

# Solvolysis of isodrin derivatives. Evidence of long-range $\sigma$ -participation in the stabilization of carbocations

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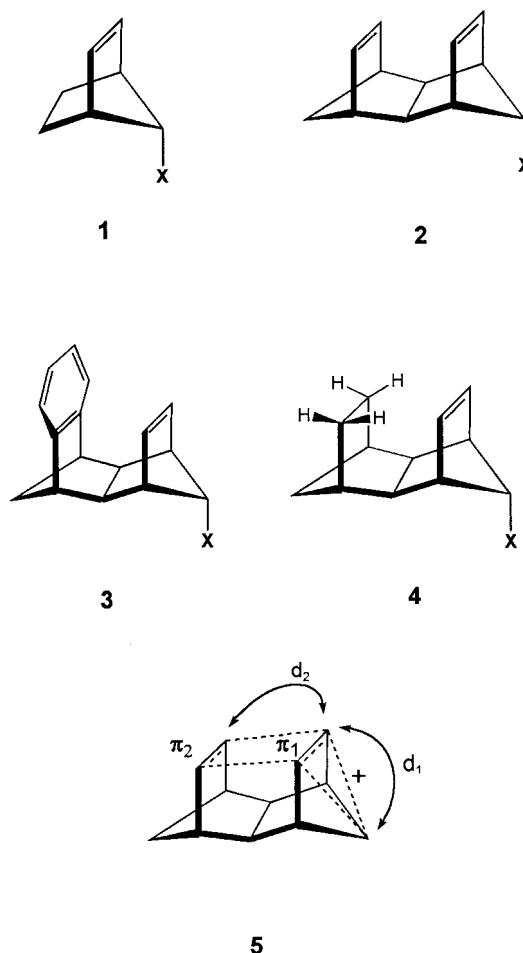
**ABSTRACT:** Enhanced rates of solvolysis have been reported for some isodrin derivatives, e.g. compounds **2**, **3**, **6** and **7** compared with *anti*-7-norbornene (**1**). The effect has been ascribed to the formation of laticyclic (2 + 2 + 0)  $\pi$ -delocalization on a carbocation such as **5**. However, comparable rates of solvolysis were also observed for analogous monoenes **4**, **8**, **9** and **12**, where no adequate explanation has been provided. Molecular modeling at both semiempirical and *ab initio* levels shows a good correlation between the stabilization energy of the cations and their kinetic data. The enhanced rate of solvolysis for **4**, **8**, **9** and **12** can be rationalized by strong effects of  $\sigma$ -bond participation in the transition state. For both series of compounds, the stabilization effect can be effectively transmitted either through space or through bonds. © 1998 John Wiley & Sons, Ltd.

**KEYWORDS:** laticyclic hyperconjugation; isodrin; solvolysis; through-bond and through-space interactions

## INTRODUCTION

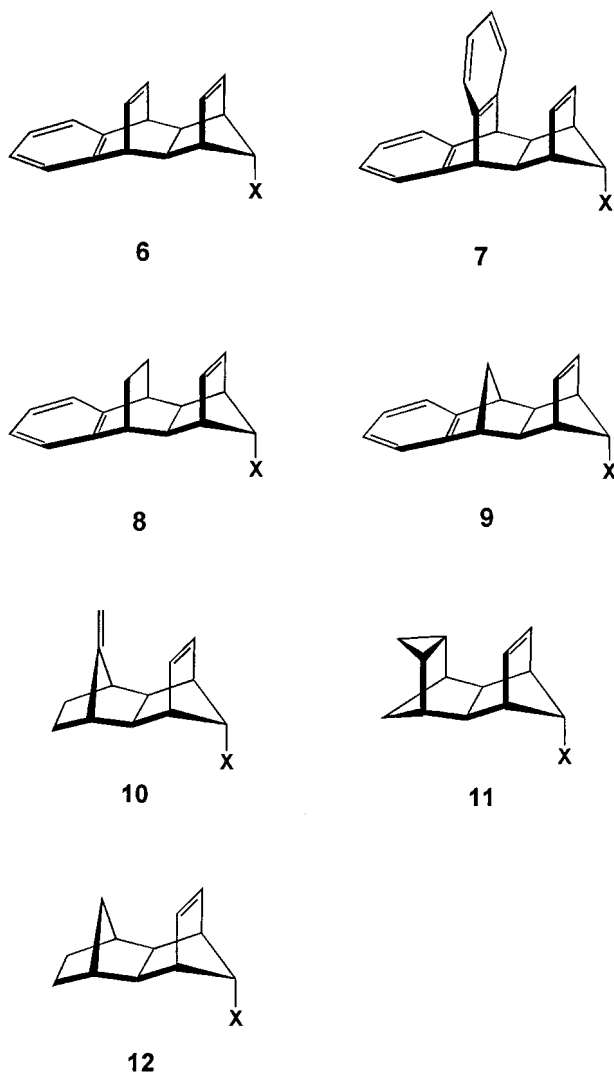
The  $10^{11}$ -fold rate enhancement for the solvolysis of *anti*-7-norbornene (**1**) compared with that of norbornane has been ascribed to the formation of a non-classical carbon cation.<sup>1</sup> In 1968, Allred and Hinshaw<sup>2</sup> reported that the solvolysis rate of **2** showed a further  $10^2$ – $10^3$ -fold enhancement compared with that of **1**. The effect was rationalized by the formation of a cationic intermediate, such as **5**, in which the charge was delocalized through space over two double bonds ( $\pi_1$  and  $\pi_2$ ).<sup>3</sup> The structure has been classified as one of the laticyclic (2 + 2 + 0) system stabilized by  $4\pi$  electrons.<sup>3,4</sup> Although the concept of a non-classical carbocation in the solvolysis of 7-norbornenyl derivatives has been recognized in general,<sup>5</sup> the effectiveness of electron delocalization on an extended system such as **5** remains unclear.

