67. Steric Effects on Reaction Rates

Part VIII

The Significance of Front Strain Release in Solvolysis of Bridgehead Derivatives

by **Paul Müller***, **Jacky Blanc**, and **Jiri Mareda**

Département de Chimie Organique, Université de Genève, CH-1211 Genève 4

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The steric requirements of leaving groups for 14 bridgehead derivatives have been examined using MM2 calculations. The strain varies almost monotonously throughout the series upon variation of the leaving group from H to Cl, OH, CH_3, CH_3CH_2O, $(CH_3)_3CO$, $(CH_3)_3C$ and no significant trends for differential F-strain effects are detected expect for the perhydrophenalene derivative **13**. The experimental rates of solvolysis of bridgehead derivatives correlate well with the calculated steric energy differences between substrate R–X and the corresponding carbenium ion R⊕. However, the strain calculations using the more recent force-fields (MM2) disagree, in part, with those reported in the literature: chloride and *p*-toluenesulfonate leaving groups correlate with identical slopes, and the perhydrotriquinacene derivative **10** shows no anomalous behavior. The calculations suggest that F-strain and C,C-hyperconjugation should not play any dominant role in bridgehead solvolysis.

Introduction. – Front strain (F-strain) is the sum of steric interactions of a substituent, usually a leaving group, with the rest of the molecule [1]. If these interactions are released upon departure of the substituent, F-strain results in rate enhancement. This phenomenon is observed unambiguously in pyrolysis of substituted ethanes, where steric crowding weakens the central bond to such extent that free energies of activation vary by *ca.* 30 kcal/mol upon changing the substituents [2]. F-Strain effects may also appear in solvolysis reactions of crowded substrates [1] [3]; the most striking observations in this area has been reported by *v. Schleyer* and his coworkers [4] (see below).

F-Strain was invoked to be responsible, at least partially, for the significantly different slopes which occurred when the rates of solvolysis of bridgehead chlorides, *p*-toluenesulfonates and trifluoromethanesulfonats were plotted *vs.* the calculated steric energy differences between the bridgehead cation and the respective alkane [5]. However, at the time when this observation was made, the method of molecular mechanics, which had been used for the strain calculations, was still in its developing stages. Parameters for functional groups were not yet available, which would have allowed investigation of the steric requirements of different leaving groups in more detail.

A priori there appears to be no reason why identical slopes should be obtained in strain reactivity correlations upon changing the leaving group¹). A leaving group variation could change the position of the transition state on the reaction coordinate, which

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¹) During the revision of this manuscript, we were informed by *Bentley* that the hypothesis of different slopes for different leaving groups has been disproven by experiment [6].

should lead to different slopes. Further, it could produce a systematic change in the entropies of activation. This latter effect could be of considerable importance, because strain changes, by definition, are enthalpy effects. In all strain reactivity correlations, proportionality between $\Delta G^{\neq}$ (or log k) and $\Delta H^{\neq}$ must exist, if they are to be successful, since only $\Delta H^{\neq}$ can be approximated with strain calculations. For the present discussion, we assume, as was assumed by *Bingham* and *Schleyer* [5], that these requirements are met for solvolysis of bridgehead derivatives.

Recently, we have described a force-field for secondary and tertiary carbenium ions [7] incorporated into *Allinger*'s MM2 program [8]. The force-field was tested, and it gave very similar results for secondary carbenium ions [9] compared to those obtained with *Schleyer*'s BIGSTRN program [10]. This communication deals with application of the molecular-mechanics calculations, using the carbenium ion force-field to evaluate solvolysis rates of tertiary bridgehead derivatives. A preliminary report on this topic has been published [11].

Results and Discussion. – The BIGSTRN version available to us was a preliminary copy which we had obtained in 1974 through courtesy of *Mislow* and *Schleyer*. Although it produced consistent results with MM2 for secondary cations [7] [8], the structures for bridgehead carbenium ions turned out unsatisfactorily, showing an exaggerated tendency towards planarity. The MM2 force-field for secondary cations [7] [8] gave consistent results also for tertiary structures, but a simplified version, which we had used at an early stage of the development, gave the most satisfactory agreement for correlation of bridgehead solvolysis rates[2]). The following modifications with respect to the previously published force-field were applied: the force constants for bending the $C-C^{+}-C$ and $C-C^{+}-H$ bond angles were increased to 2.28 mdyn/rad, that for the $C-C-C^{+}$ and $C^{+}-C-H$ angles to 0.57. A simplified treatment for torsional interactions was used with $V_1 = V_2 = 0$ and $V_3 = 0.70$ kcal/mol for all potentials[2]). A correction for alkyl β-branch-

