and wagging, and b_{2g} CCC bending differ from our DZ+d CISD predictions, by more than 60% in some cases.

(2) For pentatetraene, there are significant discrepancies between the present study and existing experiments.[15,16] In particular, the observed 1660-cm^{-1} band appears to be misassigned since it is too high for the b_2 C=C stretching according to the DZ+d CISD results. In fact, this observed band, as well as two other observed bands at 1140 and 910 cm^{-1}, does not seem to fit any normal mode when compared with the DZ+d CISD harmonic vibrational frequencies of the *linear* structure.

(3) It is found that the theoretical vibrational frequencies for C_4H_4 and C_5H_4 are extremely sensitive to the basis set and the correlation method. Thus, the frequencies for the CCC bending in C_4H_4 and C_5H_4 obtained with the DZ and 6-31G basis sets are vastly different, particularly when electron correlation is explicitly included. It is also shown that the MP2 and CISD methods give significantly different frequencies for the same vibration. Specifically, the CCC bending frequencies obtained from the 6-31G basis set and from the MP2 method are significantly lower than those obtained from the DZ basis set and from the CISD method, respectively. Thus, when the 6-31G basis set is used with the MP2 method, the predicted vibrational frequencies for the bending of cumulated double bonds are much lower than those from the DZ basis set and the CISD method. Sometimes the corresponding diagonal force constants differ even in sign. The TZ basis set predicts vibrational bending frequencies for C_4H_4 and C_5H_4 in qualitative agreement with neither the 6-31G nor the DZ basis. But it gives significantly lower CCC bending frequencies than does the DZ basis sets. Therefore, extreme caution must be exercised in theoretical studies of bending of cumulated double bonds.

In conclusion, it seems that the structure of butatriene (C_4H_4) is linear, since the DZ+d CISD predicted frequencies for the linear structure are in good agreement with the IR and Raman spectra (except for a few uncertain Raman assignments) and it is only the 6-31G MP2 method which predicts an imaginary frequency for the bending of the linear structure. However, it is not clear whether the linear structure of pentatetraene (C_5H_4) is an energy minimum since serious discrepancies remain to be solved. (1) Most of the observed IR bands for C_5H_4 do not seem to agree with any DZ+d CISD predicted frequencies for the linear structure. (2) Theoretical predictions vary significantly. Specifically, the 6-31G CISD (as well as the 6-31G MP2 and TZ MP2 methods) gives an imaginary frequency for the bending of the linear structure. Other more reliable methods predict real frequencies for this structure; but the small magnitude of the TZ predicted CCC bending frequencies calls for more theoretical studies with better basis sets. At the highest level of theory considered here (DZ+d CISD), the predicted e symmetry CCC bending frequency is only 150 cm^{-1}. Since the present work has almost reached the limit of the current technology in quantum chemistry, experimental work on this molecule may be more effective in determining the ground-state structure of pentatetraene.

As for the question whether long cumulenes are more apt to bend, the answer is certainly positive from the present study and thus agrees with Liang and Allen's analysis[2] but not with that of Trinquier and Malrieu.[1]

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Applications and Evaluations of IGLO Chemical Shift Calculations for Organolithium Compounds

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Abstract: The individual gauge for localized orbitals (IGLO) method has been applied to calculate the ^{13}C NMR shifts of numerous organolithium compounds. For the compounds existing as monomers in solution, the accord with experiment is satisfactory. The dependence of the calculated chemical shifts on aggregation and solvation was studied systematically for methyl-, vinyl-, and propynyllithium: these effects are shown to be most important for the unsaturated compounds but tend to cancel. For the aliphatic compounds, the effect of solvation and aggregation on δ ^{13}C is smaller. Hence, even IGLO chemical shifts calculated for isolated saturated monomers give acceptable agreement with the experimental values for aggregated species. Calculated ^{13}C chemical shifts for unsaturated organolithium compounds can be related to the π-electron density analogous to the Spiesecke–Schneider relationship. In some cases, IGLO calculations may be used to distinguish between structural possibilities; e.g., in benzyllithium the lithium cation is attached mainly to the benzylic and ipso carbons.

Introduction

Although organolithium compounds are important synthetic reactants,[1] their detailed characterization has been difficult. Because of the high degree of ionic character, these polar molecules often are considered to be equivalents to "carbanions". However, very few organolithium compounds exist as separated ions or as ion pairs; most exhibit various degrees of aggregation and solvation in the solid state and in solution.[2] The degree of aggregation can

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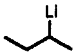
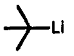
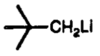
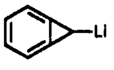
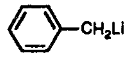
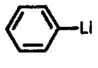
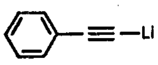
(1) Wakefield, B. J. *Organolithium Methods*; Academic Press: London, 1988.

Table I. ^{13}C Chemical Shifts of Monomeric Li Compounds

compd	opt geometry	carbon	σ,[a] ppm	IGLO δ,[b] ppm	expt δ,[b] ppm
	3-21G[c]	$CHLiCH_3$	199.3	21.1	28.8[e]
		CHLi	193.9	26.6	26.7
		CH_2	192.7	27.8	39.4
		CH_3	202.1	18.3	20.2
	3-21G	>CLi	197.9	22.5	17.1[f]
		CH_3	188.3	32.1	40.4
	3-21G	CH_2Li	187.6	32.8	34.4[g]
		C	198.4	22.1	
		ϕ-CH_3	185.6	34.4	
	3-21G	C1	174.7	41.4	31.3[h]
		C2	64.7	151.3	149.0
		C3	104.5	111.5	99.1
		C4	93.8	122.2	120.4
	3-21G[d]	CH_2Li	177.0	39.0	36.7
		C(i)	46.6	169.4	160.6
		C(o)	104.1	111.9	116.4
		C(m)	81.8	134.2	128.2
		C(p)	95.9	120.1	120.9
	3-21G(6-31G*)[i]	C(i)	27.3 (29.7)	188.7 (186.3)	196.7[f]
		C(o)	80.8 (80.7)	135.2 (135.3)	143.4
		C(m)	91.6 (91.1)	124.4 (124.1)	124.8
		C(p)	97.0 (95.9)	119.0 (120.1)	120.9
	3-21G(6-31G*)[i]		104.2 (108.5)	111.8 (107.5)	103.5
	3-21G	≡CLi	73.7	142.5	145.5[f]
		C≡	124.5	91.5	113.2
		C(i)	90.4	125.6	130.9
		C(o)	86.8	129.2	128.5
		C(m)	90.1	125.9	131.2
		C(p)	93.7	122.3	124.8

