Quantum Chemical Calculations and Nuclear Magnetic Resonance Measurements on Benzyl-type Carbanions. Part 2.[1] Influence of Countercations and Interacting Unsaturated Systems

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Quantum chemical calculations, n.m.r. and spectrophotometric measurements are carried out to study the influence of countercations and interacting unsaturated systems on the structural and electronic properties of benzyl-type carbanions. The calculated geometry of benzyl-Li compares favourably with *X*-ray data on a related structure. ^{13}C, ^{1}H n.m.r. shifts and $^{1}J_{CH}$ coupling constants of benzyl, *o*- and *p*-CH_3O-benzyl-Li, -Na, and -K compounds show a fair overall agreement with the *ab initio*-calculated charge distributions and structural parameters for the terminal members of the Li-, Na-, and K- series, the Li compound and the free carbanion, modelling the K salt. Both theory and experiment indicate that, when passing from the anion to the alkali-metal compound, an important destruction of the resonance saturation, present in the CH_3O derivatives, occurs due to the presence of the countercation, the reduction being more important with decreasing cation radius. The n.m.r. data for α-alkyl-substituted compounds suggest that steric factors make the position of the cation in the C_α region less favourable, the effect being more pronounced for larger cation radius. The resonance saturation effect in the above mentioned systems may also be influenced by intermolecular effects, *e.g.* it may change during a chemical reaction. *Ab initio* calculations on the interaction energy between the benzyl-type carbanions and unsaturated systems showing increasing delocalization possibilities for incoming negative charge indicate that the larger this delocalization possibility (ethene < butadiene < styrene), the more important the destruction of resonance saturation. Along this series the parallel conformation of the CH_3O group in the *p*-CH_3O compounds gradually becomes less disfavoured. The calculated effect is however not strong enough yet in order to show full agreement with the observed increase in the $k(-)$ value for the addition reaction to 1,1-diphenylethene when passing from polystyryl to poly-*p*-methoxystyryl carbanions. Larger basis sets and extensive geometry optimization should be carried out in order to settle this problem.

In Part 1[1] a study was undertaken, using *ab initio* quantum chemical calculations and n.m.r. (^{13}C and ^{1}H) measurements, on the electronic structure of benzyl-type carbanions. The influence of aromatic substitution by a π-electron donor-substituent, namely CH_3O, and α-alkyl substitution was studied by calculations on the corresponding anions and by n.m.r. measurements on the potassium salts. In these compounds the electronic structure of the organic part is expected to be quite close (at least for the α-unsubstituted cases) to that of the free anion. Upon introduction of a CH_3O group in an *ortho* or *para* position, a resonance saturation effect[2] occurs: the π-electron-donating capability of the CH_3O group is strongly reduced due to the presence of the much stronger π-electron-donating CH_2^- group, the effect being larger in *para* than in *ortho* substitution. α-Alkyl substitution leads to charge flow into the alkyl group which acts as an electron-attracting group, when bound to an electron-rich group. The calculations did not indicate that more charge was delocalized over the aromatic ring, as could be expected from the upfield shift of the *ortho* and *para* carbon atoms. We suggested that this effect could be ascribed to a different location of the K^+ countercation in benzyl and α-substituted compounds.

In this Part we concentrate on the influence of the countercation on the structural and electronic properties of benzylalkali-metal compounds, in particular on the resonance saturation effect encountered in Part 1, again using quantum chemical calculations and n.m.r. measurements.

Experimental

The synthesis of the methoxy-substituted benzylpotassium compounds was described in Part 1. The methoxy-substituted lithium compounds were synthesized by adding a small excess of vacuum-dried LiCl to the solutions of the potassium salts in THF, after which the precipitated KCl was filtered off. Benzyllithium was obtained by the reaction of a small quantity of ethyllithium with dibenzylmercury in cyclohexane, in which benzyllithium is insoluble. Diethylmercury and the excess of dibenzylmercury were washed off and benzyl-lithium was dissolved in THF. Benzylcesium was prepared by the reaction of dibenzylmercury with a cesium mirror in THF at −70 °C. The reaction time was limited to 4 h to reduce side-reactions with the cesium mirror. Benzylsodium was prepared in an analogous way, the reaction time being extended to 24 h to obtain 100% conversion.

