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The Sodium(benzo-15-crown-5) Salt of 2,6-Di(*tert*-butyl)-4-methylphenol, a Sodium Phenolate with an Extremely Short $Na^+\cdots O^-$ Distance: Structure and Density Functional Calculations

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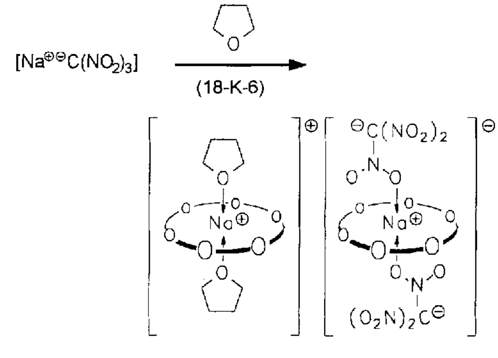
The structure of crystals, isolated in low yield, from the attempted metallation of diphenylmethane in tetrahydrofuran solution containing benzo-15-crown-5 at a sodium metal mirror is determined, surprisingly, to be the sodium (benzo-15-crown) salt of 2,6-di(*tert*-butyl)-4-methylphenol, an antioxidative stabilizer to prevent ether peroxide formation. The structure of the solvent-shared contact ion pair (monoclinic $P2_1/n$, $Z = 4$, $R_1 = 0.06$) proves a strong $Na^+\cdots O^-$ interaction at the extremely short distance of only 216 pm, a sixfold O-coordination of the Na^+ cation in a pentagonal pyramid, and a hemispherical distortion of the crown ether. Density functional calculations at the B3LYP/6-31G* level, based on the structural data, reproduce, within a one-dimensional hypersurface approach, the rather short $Na^+\cdots O^-$ distance, and predict Mulliken charges of +0.32 for Na^+ and −0.71 for O^-, as well as a considerable polarization of the trialkyl phenolate anion.

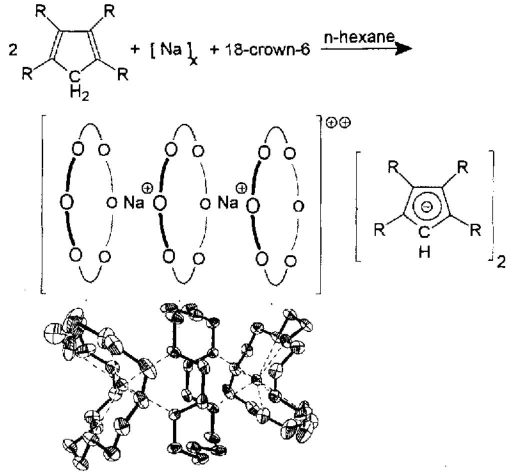
Recent Results of Alkalimetal Complexation in Crown Ethers

The selective complexation of crown ethers, in particular with alkali metal cations, has been extensively investigated[2][3][4][5]. Nevertheless, rather unexpected results are still reported, such as the crystallization of a solvent-separated contact ion quadruple from a THF solution of sodium trinitromethanide on addition of 18-crown-6, the structure of which provides evidence for 18-crown-6 solvated Na^+ centres in both the cation and the anion complexes[6] (1).



(1)

The tripledecker dication in the solvent-separated contact ion triple[6], which crystallized after sodium metal mirror deprotonation of tetraphenylcyclopentadiene in *n*-hexane solution with surplus 18-crown-6 ($R = C_6H_5$), is unprecedented (2).



(2)

Due to sixfold O coordination of the two Na^+ cations to each of the outer ligands and only two $Na^+\cdots O$ contacts to the central ligand, the macrocyclic rings are distorted differently: to hemispherical and rectangular shapes[7].

Here we report on a product obtained serendipitously in an attempt to metallate diphenylmethane in a tetrahydrofuran solution, containing benzo-15-crown as an antioxidative stabilizer, at a sodium metal mirror (see Experimental

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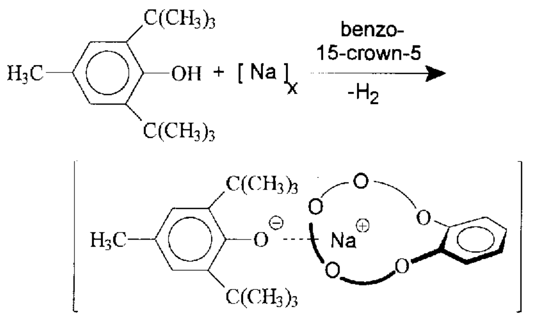
[◇] Part 117: Ref.[1].