[a] Basis DZ except *sec*-butyllithium, *tert*-butyllithium, and neopentyllithium, for which DZ+sp(C) was used; σ values relative to the bare nucleus; note the different sign convention: for absolute shielding values a positive sign denotes shielding. [b] Relative to TMS. [c] Gauche C_1 symmetry. [d] C_s symmetry, Li bridging benzylic and ipso carbons. [e] THF, PMDTA.[7] [f] THF.[7] [g] THF, PMDTA;[27] only the value for C_α is given there. [h] THF.[26] [i] Values for the 6-31G* geometries in parentheses.

differ for the same compound, depending on the temperature, the nature of the solvent, and the presence of chelating ligands. Much work has been done in recent years to characterize these compounds as completely as possible. X-ray crystallography has been invaluable,[3] but the nature of the species is not always the same in the solid state and in solution. Consequently, NMR spectroscopy is becoming increasingly important in organolithium chemistry.[4-8] For example, ^6Li–^{13}C coupling provides direct information on the state of aggregation[6] and 2D-HOESY spectroscopy[8] reveals the environment around individual lithium atoms. While lithium chemical shifts generally are not very informative (they cover a relatively narrow range[9]), the effect on δ ^{13}C due to lithiation of a given carbon can be quite revealing.[6]

In recent years, computational chemistry has contributed a great deal to the understanding of organolithium compounds.[10-13] Calculations are the most important source of energetic information since few measurements on organolithium compounds are available. The structures and potential energy surfaces of isolated monomers have been investigated in detail.[11] In some cases, dimers, higher aggregates, and solvated species have been examined computationally as well.[12,13] Because of their largely ionic character, organolithium compounds typically prefer unconventional structures and bonding arrangements. There has been a pleasing agreement between experimental and computational results. These two methods have complemented each other nicely. We now report results in a new area of joint investigations, NMR chemical shifts.

Recently, several ab initio methods for the calculation of chemical shifts have been developed.[14] We took advantage of the individual gauge for localized orbitals (IGLO) method[15,16] introduced by Kutzelnigg and Schindler. This has now been applied to a variety of compounds composed of an increasingly large number of chemical elements.[16] For hydrocarbons[17] and

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(2) Wakefield, B. J. *The Chemistry of Organolithium Compounds*; Pergamon Press: Oxford, 1974.

(3) For a review, see e.g.: Setzer, W. N.; Schleyer, P. v. R. *Adv. Organomet. Chem.* **1985**, *24*, 353.

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(14) For a recent review, see: Chestnut, D. B. *Annu. Rep. NMR Spectrosc.* **1989**, *21*, 51.

(15) (a) Kutzelnigg, W. *Isr. J. Chem.* **1980**, *19*, 193. (b) Schindler, M.; Kutzelnigg, W. *J. Chem. Phys.* **1982**, *76*, 1919.

(16) For a review of IGLO applications, see: (a) Kutzelnigg, W. *J. Mol. Struct.* **1989**, *202*, 11. (b) Kutzelnigg, W.; Fleischer, U.; Schindler, M. *NMR, Basic Principles and Progress*; Springer Verlag: New York, 1990; Vol. 23, p 165.

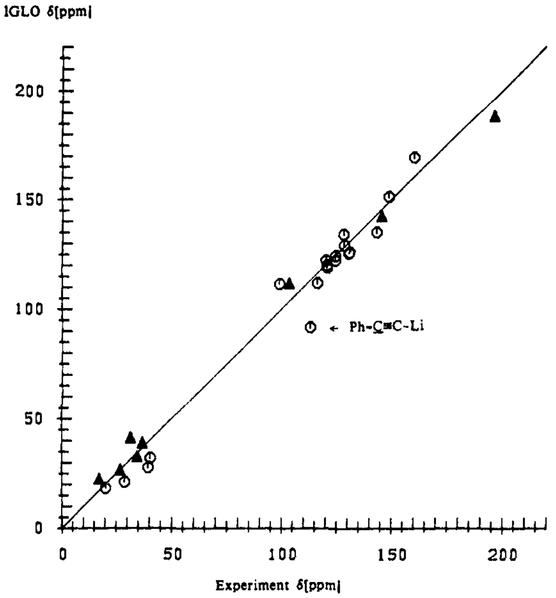

Figure 1. Theoretical vs experimental ^{13}C chemical shifts of monomeric organolithium compounds. ▲, α-carbons.

carbocations[18] even small basis sets give rather good results whereas species containing other first- or second-row atoms usually require more elaborate basis sets. However, the chemical shifts, particularly for carbocations, can be very sensitive to the geometries employed.[18] Hence, the comparison of IGLO results for different geometries with experimental ^{13}C chemical shifts affords a new tool for structural evaluation.

Our intention was to test the quality of small basis set IGLO calculations for organolithium compounds in order to see to what extent the chemical shifts are influenced by environmental effects (solvation, aggregation) and where IGLO might be useful for the solution of structural problems. Another paper[19] will deal with the dependence of the magnetic properties on size and quality of the basis set employed.

