the scope of the present work. Further development in theoretical methodology to treat the solvent effects in order to model chemical reactions more realistically must be awaited. As a result, the hypothesis presented in Scheme V can only be tested when such a methodology becomes available.

Acknowledgment. This work was supported in part by the National Science Foundation (CHE 8712389). The University of Massachusetts Computer Services made a generous grant of computer time to enable part of this work. Some of the calculations were conducted on the Cornell National Supercomputer Facility, a resource of the Center for Theory and Simulation in Science and Engineering (Theory Center), which receives major funding from the National Science Foundation and IBM Corporation, with additional support from New York State and members of the Corporate Research Institute.

Supplementary Material Available: The *Z* matrix data of the optimized molecular structures can be obtained from the authors. Contact the authors for a suitable media for data transfer.

Registry No. 1 (R = H; R^1 = Me), 31918-07-7; **1** (R = C_6H_5; R^1 = Me), 1754-88-7; *cis*-**2** (R = H; R^1 = R^2 = Me), 137895-07-9; *trans*-**2** (R = H; R^1 = R^2 = Me), 137895-08-0; *cis*-**2** (R = H; R^1 = Me, R^2 = C≡CH), 137895-09-1; *trans*-**2** (R = H; R^1 = Me, R^2 = C≡CH), 137895-10-4; *cis*-**2** (R = H; R^1 = Me, R^2 = CN), 137895-11-5; *trans*-**2** (R = H; R^1 = Me, R^2 = CN), 137895-12-6; *cis*-**2** (R = C_6H_5; R^1 = R^2 = Me), 137895-13-7; *trans*-**2** (R = C_6H_5; R^1 = R^2 = Me), 137895-14-8; *cis*-**2** (R = C_6H_5; R^1 = Me, R^2 = C≡CH), 137895-15-9; *trans*-**2** (R = C_6H_5; R^1 = Me, R^2 = C≡CH), 137895-16-0; *cis*-**2** (R = C_6H_5; R^1 = Me, R^2 = CN), 137895-17-1; *trans*-**2** (R = C_6H_5; R^1 = Me, R^2 = CN), 137895-18-2; CH_3CHO, 75-07-0; CH≡CCHO, 624-67-9; NCCHO, 4471-47-0.

---

(36) (a) Karelson, M. M.; Tamm, T.; Katritzky, A. R.; Cato, S. J.; Zerner, M. C. *Tetrahedron Comput. Methodol.* **1989**, *2*, 295. (b) Karelson, M. M.; Katritzky, A. R.; Szafran, M.; Zerner, M. C. *J. Org. Chem.* **1989**, *54*, 6030. (c) Karelson, M. M.; Katritzky, A. R.; Szafran, M.; Zerner, M. C. *J. Chem. Soc., Perkin Trans. 2* **1990**, 195. (d) Katritzky, A. R.; Karelson, M. M. *J. Am. Chem. Soc.* **1991**, *113*, 1561. (e) Rzepa, H. S.; ManYi, Yi *J. Chem. Soc., Perkin Trans. 2* **1991**, 531.

An ab Initio Study of the Structure of Monomeric, Unsolvated Benzyllithium. Is Covalency of the Carbon–Lithium Bond Important?

Andrzej Sygula* and Peter W. Rabideau*

Contribution from the Department of Chemistry, Louisiana State University, Baton Rouge, Louisiana 70803. *Received March 15, 1991*

Abstract: Ab initio calculations at the 3-21G level reveal the existence of two minima on the potential energy surface of isolated benzyllithium, the classic η^3 structure and an η^5 haptomer with lithium located over the aromatic ring. A third haptomer with lithium positioned over the C_{ipso}–C_α bond (η^2) was shown to be a transition state for racemization of the η^3 haptomer. The influence of the basis set, electron correlation effects, and zero point energies on the relative stabilities of the haptomers in question was tested. At the MP2/6-311G** with ZPE correction level, η^3 is more stable than η^5 by 1.69 kcal/mol. When purely ionic C–Li bonding was modeled, geometry optimization led to a distinctly different η^1 structure as the global minimum, demonstrating the importance of the partial covalency of carbon–lithium bonding in benzyllithium.

