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A comparative theoretical study of the allyl alkali metals

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Abstract

The *ab initio* structures calculated for the Li–Cs series of allyl alkali metal compounds prefer symmetrically bridged geometries. Bonding is mainly electrostatic; the natural charges on the metals range from 0.910 (Li) to 0.999 (Cs). Dimerization and solvation, which were studied for allyllithium, result in longer bonds to the metal. Rotational barriers, calculated for the monomers, show the uniform trends to larger values along the series, $Cs > Rb > K > Na$, as is found by experiment. The calculated barrier for monomeric allyllithium, out of line and also too high with regard to experiment, is lowered by dimerization and solvation. The reasons for the abnormally low ^1J(C–H) coupling constants (e.g. 131–133 Hz for the central carbon for all alkali metals) have been disputed. Hybridizations given by the Natural Bond Orbital method are in reasonable agreement with those deduced from the usual empirical relationship $0.2\ J(^{13}C{-}H) = \%s$. Model calculations on allyllithium and the allyl anion with imposed structural constraints show that CCC-angle widening is the main cause of the small coupling constants; hydrogen out-of-plane bending and σ-polarization due to the π-charge have smaller influences.

Introduction

The allyl anion [1] and its alkali metal derivatives [2,3], as the prototypes for π-delocalized carbanions and organometallic compounds, have been the subject of extensive experimental and theoretical studies. Structures with (symmetrically or slightly asymmetrically) bridging metal atoms, predicted by *ab initio* calculations [2,3] were indicated by isotopic perturbation [4] and variable temperature NMR investigations [5], and in the case of lithium were found in crystal structure determinations [6,7]. Rotational barriers, determined by NMR, increase in going from allyllithium to the heavier allyl alkali metals. The C–H coupling constants are unusually low relative to the normal values for alkenes, and are hardly affected by the metal.

Theoretical investigations of the allyl anion and its lithium and sodium salts first predicted a considerable widening of the CCC angle: 132.2° for the "free" anion

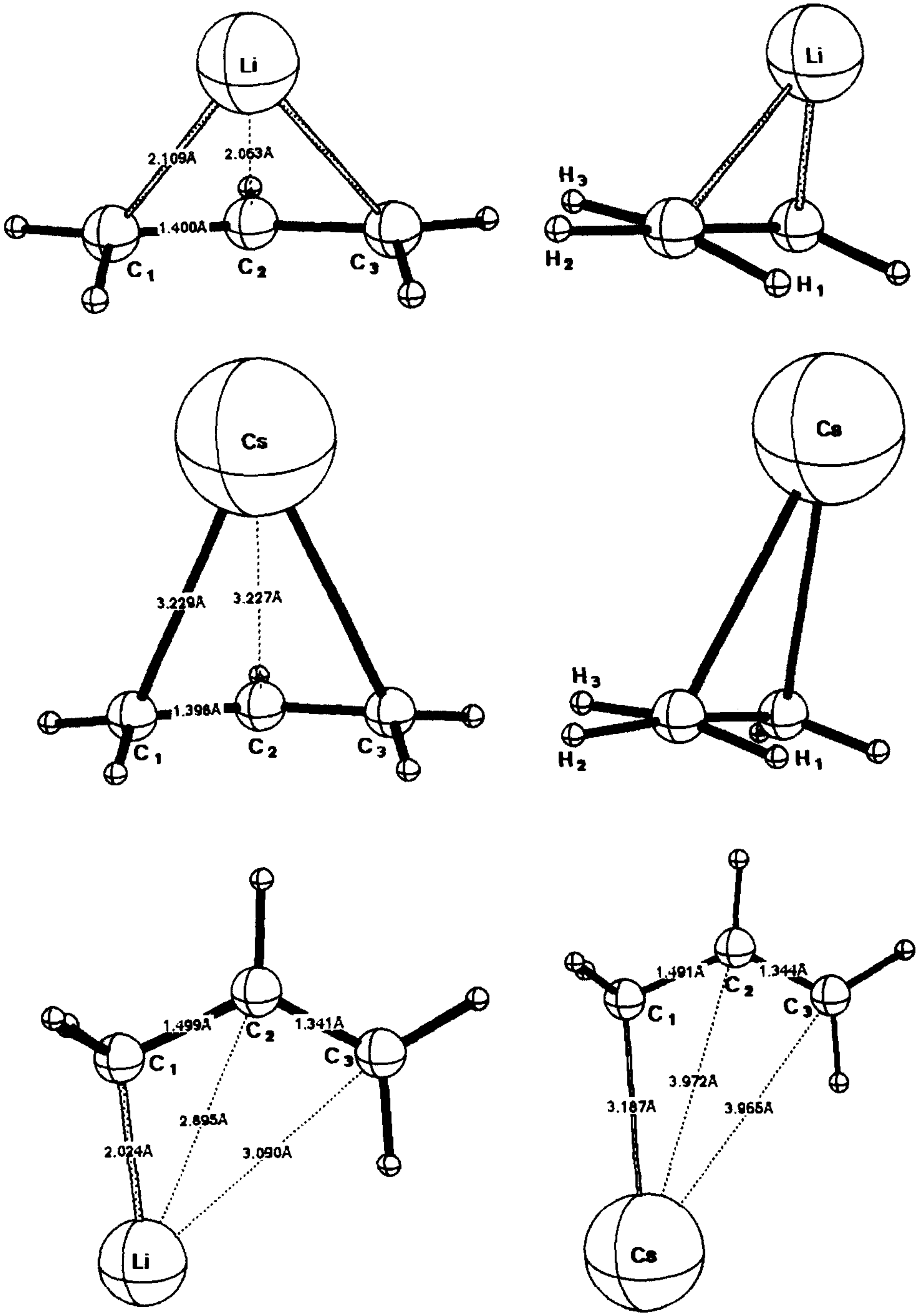
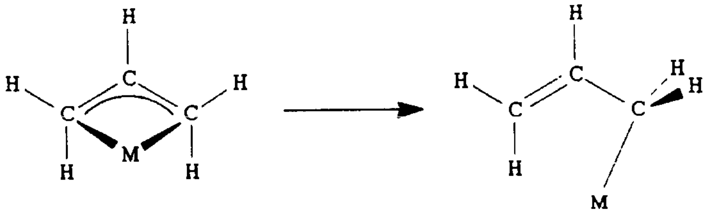