Method, Basis Sets, and Geometries

The derivation and detailed descriptions of the IGLO method are available.[15] Localized molecular orbitals are employed and the chemical shielding σ consists of a sum of diamagnetic (shielding) and paramagnetic (deshielding) MO contributions. The carbon 1s orbital usually makes the largest contribution, but this is constant (208 ppm shielding). Deshielding or paramagnetic contributions (negative sign; see footnote *a* of Table II) usually are associated with low-lying excited states (involving low-lying vacant orbitals, e.g., of π* type).[20]

We employed Huzinaga[21] Gaussian lobe basis sets (double-ζ quality without polarization functions) contracted as follows.[15b] Basis DZ (or A/A/A): C, 7s 3p contracted to [4111,21]; Li, 7s contracted to [4111]; H, 3s contracted to [21]. Basis DZ+sp(C) (or A/A+/A): same as DZ, augmented with diffuse s and p functions for carbon (exponent 0.06).

All geometries employed were calculated ab initio and were fully optimized in the given symmetry by using the Gaussian 82 program,[22] usually with the standard 3-21G[23] basis set. This sufficed for the compounds included here, as reoptimization at higher levels (e.g., 6-31G*) resulted only in minor changes in geometries and in the calculated chemical shifts (see examples in Table I).[24]

Table II. Chemical Shifts and MO Contributions of Solvated Methyllithium Species

compd	σ,[a] ppm (δ,[b] ppm)	C–Li, ppm	ΣC–H,[c] ppm
CH_3–Li	243.9 (−23.5)	18.2	24.9
CH_3–Li–OMe_2	245.0 (−24.6)	17.9	26.2
CH_3–Li–OH_2	244.8 (−24.4)	17.8	26.0
CH_3–Li$(OH_2)_2$	243.1 (−22.7)	16.0	26.3
$(CH_3$–$Li)_2$	241.8 (−21.4)	12.1	29.1
$(CH_3$–Li–$OH_2)_2$	238.8 (−18.4)	12.4	25.8
$(CH_3$–$Li)_4$ eclipsed	236.0 (−15.6)	9.5	26.0
$(CH_3$–$Li)_4$ staggered	244.2 (−23.8)	13.2	30.5
expt[d]	*−15.3*		

[a] Basis DZ+sp(C). [b] Relative to TMS; see text. [c] Sum of the three C–H bond contributions. [d] Reference 4.

Table III. Chemical Shifts and LMO Contributions of Solvated Vinyllithium Species

compound	σ,[a] ppm (δ, ppm)	C1 C–Li, ppm	ΣC–C, ppm	C1–H, ppm
C_2H_3Li	23.1 (192.9)	−67.8	−71.3	−32.4
C_2H_3Li–OH_2	18.4 (197.6)	−72.9	−69.8	−32.9
C_2H_3Li–$(OH_2)_2$	9.9 (206.1)	−81.4	−68.7	−33.5
$(C_2H_3Li)_2$[c]	27.5 (188.5)	−73.2	−60.8	−31.2
$(C_2H_3Li$–$OH_2)_2$[c]	20.9 (195.1)	−76.4	−63.5	−32.0
expt(dimer)[d]	*192.1*			
expt(tetramer)[d]	*183.2*			
C(2)	σ, ppm (δ, ppm)		ΣC–C	ΣC2–H[b]
C_2H_3Li	86.7 (129.3)		−60.9	−47.5
C_2H_3Li–OH_2	88.7 (127.3)		−61.0	−45.7
C_2H_3Li–$(OH_2)_2$	93.4 (122.7)		−59.5	−42.5
$(C_2H_3Li)_2$	71.2 (144.8)		−65.7	−57.4
$(C_2H_3Li$–$OH_2)_2$	77.9 (138.1)		−63.0	−53.3
expt(dimer)[d]	*130.0*			
expt(tetramer)[d]	*132.8*			

[a] Basis DZ. [b] Sum of the two C–H MO contributions. [c] C_{2h} symmetry. [d] Reference 28.

IGLO calculations give "absolute" chemical shielding values, σ, relative to the bare nucleus. The theoretical relative ^{13}C chemical shifts are based on CH_4 as the standard (the calculated shielding values σ for CH_4 are 218.3 ppm with the DZ basis and 222.7 ppm with the DZ+sp(C) basis) and, for comparison with experiment, converted to the usual tetramethylsilane (TMS) scale by using the experimental value $\delta(CH_4) = -2.3$ ppm relative to TMS.[25] (See ref 19 for a discussion of the appropriate primary reference.)

Basis Set Dependence. Our more detailed investigation[19] has established that basis sets larger than DZ do not result in significant changes in the calculated relative ^{13}C chemical shifts of unsaturated compounds. However, diffuse functions are essential for saturated organolithium compounds; the DZ+sp(C) basis set is used here. For the calculation of relative lithium chemical shifts, p functions on Li should be included.

Results

1. Monomeric Li Compounds. Despite the strong tendency to form higher aggregates, several hindered organolithium compounds have been shown recently to exist as monomers in solution (some of them in the presence of polydentate amines).[7,26,27] The observed ^{13}C NMR chemical shifts for the monomeric forms and the IGLO results are summarized in Table I. The agreement is satisfactory but not excellent. Most of the calculated values lie within about

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(18) (a) Schindler, M. *J. Am. Chem.* **1987**, *109*, 1020. (b) Bremer, M.; Schleyer, P. v. R.; Schötz, K.; Kausch, M.; Schindler, M. *Angew. Chem.* **1987**, *99*, 795. (c) Schleyer, P. v. R.; Laidig, K. E.; Wiberg, K. B.; Saunders, M.; Schindler, M. *J. Am. Chem. Soc.* **1988**, *110*, 300. (d) Saunders, M.; Laidig, K. E.; Wiberg, K. B.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1988**, *110*, 7652. (e) Schleyer, P. v. R.; Carneiro, J. W. de M.; Koch, W.; Raghavachari, K. *J. Am. Chem. Soc.* **1989**, *111*, 5475. (f) Bremer, M.; Schleyer, P. v. R.; Fleischer, U. *J. Am. Chem. Soc.* **1989**, *111*, 1147. (g) Bremer, M.; Schötz, K.; Schleyer, P. v. R.; Fleischer, U.; Schindler, M.; Kutzelnigg, W.; Pulay, P. *Angew. Chem.* **1989**, *101*, 1063. (h) Schleyer, P. v. R.; Koch, W.; Liu, B.; Fleischer, U. *J. Chem. Soc., Chem. Commun.* **1989**, 1098.