The methoxy-substituted benzylsodium salts could not be synthesized starting from the corresponding mercury compounds. The latter compounds decomposed immediately upon formation into metallic mercury and coupled products. The same observation applied to the substituted Sn and Cd compounds. The sodium salts could not be obtained from the corresponding benzylmethyl ethers. Ether cleavage was only observed at room temperature, when rapid termination of the sodium salts occurred. The sodium salts could be prepared by addition of $NaBPh_4$ to the potassium salts. Nevertheless, $KBPh_4$ only precipitated in a sufficient amount at room

Table 1. STO-3G Results for benzyl-Li compounds: total energy (E_{tot}), dissociation energy (ΔE_{diss}), charge on the α-carbon atom (q_α) and the Li atom (q_{Li}), and substituent interaction energy (ΔE_{int}). The symbols A, B, C denote the various structures described in the text. Symbols ⊥ and ‖ denote perpendicular and planar conformations of the CH_3O group (*cf.* ref. 1)

		$E_{\mathrm{tot}}^{(\mathrm{a.u.})*}$	ΔE_{diss}/kJ mol^{-1}	q_α(e)	q_{Li}(e)	ΔE_{int}/kJ mol^{-1}
Benzyl-Li	A	−273.181 92	992	−0.211	0.165	
	B	−273.164 02	945	−0.199	0.234	
p-CH_3O-Benzyl-Li	A (⊥)	−385.594 95	983^a	−0.211	0.166	+2.1
	(‖)	−385.592 24	1 003^b	−0.210	0.153	+8.1
p-CH_3O-Benzyl-Li	B (⊥)	−385.577 66	938^a	−0.199	0.234	
o-CH_3O-Benzyl-Li	A (⊥)	−385.613 69	1 032^a	−0.213	0.162	−47.2
	(‖)	−385.608 82	1 043^b	−0.210	0.144	−35.4
o-CH_3O-Benzyl-Li	C (‖)	−385.617 25	1 041^a	−0.214	0.099	
			1 065^b			

[a] Value obtained using a perpendicular conformation (⊥) for the CH_3O group. [b] Value obtained using a planar conformation (‖) for the CH_3O group. *1 a.u. = 2 625.5 kJ mol^{-1}.

temperature. Only in the case of *o*-$MeOC_6H_4Na$ we were able to isolate the product in a satisfactory concentration and purity, suitable for n.m.r. study.

Details of the n.m.r. measurements can be found in Part 1. The quantum chemical calculations are again performed at the STO-3G *ab initio* level.[3]

Results and Discussion

(A) *Influence of Countercations: Quantum Chemical Calculations.*—The structure of benzyl-Li was investigated starting from the molecular electrostatic potential[4] (m.e.p.) of the benzyl ion, calculated with the STO-3G wavefunctions. The m.e.p. in a plane at 2 Å above the molecular plane indicates the $C_\alpha C_i C_o$ region to be the preferred site for interaction with the Li^+ ion. Optimization at STO-3G level yielded a structure for benzyl Li in which the Li atom is situated 1.60 Å above the aromatic ring plane; the C_α atom undergoes a rehybridization: the angle between the carbon lone pair and the C_α–C_i bond increases from 90 to 105° and the CH_2 part is rotated over 20° so that the carbon lone pair points in the direction of the Li atom. This structure* leads to C_α–Li, C_i–Li, and C_o–Li distances of 1.93, 2.00, and 2.22 Å, indicating the interaction with the Li^+ ion to be the strongest for C_α. This feature also emerges from the overlap populations, obtained *via* a Mulliken population analysis,[5] the C_α–Li value (0.44) being substantially larger than those for C_o–Li (0.10) and C_i–Li (0.00). Our calculated structure compares favourably with the crystallographic data on the comparable benzyl-Li-triethylenediamine complex[6] where the Li also resides in the $C_o C_i C_\alpha$ region, the distance sequence 2.21 Å (C_α–Li) < 2.39 Å (C_i–Li) < 2.59 Å (C_o–Li) being the same as in our calculations. The distance between the Li atom and the aromatic ring plane (1.94 Å) is larger than in our system, which can be ascribed to the withdrawing effect of the ligands. Structure (A) is 47 kJ mol^{-1} more stable than a pure sp^3 structure, in which the Li atom is situated on the pyramidal axis with an optimized distance C_α–Li of 2.0 Å, hereafter referred to as structure (B). The trend in the dissociation energies parallels the trend of electron transfer of the carbanion to the Li^+ ion, which amounts to 0.835 e in the most stable complex, the corresponding dissociation energy being 992 kJ mol^{-1}. If a CH_3O group is introduced in the *para* position, the m.e.p. in the C_α region is qualitatively unchanged. The actual m.e.p. value at the electrostatic minimum in the plane at 2 Å above the molecular plane however becomes slightly less negative, the effect being more pronounced in the most stable (perpendicular) conformation of the CH_3O group; the values obtained are −530.9 (⊥) and −538.6 kJ mol^{-1} (‖) as compared with −541.0 kJ mol^{-1} in the unsubstituted case. This further illustrates the resonance saturation effect (*cf.* Part 1). In the *o*-CH_3O case, the global features of the m.e.p. are the same as in the unsubstituted and *p*-substituted case. The m.e.p. values at the electrostatic minimum [−541.1 (‖) and −541.9 (⊥) kJ mol^{-1}] are very close to that of the unsubstituted compound, the resonance saturation effect being much smaller. Upon optimization of the geometry of the *p*-CH_3O-benzyl-Li complex the position of the Li^+ ion was not found to change in a noticeable way compared with the unsubstituted case. The energy difference with the sp^3 structure is, however, somewhat smaller (±2 kJ mol^{-1}). Table 1 further shows that, just as in the case of the free carbanion, the perpendicular conformation of the methoxy group is more stable than the parallel one, the energy difference between the two conformations being, however, much smaller than in the carbanion (7.1 *versus* 26.6 kJ mol^{-1}). The resonance saturation effect is strongly reduced as the interaction between the Li^+ ion and the CH_2^- group (*cf.* the charge transfer of 0.834 e to the Li^+ ion) reduces the negative charge excess on the CH_2^- group and consequently its π-electron-donating capability. This also shows up in the negative charge excess on the CH_3O group decreasing from 0.207 e in the free carbanion (⊥) to 0.115 e in the corresponding Li derivative. The substituent interaction energies, calculated as in ref. 1, indicate that in the Li complexes the *p*-CH_3O group exerts a destabilizing effect in its perpendicular conformation (ΔE_{int} +2.1 kJ mol^{-1}) as opposed to the situation for the free carbanion[1] (ΔE_{int} −6.5 kJ mol^{-1}). In the case of the planar CH_3O group the destabilizing effect in the anion (19.0 kJ mol^{-1}) is reduced to 8.1 kJ mol^{-1}; both observations again indicate an important reduction of resonance saturation in the Li complexes. The trend in substituent interaction energies parallels the dissociation-energy sequence showing that *p*-CH_3O-benzyl-Li dissociates more easily than benzyl-Li. For the *o*-CH_3O derivative, structures of type (A) yield an extra stabilization energy, compared with the *para*-derivative, of the order of 50 kJ mol^{-1} if the Li^+ ion is brought into interaction with the *o*-CH_3O substituent.

