

A Second Modification of Potassium Fluorene and the Structure of Potassium 9-*tert*-Butylfluorene: Effect of Crystallization Conditions and Substituents on Solid-State Contact Ion Pair Interactions

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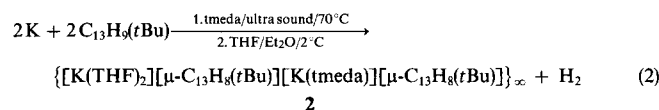
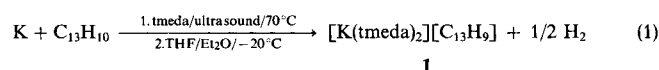
Crystallization of potassium fluorene or 9-*tert*-butylfluorene [formed from potassium metal and fluorene or 9-*tert*-butylfluorene in tetramethylethylenediamine (tmeda)] from a mixture of tmeda, tetrahydrofuran (THF) and diethyl ether yields $[K(tmeda)_2][C_{13}H_9]$ (**1**) or $\{[K(THF)_2][\mu-C_{13}H_8(tBu)][K(tmeda)][\mu-C_{13}H_8(tBu)]\}_\infty$ (**2**). Compound **1** is a monomeric solvated ion pair with one η^5 -coordinated fluorenyl and two chelating tmeda ligands and crystallizes in the monoclinic space group *C2/c*. Compound **1** is an example of polymorphism in organopotassium compounds, as a polymeric structure of **1** obtained

under slightly different crystallization conditions has been reported earlier. Compound **2** forms a polymeric chain with potassium coordinated to two anellated six-membered rings from two bridging 9-*tert*-butylfluorenyl systems and alternatingly solvated by one chelating tmeda or two THF. The crystal system for **2** is monoclinic, space group *P2₁/c*. A comparative AM1 study on the fluorenyl and 9-*tert*-butylfluorenyl anion suggests a steric origin for the haptotropic potassium shift in **2**. ¹H- and ¹³C-NMR data for **1** and **2** as well as for 9-*tert*-butylfluorene are reported.

The fundamental problem of determining major controlling factors in crystallization and their relative significance has become again a very active area of research^[1–3]. The question of „what crystallizes how and why”^[1] is especially vivid in the discussion of the solid-state interactions of the structurally rich organoalkali metal salts^[1,4]. For the latter there is a growing interest in solid-state structures of π compounds of the heavier congeners of lithium^[5–12]. On the other hand, metal complexes with fluorenyl as a ligand are also the subject of seminal structural investigations^[12–16].

In the context of molecular self-organization of organoalkali ion pairs a second solid-state modification of potassium fluorene as well as the structure of potassium 9-*tert*-butylfluorene are described in this paper. These structural investigations were initially carried out as a means of modeling the adsorption of potassium on graphite^[17] by interactions of potassium with extended molecular π systems.

formed. The precipitates were dissolved in a mixture of tetrahydrofuran (THF) and diethyl ether. Cooling yielded well-shaped orange-brown crystals of bis(tetramethylethylenediamine)potassium fluorene (**1**) and red crystals of bis(tetrahydrofuran)potassium-(tetramethylethylenediamine)-potassium bis(μ -9-*tert*-butylfluorene) (**2**), both of which are highly air-sensitive. The number of solvent molecules found in the crystal structure determinations matches the integration pattern in the ¹H-NMR spectrum.



Synthesis and Structural Characterization of $[K(tmeda)_2][C_{13}H_9]$ (**1**) and $\{[K(THF)_2][\mu-C_{13}H_8(tBu)][K(tmeda)][\mu-C_{13}H_8(tBu)]\}_\infty$ (**2**)

Metalation of the very weak hydrocarbon acid fluorene ($C_{13}H_{10}$) or of its 9-*tert*-butyl-substituted derivative $[C_{13}H_9(tBu)]$ was carried out here with metallic potassium in *N,N,N',N'*-tetramethylethylenediamine (tmeda) as a solvent^[18] (equations 1 and 2). To assure a rapid and quantitative reaction, the heterogeneous mixture was heated in an ultrasonic bath to 70°C (above the melting point of potassium metal). After 1 h all the potassium had been consumed and a deep brown-violet (**1**) or red-orange (**2**) slurry

