Face-to-face stacking of dianionic quinoid rings in crystals of alkali salts of 2,5-dihydroxyquinone in view of π –system polarization

Supporting Information

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Table S1 Crystallographic, data collection and structure refinement details for **$Li_2DHQ{\cdot}2H_2O$ (**redetermination **)**.

Compound	**$Li_2DHQ{\cdot}2H_2O$**
Empirical formula	$C_6H_4Li_2O_5$
Formula wt. / g mol^{-1}	187.99
Crystal dimensions / mm	0.11 x 0.05 x 0.02
Space group	*C* 2/*m*
a / Å	15.9708(7)
b / Å	6.4417(2)
c / Å	7.9093(3)
α / °	90
β / °	116.462(5)
γ / °	90
Z	4
V / Å^3	728.45(5)
D_{calc} / g cm^{-3}	1.714
μ / mm^{-1}	1.305
Θ range / °	6.19 – 76.05
T / K	293(2)
Radiation vawelength	1.54179 (Cu*K*α)
Diffractometer type	Xcalibur Nova
Range of *h*, *k*, *l*	–18 < *h* < 19; –5 < *k* < 8; –9 < *l* < 9
Reflections collected	1618
Independent reflections	818
Observed reflections ($I \geq 2\sigma$)	758
Absorption correction	Multi-scan
R_{int}	0.0157
R (F)	0.0363
R_w (F^2)	0.1084
Goodness of fit	1.081
H atom treatment	Free
No. of parameters	96
No. of restraints	3
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (eÅ^{-3})	0.299; -0.269

Table S2 Primitive unit cell parameters of the experimental and calculated structures.

	a / Å	b / Å	c / Å	α / °	β / °	γ / °	rel. energy[2] /kJ mol^{-1}
Na_2DHQ–A	3.73	9.93	7.71	90.0	100.7	90.0	0.0
Na_2DHQ–B [1]	6.08	8.12	7.54	122.4	113.3	90.5	107.95
Na_2DHQ–C	3.73	9.93	7.72	90.0	100.7	90.0	0.0
K_2DHQ–X-ray	3.93	11.24	8.33	90.0	102.8	90.0	–
K_2DHQ–A	4.00	10.59	8.38	90.1	103.5	90.0	0.0
K_2DHQ–B [1]	6.80	8.14	7.95	120.8	115.3	90.0	27.31
K_2DHQ–C	3.56	11.26	8.11	90.0	90.1	81.0	27.25
Rb_2DHQ– X-ray [1]	7.23	8.17	8.28	120.0	115.9	90.0	–
Rb_2DHQ–A	4.42	11.07	8.37	90.0	100.8	90.1	10.62
Rb_2DHQ–B [1]	7.50	8.12	8.19	119.7	117.2	90.0	0.0
Rb_2DHQ–C	3.82	11.99	8.11	89.8	89.0	90.2	10.12
$(NH_4)_2DHQ$–X-ray [1]	7.03	8.24	8.24	60.1	64.8	64.8	–
$(NH_4)_2DHQ$–B [1]	6.94	8.23	8.23	61.7	65.0	65.1	–
Cs_2DHQ–X-ray [1]	3.89	7.64	7.64	114.6	90.0	90.0	–
Cs_2DHQ–B [1]	8.21	8.17	8.43	119.0	119.1	90.0	2.28
Cs_2DHQ–C	4.13	12.21	8.16	90.0	89.8	89.7	0.0

1) The crystallographic centered unit cells in Table 4 are transorfmed into primitive ones prior to calculations.
2) Relative energies are given in respect to the lowest energy structure of the given salt

