.

Mixtures of PhNa, $PhCH_2(Me)NH$ and tmeda (in 1 : 1 : 1 ratios) in hexane solutions under protective argon blankets afford the highly air- and moisture-sensitive adduct **1** in near quantitative yields.† Its isolation proved difficult, more so than is usual with *lithium* amides, as the minutest trace of oxygen in the inert gas would cause surface-blackening of the red crystals of **1**.

Fig. 1 shows the buckled nature of the four-membered $(NNa)_2$ ring of **1** (the Na and N atoms lie 0.173 Å above and

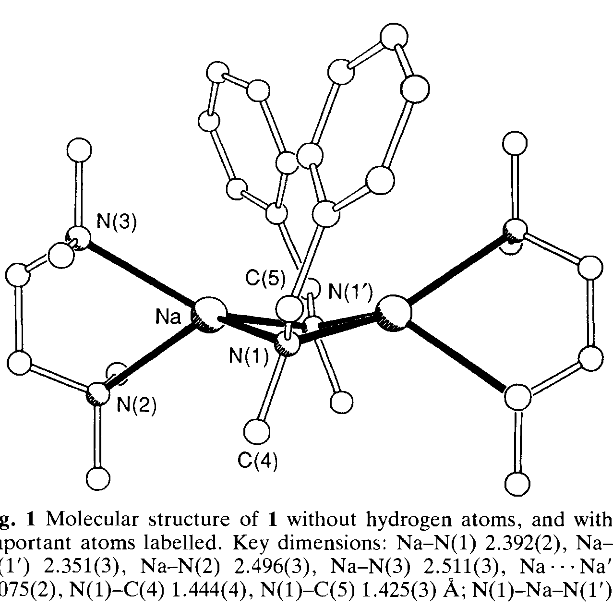

Fig. 1 Molecular structure of **1** without hydrogen atoms, and with important atoms labelled. Key dimensions: Na–N(1) 2.392(2), Na–N(1′) 2.351(3), Na–N(2) 2.496(3), Na–N(3) 2.511(3), Na···Na′ 3.075(2), N(1)–C(4) 1.444(4), N(1)–C(5) 1.425(3) Å; N(1)–Na–N(1′) 96.7(1), Na–N(1)–Na′ 80.8(1), N(2)–Na–N(3) 72.5(1), N(1)–Na–N(2) 126.2(1), N(1)–Na–N(3) 111.5(1), N(1′)–Na–N(2) 107.7(1), N(1′)–Na–N(3) 144.8(1), C(4)–N(1)–C(5) 107.0(2)°.

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† Satisfactory analyses (C, H, N, Na) were obtained. M.p., 41–42 °C. NMR spectra; ^1H (250 MHz), 25 °C, $[^2H_8]$thf solution, δ 2.15 (s, 12H, Me-tmeda), 2.30 (s, 4H, CH_2 × 2-tmeda), 2.79 (s, 3H, Me), 3.99 (br s, 2H, CH_2), 7.02 (m, 1H *para* Ph), 7.15 (m, 2H, *meta* Ph), 7.25 (m, 2H, *ortho* Ph) relative to tetramethylsilane.

below the mean plane of the ring with the summed bond angles within the ring being 355°), as revealed by an X-ray diffraction study.[‡] Each benzyl group lies on the same side of the ring as the Na · · · Na link, while the methyl groups are positioned towards the opposite side, giving molecular C_2 symmetry. Bidentate tmeda molecules complete the distorted tetrahedral environment of the metal cations. N–Na interatomic distances within the ring reflect this comparatively low coordination number (four) for sodium in being distinctly shorter {with the exception of one bond in [*N*-sodioindole(tmeda)]$_2$[6]} than the corresponding bonds in the planar dimeric rings mentioned above (range of lengths, 2.35–2.55 Å), which tend to have higher-coordinated metal centres. The amido-nitrogen atoms also occupy distorted tetrahedral sites, as do the two nitrogen donor atoms in each tmeda molecule {the analogous (donor)N–Na attachments in [*N*-sodioindole(tmeda)]$_2$[6] are marginally shorter than those in **1**, being 2.433(5) and 2.474(5) Å}. There is no obvious steric explanation to account for the preference of the non-planar, *cisoid* arrangement to a planar, *transoid* (C_i) alternative, so the controlling factor could be electronically-based. However, the dimeric molecules are arranged discretely in the lattice so intermolecular bonding is not a factor here.

The view of the crystal structure given in Fig. 1 prompts the question, 'do phenyl · · · Na interactions contribute to its stability?' Each aryl ring is arranged so that it sits approximately face-on to one Na^+ cation and edge-on to the other, but the interatomic distances involved appear to be too long to constitute significant C–Na bonding (*e.g.* shortest *ipso* C · · · Na, 3.474 Å; shortest *ortho* C · · · Na, 3.395 Å; *cf.* even the weakest C–Na bonds in methylsodium, the intermolecular ones between tetrameric units, 2.76 Å).[9] However, preliminary *ab initio* MO calculations at the 6-31G level[10] on the model uncomplexed monomer [PhCH$_2$(H)NNa] reveal that the conformation in which the face of the phenyl ring points towards the metal is more stable by 8.3 kcal mol^{-1} (1 cal = 4.184 J) than the structure in which it is end-on to the nitrogen–sodium bond. A 180° rotation of the benzyl group about the C–N bond, which leads to greater phenyl · · · Na distances, decreases the stability of these structures by 7.5 and 1.9 kcal mol^{-1} respectively.[§] These findings suggest that phenyl · · · Na interactions may be more influential in the structure of the uncomplexed precursor of **1**, [PhCH$_2$(Me)NNa]$_n$, *i.e.* in the absence of tmeda donor molecules.

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[‡] *Crystal data* for $C_{28}H_{52}N_6Na_2$: $M_r = 518.7$, monoclinic, $C2/c$, $a = 22.935(3)$, $b = 9.443(1)$, $c = 16.961(2)$ Å, $\beta = 115.263(8)°$, $U = 3322.0$ Å^3, $Z = 4$, $D_c = 1.037$ g cm^{-3}, λ(Mo-Kα) = 0.71073 Å, $\mu = 0.08$ mm^{-1}, $F(000) = 1136$, $T = 295$ K. The structure was determined by direct methods and refined[11] to a minimum of $\Sigma w\Delta^2$ [$\Delta' = |F_o| - |F_c|$, $w^{-1} = \sigma^2(F) = \sigma_c^2(F) + 15 - 94G + 120G^2 - 30H + 15H^2 + 119GH$, $G = F_o/F_{max}$, $H = \sin\theta/\sin\theta_{max}$][12] from 1499 reflections with $2\theta < 45°$ and $F > 4\sigma_c(F)$ (σ_c from counting statistics only), measured with a Stoe–Siemens diffractometer and on-line profile fitting.[13] Anisotropic thermal parameters were refined for all non-H atoms, H atoms were constrained. Final $R = 0.039$, $R'_w = (\Sigma w\Delta^2/\Sigma w F_o^2)^{\frac{1}{2}} = 0.036$, $S = 1.13$, for 179 parameters. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

[§] Total energies of different conformations of [PhCH$_2$(H)NNa]: (*a*) Phenyl ring face-on to sodium, $E = -485.8822$ au, 180° rotation of benzyl group about C–N bond, $E = -485.8702$ au; (*b*) Phenyl ring end-on to sodium, $E = -485.8690$ au, 180° rotation of benzyl group about C–N bond, $E = -485.8659$ au.