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The preference of 1-methylallyl polar organometallics and carbanions for *cis* rather than for *trans* geometries

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Abstract

In agreement with experimental equilibrium studies in solution, *ab initio* calculations, using diffuse function augmented split valence basis sets, favor *cis* geometries of 1-methylallyl lithium, sodium, potassium, and rubidium by 0.7, 1.1, 2.5, and 2.6 kcal/mol, respectively. These results, and the even greater *cis* preference of the 1-methylallyl anion over *trans*, 4.7 kcal/mol (MP2/6–31+G//3–21G) show the contrary conclusions from an early ICR study and from semiempirical theory to be incorrect. Later gas phase experiments demonstrated that stereointegrity was not maintained under the ICR conditions. Semiempirical theory is shown here to be inherently deficient for the examination of alkyl-substituted carbanions. The surprisingly large *cis* preferences of the 1-methyl-allyl anion systems are attributed to the largely electrostatic attraction between the positively charged methyl hydrogens and the remote allyl anion terminus. This attraction is largest in the free anion and attenuated to an increasingly greater extent the smaller the alkali metal gegenions become. The allyl moieties in the metal 1-methylallyl derivatives are calculated to be quite unsymmetric, in agreement with NMR observations.

Introduction

The surprising thermodynamic preference of 1-methylallyl (crotyl) organometallics for *cis* rather than *trans* skeletal geometries was recognized as early as in 1960 [1]. The question as to whether the 1-methylallyl (crotyl) anion is more stable *cis* or *trans* is not yet resolved [2–8] despite extensive evidence which demonstrates the strong thermodynamic preference of 1-methylallyl organometallics for *cis* (*Z*) rather than for *trans* (*E*) skeletal geometries [1,2,9]. Thus, Schlosser has found that the more electropositive (and larger) the metal, the higher the content of *cis*

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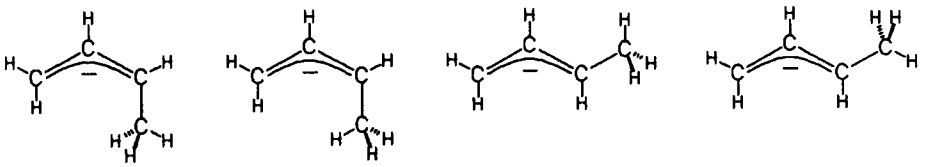
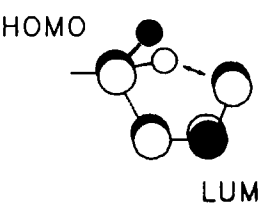
isomer at equilibrium in hexane at 225 K. For crotyl-lithium the Z/E ratio is 67/33 (in ether at 273 K, and 85/15 in THF at the same temperature). For crotylsodium, for crotylpotassium, and for crotylcesium the corresponding values at 225 K in petroleum ether are 93/7, 96/4 and > 99.9/0.1 [2b]. This progression indicates that the free crotyl anion should prefer the *cis* configuration strongly, by more than 4 kcal/mol judging from the crotylcesium results. A similar experimental estimate is available. The temperature dependence of the *cis–trans* equilibrium of neopentylallyl lithium, gave $\Delta H^\circ = 1.6$ kcal/mol [2d]. The *cis* fraction of neopentylallyl lithium in THF varied between 0.54 at 303 K and 0.70 at 243 K. There was less temperature change for the heavier alkali metals, but Na and K neopentylallyls showed larger amounts of the *cis* fractions, approximately 0.8. While counterion dependence of intramolecular interactions in allyl polarmetallics is clearly indicated, these data have generally been interpreted in terms of an approach to the free carbanions with the increase in size of the alkali metal cation [2b,d].

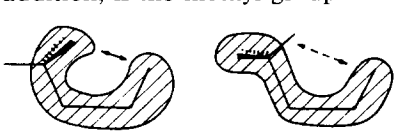


1, *Z*-eclipsed **2**, *Z*-staggered **3**, *E*-staggered **4**, *E*-eclipsed

An early *ab initio* study of the crotyl anion, radical, and cation at the 4-31G level with partially optimized geometries [4] found the *cis*-crotyl anion, with an unexpected methyl conformation, eclipsed with regard to the adjacent hydrogen, **1**, to be 1.4 kcal/mol more stable than the most stable form of the *trans* isomer, **3**. Two related explanations of the observed *cis* preference of 1-alkylallyl polarmetallics assume attractive interactions between the two inner methyl hydrogens in the *Z*-eclipsed conformer:



The first of these involves pseudo-aromatic orbital overlap [4,9] and the second intramolecular hydrogen bonding [2b]. Two factors argue against these interpretations. As shown, the distance between methyl hydrogens and the negatively charged allyl terminus is too large for effective overlap or hydrogen bonding. In addition, if the methyl group is rotated 60°



to the staggered conformer, the *cis* form is still more stable than the *trans*. Neither pseudo-cyclic aromaticity nor hydrogen bonding is possible in this form. Hence, other factors must predominate.

