Supplementary data for:

Sodium compounds of the Benzophenone dianion (diphenyloxidomethanide)

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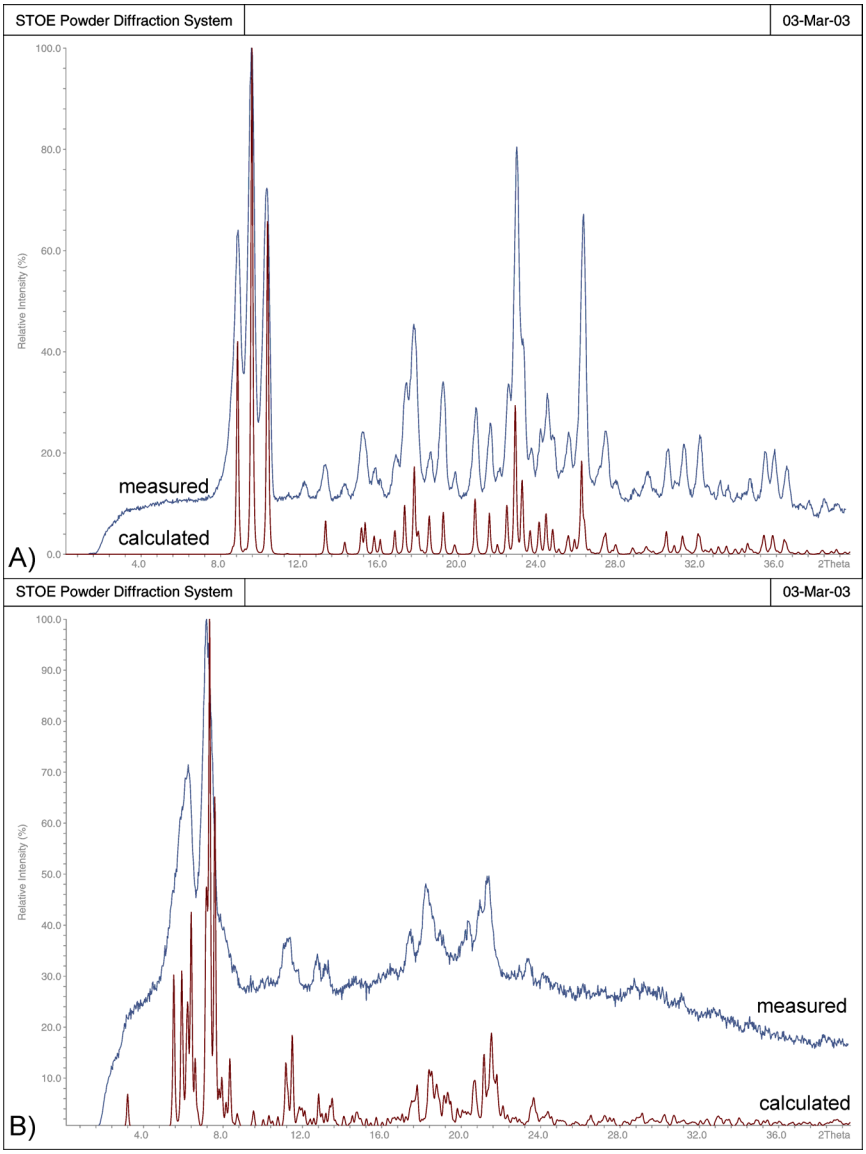
1. X-ray powder diffractograms of 1 and 3

Powder diffractograms were measured at room temperature on a STOE STADI P2 diffractometer ($CuK_{\alpha 1}$, Germanium-monochromator) with a linear position-sensitive detector. For the calculation of the theoretical diffractograms the atomic coordinates from the single crystal structures were used. The experimental (blue) and calculated (red) diffractograms for compounds **1** (A) and **3** (B) are shown below:

