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THEORETICAL STUDIES OF THE EFFECTS OF *ortho*-METHYL SUBSTITUTION ON S_N1 and S_N2 PROCESSES AT PRIMARY AND SECONDARY BENZYLIC CARBONS*

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The effects of *o*-methyl substitution on the transition-state (TS) structure and reactivity of S_N1 and S_N2 processes were investigated for primary and secondary benzyl (α-*tert*-butyl) derivatives MO theoretically using the AM1 method. The *o*-methyl groups have both stabilizing (by electron donation) and destabilizing (steric) effects on the S_N2 TS; the former prevails for the primary whereas the latter effect becomes dominant for the secondary compounds. In contrast, complex interplay of the two effects are operative in the S_N1 TS of both primary and secondary derivatives leading to the reactivity order which is consistent with that observed by solvolytic experiments, *o,o′*-dimethyl < H < *o*-methyl. The bond length–reactivity rule applies only for the primary benzyl S_N2 series for which steric effects are insignificant. For reactions of benzyl derivatives is general the coplanarity between the carbenium sp^2 centre and the benzene ring, $\pi-\sigma^*_{C-X}$, is of the utmost importance in stabilizing TS structure for which other structural requirements may be relaxed.

INTRODUCTION

Nucleophilic displacement at a benzylic carbon exhibits interesting mechanistic variations depending on the substrate structure and solvent. Primary benzylic compounds (**I**, $ArCH_2X$, where X is a leaving group) tend to react with both anionic and neutral nucleophiles in solution by a dissociative type of S_N2 mechanism with positive charge development at the reaction centre in the transition state (TS).[2] In contrast, secondary and tertiary benzylic centres (**II**, ArCHRX; **III**, ArCRR′X where R, R′ = CH_3 or other alkyl group) have been shown to react in solution via an S_N1 mechanism.[3] Gas-phase anionic displacement of ring-substituted benzyl derivatives carried out under identical S_N2 conditions with chloride ion, $Cl^- + ArCH_2Cl \rightarrow ArCH_2Cl + Cl^-$, however, gave a convex-upward type of Hammett plot,[4] indicating a change of sign from positive (for electron-donating substituents) to negative (for electron-withdrawing substituents) charge development at the benzylic carbon, when the intrinsic barriers from double-well potential energy curves are interpreted in terms of rates. On the other hand, MNDO MO theoretical studies[5] have shown that such Hammett plots for S_N2 reactions of chloride ion with *para*-substituted benzyl chlorides lead to a positive ρ value, i.e. negative charge development at the benzylic carbon.

In the S_N1 solvolysis of α-*tert*-butyl(α-methyl)benzyl chlorides (α to phenyl), delocalization of positive charge developing at the α-carbon (benzylic carbon) into the ring in the TS is shown to be small owing to deviations from the coplanarity between the reaction centre and benzene ring.[6] In contrast, however, the loss of coplanarity is insignificant and the through-conjugation interaction between developing carbenium ion and the benzene π-system is fully operative in the S_N1 solvolyses of α-*tert*-butylbenzyl tosylates, even when the *ortho*-positions are substituted with methyl groups.[7] Fujio *et al.*[8] hypothesized that the resonance demand is maximum in the solvolyses of α-methylbenzyl and 2,2-dimethylindan-1-yl chlorides so that they can serve as reference compounds for the limiting r_{max} value ($r_{max} = 1\cdot14$). They then proceeded to calculate the dihedral angle of twisting out of coplanarity (φ) in the TS for the solvolysis of α-*tert*-butylbenzyl tosylates (**i**) and their *o*-methyl (**ii**) and *o,o′*-dimethyl analogues (**iii**) by using this r_{max} (= 1·14) value in equation (1)[9]:

$$r = r_{max} \cos^2 \phi \qquad (1)$$

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where r is the reaction-dependent resonance demand parameter of the Yukawa–Tsuno equation (2):[10]

$$\log(k/k_0) = \rho(\sigma^0 + r\Delta\sigma_{\bar{R}}^{+}) \qquad (2)$$

They arrived at ϕ values of 12°, 20° and 20° for **i**, **ii** and **iii**, respectively, and concluded that increased steric congestion around the carbenium ion by *o*-methyl substitution does not cause a significant loss of resonance stabilization in the TS.

In an anatomy of the S_N1 reaction involving crystal structure–reactivity correlation for 1-arylethanol derivatives [$ArCH(CH_3)OH$], Edwards *et al.*[11] formulated a working rule related to the length of bond being broken: the longer the bond in a given system, the faster it breaks.

In this work, we investigated S_N1 and S_N2 reactivities of primary and secondary benzylic systems MO theoretically using the AM1 method in order to understand more fully these various factors found to influence reactivities of benzyl derivatives in solid-, solution- and gas-phase experiments.

