Journal of Organometallic Chemistry, 386 (1990) 287–297
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands
JOM 20623

X-ray crystallographic studies and dynamic ^{1}H NMR spectroscopic studies of the novel sodium aza-allyl monomer {[PhC(H)NC(H)Ph]Na · PMDETA}: a discrete contact ion-pair structure held together by a short N–Na bond, and showing close (*ortho*-Ph)C–H ··· Na contacts in both solid state and solution

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(Received November 14th, 1989)

Abstract

{[PhC(H)NC(H)Ph]Na · PMDETA} (**1**) (PMDETA = $(Me_2NCH_2CH_2)_2NMe$), exhibits a contact ion-pair arrangement in the crystal, with the complexed metal cation bound to the nitrogen centre of the aza-allyl $(C{\because}N{\because}C)^-$ fragment (N–Na bond length, 2.384(2) Å). Further close contacts exist between the sodium and one *ortho*-C from each phenyl ring (distances 3.133(4) and 3.166(4) Å). Variable-temperature ^{1}H NMR spectroscopic studies indicate that **1** adopts a remarkably similar structure in tetrahydrofuran-d_8 solution. Thus, at −50 °C the restricted rotation about each C(*ipso*)–C(benzylic) bond results in the appearance of two distinct resonances each for both the *ortho*- and *meta*-H's. From their coalescence temperatures the energy barrier to rotation has been estimated (12.8 kcal mol^{-1}). Evidence that this rigid solution conformation mimics the crystal structure in having short *ortho*-C–H ··· Na distances comes from the exceptionally large chemical shift difference (1.05 ppm) associated with the dual *ortho*-H signals.

Introduction

Lithium amide reagents commonly used for selective proton abstraction in many areas of laboratory synthesis [1] have the formula $(R^1R^2NLi)_n$, unless they are

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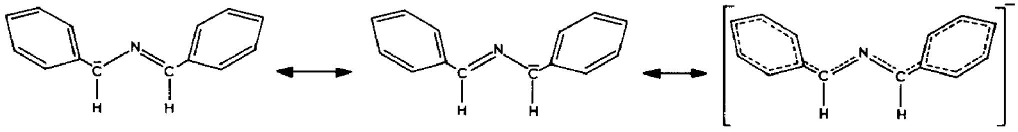
employed in a donor medium where frequently the reactive species is a complex, $[R^1R^2NLi(D)_x]_{n'}$ (D = a Lewis base, n' is usually less than n). Often it is simply a matter of adding a stoichiometric amount x of a Lewis base solvent (nitrogen or oxygen donors are usually preferred) to a hydrocarbon solution of the initial amide to give the complex. The best example for comparison with the work reported here is the trimeric solid dibenzylamidolithium $[(PhCH_2)_2NLi]_3$, since this forms crystalline (1/1) complexes with ether or HMPA $[O{=}P(NMe_2)_3]$ [2]. That being the case for lithium, we were surprised to find in our studies of the lesser known sodium amide compounds that its analogue dibenzylamidosodium, $[(PhCH_2)_2NNa]_n$, does not form the straightforward donor-acceptor complex $[(PhCH_2)_2NNa \cdot PMDETA]_n$ on treatment with the tridentate chelating agent PMDETA [3]. Instead, the amido group undergoes a remarkable transformation, one proton being stripped from each benzylic-CH_2 carbon site to give the naked $[PhC(H)NC(H)Ph]^-$ anion in the only solid product of the reaction, $\{[PhC(H)NC(H)Ph]Na \cdot PMDETA\}$ (**1**). A preliminary account of the establishment of the empirical formula of **1** by routine analyses has already appeared [3]. However, in view of the intriguing structural and bonding picture that this molecular formula posed, we subsequently carried out a more detailed examination of **1** itself and report our findings here. In particular, we have succeeded in determining by an X-ray diffraction study the crystal structure of this typically moisture- and oxygen-sensitive sodium organometallic. This study has revealed a rare monomeric arrangement for sodium comprising a $[PhC(H)NC(H)Ph]^-$ near-planar anion and a $[Na \cdot PMDETA]^+$ cation in a contact ion-pair formation which places the metal close to one *ortho*-C–H unit of each phenyl ring. Similar short (*ortho*-Phenyl)C–H ··· Na separations in tetrahydrofuran-d_8 solution are implied by the results of a dynamic ^1H NMR spectroscopic study.