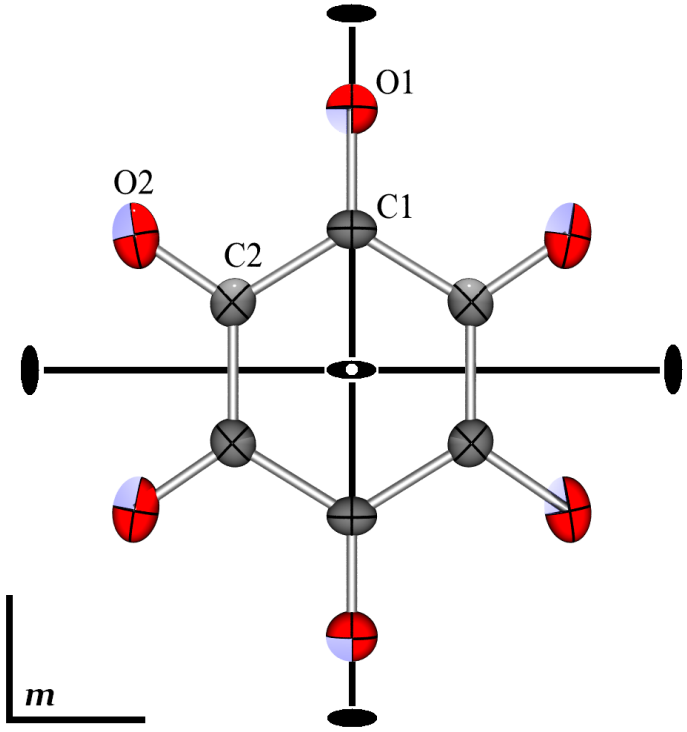

Figure S1 ORTEP-3 drawing of a disordered DHQ^{2-} anion in Cs_2DHQ with symmetry elements shown. Due to a disorder, hydrogen atom could not be located; O2 atom and C-attached H are partly populated (pp = 0.25). Displacement ellipsoids are drawn at the probability level of 50 % and hydrogen atoms are depicted as spheres of arbitrary radii.

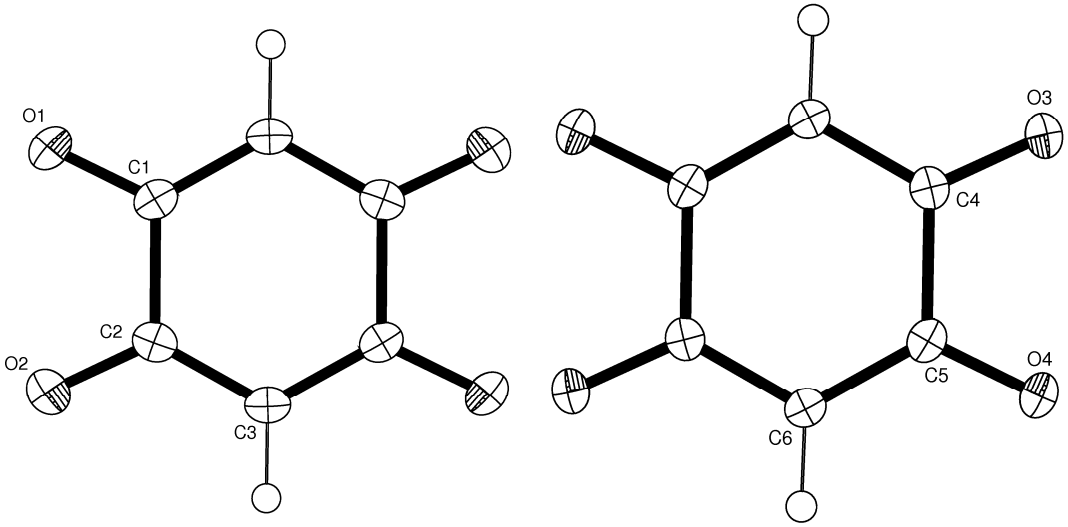

Figure S2 ORTEP-3 drawing of two symmetry-independent DHQ^{2-} anions in $Li_2DHQ{\cdot}2H_2O$. Displacement ellipsoids are drawn at the probability level of 50 % and hydrogen atoms are depicted as spheres of arbitrary radii.

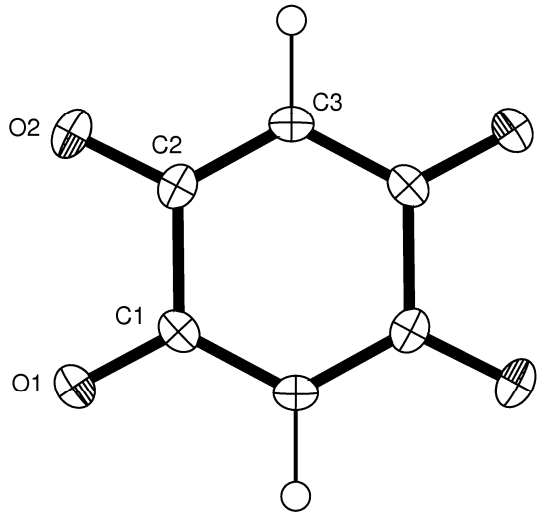

Figure S3 ORTEP-3 drawing of DHQ^{2-} anion in Rb_2DHQ. Displacement ellipsoids are drawn at the probability level of 50 % and hydrogen atoms are depicted as spheres of arbitrary radii.