CALCULATION

The calculations were carried out using the standard AM1 procedure[12] throughout. The use of *ab initio* methods was precluded since the systems studied are large (up to 15 heavy atoms are involved). The geometries of all reactants were fully optimized without any assumption and charaterized by confirming all positive eigenvalues in the Hessian (force constant) matrix.[13] Transition states were located approximately by the reaction coordinate method[14] and refined by minimizing the gradient norm.[13] The force constants were used to calculate molecular vibration frequencies and hence molecular entropies and entropies of activation.[15] The TSs were characterized by confirming only one negative eigenvalue in the Hessian matrix.[16]

For the S_N2 reactions investigated:

$$X^- + ArCHRX \rightleftharpoons ArCHRX + X^- \qquad (3)$$

$$X = Cl, Br \text{ or } OH$$

$$R = H \text{ or } (CH_3)_3C$$

$$Ar = C_6H_5, \textit{o}\text{-}MeC_6H_4 \text{ or } \textit{o,o}'\text{-}diMeC_6H_3$$

symmetry conditions for the identity exchange reactions were applied.[17]

In a search for a model S_N1 reaction, we found that gas-phase dissociation of neutral substrates to ion pairs, e.g. $CH_3F \rightarrow CH_3 + F^-$, is not suitable since ion-pair formation with cut solvent stabilization leads to a continuous endoergic process with eventual dissociation of two free ions without formation of intermediates (or TSs).[18] This type of behaviour is encountered even in solution for cationic substrates dissociating into localized cations, e.g. $CH_3N_2^+$ in H_2O and in HF.[18]

In this work, we chose to investigate the dissociation of cationic benzyl substrates, which proceeds through rate-limiting ion-molecule intermediate formation.[3c–e,19] This type of reaction is well known in the S_N1 solvolytic processes of benzyl derivatives, e.g. equation (4)[19]

$$ArCHRS^+Me_2 \xrightarrow{\text{slow}} \underset{\text{ion–molecule complex}}{Ar\overset{+}{C}HR\text{—}SMe_2} \xrightarrow{\text{SOH}} \text{products} \qquad (4)$$

For simplicity, however, we used H_2O instead of $(CH_3)_2S$ as the neutral leaving group (LG) and thus the S_N1 reactivity was studied with the gas-phase dissociation processes of $ArCHRO^+H_2$, equation (5)

$$ArCHRO^+H_2 \xrightarrow{\text{slow}} \underset{\text{ion–molecule complex}}{ArC^+HR\text{—}OH_2} \longrightarrow \underset{\substack{\text{dissociated cation and}\\ \text{molecule}}}{ArC^+HR + H_2O} \qquad (5)$$

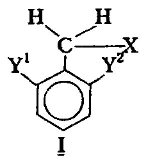
$$R = H \text{ or } (CH_3)_3C$$

$$Ar = C_6H_5, \textit{o}\text{-}MeC_6H_4 \text{ or } \textit{o,o}'\text{-}diMeC_6H_3$$

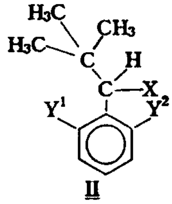
It has been shown that the charge distribution along the dissociative path is similar in the gas phase and in solution.[18]

RESULTS AND DISCUSSION

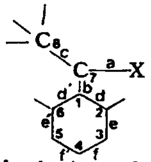
We adopt the following notations and numbering schemes throughout in the discussion of the results:



I



II



Numbering scheme.

$$A: Y^1 = Y^2 = H$$

$$B: Y^1 = H, Y^2 = CH_3$$

$$C: Y^1 = Y^2 = CH_3$$

$$X = Cl, Br, OH \text{ or } O^+H_2$$

For example, the S_N2 process of chloride ion with *o*-Me-α-*tert*-butylbenzyl chloride will involve the **IIB** + Cl system. The important bonds and angles to note are a, b, ab and ϕ (=90 − abd).

S$_N$2 processes

The S$_N$2 processes were investigated for the **IA–IC** and **IIA–IIC** systems with X = Cl, Br and OH [equation (3)]. The AM1 heats of formation and entropies for the reactant (RX) and TS are summarized in Table 1 together with activation parameters, $\Delta H^{\neq}$, $\Delta S^{\neq}$ and $\Delta G^{\neq}$. For the primary benzyl system, **IA–IC**, the reactivity based on the activation enthalpies, $\Delta H^{\neq}$, increases in the order **IA** < **IB** < **IC**, which reflects that *o*-methyl groups act as electron donors with an insignificant steric inhibition effect. This trend is not changed even if the entropy terms are accounted for, so that the identity exchange reactivity ($\Delta G^{\neq}$) is in the same order. Since electron-donating substituents increase the reactivity, the reaction center is positively charged in the TS, which becomes stabilized by the electron-donating *o*-methyl groups with small entropy effects. The formal charges, *q*, of benzylic carbon become more positive ($\Delta q > 0$) in the TS; for X = Cl, Br and OH, Δq ($= q_{TS} - q_{RX}$) and q_{TS} are $+0\cdot 25$ and $+0\cdot 17$, $+0.23$ and $+0\cdot 06$, and $+0\cdot 22$ and $+0\cdot 23$, respectively. In contrast, Δq and q_{TS} values for the LG X become more negative as expected, with $-0\cdot 57$ and $-0\cdot 7$, $-0\cdot 58$ and $-0\cdot 63$, and $-0\cdot 52$ and $-0\cdot 65$ for X = Cl, Br and OH, respectively.