Table 1. *Steric Energies* (E_{st}) *and Strain of Bridgehead Derivatives* [kcal/mol] *by MM2*

No	Compound	RH		R⊕	$\Delta G^{\neq a}$)	$\Delta G^{\neq a}$)
		E_{st}	Strain	E_{st}	RCl	ROTs
1	1-Norbornyl	23.09	18.46	50.22		15.62
2	1-Bicyclo[2.2.2]octyl	19.64	14.34	33.88	5.28	5.79
3	1-Bicyclo[3.2.1]octyl	19.27	13.98	36.03		7.42
4	1-Bicyclo[3.3.1]nonyl	18.27	12.32	22.76	−1.59	
5	1-Bicyclo[3.2.2]nonyl	24.35	18.41	28.78	−0.4421	
6	1-Noradamantyl	28.02	22.04	46.95		8.66
7	1-Bicyclo[3.3.2]decyl	29.96	23.35	28.00	−5.46	
8	1-Adamantyl	17.09	10.45	24.80	0	0
9	7-Methyl-3-noradamantyl	27.80	21.49	51.15		11.74
10	10-Tricyclo[5.2.1.0^{4,10}]decyl	26.55	19.91	45.94		8.86
11	1-Bicyclo[3.3.3]undecyl	37.29	30.02	29.27	−10.75	
12	3-Homoadamantyl	28.04	20.74	28.19	−3.65	
13	*trans-trans-trans*-1-Tricyclo[7.3.1.0^{5,13}]tridecanyl	15.51	6.90	18.18	−1.96	
14	*cis-cis-trans*-1-Tricyclo[7.3.1.0^{5,13}]tridecanyl	19.20	10.59	20.68	−3.92	

[a]) Relative to 1-adamantyl [5].

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[2]) The results reported in [11] were obtained with the same modified force-field.

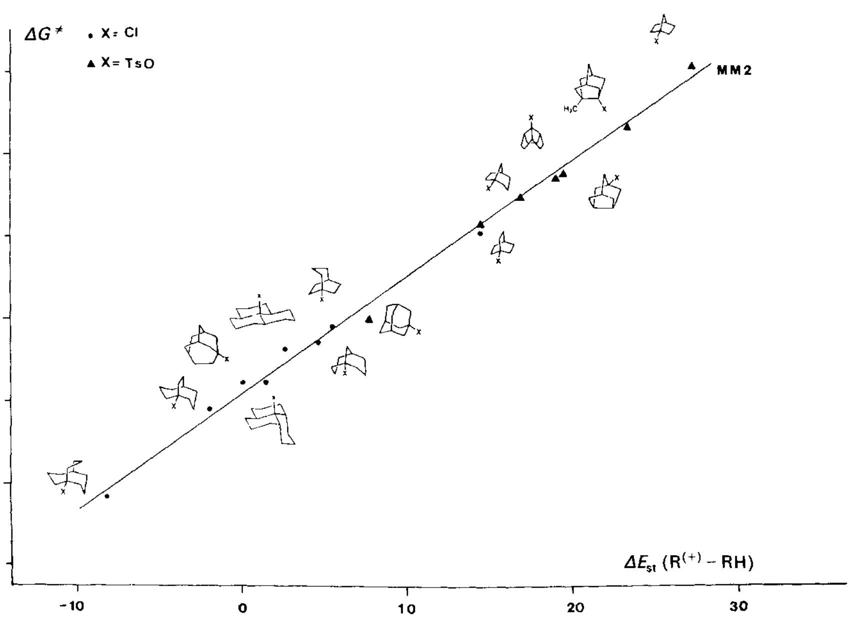


Fig. 1. *Plot of rates of solvolysis of chlorides and* p-*toluenesulfonates* vs. *steric-energy differences* [kcal/mol] *between carbenium ions and hydrocarbon* (ΔE_{st})

