Sodium compounds of the benzophenone dianion (diphenyloxidomethanide)†‡

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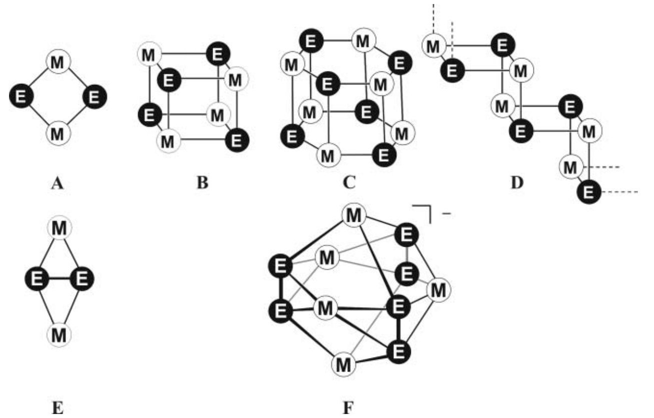
The benzophenone dianion [diphenyloxidomethanide, $(\mathrm{Ph_2CO})^{2-}$], which occurs in the well known deeply violet sodium/benzophenone tetrahydrofuran solutions, was crystallised with sodium cations in form of the two polymeric chain compounds $[\mathrm{Na_2(Ph_2CO)(tetraglyme)}]_\infty$ **1** and $[\mathrm{Na_2(Ph_2CO)(thf)_2}]_\infty$ **2**. It was found to aggregate with its conjugated acid, the alcoholate $(\mathrm{Ph_2CHO})^-$, around a central unit of sodium hydroxide, resulting in the mixed cage compound $[\mathrm{Na_{13}(Ph_2CO)_4(Ph_2CHO)_4(OH)(mtbe)_4}]\cdot\mathrm{mtbe}$ **3**. The structural parameters of the benzophenone dianion indicate that a considerable amount of its negative charge is located within the phenyl rings, rather than on the formally anionic benzylic carbon atom. The topological analysis of the electron density of the monomeric model structure $[\mathrm{Na_2(Ph_2CO)}]$ reveals an even positive charge for this particular atom, hence $(\mathrm{Ph_2CO})^{2-}$ is, despite its usual representation, not a vicinal dianion.

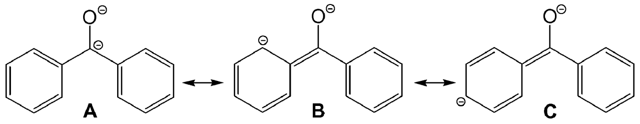
Introduction

The structural chemistry of ionic organoelement compounds with composition $[\mathrm{M}^{(n+)}{}_{m/n}(\mathrm{ER}_x)^{(m-)}]$ (M: alkali or alkaline earth metal; E: anionic atom from main groups IV–VI; R: organic residue) is currently under intensive investigation.[1] For $m/n = 1$ rings (**A**), cubes (**B**), hexaprismanes (**C**) and ladder structures (**D**) are often observed (Scheme 1), while the compounds with $m/n = 2$ have frequently spherical polyhedral shapes.[2] The architectures of $[\mathrm{M^+{}_2(R_xE^-{-}E^-R_y)}]$ species, which contain vicinal dianions, are often based on bicyclobutane-shaped ion triples (**E**), a fact that was rationalised by an electrostatic point charge model.[3] For example, this characteristic structural motif is found in $[\mathrm{Li_2(Ph_2H_2C_2)(tmeda)_2}]$,[4] $[\mathrm{Na_4(Ph_2N_2)(HPh_2N_2)_2(dme)_4}]$[5] and $[\mathrm{Na_6(Ph_2P_2)_3(dme)_6}]$. The latter contains besides $[\mathrm{Na(dme)_3}]^+$-cations the anionic cluster $[\mathrm{Na_5(Ph_2P_2)_3(dme)_3}]^-$,[6] which has the structure **F**, where three building blocks **E** are linked by corner-sharing sodium cations.



Scheme 1 Association of four-membered rings (**A**) to prismane (**B, C**) and ladder (**D**) structures and of bicyclobutane-shaped units (**E**) to the cage found in the trimeric anion $[\mathrm{Na_5(Ph_2P_2)_3(dme)_3}]^-$ (**F**).

While stability against spontaneous electron detachment requires close counterion contacts for many polyanions,[7] this is especially important for vicinal dianions. Moreover, almost all structurally characterised 1,2-dianions from main groups IV–VI contain substituents which provide additional stabilisation, *e.g.* silyl groups or electron-delocalising residues like aryl systems.[8] The dianion of benzophenone, $(\mathrm{Ph_2CO})^{2-}$, which is formally, *i.e.* in its Lewis structure **A** (Scheme 2), a vicinal dianion, provides an important example for the latter.



Scheme 2 Lewis structures for $(\mathrm{Ph_2CO})^{2-}$: vicinal (1,2-) dianion structure (**A**), one of four 1,4-dianionic structures (**B**) and one of two 1,6-dianionic structures (**C**).

Its synthesis by the two-electron reduction of benzophenone, $\mathrm{Ph_2C{=}O}$, with sodium metal was first reported in 1914 by Schlenk *et al.*[9] After the initial formation of the deeply blue coloured ketyl radical anion $(\mathrm{Ph_2CO})^{\bullet-}$, an intensely violet-red product is formed which was identified as $[\mathrm{Na_2(Ph_2CO)(S)}_n]_m$ (S = solvent). This very oxygen- and moisture-sensitive compound of unknown structure has now widespread use as an *in situ* prepared self-indicating drying and deoxygenating agent for organic solvents.[10] The only crystallographically characterised s-block metal complex of $(\mathrm{Ph_2CO})^{2-}$ to date is the dimeric lithium compound $[\mathrm{Li_2(Ph_2CO)(thf)(tmeda)}]_2$.[11] Furthermore a dimeric ytterbium compound, $[\mathrm{Yb(Ph_2CO)(hmpa)_2}]_2$, was described.[12] We report

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† Electronic supplementary information (ESI) available: 1. X-Ray powder diffractograms of **1** and **3**; 2. ^{23}Na 3QMAS NMR spectrum of **1**; 3. Atomic coordinates for the calculated structure of $[\mathrm{Na_2(Ph_2CO)}]$; 4. QTAIM analysis of the model structure $[\mathrm{Na_2(Ph_2CO)}]$. See DOI: 10.1039/b512173f

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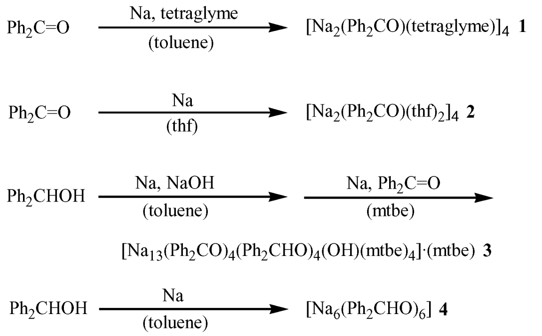
here the structural characterisation of several sodium compounds of the benzophenone dianion, combined with quantum chemical investigations concerning its electronic structure.