Section). The product unexpectedly isolated in low yield, according to the structure determined, is the (benzo-15-crown-5)Na^+ salt of 2,4-di(*tert*-butyl)-4-methylphenol, the additive to prevent ether peroxide formation (3).



(3)

The structural analysis proves a sixfold O-coordinated Na^+ centre in a distorted pentagonal pyramid, with the hemispherically distorted benzomacrocycle as its base The $Na^+\cdots{}^-O$ distance is the shortest so far observed, indicating a strong interaction within the contact ion pair. This has been confirmed by density functional calculations.

Structural Results and Discussion

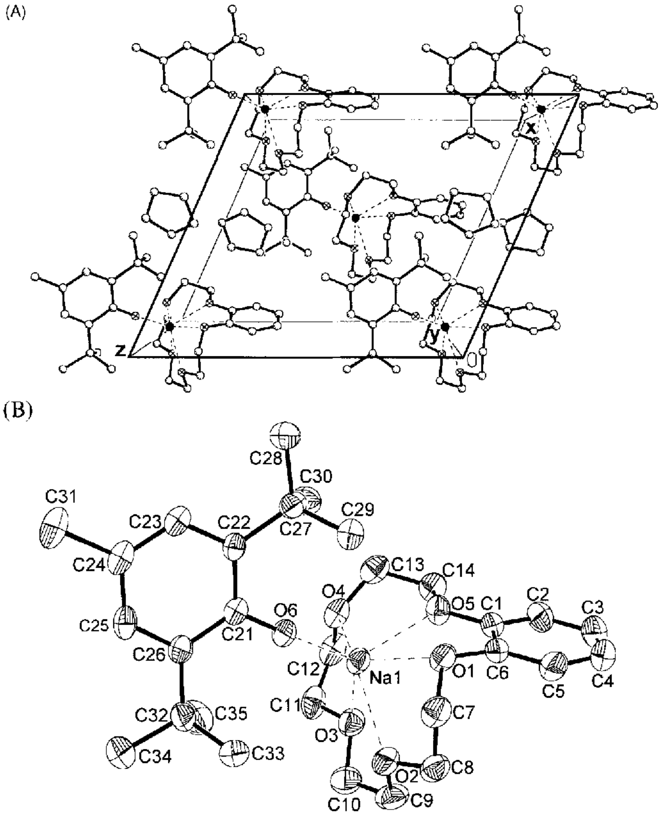
Structure of the Contact Ion Pair: The title compound crystallizes in the monoclinic space group $P2_1/n$ with four molecular ion pairs in the unit cell (Figure 1: A). One THF molecule, not coordinated to the counter cation, is located in the holes of the structure.

The sodium counter cation is connected to one phenolate anion and surrounded by one crown ether ligand. The result is a distorted pentagonal pyramid, as the coordination polyhedron, with the phenolate oxygen anion at the top and the five crown ether oxygen centres in the basal plane (Figure 1: B). The sodium cation is located 1.04 Å above the mean plane, calculated through the oxygen centres of the macrocyclic ring, with contact $Na^+\cdots O$ distances varying only slightly in the range 2.47–2.51 Å. In contrast, the considerably shorter $Na^+\cdots O^-$ distance to the phenolate oxygen anion centre amounts to only 2.16 Å (Table 2). The phenolate anion coordinates nearly in the direction of its C–O vector with an angle $C-O^-\cdots Na^+$ of 173 °, and the Na^+ counter cation is located only 0.44 Å above its mean plane (Figure 1: B).

The one-sided Na^+ ion pairing significantly distorts the conformation of the benzo-15-crown-5 to a hemispherical cone (2) with the benzene ring pointing away from the counter cation (Figure 1: B).

The phenolate anion skeleton is planar within experimental error (Figure 1: B), and the individual centres exhibit a maximum deviation of only 2 Å. On phenolate anion formation, the C–O bond is shortened by about 0.09 Å to 1.30 Å and the *ipso* angle, C22–C21–C26, at the O-substitution centre C21[8] decreases from 122 ° to about 118° as expected (Table. 2).