ing was applied to the ideal bond angles, using for C–C–C⊕ 109.5 for two alkyl groups, 110.5 for one, and 111.5 for two hydrogens. Similarly, values of 109.5, 110.2, and 111.0 were used for H–C–C⊕. The force-field was tested by recalculating the steric energy differences between bridgehead carbenium ions and the corresponding hydrocarbons (ΔE_{st}) which had previously been determined by *Bingham* and *Schleyer* [5] for correlation with rates of solvolysis of bridgehead derivatives (*Table 1*). The analogous correlation obtained with MM2 is shown in *Fig. 1*. Reactivities are expressed in terms of $\Delta G^{\neq}$ relative to the 1-adamantyl derivative. Although the general trend is similar to that obtained by *Bingham* and *Schleyer*, our calculations afford almost identical slopes for chloride and *p*-toluenesulfonate solvolysis, and it is possible to correlate the data with only one equation:

$$\Delta G^{\neq} = 0.71\ \Delta E_{st} - 4.61\ (r = 0.997)$$

In contrast, *Bingham* and *Schleyer* reported a change of the slopes by a factor of *ca.* 3 upon changing the leaving group from chloride to *p*-toluenesulfonate, and they ascribed this trend to F-strain which was thought to be present in the case of sulfonate leaving group, but neglected in the calculations. Our observation of identical slopes may be due to two causes: either the F-strain hypothesis invoked by *Bingham* and *Schleyer* [5] is correct, and it follows that our carbenium ion force-field must be inadequate, the observation of identical slopes for chlorides and *p*-toluenesulfonates being due to a systematic error proportional in magnitude to the strain of the carbenium ions involved. Alternatively, provided that the force-field reproduces carbenium ion stabilities correctly, the F-strain hypothesis should be abandoned in the context of bridgehead solvolysis. The significance of F-strain in the series was tested by calculating the strain energies for