Results and discussion

The title compound, $\{[PhC(H)NC(H)Ph]Na \cdot PMDETA\}$ (**1**), to the best of our knowledge is unprecedented in sodium chemistry (perhaps in alkali metal chemistry) in being a 2-aza-allyl anion derivative, i.e., with the nitrogen atom in the centre of the unsaturated CNC linkage. There are many examples of 1-aza-allyl lithium species, characteristically having aza-allyl CCN units, in contrast to the CNC sequence in **1** [4]. A limited selection has been successfully studied by X-ray diffraction: in most cases the anion binds to the metal solely through its nitrogen atom, but occasionally an η^3-CCN interaction with the metal is observed, as in the products of lithiation of $2\text{-}(Me_3Si)_{3-n}CH_nC_5H_4N$ ($n = 1$ or 2) [5]. Strictly, many other unsaturated species containing additional heteroatoms also belong to this group of compounds, including lithium derivatives of hydrazones, oximes and oxime ethers [6].

The $[PhC(H)NC(H)Ph]^-$ anion in **1** is itself noteworthy since in theory its negative charge can be delocalised over its entire length as shown in Scheme 1. Our X-ray crystallographic study reveals that the anionic ligand has an almost planar geometry (see Figs. 1, and 2 in particular) that facilitates such delocalisation, and this is reflected in the fact that the bond lengths are shorter than those usually observed. Typically, carbon–nitrogen single bonds are 1.48 Å long [7], yet here the two CN links measure only 1.327(4) and 1.334(4) Å, closer to the double bond



Scheme 1.

distance (1.25 Å); similarly, the two C(*ipso*)-C(benzylic) bonds exhibit partial multiple bonding character in that they have lengths of 1.430(4) and 1.421(4) Å) (cf. single CC bonds, typically 1.54 Å long [7]). Table 1 gives the complete list of bond lengths and bond angles found in **1**. The central CNC unit of the anion forms a contact ion-pair with the Na^+ cation by bonding in a mono-hapto manner through its N component; this N–Na bond (length 2.384(2) Å) is inclined at an angle of 50.1° to the CNC aza-allyl plane. Our ab initio MO geometry optimisation on the model system of **1**, {[HC(H)NC(H)H]Na}, described previously [3], predicted a significantly larger dihedral angle (with Na 77.1° out of the $C \overset{\cdots}{-} N \overset{\cdots}{-} C$ plane): however, owing to the restriction on the number of atomic orbitals that could be employed in the calculation, the model used did not take account of the important effects of the phenyl groups or of complexation by a bulky tridentate Lewis base. Though there are no structural reports of such N–Na bonds elsewhere in the literature, a few crystal structures featuring other types of anionic N–Na contacts are available for comparison. Of particular interest is a series of silylamide derivatives: the simplest, $[(Me_3Si)_2NNa]_\infty$ [8], displays marginally shorter N–Na bonds [average length, 2.355(4) Å], attributable to the lower metal coordination number in its infinite chain structure (i.e., 2 cf. 4 (to nitrogen, see below) for **1**); the significantly longer N–Na bonds in the mixed-metal sodium lanthanides $NaEu[N(SiMe_3)_2]_3$ (average length 2.47 ± 0.02 Å) and $NaYb[N(SiMe_3)_2]_3$ (average length 2.46 ± 0.02 Å) can be rationalised in terms of the fact that each sodium has additional (multifarious) contacts with methyl carbon atoms [9]; the plethora of N–Na bond lengths [range 2.304(3)–2.601(3) Å] in the trimeric cluster $[(Me_3SiNNa)_2SiMe_2]_3$ appears to be an artefact of the different coordination numbers of both atoms in each N–Na connection [10]. Imido nitrogen atoms, on the other hand, are compelled to make more extended use of their valence electrons in the novel monolithium-trisodium cubane cluster $LiNa_3[O{=}P(NMe_2)_3]_3[N{=}C(NMe_2)_2]_4$ [11], and therefore all their μ_3-interactions with sodium atoms are

