REVIEW COMMENTARY

STRAIN AND STRUCTURAL EFFECTS ON RATES OF FORMATION AND STABILITY OF TERTIARY CARBENIUM IONS IN THE LIGHT OF MOLECULAR MECHANICS CALCULATIONS

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An empirical MM2 force-field was developed for the calculation of steric or strain energies of carbenium ions, and applied to the rationalization of the rates of solvolysis of bridgehead derivatives. The latter constitute a homogeneous series of model compounds for solvolysis, spanning a rate range of *ca* 20 log units. Their rate constants correlate with the calculated steric energy differences between bridgehead bromides and the corresponding carbenium ions. The rate constants of tertiary derivatives of general structure may similarly be rationalized in terms of strain changes, although the correlation exhibits more scatter than that for the bridgehead derivatives alone. In the bridgehead series, the relative free energies of activation for solvolysis correlate with the heterolytic bond dissociation energies $D°(R^+ - Br^-)$ in the gas phase. However, this correlation breaks down when simple mono- and acyclic substrates are included. This is attributed in part to the proximity of the leaving group in the transition state of solvolysis, which stabilizes the developing positive charge at the cationic centre in comparison with the charge of the free ion. The significance of the force-field calculations with respect to the structure of bridgehead carbenium ions was tested by comparison of structural data obtained from *ab initio* calculations. The structures of cations suffering strong distortions owing to C–C hyperconjugation are poorly reproduced by the molecular mechanics calculations, the parameters of which are based on solvolytic reactivity and not on carbenium ions.

INTRODUCTION

The classical approach to the understanding of the factors governing chemical reactivity consists in the application of linear free energy relationships (LFERs).[1] These use the assumption that one can separate the reacting molecule in two parts, namely a reactive centre and a substituent. The latter does not participate directly in the reaction. Using appropriate reference reactions, it is possible to derive constants which are characteristic for the substituents, and these constants may be used to characterize other reactions with respect to their sensitivity towards substituent effects. LFERs play a prominent role in mechanistic chemistry, particularly for the interpretation of electronic effects. They are also used for steric effects, and substituent constants expressing the steric requirements of various groups have been developed, for example by Taft[2] and Charton.[3]

The applicability of steric substituent constants is limited, however, to situations where the molecules under consideration do not undergo conformational changes during the reaction, since this could violate the assumption of absence of direct interactions between the reactive centre and the substituent. Unfortunately, this condition is often not satisfied. For example, in the homologous series of monocyclic compounds undergoing sp^2–sp^3 interconversions at one reactive centre, the overall strain changes are almost exclusively determined by ring strain (*I*-strain),[4] and the influence of the substituents is almost negligible, as long as their steric requirements remain within reasonable limits. Indeed, a variety of reactions involving rate and equilibrium constants of monocyclic compounds may be interpreted in terms of the *I*-strain hypothesis, which was formulated over 40 years ago and has since been verified repeatedly.[5]

An alternative approach, initially proposed by Ivanoff

and Magat[6] and further developed by Becker,[7] consists in evaluating the energies of the reactants and the respective transition states, and relating the resulting energy differences to the rates of reaction. The recent development of efficient and reliable empirical and theoretical computational procedures has greatly facilitated this approach and has substantially improved our understanding of steric effects.[8]

STRAIN EFFECTS ON BRIDGEHEAD SOLVOLYTIC REACTIVITY

The solvolytic reactivity of bridgehead derivatives has been the subject of many investigations in the past, mainly by Schleyer and his school, and much of our current knowledge on solvolytic processes is derived from these studies. Bridgehead derivatives are particularly appropriate for such investigations. They are mechanistically homogeneous; for structural reasons, the rear of the reacting centre is shielded from interventions by solvent molecules, so that the reaction mechanism may not involve solvent participation (k_s contributions). The solvolysis of bridgehead derivatives occurs usually with preservation of the molecular structure; rearrangements are rare and easily detectable when they occur, and non-classical effects are largely absent. In addition, the range of reactivity of bridgehead derivatives is enormous, and this makes the series particularly attractive for quantitative structure–reactivity correlations. This latter advantage, however, is compensated by a major inconvenience: the rates of solvolysis must be determined with different leaving groups in order to cover the whole range of reactivities, and conversions from different solvents and/or leaving groups are required. In addition, the rate constants available in the literature often refer to different temperatures, so that extrapolations are required in order to establish a reactivity scale covering the full range.

The F-strain problem

Schleyer and his school developed a molecular mechanics model in order to express the solvolytic reactivities of bridgehead derivatives in terms of strain changes owing to hybridization changes from sp^3 to sp^2 at the reacting centre.[9] Irrespective of the leaving group used in the rate studies, the strain of all the compounds under investigation was assumed to be that of the appropriate bridgehead hydrocarbon. The structure of the transition state of solvolysis, in turn, was approximated by that of the corresponding carbenium ion (1), and a force-field parametrization for the latter was derived.

$$R_3C\text{–}H \rightarrow R_3C^\oplus \qquad (1)$$

Satisfactory plots were obtained when the log k for

the rates of solvolysis of chlorides, bromides, p-toluenesulphonates and trifluoromethanesulphonates were correlated with the calculated changes in steric energies between the bridgehead hydrocarbons and carbenium ions but, surprisingly, the slopes of the straight lines changed from 3·12 (chlorides), to 2·44 (bromides), 1·11 (p-toluenesulphonates) and 0·94 (trifluoromethanesulphonates). This change in slope was attributed to the inadequacy of the computational model. If F-strain,[10,11] i.e. strain between the leaving group and the molecular skeleton, was present in some of the compounds investigated, the computational model, which uses hydrogen as a surrogate for the leaving group, would not have accounted for it. Since F-strain expectedly varies in function of the bulk of the leaving group, the systematic neglect of F-strain was held responsible for the changing slopes for the different leaving groups in the strain–reactivity correlations.

Subsequent studies showed, however, that the changing slopes are not attributable to F-strain, but rather to inadequate parametrization of the early force fields: Schleyer's force-field for carbenium ions, adequately adjusted,[12] was incorporated into Allinger's molecular mechanics program (MM2),[13] which is parametrized for some functional groups, although not sulphonate esters. The steric requirements for a variety of leaving group models were tested for a representative series of bridgehead compounds. Figure 1 shows a plot of the steric energy* difference ΔE_{st} between bridgehead carbenium ions (R_3C^+) (calculated with the UNICAT 1 parametrization[12]) and bridgehead derivatives (R_3CX) vs $\Delta E_{st}(R_3C^+ - R_3CH)$.[14]

Figure 1(a) combines the data for the small leaving group models Cl, OH and CH_3. A series of straight lines with almost identical slopes are produced (the lines are displaced for clarity by +10 (CH_3) and +20 (OH) kcal mol^{-1}, respectively). No systematic deviations occur. The compounds most susceptible to F-strain are the perhydrophenalene derivatives **33** and **42**, which show slight deviations even for a leaving group as small as CH_3. The results for the bulkier substituents OEt, Ot-Bu and t-Bu are summarized in Figure 1(b). Here, the compounds with small bridges, such as 1-norbornyl (**59**) or 1-bicyclo[2.2.2]octyl (**50**), still behave fairly well, and only those with the largest bridges, particularly the

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* It should be noted that the early publications in the field used the term 'strain energy' for what is now called 'steric energy'. The steric energy is the sum of contributions due to bond-length and bond angle deformations and torsional and non-bonding interactions. In order to convert steric energies into strain energies, a strainless reference compound must be selected. Enthalpies of formation and strain energies are calculated from steric energies by means of appropriate increments. In this paper only steric energies will be used.
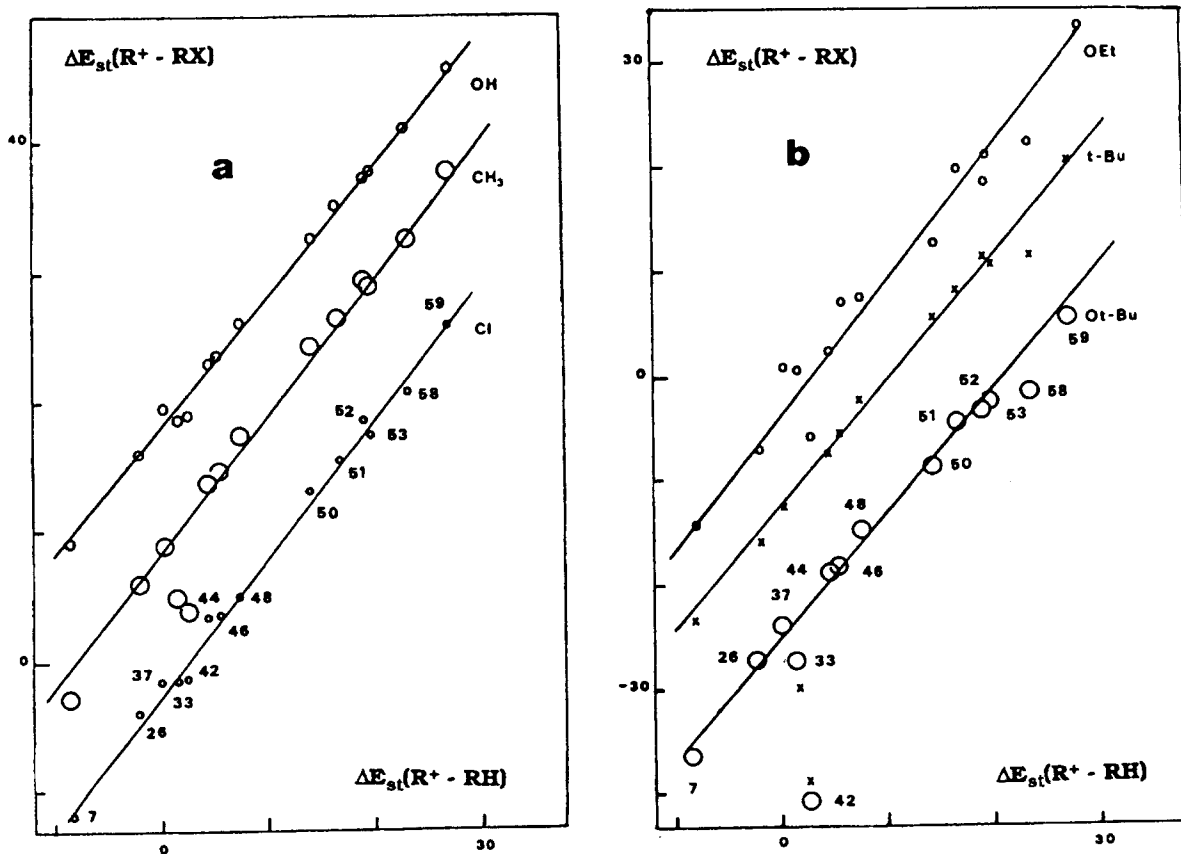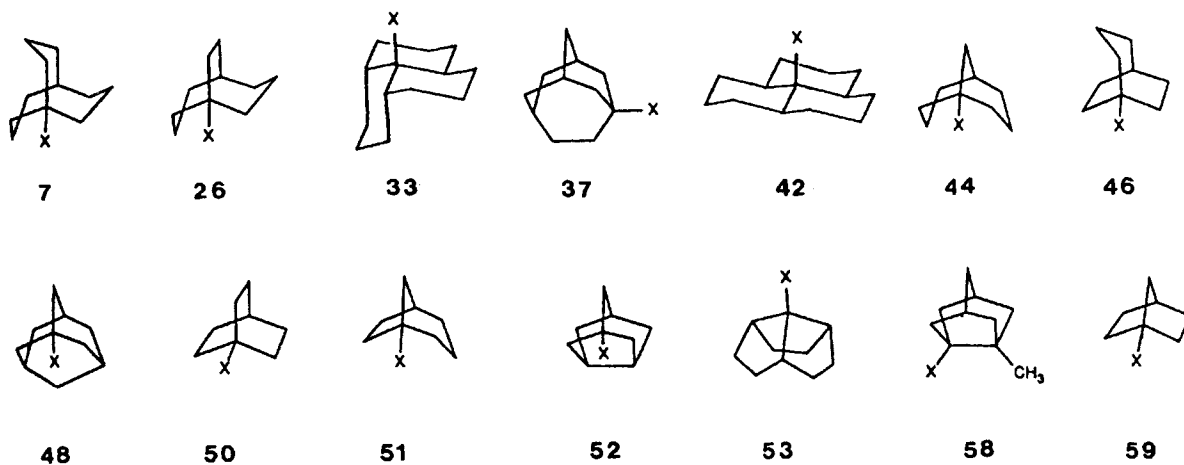
Figure 1. (a) Plot of $\Delta E_{st}(R^+ - RX)$ vs $\Delta E_{st}(R^+ - RH)$ for bridgehead derivatives. Data for X = CH$_3$ and X = OH are displaced by +10 and +20 kcal mol^{-1}. For numbering and structure, see Scheme 2. (b) Plot of $\Delta E_{st}(R^+ - RX)$ vs $\Delta E_{st}(R^+ - RH)$ for X = OEt (displaced by +10 kcal mol^{-1}), t-Bu and Ot-Bu (displaced by −5 kcal mol^{-1})