However, the most stable structure is the one in which the Li ion is situated in the plane of the aromatic ring, equally interacting with both oxygen lone pairs (in an equivalent LMO description[7]) and along the pyramidal axis of a sp^3-hybridized C_α atom, with optimized distances C_α–Li and O–Li of 2.05 and 2.15 Å, respectively [structure (C) in Table 1]. This yields an extra energy lowering of 9 kJ mol^{-1}. This geometry is comparable with that computed for the $H_2O \cdots Li^+$ complex with the Li^+ ion located on the H_2O C(2)-axis.[8]

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* Hereafter referred to as structure (A).

Table 2. ^{13}C Resonances (in p.p.m. from Me_4Si) and $^1J_{C_\alpha H}$ coupling constants (in Hz) for benzylalkali-metal compounds and toluene derivatives in THF at −30 °C

	C_α	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	CH_3O	$^1J_{C_\alpha H}$
Benzyl-K[11]	52.8	153.2	111.0	130.8	95.6	130.8	111.0		153
-Na	40.9	156.1	114.9	128.9	102.4	128.9	114.9		144
-Li[11]	36.9	161.5	117.0	128.6	104.7	128.6	117.0		134
Toluene	21.5	138.5	129.7	129.0	126.1	129.0	129.7		126
p-CH_3O-Benzyl-K	44.7	151.5	109.6	119.7	139.4	119.7	109.6	58.7	150
-Li	31.9	156.8	116.9	115.5	145.4	115.5	116.9	56.8	127
p-CH_3O-Toluene	20.3	129.9	130.3	114.3	158.7	114.3	130.3	55.0	126
o-CH_3O-Benzyl-K	44.3	144.0	145.2	110.4	94.7	124.2	109.7	54.5	152
-Na*	34.7	146.5	146.5	109.5	98.5	123.4	113.2	54.8	
-Li	31.1	149.6	150.4	108.9	103.1	122.1	116.5	54.5	
o-CH_3O-Toluene	16.6	126.6	158.5	110.0	127.6	120.7	131.0	55.0	

* CH_3O Group at position 2.

The co-ordination of the Li^+ ion by the methoxy group leads to a dissociation energy which is much larger (by *ca.* 50 kJ mol^{-1}) than for benzyl-Li. This higher dissociation energy parallels with higher charge transfer to the Li^+ ion in the *o*-CH_3O case, the values for benzyl-Li and *p*-CH_3O-benzyl-Li being almost identical. The charge on the α-carbon atom is almost identical in the three cases.