For the partially saturated monoene **4**, the solvolysis rate is expected to be significantly slower than that of **2**, and about the same as that of **1**. In fact, the observed rate for **4** is close to that of **2** within a factor of *ca* 2.<sup>6</sup> This result suggests uncertainty regarding the existence of **5**. Allred *et al.*<sup>6</sup> ascribed the enhanced rate of **4** to steric reasons. However, Paquette and Dunkin<sup>7</sup> measured the solvolysis of **6–9** and concluded that all the doubly bridged compounds such as **2**, **4** and **6–9** received



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essentially the same amount of stabilization from the  $\pi_1$ -orbitals as that of **1** (leveling effect). Any stabilization effect derived from the second bridge ( $\pi_2$  or  $-\text{CH}_2\text{CH}_2-$ ) was therefore rendered insignificant.


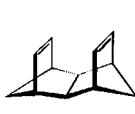


Our previous studies indicated that  $\sigma$ -orbitals may play a significant role in the stabilization of carbocations.<sup>8</sup> The  $\sigma$ -bondings in polycyclic hydrocarbons mixed with each other more extensively than linear molecules owing to their structural complexity.<sup>9</sup> More and more evidence has been obtained in recent years showing that the  $\sigma$ -bonds in polycyclic compounds can alter their chemical behaviors.<sup>10,11</sup> Our continuing interest in this field prompted us to reinvestigate the nature of the solvolysis processes of these isodrin derivatives. The details of our analysis are described here.

## RESULTS AND DISCUSSION

### Relative stability among the cations

The heats of formation for structures **2–12** ( $X = \text{Cl}$ ) and the corresponding cations were calculated by semiempirical models AM1<sup>12</sup> and PM3<sup>13</sup> implanted in MOPAC 6.0<sup>14</sup> and by the *ab initio* method<sup>15</sup> implanted in SPARTAN.<sup>16</sup> From these data, the heats of reaction ( $\Delta H_d$ ) for  $\text{R}-\text{Cl} \rightarrow \text{R}^+ + \text{Cl}^-$  were obtained as shown in Tables 1, 2 and 3. The relative magnitude of  $\Delta H_d$  corresponds to the enthalpies of heterolytic dissociations in the gas phase. The  $\Delta H_d$  value for  $\text{1-Cl} \rightarrow \text{1}^+ + \text{Cl}^-$  is used as a standard ( $\Delta\Delta H_d = 0$ ), while the dissociation energies of other compounds are expressed as differences ( $\Delta\Delta H_d$ ) from that of **1**. The more negative the  $\Delta\Delta H_d$

**Table 1.** Calculated thermodynamic and structural parameters for compounds **1**, **2**, **3** and **4** ( $X = \text{Cl}$ ) and their cations (all structures are fully optimized; units of  $\Delta H$  are  $\text{kcal mol}^{-1}$ )

	 <b>1-Cl/1<sup>+</sup></b>	 <b>2-Cl/2<sup>+</sup></b>	 <b>3-Cl/3<sup>+</sup></b>	 <b>4-Cl/4<sup>+</sup></b>
$\Delta H_f^a$ (AM1)	19.5/255.2	76.7/308.8	85.4/315.8	38.4/270.0
$\Delta H_d^b$ (AM1)	176.9	173.3	171.6	172.6
$\Delta\Delta H_d^c$ (AM1)	0.0	-3.6	-5.3	-4.3
$\Delta H_f^a$ (PM3)	17.8/255.5	67.8/301.3	76.0/307.9	33.7/266.4
$\Delta H_d^b$ (PM3)	178.9	174.7	173.1	174.2
$\Delta\Delta H_d^c$ (PM3)	0.0	-4.2	-5.8	-4.7
$\Delta H_d^b$ (HF/3-21G)	159.1	148.7	144.2	148.9
$\Delta\Delta H_d^c$ (HF/3-21G)	0.0	-10.4	-14.9	-10.2
Rel. rate solv.	1	200 <sup>d</sup>	380 <sup>e</sup>	130 <sup>f</sup>

<sup>a</sup> Standard heat of formation.