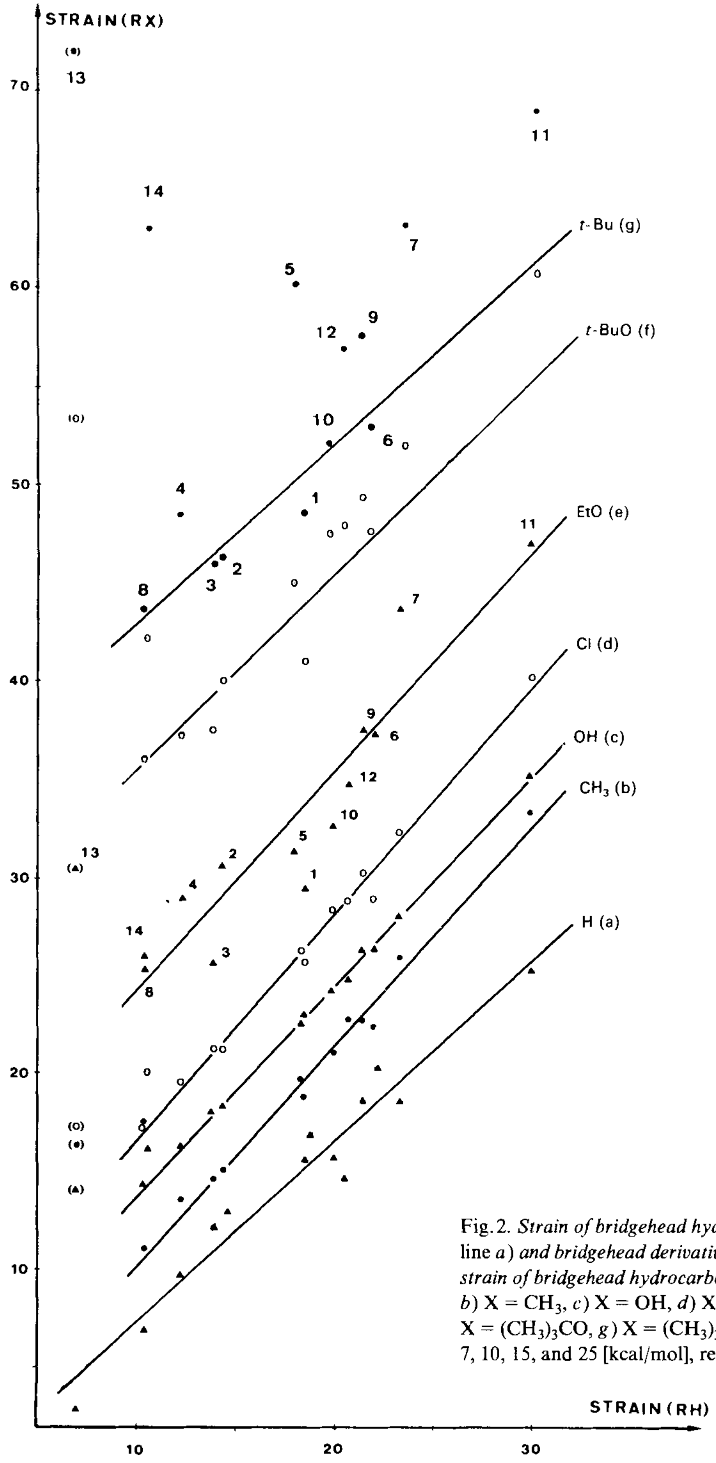


Fig. 2. *Strain of bridgehead hydrocarbons RH* (BIGSTRN, line *a*) *and bridgehead derivatives RX* (MM2, lines *b–g*) vs. *strain of bridgehead hydrocarbons RH, calculated by MM2. b*) X = CH_3, *c*) X = OH, *d*) X = Cl, *e*) X = CH_3CH_2O, *f*) X = $(CH_3)_3CO$, *g*) X = $(CH_3)_3C$. Lines *b* to *g* shifted by 1, 4, 7, 10, 15, and 25 [kcal/mol], respectively in y.

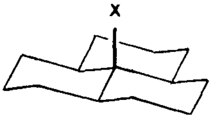
various leaving groups of different size. Since no parameters are available for sulfonate groups, their steric requirements were approximated in the present work with hydrocarbon or ether models. Strain calculations were performed for 14 bridgehead compounds and the leaving group was varied along the series H, Cl, OH, CH_3, CH_3CH_2O, $(CH_3)_3CO$, $(CH_3)_3C$. Even though geometries were fully optimized, it was beyond our possibilities to perform dihedral driver search for global minima for such a large number of structures. In *Fig. 2*, the strain energies calculated by MM2 are plotted *vs.* the strain energies of the corresponding hydrocarbons. Tables containing the details of the calculations are available as supplementary material from the authors upon request. Line *a* represents the strain energy of the hydrocarbons, as calculated by BIGSTRN; satisfactory agreement is found between BIGSTRN and MM2 in the series (line *a*, strain (BIGSTRN) = 0.92 × strain (MM2) + 2.00, $r = 0.97$).

The F-strain hypothesis assumes that the strain of bridgehead chloride R–Cl is adequately represented by that of bridgehead hydrocarbons R–H, while strain of *p*-toluenesulfonates is systematically underestimated by the R–H model. Further, to produce the expected slope change mentioned above the sensitivity of the *p*-toluenesulfonate substrates should increase in the order **8** < **2** < **3** < **6** < **10** < **9** < **1**. As *Fig. 2* shows, the small leaving group models CH_3, OH, Cl and even EtO (lines *b–e*) lead to rather small F-strain effects throughout the series in comparison to H. Thus, it appears that the 1-norbornyl system **1** is less susceptible to F-strain than 1-bicyclo[2.2.2]octyl (**2**) or 1-adamantyl (**8**). If **13** is excepted (see below), only **7** shows some enhanced response with EtO, but the effect is not dramatic.

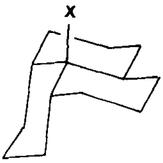
The situation changes considerably with the bulkier *t*-BuO and *t*-Bu substituents. Clearly, the *t*-Bu group produces important strain variations in the substrates under consideration, and it constitutes, therefore, a useful probe for F-strain [12]. On the other hand, it is not an appropriate model for the TsO group. The compounds most affected by F-strain are the bicyclic systems with large bridges, such as bicyclo[3.3.2]decyl (**7**), bicyclo[3.3.3]undecyl (**11**), and the perhydrophenalene derivatives **13** and **14**. Unfortunately, the rate data available for **7** and **11** refer to chlorides only, and it is, therefore, impossible to verify, if the trends predicted by the bulky-leaving-group models are indeed reproduced by experiment. This verification is, however, possible for **13** and **14**. The *trans,trans,trans*-perhydrophenalene derivative **13** is the only substrate of the series showing clearly different response to leaving-group change.

