

The solid state structures  
of *ortho*-lithio- $\beta$ -(*N,N*-dimethylamino)ethoxybenzene  
and the corresponding sodium compound:  
a new type of organolithium tetramer and a first example  
of an organosodium hexamer

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Abstract

The crystal structures of *ortho*-lithio- $\beta$ -(*N,N*-dimethylamino)ethoxybenzene (**2**) and the corresponding sodium compound (**3**) are presented. **2** displays a new type of organolithium tetramer and **3** is the first example of an organosodium hexamer in the solid state. In benzene and toluene **3** is trimeric.

Keywords: Sodium; Lithium; Crystal structure

1. Introduction

Whereas many structural data of organolithium compounds have been published [1], information about structures of heavier organoalkali compounds is scarce. Possible reasons are the slight solubility of the latter in commonly used organic solvents. Furthermore, they are generally more reactive towards these solvents than their lithium analogues. In most of the few published structures of organosodium compounds the metal is bound to a delocalized carbanion [2]. Recently we succeeded in isolating a totally intramolecularly coordinated organosodium compound and determined its structure [3]: the first example of a trimeric organosodium compound. The readily accessible  $\beta$ -(*N,N*-dimethylamino)ethoxybenzene [4]. (**1**) seemed an interesting substrate for continuing our structural studies on polar organometallic compounds.

2. Results

It is known [5] that **1** can be easily *ortho*-lithiated with high efficiency. As we wanted to avoid any coordination of an organic solvent, we added *n*-butyllithium (BuLi) to a solution of **1** in hexane at room temperature. Immediately, a precipitate (presumably a BuLi·**1**-complex) was formed which dissolved quickly. Unfortunately, the extreme reactivity of this complex did not allow detailed characterization, although it could be isolated as a dry microcrystalline powder [6]. It underwent a rapid transformation into 2- $\beta$ -(*N,N*-dimethylamino)ethoxyphenyllithium (**2**) which could be isolated and subsequently converted into 2- $\beta$ -[*N,N*-dimethyl-

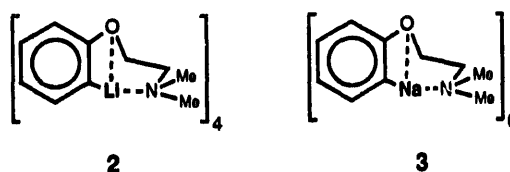
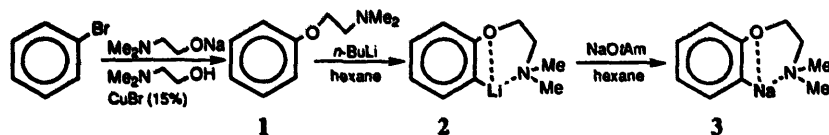


Fig. 0. Compounds **2** and **3**.

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Scheme 1. Synthesis of 1, 2 and 3 starting from bromobenzene.

aminoethoxyphenylsodium (3) (Fig. 0) by treatment with one equivalent of sodium-*tert*-amylate Scheme 1).

2 is a tetramer in the solid state and possesses pseudo  $S_4$ -symmetry, see Fig. 1.

The core of the structure of crystalline 2 deserves special attention. At first glance the lithium atoms seem to form an almost ideal tetrahedron. However, the metallated carbons (*Cipso*) do *not* bind in a four-center two-electron ( $4c-2e$ ) way to each  $Li_3$  face of the  $Li_4$  tetrahedron, as is the case in the 'classical' representation of organolithium tetramers [1] (Fig. 2(a)). Owing to the sterical demands from the OCCN-arm, the carbanions are forced to bend towards the edges of the  $Li_4$  tetrahedron (Fig. 2(b)). In 2 *Cipso* is bound in a three-center two-electron ( $3c-2e$ ) fashion, which is usual for dimeric organolithium compounds (see Fig. 2(c)). As a consequence, two of the total of six edges of the

$Li_4$  tetrahedron remain unoccupied (dashed lines in Fig. 2(c)).

