The Historic Camphenyl Cation: A Detailed Structure Evaluation Including Solvation Energy Calculations

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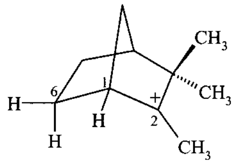
The structure of the camphenyl cation **1** has been studied in detail, using both experimental and computational approaches. Like others, we find only one structure on the camphenyl−isobornyl cation PE surface, but this single structure shows some unusual features. These include a very soft PE surface for movement along the C2−C6 axis (a nonbonding distance in a classical description of the cation), and a result of this is that very high computational methods (optimization at MP4 or QCI levels) are required in order to get structural minima that “fit” the experimental data. This PE surface has been probed computationally using fixed C2−C6 distances, and when one also calculates chemical shifts for these “fixed” structures, one sees calculated ^{13}C NMR chemical shifts for the C2 carbon that are hugely dependent on this fixed distance value, giving near-linear slopes of ca. 25 ppm/0.1 Å distance change. Since this distance can vary over at least 0.6 Å with relatively small calculated energy changes, there is a total range of ca. 150 ppm involved here. In a second part of this work, and in response to a recent paper in which the historic Meerwein “carbocation intermediate” proposal was rejected, we have calculated solvation energies (SCI-PCM method) for four carbocation systems, including **1**. We find carbocation solvation energies ($\epsilon = 10$ “solvent”) of 45−53 kcal/mol, and where comparison can be made, the data correlate well with the literature. On the basis of these results, we re-affirm the Meerwein “carbocation” mechanism, but in order to accommodate only a single carbocation intermediate, we offer a description that amounts to a subtle variation of both the nonclassical ion proposal and Meerwein’s “two cation” mechanism, namely that the camphenyl cation, **1**, as a ground-state structure, can be described as only very weakly interacting in the C2−C6 bridging sense, but that the PE surface along this “bond” is so shallow that an energy input of only 4−6 kcal/mol can produce a bridged “structure”. This mechanism explains the preferred formation of exo products in both the camphenyl and isobornyl systems, isotopic exchange of chloride in camphenyl chloride, and it allows for partial racemization of the camphenyl−isobornyl products in the reaction.

The camphenyl (camphenehydro) cation **1** has a hallowed position in the history of organic chemistry, as nicely summarized by Brown in a 1979 review article,[1] “..., Hans Meerwein published a paper ‘Uber die Gleichgewichts-Isomerie zwischen Bornylchlorid, Isobornylchlorid and Camphen-Chlorhydrat’, which had immense consequences for the development of physical organic chemistry. The paper contains the first proposal of carbonium ions as intermediates in molecular rearrangements. It also provided the basis for the later proposal of a nonclassical ion as an intermediate, ...”.

In this 1922 paper,[2] Meerwein and van Emster showed that the rate of rearrangement of camphenyl chloride (camphene hydrochloride) **2** into isobornyl chloride **3** increased with increasing polarity of the solvent used in this solution-phase rearrangement. The actual skeletal rearrangement was pictured as shown in Figure 1, i.e., a cation → cation rearrangement prior to recapture of the Cl⁻ anion.



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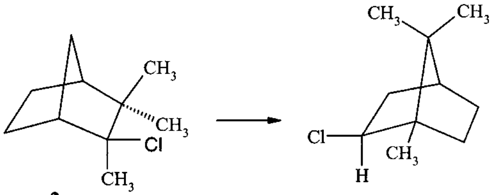

2 **3**

The second historical feature of the camphenyl cation, referred to by Brown, has been its postulated mesomeric nature (the first nonclassical cation) as proposed in a 1939 paper by Wilson et al.[3] (see Figure 1). This mesomeric formulation (1939) has also been attributed to Ingold.[4,5]

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[1] Brown, H. C. *Top. Curr. Chem.* **1979**, *80*, 1.

[2] Meerwein, H.; van Emster, K. *Ber.* **1922**, *55*, 2500.

[3] Nevell, T. P.; de Salas, E.; Wilson, C. L. *J. Chem. Soc.* **1939**, 1188.

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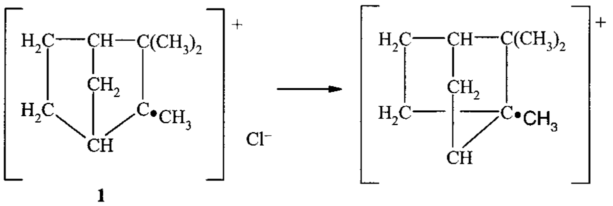

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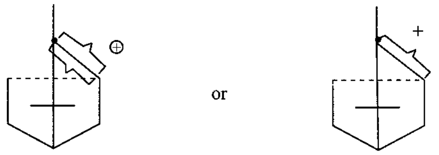
Meerwein and van Emster (1922)



Reference 3

Attributed to Ingold [4,5]

Figure 1. (Top) Meerwein's representation of the camphenyl cation to isobornyl cation rearrangement. (Bottom) Wilson and Ingold representations of the camphenyl cation.

We would like to re-open a discussion of the camphenyl chloride **2**–isobornyl chloride **3** rearrangement because of two recent developments: (1) Theoretical calculations[6,7] have shown that the secondary isobornyl cation in Meerwein's proposal does not exist as a stationary point on the camphenyl–isobornyl cation potential energy (PE) surface. (2) Any camphenyl chloride **2** → isobornyl chloride **3** mechanism must account for both a C–C bond shift and a chlorine atom shift. In the Meerwein mechanism these are of course separate steps, but recently, Smith[6] has proposed, on the basis of molecular orbital (MO) calculations, that the **2** → **3** rearrangement is a concerted reaction that *does not* involve "free" carbocation intermediates,[8] a result in complete contradiction with a wealth of physical organic chemical research.

In the present paper, we have completed the first detailed study of both the structure and dynamics of the camphenyl cation **1**, based on combined experimental and theoretical approaches. In the second part of this paper, we report solvation–simulation MO studies for ionization of the camphenyl chloride **2** system, as well as the reference compounds, *exo*-2-chloro-2-methylnorbornane, *tert*-butyl chloride, and a dichlorocycloheptatriene.

Results and Discussion

Part I. The Observable Camphenyl Cation 1. This cation is easily prepared in superacid solutions at ca. −120 °C, and we have previously reported low-field ^1H and ^{13}C NMR results.[9,10] In the present study (400 MHz), all ^1H and ^{13}C NMR assignments can be made unambiguously by means of $^1H-^1H$ COSY, ^{13}C DEPT, and $^{13}C-^1H$ HETCOR experiments, together with a knowledge of the degenerate rearrangements that take place in this cation. A ^{13}C NMR spectrum (152 K) is shown in Figure 2 to illustrate the excellent S/N and lack of impurities. The experimental ^{13}C NMR assignments for **1** are shown in Table 1, and these have proved to be extremely useful in our theoretical studies regarding this cation.