phenalene derivatives **33** and **42**, which are particularly prone to F-strain,[15] show very severe deviations. Fortunately, this has no practical consequences: the compounds most susceptible to F-strain are also the most reactive of the series; their rates of solvolysis were measured with chloride as the leaving group. Hydrogen is an adequate surrogate for chloride. The strain changes that occur on replacement of H by Cl are relatively small, and in no case exceed 3.5 kcal mol^{-1} (1 kcal = 4.184 kJ). On the other hand, the solvolytic studies carried out with p-toluenesulphonates or trifluoromethanesulphonates concern structures which are insensitive to F-strain. It follows that the change in slope in function of the leaving group in the original strain–reactivity correlations must be attributed to other causes.

It should be noted that these considerations apply only to the particular series of bridgehead compounds included in this discussion. They are not meant to invalidate the concept of F-strain as such. The latter has been unambiguously demonstrated for the perhydrophenalene derivatives **33** and **42**:[11] the p-nitrobenzoate of the t,t,t-isomer (**42**) solvolyses ca 10^4 times faster (after leaving group correction) than the corresponding chloride. This has been attributed to the enhanced strain of the OPBN group which suffers 1,3-interactions with the coaxial hydrogens of the skeleton. The steric requirements of the OPNB group may be approximately expressed by those of an acetate for molecular mechanics calculations.[16] In both **33**-OAc and **42**-OAc, the carbonyl group interacts with the molecular skeleton, while the CH$_3$ group is directed away from it, and the same is expected for OPNB. According to the calculations, the OPNB strain exceeds that of the

chloride by ca 7.5 kcal mol^{-1} in the case of **42**, and this difference accounts well for the experimental rate enhancement. In the case of the corresponding c,c,t-isomer **33**, the OPNB derivative is not only slightly less reactive than the chloride but, according to the calculations, it is also slightly less strained. Takeuchi's group[17] has recently described further examples of solvolytic rate enhancements owing to F-strain for (Z)-2-ethylidene-1-adamantyl and bicyclo[2.2.2]octyl derivatives.

Rates of solvolysis

A strain–reactivity correlation covering the full range of solvolytic bridgehead reactivities requires the existence of a standardized reactivity scale, to which data for different leaving groups and solvents may be converted. Bentley and co-workers[18] proposed solvolysis of p-toluenesulphonates in 80% EtOH at 70 °C as a reference system. It was found that relative rates of bridgehead derivatives are independent of the leaving group and of the solvent systems used, so that conversions from one system to the other are possible by means of appropriate conversion factors. At the same time, they repeated parts of the early kinetic studies and corrected some of the older rate data in the literature which had been obtained by extrapolation from very high temperatures. Their reactivity scale removes some of the inconsistencies of the previous determinations which had led to the different slopes for different leaving groups in Schleyer's original strain–reactivity correlations, and provides independent and experimental support for the absence of differential F-strain effects in bridgehead solvolysis.
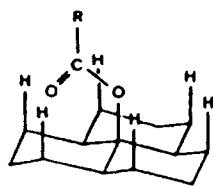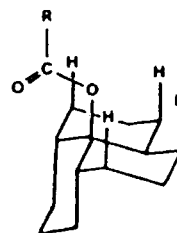
42   **33**

42	Log k	Strain R–X	ΔE_{st}	33	Log k	Strain R–X	ΔE_{st}
Cl	0.84	10.20	−1.34	Cl	2.08	13.13	−1.77
OPNB	4.91	17.98	−9.12	OPNB	1.62	12.65	−1.29

Strain effects in bridgehead solvolysis

The bridgehead derivatives constitute a mechanistically homogeneous model system, against which the solvolysis of other derivatives may be tested. In order to establish a well defined reference system, we select 24 compounds evenly distributed over the full rate range for the strain calculations. The selection includes some compounds which do not really have bridgehead structure, such as 2-alkyl-2-adamantyl and 9-alkyl-9-bicyclo[3.3.1]nonyl derivatives, but at least they are rigid. Their backside is sterically crowded and they are believed to react by k_c pathways. As a common leaving group model for all of the compounds, we propose the bromo substituent. Other leaving group models have been used in the past, in particular OH,[19] but bromides, owing to their symmetry, are easier to treat than OH groups. In addition, the calculations relate directly to the measurements of carbenium ion stabilities in the gas phase, which are discussed below. The plot of log k vs $\Delta E_{st}(R^+ - RBr)$[20] (Figure 2, Table 1) is an excellent

straight line with

$$\log k = -0.394\Delta E_{st}(R^+ - RBr) + 1.074$$
$$r = 0.990; \; \sigma(\log k) = 0.844$$

(2)

The correlation covers a rate range of ca 19 log units, and the existence of straight line behaviour over this large rate range is not self-evident. According to the Hammond[21] postulate, the less reactive compounds should have later transition states than the more reactive compounds, but the calculations assume identical positions of the transition states on the reaction coordinate for all compounds. A variable position of the transition states would lead to a curved plot rather than to a straight line in our treatment. We have considered the possibility that the observation of straight-line behaviour could be due to an artefact. An unfortunate choice of the force-field parameters for the carbenium ions could compensate for a change in transition-state structure and deform the true curve into an artificial straight line. This eventuality was tested by using different force fields for the carbenium ions.[12] However,
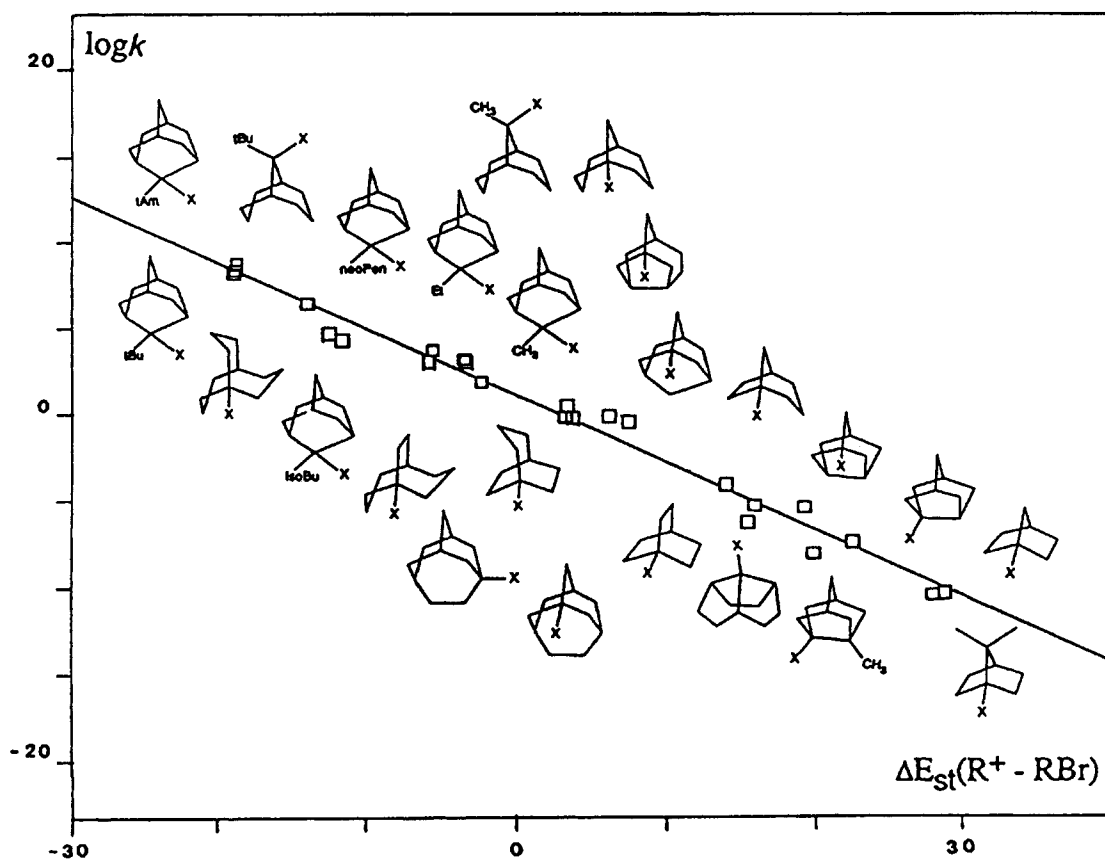

Figure 2. Plot of log k for solvolysis of bridgehead derivatives vs $\Delta E_{st}(R^+ - RBr)$. UNICAT 4 parametrization.[12] Data from Table 1

Table 1. Rate constants and strain calculations for solvolysis of tertiary substrates