The organolithium aggregate 2 is of a new type: a distorted cube which is opened on two opposite sides giving rise to a distorted eight-membered ring. This type is common for organocopper compounds [7]. The *Cipso*-Li bond lengths vary from 2.198(4) Å to 2.263(3) Å (averaged 2.231(3) Å), which are normal values. The O-Li and N-Li distances are averaged 2.016(3) Å and 2.234(3) Å respectively. The mean bite angle (angle O-Li-N) of the OCCN-arm is 77.87(11)°. The geometry around the lithium atoms is distorted tetrahedral where two *Cipso* atoms, one oxygen, and lithium almost lie in-plane. 2 dissolves well in aromatic solvents such as benzene or toluene. Table 2 gives the chemical shifts for both the  $^1H$  and  $^{13}C$  spectra.

In order to confirm the type of bonding of *Cipso* to

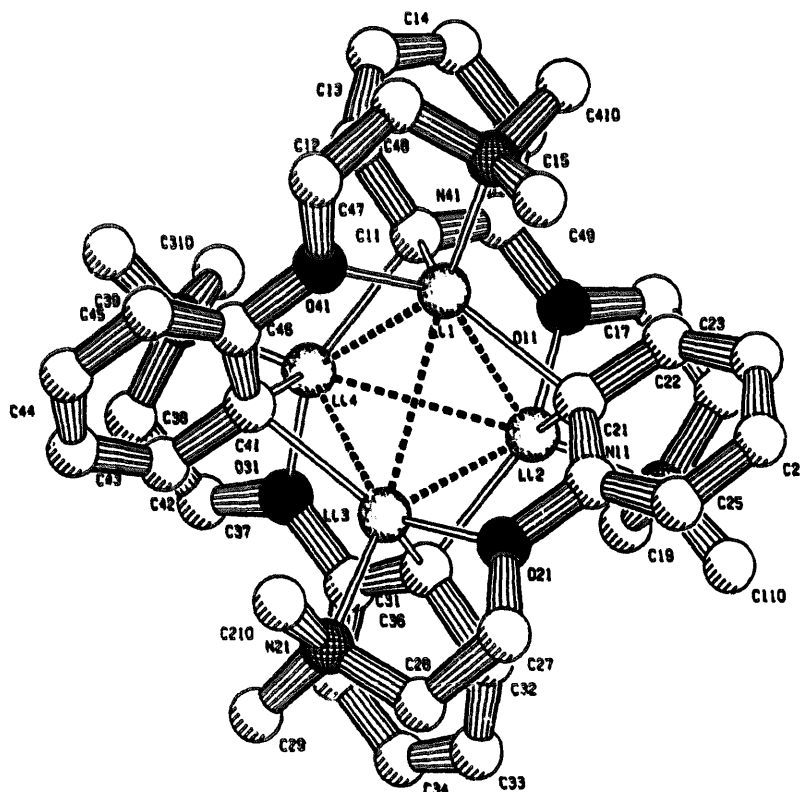


Fig. 1. Crystal structure of 2. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (deg): O11-Li2, 2.010(3); O21-Li3, 2.016(3); O31-Li4, 2.014(3); O41-Li1, 2.024(3); N11-Li2, 2.234(3); N21-Li3, 2.215(4); N31-Li4, 2.256(3); N41-Li1, 2.230(4); C21-Li2, 2.217(4); C31-Li2, 2.246(3); C31-Li3, 2.198(4); C41-Li3, 2.263(3); O11-Li2-N11, 77.70(11); O21-Li3-N21, 78.10(12); O31-Li4-N31, 77.91(11); O41-Li1-N41, 77.76(12). Atom coordinates are listed in Table 1.

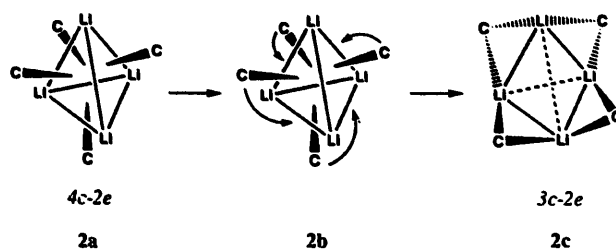


Fig. 2. Transformation of a 4c–2e organolithium tetramer into a 3c–2e organolithium tetramer. The  $\text{Li}_4$  core remains intact and the carbanions position along the edges leaving two edges unoccupied (dashed lines in 2c).

