permits it to react with sityl to form the tetrahedral complex.[10] The absence of such shifts for the less nucleophilic acetonitrile confirms that sityl lacks the fourth coordination partner and is a true silylenium ion in solvents of low nucleophilicity. We do not claim that the ion is unsolvated but that it is nonspecifically solvated in the same way that trityl is under the same conditions.

Pentacoordinate Carbon in Trigonal-Bipyramidal Symmetry. The Eight-Membered Ring X-ray Structure of Tetrakis(benzylsodium-*N*,*N*,*N'*,*N'*-tetramethylethylenediamine)

Christian Schade and Paul von Ragué Schleyer*

Institut für Organische Chemie der
Friedrich-Alexander Universität Erlangen-Nürnberg
D-8520 Erlangen, Federal Republic of Germany

Hans Dietrich and Waruno Mahdi

Fritz-Haber-Institut der Max-Planck-Gesellschaft
Abteilung Physikalische Chemie
D-1000 Berlin 33, Federal Republic of Germany

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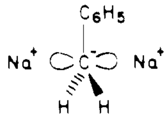
Unlike organolithium compounds,[1] relatively few structures of the synthetically important organic derivatives of the heavier alkali metals have been reported.[2] A new hexane-soluble butylsodium reagent[3] facilitates the preparation of crystalline organosodium compounds.[3b] Thus, metalation of toluene in hexane at -18 °C in the presence of *N*,*N*,*N'*,*N'*-tetramethylethylenediamine (TMEDA) gave yellow needles of $(NaCH_2C_6H_5{\cdot}TMEDA)_4$.[4a] The X-ray structure[4b] (a stereoview is shown in Figure 1) represents the first organoalkali metal tetramer that prefers an eight-membered ring over a tetrahedral arrangement.[1,2] Each α-benzyl carbon is pentacoordinate (**1**) and possesses the trigonal-bipyramidal geometry first suggested by calculations on MCH_3M^+ (M = Li, Na, etc.) models.[5] The predicted preference for pentacoordinate carbon to adopt D_{3h} (**2**) over C_s (**3**) symmetry when at least two metals are present[5] (in contrast to CH_5^+)[6] has now been verified experimentally in other instances as well.[7]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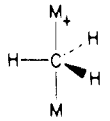
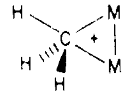

2, D_{3h}


3, C_s

	E_{rel}, kcal/mol 2	3
M = H (MP4/6-311G**//6-31G*)[6]	10 8	0 0
M = Li (MP4/6-31G*//6-31G*)[5]	0 0	3 4
M = Na (MP4/6-31G*//6-31G*)[5]	0 0	4 4

The benzylsodium-TMEDA complex (Figure 1) is a tetramer with approximate D_{2d} symmetry. The four sodium atoms define a square, each edge of which is intersected by a benzyl α-carbon. The resulting eight-membered ring puckers into a crown conformation, presumbly to alleviate crowding. The phenyl rings exhibit short carbon contacts to the methyl groups of neighboring TMEDA ligands in the 3.48-3.70-Å range and bend, in alternation, up and down out of the Na_4 plane. The benzyl groups (including the hydrogens) are exactly planar, but because of the ring puckering the coordination of two sodiums with each benzyl α-CH_2 group (as in **1**) is not exactly perpendicular. However, the deviation from linearity is small (the mean NaCNa angle is 146.5°). The average geometry of the benzyl groups shows nearly exactly the same variations in CCC angles and CC bond lengths (see caption, Figure 1), due to π-electron delocalization, as reported by Power et al.[7c] for benzyllithium; Stucky's 1970 values deviate a little more.[8] The average C-Na distances, 2.64 Å to the α-carbon and 2.76 Å to the ipso carbons, indicate that the sodiums bridge these positions to some extent. The situation in the two benzyllithium structures is similar, but there are greater variations.[7c,8] Two coordination sites on each sodium are occupied by the nitrogen atoms of a TMEDA ligand. Like the C-Na distances, the N-Na distances (around 2.50 Å) are quite normal for sodium compounds.[2] These are about 0.4 Å larger than the corresponding C-Li and N-Li values[1] due to the larger ionic radius of sodium.