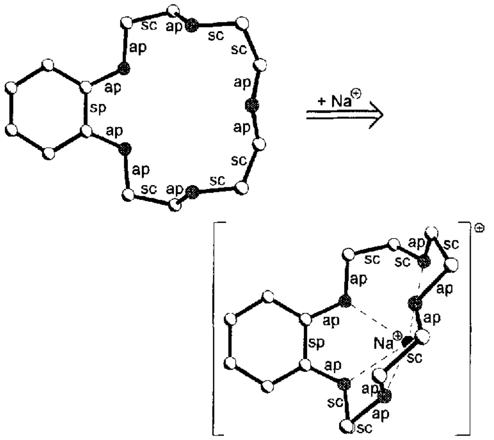
Figure 1. Crystal structure of (benzo-15-crown-5-THF)sodium 1,6-di(*tert*-butyl)-4-ethylphenolate at 150 K: (A) unit cell viewed along the *b* axis and (B) structure of the contact ion pair with numbering (Na^+ coordination dotted lines, displacement ellipsoids drawn at the 50% probability level)



Structural Changes of the Benzo-15-crown-5 Ligand on Ion Pair Formation: A search in the Cambridge Structural Database for known structures of benzo-15-crown-5 sodium complexes reveals 17 entries[9]: Three refer to analogous picrate ion pairs[8], two to solvent-separated ion pairs, in which one additional water molecule completes the coordination sphere of the sodium cation, and two with tetraphenylborate and perchlorate anions, in which the counter cation is surrounded by two crown ether ligands. In all structures with sixfold-coordinate Na^+ cations connected to an additional neutral or negatively charged centre, they are located within distorted pentagonal pyramids. In complexes with neutral ligands such as water molecules, shorter $Na^+\cdots O$ distances to the macrocyclic polyether, between 2.26 and 2.43 Å, are observed[10][11].

The rather short $Na^+\cdots O^-$ contact distance of only 2.16 Å, determined between the crown ether complexed sodium counter cation and the phenolate oxygen anion centre (Figure 1 and Table 2), indicates a strong ion pair interaction, which is confirmed by the density functional calculation results discussed later: The Na^+ cation is pulled out of the hemispherically distorted benzo-15-crown-5 ligand to a position 1.04 Å above the mean basal plane, calculated through its oxygen centres, from which $Na^+\cdots O$ distances of between 2.40 and 2.51 Å result. A search in the Cambridge Structural Database for sodium phenolate fragments shows the nearest equivalent distances to be at 2.25 and 2.28 Å[12] i.e. elongated by 0.09 and 0.12 Å relative to the $Na^+\cdots{}^-O$ distance in the title ion pair.

The conformation of the benzo-15-crown-5 changes drastically on one-sided complexation by the Na^+ cation. Within the ususal notation (*ap*: antiperiplanar; *sc*: synclinal; *sp*: synperiplanar)[7], the C_s-symmetric conformation of the uncomplexed macrocyclic ether[13] can be characterized by two arrangements, (*sc,sc,ap*) and (*ap,sc,ap*), for the subunits $-O-CH_2-CH_2-O-$, and (*ap,sp,ap*) for the geometrically restricted one, which inorporates the benzene ring. The pairs of adjacent antiperiplanar O−C bonds around the two *ortho*-benzene oxygen centres orient the six-membered ring nearly parallel to the 15-membered one of the polyether macrocyle, with an angle of only 20 ° relative to an idealized plane through its five oxygen centres (4).



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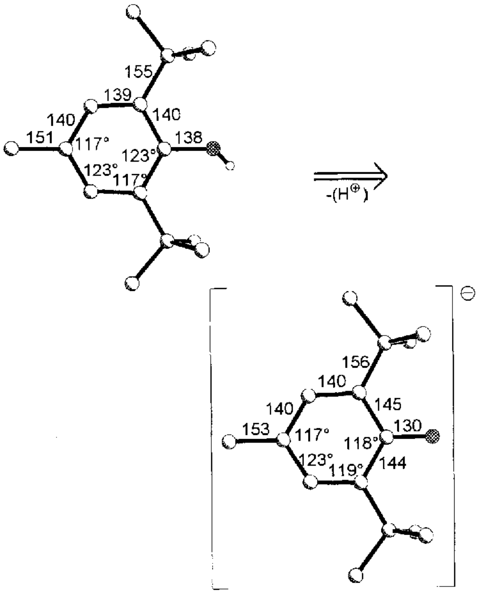