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(24) The chemical shifts in carbocations are often very sensitive to small changes in geometries, e.g., of bridging carbons or hydrogens, but this is not the case with "carbanions".

(25) Solution value, ref 4.

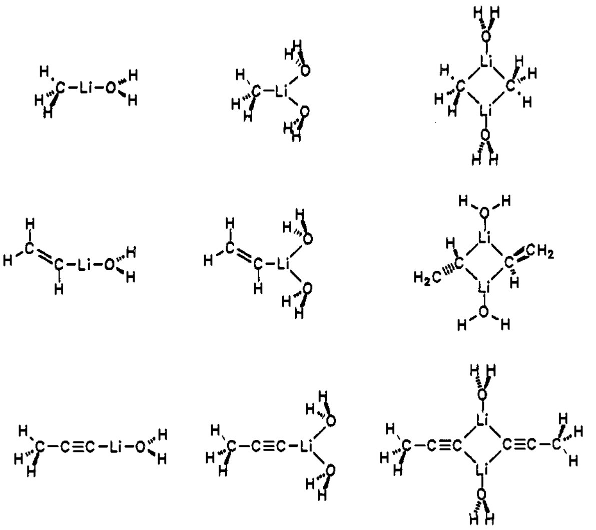


Figure 2. Conformations of the solvated methyl-, vinyl-, and propynyllithium structures employed in the IGLO calculations. The monomeric and dimeric forms have been fully optimized in C_s and C_{2h} symmetry, respectively (3-21G basis set).

Table IV. Chemical Shifts and LMO Contributions of Solvated Propynyllithium Species

compound	σ,[a] ppm (δ,[b] ppm)	C1–Li, ppm	∑C1–C2,[c] ppm	C2–C3, ppm
MeCC–Li	90.3 (125.7)	–45.1	–53.6	–10.9
MeCC–Li–OH$_2$	88.8 (127.2)	–46.6	–53.5	–10.9
MeCC–Li(OH$_2$)$_2$	88.0 (128.0)	–49.1	–51.6	–11.2
(MeCC–Li)$_2$	99.3 (116.7)	–44.9	–44.4	–11.2
(MeCC–Li–OH$_2$)$_2$	92.9 (123.1)	–47.8	–47.8	–11.2
(+≡–Li)$_2$ *expt*[d]	*118.6*			

C2	σ, ppm (δ, ppm)	C2–C3	∑C1–C2, ppm	C1–Li, ppm
MeCC–Li	124.1 (91.9)	–31.3	–25.2	–19.7
MeCC–Li–OH$_2$	125.2 (90.8)	–30.4	–25.9	–19.8
MeCC–Li(OH$_2$)$_2$	123.4 (92.7)	–30.6	–26.3	–20.2
(MeCC–Li)$_2$	105.7 (110.3)	–36.9	–37.3	–20.4
(MeCC–Li–OH$_2$)$_2$	113.8 (102.2)	–33.8	–32.5	–20.4

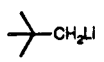
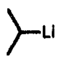
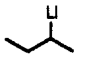
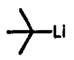
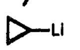
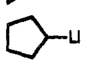
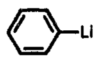
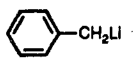
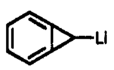
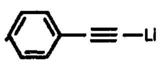
[a] Basis DZ. [b] ppm relative to TMS. [c] Sum of the three C–C MO contributions of the triple bond. [d] Fraenkel, G.; Pramanik, P. *J. Chem. Soc., Chem. Commun.* **1983**, 1527.

±5 ppm of experiment; the greatest deviation (over 20 ppm) is found for the β-carbon of phenylethynyllithium. The α-carbons, i.e., the carbons bearing the Li substituent, are described reasonably well (although the greatest deviation is ~10 ppm). Figure 1, a plot of calculated vs experimental shifts shows the degree of agreement graphically. The correspondence is remarkable, especially since the comparison involves δ values calculated for isolated molecules while the measurements refer to strongly solvated species in solution.

2. Effects of Dimerization and Solvation. Most organolithium compounds are polymeric both in solid state and in solution.[3] What is the effect of aggregation and also of solvation on the chemical shifts? In some cases, the chemical shifts for defined aggregates (dimer, tetramer, etc.) are known (e.g., for butyl-, vinyl-, and phenylethinyllithium; see tables). We examined these effects theoretically in a systematic way for methyl-, vinyl- and propynyllithium and to some extent for other lithium compounds. The results in Tables II–IV also include important MO contributions of the individual bonds to the chemical shift.

Solvation was modeled by coordinating one or more water molecules to the lithium (see Figure 2 for the conformations of the solvated forms). The use of water as a model solvent, dictated for larger systems by computational limitations, is justified by performance tests. For example, the IGLO results for methyllithium coordinated with one water or with one dimethyl ether solvent molecule are practically the same (see Table II). Also, a lithiated organic compound containing water as a ligand has been reported.[39]

Table V. C–Li LMO Contributions to the Absolute Shielding σ of the α-Carbons of Organolithium Compounds

compound	σ,[a] ppm	C$_\alpha$–Li
CH$_3$Li	243.9	18.2
C$_2$H$_5$Li	224.1	9.0
	208.7	3.4
	209.2	4.1
	187.6	–2.8
	206.6	1.9
	194.5	–2.2
	197.9	–0.1
	228.4	6.9
	190.8	–4.1
	23.1	–67.8
	29.7	–55.4
	177.0	–6.1
	174.7	–17.1
H—≡—Li	91.8	–49.2
CH$_3$—≡—Li	90.3	–49.2
	73.5	–46.9
	116.7	–18.2

[a] Basis DZ+sp(C) for saturated, DZ for unsaturated compounds; see footnote *a* of Table II.

The effect of complexing water molecules to either the monomer or the dimer of methyllithium is rather small (3 ppm upfield shift for the latter). The contributions of the C–Li and the C–H bonds to the changes in the chemical shifts are equally important.