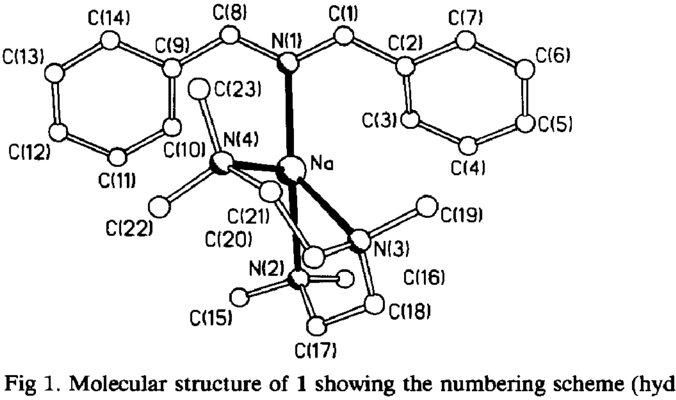


Fig 1. Molecular structure of 1 showing the numbering scheme (hydrogen atoms are omitted for clarity).

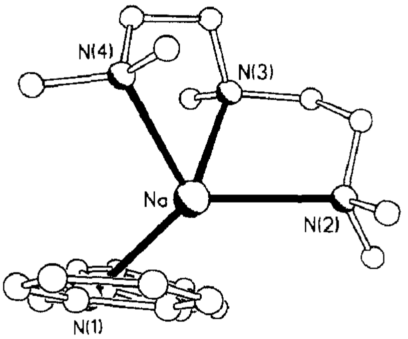


Fig. 2. Alternative view of the monomeric structure, highlighting both the near-planar geometry of the anion and the tetra-nitrogen coordination of the metal cation.

Table 1. Bond lengths (Å) and angles (°) for 1.

Na–N(1)	2.384(2)	Na–N(2)	2.529(3)
Na–N(3)	2.455(3)	Na–N(4)	2.497(3)
N(1)–C(1)	1.327(4)	N(1)–C(8)	1.334(4)
C(1)–C(2)	1.430(4)	C(2)–C(3)	1.407(5)
C(2)–C(7)	1.403(5)	C(3)–C(4)	1.383(5)
C(4)–C(5)	1.378(6)	C(5)–C(6)	1.380(6)
C(6)–C(7)	1.361(6)	C(8)–C(9)	1.421(4)
C(9)–C(10)	1.397(4)	C(9)–C(14)	1.410(5)
C(10)–C(11)	1.376(5)	C(11)–C(12)	1.378(5)
C(12)–C(13)	1.366(6)	C(13)–C(14)	1.365(6)
N(2)–C(15)	1.461(5)	N(2)–C(16)	1.457(5)
N(2)–C(17)	1.453(4)	N(3)–C(18)	1.469(4)
N(3)–C(19)	1.462(4)	N(3)–C(20)	1.472(4)
N(4)–C(21)	1.467(4)	N(4)–C(22)	1.444(5)
N(4)–C(23)	1.462(4)	C(17)–C(18)	1.498(5)
C(20)–C(21)	1.483(5)		
N(1)–Na–N(2)	135.9(1)	N(1)–Na–N(3)	138.8(1)
N(2)–Na–N(3)	74.7(1)	N(1)–Na–N(4)	102.8(1)
N(2)–Na–N(4)	115.9(1)	N(3)–Na–N(4)	74.7(1)
Na–N(1)–C(1)	103.2(2)	Na–N(1)–C(8)	112.1(2)
C(1)–N(1)–C(8)	123.4(3)	N(1)–C(1)–C(2)	122.2(3)
C(1)–C(2)–C(3)	123.1(3)	C(1)–C(2)–C(7)	120.3(3)
C(3)–C(2)–C(7)	116.6(3)	C(2)–C(3)–C(4)	120.9(3)
C(3)–C(4)–C(5)	120.9(4)	C(4)–C(5)–C(6)	118.7(4)
C(5)–C(6)–C(7)	121.2(4)	C(2)–C(7)–C(6)	121.7(3)
N(1)–C(8)–C(9)	122.5(3)	C(8)–C(9)–C(10)	123.9(3)
C(8)–C(9)–C(14)	120.0(3)	C(10)–C(9)–C(14)	115.9(3)
C(9)–C(10)–C(11)	121.7(3)	C(10)–C(11)–C(12)	121.0(3)
C(11)–C(12)–C(13)	118.1(4)	C(12)–C(13)–C(14)	122.1(4)
C(9)–C(14)–C(13)	121.1(3)	Na–N(2)–C(15)	112.9(2)
Na–N(2)–C(16)	113.2(2)	C(15)–N(2)–C(16)	106.8(3)
Na–N(2)–C(17)	103.4(2)	C(15)–N(2)–C(17)	109.5(3)
C(16)–N(2)–C(17)	111.0(3)	Na–N(3)–C(18)	107.4(2)
Na–N(3)–C(19)	111.6(2)	C(18)–N(3)–C(19)	109.3(3)
Na–N(3)–C(20)	106.9(2)	C(18)–N(3)–C(20)	110.8(2)
C(19)–N(3)–C(20)	110.8(3)	Na–N(4)–C(21)	105.5(2)
Na–N(4)–C(22)	107.0(2)	C(21)–N(4)–C(22)	111.2(3)
Na–N(4)–C(23)	114.7(2)	C(21)–N(4)–C(23)	108.2(3)
C(22)–N(4)–C(23)	110.2(3)	N(2)–C(17)–C(18)	114.3(2)
N(3)–C(18)–C(17)	113.7(3)	N(3)–C(20)–C(21)	113.5(2)
N(4)–C(21)–C(20)	114.6(3)		

