Quantum Chemical Calculations and Nuclear Magnetic Resonance Measurements on Benzyl-type Carbanions. Part 1. The Effect of an Aromatic Methoxy Substituent (Resonance Saturation) and α-Alkyl Substitution

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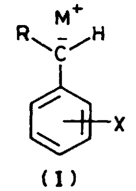
Ab initio STO-3G quantum chemical calculations are reported for benzyl-type carbanions. The influence of aromatic ring substitution by a methoxy group (*ortho* or *para*) and of α-alkyl substitution on the electronic properties of the carbanions are investigated. Energetics (*e.g.* the energy difference between perpendicular and parallel methoxy group conformations, substituent interaction energies) and charge distributions (*e.g.* total and π-electronic charge excess on the aromatic ring carbons, negative charge excess on the methoxy group) reveal the importance of a resonance saturation effect in these systems due to the simultaneous presence of two π-electron-donating substituents in the aromatic nucleus, the effect being always larger in the case of *para*-substitution. Upon introduction of an α-alkyl substituent sp^2-hybridization is still more favoured and a negative charge transfer to the alkyl group, which acts as an inductive acceptor, occurs. The charge distribution in the aromatic nucleus is hardly changed when compared with the α-unsubstituted case. The ^{13}C and ^{1}H n.m.r. chemical shifts of the benzyl-potassium compounds generally correlate well with the calculated charge distribution in the anions. The non-additivity of the π-electron-donating CH_2^- and CH_3O substituents also shows up in the ^{13}C shift data, the effect again being larger for *para* than for *ortho* substitution. When analysing the effect of α-alkyl substitution, a small polarizing effect due to the presence of the countercation should probably be taken into account.

In anionic polymerization processes the rate of initiation and propagation and the microstructure of the polymers obtained are related to the polarity of the carbon–metal bond in the carbanionic species.[1–3] The polarity of the carbon–metal bond itself is influenced by the solvent polarity, the type of metal counterion, and the structure of the organic moiety. Focusing our interest on polystyrene polymerizations, a proper understanding of the importance of these last two parameters results from a knowledge of the geometrical arrangements of the atoms and of the electron distribution in benzyl-type carbanions (I), which may be considered as model compounds for the reactive chain end of the growing polymer. Information about the electronic structure of these benzyl carbanions and their alkali-metal salts can be obtained by performing quantum chemical calculations and, in an indirect way, by ^{1}H and ^{13}C n.m.r. experiments.



(I)
R = H or alkyl
M = alkali-metal

We consider here the effect of alkyl and aromatic ring substitution on the electronic structure of the benzyl carbanions. R is varied along the series H, methyl, ethyl, propyl and the effect of aromatic ring substitution is studied for a CH_3O group in the *ortho* or *para* position, since the polymerization of the corresponding monomers (*o*- and *p*-methoxystyrene) has for several years been studied in this laboratory,[4] in view of the possibility of specific complexation effects. The results of quantum chemical calculations are compared with ^{1}H and ^{13}C n.m.r. measurements on the corresponding potassium salt in which the organic part is quite close to the 'isolated' carbanion studied in the quantum chemical calculations.

Experimental

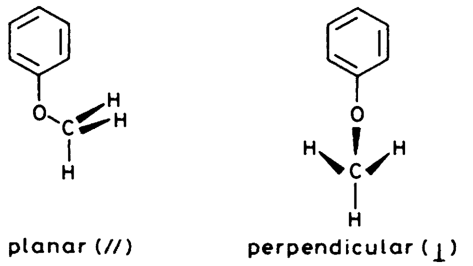
(a) *Synthesis.*—Model compounds with potassium as countercation were synthesized by the reaction of the corresponding methyl ethers dissolved in dried THF with a potassium mirror for *ca.* 24 h under high vacuum. The preparations were carried out at −70 °C because of the instability of those compounds at higher temperatures. Potassium methoxide was filtered off and THF was distilled from the filtered solution at −30 °C into a liquid-nitrogen-cooled receiver. Dried [$^{2}H_8$]THF was added to the potassium compounds and *ca.* 0.5M solutions were sealed into n.m.r. tubes.

(b) *Measurements.*—^{1}H N.m.r. spectra were recorded with a Varian XL-100 spectrometer at 100.1 MHz and ^{13}C n.m.r. spectra with a Bruker WP-80 at 20.12 MHz using a deuterium lock. The temperature of the samples was regulated at −30 °C by a stream of nitrogen using a Bruker B-VT-1000 variable-temperature controller. The sample solutions contained *ca.* 5% cyclohexane as internal reference (δ_C 27.5 p.p.m.; δ_H 1.4).