Unfortunately, the apparently pleasing agreement between the experimental results in solution and the 1977 *ab initio* findings [4] (however, these calculations were carried out at levels which would not now be considered adequate) was challenged in the same year by a gas phase ICR study of the crotyl anion. The authors concluded that the *trans* isomer was slightly more stable than the *cis* [5]. Furthermore, MNDO [6] and more recent MINDO/3 [7] calculations also favored the *trans* isomer for the crotyl anion.

In a recent review, Radom et al. [8] suggest that "higher level theoretical calculations would be desirable to provide a definitive resolution of this interesting problem". We have now refined our earlier *ab initio* computations [4] on the four crotyl anion isomers, and have examined the structural preferences for crotyllithium, sodium, potassium, and rubidium as well. The results resolve the problem clearly.

Computational methods

All *ab initio* calculations were performed with the GAUSSIAN 82 program system [10]. The four forms of methylallyl (crotyl) anion were first fully optimized with the split valence 3–21G basis set [10] which generally gives satisfactory results with carbanion geometries. More reliable relative energies were obtained employing a diffuse *s* and *p* function augmented basis set, 6–31 + G, known to be important for the adequate energetic description of carbanions [11,12]. These single point calculations also included electron correlation corrections at the MP2 level [10], i.e. MP2/6–31 + G//3–21G. Calculated absolute energies for **1**–**4** are listed in Table 2, and relative anion energies are given in Table 3. These are compared with semiempirical MINDO/3 [13], MNDO [14], AM1 [15], and PM3 [16] calculations, which reproduce and extend literature results [6,7].

Similar *ab initio* calculations were carried out on methylallyl–M (M = Li, Na, K, Rb) in various conformations. Full geometry optimizations were performed with the 3–21G basis set for M = Li, and Na. Since no standard 3–21G basis set for K and Rb is available in the GAUSSIAN 82 program [10], we used Huzinaga's equivalent basis sets, $13s8p$, contracted to $5s3p$ for K, and $16s11p1d$, contracted to $6s4p1d$ for Rb [17]. For better description of crotyl anion fragments, the energies of the crotyl-alkali metallics were also evaluated at the 6–31 + G level. The standard basis set, which includes a set of diffuse functions on the carbons and the metal atom, was used for Li and Na, but the above Huzinaga basis was used for K and Rb. Since the alkali metals in these molecules bear nearly a full positive charge, the use of unextended basis sets for the cations does not unbalance the basis set for the molecule as a whole. The geometrical parameters and calculated total energies for the organometallic structures corresponding to **1** and **3** are given in Tables 4 and 5. As discussed below, these are the most stable *cis* and *trans* isomers, respectively.

Results and discussion

There are reasons to question both the gas phase and the semiempirical results. MNDO and MINDO/3 are fundamentally unsuitable for such problems [8,11,12]. As in the case with STO–3G, which also favors the *trans*-methylallyl anion [4], minimal basis set ZDO representations lack the necessary flexibility to deal properly with electron-rich anionic systems, where outer electrons are only weakly bound. Whereas alpha-alkyl substituents generally destabilize carbanions [8,12,18,19] as well as the corresponding polar organometallics [20] such minimal basis MO representations indicate erroneously that methyl groups stabilize carbanions by electron withdrawal. Therefore, "systematic errors accompany introduction of methyl substituents at anionic centers" [21]. The poor description of negative charges is overcompensated by basis set superposition error (BSSE) [11,12]. Since the carbon (minimal valence) basis set is neither large nor flexible enough to deal with the negative charge, basis functions on nearby atoms become involved.

The defects of semiempirical theory are most pertinently illustrated by the stabilization energies of the ethyl, isopropyl, and t-butyl anions relative to methyl (eq. 1, equivalent to relative proton affinities) calculated by different methods.

$$RH + CH_3^- \longrightarrow R^- + CH_4 \qquad (1)$$

A summary of literature results using MINDO/3 [7], MNDO [6], and AM1 [21] along with our extensions is listed in Table 1. These, as well as our calculations using the most recent PM3 [16] semiempirical method indicate increasingly large stabilization of anions along the series, methyl, ethyl, isopropyl, t-butyl. This is contrary to gas phase experimental results [18a,b] and to *ab initio* calculations on anions with diffuse-function augmented basis sets [11,12,18c,19]. The semiempirical results are also negated by kinetic acidities [18d] and by calculations on organolithium and -sodium derivatives [20]. The exaggerated C^+H^- polarization of methyl hydrogens at semiempirical and minimal basis set levels (note the similar behavior of STO–3G in Table 1) leads to the erroneously indicated preference for **3** due to electrostatic repulsion between the methyl hydrogens and the negative charge on the terminal CH_2 group of the allyl anion. The difficulty is partially overcome when the more flexible split valence basis sets are employed, but more accurate descriptions of anionic systems require the further addition of diffuse functions to the basis set [8,11,12].