RX	Structure of R^+	$E_{st}(RBr)^b$	$E_{st}(R^+)^b$	$\Delta E_{st}(R^+ - RBr)^b$	Log k^c
1[a]	2-t-Amyl-2-adamantyl	47·66	28·88	−18·78	8·76
2[a]	2-(t-Butyl)-2-adamantyl	43·89	25·02	−18·87	8·40
3[a]	9-(t-Butyl)-9-bicyclo[3.3.1]nonyl	45·40	26·49	−18·91	8·18
4	2-(t-Butyl)-3,3-dimethyl-endo-norbornyl	59·00	38·88	−20·12	8·11
5	Tri(t-butyl)methyl	62·37	47·44	−14·93	6·81
6	1-(t-Butyl)-1-cycloheptyl	28·41	19·33	−9·08	6·13
7[a]	1-Bicyclo[3.3.3]undecyl	43·25	29·27	−13·98	6·44
8	1-(t-Butyl)-1-cyclopentyl	21·02	19·05	−1·97	5·43
9	1-trans-Bicyclo[3.3.0]octyl	29·59	30·12	0·53	5·30[d]
10[a]	2-Neopentyl-2-adamantyl	35·82	23·28	−12·54	4·75
11	1-(t-Butyl)-1-cyclohexyl	18·84	15·22	−3·62	4·32
12	2-Methyl-2-bicyclo[2.2.2]octyl	25·34	21·06	−4·28	4·58
13	2-Methyl-2-exo-norbornyl	28·32	30·06	1·74	4·58[d]
14	2-(t-Butyl)-2-endo-norbornyl	40·39	32·53	−7·86	4·49
15[a]	2-Isobutyl-2-adamantyl	34·46	22·78	−11·68	4·35
16	2,7,7-Trimethyl-2-endo-norbornyl	40·83	34·77	−6·06	4·27
17	1-trans-Bicyclo[4.3.0]nonyl	20·38	20·02	−0·38	4·26
18[a]	2-Ethyl-2-adamantyl	26·31	20·60	−5·71	3·77
19	1-Methyl-1-cycloheptyl	15·17	18·39	3·22	3·77
20	Di(t-butyl)(methyl)methyl	30·04	21·93	−8·11	3·48
21	1-cis-Bicyclo[4.3.0]nonyl	20·43	20·02	−0·41	3·38
22	1-Methyl-1-cyclopentyl	13·04	16·08	3·04	3·25
23[a]	9-Methyl-9-bicyclo[3.3.1]nonyl	25·37	21·75	−3·62	3·23
24	(Diethyl)(methyl)methyl	8·55	7·56	−0·99	3·17
25[a]	2-Methyl-2-adamantyl	23·79	20·32	−3·47	3·10
26[a]	1-Bicyclo[3.3.2]decyl	34·14	28·19	−5·95	3·08
27	Ethyl(dimethyl)methyl	6·11	5·86	−0·25	2·96
28	1-Bicyclo[3.1.1]heptyl	42·07	61·99	19·92	2·88[d]
29	2,3,3-Trimethyl-2-endo-norbornyl	39·65	32·31	−6·34	2·60
30	2-Methyl-2-endo-norbornyl	29·14	30·06	0·92	2·49
31	(t-Butyl)(dimethyl)methyl	12·12	10·20	−1·92	2·45
32	t-Butyl	3·36	5·32	1·96	2·38
33	c,c,t-13-Tricyclo[7.3.1.0^{5,13}]tridecanyl	23·88	21·21	−2·67	2·08
34	1-cis-Bicyclo[4.4.0]decyl	17·18	14·27	−2·91	2·57
35	1-Methyl-1-cyclohexyl	9·08	9·67	0·59	2·05
36	1-transcBicyclo[4.4.0]decyl	15·05	14·27	−0·78	1·83
37[a]	3-Homoadamantyl	30·91	28·46	−2·45	1·91
38	7-(t-Butyl)-7-norbornyl	40·71	45·33	4·62	1·83
39	1-Tricyclo[3.3.2.0^{2,8}]decyl	41·78	41·07	−0·71	1·72
40	1-Methyl-1-cyclobutyl	31·94	34·05	2·11	1·23
41	1-cis-Bicyclo[3.3.0]octyl	23·59	30·12	6·53	0·93
42	t,t,t-13-Tricyclo[7.3.1.0^{5,13}]tridecanyl	21·06	18·56	−2·50	0·80
43	t,t,t-1-Tricyclo[7.3.1.0^{5,13}]tridecanyl	19·16	18·57	−0·59	1·49
44[a]	1-Bicyclo[3.3.1]nonyl	20·08	23·36	3·28	0·51
45[a]	6-Protoadamantyl	30·31	36·37	6·06	−0·09
46[a]	1-Bicyclo[3.2.2]nonyl	27·08	30·25	3·17	−0·13
47[a]	1-Homoadamantyl	29·44	33·13	3·69	−0·20
48[a]	1-Adamantyl	18·24	25·68	7·44	−0·41
49	7-Methyl-7-norbornyl	29·18	39·74	10·56	−2·50
50[a]	1-Bicyclo[2.2.2]octyl	20·97	34·91	13·94	−4·00
51[a]	1-Bicyclo[3.2.1]octyl	21·21	37·10	15·89	−5·17
52[a]	1-Noradamantyl	29·10	48·36	19·26	−5·28
53[a]	10-Tricyclo[5.2.1.0^{4,10}]decyl	31·54	46·96	15·42	−6·16
54	4-Homocubyl	133·24	156·54	23·30	−6·58
55[a]	3-Noradamantyl	31·19	53·68	22·49	−7·28
56	1Cubyl	180·55	201·53	20·98	−7·39
57	1-Methyl-4-tricyclo[2.2.2.0^{2,6}]octyl	27·08	48·57	21·49	−7·59
58[a]	7-Methyl-3-noradamantyl	32·97	52·83	19·86	−7·96
59[a]	1-Norbornyl	24·76	52·16	27·40	−10·45
60[a]	7,7-Dimethyl-1-norbornyl	30·70	57·11	26·41	−10·49
61	1,7,7-Trimethyl-4-tricyclo[2.2.1.0^{2,6}]heptyl	37·21	74·01	36·80	−15·16
62	4-Tricyclo[2.2.1.0^{2,6}]heptyl	32·48	70·21	37·73	−15·99

[a] Reference compounds used in correlation (2).
[b] Energies in kcal mol^{-1}.
[c] Standard conditions: 80% EtOH, 70 °C, OTs leaving group (data from Ref. 20).
[d] Not included in correlation.

when the parameters were changed, the plots deteriorated, but no curvature became apparent.

The quality of the plot shown in Figure 2 is below that reported previously. This is ascribed to our inclusion of more compounds in order to define the straight line. The standard deviation of ca 0·85 on log k is acceptable considering the rate range of 19 log units; however, inverse reactivity predictions might occur if compounds of similar reactivities were involved. The scatter in the plot is within the expected limitations of the method: rate constants extrapolated from different sources to standard conditions agree usually within ca 0·5 log units. The different substitution patterns at the β-position and the orientation of β-C,C and C,H bonds suggest that some inductive or hyperconjugative corrections should be applied,[22] but these have been neglected. Similarly, entropy effects are not considered. MM2 calculations for hydrocarbons reproduce the experimental enthalpies of formation with a standard deviation of ca 0·4 kcal mol^{-1}.[23] For functionalized compounds, the uncertainties are higher, and this undoubtedly also applies to carbenium ions. Even if there is some cancellation of computational errors in the ΔE_{st} values, it is probably unrealistic to expect a better fit.

The strain–reactivity plot in Figure 2 shows clearly the analogy between the bridgehead solvolysis and the sp^2–sp^3 interconversions in the series of monocyclic derivatives: in both series, the reactivity is determined by strain changes associated with changes in hybridization at the reacting centre, while steric effects of substituents are negligible.

Bridgehead structures requiring special parameters

The carbenium ion force field used for Figure 2 has some limitations. It is inadequate for the tertiary cyclobutyl, 7-norbornyl and 1-nortricyclyl cations. Since MM2 uses special parameters for all cyclobutyl derivatives, special parameters must also be employed for the tertiary cyclobutyl cations. Both high-level *ab initio* calculations and IR measurements indicate that the bicyclobutonium cation is an energy minimum, while the planar cyclobutyl cation is a transition state on the $C_4H_7^+$ potential energy surface;[24,25] Magic angle spinning NMR experiments[26] confirmed these results. For the methylcyclobutyl cation, recent theoretical and experimental investigations by Cecchi *et al.*[27] indicate that the geometry of the four-membered ring is comparable to that of the parent bicyclobutonium cation. This is in agreement with earlier experimental evidence for the non-planarity of the methyl cyclobutyl cation, provided by several laboratories.[24,28] Parametrization for cyclobutyl derivatives in the framework of molecular mechanics is therefore a delicate task. In practice, parameters have been derived by trial and error.[20] Such parameters include some compensation for non-classical stabilization, although the MM2-optimized geometry is

clearly different from that obtained by *ab initio* methods. Remarkably, these force-field parameters can accommodate the solvolysis of not only the 1-methylcyclobutyl (**40**), but also the cubyl (**56**) and 4-homocubyl (**54**) derivatives. The cubyl system has been calculated with the early force field of Schleyer and co-workers,[9] and the solvolysis of cubyl derivatives was predicted[29] to proceed at extremely slow rates. The discovery that cubyl derivatives in fact solvolyse faster than the 1-norbornyl analogues was most surprising.[30] It is therefore remarkable to see that the empirical cyclobutyl parameters also apply to this skeleton, in addition to the homocubyl solvolysis.[31] The cyclobutyl parameters may also be used for the tertiary 7-norbornyl cations, which are not treated adequately with the normal set of parameters. The calculated C(1)–C(7)–C(4) bond angle (standard parameters, UNICAT 4) at the cationic center of the 7-methyl-7-norbornyl cation is much higher than that predicted by MINDO/3 and STO-3G calculations.[19,20] This results in an overestimation of the strain energy of the ion and, consequently, the compound deviates significantly from the strain–reactivity plot. Since the bond angles at the cationic centre of the cyclobutyl and the 7-norbornyl cation are of the same order of magnitude, the cyclobutyl parameters have also been applied to the latter, and they afforded acceptable agreement with respect to the solvolytic reactivity of the tertiary 7-norbornyl derivatives (**38** and **49**). No attempt was made, however, to derive specific parameters for these ions. In the preceding discussion, the tertiary 7-norbornyl cations are assumed to have a classical structure of C_s symmetry. This view is supported by semi-empirical and *ab initio* calculations.[19] However, on the grounds of both theoretical and spectroscopic evidence, Sieber *et al.*[32] recently reported that the global minimum for the parent 7-norbornyl cation corresponds to a σ-bridged ion. This prediction was corroborated by the study of Friedel–Crafts alkylations of aromatics with 7-chloronorbornane and investigation of the effect of bridgehead substitution on the solvolytic reactivity of 7-norbornyl triflates.[33] The cyclobutyl parameters have also been applied to the 1-bicyclo[3.1.1]heptyl cation (**28$^+$**), which also contains a cyclobutyl fragment. However, we found it impossible to find parameters that would reproduce at the same time the reactivity of the cyclobutyl, cubyl and the 1-bicyclo[3.1.1]heptyl derivatives **28** (see below).[20]