Fig. 1. Calculated structures of the bridged and planar forms of allyllithium (MP2/6-31G**) and allylcesium (MP2/6 – 31G*-Huzinaga).

[1b]. The C(1)–C(3) antibonding character of the HOMO and the repulsion between the anionic centers are responsible. The allyllithium and allylsodium structures, calculated with the alkali metal cation in a bridging position, have somewhat lower values for the CCC-angle (125.9 and 128.1°, for C_3H_5Li and C_3H_5Na, respectively), because of the attractive interaction between the cation and the anionic centers. This effect is strongest for allyllithium, which has the shortest C–M distances. Furthermore, the metal cation interaction results in considerable deviations from planarity for the allyl anion [2,3]. The hydrogen atom on C_2 is bent up towards the metal, while the *endo*-hydrogens on C_1 and C_3 are bent away (see Fig. 1). These structural predictions [2,3] have recently been confirmed by the X-ray structure determination of allyllithium as a monomer complexed with PMDTA [6]: the experimental CCC-angle is 131.5° and the hydrogen atoms are bent out of the plane. The size and orientation of the PMDTA ligand causes the lithium cation to be somewhat moved away from the "ideal" symmetrically bridging position in the mirror plane. In addition, a CCC-angle of 131° is found in the X-ray structure of 1,3-diphenylallyllithium [7], which forms polymeric chains with symmetrically bridging lithium atoms, complexed with diethyl ether.

Early isotopic perturbation experiments [4] indicated a symmetrical [8,9] or rapidly equilibrating nearly symmetrical [10] allyllithium species in THF, assumed to be a monomer. A later study by Winchester et al. [5], using variable-temperature-NMR and cryoscopy, established that allyllithium is an unsymmetrical dimer in THF. Allylsodium and allylpotassium are symmetrical monomers under these conditions.

Rotation about a carbon carbon bond in the allyl moiety "shuts off" π resonance. The barrier to rotation thus provides a measure of the resonance energy [11 *]. Upon going to the larger heavier alkali metals K, Rb and Cs, the allyl moiety is expected to resemble the "free" allyl anion more closely (Scheme 1), because the cation in the ion pair is farther away.



	C_3H_5Li	C_3H_5Na	C_3H_5K	C_3H_5Rb	C_3H_5Cs	$C_3H_5^-$
Exp. ($\Delta G^\ddagger$)	10.7 [12]	11.5 [9]	16.7 [12] 17.1 [9]	18.1 [9]	18.0 [12]	
Calc. ($\Delta H^\ddagger$)	17.7 [3]	11.9 [3]				22.2 [1a] 19.3 [13] 19.0 [1c]

Scheme 1. Experimental and calculated rotational barriers for allyl alkali metals and allyl anion.

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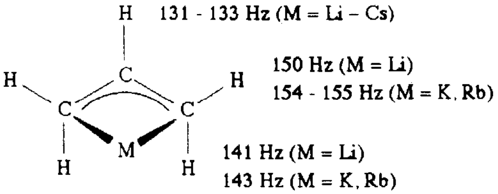
[*] Reference number with asterisk indicates a note in the list of references.



Scheme 2. Experimental C–H coupling constants for allyl alkali metals.

The largest measured barrier, ca. 18 kcal/mol, is a reasonable lower limit for the energy of rotation of rotation of the hypothetical "free" allyl anion in solution. The best calculated values, ca. 19 kcal/mol, are very similar. The theoretical barrier ($\Delta H^{\ddagger}$ value) reported for allylsodium [3] also is in reasonable agreement with experiment, but the theoretical value for allyllithium, 17.7 kcal/mol, is ca. 7 kcal/mol too high. This discrepancy may be due to the dimeric character of allyllithium in THF solution [14].

^{13}C–^{1}H coupling constants for allyl alkali metals are remarkably low [9,15], especially for H–C_2, and show very little variation with changes of the metal. $J(C_2$–$H)$ is about 25 Hz lower than the "normal" value for sp^2-carbon (propene, 157.4 Hz [16]), while the values for the terminal hydrogens are 10 to 15 Hz lower than expected (Scheme 2).