longer (range 2.40–2.46 Å) than the N(1)–Na bond in the monomeric structure of **1**.

PMDETA chelation means that the sodium cation in **1** is tetracoordinated by nitrogen atoms (see Fig. 2). Inspection of the N–Na–N bond angles (range 74.7(1)–138.8(1)°) reveals that the metal has an extremely distorted tetrahedral environment. All three Lewis base–Lewis acid attachments (lengths 2.455(3), 2.497(3) and 2.529(3) Å) are decidedly longer than the anionic N–Na bond discussed above. Here, the bite of PMDETA makes a deeper impression on the metal than in the structurally-characterised dimer $(PhNa \cdot PMDETA)_2$ (corresponding lengths being 2.609(3), 2.646(3) and 2.712(3) Å) where association inhibits the close attachment of the base [12]. Similar pentacoordination of the sodium cations in the phenylmagnesate complex $(PMDETA \cdot Na)(Ph)_2Mg(Ph)_2(PMDETA \cdot Na)$ [13] also gives rise to longer (PMDETA)N–Na interatomic distances (range 2.533(11)–2.627(9) Å). An assortment of lithium compounds complexed by PMDETA have also been investigated by X-ray diffraction. Monomeric [Ph(naphthyl)NLi · PMDETA] provides a good example for comparison with **1** since its single metal centre is similarly surrounded by four nitrogen atoms [14]. Each of its (PMDETA)N–Li bond distances (2.18(1), 2.21(1) and 2.22(1) Å) is noticeably shorter than the (PMDETA)N–Na bonds in **1**; this reflects the smaller radius of lithium than of sodium more than it reflects any PMDETA preference for chelating to the smaller alkali metal. Bidentate TMEDA, $Me_2NCH_2CH_2NMe_2$, is another nitrogen-donor known to complex strongly to both lithium and sodium compounds [15]; invariably it forms a five-membered ring with the metal atoms.

The metal cation in **1** is four coordinate in respect of nitrogen atoms. However, a case can be argued that the coordination number is actually higher if the short contacts between the sodium cation and one *ortho* C–H unit of each phenyl ring are included. The close proximity of these atoms can be seen in the line-drawing of the molecular structure shown in Fig. 3. Hydrogen positions were not independently refined, but if normal (aryl)C–H geometries are assumed the H(3) · · · Na and H(10) · · · Na distances can be estimated to be 2.78 and 2.68 Å, respectively. More accurately determined are the corresponding C(3) · · · Na and C(10) · · · Na distances, which are found to be 3.133(4) and 3.166(4) Å, respectively, on refinement

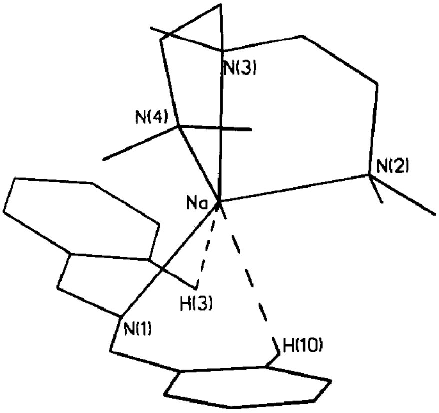


Fig. 3. Short (*ortho*-phenyl)C–H · · · Na contacts in the molecular structure (only the relevant hydrogen atoms are shown).