(c) *Quantum Chemical Calculations.*—Quantum chemical calculations were performed at the *ab initio* STO-3G[5] minimal basis set level. Standard geometries[6] were used throughout unless stated otherwise. The C(1)–C$_\alpha$ distance in the benzyl carbanion was taken to be 1.40 Å.[7] For the CH_3O group two

Table 1. STO-3G Energy and charge distribution for benzyl carbanions: total energy E_{tot} (in atomic units) (1 a.u. = 2 625.5 kJ mol^{-1}), total and π-electronic negative charge excess at C_α (q_α^{tot}, q_α^π), negative charge excess in the methoxy group (q_{OMe}), and π-electronic charge excess in the aromatic nucleus (q_ϕ^π) are given. The energy difference between planar (∥) and perpendicular (⊥) methoxy conformation, ΔE_{OMe}, and the substituent interaction energy ΔE_{int} (see text) are also tabulated

Geometry at C_α	Carbanion	E_{tot} (a.u.)	q_α^{tot}	q_α^π	q_{OMe}	q_ϕ^π	ΔE_{OMe}/kJ mol^{-1}	ΔE_{int}/kJ mol^{-1}
Planar	Benzyl	−265.668 71	0.319	0.504		0.496		
	p-CH_3O-Benzyl (⊥)	−378.085 01	0.316	0.497	0.207	0.518	26.6	−6.5
	p-CH_3O-Benzyl (∥)	−378.074 87	0.324	0.517	0.196	0.538		+19.0
	o-CH_3O-Benzyl (⊥)	−378.085 19	0.317	0.490	0.191	0.531	24.2	−7.0
	o-CH_3O-Benzyl (∥)	−378.075 98	0.314	0.490	0.179	0.582		+16.1
Tetrahedral	Benzyl	−265.658 90	0.348			0.385		
	p-CH_3O-Benzyl (⊥)	−378.074 97	0.345		0.198	0.409	23.4	−5.9
	p-CH_3O-Benzyl (∥)	−378.066 06	0.352		0.187	0.434		+16.4
	o-CH_3O-Benzyl (⊥)	−378.072 76	0.341		0.182	0.423	17.1	−0.1
	o-CH_3O-Benzyl (∥)	−378.066 25	0.344		0.170	0.472		+15.9



planar (//) perpendicular (⊥)

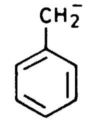
(II)

conformations were considered: 'planar' (∥) with an sp^2-type oxygen, and 'perpendicular' (⊥) with an sp^3-type oxygen, the CÔC ring angle being 120 and 109.5°, respectively. No further geometry optimizations were carried out for the different carbanions due to computational limitations.

Results and Discussion

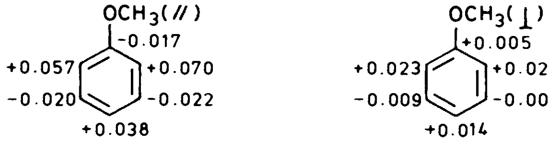
(a) *Quantum Chemical Calculations.*—Table 1 shows that the unsubstituted benzyl carbanion with planar geometry at C_α turns out to be more stable, the energy difference with the tetrahedral structure being 26 kJ mol^{-1}. The negative charge excess at C_α is larger in the tetrahedral case (0.348 *versus* 0.319), the charge delocalization in the ring being smaller but still important (0.385 e). In the planar case almost half an electron (0.485) is distributed over the aromatic nucleus. The C_α–C_i bond acquires strong double-bond character as evidenced by the C_α–C_i π-overlap population which amounts to 0.24 e which is slightly larger than the corresponding value between two neighbouring atoms in benzene (0.22 e). The whole of these results are in agreement with the well known picture of a CH_2^- group as a powerful π-electron-donating substituent.[8] In the p-CH_3O substituted case, the perpendicular geometry leads to an energy which is 26.6 kJ mol^{-1} lower than the parallel conformation.

Our results for the energy differ slightly from those presented by Kemister *et al.*[8] For the unsubstituted case, they obtained an energy of −265.670 16 a.u., *i.e. ca.* 3.8 kJ mol^{-1} lower than ours, whereas in the p-CH_3O case, in which these authors only consider the planar geometry,* a value of −378.077 01 a.u. was reported, which is 5.6 kJ mol^{-1} lower than ours but 21.0 kJ mol^{-1} higher in energy than our perpendicular geometry. The small differences can be ascribed to small deviations in the geometrical parameters characterizing the CH_2^- and CH_3O groups. It can be seen that the parameters characterizing the charge distribution also differ only slightly.