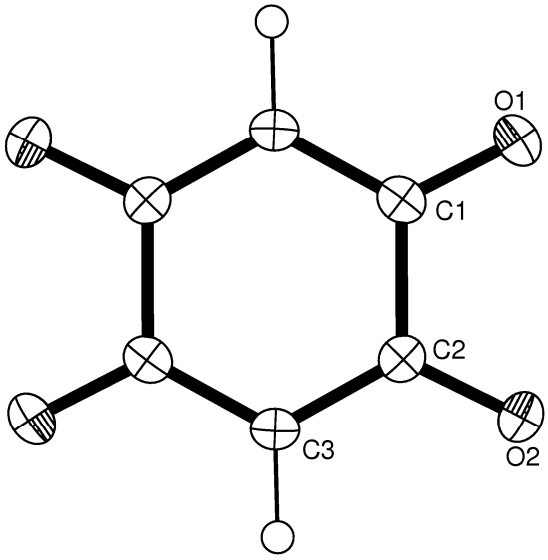

Figure S4 ORTEP-3 drawing of DHQ^{2-} anion in $(NH_4)_2DHQ$. Displacement ellipsoids are drawn at the probability level of 50 % and hydrogen atoms are depicted as spheres of arbitrary radii.

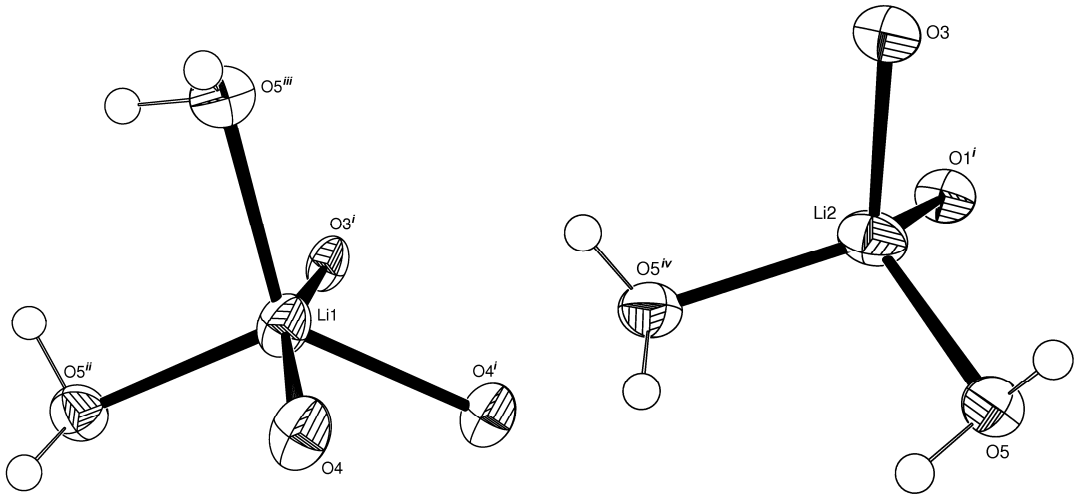

Figure S5 ORTEP-3 drawing of different coordination spheres in two symmetry-independent lithium cations in $Li_2DHQ{\cdot}2H_2O$. The penta-coordination of Li1 is between trigonal bipyramid and square-pyramid with Li···O distances ranging from 1.995(4) to 2.110(2) Å. The tetrahedral environment about Li2 with Li2···O distances form 1.908(4) to 2.027(2) Å. Displacement ellipsoids are drawn at the probability level of 50 % and hydrogen atoms are depicted as spheres of arbitrary radii. Symmetry operators: *i*) $1 - x, y, 2 - z$; *ii*) $-1/2 + x, -1/2 - y, z$; *iii*) $-1/2 + x, 1/2 + y, z$; *iv*) $x, -y, z$.