($R = 0.041$). Another contact ion-pair arrangement $Ph_3CNa \cdot TMEDA$ displays even shorter (phenyl)C ··· Na contacts (range of lengths 2.88–3.09 Å) [16]. Interestingly though, unlike **1** this complex also exhibits a short distance (2.96 Å) between sodium and a (phenyl) carbon atom of a neighbouring carbanion. The lack of any such intermolecular contacts in **1** may be due to the greater denticity (3 for PMDETA compared with 2 for TMEDA) of the Lewis base attached to its metal centre. In turning again to the short C ··· Na distances observed in **1** we must stress that when compared to carbon–sodium bonds in general these contacts appear to be too long to be of major significance for the polar bonding in its solid-state structure. For example, in the simplest sodium organometallic, the methylsodium tetramer $(MeNa)_4$, the C–Na intramolecular bond distances are considerably shorter, viz. 2.58 and 2.64 Å, and even the C–Na intermolecular bonds between tetramers are only 2.76 Å long [17]. Therefore, the core-bonding in **1** could be described as wholly nitrogen–sodium with the short C(H) ··· Na contacts merely an artefact of the rigid stereochemistry of the organonitrogen–sodium(PMDETA) attachment. However, without precise hydrogen positions the alternative view that these contacts constitute actual agostic three-centred C(H) ··· Na interactions cannot be dismissed.

Though **1** contains highly polar nitrogen–sodium bonds, it still dissolves readily in aromatic solvents such as benzene or toluene. This property which is not common for sodium organometallics is understandable in this case in view of the position of the metal cation in the molecular structure, where it is at the centre of a distorted tetrahedron comprising organic ligands. Cryoscopic relative molecular mass (CRMM) measurements intimate that $\{[PhC(H)NC(H)Ph]Na \cdot PMDETA\}_n$ retains its monomeric nature in this medium (benzene solution) at a concentration of 0.014 *M*, with a CRMM of 395 ± 20, corresponding to a state of association, *n*, of 1.01 ± 0.05. Furthermore, dynamic NMR spectroscopic studies in tetrahydrofuran-d_8 solution provide compelling evidence that the phenyl rings of the $[PhC(H)NC(H)Ph]^-$ anion moiety are locked in a rigid conformation at low temperature (at ca. −50 °C). The clamped position, placing one *ortho* C–H unit of each ring near to the metal centre, appears to correspond to the solid-state structure described above. This structural information can be deduced from the series of ^1H NMR spectra ((**a**)–(**d**)) shown in Fig. 4 (omitted from which are the three distinct signals of the complexed PMDETA molecule, which appear outside the chemical shift range displayed). The benzylic PhC*H* protons are equivalent, since only one signal is observed for them at all temperatures examined (moving from 6.79 ppm at 25 °C to 6.64 ppm at −50 °C); this signal shows an expected NOE enhancement (ca. 5%) on irradiation of the resonance of the adjacent *ortho* (Ph) hydrogens. At 25 °C both phenyl rings are also equivalent, as seen from spectrum (**a**), which shows a broad *ortho* H signal at 7.04 ppm, a multiplet *meta* H signal centred at 6.95 ppm and a triplet *para* H signal centred at 6.34 ppm. However, the spectrum at −50 °C, (**d**), reveals that both the *ortho*- and the *meta*-H signals separate into two independent sets; the former lie well apart (the doublets located at 7.52 and 6.47 ppm, respectively), while the latter are much closer together (the triplets at 6.88 and 6.81 ppm, respectively). Each phenyl ring therefore displays the same two distinct *ortho*-H and the same two distinct *meta*-H environments, a point reinforced by the observation that there is still only one *para*-H signal (the triplet at 6.20 ppm) at this lower temperature, confirming that the phenyl rings remain equivalent.