the  $\text{Li}_4$  core a sample of the  $^6\text{Li}$  isotope of **2** was prepared. At  $-10^\circ\text{C}$  the *Cipso* signal becomes visible as a well-shaped 1/2/3/2/1-quintet with  $^1J(^{13}\text{C}, ^6\text{Li}) = 6.8$  Hz. This coupling constant and quintet is indicative of a carbon coupling with two  $^6\text{Li}$  nuclei, which proves that the type of bonding of *Cipso* is indeed 3c–2e. The chemical shift of *Cipso* is constant within 0.2 ppm over the temperature range from  $-80$  to  $+40^\circ\text{C}$ , which means that only one aggregate is present. Cryoscopic measurements in benzene reveal a tetrameric aggregate, with a degree of association of  $3.91 \pm 0.18$  (concentrations varying from 72 to 153 mmolal). As can be seen in the X-ray structure, the ethylene protons ( $-\text{CH}_2\text{CH}_2-$ ) of the OCCN-arm are

not equivalent, and in the  $^1\text{H}$ -spectrum four distinct signals are observed. At  $60^\circ\text{C}$  the OCCN-arm starts to coalesce. The coordination of the OCCN-arm becomes looser, which results in one resonance for each methylene ( $-\text{CH}_2-$ ) group.

**3** crystallizes from benzene as a hexameric aggregate together with four benzene molecules. Although hexamers are common in organolithium chemistry, hitherto no hexameric organosodium compound was isolated in the crystalline state. Fig. 3 depicts the crystal structure of **3**.

The hexamer consists of two stacked trimers and possesses a pseudo threefold inversion ( $C_{3i}$ ) axis perpendicular to the six membered C–Na ring. The  $\text{Na}_6$  core forms a distorted octahedron and the metallated

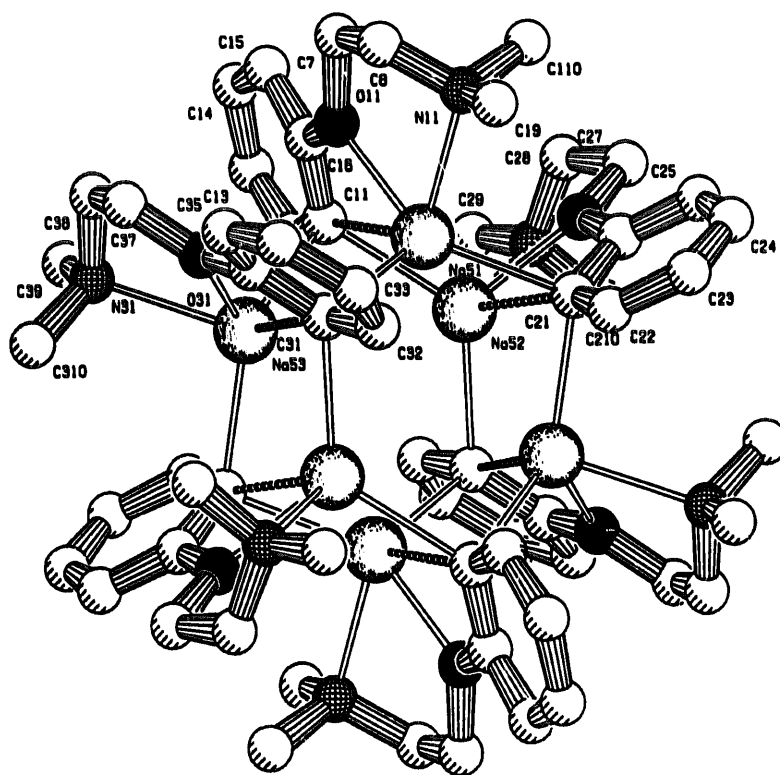


Fig. 3. Crystal structure of **3**. Hydrogen atoms and benzene solvates are omitted for clarity. Selected bond lengths ( $\text{\AA}$ ) and bond angles (deg): Na1–O11, 2.330(4); Na2–O21a, 2.335(4); Na3–O31, 2.312(4); Na1–N11, 2.540(5); Na2–N21a, 2.541(5); Na3–N31, 2.541(5); Na1–C21a, 2.523(5); Na1–C31, 2.566(5); Na2–C11, 2.579(5); Na2–C31a, 2.576(5); Na3–C11, 2.555(5); Na3–C21, 2.525(5); O11–Na1–N11, 68.66(14); O21a–Na2–N21a, 68.12; O31–Na3–N31, 68.11(13). Atom coordinates are listed in Table 3.