The structures of **1** and **2** were determined by single-crystal X-ray diffraction analysis. In **1** the potassium ion shows a π interaction with the central five-membered ring of *only one* pentahapto-bound fluorenyl ligand (Figure 1). The potassium-to-carbon distances (ranging from 307 to 332 pm) are longer and vary more than in (cyclopentadienyl)potassium complexes (maximal variation there 296 to 310 pm)^[5,9,10]. The longer K–C contacts in **1** indicate an effective solvation of the potassium ion by the four nitrogen atoms of two chelating tmeda molecules which complete the coordination sphere around potassium and lead to the formation of a monomeric ion pair. Since the potassium ion sits on a special position (0, y , 1/4) along a twofold rotational

axis, the fluorenyl ligand – lying perpendicular to this axis – shows a crystallographically induced disorder, as shown in Figure 2. The disorder has been omitted in Figure 1 for clarity.

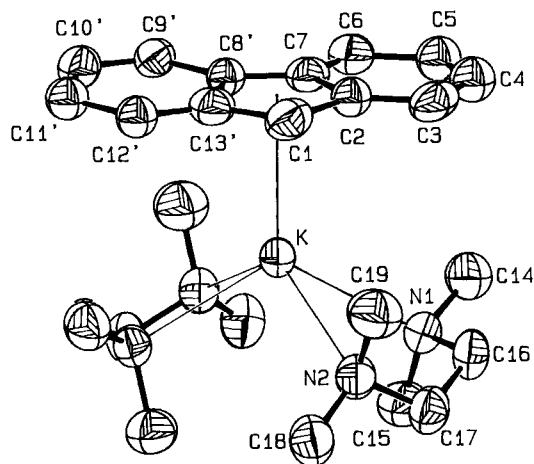


Figure 1. Molecular structure of **1** (ORTEP^[36], 50% probability ellipsoids for non-hydrogen atoms; hydrogen atoms omitted). Selected distances [pm] and angles [°]: K–N1 282.4(1), K–N2 305.8(2), K–C1 332.0(4), K–C2 321.3(5), K–C7 307.1(5), K–C8' 313.2(5), K–C13' 330.5(5); N1–K–N2 61.97(5). There are no short intermolecular contacts

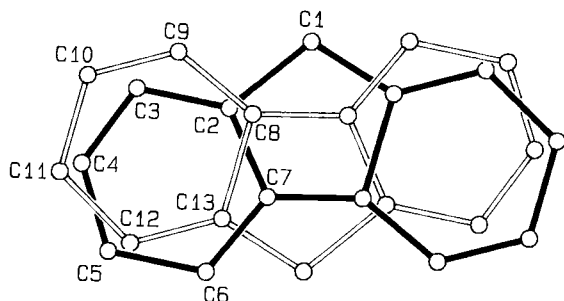


Figure 2. Crystallographically induced disorder of the fluorenyl ligand in **1**

The molecular structure of **1** is remarkable for several reasons: (i) It is only the second monomeric structure of a potassium compound with a cyclic π perimeter together with (pentabenzylcyclopentadienyl)potassium(THF)₃^[9]. Normally, potassium exhibits polymeric zig-zag chain structures in complexes with substituted cyclopentadienyl^[5,10], cyclooctatetraenyl^[6], or pentadienyl^[7] as a carbanion. A similarity exists to the structure of (pentamethyldiethylenetriamine)-sodium fluorenyl, where the sodium is sandwiched between the fluorenyl anion and the tridentate triamine ligand to give a monomeric solvated contact ion pair^[12].

(ii) A structural modification of **1** has already been described^[14]. In this structure, however, the two tmeda groups did not function as a chelating entity but were bridging two potassiums. Thus, each potassium was in contact with two nitrogen atoms, and the five-membered rings from two fluorenyl groups was bridging two other potassiums, resulting in the formation of a polymeric network according

to the formula $\{[K(\mu, \eta^1, \eta^1\text{-tmeda})_2][\mu\text{-C}_{13}\text{H}_9]\}_\infty$. The finding of a second potential minimum in the form of the monomer modification is solely attributed to slight changes in the crystallization conditions. Crystals of the polymeric form were obtained by evaporation (ca. 12 h) of a benzene/tmeda (1:1) solution of **1**^[14]. The modification reported here was obtained reproducibly from a solution of **1** in more polar tmeda/THF/Et₂O (1:1:1) upon cooling. Crystals were visible after two days at –26°C. So far only electrostatic and steric factors within the contact ion pair were emphasized as being structurally decisive in comparative discussions of organoalkali compounds^[12].