	π-charge	total charge
α	0.504	0.319
i	−0.087	−0.002
o	0.180	0.140
m	−0.009	0.072
p	0.242	0.168

(III)



(IV)

When discussing the effect of CH_3O some data on anisole can serve, together with those of the unsubstituted benzyl carbanion, as reference material. The perpendicular and parallel geometries turned out to be almost degenerate, the perpendicular geometry being 1.05 kJ mol^{-1} more stable than the parallel one (total energies obtained −340.304 14 and −340.303 74 a.u.). In recent years various *ab initio* calculations have been reported on the conformational behaviour of anisole.[9–14] The most elaborate optimization (at STO-3G level) on planar anisole led to an energy of −340.311 80 a.u., which is 8.11 kJ mol^{-1} lower than a (not fully) optimized perpendicular conformation. On this basis the standard geometry adopted in the present work somewhat overstabilizes the perpendicular geometry (*cf.* also ref. 9). The results however, can be used in a comparative study on the influence of a second substituent, in our case a CH_2^- group, on the energetics of these systems.

The charge distribution of both conformers of anisole shows the enhanced π-electron-donating capability of the p-CH_3O group in the planar conformation with a more pronounced negative π-charge excess on the *ortho* and *para* carbon atoms. (The actual values of the charge are very close to those obtained by Kollman *et al.*[12]) The same trend, but less pronounced, is found in the *total* changes, the values being 0.092 *versus* 0.079† (*o*), and 0.079 *versus* 0.069 (*p*).

As compared with the hydrogen substituent in benzene (posi-

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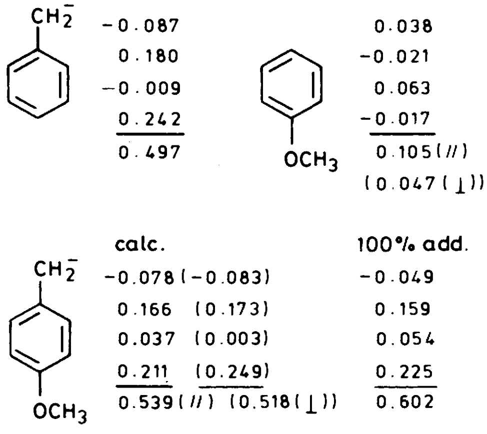
* Based on a $C_{ring}\hat{O}C$ angle of 118° (optimized value in anisole).

† Average value.

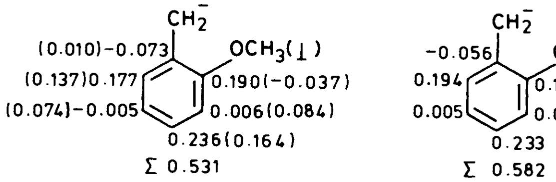
tive charge equal to 0.062), the CH_3O group takes *more* electrons from the aromatic ring system (0.170 e in the perpendicular and 0.151 e in the planar conformation), the negative charge excess being 0.232 e in the perpendicular and 0.213 e in the parallel geometry. These results illustrate the decrease of the π-electron-donating capability of the CH_3O group, in its perpendicular conformation, as also reflected in the much smaller increase of the π-electron population of the ring when passing from benzene to perpendicular anisole (0.047 e) as compared with parallel anisole (0.106 e). The same effect is also seen in the smaller π-overlap population between the oxygen and the *ipso*-carbon atom in the perpendicular conformation (0.025 *versus* 0.056 for the planar conformation). Note that in anisole the highest π-electron population is found on the *ortho*-carbon, whereas in the benzyl carbanion the *para*-carbon atom possesses most of the π-electrons delocalized over the aromatic nucleus. This finding fits the previously mentioned statement that, in contrast with neutral π-electron donor substituents where the highest π-electron density resides at the *ortho*-positions,[9] negatively charged substituents give a through-space electron-repelling effect which makes the electronic population of the *para*-position more favourable.[8,15,16]