The reactivity is seen to increase (Table 1) in the order X = OH < Cl < Br, which is exactly the order of increasing bond length of the cleaving bond, C—X, in the RX in Table 2. This is consistent with the bond length–reactivity rule of Edwards *et al.*,[11] which was originally formulated for the *S*$_N$1 reactivity of the same type of bond based on crystal structures. In contrast, however, we note that in RX the bond length b (C_1—C_7) is in the reverse order, X = OH > Cl > Br. These are also in agreement with the contention that more reactive compounds (X = Br) start closer to the TS, in both geometry and free energy.[11] Since in the TS the benzene ring rotates to improve π overlap with the LUMO (σ^*_{C-X}), the bond b (C_1–C_7) becomes contracted (benzylic effect)[20] as the torsion angle abd ($\angle XC_7C_1C_2 = 90 - \phi$) approaches 90° ($\phi = 0$). The angle ab ($= \angle XC_7C_1$) is not exactly 90° in the TS as required from an ideal trigonal bipyramidal five-coordinate (TBP-5C) TS structure of the identical *S*$_N$2 TS.[17]

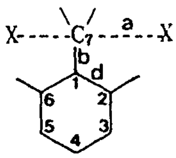
For the secondary benzyl systems with an α-tertiary group, **II**, the reactivity order is reversed to **IIC** < **IIB** < **IIA** (Table 1) owing to steric effect of the *o*-methyl groups overriding their electron-donating stabilization of the positive charge at the benzylic carbon in the TS. The relatively strong steric effect in this system is also reflected in the uniformly higher activation barriers, $\Delta H^{\neq}$ and $\Delta G^{\neq}$, compared with those for the primary benzyl systems, **I**. Here again the entropy effects are not large. The formal charges and their changes in the activation process on the benzylic carbon and the X groups are very similar to those for

Table 1. Heats of formation, ΔH_f (kcal mol^{-1}), entropies, *S* (cal K^{-1} mol^{-1}) and activtion parameters for systems **I** and **II** with X = Cl, Br and OH (1 cal = 4·184 J)

		Reactant (RX)		TS		Activation parameter		
X	System	ΔH_f	S^a	ΔH_f	S	$\Delta H^{\neq}$	$\Delta S^{\neq}$	$\Delta G^{\neq b}$
Cl	**IA**	−30·8	121·0	−27·6	93·9	3·2	−27·1	11·3
	IB	−37·5	126·6	−34·4	100·8	3·1	−25·8	10·8
	IC	−44·0	131·8	−41·1	110·7	2·9	−21·1	9·2
Br	**IA**	−1·2	125·5	−0·1	98·3	1·1	−27·2	9·2
	IB	−7·9	131·7	−6·9	104·5	1·0	−27·2	9·1
	IC	−14·3	138·0	−13·4	112·0	0·9	−26·0	8·6
OH	**IA**	−45·3	121·4	−23·8	98·3	21·5	−23·1	28·4
	IB	−51·1	131·1	−33·7	97·5	17·4	−33·6	27·4
	IC	−57·3	137·2	−41·3	102·3	16·0	−32·9	25·8
Cl	**IIA**	−45·4	146·0	−29·1	121·0	16·3	−25·0	23·8
	IIB	−51·4	150·4	−35·3	123·4	16·1	−27·0	24·1
	IIC	−51·9	156·6	−30·1	127·7	21·8	−28·9	30·4
Br	**IIA**	−14·5	150·8	2·6	124·5	17·1	−26·3	24·9
	IIB	−20·6	155·7	−2·4	128·5	18·2	−27·2	26·3
	IIC	−20·8	156·0	4·3	132·6	25·1	−23·4	32·1
OH	**IIC**	−66·1	159·0	−30·7	125·7	35·4	−33·3	45·3
	IIB	−64·4	151·2	−33·2	121·6	31·2	−29·6	40·0
	IIA	−58·6	146·9	−28·3	114·0	30·3	−32·9	40·1

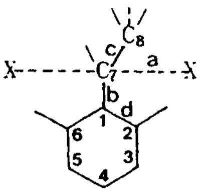
[a] The absolute molar entropy at 1 atm and 298 K assuming ideal gas behaviour.[23] Standard state of an ideal gas is established at 1 atm.
[b] $\Delta G^{\neq} = \Delta H^{\neq} - T\Delta S^{\neq}$ (at $T = 298$ K).