<sup>b</sup> Standard heat of dissociation for  $\text{R}-\text{Cl} \rightarrow \text{R}^+ + \text{Cl}^-$ .

<sup>c</sup> Relative  $\Delta H_d$  values with respect to that of **1**.

<sup>d</sup> At 100 °C in 80% aq. acetone (Ref. 7).

<sup>e</sup> At 110 °C in 80% aq. dioxane (Ref. 8).

<sup>f</sup> At 85 °C in 80% aq. dioxane (Ref. 6).

**Table 2.** Calculated thermodynamic parameters for compounds **6**, **7**, **8** and **9** (X = Cl) and their cations (units of  $\Delta H$  are kcal mol<sup>-1</sup>)

	6-Cl/6 <sup>+</sup>	7-Cl/7 <sup>+</sup>	8-Cl/8 <sup>+</sup>	9-Cl/9 <sup>+</sup>
$\Delta H_f^a$ (AM1)	88.4/320.6	97.7/328.5	55.3/287.0	81.8/314.3
$\Delta H_d^b$ (AM1)	173.4	172.0	172.8	173.7
$\Delta\Delta H_d^c$ (AM1)	-3.5	-4.9	-4.1	-3.2
$\Delta H_f^a$ (PM3)	82.1/316.0	90.1/322.6	52.9/285.9	71.8/306.0
$\Delta H_d^b$ (PM3)	175.0	173.7	174.2	175.4
$\Delta\Delta H_d^c$ (PM3)	-3.9	-5.2	-4.7	-3.5
Rel. rate solv. <sup>d</sup>	350	417	380	170

<sup>a-d</sup> See Table 1.**Table 3.** Calculated thermodynamic parameters for compounds **10**, **11** and **12** (X = Cl) and their cations (units of  $\Delta H$  are kcal mol<sup>-1</sup>)

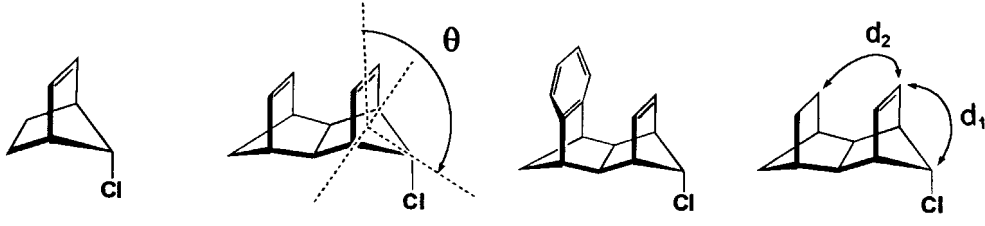
	2-Cl/2 <sup>+</sup>	10-Cl/10 <sup>+</sup>	11-Cl/11 <sup>+</sup>	12-Cl/12 <sup>+</sup>
$\Delta H_f^a$ (AM1)	76.7/308.8	59.4/291.7	81.6/313.1	33.2/265.6
$\Delta H_d^b$ (AM1)	173.3	173.2	172.7	173.6
$\Delta\Delta H_d^c$ (AM1)	-3.6	-3.7	-4.2	-3.3
$\Delta H_f^a$ (PM3)	67.8/301.3	52.1/286.0	71.8/304.9	28.6/262.5
$\Delta H_d^b$ (PM3)	174.7	175.1	174.3	175.2
$\Delta\Delta H_d^c$ (PM3)	-4.2	-3.8	-4.6	-3.7
Rel. rate solv. <sup>d</sup>	160	30	480	28

<sup>a-c</sup> See Table 1.<sup>d</sup> At 100 °C in 80% aq. dioxane (Ref. 19a).