MO Calculations of the Camphenyl Cation Structure. Initial Trials. Optimization of **1** was first carried out using two different procedures,[11] B3LYP/6-31G* and MP2/6-31G*. The resulting structures show considerable differences, the most striking being the "nonbonded" distance C2–C6 and to a lesser extent the C1–C6 bond length, as shown in Figure 3.

Having in hand the experimental ^{13}C NMR chemical shifts for **1**, we next calculated the ^{13}C shifts expected for both structures, and the comparisons are shown in Table 1.

There are several unexpected (and unusual) features concerning both the ab initio MO calculations themselves, and the subsequent comparison of observed and calculated ^{13}C NMR chemical shifts: (1) It is unusual to find such large geometry differences as we observe for the structures of **1** (see Figure 3) obtained with the MP2 and B3LYP methods, since both can be regarded as moderate level procedures.[12] These results suggest that the potential energy (PE) surface is very flat with regard to the C2–C6 structural parameter shown in Figure 3. (2) The ^{13}C NMR chemical shift comparisons for the C2 (C^+) carbon (calculated vs experimental in Table 1) are very divergent, 44 ppm too high field in the MP2 structure and 23 ppm too low field for the B3LYP counterpart, using the same NMR computational procedure in both cases. This result suggests that the calculated C2 chemical shift must be very dependent on the particular C2–C6 distance in **1**.

Both the energy profile for movement along the C2–C6 "bond" in **1** and the effect of this distance on the calculated C2 (C^+) chemical shift value can be probed by carrying out calculations where the C2–C6 distance is fixed and all other parameters are optimized; this geometry was then used for ^{13}C NMR calculations. The results of these calculations are shown in Figures 4 and 5.

At the MP2 computational level, the energy profile (Figure 4) confirms the prediction that movement along the C2–C6 "bond" involves quite small energy changes. For example, at a room temperature thermal energy (RT) level of ca. 600 cal/mol, the C2–C6 distance spans the range 1.89–2.19 Å (0.30 Å spread).

At the B3LYP level, the shape of the energy profile looks quite similar, but the whole curve is displaced by 0.22 Å. In this case, the 600 cal/mol level spans the C2–C6 range 2.13–2.39 Å (0.26 Å spread).

The relationship between the calculated ^{13}C chemical shift of the C2 carbon and the C2–C6 distance in **1** is also shown in both Figures 4 and 5. For consistency, both NMR plots show the GIAO B3LYP/6-31G* calculated

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(4) Simonsen, J. L. *The Terpenes, Vol. II*, 2nd ed.; Cambridge Press: England, 1957; p 162.

(5) Watson, H. B. *Ann. Rep.* **1939**, *26*, 197.

(6) Smith, W. B. *J. Org. Chem.* **1999**, *64*, 60.

(7) (a) Maerker, C. Ph.D. Thesis, University of Erlangen, Germany, 1997. (b) Kirchen, R. P.; Sorensen, T. S.; Whitworth, S. M. *Can. J. Chem.* **1993**, *71*, 2016.

(8) However, the transition-state structures for C1 migration published by Smith[6] show long C–Cl bonds (~3.0 Å), so the camphenyl part clearly has considerable cationic character.

(9) Haseltine, R.; Huang, E.; Ranganayakulu, K.; Sorensen, T. S. *Can. J. Chem.* **1976**, *53*, 1056.

(10) Sorensen, T. S. *Acc. Chem. Res.* **1976**, *9*, 257.

(11) Smith[6] has previously reported the B3LYP /6-31G* structure for **1**.

(12) Maerker[7a] has found that the MP2 level of theory overestimates the bridging character of 2-methyl-2-norbornyl cations. For example, the 1,2-dimethyl-2-norbornyl cation is symmetrically bridged, contrary to experiment and to the results of a B3LYP level calculation.

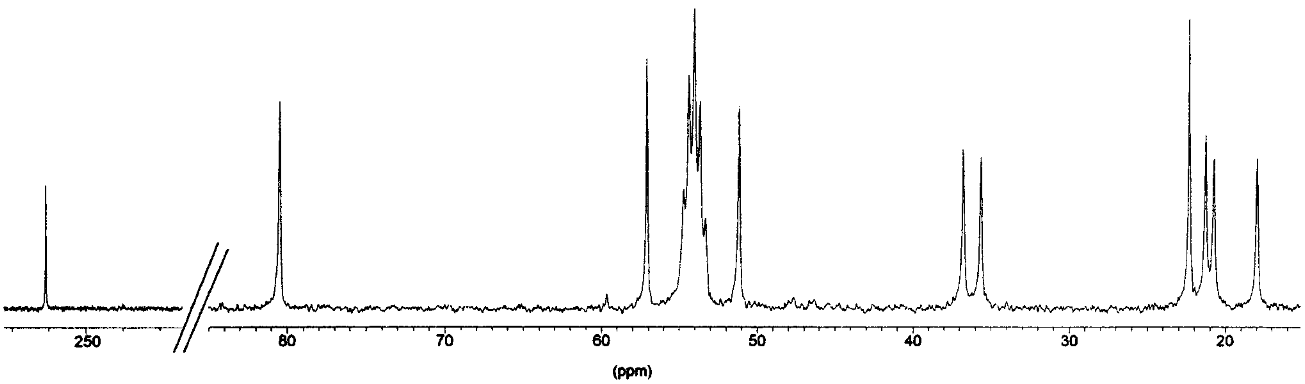
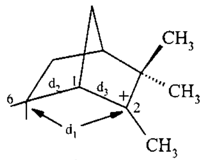


Figure 2. ^{13}C NMR spectrum of the camphenyl cation in superacid solution at 152 K. The multiplet at 54 ppm is from CD_2Cl_2.

Table 1. Experimental vs Calculated ^{13}C NMR Shifts for 1

carbon	exptl[a]	B3LYP/6-31G* structure[b,c]	diff	MP2/6-31G* structure[b,c]	diff
1	80.6	75.37		81.95	
2	261.9	285.01	+23.11	217.66	−44.24
3	57.4	65.30		52.13	
4	51.4	55.51		50.57	
5	21.4	23.52		21.69	
6	36.0	42.38		35.64	
7	37.0	40.70		35.88	
8	22.5	26.91		19.08	
9	18.1	23.21		18.51	
10	20.9	23.61		21.71	

[a] In ppm, measured at 168 K relative to internal CD_2Cl_2. [b] Calculated at the GIAO B3LYP/6-31G* level. These shifts were also evaluated at the GIAO MP2/6-31G* level and were quite similar. [c] Relative to TMS = 189.68 ppm.