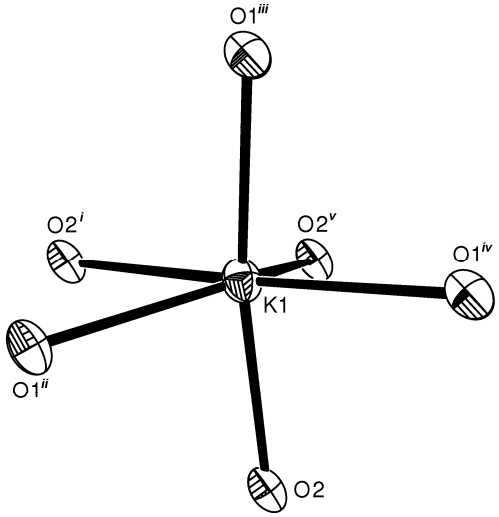

Figure S6 ORTEP-3 drawing of the cation distorted octahedral environment in K_2DHQ with K···O1^{ii} = 2.779(2), K···O1^{iii} = 2.817(2), K···O1^{iv} = 3.010(2), K···O2 = 2.700(1), K···O2^{i} = 2.724(1), K···O2^{v} = 2.745(1) Å. Displacement ellipsoids are drawn at the probability level of 50 % and hydrogen atoms are depicted as spheres of arbitrary radii. Symmetry operators: *i*) $1 + x, y, z$; *ii*) $-1 - x, -1/2 + y, 3/2 - z$; *iii*) $-1 - x, 1 - y, 1 - z$; *iv*) $-x, -1/2 + y, 3/2 - z$; *v*) $-x, 1 - y, 2 - z$.

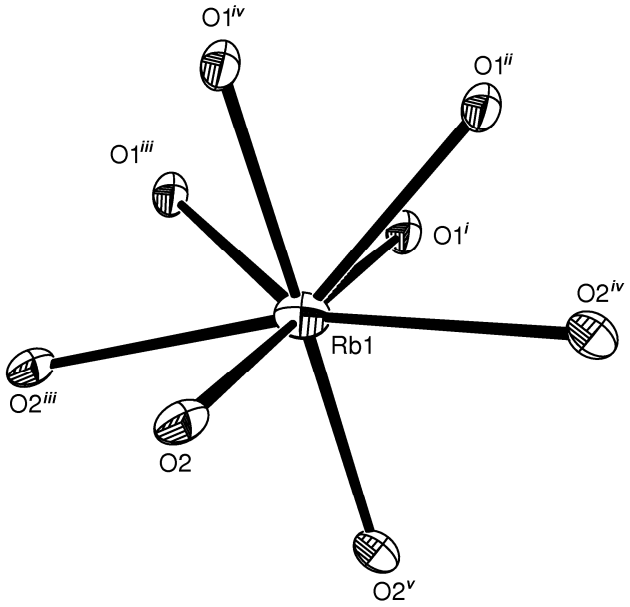

Figure S7 ORTEP-3 drawing of cation octa-coordination sphere in Rb_2DHQ. Rb^+ is located at the special position on the twofold rotation axes (8 g) 0, *y*, ¼ of *Ibam* space group. Rb1···O1^{i} and Rb···O1^{ii} = 2.974(3) Å, Rb···O1^{iii} and Rb···O1^{iv} = 2.983(3) Å; Rb···O2 and Rb···O2^{v} = 3.011(3) Å; Rb···O2^{iii} and Rb···O2^{iv} = 3.286(3) Å. Displacement ellipsoids are drawn at the probability level of 50 % and hydrogen atoms are depicted as spheres of arbitrary radii. Symmetry operators: *i*) –1/2 + *x*, 1/2 + *y*, 1/2 + *z*; *ii*) 1/2 – *x*, 1/2 + *y*, –*z*; *iii*) 1/2 – *x*, 1/2 – *y*, 1/2 + *z*; *iv*) –1/2 + *x*, 1/2 – *y*, –*z*; *v*) –*x*, *y*, 1/2 – *z*.