Table 2. Geometric parameters of various compounds for the reactant (RX) and S_N2 TS of the primary benzyl systems



Parameter	Species	X = Cl IA	 IB	 IC	X = Br IA	 IB	 IC	X = OH IA	 IB	 IC
Bond length (Å)										
a (C_7—X)	RX	1·761	1·762	1·763	1·934	1·935	1·937	1·415	1·415	1·417
	TS	2·189	2·191	2·193	2·278	2·281	2·284	1·841	1·821	1·831
b (C_7—C_1)	RX	1·482	1·483	1·484	1·478	1·479	1·480	1·494	1·497	1·498
	TS	1·469	1·470	1·470	1·470	1·471	1·472	1·480	1·484	1·486
Angle (°)										
ab ($\angle XC_7C_1$)	RX	111·7	111·9	111·9	112·8	113·0	113·1	113·4	113·5	113·6
	TS	96·1	96·2	96·4	97·5	97·8	98·0	92·9	94·4	95·5
$\angle XC_7C_1C_2$	RX	93·5	86·3	89·8	88·0	89·6	90·2	155·7	69·6	−50·1
	TS	90·0	90·0	90·0	90·0	90·0	90·0	90·0	90·0	90·0

Table 3. Geometric parameters of various compounds for the reactant (RX) and S_N2 TS of the α-*tert*-butylbenzyl systems



Parameter	Species	X = Cl IIA	 IIB	 IIC	X = Br IIA	 IIB	 IIC	X = OH IIA	 IIB	 IIC
Bond length (Å)										
a (C_7—X)	RX	1·778	1·781	1·780	1·959	1·963	1·963	1·426	1·427	1·425
	TS	2·292	2·302	2·313	2·401	2·418	2·431	1·895	1·899	1·902
b (C_7—C_1)	RX	1·494	1·495	1·500	1·491	1·492	1·497	1·502	1·505	1·509
	TS	1·471	1·472	1·479	1·473	1·473	1·482	1·483	1·485	1·495
c (C_8—C_7)	RX	1·539	1·539	1·541	1·537	1·537	1·539	1·549	1·550	1·552
	TS	1·521	1·524	1·526	1·526	1·529	1·531	1·531	1·531	1·535
Angle (°)										
bc ($\angle C_8C_7C_1$)	RX	114·0	114·8	116·3	114·0	114·6	116·0	113·3	114·0	115·2
	TS	124·3	124·1	131·4	124·0	123·8	130·7	124·2	124·2	131·2
ab ($\angle XC_7C_1$)	RX	109·8	109·2	111·5	109·8	109·5	111·9	106·9	106·2	108·2
	TS	92·1	92·8	91·8	92·7	93·9	92·3	90·0	89·4	90·1
$\angle C_8C_7C_1C_2$	RX	100·1	105·1	77·3	104·0	106·7	76·5	84·8	75·9	79·9
(= cbd = θ)	TS	4·1	−0·3	0·8	0·2	−0·3	−0·2	1·9	1·8	0·3
$\angle XC_7C_1C_2$	RX	46·6	51·2	126·8	53·1	55·6	123·0	141·9	133·4	134·5
	TS	109·0	104·3	76·9	106·7	106·1	74·6	85·5	83·7	79·6
ϕ = 90 − abd		19·0	14·3	13·1	16·7	16·1	15·4	4·5	6·3	10·4

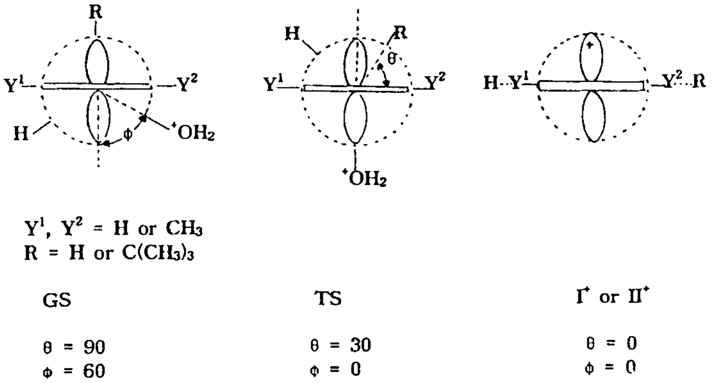
the corresponding systems **I** above. Geometrical parameters for the identical S_N2 reactions of α-*tert*-butylbenzyl systems, **II**, are given in Table 3. Notably the lengths of bonds a (C_7—X) and b (C_1—C_7) are uniformly longer than those corresponding value for the systems **I**, probably owing to an α-*tert*-butyl group which is more sterically demanding than a hydrogen atom. The rule that a species with a longer bond a (and a shorter bond b) (X = Br) reacts faster (than X = Cl) does not apply for this reaction series **II**, in contrast to the systems **I**, again primarily for steric reasons;[11] bulkier Br^- has greater activation barriers than Cl^-, albeit the C_α—Br bond length is longer than that of C_α—Cl in both the TS and in RX.