For the methoxy-substituted benzyl carbanions, the planar geometry at C_α invariably leads to the lower energy. The perpendicular geometry for the methoxy group is again favoured, the energy difference being 26.6 kJ mol^{-1} for *para* and 24.2 kJ mol^{-1} for *ortho* substitution which is in both cases much larger than for anisole. The methoxy group has only a minor influence on the electronic density at C_α. In general a small electron population decrease (both total and π) is observed, except in the case of *p*-CH_3O substitution with parallel conformation, where the π-electron population increases by 0.013 e, the effect being reduced to 0.005 e for the total electron population. Owing to the presence of the methoxy group the aromatic ring is enriched, compared with the benzyl case, by 0.021 and 0.034 π-electrons for *p*- and *o*-CH_3O substituted anions with perpendicular conformation and by 0.041 and 0.085 e in the parallel conformation. This is much smaller than the π-electron increase in the aromatic nucleus when passing from benzene to anisole (0.106 for parallel and 0.047 e for perpendicular conformation). The π-electron-donating capabilities of the CH_2^- and CH_3O substituents are not additive, the deviations from additivity being larger in the case of *para*-substitution. A 'resonance saturation' phenomenon[17,18] can apparently be recognized in this system due to the simultaneous presence of two π-electron-donating substituents on the aromatic nucleus. From an analysis of the π-densities of disubstituted benzenes, tabulated by Pross and Radom,[16] we may deduce that resonance saturation is more pronounced in the case of *para* substitution if the stronger donor substituent has a tendency to increase negative charge more in the *para* position. If the stronger donor substituent preferentially increases the negative charge in the *ortho* position, resonance saturation occurs to a greater extent in the case of 1,2 substitution. The resonance saturation effect is visualized when the calculated π-electron excess in the methoxybenzyl carbanion is compared with the one which would result from a 100% additivity of both substituents (taking the parallel geometry for the CH_3O group).

The π-electron-donating capability of the CH_3O group is clearly diminished as seen from the π-electron population of the carbons in the *ortho* (average value 0.037) and *para* positions, being 0.017 and 0.029 smaller than in the case of 100% additivity. The total π-electron excess in the aromatic ring (0.539) is 0.063 e smaller than for 100% additivity (0.602). The π-electron increase compared with benzyl is only 0.042 (0.021) in case of the planar (perpendicular) *p*-CH_3O substituent. All effects are larger if the comparison is made starting from the perpendicular case.[*] In the case of *ortho* substitution it can be seen from the π and total charges (in parentheses for the most stable structures) (**VI**) that the resonance saturation is less pronounced than in the *para* case, *e.g.* the ring π-electron increase values [0.034 (⊥) and 0.085 (∥)] are larger but however still smaller than in anisole, *i.e.* in the absence of resonance saturation. This result parallels the preferentially *para*-directing properties of the negatively charged CH_2^- substituent as discussed above.



(**V**)



(**VI**)

Our results parallel recent findings by Taft *et al.*, who showed for disubstituted benzenes that the intensity of the π-electron-donating or -accepting character of a substituent is influenced by the π-electron demand of the aromatic system in which one substituent is already present.[17,18]

Turning now to some energetic consequences of the resonance saturation, the increase in the energy difference between the perpendicular and parallel conformation for the CH_3O group (ΔE_{OMe}) from anisole (1.0 kJ mol^{-1}) and *p*-methoxytoluene (2.2 kJ mol^{-1}) to 26.6 kJ mol^{-1} in the benzylic case (sp^2), indicates that as the π-electron-donating effect of the substituent *para* to CH_3O increases, a CH_3O conformation with the smaller π-electron-donating effect becomes favoured. The results by Pople *et al.*[19,20] on torsional barriers in *para*-substituted phenols and inversion barriers in *para*-substituted anilines and by Taft on *p*-hydroxybenzyl anion[8] (see also ref. 18) point in the same direction.

As a final quantification of the resonance saturation we calculated substituent interaction energies ΔE_{int},[19,20] in our

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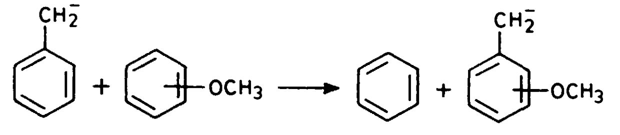
[*] Analogous conclusions arise from considering the total charges. The 100% additivity charges here amount to 0.164 (*o*) and 0.077 (*p*) [obtained on the basis of planar anisole with charges 0.092 (*o*) and 0.079 (*p*) (0.079 and 0.069 in the perpendicular case)]. The actual values calculated in the *p*-methoxybenzyl carbanion (∥) are 0.092 (*o*) and −0.002 (*p*) leading to charge deviations of 0.072 and 0.079. In the case of the most stable perpendicular form the calculated charges are 0.084 (*o*) and −0.001 (*p*), the deviations from 100% additivity being 0.080 (*o*) and 0.078 (*p*).