The structure of $(\text{benzylsodium-TMEDA})_4$ differs significantly from those of related polar metallic benzyl derivatives. In

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(1) For a review and a bibliography of crystal structures of organolithium compounds, see: Setzer, W. B.; Schleyer, P. v. R. *Adv. Organomet. Chem.* **1985**, *24*, 353.

(2) For a review of the crystal structures of organoalkali compounds of Na, K, Rb, and Cs, see: Schade, C.; Schleyer, P. v. R. *Adv. Organomet. Chem.*, in press. Note, in particular, the tetrahedral structure of $[NaCH_3]_4$: Weiss, E.; Sauermann, G.; Thirase, G. *Chem. Ber.* **1983**, *116*, 74-85.

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(4) (a) **NMR Data in Tetrahydrofuran-d_8 (THF-d_8)**: ^{23}Na (-95 °C, 105 MHz; reference NaCl/H_2O) δ +1.15; ^{1}H (-75 °C, 400 MHz; reference THF-d_8, δ 3.58 from Me_4Si) δ 6.08 (dd, 6.5, 7.7 Hz; meta H), 5.77 (d, J = 7.7 Hz; ortho H), 4.94 (t, J = 6.5 Hz, para H), 2.28 (s, TMEDA-CH_2), 2.13 (s, TMEDA-CH_3), 1.87 (s, CH_2Na); ^{13}C (-95 °C, 100.5 MHz; reference THF-d_8, δ 67.4 from Me_4Si) δ 157.0 (ipso), 128.8 (meta), 113.2 (ortho), 98.8 (para), 58.6 (TMEDA-CH_2), 46.4 (TMEDA-CH_3), 42.3 (CH_2Na). (b) **Crystal Data**, Monomer = $C_{13}H_{23}N_2Na$, M = 230.332, monoclinic, space group $P2_1/n$, a = 14.176 (3) Å, b = 15.011 (5) Å, c = 27.368 (7) Å, β = 90.82 (2)°, V = 5823 Å^3, Z = 16, D_x = 1.051 g/cm^3 (at 117 K) with one tetramer in the asymmetric unit. Graphite monochromated Mo Kα radiation, λ = 0.71069 Å. Two crystals of dimension 0.13 × 0.2 × 0.25 and 0.15 × 0.33 × 0.23 mm^3, respectively, were measured in order to improve the accuracy, especially in the range above the diffraction angle of about 18°, where the diffracted intensities fade out rapidly due to disorder in the structure. A total of 162650 reflection profiles ($2° < \theta < 25°$) were measured at 117 K. Averaging yielded a unique set of 10250 structure factors; 6011 of these were stronger than 2σ. The averaging R value $R_{av} = \sum|F_o^2 - F_{av}^2|/\sum F_o^2$ was 0.102 for the 55103 measurements above 2σ and 0.077 for the 39628 measurements above 3σ. The structure was solved by direct methods (MULTAN 76: Main, P.; Hull, S. E.; Lessinger, L.; Germain, G.; Declecq, F.; Woolfson, M. M. MULTAN 76, Universities of York, England, and Louvain, Belgium, 1976) and refined by large block matrix least-squares methods (X-ray 76: Steward, J. M.; Machin, P. A.; Dickinson, C. W.; Ammon, H. L.; Heck, H.; Flack, H. X-RAY 76, Technical Report TR 446, 1976; Computer Science Center, University of Maryland, College Park, MD) by using weights $1/\sigma^2$ (F_o^2) and including all hydrogen atoms (1063 variables in six blocks). All non-nitrogen atoms of the TMEDA groups are disordered. In case of the methyl groups this disorder was approximated adequately by the anisotropic tempertaure parameters, but each ethylene group had to be divided into two alternative positions, whose populations were chosen so that the mean "vibrations" of the carbon atoms were about equal. All hydrogen atoms of the benzyl groups and most of the TMEDA groups were refined with isotropical vibration parameters; 16 of the lower populated (disordered) methylene hydrogens were given the anisotropic vibration parameters obtained for their mother carbon atoms and refined only with respect to their positional parameters. The R values, based on the 6011$F_o^2 > 2\sigma$ (of the average values), converged to $R(F^2)$ = 0.069, $R_w(F^2)$ = 0.058. The biggest peak and the lowest hole in the final difference map are 0.55 and -0.57 e/Å^3, respectively.