Results and discussion

Synthesis and structural characterisation

Three compounds of sodium-bonded $(Ph_2CO)^{2-}$ (disodium diphenyloxidomethanide) were prepared in crystalline state, two of them are linear chain polymers solvated by aliphatic ether ligands, while the third one is a cluster consisting of a central sodium hydroxide unit surrounded by equal amounts of the target compound $[Na_2(Ph_2CO)]$ and the alcoholate $[Na(Ph_2CHO)]$ (Scheme 3). For comparison, the alcoholate $[Na(Ph_2CHO)]$ was also crystallised in the pure state. In the following discussion sodium–carbon distances of less than 3.1 Å are regarded as structurally meaningful contacts, this does not necessarily imply the presence of chemical bonding.



Scheme 3 Syntheses of compounds **1–4**.

The reduction of benzophenone with sodium metal in toluene in presence of one equivalent of the pentadentate ligand tetraglyme $[CH_3O(CH_2CH_2O)_4CH_3]$ gives rise to the compound $[Na_2(Ph_2CO)(tetraglyme)]_\infty$ **1** as dark green, golden reflecting crystals (68% yield) which contain one-dimensional polymeric chains (Fig. 1).

The $[Na_2(Ph_2CO)]$ building blocks show the bicyclobutane-type ion arrangement which is typical for vicinal dianions (grey shaded in Fig. 1), that is, the counterions Na1 and Na2A are each close to both of the formally negatively charged centres, O1 and C1 [Na1–O1 2.335(3), Na2A–O1 2.355(3), Na1–C1: 2.559(3), Na2A–C1 2.729(3) Å]. The resulting, almost planar (mean deviation 0.03 Å) four atom arrangement resembles more a bisected triangle than a rhomboid because of the wide Na–O–Na angle around the oxygen atom O1, which amounts to 170.8(1)°. Na1 and Na2A are not only close to the benzylic carbon atom C1, they also have short distances to some *ipso* and *ortho* phenyl carbon atoms: Na1 to C8 and C9 [Na1–C8: 2.837(4), Na1–C9: 3.036(4) Å], Na2A to C2 [3.048(4) Å]. The $[Na_2(Ph_2CO)]$ units in **1** dimerise *via* planar $\{Na_2O_2\}$ four-membered rings (Na2, O1, Na2A, O1A) in the manner of normal, *i.e.* singly negatively charged, alcoholates (**A** in Scheme 1). These centrosymmetric $[Na_2(Ph_2CO)]_2$ dimers are then linked together *via* their external sodium cations (Na1, Na1A), which again form $\{Na_2O_2\}$ rings with the μ_2-bridging oxygen atoms (O4, O4B) of two tetraglyme molecules. Note the μ_4-bridging mode of the tetraglyme molecule which is responsible for the polymeric nature of **1**. The structural parameters of the $(Ph_2CO)^{2-}$ dianion unit reflect the perturbation by the additional negative charges: besides pronounced carbon–carbon bond length alternation in the phenyl groups, the inner ring angles around the *ipso* carbon atoms, C_i, are significantly decreased[13] [C9–C8–C13 112.7(3)°, C3–C2–C7 113.5(4)°] and the bonds from the planar benzylic carbon atom C1 [Σ(angles) = 359.8(2)°] to C_i of both phenyl groups have lengths between a single and a double bond

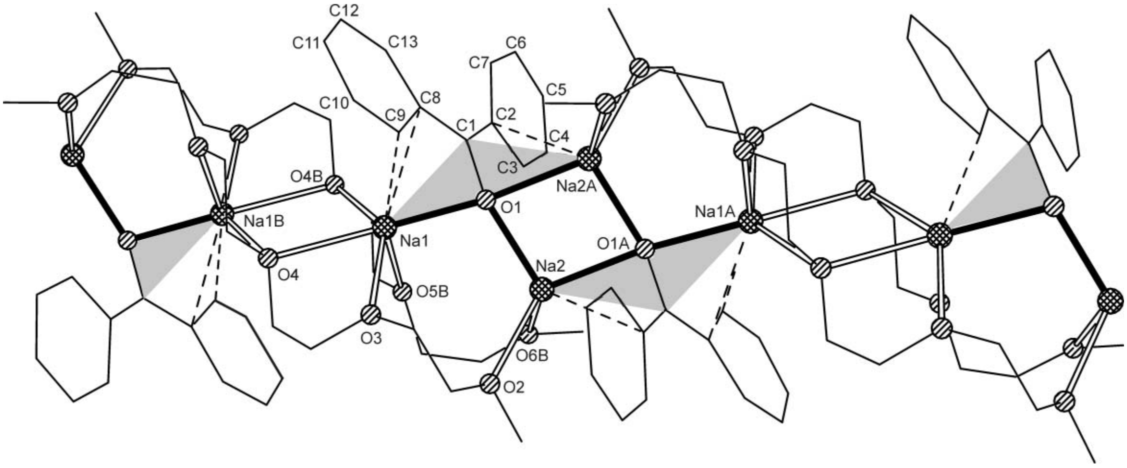


Fig. 1 Solid state structure of **1** (fragment of the polymeric chain containing four times the asymmetric unit). Selected bond lengths (Å) and angles (°): Na1–O1 2.335(3), Na2–O1 2.241(3), Na2A–O1 2.355(3), Na1–O3 2.377(3), Na1–O4 2.548(3), Na1–O4B 2.653(3), Na1–O5B 2.354(3), Na2–O2 2.378(3), Na2–O6B 2.471(4), Na1–C1 2.559(3), Na1–C8 2.837(4), Na1–C9 3.036(4), Na2A–C1 2.729(3), Na2A–C2 3.048(4), C1–O1 1.401(4), C1–C2 1.427(5), C1–C8 1.425(5), C2–C3 1.432(5), C3–C4 1.375(6), C4–C5 1.389(6), C5–C6 1.390(6), C6–C7 1.371(6), C7–C2 1.437(5), C8–C9 1.436(5), C9–C10 1.374(5), C10–C11 1.386(5), C11–C12 1.389(6), C12–C13 1.375(5), C13–C8 1.447(5); O1–Na1–O4 155.0(1), O1–Na1–O4B 124.3(1), O3–Na1–O5B 93.5(1), Na1–O1–Na2A 170.8(1), Na2–O1–Na2A 81.0(1), O1–Na2–O1A 99.0(1), O2–Na2–O6B 85.0(1), Na1–O1–C1 82.4(2), Na2A–O1–C1 89.5(2), O1–C1–C2 116.0(3), O1–C1–C8 116.1(3), C2–C1–C8 127.7(3), C3–C2–C7 113.5(4), C9–C8–C13 112.7(3), O4–Na1–O1–Na2 100.8(2), C7–C2–C1–C8 19.3(5), C13–C8–C1–C2 5.1(5).