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	d_1 (Å)	d_2 (Å)	d_3 (Å)
B3LYP/6-31G*	2.259	1.655	1.442
MP2/6-31G*	2.038	1.706	1.400

Figure 3. Structural parameters for **1** calculated at two different MO levels.

results, but in the case of the MP2 energies we have also calculated the corresponding GIAO MP2/6-31G* chemical shift values and found a quite similar relationship (see the Supporting Information).

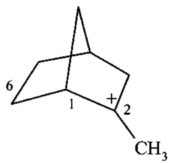
The slope of the calculated δ C$^+$ vs the C2−C6 distance is almost linear in Figure 4 and is very steep, ca. 30 ppm/0.1 Å change. At the 600 cal/mol energy level, and the resulting 0.30 Å variation in the C2−C6 distance, there is a 90 ppm spread in the ^{13}C chemical shift calculated for C2. The curve in Figure 5 covers a much larger set of C2−C6 distances and is therefore less linear, but evaluated as above, the slope is ca. 22 ppm/0.1 Å (56 ppm total variation at the 600 cal/mol level).

Because of the large structural differences found for **1** using the B3LYP and MP2 procedures and the fact that neither structure gives calculated ^{13}C-2 values even close to experiment, it would clearly be useful to move to higher level calculations, and the δ C$^+$ (calcd) vs C2−C6 distance relationship would serve as a very useful guide for evaluating this critical C2−C6 distance in these higher level calculations. Thus, using the experimental δ C$^+$ of 260.9 ppm (Table 1), the "correct" C2−C6 distance based on Figure 5 would be ca. 2.19 Å and about ca. 2.16 Å based on Figure 4; i.e., a C2−C6 distance in the range 2.16−2.19 Å would give reasonable C$^+$ (calcd) vs C$^+$ (exptl) agreement.[13]

Higher Level Calculations on 1. The camphenyl cation **1** was optimized at the MP3 (full), MP4 (s, d, q), and QCI (s, d) levels, all employing a 6-31G* basis set. In the MP4 case, the C2−C6 distance was 2.176 Å, while at the QCI level, a value of 2.194 Å was obtained. These are gratifying results, not only because of the agreement with the prior predictions (previous section), but also because they are clearly the result of a higher level calculation. For both geometries, we have calculated the GIAO B3LYP/6-31G* and GIAO MP2/6-31G* ^{13}C NMR chemical shifts. A comparison based on the calculated MP4/6-31G* geometry and a GIAO B3LYP/6-31G* chemical shift calculated vs experimental is shown in Table 2, giving an average absolute deviation of 2.6 ppm. For the same geometry using GIAO MP2/6-31G* NMR calculations, the average deviation was 3.3 ppm. The QCI structure had corresponding average deviations of 3.8 and 4.5 ppm.

Basis Set Variation in the Calculations. The camphenyl cation structure was also optimized using a more complete basis set. At an MP2/6-311+G** level, the critical C2−C6 distance was marginally shorter at 2.017 Å (2.038 Å with the 6-31G* set). At the B3LYP level, there was an even smaller difference, 2.256 vs 2.259 Å (6-311+G* vs 6-31G*). We conclude therefore that the 6-31G* basis set is adequate for all the calculations shown in Figures 4 and 5 and for the MP4 and QCI calculations.

Comparison Calculations on the 2-Methyl-2-norbornyl Cation 4. Cation **4** is expected to have a structure similar to that calculated for the camphenyl cation **1**, and a verification of this would add weight to the results obtained for **1**. Maerker and Schleyer[7] have previously carried out calculations on **4** at the B3LYP/6-31G* and MP2/6-31G* levels and have noted a reduced



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[13] A very similar situation has been seen in ^{13}C NMR shift calculations of 2-butyl cation structures, and these authors derived a "correct" distance parameter by matching calculated and observed ^{13}C chemical shifts: Carneiro, J. M. de M.; Schleyer, P. v. R.; Koch, W.; Raghavachari, K. *J. Am. Chem. Soc.* **1990**, *112*, 4064.

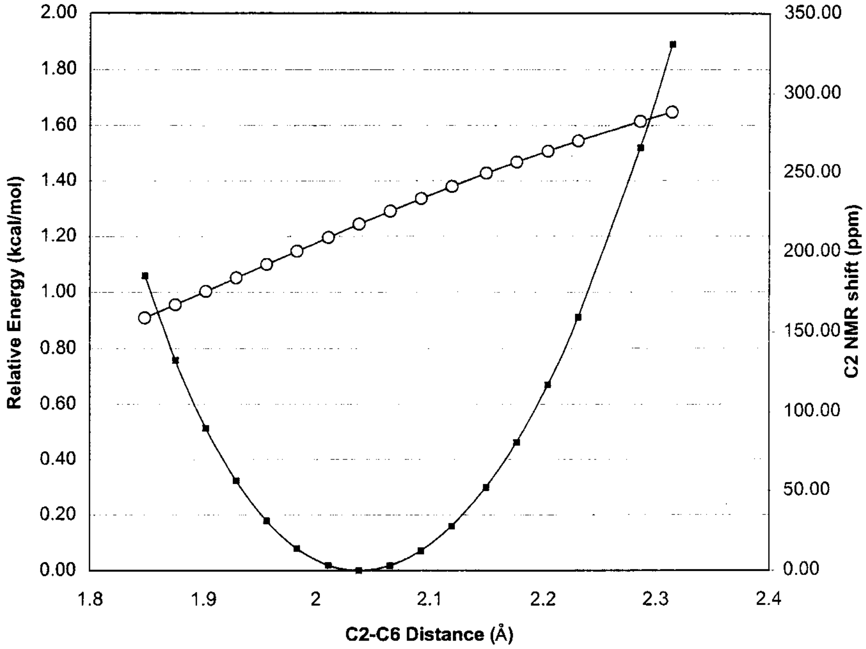

Figure 4. (■) Energy of **1** vs fixed C2–C6 distances using MP2/6-31G* calculations. (○) Calculated ^{13}C NMR shifts of the C2$^+$ carbon at each geometry.