Even with small substituents, such as Cl and OH, **13** shows enhanced strain in comparison to the other substrates (see *Fig. 2*). With CH_3 and CH_3CH_2O the deviation is in the order of 10 kcal/mol. The chloro derivative (**13**-Cl) solvolyzes with the relative rate of 0.06 compared to the *cis-cis-trans*-isomer (**14**-Cl); however, with *p*-nitrobenzoates as leaving group the relative rate of **13**-PNBO is 200 [4]. These tendencies are reproduced by the force-field calculations using the acetate group as model for PNBO *(Scheme)*. The isomer **13** is much more sensitive to F-strain than **14**. Replacement of Cl by AcO increases the strain energy by 7.8 kcal/mol in **13** but reduces strain by 0.5 kcal/mol in **14**. The tendencies for change of relative rate upon changing the leaving group of **13** and **14** are accounted for, if the steric energies of the corresponding carbenium ions relative to that of the substrate (ΔE_{st}) is taken into consideration. It should be noted, however, that **14** itself is also extremely sensitive to F-strain when very bulky leaving-group models are used *(Fig. 2)*.

Scheme



13



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X	Strain	ΔE_{st}(R(+) - RX)	k_{rel}	Strain	ΔE_{st}(R(+) - RX)	k_{rel}
Cl	10.20	- 1.34	0.06	13.13	- 1.77	1
	17.98 a)	- 13.45 a)	200	12.65 a)	- 5.62 a)	1

a) Calc. for ROAc.

The significance of F-strain has been examined by other investigators. *Beckhaus* [12] proposed φ_f parameters as a measure for F-strain of alkyl groups. φ_f Parameters are defined as 'the difference between the heats of formation of the *t*-Bu derivative of R, ΔH_f° [R/C(CH$_3$)$_3$] and those of the Me derivative ΔH_f° [R–CH$_3$]', with $\varphi_f(CH_3) = 0$. φ_f Values (in kJ/mol) have been calculated by *Beckhaus* for **1** (25.7), **2** (34.9), and **8** (40.8), and they confirm our more qualitative observation that **1** should suffer less F-strain than **2** and **8**. Further, these calculated trends are corroborated by experimental observations: the relative rates of hydrolysis of bicyclic bridgehead-substituted esters decreases in the order **1** (8.2) > **3** (4.3) > **2** (2.4) > **5** (1.5) **4** (1.0); in the bicyclic series, the reactivity sequence is **8** (3.1) > **12** (1.65) [13]. The rate variations are small, but they follow the prediction of *Beckhaus*.

Since no experimental rate data for *p*-toluenesulfonate derivatives of the substrates most sensitive to F-strain are available, and since the *p*-toluenesulfonates measured are relatively insensitive to F-strain, we believe that differential F-strain effects should be unimportant in the series (except for **13**) when compared with the steric energy difference

Table 2. *Correlation of Rates of Solvolysis* ($\Delta G^{\neq}$)$_{rel}$ *and* ΔE_{st} (R⊕–RX) *for* p-*Toluenesulfonates and Chlorides.* Data from *Table 1.*

Substrates	No. of compounds	Leaving-group model	Slope	Intercept	r
Chlorides	9	H	0.69	−4.49	0.99
Chlorides	9	Cl	0.58	−2.91	0.98
Chlorides	9	OH	0.63	2.94	0.977
Chlorides	8	CH_3	0.57	−3.25	0.97
Chlorides	8	OCH_2CH_3	0.51	2.00	0.97
p-Toluenesulfonates	7	H	0.77	−5.77	0.996
p-Toluenesulfonates	7	OCH_2CH_3	0.64	2.65	0.97
p-Toluenesulfonates	6	$OC(CH_3)_3$	0.70	7.60	0.98
p-Toluenesulfonates	7	$C(CH_3)_3$	0.69	2.26	0.97
Chlorides and *p*-Toluenesulfonates	14	H	0.71	−4.62	0.997
Chlorides and *p*-Toluenesulfonates	14	Cl	0.66	−2.93	0.989
Chlorides and *p*-Toluenesulfonates	14	OCH_2CH_3	0.59	2.85	0.984