To the best of our knowledge, **1** represents the first example of polymorphism in an organopotassium compound^[19]. Thus, caution should be exerted when discussing details such as metal solvation in crystalline organopotassium or even other alkali metal complexes. One crystal structure may not always tell the whole story of solid-state interactions, as the structure found may correspond to just one potential well, determined by external parameters such as temperature or solvent of crystallization.

(iii) Furthermore, it is interesting to note that tmeda can effectively chelate a potassium ion with the formation of an N–K–N angle of only 62°^[12] (cf. the structure of **2** and ref.^[7]). The large size of the potassium ion together with the given N...N distance in tmeda and an optimal “bite” angle of about 85° for the free electron pairs on the nitrogens have been given as a reason for the double-strand linkage of two potassium ions by two tmeda molecules in the polymeric modification of **1**, i.e. non-formation of a K-tmeda chelate structure^[4,12,14]. However, modeling calculations on K(en) (en = ethylenediamine) give similar energies for chelating and monodentate en^[20].

The two K–N bond lengths in the monomeric allotrope of **1** differ by more than 20 pm, their average as well as the K–C distances in both polymorphic forms are, however, not significantly different^[14].

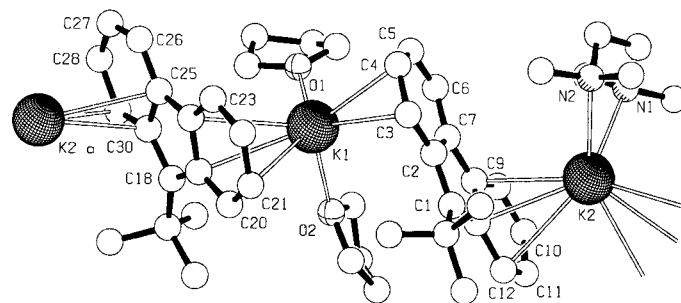


Figure 3. Section of the chain structure (along 001) of **2** in the crystal (PLUTO^[37]). Selected distances [pm] and angles [°]: K1–O1 267.8(4), K1–O2 265.5(4), K1–C2 342.9(6), K1–C3 322.6(5), K1–C4 309.1(6), K1–C5 315.4(6), K1–C6 334.4(6), K1–C7 346.8(5), K1–C19 313.6(5), K1–C20 311.6(6), K1–C21 319.0(6), K1–C22 330.1(6), K1–C23 331.3(6), K1–C24 322.0(5), K2–N1 287.8(5), K2–N2 291.8(5), K2–C8 315.6(5), K2–C9 338.3(6), K2–C10 349.3(6), K2–C11 342.8(6), K2–C12 324.2(5), K2–C13 308.7(5), K2a–C25 316.5(5), K2a–C26 329.7(6), K2a–C27 337.4(6), K2a–C28 331.7(6), K2a–C29 320.4(6), K2a–C30 311.9(5); O1–K1–O2 92.0(2), N1–K–N2 64.4(1). K–C contacts above 330 pm are not drawn

The structure of **2** shows at first glance the expected zig-zag-type polymeric chain structure (Figure 3) with alternating potassium and fluorenyl ions. It is remarkable, however, that the potassium is not situated above the five-membered ring, but above the anellated six-membered ring of the fluorenyl system. This ring shift is explained with the steric influence of the *tert*-butyl group (interaction with the solvent molecules attached to potassium). A comparative AM1 study^[21] of the fluorenyl and 9-*tert*-butylfluorenyl anion supports the notion of a steric origin for the haptotropic potassium shift. AM1 calculates the C-9 position somewhat less negative in the 9-*tert*-butyl derivative, but there is no charge transfer from the five- to the six-membered ring moiety (Figure 4). Furthermore, a comparison of the effective electrostatic potentials on the van der Waals surface (170 pm above the fluorenyl plane^[22]; plotted in Figure 4) illustrates that there is no obvious difference between unsubstituted and 9-*tert*-butyl-substituted fluorenyl. Calculations suggest that