[C1–C2 1.427(5), C1–C8 1.425(5) Å]. The phenyl ring planes are slightly twisted, by 14.8(2) and 6.2(2)°, respectively, against the {C1,O1,C2,C8} plane.[14] The C–O bond has the length of a single bond [C1–O1 1.401(4) Å]. In a sodium compound of the ketyl radical anion, $[Na_2(Ph_2CO)_2(hmpa)_4]$, the C–O bond is shorter with 1.30(1) Å.[15]

The phenyl protons of **1**, dissolved in thf, give rise to three NMR signals at room temperature, with the *para* protons appearing distinctly highfield shifted at 5.35 ppm (*meta*: 6.46, *ortho*: 6.70; see also ref. 10*b*). The isotropic ^{23}Na NMR shifts of the two sodium sites in solid **1**, determined by the MQMAS technique,[16] are with −6.6 and −15.0 ppm in the normal range of oxygen coordinated sodium cations (see ESI† for spectra).[17a] Sodium ions in a lower oxidation state than Na^{+1}, *i.e.* Na^{-1}, are more shielded, *e.g.* −61 ppm[17b] for isolated Na^- and −32 ppm[17b] for a Na_2^{2-} dimer.

If benzophenone is reduced with sodium in thf, a crystalline, dark green product of the composition $[Na_2(Ph_2CO)(thf)_2]_\infty$ **2** can be obtained; the low yield of 11% isolated substance is caused by its high solubility. This polymeric compound likewise contains $[Na_2(Ph_2CO)]$ units with bicyclobutane-type ion arrangement (grey shaded in Fig. 2).

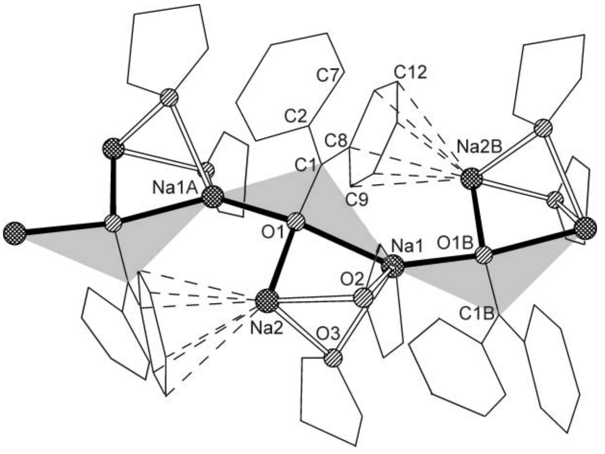


Fig. 2 Structure of **2** (fragment of the polymeric chain containing three times the asymmetric unit + one additional Na^+). Selected bond lengths (Å) and angles (°): Na1–O1 2.352(4), Na1–O2 2.640(5), Na1–O3 2.450(4), Na1A–O1 2.262(4), Na2–O1 2.201(4), Na2–O2 2.436(5), Na2–O3 2.411(5), Na1–C1 2.739(6), Na1–C1B 2.791(6), Na2B–C8 3.068(6), Na2B–C9 2.834(6), Na2B–C10 2.683(6), Na2B–C11 2.734(6), Na2B–C12 2.946(6), Na2B–C13 3.095(6); C1–O1 1.383(6), Na1–O1–Na1A 154.6(2), O1–Na1–O1B 139.5(1), Na1–O1–Na2 83.0(1), O1–Na1–O2 85.5(2), O1–Na1–O3 81.5(1), O1–Na2–O2 93.9(2), O1–Na2–O3 85.5(2), Na1–O2–Na2 72.8(1), Na1–O3–Na2 76.8(1), Na1–O1–C1 90.5(3), Na1A–O1–C1 97.0(3), O1–C1–C2 116.1(5), O1–C1–C8 117.0(5), C2–C1–C8 126.5(5), C9–C8–C13 111.8(6), C7–C2–C1–C8 −29.1(9), C13–C8–C1–C2 2.4(9).

In contrast to **1** there are no $\{Na_2O_2\}$ four-membered rings present and the dianion units are linked to an infinite chain by corner-sharing sodium atoms (Na1 and its equivalents). Pendant to this chain, the sodium atoms Na2 and its symmetry equivalents are attached to the oxygen atoms of the $(Ph_2CO)^{2-}$ dianion units. Two thf molecules bridge in μ_2-mode the two different types of sodium ions, Na1 and Na2. The latter is on the opposite side connected in addition to a phenyl group, with the six Na–C distances ranging from 2.683(6) to 3.095(6) Å.

The attempted crystallisation of $[Na_2(Ph_2CO)]$ from methyl-*tert*-butyl ether (mtbe), gave rise to the unintended generation of the crystalline compound $[Na_{13}(Ph_2CO)_4(Ph_2CHO)_4(OH)(mtbe)_4]\cdot$mtbe **3**, the composition of which suggests its origin to be accidental contamination with water. The formation of this compound can be reproduced with some difficulties (see the Experimental section) in about 25% yield by reducing benzophenone with sodium metal in the presence of sodium diphenylmethanolate **4** and NaOH in mtbe. The sodium alcoholate **4** was prepared separately from Na and diphenylmethanole, Ph_2CHOH, in boiling toluene. When crystallised from cyclopentane solution, **4** consists of hexameric aggregates with the S_6 symmetric geometry of a hexaprismane (Fig. 3), which is a typical structure for alkali metal alcoholates.[18]

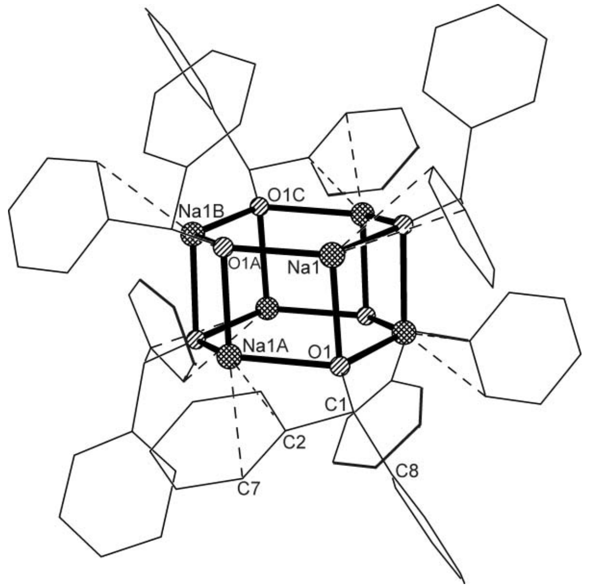


Fig. 3 Structure of **4** (six times the asymmetric unit). Selected bond lengths (Å) and angles (°): Na1–O1 2.304(2), Na1–O1A 2.292(2), O1A–Na1B 2.209(2), Na1A–C2 2.799(3), Na1A–C7 2.892(4), C1–O1 1.383(3), C1–C2 1.531(4), C1–C8 1.511(4); Na1-O1A–Na1B 117.2(1), O1A–Na1B–O1C 121.6(1), O1–Na1–O1A 94.0(1), Na1–O1–Na1A 85.7(1), Na1–O1A–Na1A 83.9(1), O1–C1–C2 108.4(2), O1–C1–C8 114.6(3), C2–C1–C8 112.0(3).