value for a compound is, the more stable is the corresponding cation. It is interesting to find that the calculated values of  $\Delta\Delta H_d$  for **2**, **3** and **4** are all smaller than that of **1** (negative values). The relative magnitudes are also consistent with their relative rates of solvolysis (Table 1). The calculated  $\Delta\Delta H_d$  values by the *ab initio* method with the 3-21G basis set for **1**, **2** and **3** are 0.0, -10.4 and -14.9 kcal mol<sup>-1</sup>, respectively, whereas their observed relative rates of solvolysis are 1, 200 and 380, respectively. In a preliminary communication we showed that both semiempirical models AM1 and PM3 also gave reasonable predictions for these compounds.<sup>8</sup> The  $\Delta\Delta H_d$  values for **2** and **3** calculated by AM1 are -3.6 and -5.3 kcal mol<sup>-1</sup> and those calculated by PM3 are -4.2 and -5.8 kcal mol<sup>-1</sup>, respectively. It is logical for the benzene ring ( $\pi_2$ ) of **3** to give a better stabilization effect than the double bond of **2**, since the interaction between  $\pi_1$  and  $\pi_2$  is expected to be stronger for the former.

It seems that the calculated  $\Delta\Delta H_d$  values are somewhat overestimated by the *ab initio* model than those estimated by semiempirical models.<sup>17</sup> However, one should realize that the solvolysis data presented in the literature are mostly kinetic parameters obtained under chosen conditions, e.g. in different solvents at certain temperatures. The rate of solvolysis (a kinetic parameter) may not correspond quantitatively to the energy of the cations (a thermodynamic parameter). A comparison in relative terms should be more meaningful according to Hammond's postulate.<sup>18</sup>

It is most surprising to learn that the  $\Delta\Delta H_d$  value of **4** is estimated to be close to that of **2**, i.e. -4.3 kcal mol<sup>-1</sup> by AM1, -4.7 kcal mol<sup>-1</sup> by PM3 and -10.2 kcal mol<sup>-1</sup> by HF/3-21G. The previously 'unexpected' high rate of solvolysis is correctly predicted by all three theoretical models. The kinetic behavior of **4** therefore can be rationalized by the relative stability of cation **4**<sup>+</sup>.

**Table 4.** *Ab initio* (HF/3-21G) optimized geometrical parameters for compounds **1**, **2**, **3** and **4** (X = Cl) and their cations


	1-Cl/1 <sup>+</sup>	2-Cl/2 <sup>+</sup>	3-Cl/3 <sup>+</sup>	4-Cl/4 <sup>+</sup>
$d_1$ (Å) (HF/3-21G)	2.32/1.94	2.30/1.88	2.30/1.87	2.30/1.89
$d_1$ (Å) (AM1)	2.35/2.23	2.33/2.17	2.33/2.16	2.33/2.16
$d_2$ (Å) (HF/3-21G)		2.91/2.91	2.88/2.76	3.00/2.96
$d_2$ (Å) (AM1)		2.70/2.71	2.76/2.74	2.94/2.94
$\theta$ (°) (HF/3-21G)	125/96	122/92	122/91	122/92

### Calculations on related systems

The calculations were applied to other analogous systems in order to ensure that the situation which appeared between **2** and **4** was not merely an isolated special case. The solvolysis rate of **8** (380 vs **2**) has been shown to be slightly faster than that of **6** (350 vs **2**), and the calculations give a consistent estimation.<sup>7</sup> The  $\Delta\Delta H_d$  values for **8** are  $-4.1$  kcal mol<sup>-1</sup> calculated by AM1 and  $-4.7$  kcal mol<sup>-1</sup> by PM3, and those for **6** are  $-3.5$  kcal mol<sup>-1</sup> by AM1 and  $-3.9$  kcal mol<sup>-1</sup> by PM3 (Table 2). Both models again predicted that the benzo-fused derivative **7** should be solvolyzed faster than **6** and **8**. The  $\Delta\Delta H_d$  values for **7** are  $-4.9$  kcal mol<sup>-1</sup> (AM1) and  $-5.2$  kcal mol<sup>-1</sup> (PM3), while its solvolysis rate showed a high value of 417 times that of **2**. The order of reactivity among **6**, **7** and **8** agrees with that among **2**, **3** and **4**.

A recent measurement on the solvolysis of compound **11**, in which a cyclopropyl group is attached on the second bridge, showed a rate enhancement with respect to **2** (Table 3).<sup>19</sup> The estimated  $\Delta\Delta H_d$  values ( $-4.2$  kcal mol<sup>-1</sup> by AM1 and  $-4.6$  kcal mol<sup>-1</sup> by PM3) give a proper prediction of its kinetic behavior (480-fold vs **1**). In the same report, Lloyd and co-workers<sup>19</sup> recorded the rate data for compounds **9** (Table 2), **10** and **12** (Table 3), which represent a different ring skeleton to those of **2** and **6**. The remote  $\pi$ -bridge ( $\pi_2$ ) of **10** is oriented perpendicularly to  $\pi_1$ , thus changing the orbital interaction between the two bridges.<sup>20</sup> However, no comment was offered on the origin that caused the rate