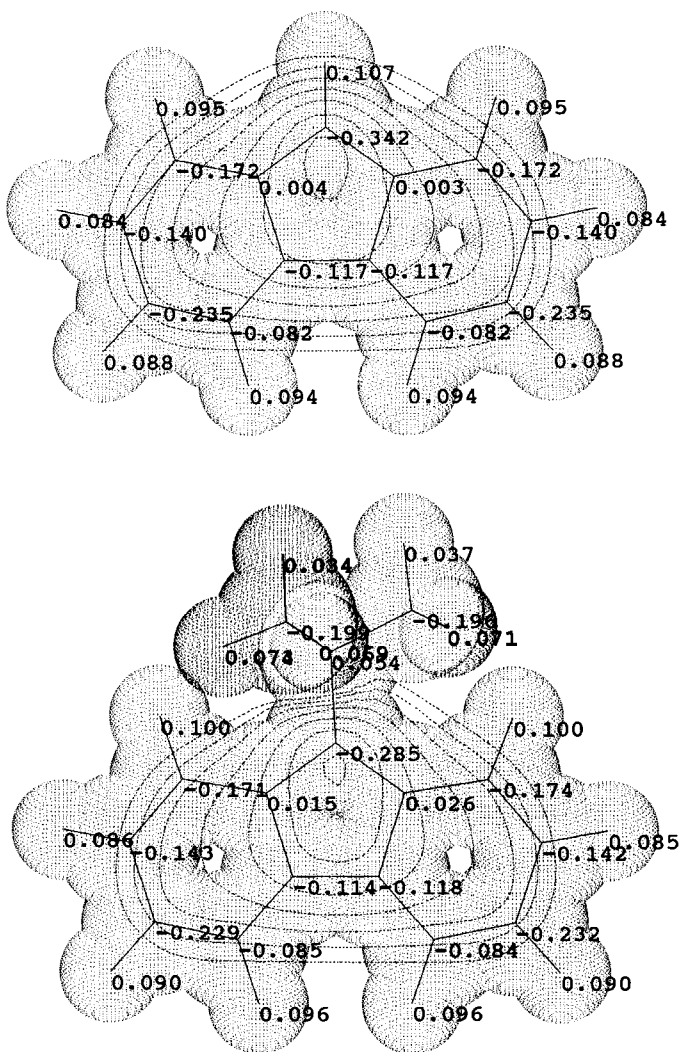


Figure 4. Charge distribution and electrostatic potential in the fluorenyl (a) and 9-*tert*-butylfluorenyl anion (b) according to an AM1 calculation^[21]. The contour lines for the electrostatic potential are -0.22 (minimum)/ -0.21 / -0.20 / -0.19 / -0.18 / -0.17 / -0.16 (inside-out). The electrostatic potential is plotted 170 pm above the ring plane corresponding to the van der Waals surface (half thickness) of an aromatic system^[22]

energy surfaces for metal cations above a delocalized anionic ring can be quite flat, especially so for long cap-ring distances^[4,19]. Dilithium 1,2-diphenylbenzocyclobutadiene-diide is an example that different metal cation locations exist for the same compound^[19].

Metal-fluorenyl six-membered ring coordination could be observed in some cases for transition metals^[15,16]. For alkali metals such a coordination mode to fluorenyl has been observed in the structure of the tetrameric (tetramethylpropylenediamine)sodium fluorenyl where a weak sixring interaction has been found together with the actual fivering coordination^[12]. Base-free lithium fluorenyl forms a dimeric unit with the lithium atoms being sandwiched between the six-membered ring planes^[23]. Alkali metal coordination to six-membered ring entities in other extended π systems or to a phenyl group has been observed e.g. in lithium indenofluorenyl^[24], lithium 1,1,3,3-bis(2,2'-biphenylene)propene^[25], sodium terphenyl^[26], in sodium structures with the tetraphenylallyl anion^[27], the 1,1,4,4-tetraphenylbutane-1,4-diyl dianion^[28], the (biphenyl-2,2-diyl)diphenylethene anion^[29], or with perylene^[30] as well as in potassium dimethylphosphoniumbis(benzylide)^[31].