Coalescence occurs for the *ortho*-H's at −7 °C (spectrum (**b**)), and for the

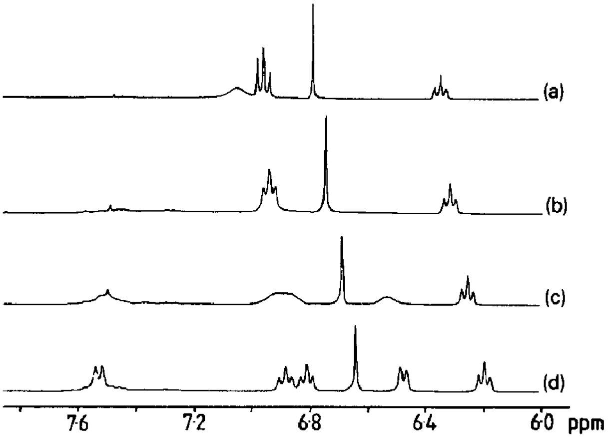


Fig. 4. The aromatic region of the variable-temperature ^{1}H NMR spectra of **1** recorded in tetrahydrofuran-d_8 solution: (**a**) 25 °C; (**b**) -7 °C, coalescence of *ortho*-hydrogen signals; (**c**) -30 °C, coalescence of *meta*-hydrogen signals; (**d**) -50 °C.

meta-H's at -30 °C (spectrum (c)). From these coalescence temperatures we have estimated the rate constants (K_c) for the mutual exchange of the two *ortho*-H's and of the two *meta*-H's by using the approximate eq. 1:

$$K_c = \frac{\pi}{2}\Delta\nu^2 + 6J^2 \tag{1}$$

This equation has been previously shown to afford reliable estimates of free energies of activation ($\Delta G^\ddagger$) for spin-coupled nuclei provided that the chemical shift differences exceed the coupling constants [18]. In this case, the $\Delta\nu$ values meet this criterion, being 379.0 and 25.8 Hz for the *ortho*- and *meta*-H signals, respectively, whereas J has a mean value of only 7.8 Hz. The rate constants are thus calculated to be 843 s^{-1} for the former and 71 s^{-1} for the latter, and correspond to a $\Delta G^\ddagger$ of 12.8 kcal mol^{-1} in each case. Here, $\Delta G^\ddagger$ is a measure of the energy barrier to rotation about the C(*ipso*)–C(benzylic) bonds (labelled C(1)–C(2) and C(8)–C(9) in the view of the crystal structure shown in Fig. 1) which can be attributed to the partial multiple bonding depicted in Scheme 1. The effect of this restricted rotation is to leave the $[PhC(H)NC(H)Ph]^-$ symmetrical anion in a fixed conformation at low temperature. Evidence that this static structure mimics the crystal structure comes from the exceptionally large chemical shift difference (1.05 ppm) observed for the twin *ortho*-H doublets. Perturbation of the phenyl groups, and their *ortho*-H sites in particular, on such a scale implies that the positively-charged metal centre is closely involved with the aromatic rings. Specifically this involvement is with the *ortho*-H atoms, rather than with *meta*-H atoms as the latter's two types present exhibit much more similar chemical shifts (difference only 0.07 ppm). The solid-state arrangement discussed above fits this description well in having *ortho*-H sites, *endo* and *exo* from the metal centre, in addition to two distinct *meta*-H sites far enough away from the metal centre to be barely affected by it. Therefore the conclusion drawn must be that **1** remains intact in solution, even to the extent of retaining the short (*ortho*-phenyl)C–H $\cdots$ Na contacts.

While this study has established the nature of **1** both in the solid state and in solution, the precise mechanism of the reaction leading to **1** remains to be determined. Full details of the preparation are given in the Experimental section; essentially it is simply a matter of adding PMDETA to a suspension of dibenzylamidosodium, $[(PhCH_2)_2NNa]_n$ in hexane. In the original communication arising from this work [3] we suggested that agostic (benzylic)$CH_2 \cdots Na$ interactions within the precursor compound are so pronounced that two benzylic C–H bonds are actually cleaved on introduction of the Lewis base, giving **1** and H_2 (though no sign of gas evolution was observed). To date we have been unable to obtain any conclusive structural evidence to support this contention owing to the limited solubility of $[(PhCH_2)_2NNa]_n$ and to our lack of success at growing single crystals suitable for X-ray diffraction study. Further attempts are underway.