carbons bind in a 4c–2e way to the smaller planes of the Na<sub>6</sub> octahedron. The same type of bonding is found in the structure of hexameric [BuLi]<sub>6</sub> [8]. Sodium is five coordinated in a distorted trigonal bipyramidal way. The C<sub>ipso</sub>–Na bond lengths are 2.523(5)–2.579(5) Å (average 2.554(5) Å) and the O–Na and N–Na distances are averaged 2.326(4) and 2.541(5) Å respectively. The bite angle of the OCCN-arm is 68.30(14)° which is almost 10° smaller than 2. 3 is soluble in aromatic solvents like benzene or toluene. Table 1 gives the chemical shifts for both <sup>1</sup>H and <sup>13</sup>C spectra. At room temperature the metallated carbon is visible at 169.9 ppm. However, the large quadrupole moment and the spin of sodium (*I* = 3/2) inhibits the observation of C–Na couplings and, therefore, no information can be obtained about the degree of association. The chemical shift of C<sub>ipso</sub> lies in the region where two metals are expected to be bound to one carbon [9]. It is constant within 0.1 ppm over the temperature range from –60 to +25°C, which indicates that only one aggregate is present. To reveal the degree of aggregation, cryoscopic measurements in benzene were performed and a degree of association of 2.88 ± 0.17 (concentrations varying from 54 to 97 mmolal) was found which implies that 3 is trimeric in solutions like benzene or toluene. Most likely, trimeric 3 has the same propeller-like structure in solution as is found in the case of 2,6-bis(dimethylamino)phenyllithium [10] or 2,6-bis[(dimethylamino)methyl]phenylsodium [3] in the solid state. Coalescence of the OCCN-arm is already visible at –5°C. Despite the difference in degree of association, the metallated carbons of both 2 and 3 have the same type of bonding to the metals in solution (3c–2e). As a consequence of the results from Ref. [9] we can justify that the down shift is proportional with increasing ionicity of the carbon–metal bond. This means that from the chemical (down)shifts, relative to the free ligand in the same solvent, the relative ionicities of the carbon–lithium and carbon–sodium bond can be calculated. Assuming 80% ionicity for the C–Li bond [11] yields 91% for the C–Na bond.

### 3. Experimental

All syntheses were carried out under nitrogen using freshly distilled and dried solvents.

Synthesis of 1: sodium (9.0 g, 0.39 mol) was added to 55.0 g of *N,N*-dimethylethanolamine (0.62 mol) and the mixture was allowed to reflux. After dissolution of the sodium, 40.7 g of bromobenzene (0.26 mol) was added at 110°C and subsequently 5.7 g of copper(I) bromide (40 mmol). After the CuBr addition the temperature rose to 150°C and the reaction was complete within 1 h. The reaction mixture was cooled to room temperature and a solution of 15 g of potassium cyanide in 150 ml of water was added. The mixture was ex-

Table 1

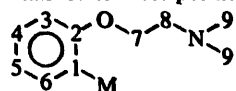
Final coordinates and equivalent isotropic thermal parameters of the non-hydrogen atoms of crystalline 2 (cf. Fig. 1)