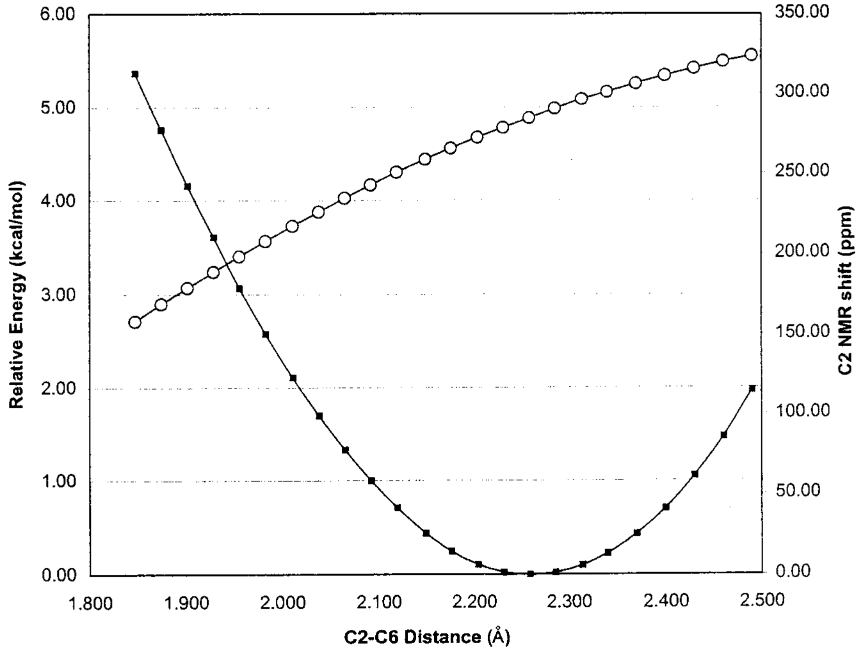

Figure 5. (■) Energy of **1** vs fixed C2–C6 distances using B3LYP/6-31G* calculations. (○) Calculated ^{13}C NMR shifts of the C2$^+$ carbon at each geometry.

C2–C1–C6 bond angle (C2–C6 partial bridging). They also calculated ^{13}C NMR chemical shifts for the B3LYP structure. A natural bond analysis on this structure indicated that some C2–C6 interaction was present.

In the present study, we have verified that the PE surface of **4**, as a function of the C2–C6 distance, closely resembles that shown in Figures 4 and 5 for cation **1**. There is also a similar large variation in the calculated δ ^{13}C values for the C2 carbon as a function of the C2–C6 distance (see the Supporting Information). The correlation level and basis set variations noted for **1** are also closely matched by the results for **4**, as shown in Table 3 for the key C2–C6 distance value.

The PE Surface Parameters for the Camphenyl Cation 1. The preceding discussion has focused on the C2–C6 "bond" in **1**, and as noted, movement along this "bond" is associated with a flat PE surface. As expected, the C1–C6 and C1–C2 bond lengths also change, but in a much less symmetrical way.

Even at large (fixed) C2–C6 distances, e.g., 2.4 Å (a value typical of this distance in the bicyclo[2.2.1]heptan-2-one structure),[14] one finds long C1–C6 bonds, and these

Table 2. Observed vs Calculated ^{13}C NMR Chemical Shifts for MP4/6-31G* Geometry of the Camphenyl Cation 1

carbon	exptl[a]	calcd[b]
1	80.6	74.69
2	261.9	266.84
3	57.4	59.69
4	51.4	53.07
5	21.4	23.37
6	36.0	36.51
7	37.0	38.76
8	22.5	24.31
9	18.1	21.12
10	20.9	23.26
avg |deviation|		2.6 ppm

[a] Temperature of 152 K. Chemical shifts were internally referenced relative to $CD_2Cl_2 = \delta$ 54.0. [b] GIAO B3LYP/6-31G*, δ values relative to TMS = 189.68 ppm.

Table 3. Comparison of Calculated C2−C6 Distance in Cations 1 and 4 as a Function of Computational Procedure

calculation type	cation **1** C2−C6 (Å)	cation **4** C2−C6 (Å)
B3LYP/6-31G*	2.259	2.247
B3LYP/6-311+G**	2.256	2.247
MP2/6-31G*	2.038	2.013
MP2/6-311+G**	2.017	1.992
MP3 (full)/6-31G*	2.172	2.128
MP4 (s, d, q)/6-31G*	2.176	2.158
QCI (s, d)/6-31G*	2.194	2.186

can be attributed to a favorable C−C hyperconjugation. This C1−C6 bond length is nearly constant over a wide range of fixed C2−C6 values, varying only from 1.649 to 1.663 Å over the C2−C6 range of 2.49−2.15 Å, as shown in Figure 6 (B3LYP/6-31G* data). As one would expect for a more "bridging ion" description of **1**, the C2−C6 and C1−C6 distances approach one another as one fixes progressively shorter C2−C6 bond lengths. For example, at a distance of 1.848 Å, the MP2 calculations give C1−C6 = 1.745 Å, while B3LYP gives 1.761 Å. As also expected, this onset of bridging is accompanied by a small progressive decrease in the C1−C2 bond length (more double-bond character). One can illustrate this effect in the camphenyl cation by plotting the LUMO orbital for a C2−C6 distance of 2.49 Å and for 1.85 Å, whereby one sees in the latter the typical LUMO orbital pattern for a π-bridged structure (see Figures 7 and 8).

In our previous discussion, we concluded that the observable superacid solution camphenyl cation has a C2−C6 distance of ca. 2.16−2.19 Å, and the MP4 calculations duplicate this quite closely. This "correct" camphenyl cation structure is clearly distorted relative to a strain-free bicyclo[2.2.1] heptane skeleton,[14] C2−C6 ca. 2.4 Å, but it is even more geometrically distant from a bridged cation structure (C2−C6 = C1−C6 = ca. 1.8 Å). On the basis of the Figure 6 correlation, it is also clear that **1** falls closer to the C−C hyperconjugation description.

Much more important than the actual structure of **1** is the extremely flat PE surface, i.e., the dynamic behavior of **1**. Attempting to evaluate the whole surface at the MP4 level would be extravagant, but one can estimate that the "true" PE profile for **1** would lie between those shown in Figures 4 and 5. On this basis, one estimates that the PE surface corresponding to a bridged camphenyl cation structure would involve an energy increase of only about 4−6 kcal/mol above the energy minimum.