ΔE_{st} between substrate RX and the corresponding carbenium ion R⊕. When ΔE_{st} is calculated for the various leaving-group models and plotted against $\Delta G^{\neq}$ for solvolysis as in *Fig. 1*, correlations of very similar quality are obtained *(Table 2)*. The slopes vary between 0.58 and 0.77 and the correlation coefficients between 0.97 and 0.997. Hydrogen appears to be the best leaving-group model for the combined plot including chlorides and *p*-toluenesulfonates, but Cl or CH_3CH_2O are almost equivalent. *t*-BuO and *t*-Bu give acceptable correlations for *p*-toluenesulfonates. Extension to chlorides was not attempted in view of the calculated results in *Fig. 2*. The insignificance of differential F-strain effects in the series of substrates under investigation led us to propose another explanation for the discrepancy of our results from those of *Bingham* and *v. Schleyer*. Originally, we expected to find it in the carbenium ion force-field. However, after detailed inspection of the data reported by *Bingham* [14], we found that the main source of disagreement is in the strain energies of the bridgehead hydrocarbons. *Bingham*'s 'strain energies' are 'steric energies' according to the definition of *Allinger* [15]. Steric energies

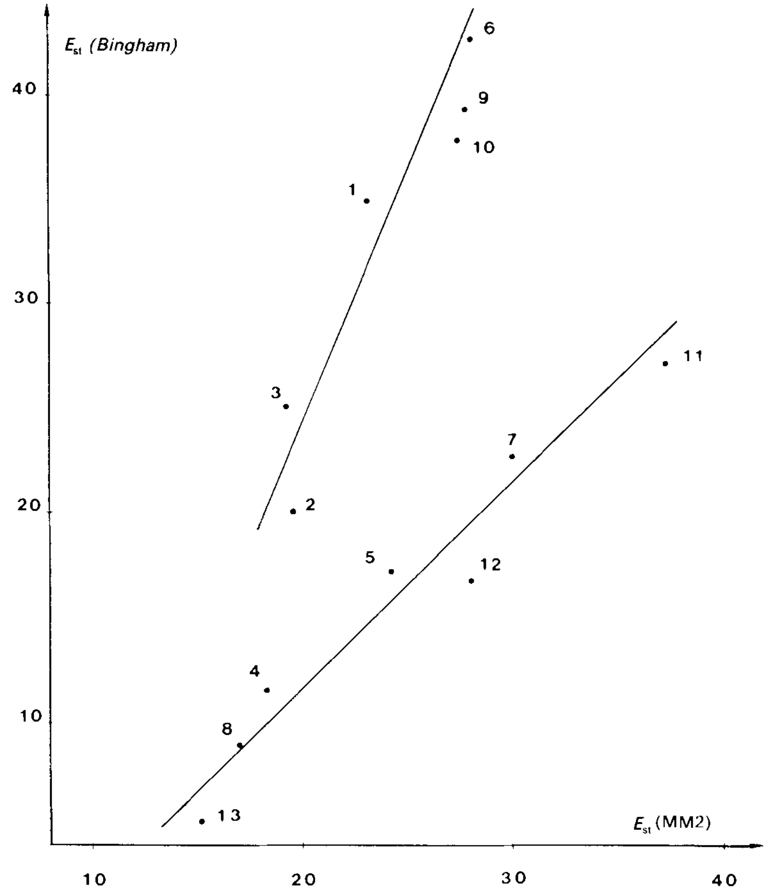

Fig. 3. *Steric energies* (E_{st}) *of bridgehead hydrocarbons calculated with the* Bingham *force-field* vs. E_{st} *calculated by MM2* [kcal/mol]

are relative values and, as such, are of limited applicability. However, since the computational procedure used by *Bingham* is conceptually similar to that of BIGSTRN and MM2, it is legitimate to compare the steric energies E_{st} obtained by the various methods. *Fig. 3* shows E_{st} values of *Bingham vs.* those calculated by MM2. The compounds fall on two clearly distinct lines. One of them contains the very rigid bicyclic and the noradamantyl systems, for which the rates with TsO derivatives have been determined. The other line contains the more flexible structures where the rate constants were measured with chlorides. Thus, a serious discrepancy exists between these methods of calculation. A similar plot (not shown) results if the MM2 data are replaced by those obtained with