The structure of the mixed aggregate **3**, which contains besides $(Ph_2CHO)^-$ in equal molar ratio the conjugated base $(Ph_2CO)^{2-}$and also a single hydroxide anion, is shown in Fig. 4(A) and (B).

Aggregate **3** consists of a $\{Na_9O_9\}$ cage formed by four face-sharing $\{Na_4O_4\}$ cubes containing a central linear NaOH unit,[19] which constitutes an approximate fourfold rotation axis. The four alcoholate units, $[Na(Ph_2CHO)]$, are arranged on that face of the cage, which contains the sodium cation of the NaOH unit. The four dianion units, $[Na_2(Ph_2CO)]$, are located on the opposite side, to which the hydroxide proton belongs. The oxygen atoms of the $(Ph_2CO)^{2-}$ dianions are each coordinated by an additional external sodium cation, such that again a bicyclobutane-type ion arrangement may be extracted from the structure (grey shaded in Fig. 4(B)). These external sodium ions, Na10–Na13 (marked with a star in Fig. 4(B)), each bind to one mtbe molecule (only the mtbe oxygen atoms, O10–O13, are shown in Fig. 4(A)).

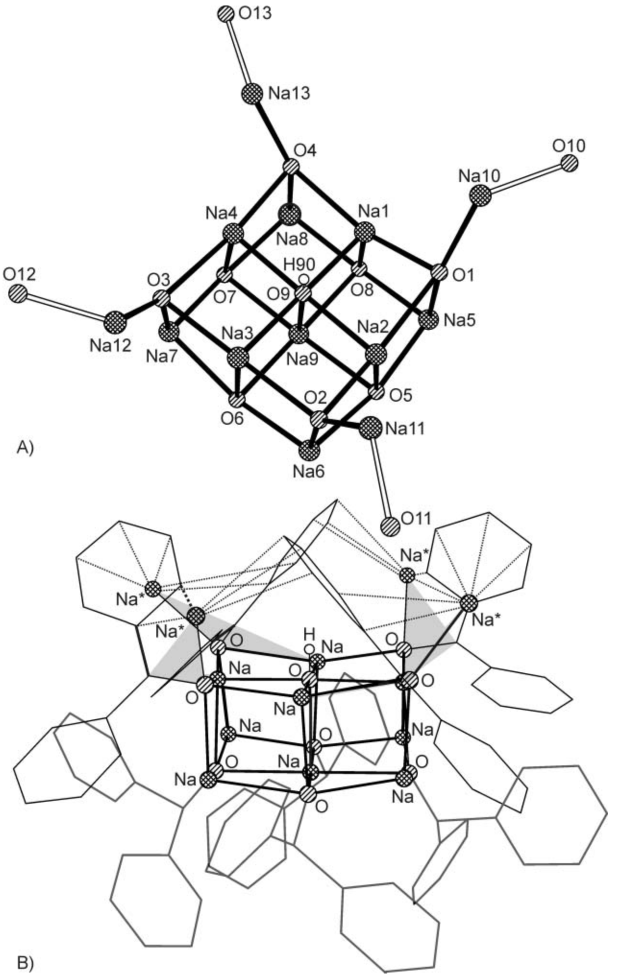


Fig. 4 Structure of **3**. Only one of the two independent molecules in the asymmetric unit is pictured; selected bond lengths (Å) and angles (°). (A) Inorganic core structure showing the central hydroxide ion (O9, H90). The oxygen atoms O1 to O4 are part of $(Ph_2CO)^{2-}$, O5–O8 from $(Ph_2CHO)^-$, O10–O13 from mtbe. Na1–O1 2.206(3), Na1–O4 2.448(3), Na1–O8 2.324(3), Na1–O9 2.313(3), Na9–O9 2.357(4), Na10–O1 2.268(3), Na10–O10 2.306(3), Na1–O1–Na2 87.6(1), O1–Na1–O4 185.2(1), Na1–O9–Na3 178.3(2), Na5–O1–Na10 145.6(1), O1–Na10–O10 123.9(1), all other Na–O distances/angles are of comparable values. (B) Simplified model of **4** showing the $(Ph_2CHO)^-$ moieties pointing to the side of the NaOH sodium atom and the $(Ph_2CO)^{2-}$ units to the side of the NaOH hydrogen atom. The bicyclobutane-type $[Na_2(Ph_2CO)]$ ion triples are shown as grey shaded rhomboids. The Na* indicate the sodium atoms carrying an additional mtbe ligand. Averaged C–O and $C–C_i$ distances and averaged $C–C_i–C$ angles in $(Ph_2CO)^{2-}$: 1.393(1) Å, 1.434(1) Å, 113.4(1)°. Averaged C–O and $C–C_i$ distances and averaged $C–C_i–C$ angles in $(Ph_2CHO)^-$: 1.405(1) Å, 1.527(1) Å, 118.0(1)°.

All sodium cations except the central one, Na9, have at least one close contact to a phenyl carbon atom [shortest distance found: 2.577(4) Å]. The central cage in **3** finds precedence and is related to $[Li_4Na_5(O^tBu)_4(PhNH)_4(OH)(4\text{-Me-py})_4]$[20] and $[Li_4K_5(O^tBu)_4(C_6H_{11}O)_4(OH)(thf)_5]$.[21]

The ^{1}H NMR spectrum of a freshly prepared solution of **3** in $[D_8]$toluene shows the signal for the hydroxide proton at −2.63 ppm, a chemical shift which was recently established for mixed hydroxide/alkoxide clusters.[22] This signal disappears within several hours at room temperature, the identification of the resulting products by NMR spectroscopy is not possible, due to rapid exchange phenomena.

Theoretical investigation

The unsolvated monomeric disodium oxidodiphenylmethanide, $[Na_2(Ph_2CO)]$, is chosen as a model compound for quantum chemical investigations. The inclusion of the counterions is important for the application of standard (bound state) electronic structure methods to anions.[23] Geometry optimisation[24] of $[Na_2(Ph_2CO)]$ at the B3LYP/6-311+G(2d,p) level[25] results in a C_2 symmetric structure (Fig. 5), with the C–O vector constituting the rotation axis.