Since ^{1}J(C–H) is almost completely determined by the Fermi contact term, which is directly related to the %*s*-character in the carbon hybrid orbital, small C–H coupling constants imply less carbon *s*-character. However, the reasons for this rehybridization in the allyl alkali metals are the topic of considerable debate. Schlosser et al. [17–19] implicate the out-of-plane bending of the hydrogen atoms, discovered computationally [2], as the leading cause. Clark et al. [3], as well as Ahlbrecht, Boche et al. [20] consider in-plane distortion, i.e., CCC-angle widening, to be more important. Furthermore, the negative charge on the allyl moiety is expected to have an additional effect [9,15].

In this paper, we report *ab initio* calculated structures for the allyl anion and the complete series of allyl derivatives of the alkali metals (except francium). For all compounds, two forms are calculated: the most stable form with symmetrically bridging alkali metal cation as well as the *cis*-planar conformation. The latter is more stable than the trans planar form and is the transition state for CH_2-rotation. For allyllithium, dimeric forms and model solvates have been examined as well. We have endeavoured to answer the major questions left unresolved by the earlier work.

Computational methods

Calculations were performed using the GAUSSIAN 82 and 88 [21] and CADPAC 4.0 and 4.1 [22] programs. For C, H, Li and Na, standard basis sets (3 – 21G [23], 6 – 31G* [24], 6 – 31G** [24], 6 – 31 + G, and 6 – 31 + G* [25]) were used. For K, Rb and Cs, we employed the Huzinaga [26] minimal basis sets, with the highest shell split and an additional *p*-function (and a *d*-function on K in MP2 optimizations). The contraction schemes were: K: 43321/4211(/1), Rb: 433321/43211/4, Cs: 4333321/43321/43. All geometries were fully optimized within C_s-symmetry, unless indicated otherwise, and characterized as minima or transition structures by calculation of vibrational frequencies. Influence of electron correlation was estimated using Møller–Plesset theory carried out to second order. For optimizations at this level, and for single point calculations on allylpotassium, allylrubidium and allylcesium, correlation included all electrons (MP2-fu) [27]; otherwise, core electrons were kept frozen (MP2-fc). Atomic charges and hybridizations were calculated at $3-21G$ and $6-31+G$ levels using the Natural Population Analysis method [28].

Geometries and charges

As expected from the size of the cations, the carbon metal distances increase on going from lithium to cesium (Table 1, Fig. 1), but the C–C bond lengths in the bridged form show only minor changes. The CCC bond angle widens from 126.0° for C_3H_5Li to 130.2° for C_3H_5Cs and thus approaches the value of 131.5° calculated for the allyl anion (Table 1, see ref. 1). The natural charges [28] (Table 2) show a comparable trend: the charge on the allyl moiety increases from -0.91 for allyllithium to -0.999 for allylcesium. In all cases, the hydrogens are bent out of the CCC-plane. Even in the completely ionic allylcesium, considerable interaction

Table 1

Geometrical parameters for bridged C_3H_5M species (Å and °)

Compound	Level	$M-C_{1,3}$	$M-C_2$	$C_{1,3}-C_2$	$C_1C_2C_3$	Ω-H_1 ^{b}	Ω-H_2 ^{b}	Θ-H_3 ^{c}
C_3H_5Li	$3-21G$	2.141	2.093	1.394	125.9	−28.1	1.0	11.3
	$6-31G^{*}$	2.127	2.079	1.392	126.5	−28.4	0.7	12.3
	$6-31G^{**}$	2.127	2.078	1.392	126.6	−28.0	0.8	12.2
	$MP2/6-31G^{**}$	2.109	2.063	1.400	126.0	−27.8	0.2	13.2
$C_3H_5Li-H_2O$	$3-21G$	2.193	2.128	1.391	126.8	−25.2	−0.8	9.8
	$6-31G^{*}$	2.169	2.107	1.391	127.3	−26.6	−0.4	11.7
$C_3H_5Li-(H_2O)_2$	$3-21G$	2.279	2.185	1.389	128.4	−23.5	−2.6	8.6
C_3H_5Li-PMDTA	(exp.) [6]	2.255	2.326	1.361	131.5	−13.7	−6.1	6.3
		2.720		1.379		−11.0	−8.6	
$(C_3H_5Li)_2$	$3-21G$	2.286	2.209	1.451	126.9	−15.8	+3.1	8.4
		2.308	(2.190 ^{d})	1.356		−31.7	−21.6	
C_3H_5Na	$3-21G$	2.475	2.426	1.393	128.1	−23.4	−4.2	7.4
	$6-31G^{*}$	2.503	2.443	1.393	129.2	−24.4	−5.1	8.6
	$6-31G^{**}$	2.503	2.441	1.392	129.2	−23.8	−4.8	8.3
	$MP2/6-31G^{**}$	2.491	2.425	1.400	128.7	−23.8	−6.0	8.5
C_3H_5K	$3-21G$ ^{a}	2.888	2.857	1.389	129.5	−20.9	−6.6	5.7
	$6-31G^{*}$ ^{a}	2.870	2.852	1.390	130.0	−23.7	−6.5	7.1
	$6-31G^{**}$ ^{a}	2.871	2.853	1.390	130.1	−23.1	−6.3	7.6
	$MP2/6-31G^{**}$ ^{a}	2.811	2.791	1.398	129.3	−25.2	−7.8	8.9
C_3H_5Rb	$3-21G$ ^{a}	3.045	3.026	1.388	129.9	−20.4	−7.0	5.5
	$6-31G^{*}$ ^{a}	3.067	3.054	1.390	130.7	−22.4	−7.7	7.0
	$MP2/6-31G^{*}$ ^{a}	3.052	3.025	1.399	130.1	−22.8	−9.4	7.6
C_3H_5Cs	$3-21G$ ^{a}	3.210	3.218	1.386	130.2	−20.4	−7.4	5.8
	$6-31G^{*}$ ^{a}	3.251	3.260	1.388	131.0	−22.2	−8.0	7.1
	$MP2/6-31G^{*}$ ^{a}	3.229	3.227	1.398	130.4	−24.1	−9.9	8.0
$C_3H_5^-$	$6-31+G^{*}$	–	–	1.388	132.2	0.0	0.0	0.0
	$6-31+G^{**}$	–	–	1.388	132.2	0.0	0.0	0.0
	$MP2/6-31+G^{**}$	–	–	1.396	131.5	0.0	0.0	0.0