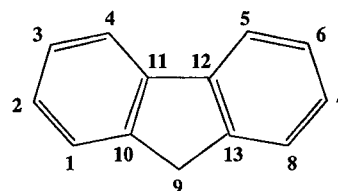
The coordination sphere of the potassium ions in **2** is completed either by two THF molecules or a tmeda molecule in an alternating fashion, with the tmeda molecule again functioning as a chelate ligand. The K-C₆ distances vary between 309 and 349 pm with the shorter contacts corresponding to the K-C₅ distances in **1**. In view of the longer contacts and no sharp discontinuity within the K-C₆ distances it is, however, difficult to assign a definitive coordination number to potassium.

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Experimental

All operations were carried out under purified argon by using standard Schlenk and vacuum techniques. Solvents were distilled from potassium (THF) or sodium metal (tmeda) or from blue sodium/benzophenone ketyl (Et₂O). — ¹H and ¹³C NMR: Bruker WP80SY, ambient temperature (¹H: 80.00, ¹³C: 20.15 MHz).

9-*tert*-Butylfluorene was synthesized according to ref.^[32]: m.p. 101–102°C. — ¹H NMR (CDCl₃): δ = 1.16 (s, 9H, CCH₃), 3.88 (s, 1H, 9-H), 7.2–8.0 (m, 8H, 2- to 8-H). — ¹³C NMR (CDCl₃): δ = 28.38 (CCH₃), 34.99 (CCH₃), 58.51 (C-9), 119.41 (C-4, -5), 125.81, 126.42, 126.87 (C-1, -2, -3, -6, -7, -8), 142.03 (C-11, -12), 146.07 (C-10, -13).



For the assignment of the NMR chemical shifts compare ref.^[13,33]

$[K(\text{tmeda})_2][C_{13}H_9]$ (1): 0.089 g (2.28 mmol) of potassium metal in a solution of 0.36 g (2.17 mmol) of fluorene in 10 ml of tmeda was treated for 1 h in an ultrasonic bath at 70°C. After this time, no metal could be observed anymore, and a deep brown-violet slurry had formed. Addition of 10 ml of THF and 10 ml of Et₂O gave an intensely colored but almost clear solution, and cooling to -26°C caused precipitation of 1 as orange-brown crystals: 0.37 g (39%, crystal yield not optimized). — ¹H NMR ([D₈]THF): δ = 2.16 (s, 24H, CH₃N), 2.31 (s, 8H, CH₂N), 5.98 (br. s, 1H, 9-H), 6.58 (t, ³J_{H,H} = 7.8 Hz, 2H, 3-, 6-H), 6.95 (t, ³J_{H,H} = 7.8 Hz, 2H, 2-, 7-H); 7.40 (d, ³J_{H,H} = 7.8 Hz, 2H, 1-, 8-H), 7.95 (d, ³J_{H,H} = 7.8 Hz, 2H, 4-, 5-H). — ¹³C NMR ([D₈]THF): δ = 46.16 (CH₃N), 58.73 (CH₂N), 83.08 (C-9), 109.86 (C-2, -7), 117.14 (C-4, -5), 119.70 (C-1, -8), 120.57 (C-3, -6), 121.68 (C-11, -12), 136.70 (C-10, -13). — C₂₅H₄₁KN₄ (436.7): calcd. C 68.76, H 9.46, N 12.83; found C 68.12, H 9.26, N 13.00.