Atom	x	y	z	U <sub>q</sub> (Å <sup>2</sup> )
Li(1)	0.2486(3)	0.7648(2)	0.1587(2)	0.0280(8)
Li(2)	0.3863(3)	0.8709(2)	0.2528(2)	0.0278(8)
Li(3)	0.2055(3)	0.7371(2)	0.3411(2)	0.0281(8)
Li(4)	0.4607(3)	0.6221(2)	0.2388(2)	0.0277(8)
O(11)	0.52263(12)	0.87757(9)	0.14797(7)	0.0317(3)
O(21)	0.05072(11)	0.87593(9)	0.34631(7)	0.0312(3)
O(31)	0.54675(12)	0.61235(9)	0.33826(7)	0.0341(3)
O(41)	0.16658(12)	0.63395(9)	0.16084(7)	0.0313(4)
N(11)	0.4734(2)	1.01084(11)	0.27102(9)	0.0347(5)
N(21)	0.05699(14)	0.70463(12)	0.45170(8)	0.0328(4)
N(31)	0.63505(14)	0.46791(11)	0.21857(8)	0.0321(4)
N(41)	0.14143(14)	0.80219(11)	0.05202(8)	0.0288(4)
C(11)	0.48006(15)	0.71419(12)	0.11691(9)	0.0243(4)
C(12)	0.5078(2)	0.63494(12)	0.05836(10)	0.0284(5)
C(13)	0.5995(2)	0.63407(14)	–0.01601(10)	0.0336(5)
C(14)	0.6690(2)	0.71577(15)	–0.03523(11)	0.0392(6)
C(15)	0.6462(2)	0.79827(14)	0.01883(10)	0.0377(5)
C(16)	0.5530(2)	0.79494(12)	0.09199(9)	0.0265(5)
C(17)	0.5836(2)	0.96885(14)	0.12814(11)	0.0378(6)
C(18)	0.5033(2)	1.05595(14)	0.18787(10)	0.0366(6)
C(19)	0.6007(2)	0.9697(2)	0.30420(14)	0.0592(9)
C(21)	0.1743(2)	0.92718(12)	0.22202(9)	0.0255(4)
C(22)	0.1832(2)	1.01099(13)	0.16220(10)	0.0293(5)
C(23)	0.0872(2)	1.11265(14)	0.16297(11)	0.0359(6)
C(24)	–0.0259(2)	1.13404(14)	0.22591(12)	0.0402(6)
C(25)	–0.0422(2)	1.05628(14)	0.28815(11)	0.0359(5)
C(26)	0.0579(2)	0.95687(12)	0.28445(9)	0.0263(4)
C(27)	–0.0588(2)	0.89532(15)	0.41569(10)	0.0376(5)
C(28)	–0.0104(2)	0.81415(15)	0.48169(10)	0.0380(5)
C(29)	0.1240(2)	0.6368(2)	0.51459(11)	0.0451(6)
C(31)	0.3865(2)	0.77889(13)	0.37330(9)	0.0265(5)
C(32)	0.3334(2)	0.85986(14)	0.43141(10)	0.0323(5)
C(33)	0.3834(2)	0.8587(2)	0.50291(11)	0.0446(6)
C(34)	0.4920(2)	0.7739(2)	0.51880(12)	0.0531(7)
C(35)	0.5505(2)	0.6904(2)	0.46470(11)	0.0449(6)
C(36)	0.4953(2)	0.69544(13)	0.39464(9)	0.0298(5)
C(37)	0.6544(2)	0.5191(2)	0.35398(12)	0.0452(6)
C(38)	0.6506(2)	0.42912(14)	0.30164(11)	0.0401(6)
C(39)	0.6022(2)	0.38276(14)	0.17787(11)	0.0415(6)
C(41)	0.2592(2)	0.57606(13)	0.27823(9)	0.0266(4)
C(42)	0.2826(2)	0.49180(13)	0.33748(10)	0.0317(5)
C(43)	0.2369(2)	0.39566(14)	0.34217(11)	0.0367(5)
C(44)	0.1608(2)	0.38129(14)	0.28624(11)	0.0387(6)
C(45)	0.1333(2)	0.46077(13)	0.22582(10)	0.0325(5)
C(46)	0.1849(2)	0.55332(12)	0.22294(9)	0.0263(5)
C(47)	0.0986(2)	0.62079(14)	0.09710(10)	0.0314(5)
C(48)	0.1464(2)	0.69315(13)	0.02682(10)	0.0320(5)
C(49)	–0.0032(2)	0.86476(15)	0.07761(12)	0.0400(6)
C(110)	0.3757(3)	1.0981(2)	0.32113(13)	0.0578(9)
C(210)	–0.0443(2)	0.6539(2)	0.42828(12)	0.0469(7)
C(310)	0.7622(2)	0.4953(2)	0.17274(13)	0.0483(7)
C(410)	0.2136(2)	0.8600(2)	–0.01578(10)	0.0403(6)

tracted three times with 50 ml of pentane and the organic layer was dried over K<sub>2</sub>CO<sub>3</sub> and subsequently concentrated *in vacuo*. Distillation at water vapor pressure gave 1 as a colorless oil, b.p. 105°C (15 mm Hg), yield: 35.2 g (82%). NMR data: <sup>1</sup>H (200 MHz, CDCl<sub>3</sub>, 25°C): δ = 2.32 (s, 6H, N(CH<sub>3</sub>)<sub>2</sub>), 2.70 (t, 2H, <sup>3</sup>J(HH) = 5.8 Hz, CH<sub>2</sub>–NMe<sub>2</sub>), 4.04 (t, 2H, <sup>3</sup>J(HH) = 5.8 Hz,