It should be pointed out that CNDO/2[9] calculations yielded identical trends as *ab initio* for the energetics and charge distribution for the free carbanions but completely failed in the Li^+ complexes where a preferential position of Li^+ was found above the centre of the ring in complete disagreement with the crystallographic[8] and n.m.r. data.[10]

(B) *Influence of Countercations: N.m.r. Measurements and Comparison with Quantum Chemical Calculations.*—In Table 2 we give the ^{13}C for the C_α atom and the ring carbons in the unsubstituted and *o*- and *p*-CH_3O-substituted benzyl-Li, -Na, and -K compounds and compare them with those of the corresponding toluene derivatives. When comparing the ^{13}C resonances of the ring carbon atoms for the unsubstituted case, we see that the upfield displacements of the *ortho* and *para* carbon atoms increase with increasing cation radius, indicating that, certainly for Li and Na, polarizing effects must be attributed to the cations so that the anion–metal bond is not purely electrostatic. Summing relative shifts of *ortho* and *para* carbon atoms a sequence 68.2 (K), 53.3 (Na), and 46.8 (Li) is obtained which corresponds, using the 160 p.p.m./e relationship,[12] to an amount of 0.43, 0.33, and 0.29 electrons delocalized over the aromatic nucleus. The ratio of the values obtained for K and Li (1.48) compares favourably with the ratio of the sum of the *ab initio*-calculated negative charge excess on the *ortho* and *para* carbon ring atoms in the free anion (0.59 e) and the Li compound (0.36 e) (calculated ratio 1.76). Increasing delocalization is accompanied by a downfield shift of the α-carbon atoms and by a decrease of the directly bonded $^1J_{CH}$ coupling constant from 153 Hz (K) to 134 Hz (Li). Using the Müller–Pritchard relationship[13] we calculated from these data a change in hybridization of C_α from sp^3 type in benzyl-Li ($sp^{2.73}$) to sp^2 type in benzyl-K ($sp^{2.27}$). As expected an intermediate hybridization for the Na compound is obtained ($sp^{2.47}$) ($^1J_{CH}$ 144 Hz). The benzyl-Li results indicate that the hybridization at C_α is not completely sp^3 in which case a coupling constant of 125 Hz would be obtained as almost exactly found in toluene (126 Hz). Relating the values 109.5 and 90° of the angle between the lone pair on C_α and the C_α–C_i bond-axis to pure sp^3 and sp^2 hybridization of C_α with $^1J_{CH}$ values of 125 and 166 Hz, a linear interpolation yields an angle of 105° in the benzyl-Li compound, which compares favourably with the calculated equilibrium geometry in section (A). Considering that when passing from sp^3 to sp^2 hybridization a downfield shift of the order of 100 p.p.m. is expected,[14a] the $sp^{2.73}$ hybridization in benzyl-Li would yield, if a linear interpolation is used, a downfield shift from toluene of the order of 27 p.p.m.

The observed value is however only 15 p.p.m. downfield. The difference of 12 p.p.m. will originate in an upfield shift due to charge effects: using the 160 p.p.m./e relationship we expect *ca.* 0.07 electrons extra on the α-carbon atom in benzyl-Li as compared with toluene. The value resulting from our *ab initio* calculations is of the order of 0.04, the C_α net atomic charges in toluene and benzyl-Li being 0.175 and 0.211 respectively, which, in view of the various approximations made, compares favourably.

On the basis of the $^1J_{CH}$ values in benzyl-Na and -K the angle between the C_α lone pair and the C_α–C_i bond is calculated to be 100 (Na) and 96° (K), showing that in benzyl-K the completely planar arrangement of atoms in the $C_\alpha H_2$ part, corresponding to an angle of 90°, is approached.

The resonances of the *meta* carbon atoms are, as intuitively expected, hardly influenced by the nature of the cation. The *ipso*-atoms show, compared with toluene, downfield shifts which can be ascribed to the higher electron density at the α-carbon atom in the benzyl-Li system, repelling electrons at the *ipso* atoms.

The ^1H shifts (shown in Table 3) for the α-hydrogens show the same sequence as a function of the cation radius as the ^{13}C shifts (note however that they all resonate upfield from toluene). The *para*-hydrogens are at higher field with increasing cation-radius in agreement with the more important charge delocalization in the K compound. The same sequence, but less pronounced, is found for the *ortho* hydrogens. The *meta* hydrogens resonate at different field from toluene, as opposed to the *meta* ^{13}C shifts. Such lack of correlation between ^1H and ^{13}C shifts for *meta* positions was already observed in a large series of monosubstituted benzenes[16] (*cf.* also Part 1).