To date, the results of three independent X-ray structure determinations of benzyllithium (**1**) have been published[1-3] reflecting an interest in the structure of organolithium compounds in general and an interest in benzylic anions in particular. In the classic study by Stucky et al.[1] the lithium atom, additionally coordinated by two triethylenediamine molecules, was found to be in bonding distance with three carbon atoms: C_α, C_{ipso}, and C_{ortho} (2.21, 2.39, and 2.59 Å, respectively). The η^3 arrangement was rationalized on the basis of the interactions of the benzyl carbanion's HOMO with the 2s and 2p orbitals of the lithium cation.[1,4] The subsequent structure determination of **1**–diethyl ether complex by Power et al.[2] revealed an infinite chain of alternating benzyl and lithium ions with the lithium also coordinated to Et_2O. In this case lithium was located approximately over the C_{ipso}–C_α bond with distances in the range 2.40–2.88 Å (C_{ipso}) and 2.19–2.23 Å (C_α), and therefore in the η^2 arrangement.[2] Finally Boche et al.[3] determined the structure of **1**·THF·TMEDA complex and found the lithium atom to be located over C_α with the C–Li distance of 2.21 Å and the Li–C_α–C_{ipso} angle equal to 94°; i.e., the η^1 haptomer. The distinctly different locations of the lithium cation with respect to the benzyl anion demonstrate the shallowness of the potential energy surface around the lowest energy arrangement as well as the importance of lithium coordination and/or crystal packing forces in this system.

Some theoretical efforts have been made to understand the structure of benzyllithium. Despite the emphasized importance of intermolecular interactions, such studies must start with consideration of the isolated molecule only. On the basis of an electrostatic model, the η^3 structure analogous to the classic structure was found to be most stable when either HMO or CNDO atomic charges were employed. However, the position of the lithium cation over the benzene ring (η^6 haptomer) was favored when STO-3G charges were used.[5] Semiempirical MNDO calculations for isolated **1** locate two minima on the potential energy surface, η^3 and η^6, with the latter being the global minimum.[3,4,6] On the other hand, when solvation is included in

---

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

(2) Beno, M. A.; Hope, H.; Olmstead, M. M.; Power, P. P. *Organometallics* **1985**, *4*, 2117.

(3) Zarges, W.; Marsch, M.; Harms, K.; Boche, G. *Chem. Ber.* **1989**, *122*, 2303.

(4) Setzer, W. N.; Schleyer, P. v. R. *Adv. Organomet. Chem.* **1985**, *24*, 353.

(5) (a) Bushby, R. J.; Tytko, M. P. *J. Organomet. Chem.* **1984**, *270*, 265. (b) Bushby, R. J.; Steel, H. L.; Tytko, P. *J. Chem. Soc., Perkin Trans. 2*, **1990**, 1155.

the MNDO calculations, the η^1 arrangement becomes most stable.[3,7]

Only very limited information based on ab initio calculations is available in the literature. Van Beylen et al.[8] reported a study on benzyllithium at the STO-3G level. They found the η^3 structure to be more stable than η^1 with pure sp^3 hybridization of C_α by 11.2 kcal/mol. The latter structure was not fully optimized, however.[8] Also, at the time our work was just completed, a paper by Schleyer et al.[9] appeared in which calculations for benzyllithium at the 3-21G level were reported. The authors found the η^3 haptomer to be more stable than η^6 by 4.0 kcal/mol. Another haptomer, η^2, with the lithium cation bridging the C_α and C_{ipso} carbons was also located and found to be higher in energy than η^3 by only 0.1 kcal/mol.

Herein we report the results of detailed ab initio studies on monomeric, unsolvated benzyllithium focusing mainly on the influence of basis set and electron correlation as well as on the influence of zero point vibrational energy (ZPE) on the relative stabilities of various haptomers. The structural consequences of the partial covalency of the carbon–lithium bond are also considered.

Methods

GAUSSIAN 88 ab initio program[10] was employed throughout the study. Analytical gradient geometry optimizations either without geometry constraints, or restricted to a given symmetry, were carried out at the 3-21G[11] level. Although previous calculations demonstrated the adequacy of the 3-21G basis set for a description of closed-shell, small acyclic organolithiums,[12-14] the effect of basis set selection on the equilibrium geometry has not been tested on systems where lithium is coordinated by aromatics. Thus 3-21G optimized geometries were reoptimized with the 6-31G* basis set.[15] In addition, all the stationary points were characterized by calculations of harmonic vibrational frequencies by analytical method[10] at both 3-21G and 6-31G* levels.