The predominant influence of steric effects on the geometries and reactivity is reflected in the angles ϕ ($= 90 - \text{abd}$) and θ ($= \text{cbd}$). Table 3 indicates that while the α-*tert*-butyl group almost eclipses with the *o*-methyl group [$\theta < 1^\circ$ with the one exception of the **IIB**—OH system ($\theta = 1{\cdot}8^\circ$)], $\pi - \sigma^*_{\text{C—X}}$ overlap is not perfect, i.e. the deviation from coplanarity, ϕ, is significant, ranging from 4·5 to 19·0°. Strikingly, the greatest deviation is exhibited with the unsubstituted (**IIA**) series, for which we would intuitively have expected the least deviation. However, close examination of Table 3 reveals that the steric strain caused by eclipsing the α-*tert*-butyl group with an *o*-methyl group and by keeping the angle ab near 90° as required by an ideal TBP-5C TS structure is accommodated by an increase in the angle bc ($\angle C_8C_7C_1$) to *ca* 130°, which is greater by 10° than that expected from a trigonal structure at C_α. The greatest amount of steric strain caused by the α-*tert*-butyl group is relieved by keeping the widest angle bc in the *o,o'*-dimethyl-substituted (**IIC**) series. Here again the greatest deviation from coplanarity is found with the bulkiest group, X = Br. Thus the $\pi - \sigma^*_{\text{C—X}}$ overlap in the TS is less efficient with X = Br than with X = Cl and hence the reactivity of X = Br is reduced and the order is reversed to X = Cl > Br ($\Delta H^{\neq}$ and $\Delta G^{\neq}$ in Table 1).

S_N1 processes

In the S_N1 dissociation of benzylic compounds, the structures at three equilibrium points, RX, TS and ion–molecule pair, along the reaction coordinate are most important. In most cases, the conformation of RX favoured is that with the C—R bond perpendicular to the plane of the ring ($\theta = 90^\circ$) in order to minimize steric crowding by R. The TS is formed by rotating the benzene ring to reduce ϕ and thus improve π-overlap with the LUMO of the cleaving bond ($\sigma^*_{\text{C—X}}$). In this conformation θ is approximately 30° but steric crowding between R and Y^2 will open up the θ to a larger angle that 30°. Finally, the free cation ($\mathbf{I}^+$ or $\mathbf{II}^+$), is formed with complete breakaway of the LG. Ideally in this structure, both θ and ϕ are 0°, where ϕ is now an angle formed by an empty 2p AO at the benzylic centre replacing the C—X bond. In this conformation excessive steric crowding between R and Y^2 will open up the angles θ ($> 0^\circ$) and bc ($> 120^\circ$). The most favoured conformations of the RX, TS and free cation ($\mathbf{I}^+$ or $\mathbf{II}^+$) for a cationic benzyl substrate with a neutral LG (H_2O) are illustrated in Scheme 1.

The heats of formation and entropies of the RX, TS and ion–molecule complex (**IC**) are summarized in Table 4 together with the activation parameters. Complex interplay between electron-donating ($\Delta H^{\neq}$ lowering) and steric effects ($\Delta H^{\neq}$ elevating) of *o*-methyl groups leads to the relative order of reactivity based on $\Delta H^{\neq}$ for primary benzyl systems as **IA** < **IC** < **IB**. However, when entropy terms are accounted for, the order of reactivity ($\Delta G^{\neq}$) changes to **IC** < **IA** < **IB**, which is exactly the order of solvolytic reactivity found by Fujio *et al.*[7] for α-*tert*-butylbenzyl tosylates. The relative reactivity orders for



Scheme 1

Table 4. Heats of formation, ΔH_f (kcal mol^{-1}) and entropies (cal K^{-1} mol^{-1}) for the S_N1 dissociation reactions of benzyl (**I**) and α-*tert*-butylbenzyl (**II**) systems with $X = OH_2$: $I—O^+H_2$ and $II—O^+H_2$

	Reactant		TS		IC[a]	Activation parameter		
System	ΔH_f	S	ΔH_f	S	ΔH_f	$\Delta H^{\neq}$	$\Delta S^{\neq}$	$\Delta G^{\neq}$ [b]
IA	151·8	85·5	156·1	83·7	154·2	4·3	−1·8	4·8
IB	143·9	92·5	147·5	91·4	145·0	3·6	−1·1	3·9
IC	136·3	99·0	140·4	95·6	135·9	4·1	−3·4	5·1
IIA	131·6	110·1	134·4	113·3	126·5	2·8	3·2	1·8
IIB	124·2	109·9	127·5	115·5	119·0	3·3	5·6	1·6
IIC	121·7	119·9	126·4	123·9	118·4	4·7	4·0	3·5

[a] Ion–molecule complex.
[b] $\Delta G^{\neq} = \Delta H^{\neq} - T\Delta S^{\neq}$ (at $T = 298$ K).

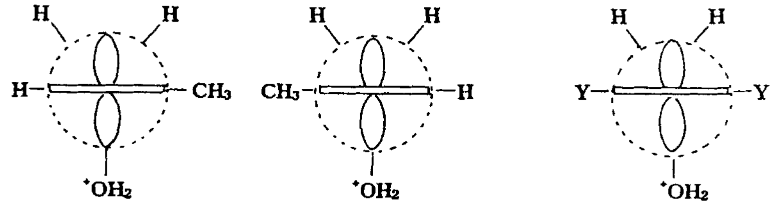
the primary (**I**) and secondary (**II**) benzyl systems are the same, suggesting that the α-*tert*-butyl group in **II** does not exert an overwhelming effect on the S_N1 reactivity.

The entropy of activation, $\Delta S^{\neq}$, seems to favour *o*-methyl derivative, **IB**, because two equivalent eclipsing arrangements or conformations of the two benzylic hydrogens with *o*-methyl substituent become available in the TS for this compound, whereas for **IA** and **IC** there is only one (Scheme 2).