[a] Huzinaga basis sets [26] (*vide supra*) used for K, Rb and Cs. [b] Dihedral angle $H-C_1-C_2-C_3$. [c] Angle between $H-C_2$ bond and $C_1-C_2-C_3$ plane. [d] Distance C_1-Li'.

Table 2

Natural charges in bridged C_3H_5M species (6-31+G basis set)

Compound	M	$C_{1,3}$	C_2	C_2-H	$C_{1,3}$-H_{endo}	$C_{1,3}$-H_{exo}
C_3H_5Li	0.910	−0.932	−0.198	0.239	0.217	0.239
C_3H_5Na	0.938	−0.926	−0.183	0.228	0.204	0.230
C_3H_5K	0.973	−0.906	−0.175	0.211	0.187	0.214
C_3H_5Rb	0.986	−0.906	−0.174	0.208	0.184	0.212
C_3H_5Cs	0.999	−0.918	−0.181	0.212	0.187	0.216
$C_3H_5^-$	–	−0.883	−0.174	0.187	0.187	0.190

between the alkali metal cation and the allyl anion exists. The degree of out-of-plane bending is largest for allyllithium, but this is attenuated upon solvation (Table 1, Fig. 2, see also ref. 20a) at least in part because of the greater carbon–lithium distance. The direction of out-of-plane bending for H_2 in allyllithium also is reversed on solvation, in agreement with the experimental structure for the PMDTA-complexed monomer [6].

On going from allyllithium to the heavier alkali metal derivatives, the degree of out-of-plane bending decreases for C(1)–H(1) (the inner hydrogen), but increases for C(1)–H(2) (Table 1, Fig. 1). The illustrations on the left hand side of Fig. 1 show the differences clearly. Out-of-plane bending for C(2)–H(3) is largest for allyllithium, while the value for the other alkali metal derivatives (and for the disolvated allyllithium) is nearly the same.

Rotational barriers

For the allyl alkali metals, rotation transition structures with the metal *syn* to the double bond were found to be lower in energy than the corresponding *anti* forms [3]. Contradictory results were reported for the allyl anion: Chandrasekhar et al. found the *anti* transition structure to be more stable than the *syn* TS [1a], while Gonzâlez Luque et al. reached the opposite conclusion [13].

Table 3 lists the calculated total energies for the bridged and *cis* planar conformations of the allyl alkali metals; Table 4 gives the barriers to rotation. The *syn* and *anti* rotational transition structures for the allyl anion are included for comparison.

With the exception of allyllithium, calculated rotational barriers show the same trend as the experimental values: higher barriers are found for the heavier alkali metals. As expected, the barrier for allylcesium approaches the value for the "free" allyl anion.

However, the theoretical values are generally too high, presumably because the experiments refer to solvated species. The large deviation between calculated and experimental barrier for allyllithium has been ascribed to dimerization [5]. Indeed, rotation of one allyl moiety in the dimer is calculated to have a significantly lower activation barrier, closer to the experimental value (Table 4). Solvation is shown to lower the barrier to rotation by the present calculations for monomeric allyllithium using water as a computational model for ether solvents. The same influence of solvation is expected for allyllithium dimer, as well as for the allyl derivatives of the heavier alkali metals.