Single point calculations based on 3-21G geometries were carried out with various basis sets up to the 6-311G** level.[16] Electron correlation effects were accounted for with Moller–Plesset[17] correction to the second-order (MP2) with frozen core orbital approximation.

The purely ionic behavior of lithium was modeled by removing all the orbitals except 1s from its basis set.[18] The alternative technique in which the exponents of the valence orbitals in the lithium basis are set to 950.0 and 900.0[14] was also tested and showed to give the same optimized geometry, although with slightly lower total energy. Because of economical reasons the previous strategy was chosen and used throughout the study.

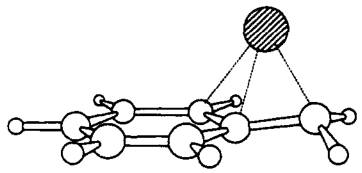
Table I. Calculated Total Energies (au) and Relative Energies (kcal/mol) for **1A–1C** at 3-21G Geometry

	1A[a] C_1[e]	**1B**[b] C_s[e]	**1C**[b] C_s[e]
3-21G	−275.033 458	0.12	4.05
6-31G	−276.479 122	0.22	7.62
6-31+G	−276.487 237	0.16	6.96
6-31++G	−276.487 429	0.14	6.91
6-31G*	−276.573 549	0.24	4.05
6-31G**	−276.586 292	0.25	3.96
6-311G*	−276.622 988	0.23	2.75
6-311G**	−276.635 820	0.29	2.62
MP2/6-31G	−277.092 046	0.30	5.95
MP2/6-31G*	−277.476 973	0.25	2.42
MP2/6-31G**	−277.534 340	0.26	2.62
MP2/6-311G*	−277.572 724	0.26	1.36
MP2/6-311G**	−277.625 342	0.32	1.43
zero point energy[c]	70.84	(70.77)[d]	71.10

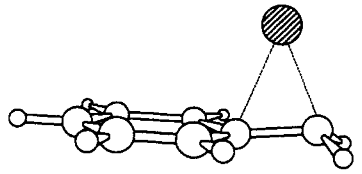
[a] Total energy (hartrees, 1 hartree = 627.51 kcal/mol). [b] Energy relative to **1A** (kcal/mol). [c] Kcal/mol, scaled by a factor of 0.9. [d] One negative vibration ignored in ZPE calculations. [e] Symmetry.

Results and Discussion

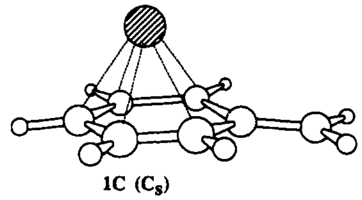
Three stationary points **1A–1C** were located on the SCF/3-21G potential energy surface.[19] **1A** is a "classical" structure with a η^3 lithium arrangement; i.e., lithium in bonding distance with three carbon atoms. The calculated distances between lithium and C_α, C_{ipso}, and C_{ortho} are 2.041, 2.158, and 2.454 Å, respectively.[19]



1A (C_1)



1B (C_s)



1C (C_s)

Structure **1A** is similar to the originally determined crystal structure of **1**·triethylenediamine (TEDA) complex[1] and to the STO-3G optimized structure for **1**.[8] Structure **1B** (η^2) resulted from C_s symmetry restricted geometry optimization of the η^1 structure found by Boche et al.[3] for the **1**·TMEDA·THF complex and resembles to some extent the structure of $(\mathbf{1}\cdot Et_2O)_x$.[2] The calculated Li–$C_\alpha$ and Li–C_{ipso} distances are 2.034 and 2.164 Å. Finally **1C** with the lithium located over the benzene ring, although not observed experimentally, was found to be a global minimum for benzyllithium by semiempirical MNDO calculations.[3,4,6] Geometry optimization for **1C**, which was performed with C_s symmetry restriction, reveals some interesting structural features. The C_{ipso}–C_α bond length (1.340 Å) is typical for a carbon–carbon double bond, and the lithium is located over the ring but shifted toward C_{para} with C–Li distances of 2.142, 2.207, 2.295, and 2.500

---

(6) Sygula, A.; Rabideau, P. W. *J. Org. Chem.* **1987**, *52*, 3521.

(7) Lipkowitz, K. B.; Uhegbu, C.; Naylor, A. M.; Vance, R. *J. Comput. Chem.* **1985**, *6*, 662.