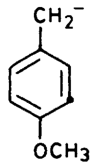
Turning now to the influence of a CH_3O substituent, for the *para* case essentially the same trend in the C_α shifts as a function of the cation radius is found as in the unsubstituted case, showing a downfield shift with increasing cation radius.

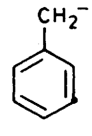
The non-additivity of the substituents is observed in all cases, but the resonance saturation decreases when passing from K to Na to Li. This effect most clearly shows up when comparing the *meta* resonances in the series (**1**)—(**4**). The Δ values indicate the difference between unsubstituted and substituted cases. Apparently the resonance saturation, for which a Δ value smaller than in the toluene case is indicative, decreases from the K to the Li compound, which is related to the increasing covalent character of the carbon–metal bond whereby the π-electron-donating capability of the CH_2^- group is reduced. The resonance satura-

Table 3. ^{1}H Resonance (in p.p.m. from Me_4Si) for benzylalkali-metal compounds and toluene derivatives in [$^2H_8$]THF at −30 °C

	H_α	2-H	3-H	4-H	5-H	6-H	CH_3O
Benzyl-K[15]	2.24	5.59	6.12	4.79	6.12	5.59	
-Na	1.88	5.92	6.20	5.16	6.20	5.92	
-Li[15]	1.62	6.09	6.30	5.50	6.30	6.09	
Toluene	2.32	~7.15	~7.15	~7.15	~7.15	~7.15	
p-CH_3O-Benzyl-K	1.80	5.45	5.90		5.90	5.45	3.32
-Li	1.26	6.00	6.00		6.00	6.00	3.40
p-CH_3O-Toluene	2.18	7.00	6.72		6.72	7.00	3.60
o-CH_3O-Benzyl-K	~2.0		~6.0		~6.0	5.78	3.72
-Na	~1.75		~6.0		~6.0	~6.0	
-Li*	1.50		~6.2		~6.2	6.10	3.74
o-CH_3O-Toluene	2.14		~6.8		~6.8	7.05	3.73

* OCH_3 Group at position 2.


(**1**)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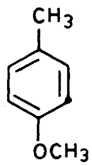
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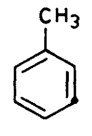
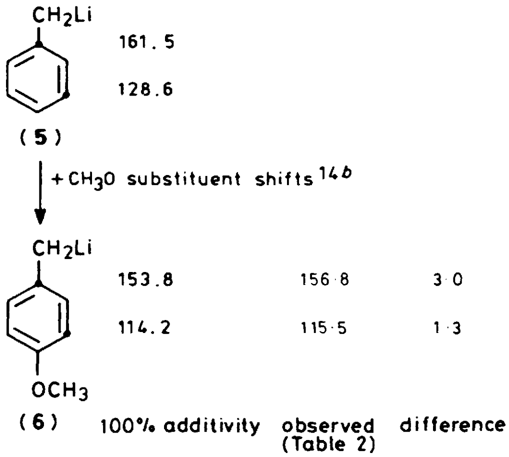

(**4**)

K 119.7 130.5 Δ = 11.1 114.3 129.0 Δ = 14.7

Li 115.5 128.6 Δ = 13.1



tion effect, occurring upon introduction of a second π-electron-donating substituent, will then be smaller. This effect also shows up when comparing the *meta* resonances of the toluene compounds with the corresponding benzyl compounds. This difference should be close to zero in the case of perfect additivity. The much smaller observed difference value for the Li compound (1.2) as compared with the K compound (5.4) also illustrates the decrease of resonance saturation.*

A similar conclusion emerges if we add the *relative* shifts of *ortho* and *para* carbons; the obtained values in the Li case are −46.8 (unsubstituted) and −40.1 (*p*-CH_3O), their difference (6.7) being smaller than in the K compound (7.5). A final 'visualization' of the resonance saturation destruction is obtained by 'calculating' the ^{13}C shifts in the case of 100% additivity of the CH_2^- and CH_3O substituents (*cf.* Part 1) and comparing the obtained values with the experimental ones.