Table 1

Calculated and experimental stabilization energies of carbanions relative to methyl (eq. 1, kcal/mol)

Anion	MNDO [a]	AM1 [b]	PM3 [c]	STO-3G	4-31+G [a]	Experiment [d]
CH_3^-	0.0	0.0	0.0	0.0	0.0	0.0
$CH_3CH_2^-$	−11.1	−14.6	−14.7	−9.0	+5.6	+3.5
$(CH_3)_2CH^-$	−28.6	−25.5	−26.1	−8.7	+5.9	+2.7
$(CH_3)_3C^-$	−60.8	−34.0	−35.4	−23.9	+3.0	(−3.5)

[a] Ref. 12a. [b] Ref. 21. [c] Calculated PM3 heats of formation: CH_4, −13.0 [16]; CH_3^-, 51.5; C_2H_6, −18.1 [16]; $CH_3CH_2^-$, 31.7; C_3H_8, −23.6 [16]; $(CH_3)_2CH^-$, 14.8; iso-C_4H_{10}, −29.5 [16]; $(CH_3)_3C^-$, −0.4 kcal/mol. [d] Ref. 18. With the exception of methyl, these are indirectly obtained estimates which may suffer from errors in the method, e.g. steric effects for t-butyl.

Table 2

MNDO, PM3 heats of formation (kcal/mol) and absolute (−a.u.) energies of crotyl anions

Species	MNDO [a]	PM3	3–21G//3–21G	6–31+G//3–21G	MP2/6–31+G//3–21G
1	9.6	13.3	154.56712	155.40500	155.78133
2		13.5	154.56538	154.40140	155.77695
3	9.3	12.5	154.56579	155.39857	155.77393
4		13.0	154.56355	155.39708	155.77272

[a] Ref. 6.

Recent multiphoton electron detachment studies [22] cast doubt on the conclusions of the 1977 ICR investigation [5]. Indeed, possible difficulties were already recognized by the original investigators [5]. For the claim of *trans* preference to be valid, stereochemical integrity must have been maintained during the experiment. However, while proton abstraction from *cis*-butene in the gas phase was found to produce 100% *cis*-crotyl anion, *trans*-butene afforded 86% *cis*- and only 14% *trans*-crotyl anions [22]. In another series of experiments in the gas phase DePuy showed that multiple proton exchange processes can lead to *cis–trans* isomerization [23]. This is due to the formation of long-lived collision complexes between anions and neutral acids, in which more than one proton exchange may occur, and is demonstrated by deuterium incorporation in substituted propenes in the reaction with DO^- [23]. Fluoride ion reactions with the substituted trimethyl silanes, *cis*- and *trans*-$CH_3CH{=}CHCH_2Si(CH_3)_3$ apparently gave the *cis*- and *trans*-crotyl anions, but the relative energies could not be determined [24].

Crotyl anions

Geometries of carbanions are satisfactorily reproduced by low level 3–21G calculations [10]. Calculated C–C bond lengths in the allylic parts of the four conformations of crotyl anion **1–4** are remarkably similar, indicating significant pi-delocalization. Allyl–methyl bond lengths are, in turn, relatively long, and are also similar (Fig. 1). These results are significantly different from the semiempirical findings, which predict C_2–C_3 to be shorter than C_1–C_2 and shortening of allyl–methyl bonds C_3–C_4 [6,7]. This is a consequence of the overestimation by semiempirical theory of the interactions of the methyl group with the negatively charged allylic moiety. In contrast to geometries, satisfactory carbanion energies require more computational effort [11,12]. We regard the only reliable results in Table 3 to be those obtained with the 6–31 + G basis set, which includes diffuse functions on nonhydrogen atoms. Note the large increase in relative energies due to the addition of the latter. MP2 electron corrections, on the other hand, only result in small (approx. 0.5 kcal/mol) changes of relative energies. At MP2/6–31 + G//3–21G, the *cis–trans* energy difference (**1** *versus* **3**) is 4.6 kcal/mol, a value which corresponds very well with Schlosser's results for crotylcaesium in solution [2b]. Hence, we are confident that the *cis*-crotyl anion is considerably more stable than the *trans*. This result demonstrates the inadequacy of previous MNDO [6] and MINDO/3 [7] calculations, as well as of AM1 [15,21] and PM3 [16] for this purpose. The misgivings concerning the gas phase results [5] are also confirmed: isomerization of *trans* to *cis* [22,23] evidently did occur under the experimental conditions employed.