(8) Vanermen, G.; Toppet, S.; Van Beylen, M.; Geerlings, P. *J. Chem. Soc., Perkin Trans. 2* **1986**, 707.

(9) Buhl, M.; van Eikema Hommes, N. J. R.; Schleyer, P. v. R.; Fleischer, U.; Kutzelnigg, W. *J. Am. Chem. Soc.* **1991**, *113*, 2459.

(10) GAUSSIAN 88: Frisch, M. J.; Head-Gordon, M.; Schlegel, H. B.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Defrees, D. J.; Fox, D. J.; Whiteside, R. A.; Seeger, R.; Melius, C. F.; Baker, J.; Martin, R. L.; Kahn, L. R.; Stewart, J. J. P.; Fluder, E. M.; Topiol, S.; Pople, J. A. Gaussian, Inc.: Pittsburgh, PA.

(11) Binkley, J. S.; Pople, J. A.; Hehre, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 939. Gordon, M. S.; Binkley, J. S.; Pople, J. A.; Pietro, W. J.; Hehre, W. J. *J. Am. Chem. Soc.* **1982**, *104*, 2797.

(12) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley & Sons: New York, NY, 1986.

(13) (a) Kaneti, J.; Schleyer, P. v. R.; Clark, T.; Kos, A. J.; Spitznagel, G. W.; Andrade, J. G.; Moffat, J. B. *J. Am. Chem. Soc.* **1986**, *108*, 1481. (b) Sapse, A.-M.; Raghavachari, K.; Schleyer, P. v. R.; Kaufmann, E. *J. Am. Chem. Soc.* **1985**, *107*, 6483.

(14) Rajca, A.; Streitwieser, A., Jr.; Tolbert, L. M. *J. Am. Chem. Soc.* **1987**, *109*, 1790.

(15) (a) Hariharan, P. C.; Pople, J. A. *Chem. Phys. Lett.* **1972**, *66*, 217. (b) Francl, M. M.; Pietro, W. J.; Hehre, W. J.; Binkley, J. S.; Gordon, M. S.; DeFries, D. J.; Pople, J. A. *J. Chem. Phys.* **1982**, *77*, 3654.

(16) Krishnan, R.; Binkley, J. S.; Seeger, A.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 650.

(17) (a) Moller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618. (b) Binkley, S. J.; Pople, J. A. *Int. J. Quantum. Chem.* **1975**, *9*, 229.

(18) Clark, T.; Rohde, C.; Schleyer, P. v. R. *Organometallics* **1983**, *2*, 1344.

(19) See also ref 9.

Å for C_{para}, C_{meta}, C_{ortho}, and C_{ipso}, respectively. Because of the significantly longer C_{ipso}–Li distance, **1C** shows η^5 rather than η^6 arrangement.

The above stationary points were characterized by vibrational frequency calculations. For both **1A** and **1C**, all real frequencies were found proving that they are true minima on the potential energy surface. On the other hand, one imaginary frequency (57i) was found for **1B** indicating that it is a transition state at the level of theory employed. Inspection of the transition vector shows that **1B** is a TS for racemization of **1A**. The very low barrier for racemization (0.12 kcal/mol at the 3-21G level, Table I) as well as the low value of the imaginary frequency indicates a shallow potential energy area around the minimum.

The very low energy difference between **1A** and **1B** may cause some question about the above results. At the relatively low quality of the basis set employed, the errors—such as basis set superposition error, BSSE—may be responsible for predicting **1A** to be lower in energy than **1B**. In an attempt to address this question we estimated the BSSE at the 3-21G level by comparing the energies of the "naked" benzylic anions extracted from **1A**–**1C** with the energies of the same anions augmented with lithium orbitals (ghost lithium atoms) located in the same position as the lithium cations. The lowering of energy was 9.59, 9.67, and 8.08 kcal/mol for **1A**-, **1B**-, and **1C**-like anions, respectively. The above results show that at the 3-21G level, the stability of **1B** is overestimated the most, while the stability of **1C** is the least overestimated by BSSE. In other words when reducing the BSSE one should expect a slight increase in energy difference between **1B** and **1A** (by ca. 0.1 kcal/mol) and at the same time a decrease (by ca. 1.5 kcal/mol) in the respective difference between **1C** and **1A**. There are two important implications of the above results. First, this serves as evidence that **1B**, being a transition state for racemization of **1A**, is not an artifact of the low quality basis set so one can expect the **1A** structure to also be a minimum on the potential energy surface at higher levels of theory. Second, it is obvious that a precise estimation of the energy difference between **1C** and **1A** requires a higher quality basis set than 3-21G although we do not expect the former to become the global minimum for **1**.