A third class of compounds requiring special treatment is constituted by the 1-tricyclyl derivatives.[34,35] The corresponding cations are rejected by MM2, because the program uses special parameters for cyclopropanes which are part of the tricyclane structure. The ideal bond angle of the C-atoms bonded to the cyclopropane is slightly increased, which makes it possible to reproduce the experimental enthalpies of formation of the parent nortricyclane. For consistency, the same adjustments are required for the calculation of the
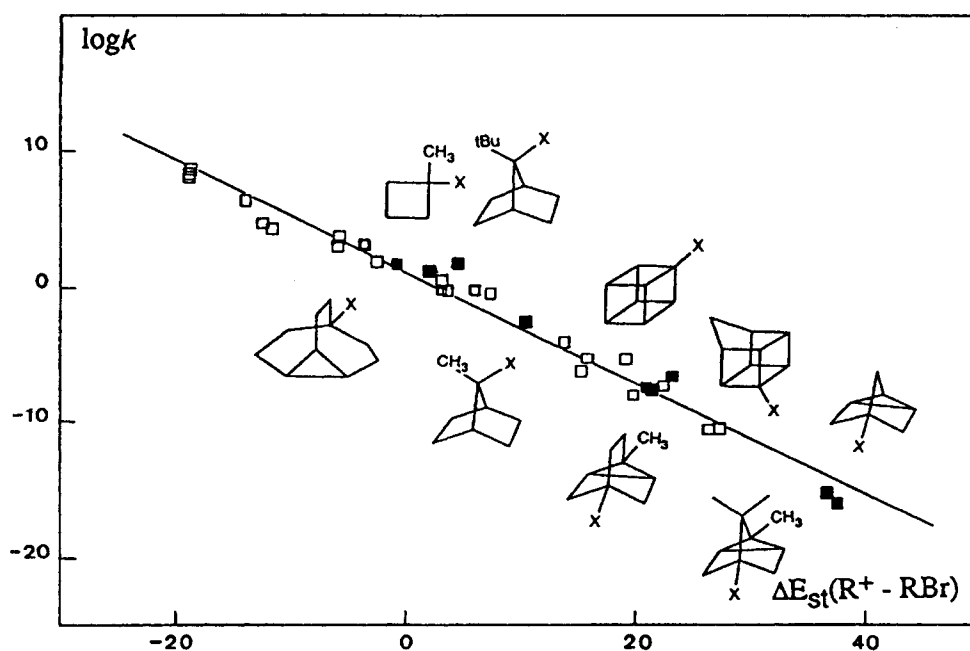
Figure 3. Plot of log k vs $\Delta E_{st}(R^+ - RBr)$ for solvolysis of bridgehead (open squares), cyclobutyl and tricyclyl (filled squares) derivatives. Data from Table 1

tricyclyl cations. The tricyclyl derivatives (**39**, **57**, **61** and **62**) are of special interest in the context of this study, since some of them solvolyse at even lower rates than the 1-norbornyl derivatives. Their inclusion allows the extension of the experimental rate range of the strain–reactivity correlation by 4 log units. The plot combining the bridgehead with the cyclobutyl, 7-norbornyl and 1-tricyclyl derivatives according to equation (3)[20] is shown in Figure 3.

$$\log k = -0.408 \Delta E_{st}(R^+ - RBr) + 1.220 \quad (3)$$
$$r = 0.988; \ \sigma(\log k) = 1.022$$

The fit is only marginally worse than that for the bridgehead derivatives alone, but it must be stressed that, since the parametrization for these special classes of compounds has been derived empirically, the significance of the result is questionable, except for the fact that within a given class of compounds the same parameters are valid.

SOLVOLYSIS OF NON-BRIDGEHEAD TERTIARY DERIVATIVES

Strain–reactivity correlation

Once the correlation for bridgehead derivatives has been established, the solvolytic behaviour of other tertiary

derivatives may be tested against this mechanistic model. Unfortunately, the experimental rate range for non-bridgehead compounds is only about half of that of the bridgehead derivatives, so that the relative experimental and computational uncertainties increase.[19,20] Much of the rate constants have been determined with OPNB derivatives. These data may be converted into rate constants for chloride solvolysis by means of linear free energy correlations.[16] The rate constants for chloride solvolysis are converted to standard conditions using Bentley's conversion factors. Factors for direct conversion of rate constants of OPNB derivatives to those of sulphonate esters are now also available.[18] The strain–reactivity correlation for the non-bridgehead derivatives alone is similar to that obtained in the bridgehead series (slope -0.27, intercept 2.64). However, the quality of the fit deteriorates ($r = 0.895$; $\sigma = 1.05$). Some monocyclic *tert*-butyl derivatives (**6**, **8**, **11**) exhibit severe upward deviation from the plot for which, at present, no satisfactory explanation may be provided. When the data for the non-bridgehead derivatives are combined with those of the bridgehead compounds, a remarkably consistent plot results [equation (4), Figure 4].

$$\log k = -0.408 \Delta E_{st}(R^+ - RBr) + 1.661 \quad (4)$$
$$r = 0.971; \ \sigma(\log k) = 1.34$$
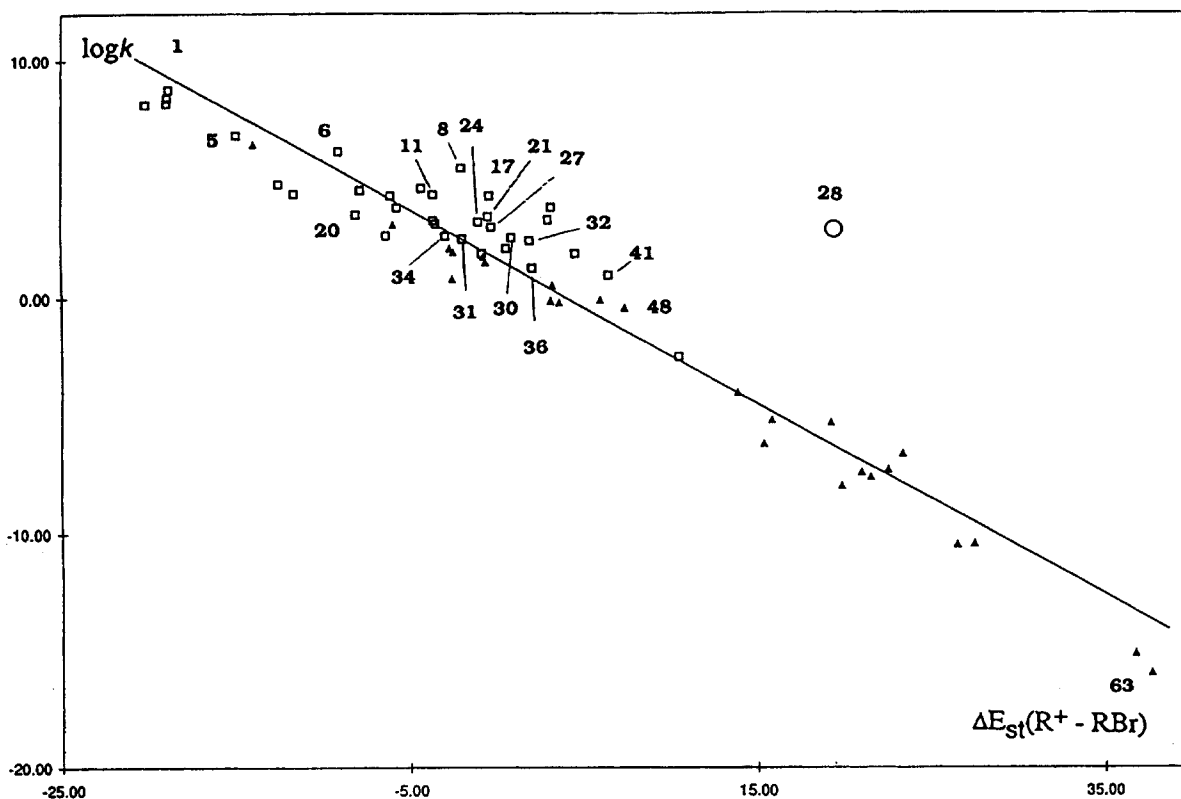
The fit of the combined plot is below that for the

Figure 4. Plot of log k for solvolysis of bridgehead (triangles) and tertiary non-bridgehead derivatives (squares) vs $\Delta E_{st}(R^+ - RBr)$. Data from Table 1

bridgehead compounds alone, the standard deviation increasing to 1·34 log units, while the slope of the correlation line is practically unchanged in comparison with that in Figure 3. The intercept increases only slightly to 1·69. It appears justified, therefore, to conclude that in both series of compounds, strain effects are predominant for the solvolytic reactivity.

The deviation of the acyclic tertiary derivatives from the overall plot is of some interest in the context of the subsequent discussion. We find upward deviations from the plot for 24 (1·3 units), 27 (1·3), 31 (0·2) and 32 (1·5), whereas 5 (−0·8) and 20 (−0·7) deviate downwards. Since the bridgehead and rigid tertiary derivatives which define the correlation line may not profit from nucleophilic solvent assistance[36] and/or backside solvation of the incipient carbenium ion, we estimate that k_s pathways should not contribute by more than a factor of 100 to the reactivity of acyclic derivatives. The possibility that inductive stabilization of the transition state by alkyl substituents might be compensated by decreased k_s contributions (or solvation) owing to steric hindrance may not be ruled out, however.

Exceptions

The force-field calculations, in their present form, apply only to compounds which solvolyse with retention of their structure via classical carbenium ions. Thus, molecules solvolysing with anchimeric assistance, owing to the presence of double bonds[37] or cyclopropane rings, are deliberately excluded from these studies, since no provision for such effects is made in the force field. This restriction also applies to σ-participation. In the series of tertiary derivatives, σ-participation occurs with the (tertiary) 2-exo-2-norbornyl compounds. They consistently solvolyse faster than expected on the grounds of the strain–reactivity correlation, while the endo epimers appear to be normal.[19] Based on experimental[26] and computational data for the parent 2-norbornyl cation, the symmetrically bridged structure was established as the energy minimum, while the classical 2-norbornyl cation is a transition state[38–40]. The observation of enhanced exo/endo rate ratios is particularly typical for the solvolysis of secondary norbornyl derivatives, and has led to a long controversy.[41] In the

tertiary series, the effect is less important, but neverthe-less appears clearly. The phenomenon of σ-participation is of some interest in the context of force-field calculations, because it points at a deficiency of the transition-state model used. It is assumed to be close to the intermediate carbenium ion with respect to structure and energy. Accordingly, the *exo/endo* rate ratio for solvolysis of epimeric derivatives should reflect their relative stabilities, but this is not the case. X-ray studies and theoretical calculations[42,43] have established an unsymmetrically bridged structure of the tertiary 2-norbornyl cation. This bridging stabilizes the transition state of the *exo* derivatives, such as **13**, but not that of its *endo* epimer **30**. The absence of bridging in the transition state of **30** implies different transition states for *exo* and *endo* derivatives, while the model assumes identical transition states for both epimers. Since the force field makes no provision for bridging, the transition-state model is inadequate for the *exo* derivative, while the *endo* isomer appears to be ade-quately treated (see Figure 4). If the occurrence of epimeric transition states for solvolysis of epimers is a general phenomenon, this implies that the transition state for solvolysis is less advanced on the reaction coordinate than the model assumes. The possibility that the same phenomenon might occur in other compounds of the series, and remained undetected, cannot be ruled out.