The staggered and the eclipsed conformers of (CH$_3$Li)$_4$ were the only tetrameric organolithium compounds examined.[12] Interestingly, the ^{13}C chemical shifts of these conformers differ by more than 8 ppm. The experimental value refers to the staggered conformer, which is more likely to be found in polar solvents.

No clear trend can be seen in the effects of aggregation: going from the unsolvated monomer to the dimer results in a small upfield shift, but the dimer–tetramer shift difference is either upfield or downfield, depending on the tetramer conformations. Although the differences are not large, the chemical shift depends more on the individual structure than on the degree of association.

The chemical shifts for vinyllithium (Table III) show a definite trend. Coordination of solvent molecules causes the α-carbon C1 to become more deshielded and the β-carbon C2 to become more shielded. The effect of dimerization is opposite, so that the chemical shifts of the solvated dimer are similar to those of the monomer. By coincidence, these match the experimental values almost exactly. The LMO contributions to σ of C1 indicate that solvation effects are dominated by the C–Li contribution whereas for dimerization the C–C contributions are more important.

In this context it is intriguing to speculate about the related phenyllithium. The situation (cancelling effects of solvation and of aggregation) may well be analogous: the ipso carbon chemical shift calculated for the C$_6$H$_5$Li monomer (186.3 ppm; see Table I) nearly matches the experimental ipso C for the solvated dimer

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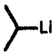
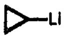
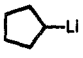
(26) Wimmer, P. Diplomarbeit, München, 1985.
(27) Fraenkel, G.; Winchester, W. R. *J. Am. Chem. Soc.* **1988**, *110*, 8720.
(28) Bauer, W., unpublished measurements.

Table VI. ^{13}C Chemical Shifts of Alkyllithium Compounds

compound	symmetry	IGLO[a] δ,[b] ppm C1	C2	C3	C4
	linear C_s	11.7	19.0	20.3	
	expt	*16.1*	*24.8*	*25.7*	
	C_s	13.8	22.1		
	expt	*10.2*	*23.7*		
	gauche C_1	3.9	25.4	18.9	12.7
	linear C_s	11.2	28.9	27.4	13.6
	expt(dimer)[c]	*12.8*	*35.9*	*37.3*	*14.9*
	expt(tetramer)[c]	*10.5*	*33.9*	*35.4*	*14.7*
	C_s	−8.0	−4.5		
	expt	*−9.4*	*2.7*		
	exo C_s	29.6	31.9	22.5	
	expt[c]	*28.3*	*40.0*	*28.8*	

[a] Basis DZ+sp(C). [b] Relative to TMS, experimental values in italics, taken from ref 5, except where otherwise noted. [c] Reference 28.

(185.5 ppm).[7] In contrast, the experimental value for the (solvated) monomer[7] appears 8 ppm to lower field.

Compared to vinyllithium, the effect of coordinating H_2O molecules to propynyllithium is very small for the monomer (see Table IV). This may also hold for monomeric phenylethynyllithium, where the calculated chemical shift of the α-carbon is in good agreement with experiment even though no solvent models are included (see Table I). The chemical shifts of the propynyllithium dimer are somewhat more susceptible to donor coordination, but the partial cancellation of solvation and dimerization effects, noted above, is seen again.

In summary, the IGLO chemical shifts for saturated organolithium monomers agree satisfactorily with experimental values; solvation and even aggregation effects do not have to be taken into account (cf. the experimental results for the *n*-BuLi aggregates; Table VI). However, this is not the case for unsaturated compounds, where solvation and aggregation effects may compensate, but are significant and should not be neglected.

This behavior can be rationalized by regarding the LMO contributions of the C–Li bond orbitals, given in Table V. The C–Li contributions for the saturated compounds are usually diamagnetic and are rather small. In such cases, solvation or even aggregation is not expected to affect the chemical shift significantly. Consequently, other simple alkyllithium compounds are described reasonably well even when calculated as monomers. Some IGLO results are shown in Table VI. The agreement with experiment is quite good, especially for the α-carbons.

On the other hand, the C–Li contributions to σ of unsaturated compounds are strongly paramagnetic (deshielding) due to low-lying unoccupied π* orbitals.[20] These paramagnetic contributions and hence the chemical shifts are more sensitive to changes in the coordination sphere of the lithium.

Lithium Chemical Shifts. Usually lithium chemical shifts (^6Li) of organolithium compounds are not very informative, since for most compounds the shifts cover only a very small range of ca. 2–3 ppm.[9] Spectacular exceptions are upfield shifts up to 13 ppm due to anisotropy effects on lithium "sandwiched" by two aromatic anion moieties.[29,30] For calculations on lithium chemical shifts of representative compounds and for a detailed discussion of the effects governing these chemical shifts see ref 19. There it is shown that a correct description of the trends in δ ^6Li usually requires inclusion of p functions on Li in the IGLO basis set.

3. Applications. This section illustrates how IGLO calculations may be applied to various structural problems in light of the results given above.

***n*-Butyllithium.** Since the chemical shifts of saturated organolithium compounds are not very sensitive to solvation and aggregation, one may be able to make reliable assignments based on the simple monomers. For *n*-butyllithium two conformers have been calculated: *all-trans* **1** with C_s symmetry and an "*all-gauche*" **2** (Figure 2), the latter being of interest because of an agostic interaction between the lithium and one hydrogen of the methyl group (distance Li–H = 2.14 Å; intramolecular Li···HC interactions have been proposed, e.g., for cyclohexyllithium hexamer with mean X-ray Li–H distances between 2.00–2.33 Å;[31a] very