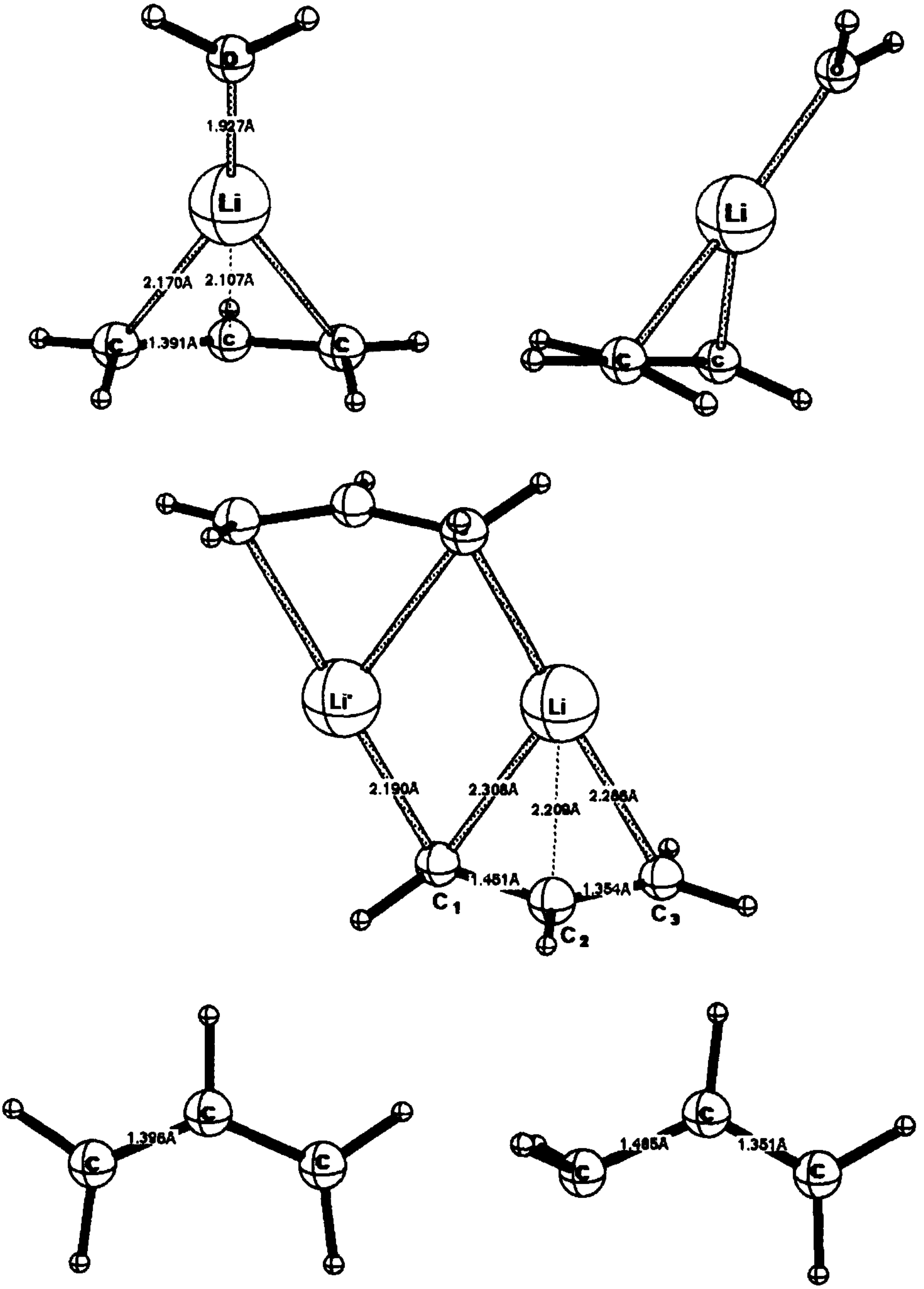


Fig. 2. Calculated structures of mono-solvated allyllithium (6−31G*), dimer allyllithium (3−21G) and planar and twisted (*anti*) allyl anion (MP2/6−31+G**).

Both the *syn* and *anti* conformations of the twisted allyl anion are true transition structures at RHF and MP2 levels (1 imaginary frequency), the *syn* form corresponds to the lowest barrier, in line with the results reported by González-Luque et

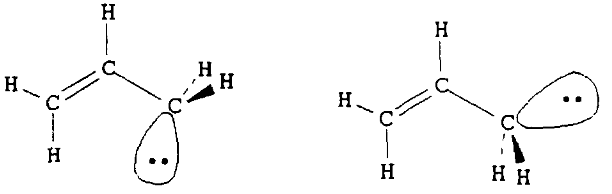
Table 3

Absolute (-a.u.) energies for bridged and planar allyl alkali metals and the allyl anion [a]