enhancement. In our calculations, cation **10**<sup>+</sup> is shown to be more stable than **1**<sup>+</sup>, which is consistent with rate measurements where the reactivity of **10** was found to be 30 times that of **1**. For **9** and **12**, the calculated  $\Delta\Delta H_d$  values are close to that of **10** even in the absence of the  $\pi_2$  moiety (Table 3). A comparison between **10** and **12** reaffirmed the phenomenon that the  $\pi_2$ -orbital is not the only factor capable of promoting the stability of the cation. A saturated hydrocarbon bridge, i.e.  $-\text{CH}_2-$  or  $-\text{CH}_2\text{CH}_2-$ , can supply a similar stabilizing effect.

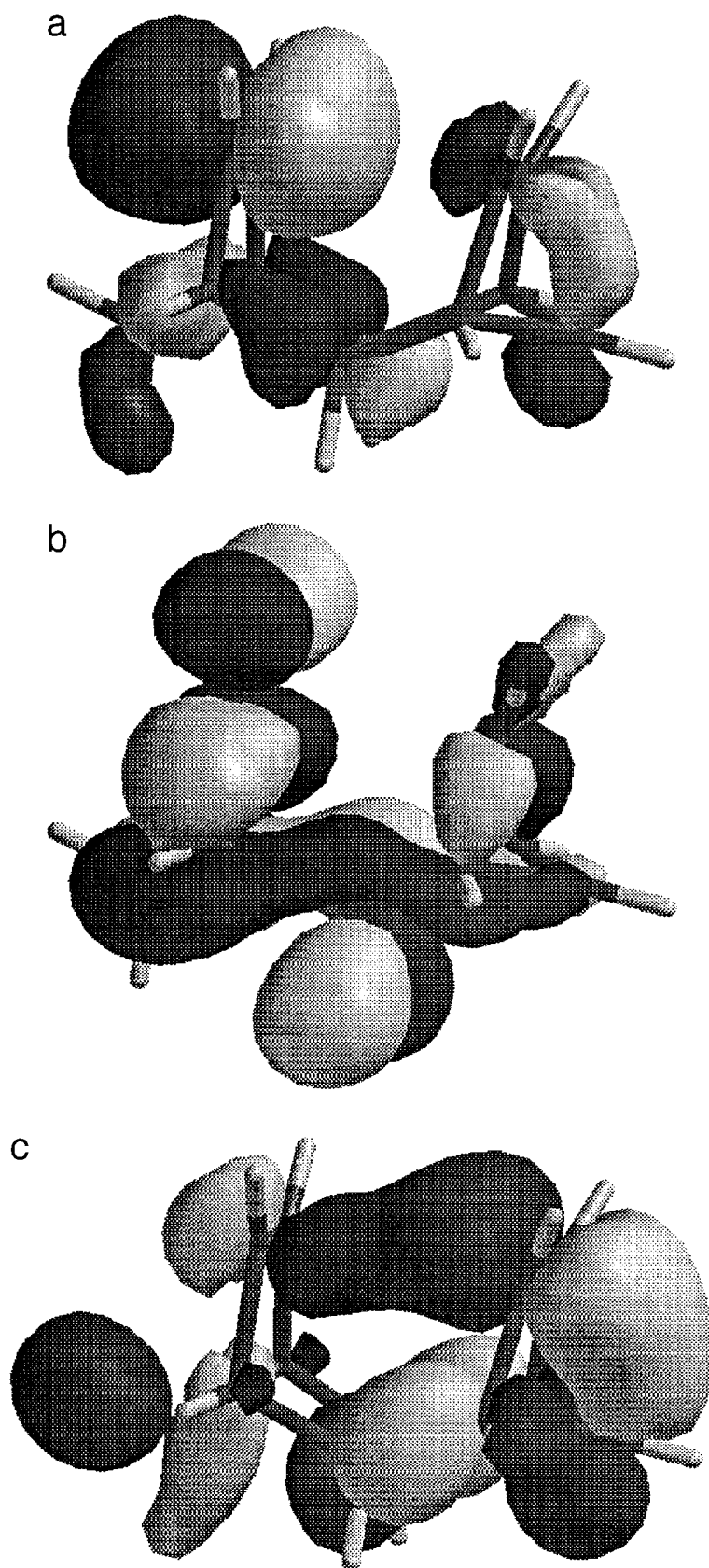
### Structural effects

From the above analyses, we can draw the following two conclusions: (1) the rate enhancement of solvolysis can be ascribed to the stability of the cations; and (2) the addition of an extended hydrocarbon bridge to the structure of **1**, whether it is saturated or not, contributes to the stability of the corresponding cation with respect to **1**<sup>+</sup>.