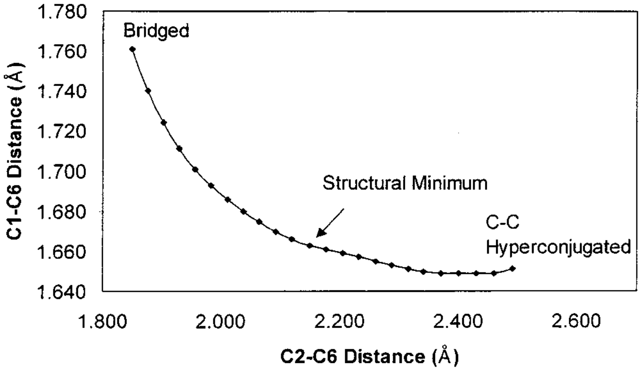

Figure 6. Plot of calculated C1−C6 bond lengths vs fixed C2−C6 distances (B3LYP /6-31G*).

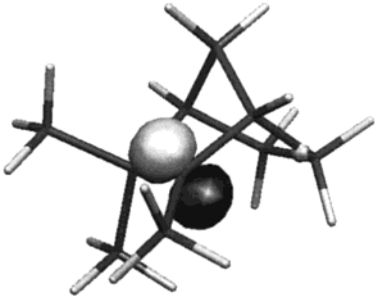

Figure 7. LUMO orbital of **1** at a fixed C2−C6 distance of 2.49 Å.

Figure 8. LUMO orbital of **1** at a fixed C2−C6 distance of 1.85 Å.

This point will be brought up again later, but before doing this we will switch to the second topic of this study, an evaluation of the energetics associated with the solution-phase dissociation of camphenyl chloride into the camphenyl cation **1** and chloride anion.

Part II. Estimation of Gas-Phase Solvation Energies and Overall Solution Ionization Energy for the Camphenyl System and Other Reference Compounds. This study was undertaken in partial response to the recent publication of Smith,[6] in particular, his theoretical calculations showing that the ionization of camphenyl chloride in nitromethane solvent would be endothermic by ca. 130 kcal/mol (B3LYP/6-31G*). If this

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(14) The B3LYP /6-31G* calculated structure for camphenilone has C2−C6 = 2.46 Å. An optimization of **1** using AM1 appears to give a classical structure, since C2−C6 = 2.41 Å.

number were correct, one clearly could not have a solution-phase ionization process, a fundamental part of the Meerwein mechanism (or of any S_N1 reaction).

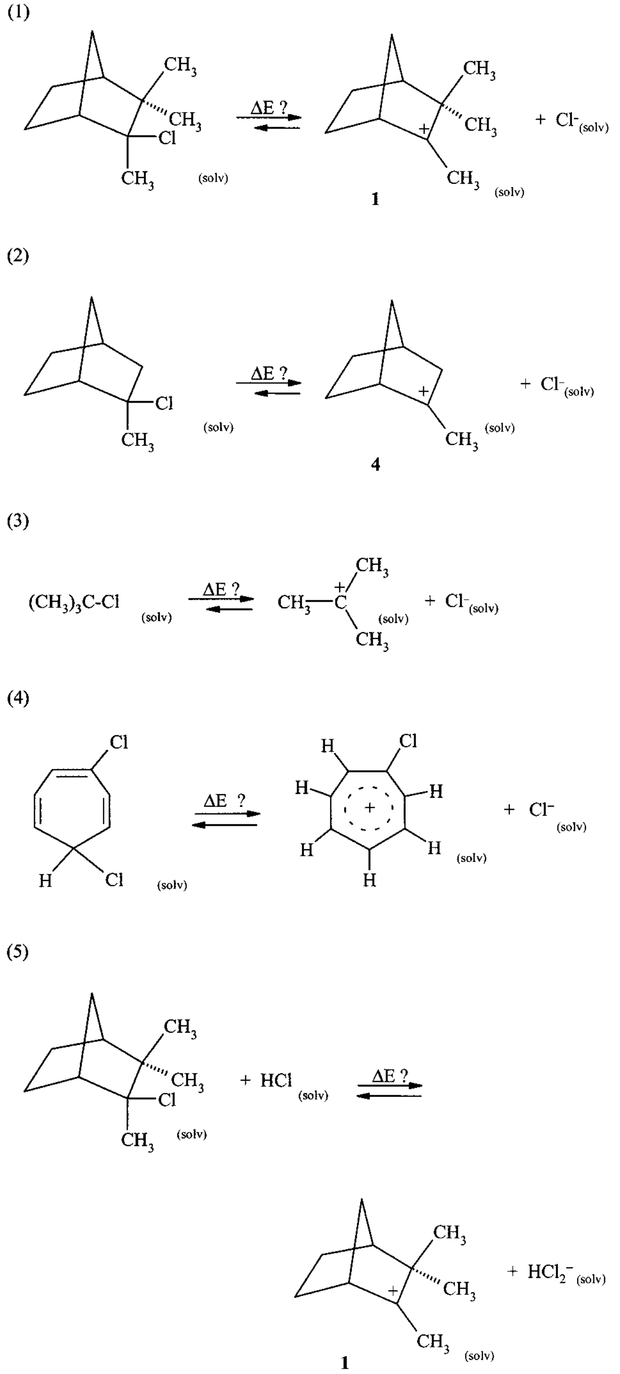
Our plan was to carry out our own solvation simulation calculations, since those reported by Smith appeared to greatly underestimate known gas-phase ionic solvation energies. The simulation procedure chosen for our study was the continuum-based SCI-PCM method, with full optimization of all structures (gas phase and solvation simulation) at the B3LYP/6-311+G** level of calculation. Wiberg and co-workers have reported[15] several studies using this procedure, and Schleyer[16] has predicted from such calculations that one could have differential cation solvation in some isomeric systems. We have also used the SCI-PCM method to calculate differential solvation effects involving carbocation equilibria.[17]

There have been a number of previous analyses of alkyl halide solvolysis processes, although none involved the camphenyl system. Abraham has reported[18] calculated thermodynamic parameters for the aqueous hydrolysis of tBuCl using Monte Carlo solvation-simulation methods. Jorgensen also studied[19] tBuCl solvolysis processes, specifically the energetics of contact and solvent-separated ion pairs. Williams has also used [20] a Monte Carlo method to study the detailed mechanism of tBuCl hydrolysis.

Perhaps the most useful literature comparison for our contemplated study is an estimate of the gas-phase solvation energy of the tBu^+ cation in water. We planned to use this tBuCl system as a reference to compare with our own results.