A drastic example for an anchimerically accelerated bridgehead derivative is the 1-bicyclo[3.1.1]heptyl system **(28)**, which solvolyses via the 1-bicyclo[3.1.1]heptyl cation **(28$^+$)** with preservation of its structure.[44] Its rate of solvolysis is enhanced by *ca* eight orders of magnitude over the reactivity expected on the grounds of the strain calculations, even if the cyclobutyl parameters are used. Experimental evidence for anchimeric participation on solvolysis of the com-pound has been reported. Preliminary theoretical studies[45] show that the classical ion **(28$^+$)** is not an energy minimum. Similarly, the unexpected high rate of solvolysis of 1-halobicyclo[1.1.1]pentanes, which was originally attributed to ring-opening concerted with departure of the leaving group,[46] is now ascribed to hyperconjugative stabilization of the 1-bicyclo[1.1.1]pentyl cation.[47] Preliminary evidence suggests that even the 1-bicyclo[2.1.1]hexyl derivatives may solvolyse at least with partial retention of struc-ture,[48] so that their high rate of solvolysis, reported *ca* 20 years ago,[49] may not be due to release of ring strain in the transition state as originally suggested, but rather to the inherent stability of the ion.

σ-Bridging and hyperconjugation are not the only reasons which can lead to energetically different transi-tion states for epimeric derivatives. The rates of solvolysis of the isomeric *cis*- and *trans*-decalin **(34** and **36)**, -hydrindane **(17** and **21)** and -bicyclo[3.3.0]octane derivatives **(9** and **41)** have been

determined, and it was found that the difference in ground-state energy between the epimers was only in part reflected in their relative solvolytic reactivity. Epimeric transition states were therefore proposed for these compounds.[50,51] The hypothesis has not been extensively tested, however. The occurrence of epim-eric rather than identical transition states on solvolysis of epimeric transition states is in contradiction to the computational model, and might be responsible for some of the scatter in the correlations.

In addition, a conceptual problem exists with confor-mationally flexible molecules. The treatment assumes carbenium ions in the most stable conformation as transition states, but whether the transition states reach indeed minimum steric energies depends on the rate of reaction relative to that of conformational change.[5] For example, conformational analysis of the 1-*tert*-butylcy-cloheptyl cation **(6$^+$)** using molecular mechanics and the CHEM-X package[52] reveals the existence of nine different stable conformations in a relatively small energy range, and it is impossible to attribute one of them to the transition state of the reaction.[45] For-tunately, the problem has only minor practical consequences in the context of solvolysis. In the series of rigid bridgehead compounds there is no evidence for secondary minima, and in the conformationally flexible systems investigated so far, the energy differences between the various conformations involved are modest. Therefore, the systematics errors introduced by the computational model may not be visible in the strain–reactivity plot owing to the scatter in the data.

RATES OF SOLVOLYSIS AND GAS-PHASE STABILITIES OF CARBENIUM IONS

Bridgehead derivatives

The force-field parameters used for carbenium ions in the context of solvolysis reactions have been derived and adjusted so as to reproduce rates of solvolysis. They therefore refer, more precisely, to transition states rather than to carbenium ions. We have discussed above several situations where the structural and energetic equivalence between transition state of solvolysis and carbenium ion intermediate is questionable, and this view is supported by other investigations. According to Abraham's analysis,[53] the transition state for solvolysis of *tert*-butyl chloride in water is structurally close to the contact ion pair, with 70–80% charge separation.[54] *Ab initio* calculations, combined with Monte Carlo simula-tions, predict the occurrence of a contact ion pair at a C–Cl distance of 2·9 pm and a solvent-separated ion pair near 5·5 pm. An energy barrier of 2 kcal mol^{-1} (1 kcal = 4184 kJ) separates the contact from the separated ion pair, the latter being more stable by 4 kcal mol^{-1}. The region around the transition state was not investigated,[55] however, and an uncertainty remains

with respect to the detailed transition-state structure. The slope of the strain–reactivity correlations (Figures 2–4), when converted into units of energies of activation, is 0·64, which indicates that *ca* 65% of the steric energy difference between the transition state model and the bridgehead derivative is expressed in the rates of solvolysis. This is in reasonable agreement with a transition state having developed substantial carbenium ion character and, at least with respect to strain, the computational model is satisfactory.

The stability of some bridgehead or tertiary rigid carbenium ions has been determined recently by ICR techniques using equilibrium constants for bromide exchange between carbenium ions and basicity measurements of olefins.[56] By combining the experimental enthalpies of formation of the carbenium ions with the MM2-calculated enthalpies of formation of the corresponding alkyl bromides, it is possible to obtain the heterolytic bond dissociation energy $D°(R^+ - Br^-)$ of the respective bromides or the enthalpy change $\Delta H(R^+ - RBr)$ in the gas phase (Table 2).

A plot of the rates of solvolysis (log k) vs $D°(R^+ - Br^-)$ for bridgehead and rigid tertiary derivatives is shown in Figure 5 [log $k = -0.588D°(R^+ - Br^-) + 81.7$; $r = 0.595$; $\sigma = 1.48$]. The rate range for this plot spans *ca* 12 log units, which is about half of that covered by the strain–reactivity plot. An extension to include more stable and still less stable carbenium ions to cover the full range of solvolytic reactivity is near completion.[57]

As Figure 5 shows, there is a linear correlation between solvolytic reactivity (in solution) and the heterolytic bond dissociation energy (in the gas phase) for the bridgehead derivatives. If log k for solvolysis is converted into units of free energy of activation, the slope of the correlation becomes 0·92, which corresponds to a *ca* 90% energetic equivalence between solvolytic reactivity and gas-phase equilibrium. This is higher than expected from the strain–reactivity plot (Figure 2), which revealed a *ca* 65% energetic equivalence between solvolysis and strain changes. The reasons for these discrepancies are not yet clear, and discussion is deferred until the final correlation based on the full rate range is available.

Despite these shortcomings, it appears justified to conclude that bridgehead solvolysis in solution and the corresponding gas-phase equilibria are governed by the same factors, and the strain–reactivity calculations show that the dominant factor consists in the strain changes.

In our initial study, the cation derived from 1-brom-onorbornane was off the correlation line of Figure 5. This was tentatively attributed to rearrangement of the 1-norbornyl cation in the ICR spectrometer. More recently, Abboud and Müller[57] found conditions under which the gas-phase stability of the 1-norbornyl and other, even more strained cations can be measured. So far, all of the bridgehead and rigid polycyclic cations investigated fit the correlation of log k for solvolysis vs $D°(R^+ - Br^+)$.

Table 2. Heats of formation of carbenium ions and rate constants of solvolysis of tertiary derivatives (kcal mol^{-1})

No.	Substrate	Log k	$\Delta H_f(R^+)$(exp)	$\Delta H_f(R^+)$(MM2)	$\Delta H(R^+ - RBr)$	$D°(R^+ - Br)^d$
12	2-Methyl-2-bicyclo[2.2.2]octyl	4·58	155·5[a]	158·3	180·9	129·9
13	2-Methyl-2-*exo*-norbornyl	4·57	169·4[b]	172·8	187·0	136·0
22	1-Methyl-1-cyclopentyl	3·25	167·0[b]	167·1	192·0	141·0
24	(Diethyl)(methyl)methyl	3·17	157·0[b]	152·2	190·9	139·9
25	2-Methyl-2-adamantyl	3·10	149·5[b]	149·8	182·7	131·7
27	Ethyl(dimethyl)methyl	2·96	158·0[b]	158·5	192·9	141·9
30	2-Methyl-2-*endo*-norbornyl	2·49	171·0[b]	172·8	186·1	135·1
31	(*t*-Butyl)(dimethyl)methyl	2·45	144·5[b]	143·4	190·0	139·0
32	*t*-Butyl	2·38	165·8[b]	165·8	197·1	146·1
35	1-Methyl-1-cyclohexyl	2·05	156·9[b]	155·4	192·3	141·3
40	1-Methyl-1-cyclobutyl	1·23	193·0[b]	193·5	192·6	141·6
48	1-Adamantyl	−0·41	160·7[c]	161·7	191·6	140·6
49	7-Methyl-7-norbornyl	−2·50	179·9[a]	183·4	195·0	144·0
50	1-Bicyclo[2.2.2]octyl	−4·00	177·8[a]	178·6	199·7	148·7[b]
53	10-Tricyclo[5.2.1.0^{4,10}]decyl	−6·16	182·9[c]	179·7	200·5	149·5[b]
55	3-Noradamantyl	−7·28	189·1[c]	195·9	200·6	149·6[b]
56	1-Cubyl	−7·39	358·1[c]	360·2	200·7	149·7[b]
61	6-Tricyclo[3.1.1.0^{3,6}]heptyl	—	261·5[c]	262·4	200·6	149·6[b]

[a] From proton affinity, Ref. 56.
[b] Ref. 59.
[c] From bromide transfer, Ref. 56.
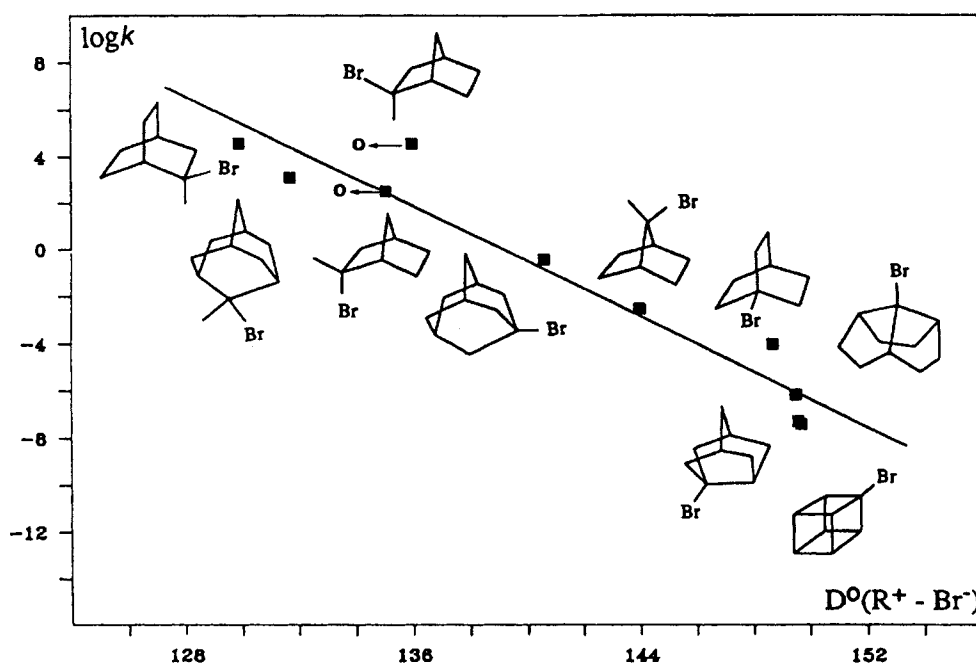[d] Calc. from $\Delta H_f(R^+)$ (exp) and $\Delta H_f(R - Br)$ (MM2).