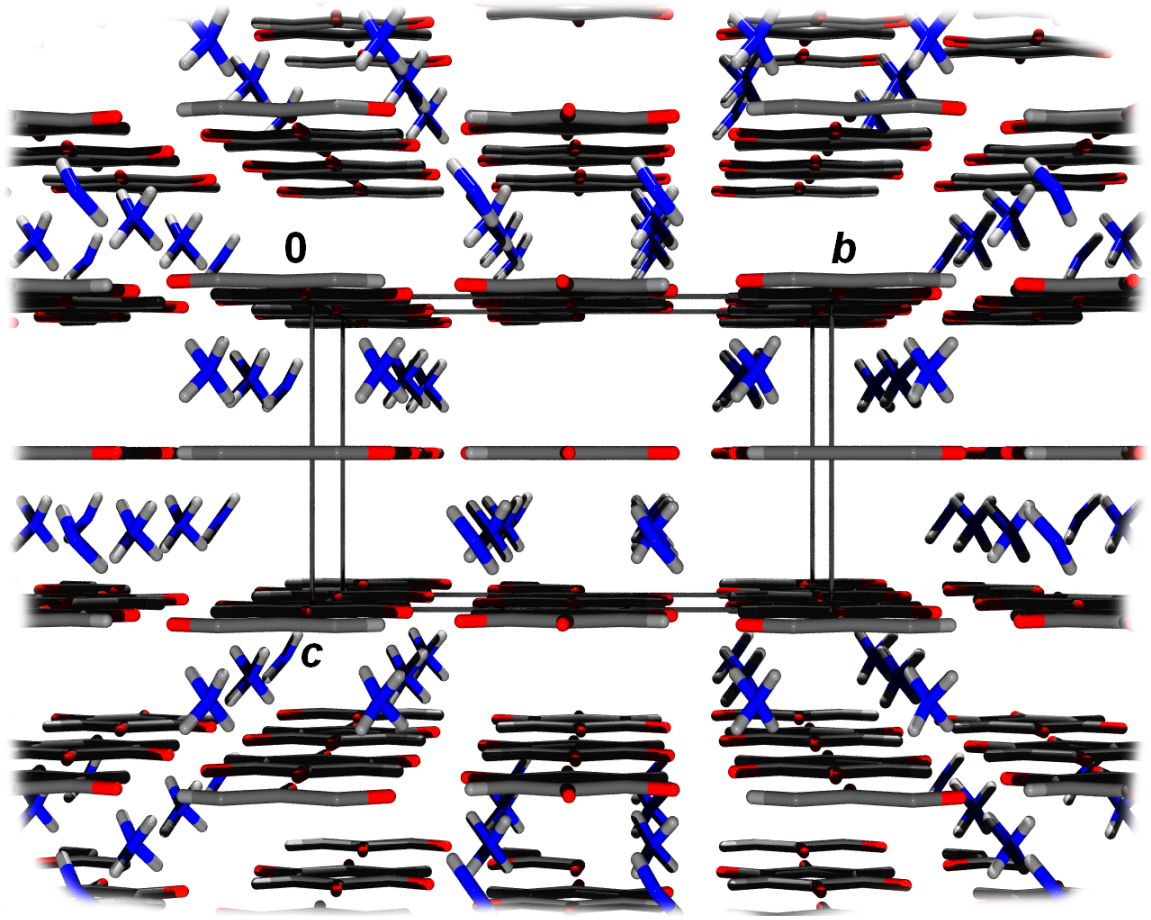

Figure S8 Crystal packing of **$(NH_4)_2$DHQ** viewed in the direction [100]. DHQ^{2-} anions are located on a crystallographic mirror plane and are therefore parallel.

Computational details

The basis sets used in the calculations are Gaussian sets designed for solid state calculations with the Crystal program (http://www.crystal.unito.it/). They were taken from the web page: http://www.tcm.phy.cam.ac.uk/~mdt26/crystal.html. The references to papers with the details on their use are included in the tables listed below. The format is appropriate for Gaussian 09.