Table 2. STO-3G Energy and charge distribution for α-alkyl-substituted benzyl carbanions $CH_3OC_6H_4CHR^-$. q_R^{tot} Stands for the negative charge excess on the alkyl group; the remaining symbols and units are the same as in Table 1. All results refer to planar geometry at C_α unless indicated otherwise

R	CH_3O position and conformation	E_{tot} (a.u.)	q_α^{tot}	q_α^π	q_{OMe}	$q_\bullet^\pi$	q_R^{tot}	ΔE_{OMe}/kJ mol^{-1}	ΔE_{int}/kJ mol^{-1}
CH_3		−304.249 13	0.237	0.487		0.492	0.146		
C_2H_5		−342.827 88	0.240	0.492		0.490	0.146		
C_2H_5(tetrahedral C_α)		−342.813 19	0.277			0.317	0.181		
C_3H_7		−381.407 01	0.241	0.492		0.489	0.146		
C_2H_5	*para* (⊥)	−455.244 07	0.237	0.485	0.204	0.513	0.143	25.9	−6.3
	para (∥)	−455.234 19	0.245	0.505	0.193	0.535	0.149		+18.6
C_2H_5	*ortho* (⊥)	−455.244 22	0.238	0.478	0.189	0.526	0.141	23.2	−6.6
	ortho (∥)	−455.235 39	0.235	0.478	0.176	0.576	0.143		+15.5



(VII)

case defined as the energy change in the formal reaction. Table 1 shows that the largest positive value for ΔE_{int} is obtained in the case of parallel *p*-CH_3O substitution. If the CH_3O group is turned out of the plane a negative interaction energy is obtained. This result at first seems to be in contradiction to the resonance saturation effect. However, we recall that in all our calculations standard geometries were used which apparently overstabilize the perpendicular CH_3O group conformation. The main point in this section, namely the *trend* in substituent interaction energy which noticeably decreases from parallel to perpendicular conformation, may be regarded with confidence. This effect parallels the accumulation of more negative charge on the CH_3O group in *p*-methoxybenzyl carbanion compared with anisole [0.108 (⊥); 0.089 (∥)], the actual values being 0.207 (⊥) and 0.196 e (∥).

Turning now to the influence of α-alkyl substitution, we considered the α-methyl, -ethyl, and -propyl derivatives of the benzyl carbanion and the *o*- and *p*-methoxybenzyl carbanions. In all cases studied the planar geometry at C_α is favoured, the energy difference with the tetrahedral case being substantially larger than in the non-substituted case. For the α-ethyl case* an energy difference of 39 kJ mol^{-1} was calculated which is 13 kJ mol^{-1} larger than in the unsubstituted case. In the remainder only the results for the planar case will be analysed. In all cases the alkyl group carries more electrons than the hydrogen atom in the benzylic case. The negative charge transfer amounts to 0.146 e, irrespective of the nature of the alkyl group (ethyl, propyl, butyl) (compare the charge on the α-hydrogen atoms in the benzyl carbanion: 0.069). Our results that alkyl groups may act as electron acceptors when bound to an electron-rich centre are in agreement with those obtained by Pople and Hehre[21] and Umeyama and Morokuma[22] in STO-3G studies on aliphatic amines. The electronic charge distribution in the aromatic nucleus is hardly changed when passing from the benzyl carbanion to the α-substituted cases. Table 2 shows that the π-electron excess in the ring changes from 0.497 (in the benzyl carbanion) to 0.492, 0.490, and 0.489 in the methyl, ethyl, and propyl derivatives. The small change in the C_α π-electron population is expected on this basis: from 0.504 in benzyl to 0.487, 0.492, and 0.492 in the α-methyl, α-ethyl, and α-propyl derivatives. The change in the C_α total electon population from 0.319 in benzyl to 0.237, 0.240, and 0.241 in the α-substituted cases is a σ-effect, indicating that in these compounds the α-alkyl group exerts a σ-inductive acceptor effect.

The influence of the methoxy substituent both for charge distribution and energetics is almost the same as in the α-unsubstituted case, *e.g.* the energy difference between the planar and perpendicular methoxy group conformations amounts in the α-ethyl case to 25.9 (*ortho*) and 23.2 kJ mol^{-1} (*para*), the corresponding values for the unsubstituted compounds being 26.6 and 24.2 kJ mol^{-1}. The same insensitivity to alkyl substitution is present in the main parameters characterizing the charge distribution, q_α, q_α^π, q_{OMe}, and $q_\bullet^\pi$ (compare Tables 1 and 2).