Figure 5. Plot log k for solvolysis vs heterolytic bond dissociation energies $D^\circ(R^+ - Br^-)$ in the gas phase. Data from Table 2

Figure 5 exhibits one disturbing exception. The *exo*-2-norbornyl derivative **13** solvolyses more rapidly than would be predicted on the grounds of the bond dissociation energy. This is unexpected, since any extra stabilization of the tertiary 2-norbornyl cation, due to bridging,[42,43] must be accounted for in the heterolytic bond dissociation energy of the corresponding bromide. If this stabilization is expressed in the rate of solvolysis of the *exo*-bromide **13**, the compound will fit the correlation normally. The *endo*-isomer **30**, in contrast, should lie below the regression line, because, according to current belief, the extra stability of the free ion is not expressed in the transition state for solvolysis. The deviation should be appreciated in the light of experimental error. The reported values for the enthalpy of the 2-methyl-2-norbornylcation in the gas phase vary considerably ranging from 171·3 to 168 kcal mol^{-1}.[58] The value of 171·0 kcal mol^{-1} used in the plot is that recommended in the compilation of Lias *et al.*[59] It had been obtained by measuring the proton affinity (*PA*) of methylenenorbornane (207 kcal mol^{-1}). The enthalpy of formation of the neutral compound (12 kcal mol^{-1}) was derived by an estimate using group increments.[60] We have repeated these measurements in collaboration with Abboud,[57] and found the *PA* of methylenenorbornane to amount to 206·0 kcal mol^{-1}, taking a value of 204·5 kcal mol^{-1} for *PA*(NH$_3$). The enthalpy of formation of methylenenorbornane, as calculated by MM2, is

9·52 kcal mol^{-1} (MM3:[60] 8·49 kcal mol^{-1}), while that of 2-methylnorbornene, which is also present in the equilibrium, is 10·07 kcal mol^{-1}. With these data, the enthalpy of formation of the 2-methyl-2-norbornyl cation drops to 169·4 kcal mol^{-1}, and the data points for the *exo*- and *endo*-bromides **13** and **14**, respectively, move to the positions indicated by circles in Figure 5. Using these revised values, the original irregularity in Figure 5 falls within the experimental error.

Non-bridgehead derivatives

When the plot relating rates of solvolysis and gas-phase stabilities is extended to include simple acyclic and monocyclic derivatives, the correlation breaks down [Figure 6(a)]. All these compounds solvolyse considerably faster than predicted on the grounds of their heterolytic bond dissociation energy in the gas phase. In particular, the rate of solvolysis of *tert*-butyl bromide (**32-Br**) appears accelerated by almost 7 log units.

The *tert*-butyl cation **32**$^+$ is the least strained tertiary carbenium ion but, in spite of this, it is very unstable in the gas phase. In contrast, the 1-adamantyl cation (**48**$^+$), although significantly strained, is more stable in the gas phase than **32**$^+$, because it profits from inductive stabilization owing to alkyl substituents in the β-position. Such stabilization due to β-branching is evaluated to be 1·5 kcal mol^{-1} per substituent.[61] Both cations benefit from hyperconjugative stabilization, C,C-
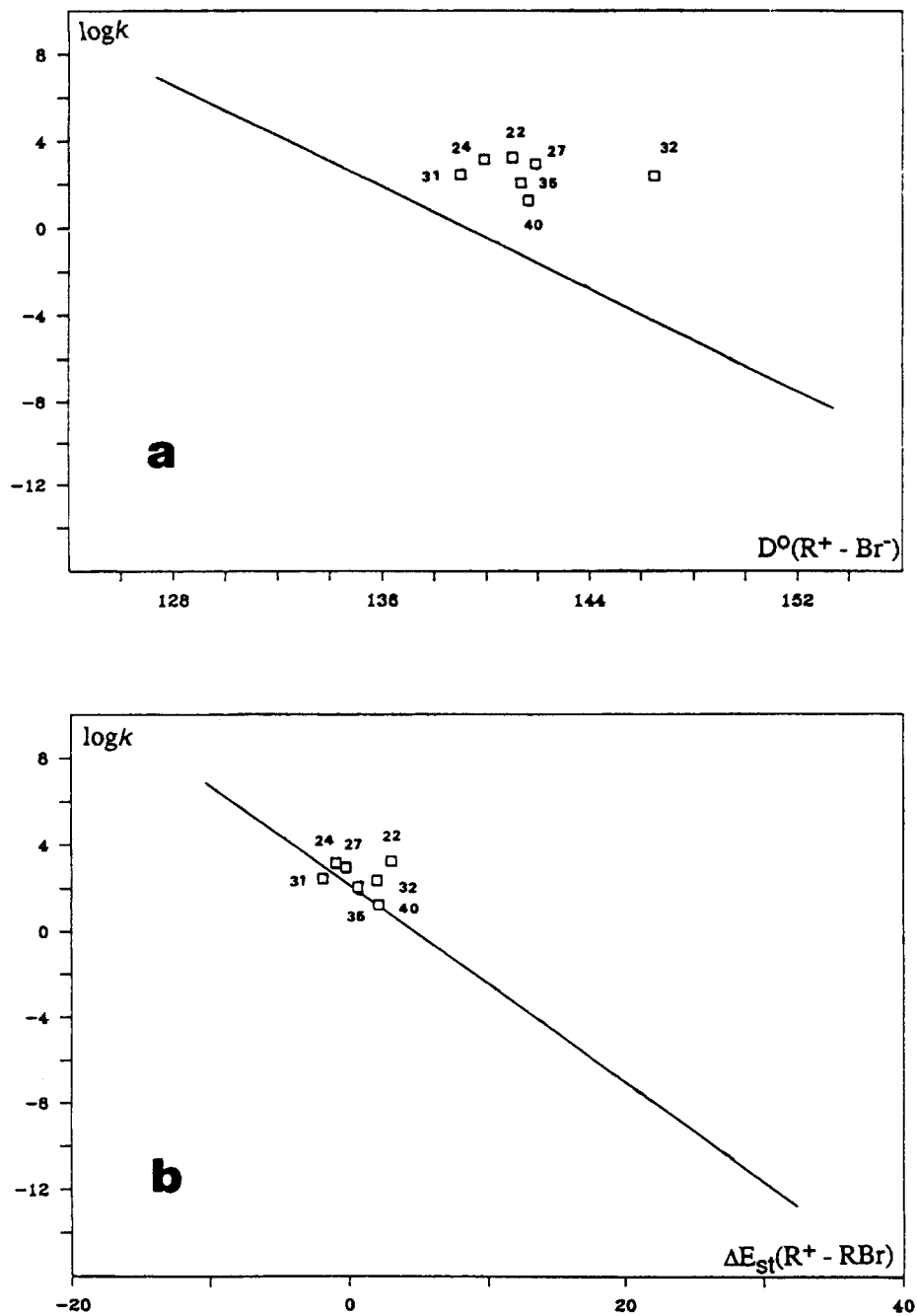
Figure 6. (a) Plot of log k for solvolysis of acyclic and monocyclic tertiary derivatives vs gas-phase equilibrium, $D°(R^+ - Br^-)$. Data from Table 2. The straight line is that determined by the bridgehead derivatives in Figure 5. (b) Plot of log k vs $\Delta E_{st}(R^+ - RBr)$ for the acyclic and monocyclic derivatives shown in (a). The straight line is defined by the bridgehead derivatives

hyperconjugation in the case of the adamantyl cation (**48**$^+$),[62-64] and C,H-hyperconjugation for the *tert*-butyl cation (**32**$^+$).[65,66] The equilibrium for hydride transfer between the *tert*-butyl and 1-adamantyl cations lies on the side of the adamantyl ion (**48**$^+$) in the gas phase ($\Delta G = -4$ kcal mol^{-1}), but in solution the free energy of the equilibrium varies from -1 to $+9$ kcal mol^{-1} depending on the solvent–electrophile combination used.[67] The change has been attributed to changes in solvation, although other effects, such as ion pairing, may also intervene.

The caged carbenium ions may only be solvated from one face, whereas in the simple acyclic ions the cationic centre is accessible to solvation from both faces. The *tert*-butyl/1-adamantyl rate ratio for solvolysis (in EtOH) leads to a difference in free energies of activation of *ca* 4 kcal mol^{-1} in favour of *tert*-butyl.[68] This corresponds to the trend predicted for more efficient solvation of the *tert*-butyl cation in the condensed phase, which, in turn, is reflected by nucleophilic assistance in the reaction rates. It appears therefore, that the rate constants of the acyclic and monocyclic tertiary derivatives should be determined as much by nucleophilic assistance as by the intrinsic gas-phase stability of the corresponding carbenium ions.

The hypothesis of nucleophilic assistance in the solvolysis of tertiary non-bridgehead derivatives follows from the observation that the relative rate ratio (1-adamantyl/*tert*-butyl) changes from *ca* 1:3000 in ethanol to *ca* 1:3 in 97% aqueous hexafluoropropan-2-ol.[69] In the less nucleophilic solvent (hexafluoropropan-2-ol), *tert*-butyl derivatives react at a lower rate, because nucleophilic assistance vanishes. This interpretation has been contested, however, on the grounds of considerations of strain, and the phenomenon of the changing 1-adamantyl/*tert*-butyl rate ratio was also ascribed to electrophilic assistance in the solvents capable of forming strong hydrogen bonds.[70] It was argued that the caged compounds should show stronger sensitivity towards electrophilic solvent assistance than the *tert*-butyl derivative, but experimental evidence contrary to this has been presented.[71] Kevill and Anderson[36] investigated the 1-adamantyl/*tert*-butyl rate ratio for dimethylsulphonium salts in different solvents and found variations from 1:2·6 (97% HFIP, 70·4 °C) to 1:8·85 (50% HFIP, 70·4 °C) and 1:210 (EtOH, 50·5 °C). This trend is inconsistent with electrophilic solvent assistance, since no such effect is to be expected with a neutral leaving group. An independent argument in favour of enhanced electrophilic assistance in adamantyl over *tert*-butyl solvolysis has been advanced.[72] Despite this criticism, the occurrence of nucleophilic assistance in solvolysis of *tert*-butyl and similar derivatives is generally accepted.

This interpretation, however, is not satisfactory. If the scatter in Figure 6(a) were due to mechanistic differences between bridgehead and monocyclic or acyclic substrates, such as nucleophilic assistance and/or eliminations, which may not occur in the bridgehead series, then the same deviations should appear in the strain–reactivity plot. This is not the case. Figure 6(b) shows the original regression line for the strain–reactivity correlation for the bridgehead derivatives (Figure 2) to which the monocyclic and acyclic compounds in Figure 6(a) are added. Clearly, the scatter in the strain–reactivity correlation [Figure 6(b)] for the same compounds is considerably less than that in Figure 6(a). For example, the *tert*-butyl derivative is accelerated only by 1·7 log units with respect to the regression line in Figure 6(b) but by 6·5 log units in Figure 6(a). If the former value is entirely ascribed to nucleophilic assistance, a rate enhancement factor of *ca* 10 000 has to be accounted for by some other cause. Nucleophilic assistance must be absent in the cage compounds for structural reasons. It cannot be the key factor determining reactivity of the tertiary 2-adamantyl derivatives, since even the secondary 2-adamantyl derivatives are believed to solvolyse via the k_c mechanism.[73] Since the *tert*-butyl derivative **32**, which among the tertiary substrates must be the most sensitive to nucleophilic assistance, shows only modest rate enhancement in the strain–reactivity plot, nucleophilic assistance alone cannot be responsible for the breakdown of the correlation between rates of solvolysis and gas-phase stabilities of acyclic and monocyclic compounds.