Using the CH_3O substituent shifts of −14.4 (*o*) and −7.7 (*p*) we arrive at '100% additivity' resonances for the Li compound which differ from the measured values by 3.0 and 1.3 p.p.m. (for positions *ortho* and *para* from CH_2^- respectively). The magnitude of these differences, which is directly related to the amount of resonance saturation, again shows an important reduction of resonance saturation as compared with the K compound, where the corresponding values were 6.0 and 3.3 p.p.m. (*cf.* Part 1). Qualitatively the same features are found in the calculated charge distribution. Summing the total charges (electron excess) in benzyl-Li (0.044 and −0.033 for the C atoms in *meta* and *ipso*) and anisole (‖), we arrive at 100% additivity values for *p*-CH_3O-benzyl-Li of 0.136 and 0.076 for the C atoms in *ortho* and *para* positions from the CH_3O group. The actual values obtained (⊥ geometry) are 0.062 and 0.001 and show a reduction in the electron-donating capacities of the CH_3O group which is smaller than in the free carbanion case (*cf.* Part 1).

For the *o*-CH_3O compounds the most important effect is the downfield shift of the carbon *para* to CH_3O, as compared with the toluene compound, indicating a decrease in the π-electron-donating capability of the CH_3O group. This effect increases with increasing cation size [124.2 (K), 123.4 (Na), and 122.1 (Li)]. Again adding the relative shifts of *ortho* and *para* positions we arrive for the Li compound at a value which is larger than in the unsubstituted compound, suggesting an increase in delocalized charge. The effect for the Na compound is even more pronounced. We cannot offer an explanation for it at present.

We finally turn to the effect of α-alkyl substitution. Table 4 shows that, just as in the K compounds (*cf.* Part 1), α-alkyl substitution in the Li compounds displaces the C_α resonance downfield, compared with the unsubstituted benzyl case; the *ipso*, *ortho*, and *para* carbons move to higher field, whereas the *meta* resonances are only very slightly affected. These effects are clearly cation dependent and are larger for the smaller cation. This could be ascribed (*cf.* Part 1) to steric factors making the position of the cation in the C_α region less favourable, thus provoking a migration of the cation out of the C_α region upon α-alkyl substitution. In the Li case charge delocalization from C_α into the ring is then facilitated due to a reduction of polarizing effects compared with the unsubstituted benzyl-Li case. These effects are expected to be smaller for larger and therefore less polarizing cations as is the case in the K compounds. These findings are supported by comparing spectrophotometric data

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* The effect also shows up in the quantum chemical calculations of the charge (electron excess) on the *meta* carbons in benzyl-Li and *p*-CH_3O-benzyl-Li (⊥) (respectively 0.044 and 0.062), their difference (0.018) being 50% larger than in the case of the carbanions but still considerably lower than in the toluene, *p*-MeO-toluene case.[1]

Table 4. ^{13}C Shifts (in p.p.m.) of benzyl and α-alkylbenzylalkali-metal compounds, from the corresponding toluene derivatives in THF (based on shifts given in refs. 11 and 17)

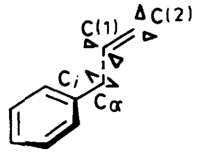
	α	*i*	*ō*	*m̄*	*p*
Benzyl-Li	15.4	23	−12.7	−0.4	−21.4
-K	31.3	14.7	−18.7	1.8	−30.5
α-Ethylbenzyl-Li	18.4	0	−15.9	−0.8	−26.1
-K	36.2	−11	−19.2	1.5	−35.1
α-Ethyl-α-methyl-benzyl-Li	22.9	−6.5	−20	−0.9	−33.9
-K	36.6	−13.7	−22.9	+0.6	−38.3

of the benzyl- and styryl-alkali-metal compounds[*] indicating that the bonding type in polystyryl systems seems to be mainly electrostatic in nature and only slightly cation dependent whereas in the case of the benzyl salt differences in absorption maxima are found (*e.g.* between the Cs^+ and Li^+ compounds) corresponding to energy differences much larger than expected on a purely electrostatic basis. This trend is fully confirmed by CNDO/2[9] calculations on the difference in interaction energy of the ground and excited states of these systems and a unit test charge, modelling the cation, as a function of the distance R, $\Delta E(R)$. When comparing $\Delta E(R)$ with $\lambda_{max.}$ differences between the Li^+ and Cs^+ compounds the differences in $\lambda_{max.}$ are much larger in the case of the benzyl compounds, as compared with the polystyryl analogues, the actual values obtained being close to those calculated in the electrostatic model in the latter case and being substantially larger in the former case.

(C) *Influence of Intermolecular Interactions on Resonance Saturation.*—Previous sections showed that resonance saturation in anionic systems may be reduced by interaction with cations. For the same reason resonance saturation may be expected to change during a chemical reaction of the anionic systems, *e.g.* with an electron-accepting species. This phenomenon has important consequences if one tries to estimate the reactivity of such systems on the bases of the properties of the anion. These considerations prompted us to perform some calculations on the change in resonance saturation during a chemical reaction.