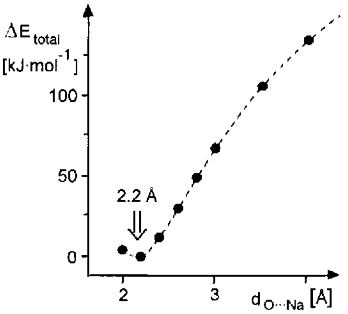
(5)

In the Na^+ complex, the conformational sequence around the benzene ring anchor remains constant (*ap,sp,ap*), but the adjacent subunits $-O-CH_2-CH_2-O-$ already change their conformation from (*ap,sc,ap*) to either (*ap,sc,sc*) or even to (*sc,ap,ap*) and twist half of the polyether macrocycle almost perpendicular to the benzene ring. This rather drastic deformation can be characterized by an interplanar angle of 60 °, relative to the mean plane of the polyether oxygen centres.

Structural Changes on Deprotonation of 2,6-Di(tert-butyl)-4-methylphenol:[14][15] Deprotonation to its anion causes considerable charge perturbation[15][17]: the bond length C−O is shortened by 0.08 Å to 1.30 Å, the *ipso* angle at the O^- substitution centre decreases by 5 ° to 118 °, and the adjacent C−C bonds are stretched by about 0.05 Å to 1.45 Å. (Table 2) (5). The structural distortions are comparable to those in other phenolate salts[12][17] and can be traced to the negative charge, which according to the density functional calculation is largely located at the phenolate oxygen centre.

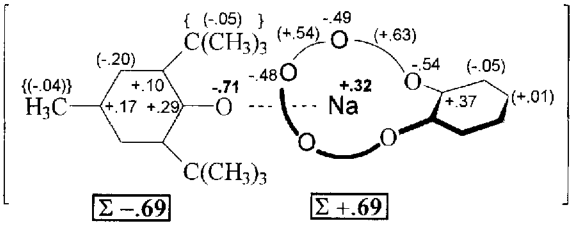
Density Functional Calculations

Based on the structural coordinates determined experimentally (Figure 1 and 2), the O···Na distance between the phenolate anion and the sodium cation coordinated to the benzo-15-crown-5 ligand has been varied step-wise between 2 and 8 Å (see Experimental Section) without additional geometry optimization. The resulting approximate one-dimensional hypersurface exhibits a local minimum at about 2.2 Å (6), in satisfactory agreement with the unexpectedly short gap of only 2.16 Å measured for the contact ion pair $[(H_{23}C_{15})O^-\cdots Na^+(O_5C_{14}H_{20})]$.



(6)

In addition, from the total energies calculated for the components it is estimated that the Na^+ complexation in the benzo-15-crown-5 should stabilize by −380 kJ mol^{-1} and the ion pair formation by −367 kJ mol^{-1}. Accordingly, the product, isolated in low yield from the sodium metal mirror reduction of the trialkylphenol antioxidative stabilizer in its extremely dilute THF solution, is thermodynamically rather a favourable one.



(7)

Based on the crystal structure, and with a 631-G* basis set at a B3LYP level, the charge densities shown in (7) result for the contact ion pair in the local minimum depicted in (6) at the shortest O···Na distance reported so far.[12]

The total charges [(7): Σ] calculated are −0.69 for the phenolate anion and +0.69 for the (benzo-15-crown-5) so-

Table 1. Crystal data and structure refinement for $C_{15}H_{23}ONa \cdot C_{10}H_{20}O_5 \cdot C_4H_{10}O$

molecular weight	584.7	crystal habit	light yellow blocks
temp [K]	150	2θ range	($3° \le 2\theta \le 46°$)
cryst. system	monoclinic	refl. measured	5567
space group	$P2_1/n$ (No. 14)	refl. independent	4542
a [Å]	12.188(1)	R_{int}	0.0210
b [Å]	20.801(2)	refl. > $F_o > 4\sigma(F_o)$	3332
c [Å]	14.202(1)	parameters	397
β [°]	113.64(1)	$R1$ for $F_o > 4\sigma(F_o)$	0.0602
V [Å^3]	$3298.5(7) \cdot 10^6$	$R1$ for all data	0.0874
$F(000)$	1272	$wR2$ for $F_o > 4\sigma(F_o)$	0.1600
$\rho_{calcd.}$ [g•cm^{-3}]	1.178	wR for all data	0.1874
Z	4	Goodness of fit	1.043
μ [mm^{-1}]	0.09	D(r) [e/Å^3]	0.61/−0.37
crystal size [mm]	0.6 × 0.4 × 0.3	weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0888 \cdot P)^2 + 4.37\,P]$