The gas-phase stability of ions is determined not only by strain, but also by the number of atoms on which charge may be delocalized. The sequence for the bond dissociation energies $D°(\mathrm{R}^+ - \mathrm{Br}^-)$ of **32** (146·1), **27** (141·9), **24** (139·9) and **31** (139·0 kcal mol^{-1}) is illustrative. We propose that the absence of correlation between the rates of solvolysis and the gas-phase $D°(\mathrm{R}^+ - \mathrm{Br}^-)$ values of the acyclic and monocyclic derivatives should be ascribed to the fact that in the transition state for solvolysis the positive charge at the reacting centre is not fully developed. As suggested by the analysis of Abrahams,[53] charge separation in the transition state has progressed to only 70–80%. In addition, the proximity of the leaving group may reduce the electron deficiency of the reacting centre, and therefore reduce the demand of the transition state for inductive and hyperconjugative charge stabilization in comparison with that in free ions. The solvolytic reactivity is mainly determined by strain changes, and charge effects play a minor role. However, in the gas phase, charge effects and strain may be equally important in determining the stability of the ions. The bridgehead ions exhibit significant structural similarity. The number of atoms is high, and the β-substitution pattern rather uniform. Charge may be efficiently stabilized over the molecular skeleton so that the bond dissociation energies $D°(\mathrm{R}^+ - \mathrm{Br}^-)$ are dominated by strain effects, and the correlation between log k and $D°(\mathrm{R}^+ - \mathrm{Br}^-)$ holds. The small ions such as *tert*-butyl

are unstable in the gas phase, because they may not stabilize charge in the way the bridgehead ions do. Their enhanced rates of solvolysis may be ascribed to the lower demand for charge stabilization of the solvolysis transition state in comparison with that in free ions. In more ionizing and less nucleophilic solvents the development of charge at the reaction centre increases. The capacity of the bridgehead compounds to stabilize charge becomes predominant, and their reactivity increases over that of *tert*-butyl. At the extreme, the 1-adamantyl/*tert*-butyl ratio would express the relative stability of the free ions.

COMPARISON OF MM2 AND *AB INITIO* CALCULATIONS FOR BRIDGEHEAD CARBOCATIONS

When force-field parameters for bridgehead carbocations were developed, rate constants for solvolysis of bridgehead derivatives were the only data available, and practically no reliable structural or energetic information on carbocations existed except that derived from solvolysis data. As discussed in the preceding paragraphs, there is only limited correspondence between solvolytic reactivity and the heterolytic bond dissociation energy of tertiary derivatives, and it follows, therefore, that the validity of the force-field calculations with respect to structure and energy of carbenium ions is open to question.

Experimental techniques such as x-ray,[42,43,64,66,74] NMR[26,75-82] and IR[83,84] methods recently provided direct insight in the structures of carbocations. Of particular interest in the field was the contribution of Schleyer and co-workers, who used *ab initio* methods based on individual gauge for localized orbitals (IGLO)[85-88] to calculate the ^{13}C NMR shifts for carbocations. As the NMR shifts thus obtained are very sensitive to the changes in geometry, a good agreement between theoretical and experimental shifts provides very valuable information on the geometries of carbocations.[89]

The theoretical calculations are the most widely used methods to study the structures and the properties of carbocations. In particular, in the field of short-lived reaction intermediates, an increasing amount of structural data has, over recent years, been determined through *ab initio* calculations. It has been shown that *ab initio* methods using polarized basis sets, when possible including explicit consideration of electron correlation, are useful for the accurate prediction of structures and energies of carbocations.[38,65,81,82,84,88] These high-level *ab initio* calculations were shown to be particularly important in the case of non-classical carbocations.[32,39,90-92] The MM2 method, in contrast, is not intended for the geometry optimization of such ions since, in its present state of sophistication, it is not adapted to deal with phenomena such as charge delocalization or partial bridging of carbocations.
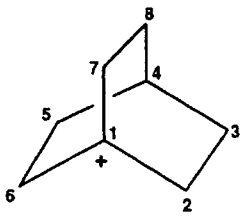
Geometry optimization using high-level *ab initio* calculations has been performed for only two of the bridgehead cations investigated by the MM2 method. Hrovat and Borden[93] examined the hyperconjugative stabilization of 1-bicyclo[2.2.2]octyl cation (**50**$^+$) by means of RHF/6–31G* and MP2/6–31G* calculations. Interestingly, both methods show the presence of hyperconjugative interactions, as demonstrated by the substantial lengthening of the bond distance between C(2) and C(3) (Table 3). This important structural deformation is accompanied by the shortening of the C(1)–C(2) and C(3)–C(4) bonds. Nevertheless, the inclusion of electron correlation is necessary to reveal the double hyperconjugation in **50**$^+$, as evidenced by shorter C(3)–C(4) and longer C(4)–H bond distances (Table 3). With the exception of C(1)–C(2) bond shortening, none of these structural modifications is reflected in the MM2-optimized geometry: neither the C(2)–C(3) and C(4)–H bond elongations nor the C(3)–C(4) bond shortening are observed.

Schiesser and co-workers[94,95] recently optimized the geometry of cubyl cation at the correlated MP2/6–31G** level. Their results indicated that the positive charge is substantially delocalized to the α- and γ-positions of the cage-type structure. The stability of cubyl cation had previously been rationalized in similar terms, at the Hartree–Fock level.[96] Again, the MM2 structure compares poorly with *ab initio* results. This is particularly the case for the key parameter: the MM2-calculated cross-ring distance C(1)–C(3) is far too short compared with the *ab initio*-optimized structure. For cubyl cation, such discrepancies are not surprising in the light of the fact that MM2 computations are based on trial cyclobutyl parameters. As mentioned earlier, within the MM2 model, a specific set of parameters is required for structures containing a four-membered ring.
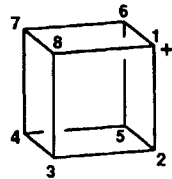
The geometries of both carbocations **50**$^+$ and **56**$^+$ present special features which are consequences of their strained polycyclic structures. These features are revealed by the *ab initio* method, especially when electron correlation is included, whereas the MM2 computations yield inaccurate geometries for both ions. However, the comparison between the two methods should not be confined to these two special cases where severe discrepancies may be expected.

For the purpose of evaluating in more detail the quality of MM2-optimized geometries of bridgehead carbocations, comparisons were made between MM2 results and *ab initio* molecular orbital theory computations at the Hartree–Fock level, obtained with the Gaussian set of programs.[97] The six bridgehead carbocations selected for this comparison were chosen because non-classical types of stabilization do not predominate in these structures. The choice was limited to relatively rigid polycyclic bridgehead cations with low conformational flexibility. As the six carbocations are classical, the absence of explicit consideration of

Table 3. Selected geometric parameters for 1-bicyclo[2.2.2]octyl cation and 1-cubyl cation

50+   **56+**

	50^+				56^+	
Parameter[a]	MM2	HF/6–31G*[b]	MP2/6–31G*[b]	Parameter[a]	MM2	MP2/6–31G**[c]
C1–C2	1·486	1·464	1·449	C1–C2	1·500	1·497
C2–C3	1·545	1·608	1·626	C2–C3	1·561	1·575
C3–C4	1·556	1·538	1·527	C3–C4	1·596	1·563
C1–C4	2·369	2·350	2·354	C1–C3	1·877	2·034
C1–C2–C3	102·2	98·6	98·4	C1–C4	2·200	2·442
C2–C3–C4	109·1	109·9	109·8	C1–C2–C3	75·6	82·9
C2–C1–C6	115·9	117·8	118·0	C2–C1–C6	106·9	100·2
C3–C4–C5	109·4	109·1	109·1	C2–C3–C4	85·9	88·1
C2–C3–C4–C5	−59·5	−59·6	−59·5	C2–C3–C8	101·4	93·6
C6–C1–C2–C3	70·5	75·5	76·0	C1–C2–C3–C4	−78·1	−83·6
				C6–C1–C2–C3	106·8	97·1
				C2–C3–C4–C7	97·1	92·7

[a] Bond lengths in ångstroms and angles in degrees.
[b] Ref. 93.
[c] Refs 94 and 95.

electron correlation is less critical for such species. Indeed, even with the use of the recent computer technology, calculations incorporating electron correlation, in particular the characterization of stationary points by vibrational frequency analysis at such a high level, are difficult to carry out for carbocations with up to eleven carbon atoms such as the 1-manxyl cation 7^+ ($C_{11}H_{20}^+$).

The HF/6–31G*[98–100] polarized basis set, which has been shown in the past to reproduce the properties of the classical carbocations in a satisfactory manner, was used to optimize the geometries for the six selected carbocations. It was assumed that the optimized geometry parameters are adequately reproduced with the HF/6–31G* basis set, at least for the purpose of this comparison. Although limitations to its use have recently been found,[101] it has successfully revealed hyperconjugative interactions in carbocations.[102,103]

In polycyclic bridgehead carbocations, these interactions may play a more or less important role, depending on the particular structure of the ion. Three carbocations with weak hyperconjugative interactions were investi-

gated in this series. The three remaining ions were selected because they display more pronounced degrees of C–C and/or C–H hyperconjugative stabilization.