Table 2

NMR ( $^1\text{H}$  300 MHz,  $^{13}\text{C}$  75 MHz) data of **2** ( $M = \text{Li}$ ) and **3** ( $M = \text{Na}$ ) in  $[\text{D}_8]$  toluene at  $-10^\circ\text{C}$ . Numbers correspond to the positions or protons attached to those positions as depicted in the structural formula above the table



	1	2	3	4	5	6	7	8	9
<b>Proton</b>									
$\delta$ (ppm)			d, 6.56	dd, 7.24	dd, 7.02	d, 7.88	m, 3.72	m, 2.39	s, 1.47
$M = \text{Li}$							m, 3.45	m, 1.77	
$\delta$ (ppm)			d, 6.58	dd, 7.27	dd, 7.14	d, 8.07	s, broad	s, broad	s, 1.60
$M = \text{Na}$							3.47	2.05	
<b>Carbon</b>									
$\delta$ (ppm)									
$M = \text{Li}$	164.9	168.8	105.7	126.7	121.2	144.7	63.3	57.6	44.3
$\delta$ (ppm)									
$M = \text{Na}$	169.9	168.3	106.6	125.7	121.6	143.2	62.0	58.5	44.1

$\text{O}-\text{CH}_2-$ ), 6.93 (m, 3H, arom), 7.26 (dd, 2H, arom);  $^{13}\text{C}$  (50 MHz,  $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ):  $\delta = 45.9, 58.4, 65.9, 114.6, 120.7, 129.4, 158.7$ .

**Synthesis of 2:** to a stirred solution of 4.0 g of **1** (25 mmol) in 25 ml of hexane was added 16 ml of *n*-BuLi (25 mmol) at room temperature. Immediately, microcrystals of the assumed  $\text{BuLi} \cdot \mathbf{1}$  complex precipitated which soon redissolved. After 1 h a white suspension was formed. This was washed twice with pentane and subsequently dried *in vacuo*. Crystals suitable for X-ray diffraction were obtained by adding *n*-BuLi to a solution of **1** in hexane without stirring. After a few hours, colorless crystals precipitated. NMR data in  $[\text{D}_8]$  toluene,  $25^\circ\text{C}$ , see Table 2.

**Synthesis of 3:** to a stirred white suspension of 2.0 g of **2** (14 mmol) in 15 ml of hexane a solution of 1.8 g of sodium-*tert*-amylate ( $\text{NaOtAm}$ ) (16 mmol) in 15 ml of hexane was added at room temperature. The reaction mixture was stirred for 30 min, after which the mother layer was discarded and the precipitate was washed three times with pentane and subsequently dried *in vacuo*. Crystals suitable for X-ray diffraction were prepared by dissolving **3** in benzene under reflux. After a few hours, large colorless crystals of  $[\mathbf{3}]_6 \cdot [\text{C}_6\text{H}_6]_4$  precipitated. NMR data in  $[\text{D}_8]$  toluene,  $25^\circ\text{C}$ , see Table 2.

#### 4. X-ray analysis

Crystal data for **2**:  $\text{C}_{40}\text{H}_{56}\text{Li}_4\text{N}_4\text{O}_4$ ,  $M_r = 684.67$ , colorless, transparent ( $0.15 \times 0.25 \times 0.75$ ), triclinic, spacegroup  $P\bar{1}$  (no. 2),  $a = 10.532(5)$ ,  $b = 12.6329(10)$ ,  $c = 16.8091(13)$  Å,  $\alpha = 84.986(6)^\circ$ ,  $\beta = 78.254(5)^\circ$ ,  $\gamma = 75.007(6)^\circ$ ,  $V = 2017.6(2)$  Å<sup>3</sup>,  $Z = 2$ ,  $\rho_{\text{calcd}} = 1.127$  g cm<sup>-3</sup>,  $F(000) = 736$ ,  $\mu(\text{Mo K}\alpha) = 0.7$  cm<sup>-1</sup>, 9844 reflections measured, 9185 independent ( $1.2^\circ < \theta <$