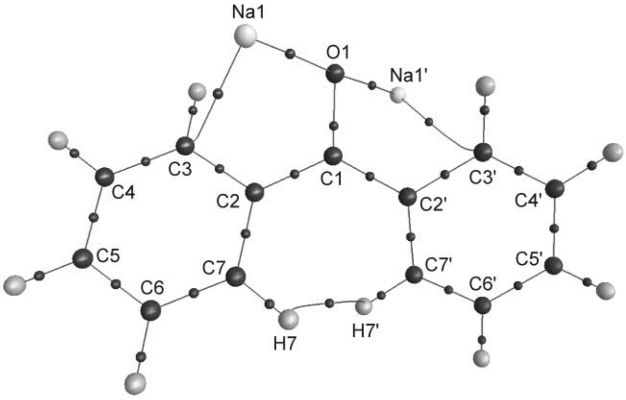


Fig. 5 Molecular graph of C_2-symmetric $[Na_2(Ph_2CO)]$, calculated at the B3LYP/6-311+G(2d,p) level; the rotation axis coincides with the O1–C1 vector. Bond critical points [(3, −1)] are indicated by small black spheres, the lines correspond to the bond paths. Distances (Å) and angles (°): Na1–O1 2.1574, Na1–C1 2.5858, Na1–C2 2.6381, Na1–C3 2.5649, O1–C1 1.3792, C1–C2 1.4327, C2–C3 1.4388, C3–C4 1.3948, C4–C5 1.3871, C5–C6 1.4064, C6–C7 1.3774, C2–C7 1.4339; Na1–O1–Na1′ 177.497, Na1–O1–C1 91.251, O1–C1–C2 116.717, C2–C1–C2′ 126.565, C3–C2–C7 114.757, C4–C3–C2 121.996, C5–C4–C3 121.397, C6–C5–C4 117.912, C7–C6–C5 121.780, C2–C7–C6 122.086, Na1–O1–C1–C2 49.065, O1–C1–C2–C3 14.338, C2′–C1–C2–C7 21.595.

The planes of the phenyl rings are twisted by 18.1° against the $\{C1,O1,C2,C2'\}$ plane and the torsion angle between the sodium cations and the adjacent *ipso*-phenyl carbon atoms along the C–O bond is 49.07°. The bond lengths within the dianion are in satisfactory agreement with the solid state structures of compounds **1–3**, the sodium–oxygen bonds are shorter because of the lower metal coordination number (the values are given in the caption to Fig. 5).

There is a distinct C–C bond length alternation in the phenyl rings and the values of the nucleus independent chemical shift (NICS),[26] calculated[27] at the ring centroids and 1 Å above and below [NICS(1)], respectively, are with +0.2 and −3.0/−2.7 markedly reduced in magnitude from the values for benzene, which has −7.6 and −10.0 at the same level of theory. This indicates a strong perturbation of the aromatic systems by the negative charges of the dianion. The electron populations, $[N(\Omega_i)]$, of the atomic basins, Ω_i, were determined by a topological analysis of the electron density (QTAIM[28]).[29] The basin of the benzylic carbon atom C1 is populated by only 5.617 electrons, corresponding to a positive charge of +0.383. Hence, the sodium-bonded benzophenone dianion is *not* a vicinal dianion (like in resonance structure **A** of Scheme 2). There are no bond critical points[28] between the benzylic carbon atom C1 and the likewise positively charged (+0.831) sodium atoms, although the corresponding Na1–C1/Na1′–C1 distances are short: with 2.5858 Å they are very close to the experimental values in **1**. Most of the negative charge of $(Ph_2CO)^{2-}$ is concentrated in the basin of the oxygen atom, which carries more than one unit charge (−1.258), due to its high electronegativity. The remaining negative charge is associated with the phenyl groups, in particular with those *ortho*-carbon atoms, C3 and C3′ (charge: −0.181), which are closer to the sodium cations (Fig. 5), while the other *ortho*-carbon atoms, C7 and C7′, are considerably less negatively charged (−0.079). Hence, the sodium cations cause a significant polarisation of the negative charge within the phenyl rings. There are bond critical points present between C3/C3′ and Na1/Na1′. The values of the electron density, its Laplacian and the kinetic energy per electron at these points [$\rho(\boldsymbol{r}_b)$: 0.0153 au, $\nabla^2\rho(\boldsymbol{r}_b)$: 0.0736 au, $G(\boldsymbol{r}_b)/\rho(\boldsymbol{r}_b)$: 1.0131 au] characterise the Na–C bonds (like the Na–O bonds) as *closed-shell* interactions.[28] The *para*-carbon atoms, C5/C5′, are more negatively charged (−0.081) than the *meta* atoms, C4/C4′ and C6/C6′ (−0.054 and −0.052).

The amount of electron delocalisation between two atoms, *i.e.* the number of exchanged (shared) electrons, can be quantified by the delocalisation index $\delta(\Omega_i,\Omega_j)$,[30] which is derived from the exchange density.[31] Correspondingly, the localisation index $\lambda(\Omega_i)$[30] [$= \delta(\Omega_i,\Omega_i)$] determines the amount of electrons which are exchanged only within a basin. In case of the oxygen atom O1, 8.293 electrons are localised within its basin, corresponding to 90% of its electron population. The remaining 0.965 electrons are delocalised mainly over the directly bonded benzylic carbon atom C1 with $\delta(O1,C1) = 1.046$ (*i.e.* O1 shares $\frac{1}{2} \times 1.046$ electrons with C1 and *vice versa*), over the *ipso* [$\delta(O1,C2) = 0.120$] and *ortho* [$\delta(O1,C3/7) = 0.054/0.018$] carbon atoms of the phenyl rings, and over the sodium cations [$\delta(O1,Na1) = 0.174$].