Cations exhibiting moderate hyperconjugative interactions

Careful investigation of the potential energy surface of perhydrotriquinacenyl cation **53**$^+$, using the *ab initio* method, revealed the presence of several stationary points. Vibrational frequency analysis at the 6–31G* level shows cation **53**$^+$ of C_3 symmetry as being the lowest minimum, whereas the C_{3v} isomer is a higher order stationary product.[102] Molecular mechanics calculations that identify only one minimum of C_3 symmetry are consistent with *ab initio* results. The 6–31G* computations show a weak threefold C–C hyperconjugation enabled by the propeller-like arrangement of the three rings of ion **53**$^+$. This hyperconjugative interaction is reflected in the *ab initio*-optimized structure by the slight lengthening of bonds C(1)–C(2), C(4)–C(5) and C(7)–C(8) to 1·569 Å, compared with

1·545 Å for C(1)–C(9), C(3)–C(4) and C(6)–C(7) (Table 4). The lengthened bonds are associated with the smaller C$^+$–C–C bond angles, as C(10)–C(1)–C(2) and its two symmetry-related angles are decreased to 98·5°, whereas C(10)–C(1)–C(9) amounts to 102·4°. Apart from these small structural deformations due to hyperconjugative interactions, the MM2 calculations reproduce the *ab initio*-optimized geometries reasonably well. In Table 4, the MM2 optimized geometries for the other two carbocations **7**$^+$ and **9**$^+$, which display weak to moderate hyperconjugative interactions, also come relatively close to those optimized by *ab initio* calculations. The case of the 1-bicyclo[3.3.0]octyl cation **9**$^+$ is

particularly interesting since both methods, MM2 and *ab initio*, predict the existence of two minima, the lower one having C_s symmetry and the higher one C_1 symmetry. In the *ab initio*-optimized geometry of the more stable isomer, the C–C hyperconjugation remains weak, whereas the C–H hyperconjugation is clearly present. Indeed, the C(2)–H$_a$ and especially C(5)–H bond distances at the α-position are longer, at 1·094 and 1·104 Å, respectively, than those computed for the β-position where C(3)–H$_c$ is 1·081 Å. In addition, the C$^+$–C–H bond angles are smaller (105·4° and 101·4°), as compared, for example, with C(2)–C(3)–H$_c$, which amounts to 111·9°. Again, these geometry distortions

Table 4. Optimized structures[a] of the series of bridgehead carbocations with moderate C–C hyperconjugation with key geometric parameters[b]

7+ (C₃)   9+ (Cₛ)   53+ (C₃)

7⁺			9⁺			53⁺		
Parameter[b]	MM2	6–31G*	Parameter[b]	MM2	6–31G*	Parameter[b]	MM2	6–31G*
C1–C2	1·488	1·473	C1–C2	1·480	1·474	C1–C2	1·541	1·569
C2–C3	1·533	1·557	C1–C5	1·475	1·460	C1–C9	1·541	1·545
C3–C4	1·538	1·534	C2–C3	1·549	1·548	C1–C10	1·475	1·468
C1–C2–C3	111·9	110·0	C4–C5	1·539	1·540	C2–C3	1·553	1·546
C2–C3–C4	115·0	116·6	C2–H$_a$	1·115	1·094	C1–C2–C3	104·4	105·2
C2–C1–C8	119·9	119·9	C2–H$_b$	1·115	1·085	C1–C10–C4	117·9	117·1
C1–C2–C3–C4	56·8	58·9	C3–H$_c$	1·116	1·081	C2–C1–C10	97·6	98·5
C3–C2–C1–C8	61·2	60·7	C5–H	1·116	1·104	C3–C4–C10	99·9	102·5
Θ	1·6	0·4	C1–C2–C3	98·8	103·9	C3–C2–C1–C10	–35·7	–33·3
			C2–C1–C5	117·7	112·2	C2–C1–C10–C4	26·4	22·2
			C3–C4–C5	102·8	102·4	Θ	8·4	9·9
			C1–C2–H$_a$	110·1	105·4			
			C1–C2–H$_b$	112·2	113·0			
			C2–C3–H$_c$	112·6	111·9			
			C1–C5–H	109·4	101·4			
			C1–C2–C3–C4	24·8	24·6			
			C5–C1–C2–C3	–0·3	–3·9			
			Θ	2·4	2·5			

[a] Perspective drawings of the 6–31G* optimized structures.
[b] Bond lengths in ångstroms, angles in degrees and mean value Θ of the out-of-plane bending angles in degrees.

stemming from C–H hyperconjugation are absent in the MM2-optimized geometries. Incidentally, the C–H bond lengths generated by MM2 are systematically longer than those obtained with the *ab initio* method.

Cations exhibiting pronounced hyperconjugative interactions

The comparison of geometries generated by both methods is especially instructive for ions where *ab initio* calculations predict strong hyperconjugative interactions. This is the case for 3-noradamantyl **55**⁺, 1-noradamantyl **52**⁺ and 1-bicyclo[3.2.1]octyl **51**⁺ carbocations. The *ab initio*-optimized geometry of the 3-noradamantyl cation **55**⁺ is particularly affected by C–C hyperconjugation: the C(1)–C(2) and C(6)–C(8) distances attain 1·606 Å, in comparison with 1·547 Å

for C(4)–C(9) and C(4)–C(5), and the bond angles C(1)–C(2)–C(3) and C(3)–C(8)–C(6) (89·7°) are clearly smaller than angle C(3)–C(4)–C(9) (99·4°). The absence of these hyperconjugative deformations in the MM2-optimized geometries of the three ions in Table 5 increases markedly the divergences between the geometry parameters generated by molecular mechanics and by *ab initio* calculations.

The differences between the geometries optimized by MM2 and by *ab initio* methods may also be evaluated by calculating the average of the absolute values of the differences in geometry parameters listed in Tables 4 and 5. For cations **7**⁺, **9**⁺ and **53**⁺, the difference in bond length ranges from 0·012 to 0·015 Å, while the average of the absolute values of the differences for bond distances is 0·013 Å. The difference in bond angles lies between 1·17° and 3·6° with an average of 2·01°. In

Table 5. Optimized structures[a] of the series of bridgehead carbocations with pronounced C–C hyperconjugation with keygeometric parameters[b]

51+ *(C₁)*　　　　　52+ *(Cₛ)*　　　　　55+ *(Cₛ)*

	51⁺			52⁺			55⁺	
Parameter[b]	MM2	6–31G*	Parameter[b]	MM2	6–31G*	Parameter[b]	MM2	6–31G*
C1–C2	1·488	1·455	C1–C2	1·481	1·463	C1–C2	1·546	1·606
C1–C7	1·483	1·488	C1–C7	1·495	1·478	C1–C7	1·560	1·548
C1–C8	1·480	1·460	C2–C3	1·552	1·589	C2–C3	1·484	1·451
C2–C3	1·541	1·601	C3–C4	1·588	1·607	C3–C4	1·491	1·535
C5–C8	1·545	1·589	C6–C7	1·553	1·600	C4–C9	1·545	1·547
C6–C7	1·554	1·572	C1–C2–C3	91·4	87·9	C1–C2–C3	92·2	89·7
C1–C2–C3	105·2	99·0	C1–C7–C6	104·7	101·6	C2–C1–C7	109·3	109·9
C1–C7–C6	96·4	97·1	C2–C1–C7	111·4	111·5	C2–C3–C4	112·9	113·2
C1–C8–C5	90·8	89·6	C2–C3–C4	105·9	104·8	C2–C3–C8	115·5	119·7
C2–C1–C7	117·9	122·4	C7–C1–C8	115·5	119·0	C3–C4–C9	100·3	99·4
C2–C1–C8	116·5	119·1	C1–C2–C3–C4	30·1	32·4	C1–C2–C3–C4	42·3	45·1
C1–C2–C3–C4	−39·3	−41·5	C2–C1–C8–C4	58·5	66·4	C3–C2–C1–C7	58·8	57·8
C3–C2–C1–C8	70·5	75·8	C3–C2–C1 –C7	−75·6	−78·1	C4–C9–C1–C7	−62·2	−61·6
C3–C2–C1–C7	−68·2	−70·0	Θ	14·4	10·9	Θ	14·7	12·6
Θ	12·1	9·5						

[a] Perspective drawings of the 6–31G* optimized structures.
[b] Bond lengths in ångstroms, angles in degrees and mean value Θ of the out-of-plane bending angles in degrees.

the case of ions 51^+, 52^+ and 55^+, the larger average differences are observed for both bond distances (0.030 Å), and bond angles (2.33°). It is interesting that in general there is less difference between MM2- and $6\text{--}31G^*$-optimized parameters than between those generated by MM2 and 3–21G methods.

The pyramidalization at the cationic centre is another structural characteristic of bridgehead cations and its extent depends on the particular arrangement of the polycyclic framework. In an optimized geometry, this pyramidalization can be expressed as the average angle Θ, of the out-of-plane bending angles ω_i of the central C^+ atom, relative to the plane defined by the three neighbouring carbons. In the MM2 program, the pyramidalization at the cationic centre is mainly controlled by the out-of-plane constant, for which the value of 0.9 was suggested. In the series of bridgehead carbocations listed in Table 4, ab initio-determined pyramidalization evaluated as the average angle Θ is well reproduced by MM2. However, for ions where pyramidalization is more pronounced, such as 51^+, 52^+ and 55^+, MM2 tends to overestimate this out-of-plane deformation of the cationic centre (Table 5).

The MM2-computed steric energies of the carbocations may be converted into enthalpies of formation by means of bond increments,[104] which are based on the 165.8 kcal mol^{-1} experimental value for the tert-butyl cation. These data are given in Table 2 together with the experimental values available in the literature. The MM2 calculations also use increments for the inductive stabilization of the cationic centre by β-alkyl substituents. A value of 1.5 kcal mol^{-1} per substituent has been recommended and is used in MM2 calculations with the assumption that the effects are additive.

The comparison appears to be satisfactory: the experimental enthalpies of simple acyclic and monocyclic ions are well approximated by MM2. The agreement observed for the cubyl cation is remarkable, considering that the cubyl parameters were adjusted on the grounds of solvolysis data for cubyl- and methylcyclobutyl bromide.

For several other ions, the agreement is less satisfactory, however. The largest discrepancy between experimental and MM2-computed heats of formation is found for the 3-noradamantyl cation 55^+ where the deviation reaches 6.8 kcal mol^{-1}. As discussed above, the ab initio method revealed a strong C–C hyperconjugative stabilization, which is not reflected in the MM2-computed value. For the perhydrotriquinacenyl cation 53^+, where ab initio calculations showed a weaker hyperconjugative interaction, the difference between the two values drops to 3.2 kcal mol^{-1}. In another case, the poor agreement of MM2-computed values with experimental results can also be a consequence of other factors which stabilize carbocations. For example, the heat of formation calculated by MM2 for 2-methyl-2-norbornyl cation is 3.4 kcal mol^{-1} higher than that

measured experimentally, which may be attributed to the unsymmetrical bridging of tertiary 2-norbornyl cations.[42,43]

At this stage, no attempt was made to compare MM2-computed heats of formation with energies obtained by ab initio calculations using the $6\text{--}31G^*$ basis sets. Indeed, ab initio computations at correlated level are needed to appreciate satisfactorily the energetic consequences of the hyperconjugative stabilization. Such calculations are in progress.

The comparison of the MM2-calculated energies and structures with the experimental and ab initio results reveals appreciable deficiencies in the molecular mechanics treatment. These are principally due to the neglect of hyperconjugation and partial bridging in the carbocation force field. Clearly, the MM2 calculations perform much better for solvolysis, where such effects are less important than in the case of free ions.

CONCLUSION

The application of molecular mechanics calculations to steric effects in bridgehead solvolysis was developed in the early 1970s, when molecular mechanics was in its infancy. It is remarkable to find that some 20 years later the basic approach has stood the test of time. It may be applied safely not only to bridgehead derivatives, but also to tertiary derivatives of general structure, albeit less reliably. From this viewpoint, the solvolysis of tertiary derivatives appears remarkably simple and mechanistically homogeneous. Once the anchimerically assisted compounds have been recognized and removed, there are very few serious deviations from the strain–reactivity plot. It is thus possible, by this type of correlation analysis, to determine 'normal' behaviour and to quantify the deviation from this norm. On the other hand, the calculations, in their present form, provide only limited insight into the structures of carbocations, in particular when they are distorted. Although in simple cases there may be agreement between the experimental or ab initio- and the force field-calculated structures, this agreement should be considered with caution until a more advanced version of molecular mechanics, specifically parametrized for carbenium ions, is developed.

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