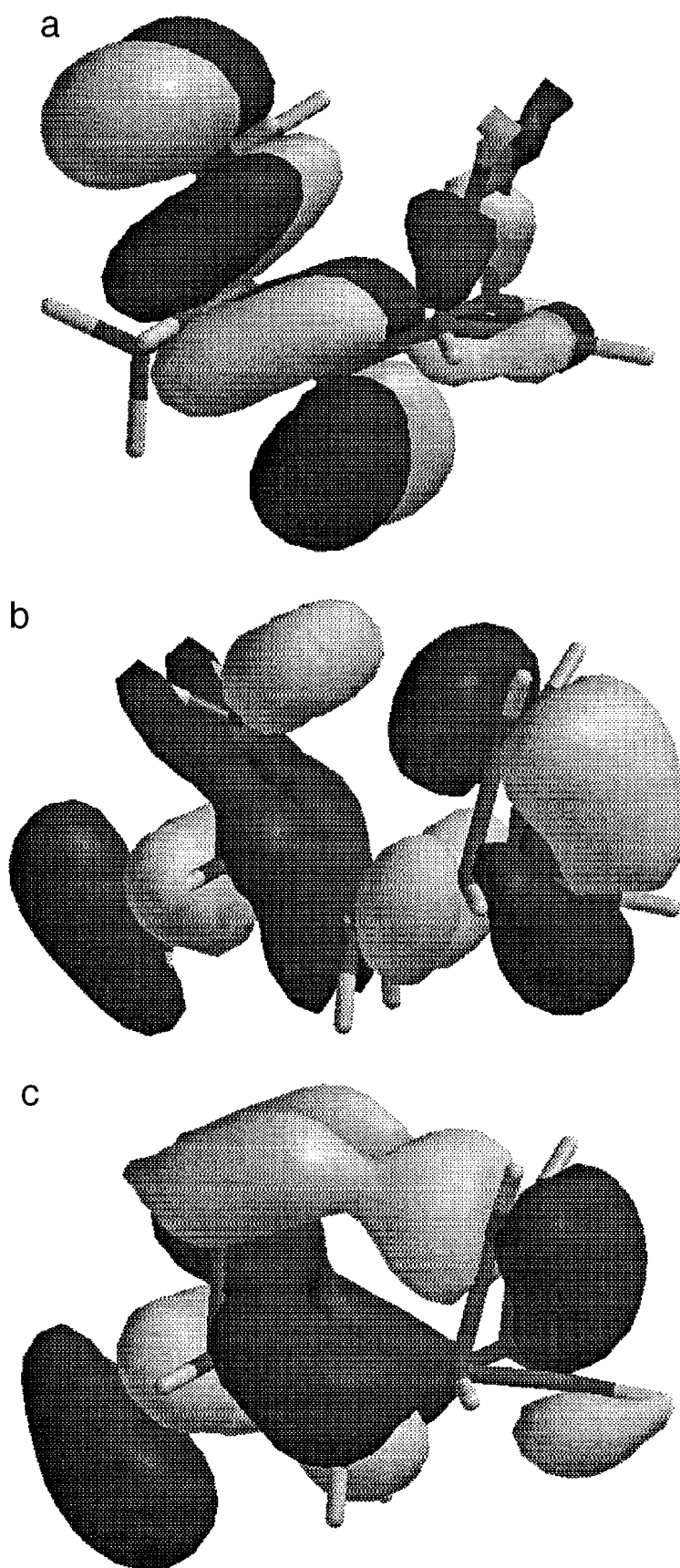
Earlier studies on the diene system (e.g. **2** and **3**) showed that the p-orbitals of  $\pi_1$  and  $\pi_2$  are located so close to each other that they inevitably overlap through space.<sup>21</sup> The  $(\pi_1 - \pi_2)$  and  $(\pi_1 + \pi_2)$  energy splitting calculated for **2** is 1.8 eV (see Table 5). In other words, the energy level of  $\pi_1$  is perturbed by the presence of  $\pi_2$ . If we agree with the concept of a 'non-classical carbocation' which exists in the solvolysis of **2**,<sup>1,22</sup> we

**Table 5.** *Ab initio* (HF/3-21G) optimized eigenvalues (eV) of selected molecular orbitals for **2** and **4** and their cations

Species	HOMO	HOMO-1	HOMO-2	HOMO-6
<b>2</b> -Cl	$-8.4$ ( $\pi_1 - \pi_2$ )	$-10.2$ ( $\pi_1 + \pi_2$ )	$-11.02$ ( $\sigma$ )	—
<b>2</b> <sup>+</sup>	$-12.7$ ( $\pi_1 - \pi_2$ )	$-15.4$ ( $\sigma$ )	$-16.0$ ( $\pi_1 + \pi_2$ )	—
<b>4</b> -Cl	$-9.4$ ( $\pi$ )	$-10.9$ ( $\sigma$ )	—	—
<b>4</b> <sup>+</sup>	$-15.1$ ( $\sigma$ )	$-15.2$ ( $\pi - \sigma$ )	—	$-17.1$ ( $\pi + \sigma$ )