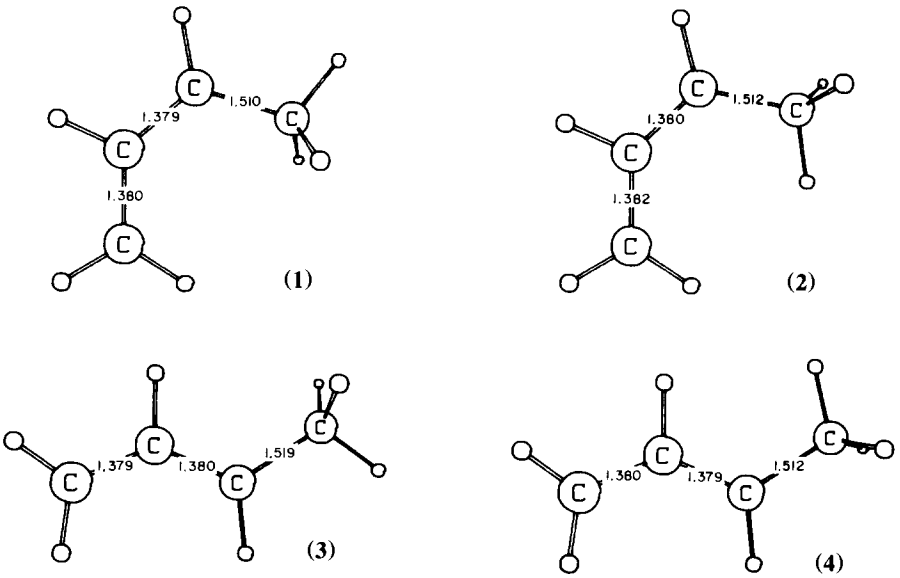


Fig. 1. Calculated geometries (3–21G) for **1**–**4**. Bond lengths are in ångströms.

Methylallyl (crotyl) alkali metals

The calculations of methylallyl (crotyl) alkali metals, M = Li, Na, K, Rb support our general conclusions. Only metal bridged structures were found for all species. For the *cis* isomers, structures with methyls eclipsed with respect to the allyl moiety, **1**, were also studied with M = Li and Na. As in the *cis*-methylallyl anion, these conformations are less stable than the staggered methyl structures. For example, **2**, M = Li is 2.4 kcal/mol higher in energy than **1**. We assumed that the situation would be similar for crotyl potassium and rubidium, and did not examine these alternative geometries. Hence, only data for **1** and **3** are included in Table 4.

For each of the systems, the *cis* isomer (**1**) is favored over the *trans* (**3**). At 3–21G, the calculated *cis* preference only increases slightly from crotyl–Li to crotyl–Rb, 1.2–1.7 kcal/mol, but this is due to the limitations of the 3–21G basis

Table 3

Relative energies of $C_4H_7^-$ isomers, calculated at various levels of theory (kcal/mol)

	1	2	3	4	Ref.
MINDO/3	0.0	−0.2	−1.0	−0.8	7 [a]
MNDO	0.0	0.3	−0.3	−0.3	6 [a]
AM1	0.0	−0.1	−1.0	−0.6	This work
PM3	0.0	−0.2	−0.8	−0.5	This work
STO-3G	0.0	0.1	−0.3	0.8	4
4-31G part.opt.	0.0	–	1.5	–	4
3-21G//3-21G	0.0	1.1	0.8	2.2	This work
6-31+G//3-21G	0.0	2.3	4.0	5.0	This work
MP2/6-31+G//3-21G	0.0	2.8	4.6	5.4	This work

[a] Recalculated and extended in this work.

Table 4

Comparison of *cis–trans* crotyl alkali metal equilibria [a]

	3-21G//3-21G	6-31+G//3-21G	Experiment [b]
Li-**1**	−162.04598	−162.89511	
Li-**3**	−162.04399	−162.89392	
cis–trans	1.2	0.7	0.4 (ether, 273 K) 0.9 (THF, 273 K)
Na-**1**	−315.48776	−317.27672	
Na-**3**	−315.48540	−317.27396	
cis–trans	1.5	1.7	1.2 (hexane, 225 K)
K-**1**	−753.14444	−753.94689	
K-**3**	−753.14173	−753.94291	
cis–trans	1.7	2.5	1.4 (ether, 225 K) 2.2 (THF, 225 K)
Rb-**1**	−3090.34818	−3091.15364	
Rb-**3**	−3090.34540	−3091.14944	
cis–trans	1.7	2.6	–
Cs-**1**			
Cs-**3**			
cis–trans			> 3.2 (hexane, 225 K)

[a] Absolute energies in a.u.; *cis–trans* energy differences in kcal/mol. [b] Gibbs energies calculated from Schlosser's equilibrium data [2b].

set. The systems are mainly ionic in character and the negative charge on the allylic carbons is not described adequately. Thus, when diffuse *sp* functions are added to the carbon atoms (and to Li and Na as well), the calculated *cis* preferences vary from 0.7 to 2.6 kcal/mol and approach the experimental values more closely (Table 4).