Experimental

Synthesis of {*[PhC(H)NC(H)Ph]Na · PMDETA*} *(1)*

Dibenzylamine (1.89 g, 9.6 mmol) was added to a stirred suspension of phenylsodium (0.96 g, 9.6 mmol) in hexane (8 ml) in a Schlenk-tube under dry argon. After a few minutes a red precipitate of dibenzylamidosodium $[(PhCH_2)_2NNa]_n$ [3] was formed. Toluene (10 ml) followed by PMDETA (2.00 ml, 9.6 mmol) were then introduced, the red precipitate then redissolved to give a much darker red solution. Stirring was immediately ceased at this stage and the solution was allowed to stand overnight. The red-green dichroic needles obtained were filtered off, washed with chilled toluene, and shown to be of **1**. Yield of first batch (without recourse to fridge-cooling), 2.21 g, 59%; m.p. 167 °C. Anal. Found: C, 71.1; H, 8.6; N, 13.9; Na, 5.9. $C_{23}H_{35}N_4Na$ calcd.: C, 70.8; H, 9.0; N, 14.4; Na, 5.9%. The needles rapidly decompose on exposure to air or moisture.

IR Spectrum. 3040m, 3020m, 2925s (broad), 2855s, 2778m, 1580s, 1560mw, 1510w, 1498w, 1480m, 1466s, 1456s, 1450s, 1405s (broad), 1388s, 1378s, 1364s, 1314s, 1310s, 1296m, 1294m, 1285m, 1280mw, 1268m, 1261m, 1258m, 1251m, 1249m, 1242m, 1238w, 1232vw, 1216m, 1209s, 1204s, 1200m, 1185mw, 1180w, 1165m, 1158vs, 1150ms, 1145m, 1110mw, 1067mw, 1060m, 1035mw, 1018m, 978s, 960mw, 950m, 940mw, 930m, 890w, 878mw, 869m, 829m, 824w, 802m, 785m, 770w, 752w, 746m, 735ms, 728w, 722w, 711mw, 685s, 662w, 638m, 610m (cm^{-1}; Nujol mull). The spectrum was recorded on a Perkin–Elmer 457 grating spectrometer.

NMR spectra. ^1H (360.13 MHz, 25 °C): PMDETA ($(Me_2N)_2$, 12H, s, δ 2.31 ppm; *Me*N, 3H, s, δ 2.24 ppm; $(CH_2CH_2)_2$, 8H, d of m, centred δ 2.45 and 2.53 ppm), Ph (*o*, 4H, br s, δ 7.04 ppm; *m*, 4H, m, centred δ 6.95 ppm; *p*, 2H, m, centred δ 6.34 ppm), and PhC*H* (2H, s, δ 6.79 ppm). (−50 °C) PMDETA ($(Me_2N)_2$, 12H, s, δ 2.27 ppm; *Me*N, 3H, s, δ 2.25 ppm; $(CH_2CH_2)_2$, 8H, d of m, centred δ 2.42 and 2.47 ppm), Ph (*o*, 2H, d, centred δ 6.47 ppm, and *o′*, 2H, d, centred δ 7.52 ppm; *m*, 2H, t, centred δ 6.88 ppm, and *m′*, 2H, t, centred δ 6.81 ppm; *p*, 2H, t, centred δ 6.20 ppm), and PhC*H* (2H, s, δ 6.64 ppm). ^{13}C (90.6 MHz, 25 °C): PMDETA ($(Me_2N)_2$, δ 44.76 ppm; (*Me*N), δ 41.94 ppm; $(CH_2CH_2)_2$, 55.48/57.42 ppm), Ph (*p*, δ 110.06 ppm; *o*, δ 117.50 ppm; *m*, δ 127.91 ppm; *ipso*, δ 144.27 ppm), and Ph*C*H (δ 114.35 ppm). ^{23}Na (95.3 MHz, 25 °C): broad resonance (half-height line-width, ca. 430 Hz), δ −1.82 ppm. All spectra were recorded on a Bruker WH360 instrument. ^1H and ^{13}C shifts are given relative to $SiMe_4$; the ^{23}Na shift is given relative to NaCl in D_2O. The solvent employed was tetrahydrofuran-d_8

and all solutions were prepared in a glove-box and tubes subsequently sealed under argon.

Cryoscopic molecular mass measurements were performed in the manner described by Reed et al. [19].