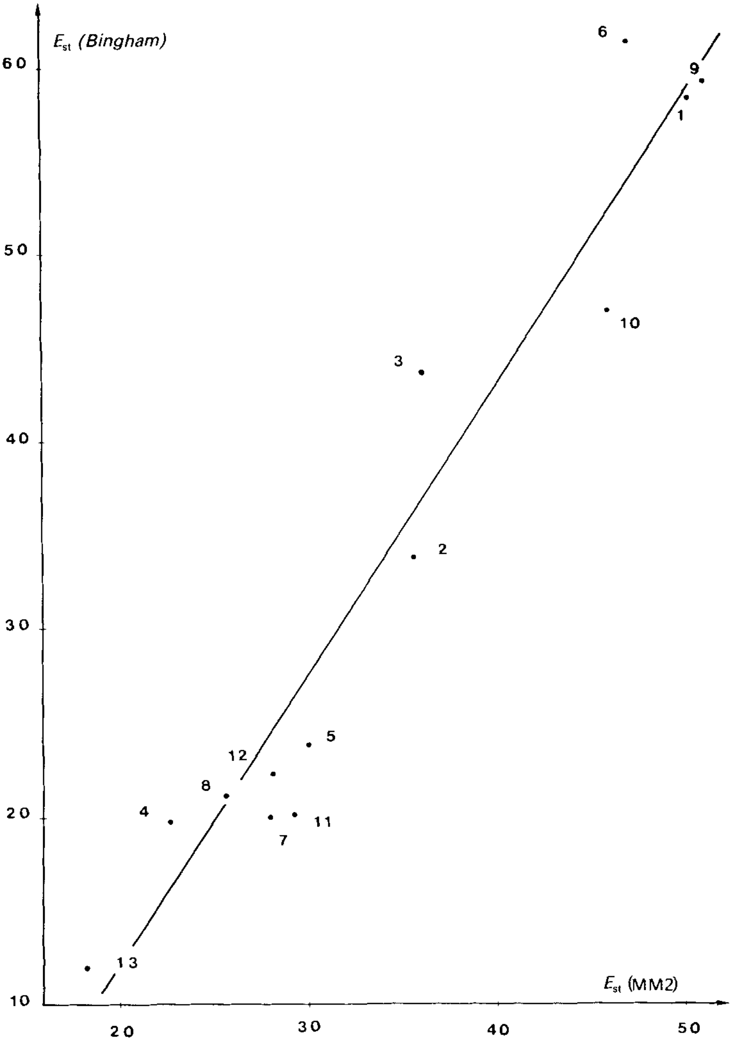

Fig. 4. *Steric energies* (E_{st}) *of bridgehead carbenium ions calculated with the* Bingham *force-field* vs. E_{st} *calculated by MM2* [kcal/mol]

BIGSTRN [10b] [10c]. It is believed that enthalpies of formation of alkanes calculated by BIGSTRN or MM2 are as reliable as those determined experimentally [10b] [16]. Indeed, good agreement exists between experimental and calculated ΔH_f° values for **1**, **2**, **4**, and **8** [15]. For **10**, the numbers are −24.40 kcal/mol (experiment [17]), −23.74 (BIGSTRN [10b]) and −22.06 (MM2). For **11**, the experimental ΔH_f° value of −21.26 kcal/mol [18], while the calculations give −25.21 (BIGSTRN [10b]) and −24.31 (MM2). Although agreement for the latter cases is not perfect, the discrepancies are small compared to those obtained with the *Bingham* force-field [14]. It is, therefore, legitimate to ascribe them to deficiencies of the latter. The molecular mechanics programs developed by *v. Schleyer* underwent successive stages of reparametrization and extension [10b], and the version used by *Bingham* [5] [14] was not meant to be the final one. At the time when it was applied to calculation of bridgehead reactivities, the authors recognized that it was 'not as accurate as the best molecular mechanics program available' [5], and very soon a much more reliable version (*Engler* force-field) was published [10b], and this is the one incorporated in BIGSTRN [10c]. Since *Bingham* and *v. Schleyer* were already aware of the problems concerning their force-field, they focused their attention on the steric energy differences between carbenium ions and the corresponding hydrocarbons rather than on the absolute values of the energies themselves. It was expected that errors in the absolute energies would be diminished or eliminated, when energy differences were considered. The success of the strain reactivity correlation demonstrates that this expectation is, in