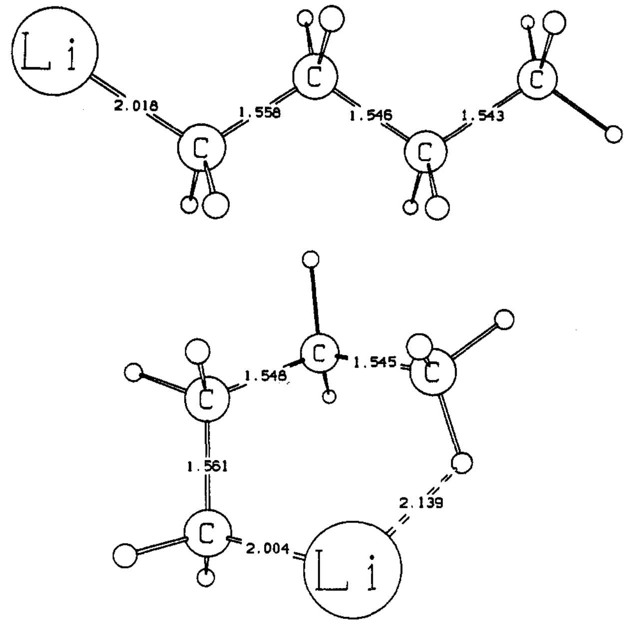


Figure 3. *n*-Butyllithium, trans conformer **1** (C_s) and gauche form **2** (C_1), 3-21G optimized.

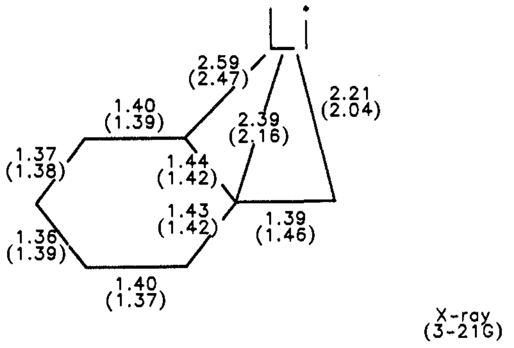


Figure 4. Comparison of the ab initio geometry of benzyllithium **5** (values in parentheses) to the X-ray structure (from ref 33).

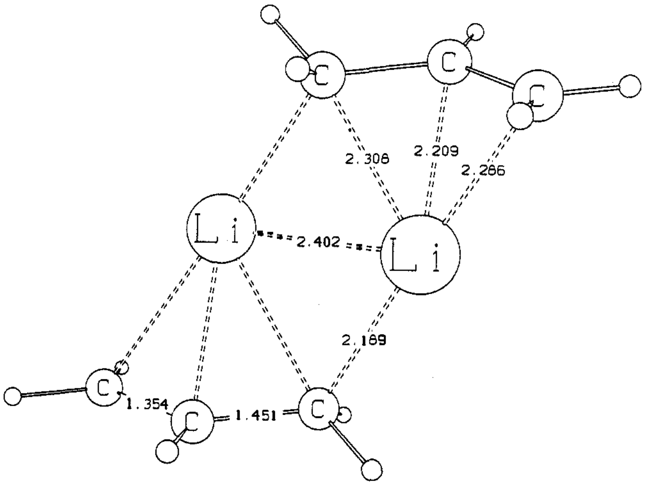


Figure 5. Allyllithium dimer, C_i symmetry (3-21G optimized).

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(29) Paquette, L. A.; Bauer, W.; Sivik, M. R.; Bühl, M.; Feigel, M.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1990**, *112*, 8776.

(30) (a) Exner, M. M.; Waak, R.; Steiner, E. C. *J. Am. Chem. Soc.* **1973**, *95*, 7009. (b) Fraenkel, G.; Hallden-Abberton, M. P. *J. Am. Chem. Soc.* **1981**, *103*, 5657.

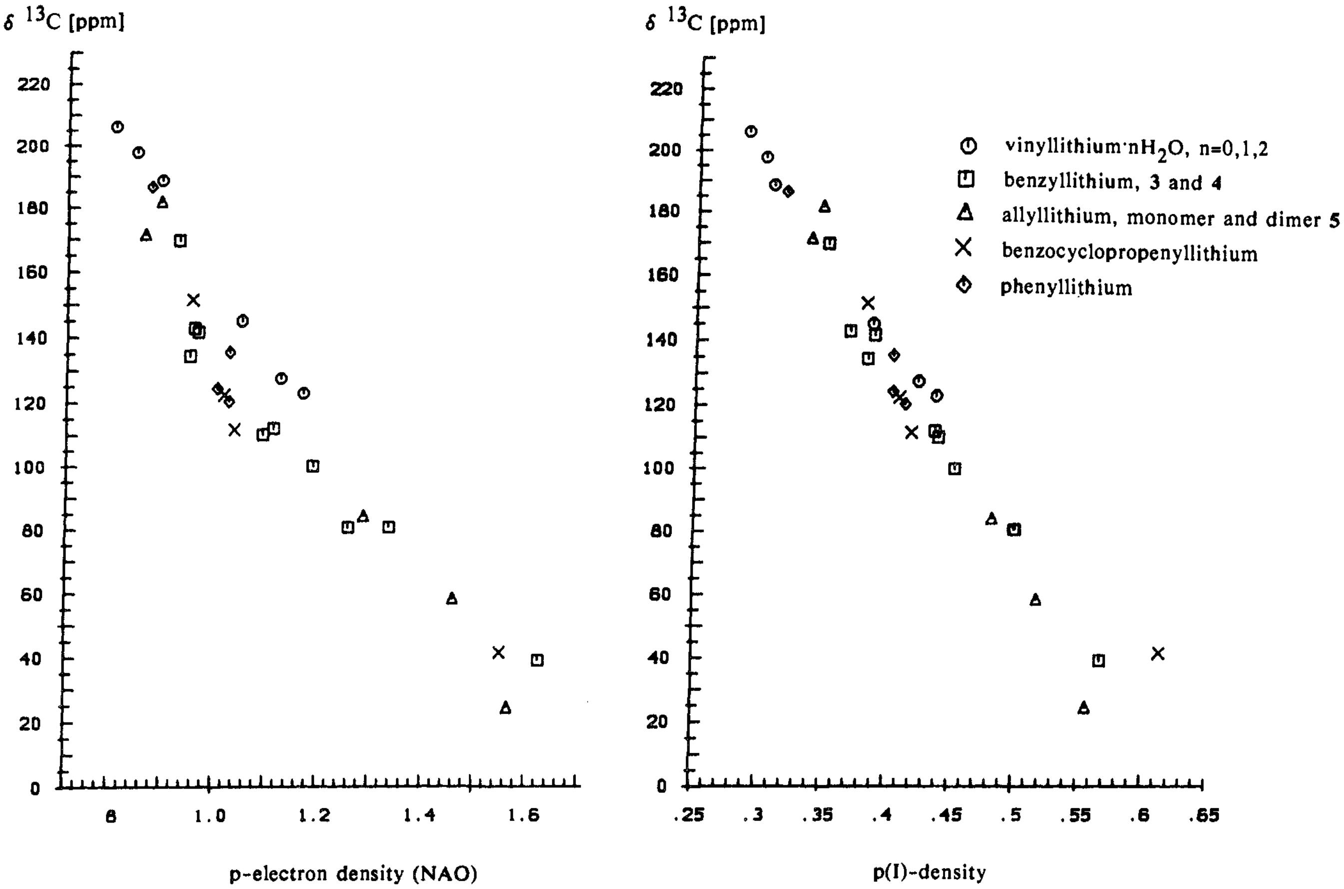
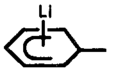
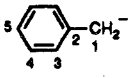