X-ray crystallographic study

Crystal data for **1**: $C_{23}H_{35}N_4Na$, $M = 390.6$, monoclinic, $P2_1/n$, a 10.814(1), b 15.803(1), c 14.040(1) Å, β 95.63(1)°, V 2387.8 Å^3, $Z = 4$, $D_c = 1.086$ g cm^{-3}, $F(000) = 848$, $\lambda = 1.54184$ Å (Cu-K_α radiation), μ 0.63 mm^{-1}. Cell parameters were refined from 2θ values (34–45°) of 32 reflections centred at $\pm\omega$ at room temperature on a Stoe–Siemens diffractometer. Data were collected by an on-line profile-fitting procedure [20] with ω/θ scans; $2\theta_{max}$ 110°. No corrections were required for standard reflection intensity decay or absorption. 5548 measured data yielded 2987 unique reflections, of which 1784 had $F > 4\sigma_c(F)$ (σ_c based on counting statistics only); $R_{int} = 0.025$.

The structure was solved by direct methods and refined by blocked-cascade refinement [21] on F, with a weighting scheme $\omega^{-1} = \sigma^2(F) = \sigma_c^2(F) + 1 + 13G - 8G^2 - 2H + 2H^2 - 25GH$ $(G = F_0/F_{max},\ H = \sin\theta/\sin\theta_{max})$ [22]. Anisotropic

Table 2

Atomic coordinates (×10^4) for **1**

Atom	x	y	z
Na	1089(1)	2884(1)	6033(1)
N(1)	458(2)	2817(1)	4360(1)
C(1)	50(3)	2028(2)	4238(2)
C(2)	−878(3)	1682(2)	4783(2)
C(3)	−1565(3)	2174(2)	5380(2)
C(4)	−2436(3)	1807(2)	5908(3)
C(5)	−2671(4)	950(3)	5852(3)
C(6)	−2017(4)	464(3)	5259(3)
C(7)	−1153(3)	814(2)	4736(2)
C(8)	1295(3)	3163(2)	3842(2)
C(9)	1847(3)	3964(2)	4065(2)
C(10)	1475(3)	4505(2)	4770(2)
C(11)	2101(3)	5245(2)	5012(2)
C(12)	3122(3)	5482(2)	4560(2)
C(13)	3478(4)	4971(3)	3852(3)
C(14)	2867(3)	4238(2)	3593(2)
N(2)	392(2)	3682(2)	7448(2)
N(3)	1471(2)	1919(1)	7400(1)
N(4)	3349(2)	2538(2)	6120(2)
C(15)	798(5)	4564(2)	7483(3)
C(16)	−953(3)	3689(3)	7469(3)
C(17)	993(3)	3229(2)	8268(2)
C(18)	874(3)	2287(2)	8200(2)
C(19)	950(3)	1079(2)	7181(3)
C(20)	2827(3)	1871(2)	7630(2)
C(21)	3523(3)	1815(2)	6774(2)
C(22)	4016(4)	3272(3)	6507(3)
C(23)	3791(4)	2297(3)	5207(2)

thermal parameters were refined for non-hydrogen atoms; H atoms were constrained to give C–H 0.96 Å, H–C–H 109.5°, aromatic H on ring angle external bisectors, $U(\mathrm{H}) = 1.2U_{\mathrm{eq}}$ (C); extinction parameter $x = 3.5(2) \times 10^{-6}$, $F_c' = F_c/(1 + xF_c^2/\sin 2\theta)^{1/4}$. Final $R = 0.041$, $\omega R = (\Sigma\omega\,\Delta^2/\Sigma\omega F_0^2)^{1/2} = 0.036$ for 269 parameters, $S = 1.06$, largest shift/esd = 0.09, all features in a final difference synthesis were within ± 0.15 eÅ^{-3}.

Table 2 gives the refined atomic coordinates. Lists of thermal parameters and hydrogen atom coordinates have been deposited at the Cambridge Crystallographic Data Centre.

Acknowledgements

We thank the SERC (P.C.A., R.E.M.) and the Research Corporation Trust (R.E.M.) for financial support, the SERC for the use of high-field NMR spectroscopic facilities, the Royal Society for the award of a 1983 Research Fellowship (R.E.M.), and Drs. R. Snaith and I.H. Sadler for helpful discussions.

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