The results of single point calculations for **1A**–**1C** at 3-21G geometries with various basis sets are shown in Table I. It is apparent from Table I that the energy difference between **1B** and **1A** increases slightly, while the analogous difference between **1C** and **1A** decreases with increasing quality of the basis set in accord with the prediction based on the BSSE estimation.

Because of the predominantly ionic character of the carbon–lithium bond, the relative correlation energy corrections for different organolithium haptomers are believed not to be important.[13] It can be seen from Table I that the influence of correlation effects calculated at the MP2 level on the relative stability of **1B** vs **1A** is negligible. This is expected because in addition to the aforementioned ionic character of lithium, the structures in consideration are very similar and so the correlation effects are also similar. On the other hand the correlation corrections seem to be more important when the energies of **1C** and **1A** are being considered. At the MP2 level this correction narrows the gap between the two by ca. 1.5 kcal mol despite the basis set used (Table I). Although in the case of benzyllithium this correction does not change the energy ordering of the haptomers, this result should be kept in mind when comparing HF energies of haptomers with similar stabilities but significantly different coordination of lithium cations.

Because of the structural differences between **1A** and **1C**, we attempted to estimate the importance of basis set quality for geometry optimization in this system even though it has been recognized for some time that the 3-21G basis set is adequate in aliphatic organolithiums.[12-14] For this reason, **1A**–**1C** were reoptimized with the 6-31G* basis set, but the improvement obtained was insignificant. First of all, optimal geometries changed only slightly, and force constant analysis showed **1A** and **1C** to be local minima and **1B** to be a transition state. Moreover, total energy lowering at the 6-31G*//6-31G* level when compared to the 6-31G*//3-21G results is also negligible: 0.11, 0.12, and 0.13 kcal/mol for **1A**, **1B**, and **1C**, respectively. Hence the calculated relative stabilities of the haptomers in question are practically unchanged when compared to the results obtained at the 3-21G geometries, and this demonstrates again the adequacy of the basis set used throughout the study for geometry optimization.

The best estimate of the energy difference between **1C** and **1A** (MP2/6-311G**//3-21G with ZPE correction) is 1.69 kcal/mol in favor of **1A**; this number is significantly lower than the one obtained at the 3-21G level. Nevertheless, even at a relatively high level of theory, the classic haptomer **1A** is the global minimum on the potential energy surface of unsolvated benzyllithium. Thus it may be concluded that the reported MNDO prediction of **1C** as the global minimum for isolated benzyllithium[3,4,6] is an artifact of the method, most probably caused by the known overestimation of carbon–lithium bond energy. As a consequence, the comparison of MNDO energies of organolithium haptomers with different numbers of formal C–Li bonds must be done with considerable caution.

The nature of the carbon–lithium bond has been a matter of considerable controversy.[12,18,20-24] Presently, most researchers agree that the bond in question is mostly ionic. However, the degree of ionic character estimated strongly depends on the method applied. For example, the reported degree of ionic character of the C–Li bond in methyllithium varies in the range 55–80%.[24b] There is obviously no unique way of defining such a quantity as the degree of ionic character and every attempt suffers from some arbitrariness. From a practical point of view, the structural implications of covalency of the C–Li bond is an important feature. This may be considered by a comparison of the lowest energy structure of a particular organolithium compound with the one obtained when lithium is forced to be entirely ionic. If both structures are similar, it can be concluded that the contribution of covalency to the C–Li bond is not structurally important; in other words, the minimum energy structure may be deduced from an electrostatic model. Although the structural consequences of a purely ionic model lead to a correct description of certain organolithiums (e.g., methyllithium[18,20a] and dilithiopropane[14,25]), we have recently demonstrated the inadequacy of this model in predicting the structure of dilithiated polyaromatics at the semiempirical MNDO level.[26]