(5) (a) Jemmis, E. D.; Chandrasekhar, J.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1979**, *101*, 527-533, and unpublished calculations on $CH_3Na_2^+$. (b) Jemmis, E. D.; Chandrasekhar, J.; Würthwein, E.-U.; Schleyer, P. v. R.; Chinn, B.; Pople, J. A. *Ibid.* **1982**, *104*, 4275-4276. (c) Schleyer, P. v. R.; Tidor, B.; Jemmis, E. D.; Chandrasekhar, J.; Würthwein, E.-U.; Kos, A. J.; Luke, B. T.; Pople, J. A. *Ibid.* **1983**, *105*, 484-488. (d) For experimental verifications of the predicted stability of the $CH_3Li_2^+$ cation, see: Chinn, J. W., Jr.; Lagow, R. J. *Organometallics* **1984**, *3*, 75-77. Lagow, R. J. *J. Organomet. Chem.* **1983**, *249*, 1-9.

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(7) Examples of pentacoordinate trigonal-bipyramidal carbon in X-ray structures: (a) A near planar methyl group bridging two zirconium atoms: Waymouth, R. M.; Santarsiero, B. D.; Grubbs, R. H. *J. Am. Chem. Soc.* **1984**, *106*, 4050-4051. There are linear B-CH_3-Li arrangements in the $LiB(CH_3)_4$ aggregate, but neutron diffraction shows the methyl groups to have local C_{3v} rather than D_{3h} symmetry: Rhine, W. E.; Stucky, G.; Petersen, S. W. *J. Am. Chem. Soc.* **1975**, *97*, 6401-6406. (b) The Li_2CH_2R grouping in the "Y-conjugated dianion", $[(C_6H_5CH)_2CCH_2Li_2{\cdot}2TMEDA]$: Wilhelm, D.; Schleyer, P. v. R.; Clark, T.; Dietrich, H.; Mahdi, W., unpublished results. (c) Polymeric $[C_6H_5CH_2Li{\cdot}Et_2O]_n$ (see text): Beno, M. A.; Hope, H.; Olmstead, M. M.; Power, P. P. *Organometallics* **1985**, *4*, 2117-2121. These results are pertinent to the mechanisms of S_E2 reactions which proceed with inversion of configuration: Fukuto, J. M.; Jensen, F. R. *Acc. Chem. Res.* **1983**, *16*, 177.

(8) Patterman, S. D.; Karle, I. L.; Stucky, G. D. *J. Am. Chem. Soc.* **1970**, *92*, 1150-1157.

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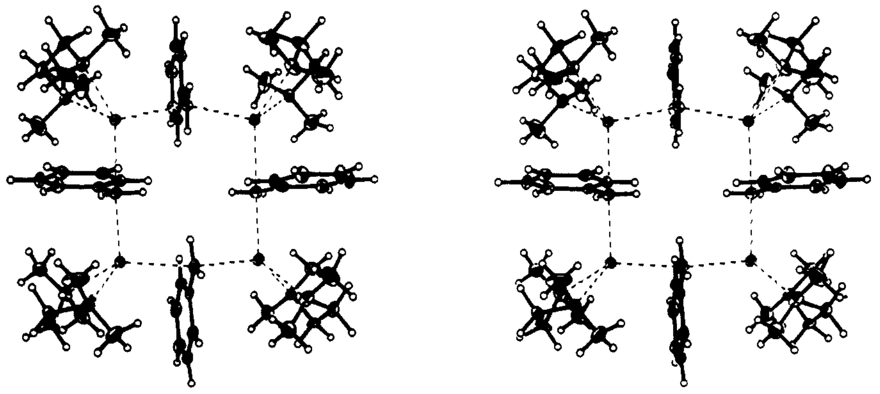