Table 2. Selected bond lengths [Å] and angles [°] for [(benzo-15-crown-5)(THF)sodium]$^+$[1,6-di(*tert*-butyl)-4-methyl-phenolate]$^-$ (with estimated standard deviations)

O(1)−Na(1)	2.467(3)	O(2)−Na(1)	2.472(3)
O(3)−Na(1)	2.429(3)	O(4)−Na(1)	2.510(3)
O(5)−Na(1)	2.449(3)	O(6)−Na(1)	2.156(3)
O(6)−C(21)	1.303(4)	C(21)−C(22)	1.443(5)
C(21)−C(26)	1.454(5)	C(22)−C(23)	1.402(5)
C(22)−C(27)	1.545(5)	C(23)−C(24)	1.395(5)
C(24)−C(25)	1.396(5)	C(24)−C(31)	1.527(5)
C(25)−C(26)	1.396(5)	C(26)−C(32)	1.536(5)
C(27)−C(30)	1.542(5)	C(27)−C(28)	1.543(5)
C(27)−C(29)	1.548(5)	C(32)−C(35)	1.540(6)
C(32)−C(33)	1.548(5)	C(32)−C(34)	1.550(5)
O(6)−C(21)−C(22)	121.3(3)	O(6)−C(21)−C(26)	121.2(3)
C(22)−C(21)−C(26)	117.5(3)	C(23)−C(22)−C(21)	119.4(3)
C(23)−C(22)−C(27)	121.1(3)	C(21)−C(22)−C(27)	119.5(3)
C(24)−C(23)−C(22)	123.1(3)	C(23)−C(24)−C(25)	117.3(3)
C(23)−C(24)−C(31)	121.9(3)	C(25)−C(24)−C(31)	120.8(3)
C(24)−C(25)−C(26)	123.3(3)	C(25)−C(26)−C(21)	119.2(3)
C(25)−C(26)−C(32)	121.6(3)	C(21)−C(26)−C(32)	119.2(3)
C(30)−C(27)−C(28)	107.4(3)	C(30)−C(27)−C(22)	110.0(3)
C(28)−C(27)−C(22)	112.7(3)	C(30)−C(27)−C(29)	110.0(3)
C(28)−C(27)−C(29)	106.7(3)	C(22)−C(27)−C(29)	110.0(3)
C(26)−C(32)−C(35)	110.2(3)	C(26)−C(32)−C(33)	109.5(3)
C(35)−C(32)−C(33)	110.9(4)	C(26)−C(32)−C(34)	112.5(3)
C(35)−C(32)−C(34)	107.2(3)	C(33)−C(32)−C(34)	106.4(3)

dium cation complex. Far from postulating partial charges as real in a molecular crystal, even when obtained from density functional calculations, this result suggests a considerable charge delocalization in both contact ions, and even some bonding contribution between them. In detail, a charge density of −0.71 is predicted at the phenolate oxygen centre and a partial charge of only +0.32 at the sodium ion. Both the six-membered phenolate ring and the benzo-15-crown-5 ligand, however, are strongly polarized due to an extended charge delocalization. This points to the negative crown ether centres partly reflecting the effective nuclear charges in the skeletal framework and the considerably $C^{\delta-}-H^{\delta+}$ polarized bonds being averaged for the alkyl groups [(7): values in brackets]. The calculated densities are commented as follows: The Na^+ charge is largely distributed over the 15-centre macrocyclic ring, for which a total of +0.54 results, and the phenolate O^- charge partly delocalized into the 2,4,6-trialkyl-substituted phenyl ring as confirmed by the considerable distortions of the *ipso* angle and the adjacent C−C bonds (5) determined (Figure 1 and Table 2).