The experimental data on which we focus our attention in this section are the anionic addition rate constants $k(-)$ of polystyryl- and poly-p-CH_3O-styryl carbanions to 1,1-diphenylethene (with Cs^+ as counterion). In THF at 0 °C $k(-)$ increases from 9.5×10^4 to 1.0×10^6 l mol^{-1} s^{-1} in the p-CH_3O case.[18] This increase in $k(-)$ was ascribed by Favier *et al.* to a higher intrinsic reactivity of the growing end of the macromolecule due to an increase of charge density at the active centre, originating in the π-electron donor capability of the CH_3O group. Note that the corresponding change in activation energy amounts to only 5.4 kJ mol^{-1}, a value which could even be smaller by a factor of 2 or 3 due to errors in the measured ion-pair dissociation constant.[19]

We first looked for a correlation between the 'isolated molecule' property q_α (charge on C_α) and the observed $k(-)$ sequence. Part 1 revealed that q_α is almost unchanged when passing from benzyl to p-CH_3O-benzyl, and when considering p-CH_3O-benzyl in its most stable (⊥) conformation for the CH_3O group, even a small charge decrease is calculated (0.319 *versus* 0.316 e). This effect is somewhat more pronounced when considering q_α^π, the π-charge on the α-carbon atom (0.504 *versus* 0.497 e). Obviously the 'isolated molecule' property q_α cannot explain the reactivity sequence. We then passed to some orientating calculations 'along the reaction path' of addition reactions of these benzylic systems to ethene, butadiene, and styrene, serving as model compounds for the experimentally studied 1,1-diphenylethene. This series of unsaturated systems is expected to show increasing delocalization possibilities for negative charge excess transferred from the anion upon intermolecular interaction.



(7)

As a geometry search of the transition state of these model reactions was still a far too demanding step we performed this study using the 'non-crossing rule' as working hypothesis, which, according to Klopman,[20] states that for similar reactants the ratio of the energies necessary to reach any particular but common point along the respective reaction paths is proportional to the activation energies. We therefore calculated all the above mentioned interacting systems at a common point of their reaction paths. Its geometry (**7**) was chosen as follows: the vinyl monomer was located in a plane parallel to the plane of the anion. The carbon atom of the vinyl monomer at which the attack of the anion occurs was placed along the lone pair axis of the α-carbon atom. A staggered conformation was chosen for the hydrogen atoms on C_α and C(1), whereas the double bond is orientated *anti* to the C_α–C_i bond.

Bond distances and angles (r_{int} and α_{int}) of this intermediate state were calculated using the relations (1)—(3) where N is a

$$r_{int} = r_{react} + \frac{r_{prod} - r_{react}}{N} \qquad (1)$$

$$\alpha_{int} = \alpha_{react} + \frac{\alpha_{prod} - \alpha_{react}}{N} \qquad (2)$$

$$r_{C_\alpha C(1)_{int}} = r_{C_\alpha C(1)_{prod}} + r_{C(1)C(2)_{prod}} - r_{C(1)C(2)_{int}} \qquad (3)$$

number larger than or equal to 1. In the limiting cases ($N = \infty$ and $N = 1$) the geometries of the reactants ('react') and of the reaction products ('prod') are recovered from these expressions. Structural parameters for ethene, butadiene, styrene, and the allyl system were taken from the literature.[21–24]

In Table 5 we report the results obtained with $N = 8$, a situation corresponding to an early stage of the reaction. The fact that the reactions studied are exothermic[25] should indeed, according to Hammond's principle,[26] yield a transition state quite close to the reactants ('reactant-like') so that the N value chosen must be relatively large. Additional calculations for the points $N = 2$ and $N = 4$ for the ethene case indicated that these structures have already lower energies: they are situated already at a greater distance from the transition state.

Considering first the non-substituted cases, we see that the charge transfer between the anion and the unsaturated system increases from ethene (0.501 e) to butadiene (0.665 e) and to styrene (0.718 e). This sequence parallels the increasing delocalization possibilities, offered by the unsaturated system, to incoming negative charge. The evolution in the C_iC_α and $C_\alpha C(1)$ overlap populations indicates the expected decrease in double-

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[*] $\lambda_{max.}$(nm) and $\varepsilon_{max.}$ (l mol^{-1} cm^{-1}) values in THF at −60 °C are: C_6H_5Cs: 368, 14 300; K: 362, 15 600; Na: 352, 15 800; Li: 330, 13 600; p-$MeOC_6H_5Cs$: 373, 8 500; K: 368, 13 600; Na: 356, –; Li: 323, 11 100; o-$MeOC_6H_5Cs$: 355, 8 300; K: 352, 13 100; Na: 347; Li: 327, 10 800; PStCs: 345; PStK: 343; PStNa: 342; PStLi: 337.