The spatial shape of the electron delocalisation originating from the basin of O1 is visualised in Fig. 6(A) by an isosurface plot (value: 0.001 au) of the atomic exchange density of O1, $\Gamma_{X[O1]}(\boldsymbol{r})$,[32] which gives a graphical representation of the above delocalisation indices $\delta(O1,X)$.[33] It shows a single domain, which extends primarily over the adjacent C1, the *ipso*-carbon atoms of the phenyl groups and the sodium cations. A more detailed view is provided by its Laplacian, $\nabla^2\Gamma_{X[O1]}(\boldsymbol{r})$, displayed in Fig. 6(B) and (C) by isosurfaces for the value −0.005 au.[34] These surfaces enclose regions where the atomic exchange density ${}^2\Gamma_{X[O1]}(\boldsymbol{r})$ is locally concentrated.[35] The principal shape of the delocalisation resembles the concept of π-conjugation more and more as one moves away from the origin basin O1, *e.g.* around the *para*- and one *meta*-carbon of each phenyl ring (Fig. 6(B), (C)), where it extends much more pronounced above and below the ring plane than in the plane. The isosurface is almost absent along the ionic Na1–O1 bond, while it is present, but with a distinct constriction, along the polar O1–C1 bond. The Laplacian of the atomic exchange density for the benzylic carbon atom, $\nabla^2\Gamma_{X[O1]}(\boldsymbol{r})$, shows no such constriction along the less polar C1–C2 bond (Fig. 6(E), (F)). The π-type delocalisation over the phenyl rings is more pronounced for C1 at the same isosurface value, it is already apparent in ${}^2\Gamma_{X[O1]}(\boldsymbol{r})$ itself (Fig. 6(D)). In contrast to O1 (*vide supra*) only 64% [$\lambda(C1) = 3.611$] of its electron population are localised within the basin of C1. There are 1.227 electrons delocalised between C1 and the directly bonded *ipso*-carbon atom C2. The order of delocalisation from C1 over the rest of the ring carbon atoms is *ortho* > *para* > *meta* (0.073/0.061, 0.025 and 0.014/0.023), although the *meta*-atoms are involved to very differing degrees, with C6 almost approaching the value for the *para*-carbon C5 (see the ESI† for additional calculated values).

Conclusions

The bicyclobutane-shaped ion triple (**E** in Scheme 1), which is a typical structure element for alkali metal compounds of vicinal dianions, can be extracted from the solid state structures of the sodium-bonded benzophenone dianion (compare Figs. 1, 3, 5), if Na–C distances smaller than 2.8 Å are considered as meaningful contacts. Because the model structure $[Na_2(Ph_2CO)]$

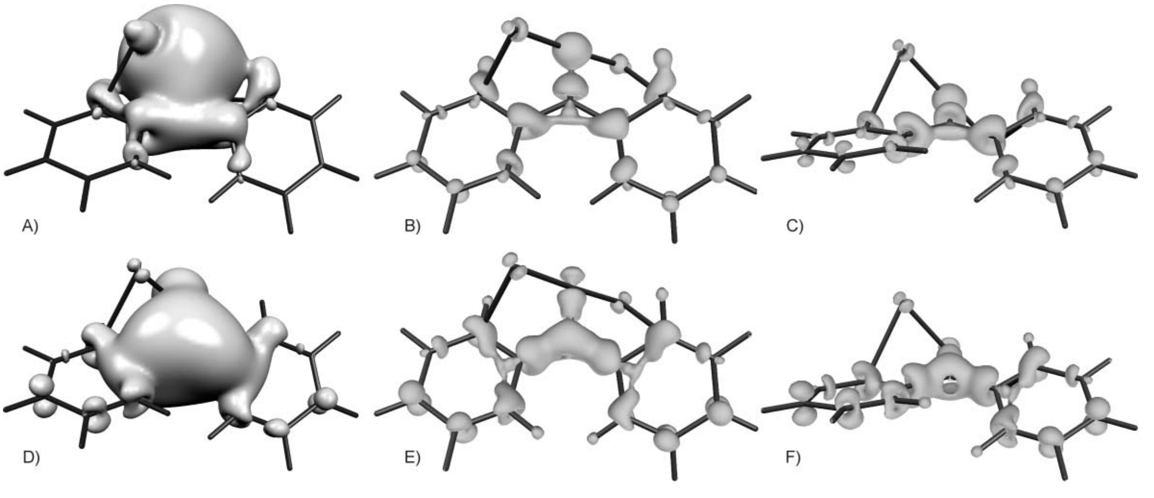


Fig. 6 Isosurface plots of the atomic exchange density and its Laplacian. (A) $\Gamma_{X[O1]}(\boldsymbol{r}) = 0.001$; (B) $\nabla^2\Gamma_{X[O1]}(\boldsymbol{r}) = -0.005$; (C) $\nabla^2\Gamma_{X[O1]}(\boldsymbol{r}) = -0.005$; (D) $\Gamma_{X[C1]}(\boldsymbol{r}) = 0.001$; (E) $\nabla^2\Gamma_{X[C1]}(\boldsymbol{r}) = -0.005$; (F) $\nabla^2\Gamma_{X[C1]}(\boldsymbol{r}) = -0.005$.

contains no bonds between sodium (Na1) and the benzylic carbon (C1), although the Na–C distance is very small, it is reasonable to assume that these bonds are likewise absent in the experimental structures of compounds **1**, **2** and **3**. The observed significant distortions of the phenyl rings are in accord with the calculated charge distribution and support the conclusion that the benzophenone dianion, when bonded to sodium, cannot be described as a vicinal dianion, but may rather be viewed as a conjugated system, which is dominated by the strongly negatively charged oxygen atom.

Experimental

The solvents were stored as violet sodium–benzophenone solutions (containing tetraglyme for solubility in case of toluene and cyclopentane) and were transferred in a vacuum line by condensation techniques. For synthetic purposes benzophenone was recrystallised twice from methanole solution. Tetraglyme was dried with lithium aluminium hydride and distilled under vacuum.

1: Sodium (0.25 g, 11.0 mmol), benzophenone (1.00 g, 5.5 mmol) and tetraglyme (1.22 g, 5.5 mmol) were sonicated for one day at room temperature in toluene (100 mL). The deep violet solution was then filtered and concentrated. After storage for two days at room temperature, dark green crystals with golden reflection were obtained (1.68 g, 68%): mp 140 °C; IR (neat): $\tilde{\nu}_{max}/cm^{-1}$ 2922w, 2890w, 2871w, 1585w, 1557s, 1443s, 1332m, 1310s, 1254m, 1233m, 1149m, 1116s, 1089s, 1063s, 1049s, 1015m, 1004m, 973w, 953m, 934m, 887m, 851m, 821w, 790w, 716m, 680s; ^{1}H NMR ([D$_8$]thf, 250.13 MHz): δ 3.25 (6H, s, tetraglyme: OCH$_3$), 3.43 (4H, m, tetraglyme), 3.53 (12H, m, tetraglyme), 5.35 (2H, m, *p*-Ar–H), 6.46 (4H, m, *m*-Ar–H), 6.70 (4H, br, *o*-Ar–H); ^{13}C NMR ([D$_8$]thf, 62.90 MHz): δ 56.2, 68.1 (two nearly superimposed signals), 68.2, 69.8 (all five: tetraglyme), 101.8 (*p*-Ar–C), 109.8 (*o*-Ar–C), 126.0 (*m*-Ar–C), 135.1 (*ipso*-Ar–C), benzylic ^{13}C-signal not observed. The X-ray powder diffractogram, together with that calculated from the single crystal structure, is contained in the ESI.†