The relevant geometric parameters for the reaction series of $I—O^+H_2$ are summarized in Table 5. The degree of bond cleavage of the C_α—LG bond, a, in the TS becomes less with successive *o*-methyl substitution, **IA** → **IC**. This indicates that stabilization of the developing positive charge at the benzylic carbon by the *o*-methyl groups leads to an earlier TS along the reaction coordinate as required by the Hammond postulate.[21] Accordingly, the resonance contraction of bond b decreases from **IA** to **IC**. This must be due to electron-donating effect of *o*-methyl groups stabilizing developing positive charge more effectively. However, the amount of bond contracted (*ca* −0·055 Å) in the S_N1 reactions, i.e. $I + O^+H_2$ reactions, is *ca* four times greater than (*ca* −0·013 Å) in the corresponding S_N2 reactions, e.g **I** + Cl reactions, in Table 2. This is, of course, because of the greater positive charge development in the S_N1 reactions. Greater positive charge delocalization into the benzene ring, especially at the *ortho* (C_2 and C_6) and *para* (C_4) positions, is apparent in Table 6, where the formal charges on heavy atoms are shown.

Examination of Table 5 reveals that angular changes accompanying the activation process are very small. The angle ab ($\angle XC_7C_1$) decreases by 3–4° whereas the angle ϕ (=90–abd) increases by 1–2°. The angle ϕ is already near 0° in the RX and hence the $\pi-\sigma^*_{C-X}$ interaction is optimum in RX so that very little change is required in the TS. In order to maximise $\pi-\sigma^*_{(C-X)}$ overlap stabilization, the angle ab is sacrificed to relieve steric congestion to a value greater by *ca* 15° than that required for the ideal 90°.

The $\Delta H^{\neq}$ values in Table 4 indicate that steric effect for the S_N1 reactions of α-*tert*-butylbenzyl compounds is relatively large, since the activation enthalpies increase with *o*-methyl substitution, and the order of reactivity based on $\Delta H^{\neq}$ is **IIC** < **IIB** < **IIA**. Inclusion of activation entropies, which favours **IIB**, however, changes the reactivity order to **IIC** < **IIA** < **IIB**, in agreement with the solvolytic reactivity order found by Fujio *et al.*[7] The favourable entropy for **IIB** has the same origin as that found for **IB** above (Scheme 2). The

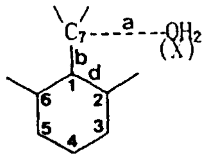


Two equivalent confotmations for IB

Y = H (IA) or CH_3 (IC)
one TS conformation for IA or IC

Scheme 2

Table 5. Geometric parameters of the reactant (RX), TS and ion–molecule complex (IC) for the S_N1 dissociation reactions of primary benzyl system with $X = H_2O$: I—O^+H_2



		Bond length (Å)		Angle (°)	
Compound	Species	b (C_7—C_1)	a (C_7—X)	ab (∠XC_7C_1)	abd (∠$XC_7C_1C_2$)
IA	RX	1·460	1·553	108·0	90·2
	TS	1·402	2·015	105·1	91·1
	IC	1·377	2·440	117·6	89·9
IB	RX	1·460	1·554	108·0	89·4
	TS	1·403	1·978	104·5	91·2
	IC	1·374	2·471	119·2	90·6
IC	RX	1·460	1·557	107·9	89·4
	TS	1·408	1·932	104·5	91·6
	IC	1·371	2·525	127·5	91·1

Table 6. Formal charge (q) on the heavy atoms in the reactant (RX), TS and Ion–molecule complex (IC) for the S_N1 dissociation reactions of primary benzyl compounds: I—O^+H_2 (electronic charge unit)

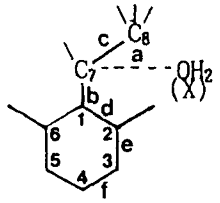
System	Species	C_1	C_2	C_3	C_4	C_5	C_6	C_7	X
IA	RX	−0·257	−0·071	−0·127	−0·042	−0·126	−0·074	+0·068	−0·145
	TS	−0·243	−0·007	−0·161	+0·026	−0·161	−0·007	+0·216	−0·364
	IC	−0·210	+0·032	−0·181	+0·070	−0·181	+0·033	+0·193	−0·448
	Δq^a	+0·014	+0·064	−0·034	+0·068	−0·035	+0·067	+0·148	−0·219
IB	RX	−0·261	−0·072	−0·131	−0·040	−0·133	−0·004	+0·068	−0·147
	TS	−0·248	−0·017	−0·161	+0·023	−0·170	+0·068	+0·203	−0·345
	IC	−0·206	+0·018	−0·182	+0·072	−0·198	+0·123	+0·170	−0·445
	Δq	+0·013	+0·055	−0·030	+0·063	−0·037	+0·072	+0·135	−0·198
IC	RX	−0·262	−0·003	−0·138	−0·037	−0·137	−0·003	+0·068	−0·148
	TS	−0·274	+0·045	−0·168	+0·019	−0·178	+0·064	+0·191	−0·327
	IC	−0·202	+0·109	−0·200	+0·077	−0·200	+0·109	+0·143	−0·442
	Δq	+0·015	+0·048	−0·030	+0·056	−0·041	+0·067	+0·123	−0·179