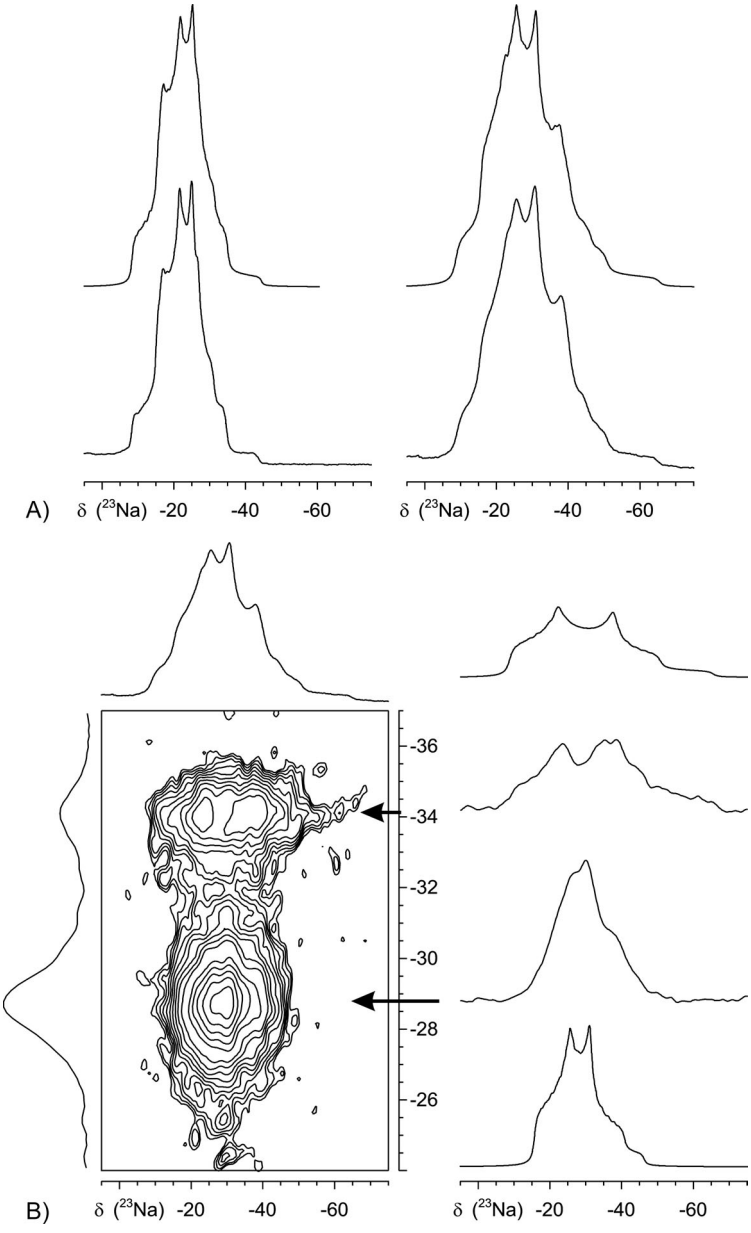


2. ^{23}Na 3QMAS NMR Spectrum of 1

A) Experimental ^{23}Na MAS NMR spectrum of **1** recorded at 132.3 (on the left) and 105.8 MHz (on the right), the simulated spectra are shown above. B) Contour plot of the 105.8 MHz ^{23}Na 3QMAS spectrum of **1** with the internal projection on the left and the conventional 1D MAS spectrum above. Traces extracted at the maxima along ω_1 are shown on the right (indicated by arrows) with simulations above and below (see the Experimental part).

Spin parameters of solid **1** (C_{qcc} = nuclear quadrupole coupling constant, η_Q = asymmetry parameter):

Site	δ_{iso} /ppm	C_{qcc} /MHz	η_Q
1	–6.6	3.21	0.42
2	–15.0	2.30	0.60



3. Atomic coordinates for the calculated structure of [$Na_2(Ph_2CO)$]

The structure was optimised at the B3LYP/6-311+G(2d,p) level using RHF/6-311+G(2d,p) orbitals as initial guess orbitals. It was confirmed as minimum by a vibrational analysis.