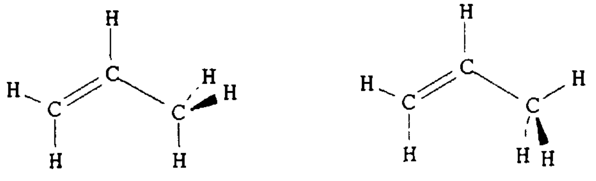
Compound		3-21G	6-31G*	6-31G**	MP2(fu)/ (6-31G*) [a]	MP2(fc)/ (6-31+G*)	Z.P.E.// (6-31G*) [a]
C_3H_5Li	br	123.22823	123.91732	123.92667	124.37691	124.32623	45.8(0)
	pl	123.19978	123.89130	123.90021	124.34481	124.29554	45.0(1)
C_3H_5Li	br	198.86989	199.96056			200.56745	61.9(0)
$-OH_2$	pl	198.84300	199.93653			200.53708	61.0(2)
$(C_3H_5Li)_2$	br	246.52231					93.9(0) [c]
	TS	246.50063					93.1(1) [c]
C_3H_5Na	br	276.67014	278.29494	278.30437	278.75510	278.70629	44.6(0)
	pl	276.64860	278.27683	278.28582	278.73488	278.68461	44.4(1)
C_3H_5K	br	714.32729	715.00007	715.00922	715.60049	715.42691 [c]	44.3(0)
	pl	714.30014	714.97633	714.98517	715.57410	715.39919 [c]	43.8(1)
C_3H_5Rb	br	3051.53078	3052.18271	–	3052.60680	3052.62835 [c]	44.2(0)
	pl	3051.50299	3052.15779	–	3052.57972	3052.59752 [c]	43.8(1)
C_3H_5Cs	br	7663.66583	7664.94163	–	7665.37156	7665.39864 [c]	44.0(0)
	pl	7663.63462	7664.91449	–	7665.34089	7665.36314 [c]	43.5(1)
$C_3H_5^-$	pl	115.74613	116.42520	116.43534	116.88560		39.9(0) [c]
	syn		116.39136	116.40098	116.85163		40.2(1) [c]
	anti		116.38820	116.39774	116.84806		40.3(1) [c]

[a] Huzinaga basis sets (*vide supra*) used for K, Rb and Cs, 6-31+G* and 6-31+G** basis sets (augmented with diffuse functions) on C used for C_3H_5-. [b] 6-31G** used for Li, Na, K. [c] 3-21G. [d] MP2(full).

al. [13]. The energy difference between *syn* and *anti* conformers is 2.3 kcal/mol (MP2/6 - 31 + G**//MP2/6 - 31 + G**), comparable to the difference of 2 kcal/mol between eclipsed and staggered conformations of propene (Scheme 3) [29]. The greater stability of the *anti* form reported previously [1a] is probably due to basis set inadequacy.



Syn-$C_3H_5^-$ (0.0) *Anti*-$C_3H_5^-$ (+ 2.3 kcal/mol)



Eclipsed C_3H_6 (0.0 [29]) Staggered C_3H_6 (+ 2.0 kcal/mol [29])

Scheme 3. Conformations of twisted allyl anion and propene.

Table 4

Rotational barriers (kcal/mol) for the allyl alkali metals and the allyl anion [a]

Compound	3−21G	6−31G*	6−31G**	MP2/6−31G*	MP2/6−31+G*	Exp. [9,12]
C_3H_5Li	17.1	15.6	15.8	19.4 [b]	18.5	10.7 [c]
$C_3H_5Li\text{-}OH_2$	16.9	14.2			18.2	
$(C_3H_5Li)_2$	13.0 [d]					
C_3H_5Na	13.3	10.9	11.2	12.3 [b]	13.4	11.5
C_3H_5K	16.6	14.4	14.6	16.1 [b]	17.4	14.3, 16.7 [c]
C_3H_5Rb	17.4	15.3	–	16.6	19.0	18.1 [c]
C_3H_5Cs	19.5	16.6	–	18.8	21.8	18.0 [c]
$C_3H_5^-$ *syn*		21.5 [e]	21.1 [f]	21.7 [f]		
$C_3H_5^-$ *anti*		23.6 [e]	23.2 [f]	24.0 [f]		

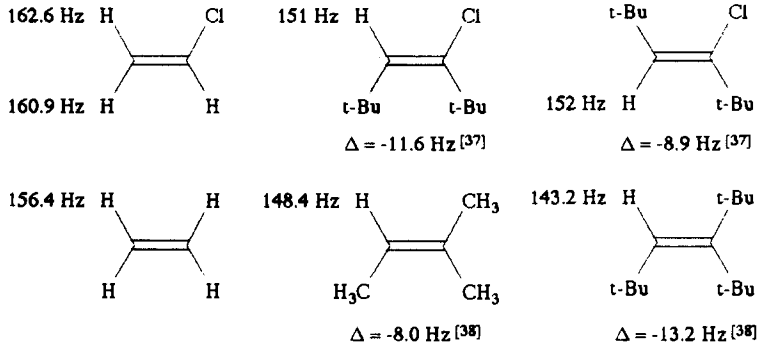
[a] Huzinaga basis sets (*vide supra*) used for K, Rb and Cs. [b] 6−31G** basis set. [c] $\Delta G^{\ddagger}$ value. [d] Barrier for rotation of one allyl moiety within a dimer, see text. [e] 6−31+G* basis set. [f] 6−31+G** basis set.

$^{13}C-^{1}H$ coupling constants

The Fermi contact term, directly related to the %*s*-character in the C hybrid orbital [30], is by far the most important contributor to the $^{13}C-^{1}H$ coupling constant. Accordingly, the empirical relation $^1J(C{-}H) = 500 \cdot s$ (Hz) [31] has long been used to estimate hybridization. Alternatively, the empirical relation $^1J(C{-}H) = 570 \cdot s - 18.4$ (Hz) [32] can also be employed. For the allyl alkali metals [9,15], values for $J(C_2{-}H)$ are about 25 Hz lower than the value expected for a sp^2-carbon hydrogen bond, while the values for the terminal hydrogens are 10 (*exo*-H) and 15 Hz (*endo*-H) lower [17,33]. Even lower values (up to 70 Hz) are found for vinyl-type organolithiums [15]. Based on the equations given above, small coupling constants imply a very low percentage of carbon *s*-character in the C–H bonds. Changes in geometry and charge-induced rehybridization are responsible.