The density functional calculations help to rationalize the fact that the contact ion pair [trialkylphenolate$^{\delta-}\cdots Na^{\delta+}$(benzo-15-crown-5)] is a thermodynamically favourable reduction product (6) with a strong cation−anion interaction (7) at an exceptionally short O···Na distance.

Conclusions and Perspectives

The unexpected crystallization of the sodium(benzo-15-crown-5) salt of 2,6-di(*tert*-butyl)-4-methylphenol from a benzo-15-crown-5 containing THF solution in contact with a sodium metal mirror (see Experimental Section), suggests that for reductive metallations in THF its antioxidative stabilizer to prevent ether peroxide formation, has to be removed by reflux over a sodium/potassium alloy, sodium hydride or analogous active solvent-drying reagents for a longer period of time.

The structure determined for the title ion pair, not registered so far in the Cambridge Structural Database, exhibits interesting facets such as the six-fold oxygen coordination of Na^+ in a pentagonal pyramid, the considerable charge perturbation in the trialkyl phenolate anion and, above all, a rather short $Na^+\cdots O$ contact distance, which indicates a strong interaction as confirmed by density functional calculations.

Numerous perspectives result, ranging from the preparation of benzo-15-crown-5 sodium salts with smaller anions −OR, which might be even more strongly perturbed by a less delocalized negative charge, to the complexation of less fitting cations such as Li^+ or Cs^+.

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Experimental Section

Tetrahydrofuran: The solvent (Riedel-de Haën 2056), which contains 250 mg of 2,6-di(*tert*-butyl)-4-methylphenol (mp. 68−71°C) per liter as an antioxidative stabilizer, has been dried (presumably for too short a period of time) by contact with a sodium/potassium alloy.

Crystal Isolation: The reaction mixture resulting from 0.33 g (2 mmol) of diphenylmethane in 200 ml of THF containing 0.54 g (2 mmol) of benzo-15-crown-5 and 55 mg (2.4 mmol) of sodium, and evaporated at 10^{-6} mbar to form a metal mirror at the surface of a carefully dried Schlenk flask, has been concentrated by THF removal at 10^{-2} mbar. From the oily, orange colored, residue (kept at room temperature under argon) four light yellow crystals, each of 2 mm diameter, grew within a time period of several weeks. These were washed with diethyl ether. Yield: 95 mg (0.16 mmol) i.e. about 7 % based on the sodium metal and 70 % based on the phenol. − [$C_{15}H_{23}ONa \cdot C_{14}H_{20}O_5 \cdot C_4H_{10}O$] (584.7): calcd. C 67.78, H 9.14; found: C 68.04, H 8.96.

X-ray Structural Solution and Refinement: Crystal data collection, and refinement parameters are given in Table 1. Suitable crystals were covered with perfluorated polyether (RS 3000; Riedel-de Haënn), mounted on a glass fiber rod and cooled to 150 K under an N_2 flow. The data were measured on a Siemens P4 four-circle diffractometer, using Mo-K_α radiation, and corrected for Lorentz and polarization effects. The structure was solved using direct methods (SHELXS-86) and refined by full-matrix least-squares against F^2 (SHELXL-93). All C, O, and Na positions were refined anisotropically. All hydrogen atoms were placed in ideal positions and refined isotropically using the riding model. Three centres of the tetrahydrofurane molecule are disordered in two orientations and were refined isotropically using a split model. Due to this disorder, the oxygen atom could not be located and, therefore, all centres were refined as carbon atoms.

Density Functional Calculations: Both the single point as well as the energy hypersurface calculations were performed at the B3LYP level, with a 6-31G* basis set, using the program GAUSSIAN 94 with the NEC SX 4 computer of the Höchstleistungs-Rechenzentrum Stuttgart. The total energy for the experimentally determined structure amounts to −1744.64483795 a.u. For the components the following total energies were calculated: Na^+ −162.081228608 a.u., benzo-15-crown-5 −921.560737462 a.u., (benzo-15-crown-5)sodium −1083.78637722 a.u., and trialkylphenolate anion −660.718543001 a.u. The one-dimensional hypersurface has been approximated by increasing the distance between the phenolate anion and the (benzo-15-crown-5)sodium subunits between 2 and 3 Å in steps of 0.2 Å, and between 3 and 8 Å in steps of 0.5 Å (cf. discussion).

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