Figure 6. Correlation of the ^{13}C chemical shifts of some unsaturated organolithium compounds with π-electron densities obtained from NPA analysis (left) and from Mulliken population analysis (right; only the inner orbital occupancy of the split valence basis set was used in the correlation).

Table VII. IGLO ^{13}C Results for Benzyllithium

compound	IGLO[a] δ, ppm C1	C2	C3	C4	C5
3 	39.0	169.6	111.9	134.2	109.9
4 	80.4	141.5	99.8	142.6	80.4
5 	39.3	170.1	110.5[b]	135.1[b]	109.5
	60.2	153.0	98.7	132.2	84.2
expt(PhCH$_2$–Li)[c]	*36.7*	*160.6*	*116.4*	*128.2*	*104.2*
expt(PhCH$_2$–K)[c]	*52.7*	*152.7*	*110.7*	*130.6*	*95.7*

[a] Basis DZ. [b] Average values for the two nonequivalent carbons in the unsymmetric static structure. [c] O'Brien, D. H.; Hart, A. J.; Russell, C. R. *J. Am. Chem. Soc.* **1975**, *97*, 4410.

recently, a structure of cyclopentyllithium showing similar interactions has been determined[31b]). Conformers **1** and **2** show remarkable differences in their ^{13}C chemical shifts (Table VI), especially for the α-carbons. Since these generally are described rather well, the IGLO results are a strong hint that the all-trans conformation, which is more stable by 0.7 kcal/mol at the 3-21G//3-21G level for the monomer, may also be dominating for the higher aggregates in solution. This is in accord with ^{6}Li–^{1}H 2D HOESY experiments where mainly contacts between the lithium and the α- and β-hydrogens are noted.[8b]

Benzyllithium. Two structural possibilities for benzyllithium have been considered: **3**, with the Li$^+$ bridging benzylic and ipso carbons, and **4** with a Li-capped aromatic ring, each in C_s symmetry. The IGLO results for **3**, **4**, and the benzyl anion (C_{2v} symmetry) are given in Table VII; only the calculated chemical shifts for structure **3** agree with experiment. Structure **4**, which is less stable than **3** by 3.9 kcal/mol at 3-21G//3-21G, clearly can be rejected.

Table VIII. ^{13}C Chemical Shifts for Allyllithium, IGLO and Experiment

compound	symm	IGLO[a] δ, ppm C1	C2
C_3H_5Li	C_s	58.3	181.6
$C_3H_5Li–OH_2$	C_s	55.1	172.3
$C_3H_5Li–(OH_2)_2$	C_s	54.5	165.7
$(C_3H_5Li)_2$ 6	C_i	54.2[b]	171.4
$C_3H_5^-$	C_{2v}	52.2	146.3
expt[c]		*51.1*	*147.0*

[a] Basis DZ. [b] Average value for C1 and C3 in the static structure. [c] Schlosser, M.; Stähle, M. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 485.

The chemical shifts of **4** should be susceptible to solvation and are expected to change toward those of the benzyl anion. In contrast, solvation should play a minor role for **3** (at least as far as the benzylic carbon is concerned), since the C–Li MO contribution, though paramagnetic, is rather small (see Table V).

Interestingly, the calculated chemical shifts of the "naked" benzyl anion show pronounced differences from those of the benzyllithium structures, but are rather similar to the measured shifts of benzylpotassium (see Table VII). This emphasizes the important role of the Li gegenion. Experimental results on the related (7-phenylnorbornyl)lithium/potassium pair have been interpreted in terms of a planar benzylic carbon for the potassium, but in a pyramidalized one for the lithium gegenion.[32]

Several X-ray structures of benzyllithium are known (monomeric as $C_6H_5CH_2Li[N(CH_2CH_2)_3N]$[33] and $C_6H_5CH_2Li·THF·TMEDA$,[34] and polymeric as $(C_6H_5CH_2Li·OEt_2)_x$[35]). The

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(31) (a) Zerger, R.; Rhine, W.; Stucky, G. D. *J. Am. Chem. Soc.* **1974**, *96*, 6048. (b) Hoffmann, D.; Schleyer, P. v. R.; Stalke, D. Unpublished results.

first of these shows this molecule to be unsymmetrical with an additional interaction between lithium and one ortho carbon. This structure, **5**, is reproduced quite well when calculated ab initio with the 3-21G basis set (see Figure 3), but since calculated without ligands, the C–Li distances are too short.

Surprisingly, this structure is only 0.1 kcal/mol more stable than the symmetrically bridged **3** at 3-21G//3-21G. (This may explain the rather pronounced influence of the ligands on the exact position of the Li^+.[34]) However, the average chemical shifts of the unsymmetrical form **5** do not deviate by more than ~1 ppm from those of symmetrical **3** (Table VII).