2 was prepared by the same method from sodium (0.25 g, 11.0 mmol) and benzophenone (1.00 g, 5.5 mmol) in thf (100 mL) to give dark green crystals after filtering, concentration and storage of the deep violet–red solution at room temperature for several weeks (0.23 g, 11%), mp 131 °C; IR (neat): $\tilde{\nu}_{max}/cm^{-1}$ 3041w, 2974w, 2869w, 1550s, 1472m, 1447s, 1356m, 1307s, 1261m, 1228m, 1152s, 1100m, 1065m, 1050m, 1029m, 994m, 979m, 956s, 873m, 807m, 776w, 739m, 683s, 617w, 608w; ^{1}H NMR ([D$_8$]thf, 300.13 MHz): δ 5.34 (2H, m, *p*-Ar–H), 6.47 (4H, m, *m*-Ar–H), 6.72 (4H, br., *o*-Ar–H); ^{13}C NMR ([D$_8$]thf, 75.48 MHz): δ 103.3 (*p*-Ar–C), 111.8 (*o*-Ar–C), 128.3 (*m*-Ar–C), 137.0 (*ipso*-Ar–C), benzylic ^{13}C-signal not observed.

3: Sodium (0.400 g, 17.4 mmol, excess), sodium hydroxide (0.027 g, 0.7 mmol) and diphenylmethanol (0.500 g, 2.7 mmol) were refluxed for 8 h in toluene (10 mL). After addition of benzophenone (0.492 g, 2.7 mmol) the solvent was removed in vacuum and replaced by mtbe (40 mL). The mixture was sonificated 12 h at room temperature and the resulting violet-red solution was filtered and then concentrated to $\frac{1}{4}$ of its volume. Dark green crystals (0.368 g, 25%) deposited after storage for one day at room temperature. This preparation was not always reproducible, since in several cases the product was contaminated by either $[Na_4(O^tBu)_4(mtbe)_3]$[36] or by an unidentified blue–green crystalline substance. **3** is unstable in solution at room temperature, the NMR spectrum was measured within 30 min after dissolution, mp 160 °C; IR (neat): $\tilde{\nu}_{max}/cm^{-1}$ 3051w, 3022w, 2971w, 2925w, 1557s, 1448s, 1347m, 1330m, 1305s, 1227w, 1199w, 1154s, 1050m, 1021w, 1001w, 959s, 888m, 849m, 768m, 739m, 695s; ^{1}H NMR ([D$_8$]toluene, 500.23 MHz, 293 K): δ −2.63 (1H, s, OH), 1.02 (s, mtbe: ^{t}Bu), 3.02 (s, mtbe: OCH$_3$), 4.43 (4H, s, Ph$_2$C*H*O), 5.16 (4H, s), 6.36–7.41 (m). The X-ray powder diffractogram together with the one calculated from the single crystal structure is contained in the ESI.†

4: Sodium (0.062 g, 2.7 mmol) and diphenylmethanol (0.500 g, 2.7 mmol) were refluxed in toluene (50 mL) until dissolution of the *meta*l (6 h). The solvent was removed in vacuum and the residue recrystallised from cyclopentane to give white crystals (0.397 g, 71%), mp 280 °C (decomp.); IR (neat): $\tilde{\nu}_{max}/cm^{-1}$ 3056w, 3017w, 2753w, 1595w, 1485m, 1446m, 1345w, 1281w, 1252w, 1195w, 1177w, 1160w, 1096s, 1057s, 1023m, 917w, 852m, 831w, 772s, 742s, 702s, 663s; ^{1}H NMR ([D$_8$]thf, 300.13 MHz): δ 6.07 (1H, s, Ph$_2$C*H*O), 7.01 (2H, m, *p*-Ar–H), 7.15 (4H, m, Ar–H), 7.36 (4H, m, Ar–H); ^{13}C NMR ([D$_8$]thf, 75.48 MHz): δ 78.9 (Ph$_2$*C*HO), 122.7, 124.3, 125.5, 153.4.

X-Ray crystallography (see Table 1)

Single crystals were selected in an argon filled glovebox under Na/K-alloy containing paraffin oil and were sealed in glass capillaries by an electrically heated platinum wire. The data were collected on STOE IPDS I image plate (**1**) and Bruker AXS Apex CCD diffractometers (**2**, **3**, **4**). In case of the latter they were corrected with the program SADABS v. 2.05.[37] The structures were solved[38] by direct methods, all non-hydrogen atoms were refined[39] against F^2 with anisotropic temperature factors while the hydrogen atoms were constrained to ride on their bonding partners. Two of the mtbe molecules in **3** show pronounced disorder, for one of them (O13) two orientations were refined with occupancies of 0.64/0.36, while in case of the other (O28) several geometrical restraints were applied.

CCDC reference numbers 234847 (**1**), 234848 (**2**), 234850 (**3**) and 234849 (**4**).

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b512173f

^{23}Na MAS NMR spectroscopy

The central transitions (–1/2 → 1/2) in the ^{23}Na NMR spectra were recorded on Bruker Avance 500 and Avance 400 spectrometers (132.3 and 105.8 MHz, respectively). The microcrystalline sample was contained in a 4 mm o.d. ZrO$_2$ rotor. ^{23}Na Triple Quantum MAS spectra were recorded at 105.8 MHz with a sample rotation frequency of 8 kHz employing the z-filter technique[40] and rotor synchronization[41] and were processed in the sheared mode. A first estimation of the ^{23}Na spin parameters was obtained from the cross-sections extracted from the 3QMAS spectrum.[16b,42] These values served as input for the simulation of the complete band-shape of the 132.3 and 105.8 MHz spectra using the SIMPSON package.[43]