Orthogonal coordinates (Å):

C1	0.137387	2.477794	0.613318
C2	-0.088895	1.276657	-0.145664
C3	-0.536787	1.491722	-1.490775
C4	-0.676509	2.754687	-2.022262
C5	-0.397804	3.909879	-1.270018
C6	0.000000	3.745748	0.048619
H7	0.540293	2.381117	1.616117
H8	-0.808460	0.641950	-2.101124
H9	-1.026559	2.855040	-3.044624
H10	-0.505012	4.895726	-1.704130
H11	0.226653	4.616614	0.656229
C12	0.000000	0.000000	0.498467
C13	0.088895	-1.276657	-0.145664
C14	0.536787	-1.491722	-1.490775
C15	-0.137387	-2.477794	0.613318
C16	0.676509	-2.754687	-2.022262
H17	0.808460	-0.641950	-2.101124
C18	0.000000	-3.745748	0.048619
H19	-0.540293	-2.381117	1.616117
C20	0.397804	-3.909879	-1.270018
H21	1.026559	-2.855040	-3.044624
H22	-0.226653	-4.616614	0.656229
H23	0.505012	-4.895726	-1.704130
O24	0.000000	0.000000	1.877634
Na25	1.723667	-1.296623	1.924753
Na26	-1.723667	1.296623	1.924753

The NICS values were evaluated at the following points:

X1	-0.260430	2.609410	-0.711130
X2	0.693470	2.590610	-1.010830
X3	-1.214330	2.628210	-0.411430
X4	0.260430	-2.609410	-0.711130
X5	-0.693470	-2.590610	-1.010830
X6	1.214330	-2.628210	-0.411430

4. QTAIM analysis of the model structure [$Na_2(Ph_2CO)$]

Table 1. Atomic charges, electron populations [$N(\Omega_i)$] and localisation indices [$\lambda(\Omega_i)$] for the atomic basins Ω_i.

	charge	$N(\Omega_i)$	$\lambda(\Omega_i)$
Na1	+0.831	10.169	9.956
O1	–1.258	9.258	8.293
C1	+0.383	5.617	3.611
C2	–0.069	6.069	3.934
C3	–0.181	6.181	4.099
C4	–0.054	6.054	3.977
C5	–0.081	6.081	4.020
C6	–0.052	6.052	3.982
C7	–0.079	6.079	4.007
H7	+0.027	0.973	0.407

Table 2. Properties evaluated at selected bond critical points, $\mathbf{r}_b$, in atomic units.[28] $\rho(\mathbf{r}_b)$: electron density; $\nabla^2\rho(\mathbf{r}_b)$: Laplacian of the electron density; $G(\mathbf{r}_b)$: Lagrangian kinetic energy density; $v(\mathbf{r}_b)$: potential energy density; $G(\mathbf{r}_b)/\rho(\mathbf{r}_b)$: kinetic energy per electron; ε: ellipticity.

	Na1-C3	Na1-O1	O1-C1	C1-C2	H7-H7′
$\rho(\mathbf{r}_b)$	0.0153	0.0338	0.2877	0.2883	0.0129
$\nabla^2\rho(\mathbf{r}_b)$	0.0736	0.2188	–0.7125	–0.7378	0.0467
$G(\mathbf{r}_b)$	0.0155	0.0472	0.2292	0.0868	0.0095
$v(\mathbf{r}_b)$	–0.0127	–0.0398	–0.6366	–0.3581	–0.0073
$G(\mathbf{r}_b)/\rho(\mathbf{r}_b)$	1.0131	1.3964	0.7967	0.3011	0.7364
ε	0.8133	0.0202	0.1466	0.2601	0.2180

Table 3. Delocalisation indices.

	$\delta(\Omega_i,\Omega_j)$		$\delta(\Omega_i,\Omega_j)$
O1,C1	1.046	C2,C4	0.062
O1,C2	0.120	C2,C5	0.054
O1,C3	0.054	C2,C6	0.066
O1,C4	0.006	C2,C7	1.232
O1,C5	0.008	C3,C4	1.406
O1,C6	0.010	C4,C5	1.410
O1,C7	0.018	C5,C6	1.319
C1,C2	1.227	C6,C7	1.487
C1,C3	0.073	Na1,O1	0.174
C1,C4	0.014	Na1,C1	0.041
C1,C5	0.025	Na1,C2	0.032
C1,C6	0.023	Na1,C3	0.081
C1,C7	0.061	H7,C7	0.941
C2,C3	1.232	H7,H7′	0.021