Table 5. STO-3G Results for 'point $N = 8$' along the reaction path [*cf.* equation (2)] for the reactions between benzyl carbanions and the unsaturated systems ethene, butadiene, and styrene. Values tabulated are the total electronic energy (E_{tot}) of the intermediate complex, its energy difference with the sum of the electronic energies of the reactants (ΔE_{tot}^{reac}), the total amount of negative charge transferred to the unsaturated system (q_{tr}), and the Mulliken overlap populations between C_α and C_i ($Q_{i\alpha}$) and between C_α and C(1) ($Q_1\alpha$). The energy difference between the two methoxy-conformers (ΔE_{tot}^{OMe}) is also indicated

Unsaturated system	Benzyl carbanion	E_{tot}(a.u.)	ΔE_{tot}^{reac}/kJ mol^{-1} *	q_{tr}(e)	$Q_{i\alpha}$	$Q_{\alpha 1}$	ΔE_{tot}^{OMe}/kJ mol^{-1}
Ethene	Benzyl	−342.619 16	315.9	0.501	0.928	0.318	
	p-CH_3O-Benzyl ($\perp$)	−455.034 23	319.2	0.495	0.928	0.318	19.1
	p-CH_3O-Benzyl ($\parallel$)	−455.026 94	311.7	0.514	0.922	0.326	
Butadiene	Benzyl	−418.614 31	196.1	0.665	0.884	0.392	
	p-CH_3O-Benzyl ($\perp$)	−531.028 74	200.9	0.662	0.884	0.392	14.4
	p-CH_3O-Benzyl ($\parallel$)	−531.023 24	188.8	0.679	0.878	0.400	
Styrene	Benzyl	−569.441 83	154.3	0.718	0.872	0.412	
	p-CH_3O-Benzyl ($\perp$)	−681.856 09	159.7	0.707	0.872	0.412	12.5
	p-CH_3O-Benzyl ($\parallel$)	−681.851 33	145.6	0.732	0.866	0.418	

* Energy values of unsaturated systems: ethene −77.070 78, butadiene −153.020 27, styrene −303.831 90 a.u.

bond character of C_iC_α and the increase in $C_\alpha C(1)$ bond strength, the effect always being in the order ethene < butadiene < styrene, which is also found when comparing the energy differences ΔE_{tot}^{reac} between the intermediate complexes and the reactants. Turning now to the influence of the *p*-CH_3O substituent, the perpendicular conformation was calculated to be the most stable conformation in all intermediate complexes, as was the case for the benzyl ions. The energy difference with the reactants (ΔE_{tot}^{reac}) slightly increases (between 3 and 6 kJ mol^{-1}) upon introducing the CH_3O substituent, which does not directly correlate with Favier's experimental data,[18] but the energy difference between perpendicular and parallel conformations for the CH_3O group is strongly reduced, the effect being larger with increasing delocalization possibilities for incoming negative charge in the unsaturated system: ΔE_{tot}^{OMe} decreases from 26.6 kJ mol^{-1} in the reactant case (*cf.* Part 1) to 19.1, 14.4, and 12.5 kJ mol^{-1} in the intermediate complexes with ethene, butadiene, and styrene. These results indicate that the resonance saturation in the benzyl reactant is drastically reduced during the chemical reaction, where the hybridization at C_α turns from sp^2 to sp^3-type. This enables the *p*-CH_3O group to exert, albeit still to a reduced amount, its π-electron-donating capability. The global electronic charge on the CH_3O group fits this pattern: it decreases from 0.207 in the reactant (*cf.* Part 1) to 0.182, 0.162, and 0.156 in the various complexes. It is interesting to note that if the less stable planar conformation of the CH_3O group is considered, the energy difference between the intermediate complex and the reactants decreases upon CH_3O substitution. The results parallel those of the highly approximate Hückel-type calculations by Favier *et al.* on the reaction of the styryl and *p*-CH_3O-styryl carbanions with styrene[27] in which, due to the fact that the theory is only applicable to planar systems, a very crude model of the CH_3O group was made and in which conformational effects could not be investigated.

We finally remark that in the planar CH_3O conformation, as opposed to the perpendicular one, more electrons are transferred to the unsaturated system as compared with the unsubstituted case. As (*cf.* Part 1) we expect that the perpendicular conformation of the CH_3O group might be overstabilized within our theoretical model it would be interesting to investigate the conformational behaviour of the CH_3O group in these systems using larger bases sets, including diffuse functions,[28,29] and performing more extensive geometry optimizations.

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