$\{[K(\text{THF})_2][\mu-C_{13}H_8(\text{tBu})][K(\text{tmeda})][\mu-C_{13}H_8(\text{tBu})]\}_\infty$ (2): 0.08 g (2.07 mmol) of potassium metal in a solution of 0.44 g (1.98 mmol) of 9-*tert*-butylfluorene in 10 ml of tmeda was treated for 1 h in an ultrasonic bath at 70°C to give a red-orange slurry. Addition of THF and Et₂O furnished an orange-red solution from which crystals could already be grown upon cooling to 2°C. Further cooling to -26°C enhanced the yield: 0.39 g (51%, crystal yield not optimized). — ¹H NMR ([D₈]THF): δ = 1.72 (s, overlapped with THF multiplet at δ = 1.78 [18 + 8H, CCH₃, CH₂(THF)]), 2.15 (s, 12H, CH₃N), 2.30 (s, 4H, CH₂N), 3.58 (m, 8H, CH₂O), 6.45 (t, ³J_{H,H} = 7.8 Hz, 4H, 3-, 6-H), 6.85 (t, ³J_{H,H} = 7.8 Hz, 4H, 2-, 7-H); 7.73 (d, ³J_{H,H} = 7.8 Hz, 4H, 1-, 8-H), 7.90 (d, ³J_{H,H} = 7.8 Hz, 4H, 4-, 5-H). — ¹³C NMR ([D₈]THF): δ = 26.35 [CH₂(THF)], 33.53 (CCH₃), 36.35 (CCH₃), 46.16 (CH₃N), 58.77 (CH₂N), 68.21 [CH₂O(THF)], 102.71 (C-9), 108.49 (C-2, -7), 117.81 (C-4, -5), 119.18 (C-1, -8), 119.95 (C-3, -6), 121.72 (C-11, -12), 133.04 (C-10, -13). — C₄₈H₆₆K₂N₂O₂ (781.3): calcd. C 73.79, H 8.52, N 3.59; found C 72.73, H 8.33, N 4.15.

Crystal Structure Determinations^[34]: CAD4, Enraf-Nonius four-circle diffractometer, Mo-K_α radiation (λ = 71.069 pm, graphite monochromator), T = 177 K, ω-2θ scan with 0.70 + 0.35 tan θ, scan time variable (max. 45 s). During data collection three standard reflections were periodically measured as a check of crystal stability. No significant change was observed for both compounds, reduction in intensity was less than 1%. Structure solution was performed by direct methods (SHELXS-86). Refinement: Full-matrix least squares; non-hydrogen atoms were refined anisotropically (SHELX-76)^[35].

$[K(\text{tmeda})_2][C_{13}H_9]$ (1): C₂₅H₄₁KN₄, M = 436.731, crystal size: 0.3 × 0.3 × 0.4 mm. Monoclinic, space group C12/c1 (No. 15), a = 1896.2(4), b = 907.9(2), c = 1643.2(3) pm, β = 113.49(2)°, V = 2595(1) · 10⁶ pm³, Z = 4, D_{calcd.} = 1.118 g cm⁻³, F(000) = 952 electrons, μ(Mo-K_α) = 2.2 cm⁻¹. 4036 reflections measured (2° < 2θ < 58°), 3168 independent, 2542 observed [F > 4σ(F)], final R = 4.13, R_w = 3.50%; 216 refined parameters, empirical absorption correction (DIFABS, max. = 1.130/min = 0.505). For C₂,4,5,8,11 and 12 (cf. Figure 2) only an isotropic refinement was possible due to the close proximity of two carbon centers each, because of the disorder problem. Residual electron density +0.31/-0.28 eÅ⁻³, largest residuals between C₄,5,11,12. Hydrogen atoms on fluorenyl calculated for idealized positions, hydrogens on tmeda found and refined.

$\{[K(\text{THF})_2][\mu-C_{13}H_8(\text{tBu})][K(\text{tmeda})][\mu-C_{13}H_8(\text{tBu})]\}_\infty$ (2): C₄₈H₆₆K₂N₂O₂, M = 781.27 g cm⁻³, crystal size 0.3 × 0.2 × 0.4 mm. Monoclinic, space group P12₁/c1 (No. 14), a = 1506.0(2), b = 1036.5(2), c = 2829.8(7) pm, β = 93.02(2)°, V = 4411(1) · 10⁶ pm³, Z = 4, D_{calcd.} = 1.176 g cm⁻³, F(000) = 1688 electrons, μ(Mo-K_α) =

2.5 cm⁻¹. 5716 reflections measured (1° < 2θ < 43°), 4334 independent, 3041 observed [F > 5σ(F)], final R = 4.95, R_w = 4.93%; 497 refined parameters, empirical absorption correction (DIFABS, max. = 1.041/min = 0.720). Residual electron density +0.44/-0.31 eÅ⁻³, largest residual at the tmeda molecule. Hydrogen atoms calculated for idealized positions.

AM1 Calculations: Calculations and contour plots were performed with the HyperChem computational package (Version 2.0, Autodesk, Inc. Sausalito, CA 94965, USA) by using the AM1 algorithm^[21] for the geometry optimization and electronic property calculation of the fluorenyl and 9-*tert*-butylfluorenyl anion.

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