The results indicate how, upon alkyl substitution at C_α, only the electronic density at C_α is changed due to an inductive acceptor effect of the alkyl group. All other characteristics of the charge distribution in CH_3O substituted benzyl carbanions discussed above are retained, and the remaining part of our discussion will be limited to the case of α-unsubstituted derivatives.

(b) *N.m.r. Measurements and Comparison with Quantum Chemical Results.*—The ^{13}C chemical shift data in Table 3 indicate that the *ortho* and *para* carbon atoms always show an upfield shift resulting from the delocalization of the negative charge excess at C_α. The *meta*-shifts are almost unaffected and show a slightly downfield shift. These results correlate with the *ab initio*-calculated charge distributions. Summation of *ortho* and *para* shift differences in benzylpotassium yields a value of −68.2 p.p.m. which, on the basis of the 160 p.p.m./e relationship,[23] leads to a delocalization of 0.42 e over the aromatic nucleus, in fair agreement with the *ab initio* results (0.496 e).

The directly bonded J_{CH} coupling constant in benzylpotassium (153 Hz) indicates, on the basis of the Müller–Pritchard relation,[24] an sp^2-type hybridization ($sp^{2.27}$) which supports our choice of the benzylpotassium compound as reference for comparison with the calculations on the carbanions. The α-carbon atom shows a downfield shift difference of 31.3 p.p.m. due to a rehybridization (*cf.* ref. 25) (from $sp^{2.97}$ in toluene to $sp^{2.27}$). Taking 100 p.p.m. as the shift difference for a complete sp^3–sp^2 rehybridization[26] and linearly interpolating, an $sp^3-sp^{2.27}$ hybridization difference would yield a downfield shift difference of *ca.* 70 p.p.m. However, when passing from toluene to benzyl the electronic population at C_α increases (the *ab initio* values being 0.175 and 0.319). This charge increase would yield, using the 160 p.p.m./e relationship,[23] an upfield contribution of 23 p.p.m. The combination of both effects results in a downfield shift of 47 p.p.m. which can be considered to be in qualitative agreement with the observed value (31 p.p.m.), in view of the approximations made. The ^1H resonances in Table 4 show that the *ortho* and *para* hydrogen signals shift to higher field as was the case for the corresponding carbon atoms. However, the *meta* hydrogen signals move to

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* The C_α–C_i distance was optimized, the value obtained being 1.46 Å.

Table 3. (a) ^{13}C Shifts (in p.p.m. from Me_4Si) for benzylalkali-metal compounds and corresponding toluene derivatives in THF at −30 °C. The value of the $^1J_{C,H}$ coupling constant is given in Hz

	C_α	C(1) (*i*)	C(2) (*o*)	C(3) (*m*)	C(4) (*p*)	C(5) (*m*)	C(6) (*o*)	$^1J_{C,H}$
Benzyl-K[25]	52.8	153.2	111.0	130.8	95.6	130.8	111.0	153
Toluene[25]	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	150
p-CH_3O-Toluene	20.3	129.9	130.3	114.3	158.7	114.3	130.3	126
o-CH_3O-Benzyl-K*	44.3	144.0	145.2	110.4	94.7	124.2	109.7	152
o-CH_3O-Toluene	16.6	126.6	158.5	110.0	127.6	120.7	131.0	

* CH_3O At position 2.

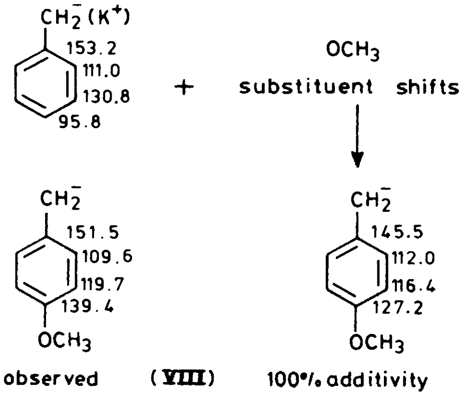
(b) ^{13}C Shift differences in (p.p.m.) between benzyl-K compounds and the corresponding toluene compounds (toluene itself in the case of benzyl-K, *p*- and *o*-CH_3O-toluene in the cases of *p*- and *o*-CH_3O-benzyl-K). A negative value indicates an upfield shift when passing from the toluene to the benzyl-K compound. $\Sigma_{o,p}$ stands for ths summation of shift differences of *ortho* and *para* carbons