**Figure 1.** Drawings of selected MOs of  $2^+$  which are fully optimized by the *ab initio* method at the HF/3-21G level using the software SPARTAN. (a) HOMO composed of  $(\pi_1 - \pi_2)$  with eigenvalue  $-12.7$  eV; (b) HOMO-1 composed of  $\sigma$  orbitals with eigenvalue  $-15.4$  eV; (c) HOMO-2 composed of  $(\pi_1 + \pi_2)$  with eigenvalue  $-16.0$  eV.



**Figure 2.** Drawings of MOs of  $4^+$  fully optimized by the *ab initio* method at the HF/3-21G level using the software SPARTAN. (a) HOMO composed of  $\sigma$  orbitals with eigenvalue  $-15.1$  eV; (b) HOMO-1 composed of  $(\pi_1 - \sigma)$  with eigenvalue  $-15.2$  eV; (c) HOMO-6 composed of  $(\pi_1 + \sigma)$  with eigenvalue  $-17.1$  eV. For three orbitals the contributions from  $\sigma$  orbitals are clearly shown.

have to accept the idea that changing the energy of  $\pi_1$  (perturbed by  $\pi_2$ ) must have a noticeable influence on the potential energy of the cations (i.e.  $2^+$  and  $3^+$ ). The presumed 'leveling effect' which totally ignored the influence of  $\pi_2$  does not comply with the observation that all the compounds that we have analyzed show significantly faster rates than norbornene (**1**).<sup>6,7</sup> However, the question waiting to be answered is how the saturated hydrocarbon bridges of the monoenes (e.g. **4**, **8**, **9** and **12**) interact effectively with the cationic center.

Allred *et al.*<sup>6</sup> proposed a solution to this question. It seems likely that the saturated  $-\text{CH}_2\text{CH}_2-$  bridge of **4** may apply a greater steric compression to  $\pi_1$  owing to the addition of two *endo* hydrogen atoms between the bridges. Consequently, the distance between  $\pi_1$  and the cationic center ( $d_1$ ) of  $4^+$  is shorter than that of  $2^+$  (and  $1^+$ ), which implies a better orbital overlapping toward the formation of three-centered bonding (non-classical carbocation). Cation  $4^+$  is therefore better stabilized than  $1^+$ . This proposal has been examined by a deuterium isotope experimental though its reliability has been questioned by Lloyd and co-workers.<sup>19,20</sup>

The subtle changes of  $d_1$  and  $d_2$  during solvolysis may be difficult to measure accurately by experiments, but can be envisioned more precisely by theoretical models. A structural analysis was performed for the chlorides **1–4** and their cations. In Table 4 the values of  $d_1$  (distance between  $\pi_1$  and the cationic center),  $d_2$  (distance between  $\pi_1$  and  $\pi_2$ ) and the dihedral angles  $\theta$  (as indicated in the table) are listed. Upon forming the cation, the  $d_1$  of **1** is reduced as a result of  $\pi_1$  delocalization toward the empty p orbital. The *ab initio* method gave a larger degree of structural change than that predicted by AM1, e.g. the  $d_1$  for  $1^+$  estimated by 3–21G is 1.94 Å ( $\Delta d_1 = 0.38$  Å cp. **1**-Cl) compared with 2.23 Å ( $\Delta d_1 = 0.12$  Å cp. **1**-Cl) by AM1. The larger values of  $\Delta d_1$  and  $\Delta\theta$  values are natural consequences derived from a larger  $\Delta\Delta H_d$  estimated by the *ab initio* model.

The amount of reduction of  $d_1$  in **2** is expected to be larger than that of **1**, i.e. 2.30/1.88 Å (3–21G) for **2**-Cl/ $2^+$  compared with 2.32/1.94 Å for **1**-Cl/ $1^+$ , as a result of stronger interaction among the  $\pi$  orbitals. The  $d_1$  values of **3**, i.e. 2.30/1.87 Å (HF/3–21G), are close to those of **2**, as expected. The change in  $d_1$  values of **4** should be noticeably greater than that of **2** if Allred *et al.* hypothesis is correct since the  $-\text{CH}_2\text{CH}_2-$  bridge of the former would apply a greater strain on  $\pi_1$  than does the  $-\text{CH}=\text{CH}-$  bridge ( $\pi_2$ ) of the latter. However, the observed  $d_1$  values of **4** (2.30/1.89 Å, 3–21G) are nearly equal to those of **2**.