Opinions differ: which of the geometrical features, present in allyl alkali metal compounds, are most responsible for lowering the C–H coupling constants through rehybridization? Schlosser et al. [17–19] emphasize the out-of-plane bending of the hydrogen atoms. But this requires the greatest out-of-plane distortion for the hydrogen on C_2, and this is not found in the X-ray structure of the allyllithium-PMDTA complex [6]: the strongest out-of-plane bending involves the inner hydrogens on C_1 and C_3. The same is seen in two X-ray structures of allyl-nickel compounds [34] and is found by calculation [2,3]. As an alternative explanation, Clark et al. [3] proposed in-plane angular distortion, i.e. CCC angle widening, as a more likely cause of rehybridization, and this interpretation was supported by Ahlbrecht et al. [20b]. The narrowing of the HCC-angle results in a lower %*s* character. Indeed, a *linear* relationship between bond angle and C–H coupling constants was found by Laszlo [35] for C=CH-systems. A few illustrative examples are given in Scheme 4. In contrast, a *quadratic* relationship was found by Mislow et al. [36] for $C{-}CH_2{-}C$ groupings, but this situation is different. Since the HCH angle decreases when the CCC angle increases, the changes in CH coupling constants attenuate as the CCC angle becomes larger. For planar C=CH–C groupings, the CCC and CCH angles obviously are linearly related.

The coupling constants in allylrubidium and allylcesium are almost the same as in allyllithium [23], even though the allyl moiety may be expected to be more nearly



Scheme 4. The effects of distortions, due to bulky groups, on J(C–H) coupling constants.

planar when the larger gegenions are present. Clark et al. [3] proposed that greater CCC bending compensated for the smaller out-of-plane C–H distortion along the Li to Cs series, with regard to the influence on the coupling constants.

Hybridization is a purely theoretical concept, artificial but useful. Since hybridization is not physically observable, there is no way it can be "measured", although estimates can be derived empirically. It seems appropriate to calculate hybridization ratios from quantum mechanical wave functions, since these are constructed from s and p orbitals. Furthermore, the effect of various geometrical changes can be probed computationally. This makes it possible to study various geometrical changes separately and to evaluate their relative importance. For this purpose, we use the hybridizations calculated with the Natural Population Analysis method [28]. These values, which are not sensitive to the basis set, show some deviations from the hybridizations calculated empirically on the basis of the coupling constants, but qualitative trends are reproduced well [39].

Laszlo's [35] linear relationship between the % carbon s-character and the CCC bond angle is confirmed [39]. This is also shown for a more limited set of CCC angles in Fig. 3 for the C_2–H bond of the compounds of interest here (Table 5). Furthermore, the results of calculations on allyllithium with geometrical constraints (points 2, 3 and 4, not included in the least squares analysis) show no significant deviation from this relationship, despite the relatively large extrapolation to point 2 (allyllithium with a fixed 120° bond angle, geometry optimized otherwise). Even the naked allyl anion (point 11) fits well. These results show that variation of the CCC-angle is the major determining factor for the C–H coupling constants.

We also assessed the effect of moving the hydrogen on the central carbon into the CCC-plane (3). The remainder of the molecule hardly changed. The s-character increased from 24.6% (corresponding to an out-of-plane angle of 11°) to 24.9% (for the planar arrangement, Table 5). If the $C_3H_5^-$ moiety in allyllithium was forced to be completely planar (point 4), optimization increased the CCC-angle to 127°. This resulted in a reduction of the s-character to 24.3%, i.e. a compensation occurs.

This emphasizes that out-of-plane bending is only of minor importance in determining the C–H coupling constants. Furthermore, if the CCC-angle is fixed to 120° and the geometry optimized otherwise, the out-of-plane deformations are actually smaller than in the fully optimized structure of allyllithium (Table 6).

Experimentally, the coupling constants for the whole series of alkali metal compounds [9] do not vary as much as implied by Fig. 3. Many of the points in Fig.

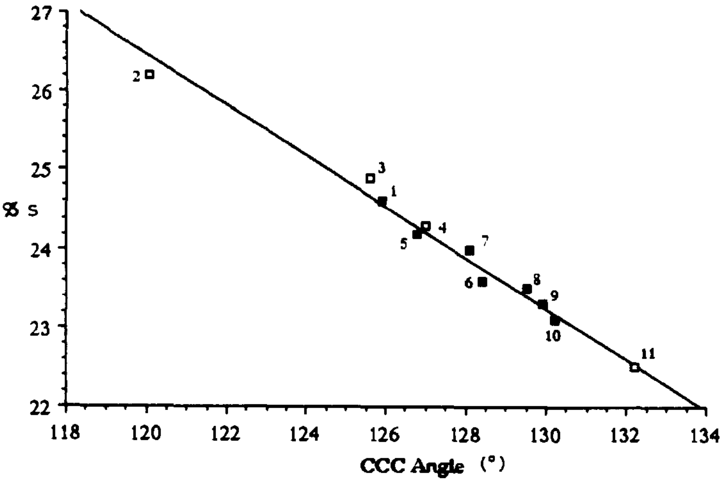


Fig. 3. Dependence of %*s*-character in the C_2–H bond on the CCC-angle in C_3H_5M species (open squares: calculations with geometrical constraints, see text).