	C_α	C(1) (*i*)	C(2) (*o*)	C(3) (*m*)	C(4) (*p*)	C(5) (*m*)	C(6) (*o*)	$\Sigma_{o,p}$
Benzyl-K[25]	31.3	14.7	−18.7	1.8	−30.5	1.8	−18.7	−68.2
p-CH_3O-Benzyl-K	24.4	21.6	−20.7	5.4	−19.3	5.4	−20.7	−60.7
o-CH_3O-Benzyl-K	27.7	17.5	−13.0	−0.3	−32.9	3.5	−20.6	−66.5

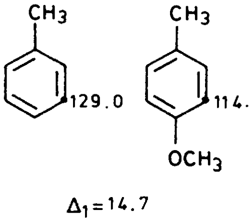
Table 4. ^{1}H Chemical shifts (in p.p.m. from Me_4Si) for benzyl compounds and the corresponding toluene derivatives (in [$^2H_8$]THF at −30 °C)

	H_α	2-H	3-H	4-H	5-H	6-H
Benzyl-K	2.24	5.59	6.12	4.79	6.12	5.59
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
p-CH_3O-Toluene	2.18	7.00	6.72		6.72	7.00
o-CH_3O-Benzyl-K*	~2		~6.0	~4.9	~6.0	5.78
o-CH_3O-Toluene	2.14		~6.8	~7.05	~6.8	7.05

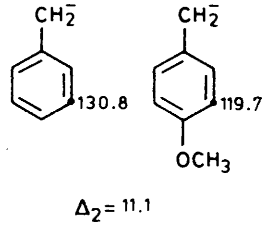
* CH_3O At position 2.



(VIII)



(IX)



(X)

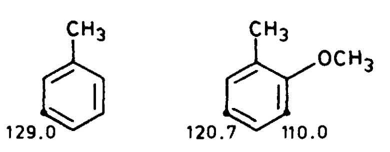
higher field as opposed to the downfield ^{13}C shifts. Such a lack of correlation between ^{1}H and ^{13}C chemical shifts for the *meta* positions was previously observed in a large series of monosubstituted benzenes.[27]

Turning now to the influence of a CH_3O substituent we see that C_α shifts less downfield which would be indicated for higher charge density at C_α and/or increasing sp^3 character. The latter effect shows up in the smaller $^1J_{C,H}$ value. The difference between $^1J_{C,H}$ in benzyl- and *p*-methoxybenzyl-potassium leads to an upfield shift of 6.5 p.p.m. using the same correlations as described above. As the calculated charge difference on C_α was very small (Table 1) this calculated shift is directly comparable with the experimental value (8.1), the agreement being fair. The *ortho* case is less evident.

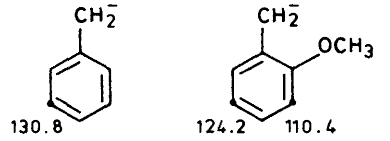
In the ^{13}C shifts in the aromatic nucleus a non-additivity of substituent effects is observed as expected on the basis of our quantum chemical calculations. The effect of a methoxy substituent on the ^{13}C shifts in an aromatic nucleus can be evaluated by considering the shift differences between anisole and benzene;[28] the values obtained were +31.4 (*i*), −14.4 (*o*), +1.0 (*m*), and −7.7 (*p*). The same pattern and values are found when passing from toluene to *p*-methoxytoluene, as shown in Table 3a, the shift differences being −14.7 and +0.6 for the carbons *ortho* and *meta* to the CH_3O group. If this pure CH_3O substituent effect is added to the observed shifts in benzylpotassium we obtain a series of ^{13}C shifts which can be considered as 100% additivity shifts, and which clearly deviate from the values actually observed.

We see that the carbon atoms *ortho* and *para* to the CH_3O group are more downfield than expected on the basis of 100% additivity, suggesting a reduced π-electron-donating capability of the CH_3O group in agreement with the charge distribution calculations discussed above. The effect also shows up when we compare the shift evolution for the carbon atom *meta* to the CH_2^- and CH_3 groups in the pairs (**IX**) and (**X**).