Table 3

Final coordinates are equivalent isotropic thermal parameters of the non-hydrogen atoms of crystalline **3** (cf. Fig. 3)

Atom	x	y	z	$U_{\text{eq}}$ (Å <sup>2</sup> )
Na(1)	-0.09287(12)	-0.1161(2)	0.41237(7)	0.0407(6)
Na(2)	-0.17031(12)	0.05008(15)	0.49264(7)	0.0388(6)
Na(3)	0.02396(12)	0.1347(2)	0.42485(7)	0.0405(6)
O(11)	-0.1682(2)	-0.0041(3)	0.33570(13)	0.0501(12)
O(21)	0.2775(2)	0.1056(3)	0.5305(2)	0.0612(14)
O(31)	0.0589(2)	0.0420(3)	0.35275(13)	0.0482(12)
N(11)	-0.1843(3)	-0.2464(4)	0.3340(2)	0.0507(17)
N(21)	0.3323(3)	-0.1110(4)	0.5035(2)	0.0496(16)
N(31)	0.0530(3)	0.2823(3)	0.3568(2)	0.0461(17)
C(11)	-0.1546(3)	0.1391(4)	0.4030(2)	0.0389(17)
C(12)	-0.1805(3)	0.2538(4)	0.4129(2)	0.0449(17)
C(13)	-0.2364(4)	0.3308(5)	0.3750(3)	0.061(3)
C(14)	-0.2701(4)	0.2931(5)	0.3220(3)	0.063(2)
C(15)	-0.2483(4)	0.1807(5)	0.3081(2)	0.0565(19)
C(16)	-0.1929(3)	0.1098(4)	0.3482(2)	0.0407(17)
C(7)	-0.2125(4)	-0.0558(5)	0.2847(2)	0.053(2)
C(8)	-0.1769(4)	-0.1807(5)	0.2866(2)	0.052(2)
C(19)	-0.1399(4)	-0.3621(5)	0.3361(3)	0.079(3)
C(21)	0.1395(3)	0.2133(4)	0.5108(2)	0.0421(17)
C(22)	0.0990(4)	0.3260(5)	0.5051(2)	0.054(2)
C(23)	0.1493(5)	0.4311(5)	0.5075(2)	0.069(3)
C(24)	0.2421(5)	0.4269(5)	0.5162(2)	0.070(3)
C(25)	0.2894(4)	0.3188(5)	0.5235(2)	0.066(2)
C(26)	0.2355(4)	0.2174(4)	0.5211(2)	0.049(2)
C(27)	0.3742(4)	0.0929(5)	0.5363(3)	0.069(2)
C(28)	0.3955(4)	-0.0399(6)	0.5447(2)	0.074(2)
C(29)	0.3533(4)	-0.2348(5)	0.5125(3)	0.076(3)
C(31)	0.0784(3)	-0.1199(4)	0.4107(2)	0.0381(17)
C(32)	0.1037(3)	-0.2396(5)	0.4178(2)	0.0505(19)
C(33)	0.1347(4)	-0.3065(5)	0.3804(2)	0.060(2)
C(34)	0.1421(4)	-0.2548(5)	0.3339(2)	0.062(2)
C(35)	0.1177(3)	-0.1372(5)	0.3235(2)	0.0490(19)
C(36)	0.0863(3)	-0.0765(4)	0.3615(2)	0.0406(17)
C(37)	0.0611(3)	0.0998(4)	0.3043(2)	0.0464(19)
C(38)	0.0165(3)	0.2199(4)	0.3052(2)	0.0476(19)
C(39)	0.0015(4)	0.3931(4)	0.3548(2)	0.061(2)
C(110)	-0.2814(4)	-0.2603(6)	0.3339(2)	0.074(3)
C(210)	0.3371(4)	-0.0810(5)	0.4485(2)	0.072(3)
C(310)	0.1525(4)	0.3082(5)	0.3687(2)	0.059(2)