3 were calculated for unsolvated species. The influence of ether solvents (modelled with water molecules for computational efficiency [40]) is quite significant on allyllithium, where changes are expected to be largest. Solvation increases the

Table 5

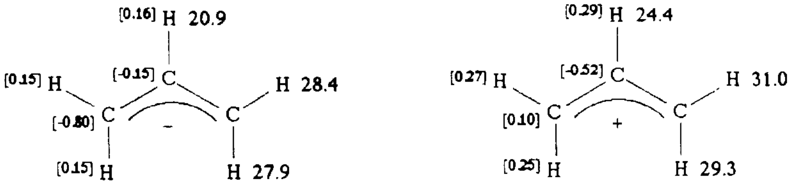
% carbon *s*-character in the C–H bonds from NBO analysis

Points	Compound	3–21G				6–31+G		
		CCC	C_2–H	$C_{1,3}$–H_{endo}	$C_{1,3}$–H_{exo}	C_2–H	$C_{1,3}$–H_{endo}	$C_{1,3}$–H_{exo}
1	C_3H_5Li	125.9	24.6	29.2	30.0	24.6	29.2	30.0
2	CCC = 120°	120.0	26.2	29.5	29.9			
3	H–C_2 in plane	127.0	24.9	29.1	30.0			
4	$C_3H_5^-$ planar	127.0	24.3	28.8	30.1			
5	C_3H_5Li–H_2O	126.8	24.2	29.0	29.9			
6	C_3H_5Li–$(H_2O)_2$	128.4	23.6	28.9	29.8			
	$(C_3H_5Li)_2$	126.9	24.9	26.3/28.2	26.9/29.3			
7	C_3H_5Na	128.1	24.0	29.0	30.2	24.0	29.0	30.2
8	C_3H_5K	129.5	23.5	28.8	30.0	23.4	28.8	29.9
9	C_3H_5Rb	129.9	23.3	28.7	30.0	23.2	28.7	29.9
10	C_3H_5Cs	130.2	23.1	28.6	29.8	23.0	28.7	29.9
11	$C_3H_5^-$	132.2				22.5	29.1	29.5

Table 6

Geometries for C_3H_5Li with geometrical constraints (in italics) (Å and °)

Compound	M–$C_{1,3}$	M–C_2	$C_{1,3}$–C_2	CCC	Ω-H_1	Ω-H_2	Θ-H_3
C_3H_5Li	2.141	2.093	1.394	125.9	−28.1	1.0	11.3
CCC = 120°	2.118	2.121	1.399	*120.0*	−23.5	−0.8	10.4
H–C_2 in plane	2.164	2.085	1.391	125.6	−21.5	−3.2	*0.0*
$C_3H_5^-$ planar	2.217	2.054	1.387	127.0	*0.0*	*0.0*	*0.0*



Scheme 5. Atomic natural charges (in square brackets) and % carbon *s* character in C–H bond hybrids (3 – 21G) for the allyl anion and cation at the same geometry.

lithium–allyl separation; this results in widened bond angles, approaching the situation found with the heavier alkali metals.

The influence of charge on C–H coupling constants, discussed by Grant and Litchman [30,41], is illustrated clearly by the 30 Hz difference between *J*(C–H) for the dication and dianion of anthracene [42]: values of 175.8, 178.2 and 175.8 Hz (1, 2 and 9-positions, respectively) are reported for the dication, while 147.5, 147.5 and 145.0 Hz are found for the dianion. A *J*(C–H) value of 98 Hz is found for (tetrameric) methyllithium, as compared to 125 Hz for methane. Hence, the C–H coupling constants in alkali metal allyl derivatives should be lowered by the negative charge. Indeed, when the allyl anion and cation are calculated at the same geometry, with the CCC-angle fixed at 132°, the carbon *s*-character in the C–H natural bond orbitals varies considerably, e.g. from 20.9%*s* for the central position in the anion to 24.4%*s* in the cation (Scheme 5). These hybridization changes are due to the σ-framework polarization by the π-charges [30,41].

Conclusions

Ab initio calculations on the set of allyl alkali metal compounds, even though mainly carried out on isolated species, give satisfactory agreement with experimental data determined in solution and in the solid state. Most notable are the CCC-angle widening and the trend in rotational barriers. Because of the larger separations involving the heavier alkali metals, these barriers increase as the electrostatic influence of the cation on the allyl anion moiety decreases. As anticipated, allylcesium most closely approximates the free allyl anion. Experimental observations on allyllithium do not follow the same trend. The exceptional behaviour is due to the effect of dimerization; solvation also is particularly important. The origins of the abnormally low C–H coupling constants, which have been debated in the literature, are established. The main cause is the widening of the CCC-angle, but CH out-of-plane bendings as well as charge polarization effects also contribute. The balancing of these influences along the allyl alkali metal series results in the nearly constant *J*(C–H) values observed experimentally.

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