The SCI-PCM method involves a geometry optimization of the molecule of interest, in the presence of the solvation field. The input geometry in our calculations was the corresponding “gas-phase” optimized structure, and in all cases, the resulting solvation simulation geometries involved only small structural changes.[21] A dielectric constant ($\in$) of 10 was used for the calculations, a midrange value for the various organic solvents used by Meerwein. The SCI-PCM model is based on the Born equation, in which the dielectric constant appears as a $(1/\in - 1)$ term. Thus, rather large changes in a midrange $\in$ value do not result in very different solvation free energies. Ion-pairing effects are important in low dielectric media so SCI−PCM calculations are obviously deficient in this regard. In aqueous media, it has been suggested[19] that solvent separated ion pairs and free ion systems do not differ much in energy, but this clearly does not apply to contact ion pairs. However, the latter are usually regarded as just a first step in the overall solvolysis substitution process.

The following ionization reactions have been studied in this work:



Reactions 1 and 5 are the equations of direct interest, the latter equation because it is known that the camphenyl chloride → isobornyl chloride rearrangement can be catalyzed by HCl. Reaction 2 was used because it involves a very similar cationic intermediate (see earlier discussion) and would be expected to yield a similar ΔE value. As mentioned, reaction 3 is the obvious reference calculation for a prototypic tertiary alkyl cation (S_N1 intermediate). This system was also included in the calculations so that comparisons could be made with a previous estimate of the *tert*-butyl cation gas-phase solvation energy, i.e., to add credence to the calculations. Reaction 4 has been studied by dynamic NMR spectros-

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(16) Schreiner, P. R.; Severance, D. L.; Jorgensen, W. L.; Schleyer, P. v. R.; Schaefer, H. F., III. *J. Am. Chem. Soc.* **1995**, *117*, 2663.

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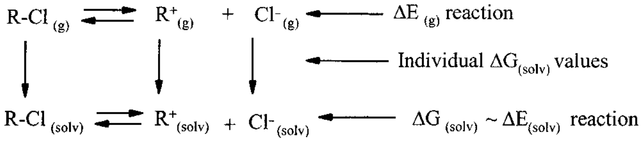
(19) Jorgensen, W. L.; Buckner, J. K.; Huston, S. E.; Rossky, P. J. *J. Am. Chem. Soc.* **1987**, *109*, 1891.

(20) Williams, I. H. Abstracts, 7th European Symposium on Organic Reactivity, Ulm, Germany, 1999, p 54.

(21) For the B3LYP /6-311+G** calculations of cation **4**, C2−C6 = 2.247 (gas-phase), 2.260 Å ($\in$ = 10) and 2.263 Å ($\in$ = 100).

Table 4. Calculated Gas-phase Reaction Energies, Gas-phase Solvation Energies (Δ*G*) and Overall Solution Ionization Energies for Reactions 1−5



equation	Δ*E*(g)[a] (kcal/mol)	Δ*G* solvation energy[b] (kcal/mol)			Δ*E*(solv) reaction[b] (kcal/mol)
		R-Cl	R$^+$	Cl$^-$	
1	123.94	−1.53	−45.41	−51.54	28.07
2	130.73	−1.58	−47.67	−51.54	33.10
3	143.85	−1.68	−52.86	−51.54	41.13
4	108.07	−3.42	−48.43	−51.54	11.52

equation	Δ*E*(g)[a] (kcal/mol)	Δ*G* solvation energy[b] (kcal/mol)				Δ*E*(solv) reaction[b] (kcal/mol)
		R-Cl	HCl	R$^+$	HCl$_2^-$	
5	101.05	−1.53	−1.84	−45.41	−41.76	14.15

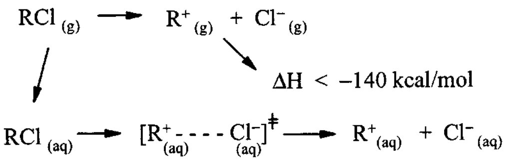
[a] Corrected for ZPVE (ZPVE/B3LYP/6-31G*) × 0.98. [b] Based on the SCI-PCM solvation simulation procedure, B3LYP/6-311+G**, $\in = 10$.

copy, and the transition-state for this reaction can be estimated.

The calculation results are summarized in Table 4, but the thermodynamic units employed in our work need some discussion. In the ionization reactions, eqs 1−5, Table 4, the energy of each molecule or atom was first calculated, and then a "reaction" Δ*E* value was derived (gas-phase). These calculations are potentially susceptible to basis set superposition errors, and while there are computational procedures to attempt to deal directly with this problem, the most practical solution is to employ a complete basis set (6-311+G** in our case).

The SCI-PCM calculations yield individual gas-phase solvation free energies, which can be combined to give a Δ*G* estimate for the solution-phase reaction. For these reactions, we believe that $\Delta G_{\mathrm{solv}} \approx \Delta H_{\mathrm{solv}}$, since the overall solvation term is totally dominated by the ionic species (electrostatic energy).

Comparison of tBu$^+$ Solvation Energy with Gold's Estimate. Gold[22] has estimated a solvation energy (H_2O) for the tBu$^+$ cation using the following thermochemical cycle:



The inequality in Δ*H* is the unknown difference in energy between the transition-state for the S_N1 hydrolysis reaction (23.2 kcal/mol) and the actual energy of the ionic intermediates. This difference was assumed to be small, based on the Hammond postulate. Gold used a value of −90 kcal/mol for $\mathrm{Cl^-}_{(g)} \rightarrow \mathrm{Cl^-}_{(aq)}$, which then leaves ca. −50 kcal/mol for the tBu$^+$ solvation energy. Our SCI-PCM calculated Δ*G* (gas-phase hydration) value[23] for the tBu$^+$ cation in water ($\in = 78$) is −58.2 kcal/mol, in reasonable agreement with Gold's value (the $-T\Delta S_{\mathrm{solv}}$ term relating ΔG_{solv} and ΔH_{solv} is expected to be a small positive number).[24]

The results shown in Table 4 are for the $\in = 10$ "solvent". Abraham[25] has reported calculations of $\mathrm{Cl^-}_{(g)}$ solvation free energies for a number of organic solvents, and these matched quite well with data based on experimental results. Our values shown in Table 4 are about 10 kcal/mol too low compared to his results for an $\in \sim 10$ solvent.[26]

In addition to the tBuCl case, the calculations shown in eq 4 (Table 4) provide yet another link with experimental data. Feigel and Kessler[27] observed NMR line-broadening when the covalent chloride shown in eq 4 was dissolved in CD_2Cl_2. This NMR line-broadening was attributed to a rapid equilibrium between the 1-, 2-, and 3-chloro-substituted 7-chlorocycloheptatrienes, where the rate-determining step involved the formation of a chlorotropylium ion intermediate. One can crudely estimate from the NMR data[28] that the barrier for this ionization would be about 12−13 kcal/mol, in good agreement with the calculated value shown in Table 4, assuming that the activation energy, relative to the energy of the separated ions, is a small value.