Table 1 Crystallographic data for compounds **1**–**4**

	1	**2**	**3**	**4**
Sum formula	$C_{23}H_{32}Na_2O_6$	$C_{21}H_{26}Na_2O_3$	$C_{129}H_{145}Na_{13}O_{14}$	$C_{78}H_{66}Na_6O_6$
M/g mol^{-1}	450.5	372.4	2218.3	1237.3
Crystal system	Triclinic	Monoclinic	Triclinic	Trigonal
Space group	$P\bar{1}$	$P2_1/n$	$P\bar{1}$	$R\bar{3}$
a/Å	10.746(2)	12.055(7)	16.383(1)	21.777(3)
b/Å	11.256(2)	8.424(5)	26.813(2)	—
c/Å	11.771(2)	19.91(1)	30.065(2)	12.378(3)
α/°	61.90(3)	—	67.108(1)	—
β/°	88.15(3)	94.62(1)°	89.543(1)	—
γ/°	70.07(3)	—	78.144(1)	—
V/Å^3	1166.6(4)	2015(2)	11869(1)	5084(1)
Z	2	4	4	3
D/g cm^{-3}	1.282	1.227	1.241	1.212
μ/mm^{-1}	0.12	0.12	0.12	0.11
T/K	293	293	150	293
Crystal size/mm	0.29 × 0.25 × 0.19	0.14 × 0.11 × 0.10	0.19 × 0.15 × 0.10	0.28 × 0.27 × 0.21
$2\theta_{max}$/°	46.50	43.94	49.42	46.50
Collected reflections	12076	10477	92934	7667
Independent reflections	3152	2459	40424	1623
R_{int}	0.1282	0.1727	0.0950	0.0388
Refined parameters/restraints	280/0	235/0	2828/14	136/0
R_1 (F) for $F_o > 4\sigma$ (no. refl.)	0.0478 (1790)	0.0611 (1114)	0.0564 (16789)	0.0485(1084)
wR_2 (F^2) for all data	0.1106	0.1525	0.1394	0.1419
Goodness-of-fit (F^2)	1.036	0.936	0.826	1.029
$\Delta\rho_{max/min}$/e Å^{-3}	0.16/−0.15	0.24/−0.23	1.06/−0.58	0.37/−0.17

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31 In the general case $\delta(\Omega_i,\Omega_j)$ is calculated from the spinless exchange–correlation density $\Gamma_{XC}(\boldsymbol{r}_1,\boldsymbol{r}_2)$ by integration of the space coordinates $\boldsymbol{r}_1$ and $\boldsymbol{r}_2$ over two atomic basins Ω_i and Ω_j and multiplying the result by minus two. At the single-determinant level, which is employed in this communication, $\Gamma_{XC}(\boldsymbol{r}_1,\boldsymbol{r}_2)$ reduces to the exchange density $\Gamma_X(\boldsymbol{r}_1,\boldsymbol{r}_2) = \Gamma_X^{\alpha\alpha}(\boldsymbol{r}_1,\boldsymbol{r}_2) + \Gamma_X^{\beta\beta}(\boldsymbol{r}_1,\boldsymbol{r}_2)$, which describes only correlation between electrons of like spin.[30b] The B3LYP method was shown to give meaningful values for $\delta(\Omega_i,\Omega_j)$, although they are usually somewhat larger[31b] than those calculated by the Hartree–Fock method, which employs the exact exchange density: (*a*) F. Cortés-Guzmán and R. F. W. Bader, *Coord. Chem. Rev.*, 2005, **249**, 633; (*b*) T. Kar, J. G. Àngyàn and A. B. Sannigrahi, *J. Phys. Chem. A*, 2000, **104**, 9953.

32 The atomic exchange density $\Gamma_{X[\Omega]}(\boldsymbol{r})$ is derived from the negative exchange density $-\Gamma_X(\boldsymbol{r}_1,\boldsymbol{r}_2)$[31] by integration of $\boldsymbol{r}_1$ over the atomic basin Ω (and renaming $\boldsymbol{r}_2$ into $\boldsymbol{r}$). At the single-determinant level it is identical with the *volume-point sharing index*: (*a*) R. L. Fulton and S. T. Mixon, *J. Phys. Chem.*, 1995, **99**, 9768; (*b*) R. L. Fulton and P. Perhacs, *J. Phys. Chem. A*, 1998, **102**, 8989; (*c*) R. L. Fulton, *J. Phys. Chem.*, 1993, **97**, 7516. The atomic exchange density is discussed as *atomic Fermi hole* in: X. Fradera, M. Duran and J. Mestres, *J. Comput. Chem.*, 2000, **21**, 1361.

33 The values of $\Gamma_{X[\Omega]}(\boldsymbol{r})$ were calculated over a cubic grid, in intervals of 0.15 au, by means of a homemade Fortran program (J. Geier, unpublished work) according to:

$$\Gamma_{X[\Omega]}(\boldsymbol{r}) = \sum_i^{\alpha}\sum_j^{\alpha} S[\Omega]_{ij}^{\alpha}\,\varphi_i^{\alpha}(\boldsymbol{r})\varphi_j^{\alpha}(\boldsymbol{r}) + \sum_i^{\beta}\sum_j^{\beta} S[\Omega]_{ij}^{\beta}\,\varphi_i^{\beta}(\boldsymbol{r})\varphi_j^{\beta}(\boldsymbol{r})$$

where the ϕ_i are spin orbitals (each with occupation number 1) and the $S[\Omega]_{ij}$ are elements of the atomic overlap matrix with respect to Ω (*i.e.* the overlap matrix integrated over Ω).[30a,32a] The ϕ_{i} were taken from the *wfn* output files of the Gaussian 03 (rev. B.04) software package[24] (Keywords: 6d, DENSITY = CURRENT, OUTPUT = WFN). The $S[\Omega]_{ij}$ were taken from the ASCII integration record files of the AIM2000 program (version 2.0).[29]The isosurface plots were then generated from the grid values with the graphics program Molekel, version 4.3: P. Flükiger, H. P. Lüthi, S. Portmann and J. Weber, *MOLEKEL 4.3*, Swiss Center for Scientific Computing, Manno, Switzerland, 2000–2002; S. Portmann and H. P. Lüthi, *Chimia*, 2000, **54**, 766.

34 $\nabla^2\Gamma_{X[\Omega]}(\boldsymbol{r})$ is a richly structured function, which is of considerable value in the investigation of electronic structures (J. Geier, unpublished work). It provides a partitioning of the Laplacian of the electron density, $\nabla^2\rho(\boldsymbol{r})$, into its atomic contributions; the sum of the $\nabla^2\Gamma_{X[\Omega]}(\boldsymbol{r})$-functions of all atomic basins equals $\nabla^2\rho(\boldsymbol{r})$. The values of $\nabla^2\Gamma_{X[\Omega]}(\boldsymbol{r})$ were calculated by a Fortran program[33] using the analytical expressions for the second derivations.

35 Negative values of the Laplacian of a scalar function indicate local concentration of this function, positive ones local depletion. In the present case an isosurface value of −0.005 au is more appropriate for graphical purposes than a value of exact zero, which would totally enclose the regions of local concentration, because the corresponding surfaces are less diffuse.

36 Colourless crystals, identified by single-crystal X-ray diffraction: triclinic, a = 11.616(4), b = 13.197(4), c = 22.236(7) Å, α = 84.736(6), β = 77.970(6)°, γ = 74.075(5)°. The compound has a heterocubane structure with only three of the four sodium atoms coordinated by mtbe. Substantial disorder of one $(\mathrm{Ph_2CHO})^-$ residue prevents a detailed discussion of its structure.

37 *Program SADABS v. 2.05*: Bruker AXS Inc., Madison, WI, USA.

38 *Program SHELXS-97*: G. M. Sheldrick, Göttingen, 1997.

39 *Program SHELXL-97*: G. M. Sheldrick, Göttingen, 1997.

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