It is seen that the influence of the CH_3O group leading to an upfield shift for the *ortho*-carbon atom when passing from toluene to *p*-methoxytoluene (Δ_1 = 14.7) is reduced in the benzylic case (Δ_2 = 11.1). The values obtained suggest that the π-electron donor capability of the CH_3O group is reduced to *ca.*



(XI)



(XII)

70% of its original value.* Note that in the 100% additivity case the C atoms *meta* to the CH_2^- group should have almost the same shift, which is obviously not the case when comparing *p*-methoxytoluene to *p*-methoxybenzylpotassium. The same effect is also seen in the calculated charges. Comparing the sum of the shift differences of *ortho* and *para* carbon atoms in *p*-methoxybenzylpotassium *versus* toluene on one hand and between benzylpotassium and toluene on the other, the value for the CH_3O substituted case is -60.7 which is only 87% of the value (-69.2) for the unsubstituted case, indicating a decrease in π-donating capability of CH_2^-. For *ortho*-substitution the situation is less clear-cut. The chemical shift of the carbon atom *meta* to the CH_2^- group and *ortho* to CH_3O is close to that in *o*-methoxytoluene, which would indicate the absence of resonance saturation. However, the carbon atom *para* to CH_3O appears at lower field (124.2) in the potassium compound than in the toluene derivative (120.7), suggesting that the π-electron donating capability of the methoxy group is reduced. The summation of *ortho* and *para* shift differences leads to a value of -66.5 p.p.m. which deviates much less from the unsubstituted case than the *para* substituted compounds. The global trend in these results is in agreement with the charge density calculations discussed earlier.

In conclusion, the n.m.r. results support the resonance saturation effect emerging from our calculations. This effect is more pronounced when both substituents are in 1,4 positions than in the case of 1,2 substitution. Theory and experiment do not, however, yield identical results. The quantum chemical calculations indicate that the CH_3O group loses part of its π-electron donating character, but not the CH_2^- group, yielding an electron population at C_α which is even slightly smaller than for the unsubstituted case. This does not fit the upfield shift of the α-carbon atom in benzylpotassium when a CH_3O substituent is introduced. It should however be noted that a small polarizing effect must be attributed to the K^+ cation. Due to the destabilizing character of the resonance saturation in *p*-methoxybenzylpotassium, polarization would occur to a larger extent than in benzyl-K, resulting in a smaller total π-electron density in the aromatic ring and in a larger π-electron density on C_α. The *p*-methoxybenzylpotassium could thus be regarded as a better polarizable system.

We finally turn to the effect of α-alkyl substitution, comparing the ^{13}C shifts in benzylpotassium with the literature values for α-ethyl and α-methyl-α-ethylbenzylpotassium (Table 5). Increasing alkyl substitution displaces the α-carbon to lower field and the *ortho* and *para* carbons to higher field, indicating increased charge delocalization. The same pattern was found for the chemical shifts of the *para* hydrogens which show an upfield displacement when passing from benzyl to α-methylbenzyl- and cumyl-potassium (4.79, 4.55, and 4.39).[31] The electron-withdrawing effect of the alkyl groups, encountered in the quantum chemical calculations, cannot be derived from these data. However, it should be realized that the shifts of aliphatic carbon atoms correlate less favourably with calculated charges than in the case of aromatic carbon atoms.[32] The calculated decrease in electronic population at C_α correlates with the observed downfield shift. As far as the charge distribution in the aromatic ring is concerned the calculations suggest smaller variations than the n.m.r. results. We think that here also the role of the cation, which will be considered in Part 2, should be taken into account: steric effects due to the alkyl group may influence the position of the cation so that less charge of the benzene ring is polarized towards the α-carbon.

Table 5. ^{13}C Shift differences (in p.p.m.) between benzyl and α-alkylbenzyl compounds $C_6H_5\bar{C}R^1R^2$ and the corresponding toluene derivatives ($\bar{o}$ and $\bar{m}$ stand for the average values of *ortho* and *meta* carbon shifts of $C_6H_5\bar{C}HR^1R^2$) (based on shifts given in refs. 25, 29, and 30)

R^1	R^2	α	*i*	$\bar{o}$	$\bar{m}$	*p*
H	H	31.3	14.7	−18.7	1.8	−30.5
H	C_2H_5	36.2	0.0	−19.2	1.5	−35.1
CH_3	C_2H_5	36.6	−13.7	−22.9	+0.6	−38.3

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* This effect, although quantitatively different, is in agreement with calculations. When comparing the charge (electron excess) on the C atoms *meta* to CH_3 (or CH_2^-) group in toluene, *p*-methoxytoluene, benzyl, and *p*-methoxybenzyl (⊥), we obtain the values +0.060, +0.091, +0.072, and +0.084. Taking differences for the neutral and negative species we obtain 0.031 and 0.012, indicating that the OCH_3 group donates fewer electrons into the aromatic system when the CH_2^- group is present.

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