[a] $\Delta q = q_{(TS)} - Q_{(RX)}$.

solvolysis rates of α-*tert*-butylbenzyl tosylates in 80% acetone at 25 °C[7] indicate that the *o*-methyl compound (corresonding to **IIB**) is 2–5 times faster but that the *o*,*o*′-dimethyl compound (corresponding to **IIC**) is 7–25 times slower than the unsubstituted compound; the steric retardation of *o*,*o*′-dimethyl groups in **IIC** seems to be much greater than the electron-donating stabilization and entropic acceleration of the *o*-methyl group in **IIB** relative to **IIA**, which is correctly reflected in much smaller difference in $\Delta G^{\neq}$ between **IIA** and **IIB** in Table 4.

Geometric parameters for these reactions are summarized in Table 7. In RX, the length of bond a that is cleaving increases in the order **IIC** < **IIA** < **IIB**, which is consistent with the bond length–reactivity rule of Edwards *et al.*[11] This is remarkable, since the rule applies despite the large steric effect on the reactivity. Bonds a and c stretch further away to avert steric congestion in **IIB** and **IIC**. However, the resonance bond contraction (Δb < 0) increases with *o*-methyl substitution (**IIA** < **IIB** < **IIC**), indicating a relatively greater degree of charge development with greater bond cleavage in the TS. The greater bond stretching (of bonds a and c) is accompanied by the greater positive charge development at the benzylic carbon, C_7; the Δq values are +0·134, +0·144 and +0·163 for **IIA**, **IIB**

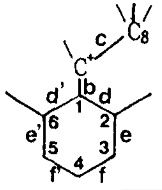
Table 7. Geometric parameters of reactant (RX) and TS and ion–molecule complex (IC) for the S_N1 dissociation reactions of α-*tert*-butylbenzyl systems with $X = H_2O$: $II—O^+H_2$



		Bond length (Å)						Angle (°)				
System	Species	d (C_2—C_1)	e (C_3—C_2)	f (C_4—C_3)	b (C_7—C_1)	c (C_8—C_7)	a C_7—X)	bc (∠$C_8C_7C_1$)	ab (∠XC_7C_1)	cbd (∠$C_8C_7C_1C_2$)	abd (∠$XC_7C_1C_2$)	Δφ
IIA	GS	1·403	1·394	1·395	1·477	1·529	1·564	119·0	106·1	66·7	125·9	
	TS	1·418	1·389	1·400	1·437	1·502	1·891	128·1	99·9	144·3	101·4	11·4
	IC	1·436	1·383	1·401	1·389	1·486	3·219	129·6	99·8	178·9	−2·6	
IIB	GS	1·413	1·403	1·391	1·478	1·530	1·566	120·0	105·9	78·2	127·8	
	TS	1·424	1·399	1·393	1·432	1·499	1·947	127·9	99·4	136·7	110·3	20·3
	IC	1·443	1·395	1·395	1·386	1·490	3·186	129·5	129·5	177·4	14·0	
	II^{+a}	1·446	1·393	1·395	1·384	1·489		129·8		178·4		
IIC	GS	1·418	1·398	1·392	1·484	1·533	1·555	121·1	108·0	75·5	130·2	
	TS	1·432	1·393	1·395	1·435	1·498	1·996	129·0	102·6	60·3	118·9	28·9
	IC	1·452	1·388	1·398	1·389	1·487	3·140	134·0	127·4	37·0	41·4	

[a] Values for cation.

Table 8. Geometric parameters of α-*tert*-butylbenzyl cations



	Bond length (Å)					Angle (°)						
Compound	b (C_7—C_1)	c (C_8—C_7)	d (C_2—C_1)	e (C_3—C_2)	f (C_4—C_3)	de (∠$C_3C_2C_1$)	ef (∠$C_4C_3C_2$)	ff′ (∠$C_5C_4C_3$)	bd (∠$C_7C_1C_2$)	bc (∠$C_8C_7C_1$)	cbd (θ)(∠$C_8C_7C_1C_2$)	Δθ
IIA	1·387	1·487	1·437	1·380	1·402	120·8	120·3	120·2	117·9	129·5	179·6	0·4[a]
IIB	1·384	1·489	1·446	1·393	1·395	119·5	121·2	120·3	119·5	129·8	−178·4	1·6
IIC	1·386	1·489	1·453	1·387	1·401	120·0	120·9	119·9	116·8	134·8	−155·6	24·4

[a] Deviation from $\theta = 180·0°$.

and **IIC**, respectively. The trends in other formal charges on heavy atoms are similar to those for **IA**–**IC**, except that delocalization of positive charge into the ring is less efficient with the secondary benzyl (**II**) series than that with the primary benzyl (**I**) series.

The angle ab ($\angle XC_7C_1$) is greater than 90° by *ca* 10–13° and also the angle θ (cbd) increases with *o*-methyl substitution in excess of the optimum 30°. The angle θ is fairly large ($\theta = 60°$) for **IIC** owing to to steric congestion between α-*tert*-butyl and *o*-methyl groups.