Allyllithium. Allyllithium is a very interesting case: the IGLO-calculated chemical shifts of the central carbon C2 for the symmetrically bridged form is unique in being so far from the experimental value. The deviation is more than 30 ppm (IGLO 181.6 ppm for C2, experiment 147.0 ppm; see Table VIII).

In contrast, the IGLO values calculated for the planar allyl anion fit a lot better (at least with the DZ basis set; 146.3 ppm for C2). Of course, allyllithium is not dissociated in solution. On the contrary, it has been shown to exist as an unsymmetrical dimer in tetrahydrofuran[36] (the solvent to which the experimental values refer). Hence, a plausible structure for the dimer was calculated (**6**, Figure 5). The IGLO results on **6** show a modest "improvement" (171.4 ppm for C2), but still deviate more than 20 ppm from experiment.

However, as noted above, the inclusion of solvation effects also is essential. This is demonstrated for the bridged monomer. When one or two water molecules (as models for ether solvents) are coordinated to the lithium, the IGLO chemical shift of C2 (172.3 or 165.7 ppm, respectively, Table VIII) approaches the experimental value. Unlike vinyllithium, where aggregation and solvation effects partially compensate each other (cf. Table III), these effects work in the same direction in allyllithium: both result in greater shielding. If additivity is assumed, then the ^{13}C chemical shifts for a solvated dimer can be estimated to be about 50 and 155 ppm for C1 and C2, respectively, close to the experimental values. Unfortunately, more detailed structural assignments are not possible at present. The large dependence of the chemical shifts on solvation is expected to obscure effects due to geometrical changes.

Discussion

The IGLO ^{13}C chemical shifts of organolithium compounds calculated with small basis sets are in reasonable agreement with experiment. However, it is necessary to include diffuse functions in the IGLO basis set for saturated compounds; solvation and aggregation effects are more important for unsaturated compounds.

The influence of solvation and aggregation is related to the C–Li bond LMO contribution to the chemical shift. This is strongly paramagnetic for the unsaturated compounds. In the theoretical framework, these paramagnetic components contribute to the downfield shift of unsaturated "carbanions" relative to the parent hydrocarbons.[6] The energy of the $\sigma_{C\text{-}Li}$ bond orbital is raised with respect to the corresponding σ_{CH} orbital (e.g., it is the HOMO in monomeric vinyllithium). Therefore, the σ–π^* energy gap is reduced and the importance of paramagnetic contributions is enhanced, cf. the discussion in ref 19.

But another relationship also seems to be valid, that between the chemical shift and the π-electron density. This was shown some time ago by Spiesecke and Schneider for simple Hückel aromatic systems[37] (although the strict linearity of this relation has been questioned more recently on the basis of IGLO calculations[18f]). In the left half of Figure 6 the chemical shifts of several unsaturated organolithium compounds (including solvated and aggregated species) are plotted against the corresponding p-electron densities, as given by the occupancies of natural atomic orbitals (NAO) from natural population analysis (NPA).[38]

Even though the correspondence is not excellent (the correlation coefficient of all points is 0.972), an overall trend is apparent. In Figure 6 (right-hand side) the chemical shifts are plotted against the p-orbital population obtained from a Mulliken population analysis (basis set 3-21G); only the inner p orbitals from the split-valence shell were considered according to the physical intuition that (since localized closer to the nuclei) these should be more important in governing the chemical shifts.[40] The correspondence is better (the correlation coefficient is 0.980); however, the scattering of the points is still quite large, indicating that the individual chemical shifts also are influenced by other factors.

Even if IGLO calculations for organolithium compounds may not be as useful a tool for structure elucidation as, e.g., for carbocations,[18] reliable differentiation between certain structural possibilities can be made.

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft, the Volkswagenstiftung, the Fonds der Chemischen Industrie, and the Convex Computer Corp. We are grateful to M. Schindler for the Convex version of the IGLO program employed at Erlangen and to T. Clark for valuable discussions. The calculations were performed on a Cyber 990E of the Regionales Rechenzentrum Erlangen, a Convex C120 at the Institut für Organische Chemie and a Cyber 205 of the Rechenzentrum der Ruhr-Universität Bochum. Computer time was granted by the HLRZ Jülich. N.v.E.H. acknowledges a Alexander von Humboldt Stiftung fellowship. Part of this work was taken from the Diplomarbeit of M.B., Erlangen, 1989.

Supplementary Material Available: Structures and energies of the calculated molecules in the form of archive entries (8 pages). Ordering information is given on any current masthead page.

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[32] Peoples, P. R.; Grutzner, J. B. *J. Am. Chem. Soc.* **1980**, *102*, 4709.

[33] Patterman, S. D.; Karle, I. L.; Stucky, G. D. *J. Am. Chem. Soc.* **1970**, *92*, 1150.

[34] Zarges, W.; Harms, K.; Marsch, M.; Boche, G. *Chem. Ber.* **1989**, *122*, 2303.

[35] Beno, M. A.; Hope, H.; Olmstead, M. M.; Power, P. P. *Organometallics* **1985**, *4*, 2117.

[36] (a) Winchester, W. R.; Bauer, W.; Schleyer, P. v. R. *J. Chem. Soc., Chem. Commun.* **1987**, 177. (b) Hommes, N. J. R. v. E.; Bühl, M.; Schleyer, P. v. R.; Wu, Y. D. *J. Organomet. Chem.*, in press.

[37] Spiesecke, H.; Schneider, W. *Tetrahedron Lett.* **1961**, 468.

[38] Reed, A. E.; Weinstock, R. B.; Weinhold, F. *J. Chem. Phys.* **1985**, *83*, 735.

[39] Barr, D.; Raithby, P. R.; Schleyer, P. v. R.; Snaith, R.; Wright, D. S. *J. Chem. Soc., Chem. Commun.* **1990**, 643.

[40] Inclusion of the complete Mulliken p-orbital populations results in a slightly worse correlation, comparable to the left-hand side of Figure 6.