Geometries

Some of the calculated structure parameters (Table 5) are intriguing. Symmetrical bridged structures for all the unsolvated monomeric allyl alkali metal species are found by theory [20,26*]. Isotope perturbation ^{13}C NMR experiments in THF solution [25] support these results: the measured ^{13}C chemical shifts for the parent allyl polarorganometallics show, if at all, only minor differences for C_1 and C_3 [27]. While generally similar in structure to the corresponding allyl alkali metals, crotyl alkali metal geometries are asymmetrical [29]. The calculated C_1C_2 distances in all the allyl anion moieties (Table 5) are significantly longer than the C_2C_3 bond lengths. In effect, the negative charge "avoids" the methyl substituted C_3 center (see also below). The terminal CH_2-group is consistently more pyramidal. These results provide further evidence for the electron releasing character of the methyl substituent, which is insignificant for the free anions (Fig. 1), but amplified by alkali metals due to the polarization of the pi-charge. Double bonds are known to be stabilized by methyl substituents. Indeed, the ^{13}C NMR shifts of C_1 and C_3 in

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

Table 5

C_4H_7–M geometrical parameters, 3–21G//3–21G for M = Li and Na, or equivalent Huzinaga basis sets for M = K and Rb (ångströms and degrees)

	M–C_1	M–C_2	M–C_3	C_1C_2	C_2C_3	< 123	< H_z123 [a]	< H_e123 [b]	< 4321	< H321	< H213
1–Li	2.138	2.088	2.138	1.406	1.381	125.3	33.0	182.4	−18.9	−180.5	11.7
3–Li	2.097	2.098	2.196	1.410	1.380	126.2	32.4	179.8	−179.8	−23.4	12.2
1–Na	2.432	2.428	2.555	1.414	1.373	127.5	28.2	174.6	−15.7	−178.3	7.7
3–Na	2.394	2.442	2.581	1.420	1.371	128.3	29.7	172.6	−176.9	−17.0	7.8
1–K	2.878	2.850	2.938	1.403	1.375	128.7	23.6	172.1	−14.4	−176.4	5.2
3–K	2.818	2.872	2.975	1.411	1.371	129.7	26.9	170.3	−174.5	−15.5	6.2
1–Rb	3.044	3.016	3.094	1.400	1.375	129.1	22.2	171.3	−14.4	−176.2	5.4
3–Rb	2.975	3.040	3.129	1.410	1.370	130.0	26.5	169.6	185.1	−14.8	6.0

[a] < H_z123: the dihedral angle between the terminal *endo*-hydrogen and the $C_1C_2C_3$ plane. [b] < H_e123: the dihedral angle between the terminal *exo*-hydrogen and the $C_1C_2C_3$ plane.

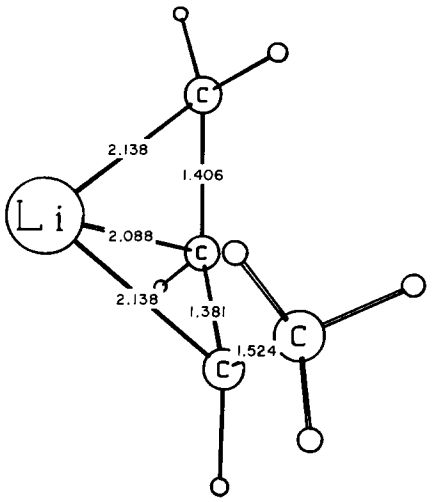


Fig. 2. The 3–21G geometry of *cis*-crotyllithium. Note the orientation of the CH_3 group and the bending of C(2)–H towards lithium.

crotyl and other 1-alkyl substituted allyl anion systems confirm our asymmetrical structures, and often show substantial differences. These depend on the experimental conditions, but the upfield shift of C_1 relative to C_3 can be as large as 80–90 ppm [29,30]. The conclusions on the charge distribution are discussed in more detail below.

Another characteristic of the allyl anion is the widened $C_1C_2C_3$ angle, 132° at 6–31 + G* [31]. As in the cases of alkali metal allyl derivatives [20], the $C_1C_2C_3$ angles in both **1** and **3** increase from M = Li to M = Rb. The angle for M = Rb is close to that calculated for the free crotyl anion, approx. 133° (Fig. 1). The M–C_1 distances are somewhat longer than M–C_3, the differences ranging from 0.05 to 0.19 A. The *cis* isomer of crotyl Li is a notable exception. This difference is larger in the *trans* isomers than in the *cis*. The allyl part of all molecules studied is significantly distorted, so that hydrogen atoms become partially staggered. C_2–H is bent above the C_1–C_2–C_3 plane, while the substituents attached to C_1 and C_3 are bent below the same plane (Fig. 2).

The calculated crotyl anion geometries, and those of the alkali metal derivatives demonstrate that methyl substitution destabilizes carbanions. This has been shown previously in a detailed study of substituted methyl anions (XCH_2^-) [11].