To address the importance of the covalency of the C–Li bond in **1**, we repeated the 3-21G optimization of **1A**–**1C** with the truncated 3-21G basis set for lithium (see Method section). By this method, optimization of **1C** led to the slightly modified structure **1C′** (E[RHF] = −274.987106 au) with the lithium cation located more over the center of the ring as compared to **1C**. The C–Li distances were 2.184, 2.246, 2.236, and 2.272 Å for C_{para}, C_{meta}, C_{ortho}, and C_{ipso}, respectively. This structure, which may be described as an η^6 haptomer, resembles the one predicted on the basis of a simple electrostatic model.[5] All positive frequencies showed this structure to be a minimum on the potential energy surface. In contrast, optimization of both **1A** and **1B** with the analogous basis set provided the distinctly different structure **1D** (E[RHF] = −274.996672 au) exhibiting the η^1 arrangement with a Li–C_α distance of 1.928 Å and a C_{ipso}–C_α–Li bond angle of

---

(20) (a) Streitwieser, A., Jr.; Williams, J. E.; Alexandratos, S.; McKelvey, J. M. *J. Am. Chem. Soc.* **1976**, *98*, 4778. (b) Streitwieser, A., Jr. *J. Organomet. Chem.* **1978**, *156*, 1. (c) Streitwieser, A., Jr. *Acc. Chem. Res.* **1984**, *17*, 353 and references therein.

(21) Graham, G. D.; Marynick, D. S.; Lipscomb, W. N. *J. Am. Chem. Soc.* **1980**, *102*, 4572.

(22) (a) Schleyer, P. v. R. *Pure Appl. Chem.* **1984**, *56*, 151. (b) Clark, T.; Chandrasekhar, J.; Schleyer, P. v. R. *J. Chem. Soc., Chem. Commun.* **1980**, 672.

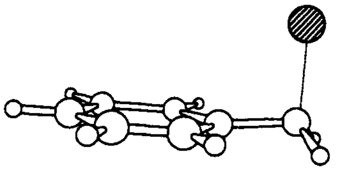
(23) Ritchie, J. P.; Bachrach, S. M. *J. Am. Chem. Soc.* **1987**, *109*, 5909.

(24) (a) Hiberty, P. C.; Cooper, D. L. *J. Mol. Struct. THEOCHEM.* **1988**, *169*, 437. (b) Penotti, F. E. G.; Gerrat, J.; Cooper, D. L.; Raimondi, M. *J. Chem. Soc., Faraday Trans. 2* **1989**, *85*, 151.

(25) Kost, D.; Klein, J.; Streitwieser, A., Jr.; Schriver, G. W. *Proc. Natl. Acad. Sci. U.S.A.* **1982**, *79*, 3922.

(26) Sygula, A.; Lipkowitz, K.; Rabideau, P. W. *J. Am. Chem. Soc.* **1987**, *109*, 6602.

96.5°. Vibrational analysis showed **1D** to be a true minimum, and the energy difference (6.00 kcal/mol below the η^6 haptomer) showed **1D** to represent a global minimum for benzyllithium where the C–Li bond is purely ionic. This structure was then reoptimized at the 6-31G* level, again with a naked core for lithium (1s orbital only), giving a similar structure with a Li–C_α distance of 1.959 Å and a C_{ipso}–C_α–Li angle of 101.2° (E[RHF} = −276.548483 au). Thus **1D** appears to be a minimum at this level, consistent with vibrational frequencies calculations. **1D** exhibits some structural features of the **1**·THF·TMEDA complex determined recently by Boche et al.[3] It may be described as a benzylic anion with nearly sp^3 hybridization at the α carbon coordinating the lithium cation.



1D

As in the aforementioned case of energy differences between **1A** and **1B**, BSSE may be responsible for predicting different minima (i.e., **1A** and **1D**) when the full and truncated 3-21G basis sets are used. It may be that the presence of unfilled Li orbitals in the position occupied by lithium in **1A** results in extra stabilization as compared to **1D**. To test this possibility we carried out the calculations for **1A** with the naked core lithium and obtained a value ***higher*** in energy than **1D** by 1.72 kcal/mol. On the other hand, when the full 3-21G basis set is employed **1A** is *lower* in energy than **1D** by 3.37 kcal/mol. The counterpoise calculations done for the anions extracted from **1A** and **1D** with the lithium orbitals added as diffuse orbitals lower the energies of the anions by 9.59 (see above) and 9.65 kcal/mol, respectively. Apparently the BSSE influences the relative energies of **1A** and **1D** by less than 0.1 kcal/mol and is more than one order of magnitude smaller than the predicted energy differences as calculated with both full and truncated basis sets. This indicates that the prediction of **1A** as the global minimum for the full representation of lithium, and **1D** as the minimum when lithium is forced to be fully ionic, is not an artifact of the method used.