The  $d_2$  values of **2**, **3** and **4** did not change much during the formation of cations as predicted by both the AM1 and *ab initio* methods (Table 4) since the two bridges are already tightly packed side by side.<sup>21</sup> The change in dihedral angle ( $\Delta\theta$ ) for all four compounds **1**, **2**, **3** and **4** is about 30° (122°/92° by 3–21G), which indicates that  $\pi_1$  is tilted toward the cationic center. No apparent difference

was observed in  $\Delta\theta$  between **2** and **4**. From this information, one can conclude that the rate of solvolysis of **4** is not related to the steric strain between  $\pi_1$  and  $\pi_2$ .

### Extended orbital interactions

Table 5 shows the calculated (HF/3–21G) eigenvalues of some selected molecular orbitals (MO) for **2** and **4** and their cations.<sup>16</sup> The corresponding drawings of the MOs are shown in Figs 1 and 2. In Fig. 1 it can be seen that the HOMO of  $2^+$  is an out-of-phase ( $\pi_1 - \pi_2$ ) combination of the two  $\pi$  orbitals, whereas the HOMO-2 belongs to the in-phase ( $\pi_1 + \pi_2$ ) one. In both orbitals the  $\pi$  electrons are shown to have delocalized across the bridges toward the empty p orbital at the center of solvolysis. The energy splitting between the two orbital of  $2^+$  is 3.3 eV, a separation larger than that between the HOMO and HOMO-1 (1.8 eV) of **2**-Cl before solvolysis. The energy level of HOMO-2 of  $2^+$  (–16.0 eV,  $\pi_1 + \pi_2$ ) is depressed so much that it goes below the level of a  $\sigma$  combination (–15.4 eV, HOMO-1). The in-phase combination ( $\pi_1 + \pi_2$ ) may be regarded as a representation of the so-called laticyclic ( $2 + 2 + 0$ ) homoconjugation.<sup>4</sup>

The energy level of  $\pi$ -orbital of  $4^+$  is also considerably lower than that of **4**. Upon forming cations, the energy level of  $\pi$  orbitals approximates that of  $\sigma$  orbitals, and the interaction between the two becomes stronger. In Fig. 2 the orbitals representing ( $\pi - \sigma$ ) (HOMO-1, **4b**) and ( $\pi + \sigma$ ) (HOMO-6, **4c**) are shown, in which the mixing of  $\text{C}-\text{H}$  bonds (on  $-\text{CH}_2\text{CH}_2-$  bridge) with  $\pi_1$  is apparent. In addition to the bridge atoms, there are considerable involvements of other  $\sigma$ -bonds (both  $\sigma_{\text{C}-\text{C}}$  and  $\sigma_{\text{C}-\text{H}}$ ) in these high-lying orbitals. The interactions may be divided into two types: the 'through-space' type, which appears as direct overlap of orbitals across the bridges, and the 'through-bond' type, which is composed of  $\sigma_{\text{C}-\text{C}}$  and  $\text{C}-\text{H}$  orbitals other than those bridge atoms.<sup>23</sup> Both types contribute to the stabilization of the cation, and in Figs 1 and 2 it seems that through-bond interaction is more emphasized in  $4^+$  than in  $2^+$ . Therefore, one can conclude that the *endo*- $\sigma_{\text{C}-\text{H}}$  bonds of  $4^+$  do provide an assisting effect for the solvolysis of **4** through electron delocalization.<sup>24</sup> A quantitative estimation of the amount of stabilization, both through-bond and through-space, may be obtained reliably by theoretical models.

### CONCLUSION

The rate enhancements for the solvolysis of **2–4** and **6–12** with respect to that of **1** can be ascribed to two types of orbital interactions. The first type of interaction is transmitted 'through space,' which appears by direct overlap of orbitals across the two bridges. The  $\pi_1$ - $\pi_2$  interaction of this type in **2**, **3**, **6**, **7**, **10** and **11** is the major cause of enhanced stability among the cations. Direct

orbital overlap between  $\pi_1$  and the *endo*- $\sigma_{C-H}$  bonds of the  $-\text{CH}_2\text{CH}_2-$  bridge of **4**, **8**, **9** and **12** also occurs, but to a lesser extent. The second type of interaction is transmitted 'through bonds,' which may be regarded as a long-range inductive effect. The cations of **4**, **8**, **9** and **12** are stabilized by  $\pi_1$  through space (non-classical carbocation) and by  $\sigma$ -bonds mainly through bonds. Both *ab initio* and semiempirical models can provide good estimations of the overall effect induced by each type of orbital interaction.

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