27.5°),  $\omega/2\theta$  scan,  $\Delta\omega = 0.50 + 0.35 \tan \theta^\circ$ ,  $T = 150$  K, Mo  $K\alpha$  radiation, graphite monochromator,  $\lambda = 0.71073$  Å, Enraf-Nonius CAD4-T diffractometer on rotating anode. Data were corrected for Lp and for a linear decay of 2% of the reference reflections ( $-2 - 1 - 6, -3 2 - 4, -1 - 6 - 2$ ) during 22 h of X-ray exposure time. Empirical absorption correction as implemented in PLATON (DIFABS, correction range 0.905–1.146). The structure was solved by automated direct methods (SHELXS86). Refinement on  $F^2$  was carried out by full-matrix least squares techniques (SHELXL93) and no observance criterion was applied during this refinement. Final  $R1 = 0.053$  for 6566 reflections with  $F_o > 4.0\sigma(F_o)$ ,  $wR2 = 0.1381$  for all 9185 reflections,  $w = 1/[\sigma^2(F_o^2) + (0.0672P)^2 + 0.2911P]$  with  $P = (\text{Max}(F_o^2, 0) + 2F_c^2)/3$ ,  $S = 1.059$  for 477 parameters. Mean and maximum shift over error 0.000 and 0.000. Maximum and minimum residual density 0.25 and  $-0.25 \text{ e } \text{Å}^{-3}$ . All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogens 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 other hydrogen atoms. Weights were refined in the final refinement cycles. After the final refinement, the structure contained one independent small void of  $12.9 \text{ Å}^3$  at 0.174, 0.278, 0.753. However, no residual density was found in that area (PLATONS/SQUEEZE).

Crystal data for 3:  $\text{C}_{60}\text{H}_{84}\text{Na}_6\text{N}_6\text{O}_6 \cdot 4\text{C}_6\text{H}_6$ ,  $M_r = 1435.75$ , colorless, transparent ( $0.7 \times 0.7 \times 0.4$ ), monoclinic, spacegroup  $P2_1/c$  (no. 14),  $a = 14.906(2)$ ,  $b = 11.3182(11)$ ,  $c = 25.604(3)$  Å,  $\beta = 107.065(10)^\circ$ ,  $V = 4129.5(8) \text{ Å}^3$ ,  $Z = 2$ ,  $\rho_{\text{calcd}} = 1.155 \text{ g cm}^{-3}$ ,  $F(000) = 1536$ ,  $\mu(\text{Mo } K\alpha) = 0.9 \text{ cm}^{-1}$ , 8404 reflections measured, 8084 independent ( $1.4^\circ < \theta < 26.4^\circ$ ),  $\omega/2\theta$  scan,  $\Delta\omega = 0.84 + 0.35 \tan \theta^\circ$ ,  $T = 150$  K, Mo  $K\alpha$  radiation, graphite monochromator,  $\lambda = 0.71073$  Å, Enraf-Nonius CAD4-T diffractometer on rotating anode. Data were corrected for Lp and for a linear decay of 20% of the reference reflections ( $2 0 6, 1 2 - 6, 5 - 2 - 2$ ) during 21 h of X-ray exposure time. Empirical absorption correction is implemented in PLATON (DIFABS, corrections range 0.846–1.147). The structure was solved by automated direct methods (SHELXS86). Refinement on  $F^2$  was carried out by full-matrix least squares techniques (SHELXL93) and no observance criterion was applied during this refinement. Final  $R1 = 0.0887$  for 3112 reflections with  $F_o > 4.0\sigma(F_o)$ ,  $wR2 = 0.2137$  for all 8084 reflections,  $w = 1/[\sigma^2(F_o^2) + (0.0847P)^2]$  with  $P = (\text{Max}(F_o^2, 0) + 2F_c^2)/3$ ,  $S = 0.94$  for 466 parameters. Mean and maximum shift over error 0.000

and 0.007. Maximum and minimum residual density 0.32 and  $-0.23 \text{ e } \text{Å}^{-3}$ . All nonhydrogen 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 other hydrogen atoms. Weights were refined in the final refinement cycles. The benzene molecules probably have some motional freedom but no disorder model was applied and refined.

Further details of the crystal structure investigations of 1 and 2 may be obtained from the Director of the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK, on quoting the full journal title.

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