The angle ϕ deviates from that of the maximum π–$\sigma^*_{\mathrm{C-X}}$ overlap ($\phi = 0$) by 11·4°, 20·3° and 28·9° for **IIA**, **IIB** and **IIC**, respectively. Strikingly, however, this is in very good agreement with those predicted by Fujio *et al.*[8] based on their solvolyses rate results with equation (1); one exception is that **IIC** shows a slightly greater deviation (by *ca* 9°) than that of Fujio *et al.* This excellent agreement between our AMI (gas-phase) ϕ values and those of Fujio *et al.*[8] based on solvolysis results may not be fortuitous, in view of the fact that the maximum *r* values (= 1·14) of Fujio *et al.*, used as the reference compounds, are identical with the values for the intrinsic stabilization of benzylic cations in the gas phase.[22] In this respect, the conclusion reached based on theoretical S_N1 studies involving solvent effects on the dissociation of CH_3F into solvated ion pairs by Demontis *et al.*[18] is relevant: 'the charges on the two counter ions are similar in gas phase and in solution.' We therefore support the contention that the loss of coplanarity by the *o*-methyl group is relatively small and through-conjugation is fully operative between the developing carbenium ion and the benzene π-system in the S_N1 reactions of α-*tert*-butylbenzyl compounds, irrespective of their *o*-methyl group. Our results clearly show that even in the most congested derivative, **IIC**, the resonance demand of the carbenium is kept optimum (in fact resonance contraction of bond b is the greatest for **IIC**) by expanding the angles bc, ab and θ instead. Thus for reactions of benzyl derivatives in solution,[7] both in the solid[11] and in the gas phase, the π–σ^*_{C}–X interaction is of the utmost importance in stabilizing the TS and in order to maximize the π–σ^*_{C}-X overlap other structural requirements can be relaxed.

The ion–molecule complex **IC** is formed by a loose electrostatic interaction between the cation and neutral molecule, H_2O, and the structure is intermediate between those for the reactant and cation in all cases, as equaton (5) suggests. The structural changes along the reaction coordinate, i.e. GS → TS → **IC** → cation, are shown for **IIB** in Table 7. The changes are gradual along the reaction coordinate and the TS geometries, especially the two angles bc and cbd, are nearer to those of **IC**, which in turn has a similar structure to the cation.

The geometric parameters for the α-*tert*-butylbenzyl cations **IIA**–**IIC**, which are illustrated as an optimum structure $\mathbf{I}^+$ or $\mathbf{II}^+$ in Scheme 1, are summarized in Table 8. The delocalization of the +1 positive charge into the ring is fully operative with bond alternation of double (b)–single (d)–double (e) bonds in all three species. The angles in the ring are almost normal (120°), whereas angles bc and cbd (θ) deviate from the standard values of 120° and 180° (or 0°), respectively, in order to alleviate steric congestion. The deviations are, as expected, the greatest for **IIC** and the least for **IIA**. One interesting aspect is that the angle bc opens up further whereas cbd decreases nearly to zero in the cations compared with those in the TS; twisting out of coplanarity is reduced as much as possible by opening up the angle bc instead. The relatively large deviation of cbd (θ) by 24·4° for **IIC**, however, does not appear to prevent from full delocalization of positive charge on the 2p atomic orbital of benzylic carbon into the ring. Results of calculation to estimate rotational barriers of these cationic species, $\mathbf{II}^+$, are given in Table 9. The barriers are 19·1, 20·2 and 10·2 kcal mol^{-1} for **IIA**, **IIB** and **IIC**, respectively. The small value obtained for *o*,*o*′-dimethyl compound (**IIC**) is due to structural relaxation in the cationic form in order to accommodate steric congestion, as discussed above. Steric repulsion of one *o*-methyl group is calculated to be 7.5 kcal mol^{-1} for **IIB**.

Table 9. Energy changes (ΔH_f, kcal mol^{-1}) for the rotation of α-*tert*-butylbenzyl cations

Angle (°)	**IIA**	**IIB**	**IIC**
0	0·0	7·5	0·0
45	3·2	5·6	0·5
90	19·1	20·2	10·2
135	3·2	9·1	0·5
180	0·0(194·5)	0·0(185·9)	0·0(186·9)

CONCLUSIONS

o-Methyl groups have both stabilizing (by electron donation) and destabilizing (by steric congestion) effects on the TS of nucleophilic substitution reactivities of benzylic compounds. For the primary benzylic compounds, the former prevails whereas for the secondary benzyl the latter becomes dominant.

The bond length–reactivity rule holds for S_N2 reactions of primary benzyl derivatives, in which complications due to steric congestion do not intervene.

The S_N1 reactivity orders for both the primary and secondary benzyl derivatives agree well with those found in solvolytic experiments.

For the stability of S_N1 TS the π–σ^*_{C}–X interaction is maximized, if necessary, by relaxing other structure requierments.

The cationic substrate with neutral LG, H_2O, provides a good MO theoretical model for the S_N1 reactions of both primary and secondary benzyl derivatives.

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