Title: **hydrogen atom**
Author: M. D. Towler
Ref.: A. R. Porter, M. D. Towler, R. J. Needs, Muonium as a hydrogen analogue in silicon and germanium: Quantum effects and hyperfine parameters, Phys. Rev. B **60** (1999) 13534-13546

```
H 0
S  8 1.0
50362.3    0.00000020
29510.2    0.00000104
 4251.44   0.00001154
  827.084  0.00007679
  193.406  0.00043129
   50.0397 0.00219849
   13.7402 0.01055974
    3.9009 0.04760939
S  2 1.0
    1.1397 0.18487289
    0.346  0.47812170
S  1 1.0
    0.109  1.0
P  1 1.0
    0.1098 1.0
```

Title: **carbon "6-21G*"**
Author: Pople et al. (modified by M. Catti)
Refs.: M. Catti, A. Pavese, R. Dovesi, V. R. Saunders, Static lattice and electron properties of MgCO3 (magnesite) calculated by abinitio periodic Hartree-Fock methods, Phys. Rev. B **47** (1993) 9189-9198

Modified by M. D. Towler for carbon graphite

```
C 0
S  6 1.0
3047.52490     0.0018347
 457.369510    0.0140373
 103.948690    0.0688426
  29.2101550   0.2321844
   9.28666300  0.4679413
   3.16392700  0.3623120
SP 1 1.0
   8.4379430   1.0   1.0
SP 1 1.0
   1.88128850  1.0   1.0
SP 1 1.0
   0.58550980  1.0   1.0
```

```
SP 1 1.0
   0.1808      1.0   1.0
D  1 1.0
   0.8325      1.0
```

Title: nitrogen "6-21G*"
Author: Pople et al.
Ref.: R. Dovesi, M. Causa, R. Orlando, C. Roetti, V. R. Saunders, Ab initio approach to molecular-crystals - a periodic Hartree-Fock study of crystalline urea, J. Chem. Phys. **92** (1990) 7402-7411

```
N 0
S  6 1.0
 4150.0    0.001845
  620.1    0.01416
  141.7    0.06863
   40.34   0.2286
   13.03   0.4662
    4.47   0.3657
SP 2 1.0
    5.425 -0.4133 0.238
    1.149  1.224  0.859
SP 1 1.0
    0.2832 1.0    1.0
D  1 1.0
    0.8    1.0
```

Title: oxygen "6-21G*"
Author: J. S. Binkley, J. A. Pople, W. J. Hehre, Self-consistent molecular-orbital methods. 21. Small split-valence basis-sets for 1st-row elements, J. Am. Chem. Soc. **102** (1980) 939-947; M. S. Gordon, J. S. Binkley, J. A. Pople, Self-consistent molecular-orbital methods .22. Small split-valence basis-sets for 2nd-row elements, J. Am. Chem. Soc. **104** (1982) 2797-2803
Ref.: R. Dovesi, M. Causa, R. Orlando, C. Roetti, V. R. Saunders, Ab initio approach to molecular-crystals - a periodic Hartree-Fock study of crystalline urea, J. Chem. Phys. **92** (1990) 7402-7411

```
O 0
S  6 1.0
5.472E+03 1.832E-03
8.178E+02 1.410E-02
1.864E+02 6.863E-02
5.302E+01 2.294E-01
1.718E+01 4.664E-01
5.912E+00 3.642E-01
SP 2 1.0
7.403E+00-4.045E-01 2.446E-01
1.576E+00 1.222E+00 8.540E-01
SP 1 1.0
3.737E-01 1.000E+00 1.000E+00
D  1 1.0
8.000E-01 1.000E+00
```

Title: sodium "8-511G"
Comment: optimized in NaCl
Refs.: M. Prencipe, A. Zupan, R. Dovesi, E. Apra, V. R. Saunders, Ab-initio study of the structural-properties of LiF, NaF, KF, LiCl,

NaCl, and KCl,Phys. Rev. B **51** (1995) 3391-3396; E. Apra, M. Causa, M. Prencipe, R. Dovesi, V. R. Saunders, On the structural-properties of NaCl - An ab initio study of the B1-B2 phase-transition, J. Phys. Condens. Matter **5** (1993) 2969-2976

```
Na 0
S  8 1.0
 56700.0    0.000225
  8060.0    0.00191
  1704.0    0.01105
   443.6    0.05006
   133.1    0.1691
    45.8    0.3658
    17.75   0.3998
     7.38   0.1494
SP 5 1.0
   119.0   -0.00673 0.00803
    25.33  -0.0798   0.0639
     7.80  -0.0793   0.2074
     3.00   0.3056   0.3398
     1.289  0.5639   0.3726
SP 1 1.0
     0.578  1.0      1.0
SP 1 1.0
     0.323  1.0      1.0
```