As the final test for the reliability of the structure **1D** as a representation of benzyllithium with purely ionic lithium we repeated the optimization at the 3-21G level augmenting the carbon atoms with diffuse sp functions,[27] again leaving the naked core for lithium. Since in **1D** we deal with the benzylic anion interacting with the countercation, the diffuse functions may be important for the description of the structure, as suggested by one of the referees. However optimization at the 3-21+G level led again to the η^1 structure of C_s symmetry **1D** (E[RHF] = −275.043923 au) with a Li–C_α distance of 2.045 Å and a C_{ipso}–C_α–Li angle of 78.3°. The calculated vibrational frequencies were found to be all real. The inclusion of the diffuse functions diminishes the C_{ipso}–C_α–Li angle significantly at the 3-21G level from 96.5 to 78.3°. On the other hand, improvement of the basis set from 3-21G to 6-31G* increases the angle to 101.2° (see above). Thus one can expect the angle in question to be close to 90° when both polarization and diffuse functions are used for description of benzyllithium with the naked core representation for lithium. Regardless, at all the levels of approximation used, **1D** is the minimum energy arrangement when lithium is forced to be fully ionic.

Since **1D** exhibits a significantly different structure than **1A**, we conclude that partial covalency of the carbon–lithium bond in benzyllithium is structurally important. This is not a common feature of organolithium compounds. Similar computational procedures applied to methyllithium[18,20a] and dilithiopropane[14,25] yielded similar structures with both ionic and fully represented lithium. On the other hand, the recent theoretical studies of Schleyer et al.[28] emphasize the importance of agostic effects[29] as the controlling factor for the eclipsed conformation of tetrameric methyllithium. However, the staggered conformation of methyllithium tetramer was observed in the crystal state.[30] Apparently in this latter case the agostic effects are being overcome by solvation and crystal packing forces.[28]

Conclusions

We have found that the classic η^3 structure **1A** corresponds to the lowest energy haptomer of isolated benzyllithium. While increasing basis set quality and including electron correlation effects were found to lower the energy difference between **1A** and **1C**, they seemed to be unimportant for the prediction of the barrier for racemization of **1A** (i.e., the relative stability of **1B**). Zero point vibrational energy influenced only modestly the relative stabilities of the haptomers by 0.26 kcal/mol in favor of **1A** in comparison with **1C**. At the MP2/6-311G**//3-21G level with ZPE correction, **1A** is lower in energy than the η^5 haptomer with lithium located over the benzene ring (**1C**) by 1.69 kcal/mol, so the MNDO prediction of **1C** as a global minimum is an artifact of the method. Geometry reoptimization at the 6-31G* level did not improve the results as compared to the 3-21G level, demonstrating again the adequacy of the latter basis set for prediction of the geometry of organolithiums.

When lithium is restricted to a purely ionic interaction with the benzylic anion, a distinctly different η^1 haptomer (**1D**) becomes the global minimum. Counterpoise calculations as well as inclusion of the diffuse functions into geometry optimization show that this result is not an artifact of the method used. Hence this latter observation suggests that partial covalency in the carbon–lithium bond is structurally important and should not be neglected in an attempt to describe the structure of **1**.

Acknowledgment. This work was supported by the Division of Chemical Sciences, Office of Basic Energy Sciences of the U.S. Department of Energy, and by SNCC (Louisiana State University) for allocation of computer time.

Registry No. 1, 766-04-1.

---

[27] Clark, T.; Chandrasekhar, J.; Spitznagel, G. W.; Schleyer, P. v. R. *J. Comput. Chem.* **1983**, *4*, 294.

[28] Kaufmann, E.; Raghavachari, K.; Reed, A. E.; Schleyer, P. v. R. *Organometallics* **1988**, *109*, 6602.

[29] In the case of organolithiums the agostic effect is a stabilizing σ_{CH}–Li interaction. For a general discussion of the effect in transition-metal complexes see: (a) Brookhart, M.; Green, M. H. L. *J. Organomet. Chem.* **1983**, *250*, 395 and references therein. (b) Koga, N.; Obara, S.; Kitaura, K.; Morokuma, K. *J. Am. Chem. Soc.* **1985**, *107*, 7109.

[30] Weiss, E.; Hencken, G. *J. Organomet. Chem.* **1970**, *21*, 265.