Energy effects

Energies relative to the corresponding methyl metals can be evaluated by means of eqs. 2–4.

$$H_2C{=}CHCH_3 + [CH_3]^-M^+ \longrightarrow CH_4 + [H_2C{=}CHCH_2]^-M^+ \quad (2)$$

$$cis\text{-}CH_3CH{=}CHCH_3 + [CH_3]^-M^+ \longrightarrow CH_4 + cis\text{-}[CH_3CH{=}CHCH_2]^-M^+ \quad (3)$$

$$trans\text{-}CH_3CH{=}CHCH_3 + [CH_3]^-M^+ \longrightarrow CH_4 + trans\text{-}[CH_3CH{=}CHCH_2]^-M^+ \quad (4)$$

Table 6

Reaction energies relative to methyl alkali metals, eqs. 2–4 (kcal/mol)

M	eq. 2: allyl [a]		eq. 3: *cis*-crotyl		eq. 4: *trans*-crotyl	
	3–21G	6–31+G	3–21G	6–31+G	3–21G	6–31+G
Li	−18.0	−14.4	−16.6	−12.0	−13.8	−9.8
Na	−14.3	−12.0	−12.8	−9.7	−11.4	−6.5
K	−19.0	−17.3	−17.3	−13.4	−15.6	−9.4
Rb	−20.0	−18.9	−18.4	−14.9	−16.7	−10.8
Cs	−24.6					
Anion [b]	(−37.4) [c]	−28.2	(−37.0) [c]	−27.9	(−45.1) [c]	−22.4

[a] Ref. 20b. [b] Anion stabilization energies, relative to the methyl anion. [c] As no diffuse basis functions are present, 3–21G results are misleading and insignificant.

The data (Table 6) provide comparisons among the alkali metal crotyl anion salts and assess the contribution of terminal methyl groups to the stability of allyl anion and their alkali metal derivatives.

Propene is considerably more acidic than methane, and its reaction with methyl anion to give the allyl anion is exothermic by 28.2 kcal/mol at 6–31 + G (Table 6). Methyl substitution destabilizes the allyl anion, the *cis* isomer by only 0.3 kcal/mol, but the *trans* isomer by 5.8 kcal/mol. This difference indicates that the inherent destabilization of allyl anions by a terminal methyl substituent is attenuated by attractive CH_3--CH_2^- interactions. Counterions attenuate the calculated relative energies significantly, but preserve, or even amplify the destabilizing effect of methyl substitution. Thus, metallation of propene to give allyllithium (eq. 2) results in an energy gain of 14.4 kcal/mol at 6–31 + G//3–21G (Table 6). For the reaction of *cis*-butene to *cis*-crotyllithium (eq. 3) the calculated energy is somewhat less (12.0 kcal/mol). The value for the *trans*-butene to *trans*-crotyllithium conversion (eq. 3) is even smaller (9.8 kcal/mol) at the same level. Methyl substitution effects on allyl alkali metals are most simply evaluated as reaction energies, relative to the corresponding unsubstituted allyl derivative (eqs. 5, 6).

$$[CH_2CHCH_2]^-M^+ + \textit{cis}\text{-}CH_3CH{=}CHCH_3 \rightarrow CH_3CH{=}CH_2 + [CH_2CHCHCH_3]^-M^+ \quad (5)$$

$$[CH_2CHCH_2]^-M^+ + \textit{trans}\text{-}CH_3CH{=}CHCH_3 \rightarrow CH_3CH{=}CH_2 + [CH_2CHCHCH_3]^-M^+ \quad (6)$$

These relative energies are listed in Table 7. Trends are evident: larger destabilization for larger counterions of more electropositive metals and larger destabilization of *trans*- rather than *cis*-crotyl alkali metals. These energy effects are consistent also with the effects of methyl substitution on the geometries of crotyl alkali metals, discussed above. However, the trends down the alkali metal group do not lead to the values for the free anions (Table 7). Thus, counterions contribute significantly to the nature of intramolecular interaction. Hence, methylallyl alkali metals can no longer be considered analogs of the free carbanions, the commonly accepted viewpoint for alkyl alkalimetal derivatives [32].