In summary, the close correspondence between our results for the tBu and tropylium systems vs experimental data gives credence to the SCI-PCM method being used in this work.

The Camphenyl and 2-Methyl-2-norbornyl Systems. In Table 4, it is seen that the larger cations (eqs 1 and 2) have smaller calculated gas-phase solvation energies than tBu$^+$, although they are still very sizable. In his paper,[6] Smith estimates the solvation energy of the camphenyl cation in nitrobenzene solvent ($\in = 34.8$) as −1.1 kcal/mol and as ca. 0 for the chloride anion. The latter estimate is clearly much too small, based simply on the various experimental values, and we would conclude that the same is true for the camphenyl cation solvation energy, in which we have obtained a −45.4 kcal/mol calculated value for a smaller $\in$-value "solvent" than CH_3NO_2.

Using our solvation calculations, we find that the Δ*E* value (Table 4) for camphenyl chloride ionization in the

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(22) Gold, V. *J. Chem. Soc., Faraday Trans.* **1972**, 1611.

(23) Calculated as in Table 4, with an $\in$ value of 78.

(24) Conway, B. E. *Ionic Hydration in Chemistry and Biophysics*; Elsevier: New York, 1981; Chapter 22.

(25) Abraham, M. H.; Liszi, *J. Chem. Soc., Faraday Trans. 1* **1978**, 1604.

(26) Continuum model solvation procedures such as SCI-PCM badly underestimate aqueous $\mathrm{Cl^-}_{(g)}$ solvation energies. For example, we calculate $\Delta G = -56.7$ kcal/mol ($\in = 78$), Table 4 procedure. Monte Carlo methods [Chandrasekhar, J.; Spellmeyer, D. C.; Jorgensen, W. L. *J. Am. Chem. Soc.* **1984**, *106*, 903] give $\Delta H_{\mathrm{solv}} = -80$ kcal/mol, close to the experimental value. This discrepancy occurs, in part, because hydrogen-bonding effects are not accounted for in continuum models. We also find that the basis set used for Cl$^-$ has a significant effect on the calculation, ΔG_{solv} ($\in = 10$) = 58.3 kcal/mol for B3LYP/6-31G* vs 51.5 kcal/mol for the B3LYP/6-311+G** basis set. The former result would correspond to a less polarizable "hard sphere" model, and the result is closer to experimental values. This large error found in anion solvation energy calculations using diffuse functions in the basis set contributes to the "outlying charge error"; see: Baldridge, K.; Klamt, A. *J. Chem. Phys.* **1997**, *106*, 6622. For our cation solvation energies there is almost no basis set effect. We could have used the full basis set for the gas-phase energy calculations (to minimize BSS errors) and computed the solvation energies at the 6-31G* level. However, for consistency purposes, we have used the 6-311+G** basis for both sets of data. The Δ*E* values shown in Table 4 are thus based on a chloride ion solvation energy that is demonstrably too small (i.e., compared to experimental values or to the 6-31G* computed value). Lower Δ*E* values would, of course, be even more consistent with our arguments.

(27) Feigel, M.; Kessler, H. *Tetrahedron* **1976**, *32*, 1575.

(28) For typical ^{1}H NMR line-broadening, $k \approx 10^3-10^4$ s^{-1}, giving $\Delta G^\ddagger = 12-13$ kcal/mol (298 K).

$\in = 10$ “solvent” is 28.1 kcal/mol. Can this be correlated with experimental results? Meerwein and van Emster[2] showed clearly that the camphenyl chloride rearrangement rate progressively increases in higher dielectric solvents. Choosing just one of their data sets, they report a first-order rate constant of 3.4×10^{-6} s^{-1} at 40 °C for the rearrangement in chlorobenzene solvent ($\in$ = ca. 6), from which one can estimate $\Delta G^{\ddagger} = 26$ kcal/mol. Given that the ionization reaction must be considerably faster than that of the overall rearrangement reaction (see next section) and that the transition-state energy for this ionization reaction will be slightly higher than that of the intermediates, then the 28.1 kcal/mol value in Table 4 appears to be at least 5−10 kcal/mol too high. Although this mismatch may well be within the uncertainties involved in our calculations, there are other possible factors.

Meerwein and van Emster were at pains to try and remove any free HCl from their camphenyl chloride solutions, since this was known to catalyze the rearrangement reaction. In Table 4, we report a calculated ΔE value for an ionization reaction (eq 5) in which HCl could act as a Lewis acid catalyst. This calculation is not meant to represent a stoichiometric reaction, since Cl^- will be immediately recaptured with regeneration of HCl. However, as the equation of a transitory and rate-determining process it does provide an estimate of how much the ionization energy could be lowered by the HCl catalyst.

After the Meerwein paper, there have been other rate studies of the camphenyl chloride rearrangement, and the occurrence of HCl catalysis has been postulated[29] as an unavoidable outcome of a camphenyl chloride dissociation into camphene and HCl. The calculated HCl-catalyzed ionization energy (ΔE) shown in Table 4 (11.5 kcal/mol) is fully 16 kcal/mol smaller than the $\Delta G^{\ddagger}_{\mathrm{rearr}}$ value based on Meerwein's rate data (see above), so even some partial HCl catalysis could be accommodated with these numbers.

We have also ignored the small, but favorable, $T\Delta S$ term associated with the ionization reactions listed in Table 4; i.e., the main intent here is to show that the solution formation of the camphenyl cation and chloride anion *is a feasible process*.

Putting It All Together: Nucleophilic Attack at the Exo C2 or C1 Position in 1. As discussed in part I, calculations of the camphenyl cation **1** show that this is a species having a very low energy profile for structural variation of the C2−C6 “bond”. We showed that a C2−C6 distance of 2.16−2.19 Å would be consistent with the observed ^{13}C NMR spectrum of **1** (superacid solution), and that MP4 or QCI calculations closely match this distance. We also pointed out that this 2.16−2.19 Å distance is considerably shorter than that found for comparable noncationic bicyclo[2.2.1]heptyl ring systems, but that conversely the C1−C6 bond in **1** is not much lengthened beyond that which can be attributed to C−C hyperconjugation. These parameters are therefore consistent with only a very early stage of bridging in the equilibrium structure of **1**.

On the basis of the original work of Meerwein,[2] and in particular the later studies of Wilson,[3] in which chloride ion exchange in camphenyl chloride was studied using added radioactive chloride (as HCl), one can set up the kinetic scheme (Scheme 1) for the conversion of camphenyl chloride into isobornyl chloride.[30] A similar scheme can be set up for the HCl-catalyzed reaction.

