Structural Assignment of the Dianion of 3-Methylbut-2-enoic Acid

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^{13}C N.m.r. spectra of the dianion of 3-methylbut-2-enoic acid suggest a delocalized structure; *ab initio* STO/3G calculations show that the only stable delocalized structure is that in which the metal lies above the plane of the molecule, as in simple allylic systems.

It is known that the dianion of 3-methylbut-2-enoic acid (1) undergoes electrophilic attack at the α or γ position, depending on the reaction conditions. The most interesting feature of this reaction is the total diastereoselection of the γ-attack, leading exclusively to the (Z)-configuration of the conjugated double bond.[1]

Recently, in studies on the regioselection of the deprotonation of conjugated esters and acids, it was reported that deprotonation *cis* both to the ester and to the acidic function occurred.[2]

Since the free dianion would be more stable in the *trans* form owing to anion–anion repulsion, the reaction course

Table 1. [13]C Chemical shifts for the mono- and di-lithium salts of 3-methylbut-2-enoic acid.[a]

	C-1	C-2	C-3	C-4	C-5
Monoanion	175.8	123.5	145.4	19.6	26.2
Dianion	175.1	88.7	147.9	73.7	—[b]

[a] The spectra were obtained on a Varian FT-80 instrument operating at 20 MHz. [b] Signal obscured by solvent.

Table 2. Net atomic charges, overlap charges, and bond distances in the ion pair and the covalent forms of the Li–Li dianion.

		Net atomic charges		Overlap charges		Bond distances/Å
(1)	Li[a]	0.207	C(4)–C(3)	0.522	C(4)–C(3)	1.39
	C(4)	−0.192	C(3)–C(2)	0.469	C(3)–C(2)	1.39
	C(3)	0.046	C(2)–C(1)	0.413	C(2)–C(1)	1.46
	C(2)	−0.182	Li–C(4)	0.049	Li–C(4)	2.37
	C(1)	0.292	Li–C(2)	0.061	Li–C(2)	2.27
	O(2)	−0.289	Li–O(2)	0.132	Li–O(2)	2.16
(2)	Li	0.045	Li–C(4)	0.283	Li–C(4)	1.96
	C(4)	−0.210	C(4)–C(3)	0.386	C(4)–C(3)	1.51
	C(3)	0.113	C(3)–C(2)	0.556	C(3)–C(2)	1.39
	C(2)	−0.156	C(2)–C(1)	0.398	C(2)–C(1)	1.46
	C(1)	0.342	C(1)–O(2)	0.347	C(1)–O(2)	1.29
	O(2)	−0.286	O(2)–Li	0.216	O(2)–Li	1.65

[a] The lithium atom is located 1.69 Å above the molecular plane.

(1)   (2)
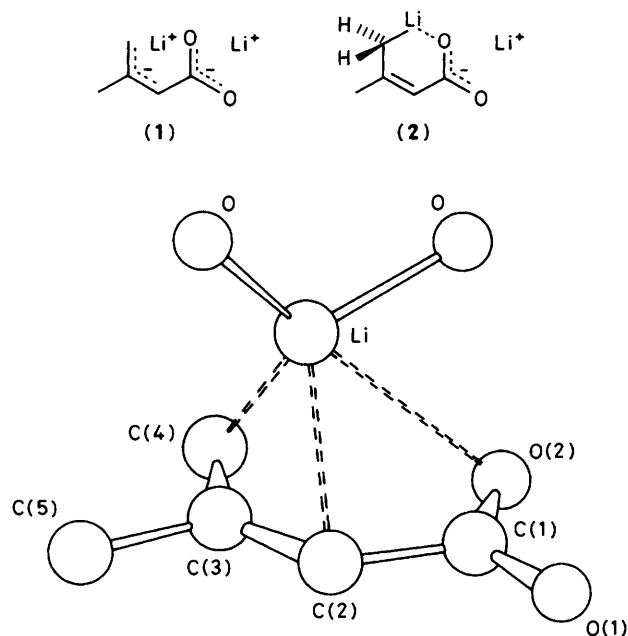
Figure 1. Perspective drawing of (3) by optimized Cartesian co-ordinates.

would depend consequently on the lithium ion co-ordination in the dienolate, in which the chelate effect stabilizes the *cis* form. The structure of the dienolate anion is unknown, with localized or delocalized forms, or an 'ate' complex possible. We have directly examined the [13]C n.m.r. spectra of the Li and Na dianions obtained in tetrahydrofuran (THF), in the absence and presence of hexamethylphosphoramide (HMPA).[1a]

The spectra are similar and the chemical shifts for the Li species are reported in Table 1, together with the chemical shifts observed for the carboxylate monoanion in the same solvent.

The two downfield peaks are assigned to C-1 and C-3, and remain practically unchanged with respect to the spectrum of the lithium carboxylate. The two upfield peaks are assigned to C-2 and C-4, since the change in the value is consistent both with acquisition of a partial negative charge and with new hybridization.[3] The spectra were therefore fully consistent with a delocalized structure, rather than with a localized one or an 'ate' complex.

To aid further understanding of the structure of the chelate form, *ab initio* STO/3G calculations[4] were performed. The dianion geometry was first optimized without the metal atoms, then the first Li atom was introduced in the plane of the carboxy group and the –COOLi substructure optimized; the second Li atom was placed above the plane of the molecule or in this plane and the C–C and C–Li parameters were again optimized.

In the absence of the Li atoms the calculations indicated that the free *trans* dianion is more stable than the *cis* dianion by 7.5 kcal mol⁻¹,† owing to the expected dipole–dipole interaction. If the lithium atom was placed above the sp² plane, a delocalized structure was obtained both for the *cis* and *trans* forms, in which the Li orbitals in the *xy* plane and the highest occupied allylic molecular orbital interacted, as previously described for simple allyl–lithium systems.[5] The results show that the *cis* form, (1) where a further interaction of the lithium orbital with the z-oxygen orbital is present, is more stable than the *trans* by 27.0 kcal/mol⁻¹. When the lithium atom was placed in the plane, to reach a real minimum a rotation of the terminal CH₂ out of the plane was necessary, and a localized system was obtained, where the C–Li bond was essentially covalent. Again the *cis* form (2) is more stable than

† 1 kcal = 4.184 kJ.

the *trans* by 61.5 kcal/mol^{-1}, owing to a bonding interaction of Li with the nearest oxygen atom. Electronic data and geometrical parameters are reported in Table 2.

Computations show that (2) is more stable than (1) by 17.5 kcal mol^{-1}, but the ^{13}C n.m.r. spectrum of the dianion, consistent with a delocalized structure, suggested that (1) was a better description of the real molecule. The difference in the stability of these structures, however, decreased significantly by co-ordination of Li to two water molecules, structure (3), and the difference was only 0.17 kcal mol^{-1} on substitution of Li for Na. These calculations on structure (3) were carried out to try to understand the role of the solvent. They showed an increased net charge and decreased overlap charges between the metal and the oxygen atom, resulting in an increase in the metal–oxygen distance and an increase in the distance between the metal and the mean plane of the molecule (0.47, 0.04, 2.72, and 1.92 Å, respectively).

The bonding orbitals scheme remained unchanged, and the small values of the overlap charges are in agreement with substantial electrostatic stabilization, owing to the interaction between the positive metal ion and the three negatively charged atoms.[6]

In conclusion, we were unable to find any stable delocalized structure in which the lithium lies in the plane; both spectral and computational data suggest a structure with a delocalized system with the metal atom above the molecular plane, as depicted in Figure 1.

References

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