Table 7

Reaction energies relative to allyl alkali metals (eqs. 5 and 6, kcal/mol)

M	eq. 5, *cis*-		eq. 6, *trans*-	
	3–21G	6–31+G//3–21G	3–21G	6–31+G//3–21G
Li	1.4	2.4	4.2	4.6
Na	1.5	2.3	2.9	5.5
K	1.7	3.9	3.4	7.9
Rb	1.6	4.0	3.3	8.1
Anion	(0.4)	0.3	(−7.7)	5.8

Charge distribution in methylallyl alkali metals

Consider now the calculated natural charge [33] distributions for the series of crotyl organometallics (Table 8). While all carbon atoms in these molecules are negatively charged, all hydrogen atoms, including those of the methyl groups, have substantial positive charges. This contradicts the statement based on semi-empirical wave functions [7], that methyl groups are electron-withdrawing, and their hydrogens are negatively charged [6] when bound to carbanion systems. Theoretical definitions of charge are controversial and are method and often basis set dependent [10]. The natural charges [33] we employ are much less basis set dependent than, e.g., Mulliken charges. The data listed in Table 8 indicate significant asymmetry in the charge distribution among the allyl carbon atoms C_1 and C_3. Most interesting, however, is the distribution of positive charge in methyl hydrogens. While hydrogen atoms in *trans* isomers are uniformly charged, in *cis* isomers a significant influence of anion negative charge is indicated: the outer hydrogen bears less positive charge than the two inner hydrogens (Table 8). The total charge on methyl substituents is slightly negative, due to the significant electron density on the carbon atom. *Cis* isomers bear a somewhat larger total negative charge on the methyl groups, which improves the anion–counterion interaction.

At least qualitative comparisons with experimental data can be obtained from ^{13}C chemical shifts of alkylallyl polarmetallics [29b,30] measured in benzene or ether solvents. NMR measurements of allyl lithium and potassium in THF substantiate the assumption that unit negative charge, accompanied by sp^3–sp^2 rehybridization, brings about an upfield shift of 33 ppm relative to the olefin value [29b]. Thus, measured ^{13}C-shifts of 20.0 (Li) to 51.4 (Cs) for C_1, 140.3 (Li) to 139.5 (Cs) for C_2, and 103.0 (Li) to 67.5 (K, Rb; 69.0 for Cs) for C_3 for neopentylallyl alkalimetals [30] are used to assign a total of 0.88–1.02 negative charge to the corresponding carbon atoms [29]. This is distributed mainly on C_1 and C_3 depending on the counterion and solvent while the central C_2 has approximately the normal olefin chemical shift. The negative charge is larger and more symmetrically distributed in more polar solvents and increases for larger counterions, i.e. from Li to Rb (C_1 from 0.80 to 0.51, C_3 from 0.79 to 0.52; for Cs alkylallyl derivatives, surprisingly, less negative charge is assigned to the allyl carbons) [30]. Within allyl moieties, most asymmetrical charge distribution is assigned to lithium compounds in nonpolar solvent, while for Cs compounds the negative charge is distributed almost symmetrically between the terminal C_1 and C_3 allylic carbons [30]. In fact, the nodal atom C_2 gives a resonance shifted downfield, and is therefore assigned a

Table 8

Natural charge distributions in crotyl-alkali metals, 6–31 + G//3–21G

Species	M		C_1/H	C_2/H	C_3/H	C_4/H
Li–**1**	0.904	C	−0.964	−0.221	−0.625	−0.708
		H	0.225	0.243	0.244	0.249
		H	0.237			0.171 out
		H				0.245
		Total	−0.502	0.022	−0.381	−0.035
Li–**3**	0.907	C	−0.985	−0.199	−0.626	−0.680
		H	0.219	0.234	0.216	0.224
		H	0.237			0.225
		H				0.228
		Total	−0.529	0.033	−0.410	−0.003
Na–**1**	0.928	C	−0.975	−0.210	−0.595	−0.699
		H	0.213	0.231	0.233	0.240
		H	0.228			0.166 out
		H				0.238
		Total	−0.534	0.021	−0.362	−0.055
Na–**3**	0.931	C	−0.999	−0.186	−0.588	−0.680
		H	0.207	0.222	0.203	0.221
		H	0.228			0.222
		H				0.220
		Total	−0.564	0.036	−0.385	−0.017
K–**1**	0.966	C	−0.938	−0.195	−0.606	−0.670
		H	0.196	0.214	0.219	0.226
		H	0.212			0.150 out
		H				0.224
		Total	−0.530	0.019	−0.387	−0.070
K–**3**	0.971	C	−0.966	−0.175	−0.589	−0.656
		H	0.188	0.205	0.187	0.209
		H	0.212			0.209
		H				0.204
		Total	−0.566	0.030	−0.402	−0.034
Rb–**1**	0.979	C	−0.934	−0.192	−0.611	−0.688
		H	0.194	0.211	0.216	0.224
		H	0.210			0.149 out
		H				0.223
		Total	−0.530	0.020	−0.395	−0.092
Rb–**3**	0.983	C	−0.964	−0.174	−0.588	−0.655
		H	0.185	0.202	0.185	0.209
		H	0.209			0.208
		H				0.201
		Total	−0.570	0.028	−0.403	−0.037

positive charge of 0.1–0.15 [30]. Our theoretical data, total charges on nodal CH (Table 8), agree with the latter conclusion, and are qualitatively consistent with experimental estimates of the charges on terminal C_1 and C_3. Note in addition that the present calculations refer to monomeric molecules, while solution data for

lithium derivatives (and perhaps for the other metal salts) may be influenced significantly by association [27,28].