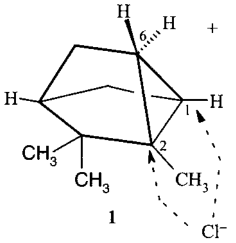
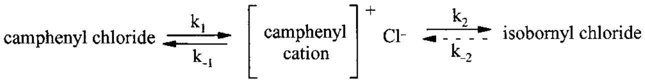


Figure 9. Attack by Cl^- occurs from the exo face at both C1 and C2. In the former case, this occurs because the PE surface of **1** appropriate for Cl^- capture is bridged.

Scheme 1



In their paper, Wilson et al. reported that k_1 was at least 15 times larger than k_2 ($CHCl_3$ solvent), but this value could have been considerably larger. Their data were, as Wilson et al. recognized, consistent with a picture of either a “single mesomeric camphenyl” cation or equilibrating camphenyl and isobornyl cations (Meerwein). Computational results now rule out the latter, and from the present work we have a more detailed picture of the camphenyl cation structure. As shown in Figure 9, the cation could react with Cl^- at either the exo C2 position (internal return), much preferred, or at the exo C1 position, at a cost of a least 4−6 kcal/mol energy movement upward on the camphenyl cation PE surface. Since isobornyl chloride is the thermodynamic product (k_{-2} small), one eventually obtains only this product. This scheme is of course quite similar to *both* the Meerwein “two carbocation” mechanism and the nonclassical (or bridged) single-cation mechanism, the subtle difference being that the actual ground-state structure of **1** appears to be only marginally bridged and that it is the shallow energy profile that allows the bridging PE surface to be energetically accessible, this surface however being very similar in structure to what one might describe as a secondary carbocation (isobornyl cation) intermediate.

Although chloride anion exchange (Wilson et. al.) can be used to measure the k_2/k_{-1} ratio in the kinetic scheme, there is another approach worth mentioning. As noted by Meerwein[31] and other early workers in the terpene area,[32] there is partial to complete racemization accompanying many terpene rearrangements, including the camphenyl chloride → isobornyl chloride transformation. In the latter case, the racemization is due mainly to an *exo*-3,2-methyl shift in the camphenyl cation.[9,10] Experimentally,[9] and from calculations,[33] the transition-state barrier for this process, measured from the camphenyl cation energy level, is about 8 kcal/mol.

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[29] Bartlett, P. D.; Pöckel, I. *J. Am. Chem. Soc.* **1938**, *60*, 1585.

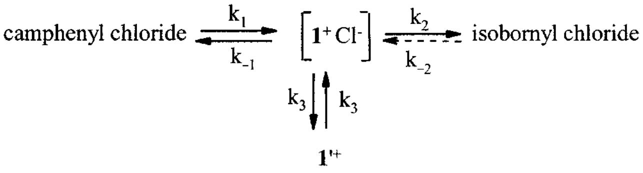
[30] As discussed earlier, details such as ion-pairing effects are not being considered here. One could probably describe the Smith[6] results in terms of a camphenyl cation contact ion pair undergoing rearrangement to isobornyl chloride. However, such an interpretation would not account for (1) Cl^- exchange, (2) Meerwein's k_{rearr} vs solvent $\in$ data, or (3) racemization processes.

[31] Meerwein, H.; Montfort, F. *Ann.* **1924**, *435*, 207.

[32] Berson, J. A. *Chemical Creativity*; Wiley-VCH: Weinheim, Germany, 1999; Chapter 5.

[33] At the MP2/6-31G* level, the transition state for the *exo*-3,2-methyl shift in **1** was 7.96 kcal/mol.

Each time the camphenyl cation is generated as a solvolysis intermediate there are therefore three major processes possible:



Our estimation of the k_3 transition-state barrier for the racemization of **1** ($\Delta G^{\ddagger} = 8$ kcal/mol) allows one to assign a similar magnitude transition-state for the irreversible chloride ion capture reaction (k_2). This in turn is consistent with the calculated energy cost of moving from the ground-state structure of **1** upward on the PE surface to where one has a bridged structure capable of Cl$^-$ capture at C1.

Experimental Section

The camphenyl cation was prepared at ca. 153 K by the slow stirred addition of a CD_2Cl_2 solution of camphene to a solution of 1:1 $SbF_5{-}FSO_3H$ in SO_2ClF solvent and contained in a 5 mm NMR tube. The camphenyl cation is stable to about 230 K, at which temperature an irreversibly rearrangement commences. As reported in a previous study,[9] one sees dynamic NMR line-broadening between 168 and 230 K. The chemical shift data reported in the present work (152 K) are for the "frozen-out" structure. NMR spectra were obtained on a Bruker AM-400 spectrometer.

Calculations were performed with the Gaussian 94 or 98 suite of programs,[34,35] the former being used for solvation simulation work. In the SCI-PCM model, a default value of 0.0004 was used for the isodensity surface, 974 points were used in the Special Grid option, and surface integrals were evaluated using the single center procedure. Gas-phase ZPVE corrections were used in the energy equations since only numerical frequencies are available in the solvation model.

Conclusion

On the basis of a detailed theoretical study of the camphenyl cation, including solvation simulations, we conclude, contrary to the assertions of Smith,[6] that this cation is an intermediate in the solution-phase camphenyl chloride → isobornyl chloride rearrangement. The detailed mechanism that we have uncovered is a hybrid of the Meerwein and nonclassical ion mechanisms. However, we *emphasize* that these details, while nice to have, should not detract from the fundamental mechanistic contribution to organic chemistry made by Meerwein and van Emster in 1922. To quote Criegee,[36] "The question now no longer is whether these rearrangements are ionic, but whether they involve classic or nonclassic ions, or intimate or solvent-separated ion pairs. It is easy to forget that these are mere questions of detail in comparison with Meerwein's fundamental discoveries."

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada for generous financial support.

Supporting Information Available: Coordinates (x, y, z) for the optimized structures. Graphical presentations of the computational data for the 2-methyl-2-norbornyl cation **4** (total energy and $^{13}C2^+$ NMR chemical shifts as a function of fixed C2−C6 distances) and the energy data used to create Table 4. This material is available free of charge via the Internet at http://pubs.acs.org.

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[34] Gaussian 94 (Revision A.1): Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. Gaussian Inc., Pittsburgh, PA, 1995.

[35] Gaussian 98, Revision A.3: Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A. Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y., Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. Gaussian, Inc., Pittsburgh, PA, 1998.

[36] Criegee, R. *Angew. Chem., Eng. Ed. Engl.* **1966**, *4*, 333.