Figure 1, Stereoview of the $[C_6H_5CH_2Na{\cdot}TMEDA]_4$ crystal structure (30% probability elipsoids). The four sodium atoms form a nearly perfect square (∠NaNaNa(av) = 90.0 (6)° and Na···Na lengths 5.05 (6) Å). The average benzyl CC bond lengths: C(2)–Cl(IPSO), 1.404 (8); C(ipso)–C(ortho), 1.431 (5); C(ortho)–C(meta) 1.375 (7); C(meta)–C(para), 1.381 (6) Å. The benzyl groups are planar (rmsd's average 0.0041 Å for the ring atoms). The disorder in the TMEDA ligands is not shown; alternative positions with populations less than 50% have been omitted. Other details are given in the text.

pseudomonomeric benzyllithium–bis(quinuclidine), lithium prefers an asymmetric ${}^3\eta$-allylic site,[8] but the distances to the α-carbon and ipso-carbon are shorter than to the ortho position. Like (benzylsodium–TMEDA)$_4$, (benzyllithium–Et$_2$O)$_n$ also shows trigonal-bipyramidal coordination of α-methylene groups but is a linear polymer.[7c] Model MNDO calculations on $C_6H_5CH_2Li_2^+$ confirm the preference for an essentially linear LiCLi configuration at the α-carbon.[9] Ring formation of $C_6H_5CH_2Li$ may be sterically prohibited because of greater crowding due to the shorter C–Li than C–Na distances. A magnesium-lithium complex, $[Li(TMEDA)_2][Li(TMEDA)Mg(CH_2C_6H_5)_4]$, exhibits magnesate–Li(TMEDA) ion pairing involving benzylic α-carbons, but with front-side coordination to carbon.[10]

Tetrahedral arrangements generally are favored over planar ring structures for tetrameric alkali-metal compounds.[1,2,11] However, lithium amides prefer cyclic structures due to the lone pair orientations.[11,12] Similar carbanion orbital–ion triplet interactions[11] (as depicted in **1**) are responsible for the nontetrahedral benzylsodium–TMEDA and polymeric benzyllithium–Et$_2$O structures. Other examples of stable eight-membered ring structures are found in some coinage metal as well as lithium–coinage metal complexes.[13]

Prochiral α-CH$_2$ groups in aggregated alkyllithium compounds are known to stereomutate intramolecularly,[14] We have suggested that this may occur by unfolding of the tetrahedral tetramer into an eight-membered ring, followed by planarization of a RCH$_2$ moiety (as in **2**).[15] Calculations are consistent with this proposed mechanism.[15b] The (benzylsodium–TMEDA)$_4$ ring structure now provides a nice experimental analogy.

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Supplementary Material Available: Tables of atomic positions and isotropic and anisotropic thermal parameters for $(C_6H_3CH_2Na\text{-}TMEDA)_4$ (3 pages). Ordering information is given on any current masthead page.

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Catalytic Directed Steroid Chlorination with Billionfold Turnovers

Ronald Breslow* and Monica P. Mehta

Department of Chemistry, Columbia University
New York, New York 10027

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We have developed methods to direct chlorination to various tertiary positions on steroids by the use of attached templates.[1] With iodophenyl groups,[2] diphenyl sulfide groups,[3] or thiophene rings[4] an incoming chlorinating species puts the chlorine on the heteroatom of the template, and this is then relayed to a geometrically accessible hydrogen. Since the template is recovered unchanged it is formally catalytic but used in stoichiometric amounts. A move toward true turnover catalysis was seen with templates attached to (and halogenating) three steroids,[4] thus showing three turnovers. We now wish to describe true turnover catalysis, in which a template species moves from substrate to substrate. In the best cases, one template catalyst functionalizes 10^9 substrate molecules.

We had examined the use of ion-pairing forces in nonpolar media to cause oppositely charged templates and substrates to associate. Poor selectivities and low conversions were seen.[5] Thus we went to metal coordination as a force that would promote well-defined but temporary binding of catalyst to substrate. The nicotinate ester of 3-α-cholestanol (**1**) was used as a substrate, while the catalyst was a metal complex of diimine **2**. Solutions

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