Intramolecular interactions in methylallyl alkali metals

The two explanations of the observed *cis* preference of alkylallyl polarmetallics mentioned in the introduction disagree with experiment [2] and the present calculations. The hyperconjugation hypothesis would be consistent with a *Z*-staggered conformation of methyl hydrogens, **2**, and significant effects of various alkyl substituents on the observed *cis / trans* ratios for alkylallyl alkali metals [2b]. The hydrogen bonding hypothesis is unacceptable, since the distances between methyl hydrogens and the pi-lobes of C_1 are much too large, 3.1–4.1 Å in the *cis* and 4.1–4.6 Å in the *trans* isomers. In addition, both hypotheses provide no explanation of counterion dependence of observed *cis / trans* ratios.

Second order perturbation analysis of the Fock matrices of methylallyl alkali metals in NAO/NBO basis [33] shows that these compounds consist of two separately bound chemical units. The only strong interunit interactions are between the metal cation (acceptor) and C_1 and C_3 (donors). For *cis*-methylallyl lithium, **1**–Li, these interactions have magnitudes of 16.4 and 10.4 kcal/mol, respectively. Since covalent interactions within a chemical unit can be much larger, we pursued a third explanation of the observed *cis* preference in crotyl alkali metals, which assumes dominant electrostatic interactions between the cation and methyl hydrogens [4]. We can quantify the electrostatic interactions between these positively charged hydrogen atoms, the C_1 allyl terminus, bearing the largest negative charge, and the metal cation. We use the coulombic expression for the interaction energy between the calculated natural charges (Table 8) and located at the corresponding nuclei (geometry partially listed in Table 4). The results are listed in Table 9. Note that the attractive interactions between methyl hydrogens and C_1 are significantly stronger in the *cis* than in the *trans* isomers. The repulsive interactions between methyl hydrogens and the metal cation are larger than the attractive interactions between methyl hydrogens and C_1 for the lithium compounds. These influences compensate each other for the sodium compounds, but are net attractive for K and Rb derivatives. Better solvation of the metal cations attenuates the repulsion between the methyl hydrogens and the metal cations. This

Table 9

Electrostatic interactions [a] between methyl hydrogens, terminal negative carbon C_1 and metal cation in crotyl alkali metals (kcal/mol) calculated from 6–31+G//3–21G natural charges

Species	Li	Na	K	Rb
cis-Allyl				
Attr	−10.27	−9.74	−8.68	−8.67
Rep	13.18	11.36	8.06	7.57
Net	2.9	1.6	−0.6	−1.1
trans-Allyl				
Attr	−6.18	−6.09	−5.54	−5.50
Rep	7.16	6.14	5.20	4.97
Net	1.0	0.0	−0.3	−0.5

[a] $E = q_i q_j r_{ij}^{-1}$.

is illustrated by the variation in Z/E ratios of methylallyl and other alkylallyl polarmetallics with different solvents [2b]. Thus, for crotyllithium, the Z/E ratio at 273 K is 67:33 in ether *versus* 85:15 in tetrahydrofuran. For crotylpotassium, the Z/E ratios at 225 K are 96:4 in hexane *versus* 99.2:0.8 in tetrahydrofuran. For ethylallyl lithium, the Z/E ratio at 273 K is 24:76 in ether *versus* 80:20 (!) in tetrahydrofuran. For ethylallylsodium, Z/E at 225 K is 61:39 in hexane *versus* 85:15 in tetrahydrofuran [2b]. For isopropylpotassium, Z/E at 243 K is 56:44 in hexane *versus* 78:22 in tetrahydrofuran [2b]. Other experimental data [2,3,25–30] underline this conclusion.

Conclusions

Isolated methylallyl carbanions strongly prefer the *cis* rather than the *trans* configuration. The calculated preference of *cis* over *trans* (4.7 kcal/mol) MP2/6–31 + G//3–21G, agrees favorably with equilibrium measurements of polar methylallyl organometallics in solution. Semiempirical treatments give incorrect results due to the inadequacies of minimal basis set restrictions of carbanions. Diffuse functions are crucially important for the correct calculational description of anions.

The *cis* preference of methylallyl carbanions can be quantitatively described in terms of electrostatic interaction between alkyl hydrogens and the negatively charged C_1 anion terminus. This reduces the inherently destabilizing influence of the methyl group, which is stronger in the *trans* configuration. Counterions compete and attenuate the attractive methyl–anion interaction due to repulsion between the metal cation and methyl hydrogens. This repulsion is in turn reduced by solvation; more effective solvents increase the Z/E isomer ratio. Methyl substitution also results in unsymmetrical geometries in the metallated derivatives. This accords with the NMR chemical shift differences.

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