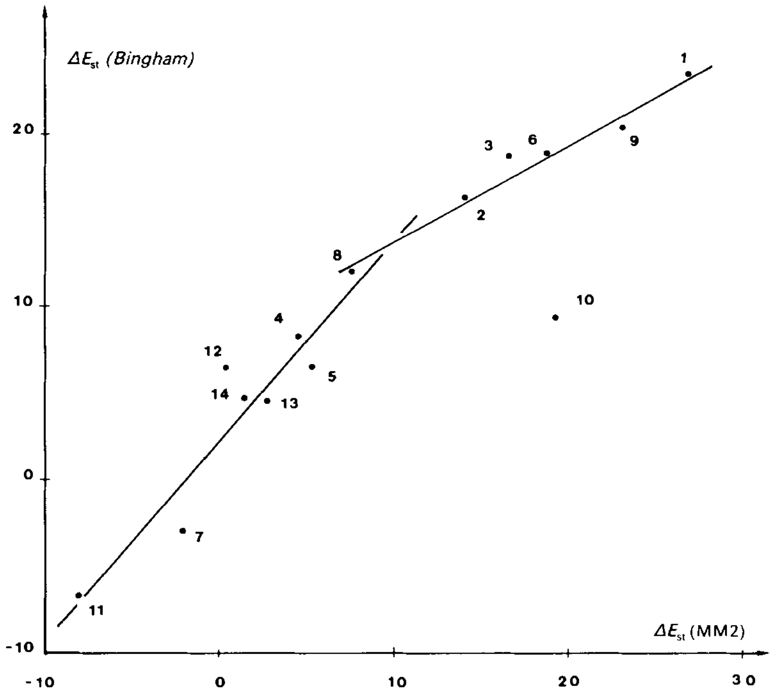

Fig. 5. *Plot of steric energy differences* ΔE_{st} ($R^{\oplus}-R-H$) *calculated with the* Bingham *force-field vs.* ΔE_{st} *calculated by MM2*

principle, justified, but comparison of the E_{st} values of cations calculated with the *Bingham* and MM2 force-fields *(Fig. 4)* show that the situation must be more complex. The methods produce rather similar results; there is scatter in the plot, but the deviations are much less severe than those for hydrocarbons *(Fig. 3)*, and, in particular, no systematic deviations occur. It seems that the discrepancies between the force-fields which become apparent in the calculations of hydrocarbons are substantially diminished when one of the bridgeheads undergoes a change in hybridization from sp^3 to sp^2.

Superposition of plots 3 and 4 is shown in *Fig. 5* which represents ΔE_{st} values obtained by both methods: as in the plot for hydrocarbons, chlorides and TsO derivatives fall on two separate lines. The ratio of the slopes is 2.1, somewhat less than the ratio of 2.3 reported by *Bingham* and *v. Schleyer* for the strain reactivity plot [5]. Similarly, **10** falls on neither of the lines in *Fig. 5*.

Comparison of the ΔE_{st} data immediately raises the question concerning the reliability of the force-fields. Clearly, for calculations of hydrocarbons, MM2 or BIGSTRN are superior to the *Bingham* program. For carbenium ions, the situation is more involved. For the time being, we restrict ourselves to the observation that the MM2 force-field reproduces the solvolysis reactivities of bridgehead derivatives very well. Results obtained with *Bingham*'s force-field for carbenium ions may be criticized, since it is based on an inadequate parametrization for hydrocarbons. Unfortunately, to the best of our knowledge, no systematic study of bridgehead carbenium ions with BIGSTRN has ever been made, so that direct comparison with MM2 is impossible. Thus, we have yet to show that our force-field is really reliable and generally applicable. A more detailed study of this question is in progress.

With this restriction, it is possible to comment on the comportment of the perhydrotriquinacene derivative **10**. It falls drastically out of the correlation of ΔE_{st} *vs.* rates of solvolysis with the *Bingham* force-field [5]. This deviation was explained by absence of stabilizing C,C-hyperconjugation in the cation derived from **10**, while all other cations of the series would benefit from C,C-hyperconjugation for reasons of favorable geometric arrangement of C–C bonds. However, our analysis shows that the deviation of **10** is rather due to overestimation of strain in the substrate rather than an underestimation of energy in the cation, as originally suggested. In the MM2 calculations, **10** behaves normally *(Fig. 1)*, and for the time being there appears to be no reason to invoke any particular phenomena.

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