Title: **potassium**
Comments: optimized in KCl (K +1), extra d-shell in K2O essential for accurate C44 elastic constant
Refs.: R. Dovesi, C. Roetti, C. Freyriafava, M. Prencipe, V. R. Saunders, On the elastic properties of lithium, sodium and potassium oxide - An ab initio study, Chem. Phys. **156** (1991) 11-19

```
K 0
S  8 1.0
 172500.0     0.000220
  24320.0     0.00192
   5140.0     0.01109
   1343.9     0.04992
    404.5     0.1702
    139.4     0.3679
     54.39    0.4036
     22.71    0.1459
SP 6 1.0
    402.0    -0.00603 0.00841
     93.5    -0.0805   0.0602
     30.75   -0.1094   0.2117
     11.92    0.258    0.3726
      5.167   0.684    0.4022
      1.582   0.399    0.186
SP 5 1.0
     17.35   -0.0074  -0.0321
      7.55   -0.129   -0.062
      2.939  -0.6834   0.1691
      1.19    1.08     1.500
      0.674   1.03     1.060
SP 1 1.0
      0.389   1.0      1.0
SP 1 1.0
      0.216   1.0      1.0
```

```
D  3 1.0
      3.94    0.160
      1.072   0.313
      0.394   0.406


Title:    Rb+ all electron basis
Author:   C. Zicovich Wilson
When:     1995
Refs:     unpublished

Rb 0
S  9 1.0
 2953550.000000       0.000034
  420969.000000       0.000298
   81358.700000       0.002060
   18877.300000       0.011200
    5164.480000       0.047800
    1622.390000       0.157300
     573.192000       0.352400
     221.489000       0.423500
      89.080900       0.151900
SP 7 1.0
    6647.380000      -0.000333       0.000875
    1508.870000      -0.006260       0.008570
     435.794000      -0.059000       0.055900
     146.168000      -0.146600       0.220000
      56.172200       0.242500       0.447900
      23.626100       0.708000       0.395500
       9.797900       0.222700       0.089900
SP 6 1.0
     180.092000       0.001090      -0.010500
      53.295200      -0.030400      -0.074900
      19.313200      -0.350600       0.076900
       7.943500       0.289600       1.003900
       3.171400       1.054700       1.227300
       1.070600       0.151700       0.196700
D  5 1.0
     288.005000       0.004180
      83.137700       0.036080
      29.003600       0.163320
      10.918500       0.393700
       4.116200       0.473820
D  1 1.0
       1.472200       1.0
SP 3 1.0
       3.381600      -0.664900      -0.194000
       1.421100      -0.580600       0.592600
       0.566900       2.913700       2.705300
SP 1 1.0
       0.208300       1.0            1.0


Title:    caesium
Author:   M.D. Towler
When:     May 1996

Cs 0
S  9 1.0
 5091567.0     0.0000487
  738658.0     0.000401
```

```
  160308.0     0.002290
   41490.2     0.011130
   12040.1     0.046000
    3845.22    0.153500
    1368.4     0.348
     545.478   0.4323
     229.8491  0.2042
SP 7 1.0
   14926.078  -0.000349 0.001090
    3459.0    -0.00632  0.00995
    1071.0    -0.0518   0.057600
     386.043  -0.1462   0.2171
     158.325   0.0889   0.457600
      73.9081  0.617    0.4702
      36.2394  0.5006   0.2275
SP 6 1.0
     363.971   0.00632 -0.0129
     137.485  -0.0238  -0.0733
      56.6146 -0.3172   0.00223
      25.8734 -0.0706   0.8454
      12.3291  0.9066   1.3707
       5.978   0.4774   0.4984
D  6 1.0
     426.715   0.0145
     127.457   0.1005
      47.9214  0.3177
      20.0956  0.4689
       9.1352  0.2873
       4.0878  0.0496
SP 3 1.0
       9.7098  0.488   -0.109
       5.69    0.1631   0.2356
       2.7177  0.0711  -0.0248
D  3 1.0
       7.9974  0.2128
       3.2744  0.5687
       1.3821  0.4271
D  1 1.0
       0.5496  1.0
SP 3 1.0
       4.8272  0.1174   0.3367
       2.4442  1.0941   1.3927
       1.1623  0.6078   0.5449
SP 1 1.0
       0.4725  1.0      1.0
SP 1 1.0
       0.1789  1.0      1.0
```