

Seven-Membered Ring or Phenyl-Substituted Cation? Relative Stabilities of the Tropylium and Benzyl Cations and Their Silicon Analogues

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The gas-phase chemistry of the tropylium cation (**1-C**) and its isomer the benzyl cation (**2-C**) has attracted attention for almost 40 years,^{1,2} but the thermochemistry of these two ions is still not well established. Indeed, despite a 1988 paper commenting²¹ that "the major mystery in the C₇H₇⁺ story yet to be solved is the heat of formation of the tropylium cation", the current situation is that this aspect *remains* to be solved. The first aim of the present communication is to use high-level ab initio calculations to obtain reliable estimates of the heats of formation for the important systems **1-C** and **2-C**.



The second aim is related to the intriguing gas-phase experimental results reported very recently by Beauchamp and co-workers, interpreted as corresponding to the silicon analogues, silatropylium cation (**1-Si**) and silabenzyl cation (**2-Si**).³ They were unable to directly measure an energy difference between **1-Si** and **2-Si** but suggested from indirect evidence that the relative stability ordering of the silicon systems is the same as that of the parent compounds, i.e., the cyclic seven-membered-ring structure (**1-Si**) is the more stable.^{3a} It is clearly of interest to address explicitly the question of the thermochemistry of these new silicon-containing ions. We report in this communication our findings in this regard. In contrast to the previous suggestion, we conclude that *silicon substitution reverses the stability ordering of 1 and 2*, i.e., silabenzyl cation (**2-Si**) is more stable than silatropylium cation (**1-Si**).

Ab initio molecular orbital calculations⁴ were carried out using the GAUSSIAN 92,⁵ MOLPRO,⁶ and ACES II⁷ programs for **1-C**, **2-C**, **1-Si**, **2-Si**, and related reference molecules with a variety

of correlation levels and basis sets (see below). Our best results were obtained at the G2 and G2(MP2) levels of theory.⁸ These both represent calculations effectively at the QCISD(T)/6-311+G(3df,2p) level of theory on MP2/6-31G(d) optimized geometries, incorporating scaled HF/6-31G(d) zero-point energies and a so-called higher level correction. G2 is found to perform slightly better than G2(MP2) but is computationally more demanding and so could not be applied to all of the systems examined in the present paper. We are unaware of any previous theoretical studies of **1-Si** or **2-Si**, while the few existing studies⁹ for the parent compounds **1-C** and **2-C** have not been carried out at quantitatively definitive levels of theory.

Both G2 and G2(MP2) have proven to be very successful in predicting heats of formation for small and medium-sized molecules, via the calculation of atomization energies.^{8,10,11} However, neither has yet been tested thoroughly in this respect for larger sized systems. We have recently noted¹² that the heat of formation for benzene is overestimated by 16 kJ mol⁻¹ (G2) or 21 kJ mol⁻¹ (G2(MP2)) using the standard approach. We find, however, that there is much better agreement between experiment and theory when the calculation of the heat of formation for benzene is based on isodesmic and isogyric reactions rather than the atomization reaction.

As a result of our experiences for benzene, we have used the isogyric approach to determine the heat of formation for benzyl cation (**2-C**). For example, we have used the G2 and G2(MP2) energy changes for reaction 1,



in conjunction with the experimental heats of formation¹³ for CH₄, CH₃CH₂⁺, and benzene to obtain a heat of formation, Δ*H*_{f,298}, for benzyl cation; both theoretical procedures give 906 kJ mol⁻¹. The G2 and G2(MP2) Δ*H*_{f,298} values for **2-C** that emerge from an examination of several such reactions¹⁴ are found to range between 900 and 914 kJ mol⁻¹. Our best estimate of Δ*H*_{f,298} for benzyl cation, obtained as the subjective average of these individual values, is 907 ± 8 kJ mol⁻¹.

Our predicted Δ*H*_{f,298} of 907 kJ mol⁻¹ for benzyl cation (**2-C**) is close to the value of 910 kJ mol⁻¹ that comes from combining recent measurements of the ionization energy of benzyl radical

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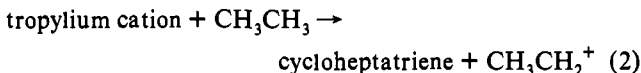
Table 1. Relative Isomer Energies (kJ mol⁻¹)

	<i>E</i> (2-C - 1-C)	<i>E</i> (2-Si - 1-Si)
AM1	49	16
HF/6-31G(d)	24	-53
MP2/6-31G(d) ^a	49	-44
MP2/6-311G(d,p) ^a	46	-48
MP2/6-311+G(3df,2p) ^a	42	-48
QCISD(T)/6-311G(d,p) ^a	32	-38
QCISD(T)/6-311+G(d,p) ^a	31	-40
QCISD(T)/6-311G(2df,p) ^a	30	
G2(MP2)(0 K) ^a	28	-38
G2(0 K) ^a	29	
G2(MP2)(298 K) ^a	29	-38
G2(298 K) ^a	29	
expt(298 K)	31-67	

^a At MP2(full)/6-31G(d) optimized geometries.

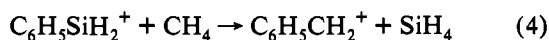
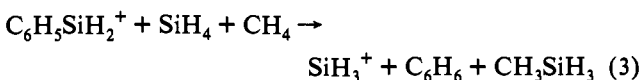
(699.40 ± 0.06 kJ mol⁻¹)¹⁵ and of the ΔH_f^{298} for benzyl radical (210.5 ± 2 kJ mol⁻¹).¹⁶ Other recent experimental determinations of ΔH_f^{298} for 2-C give values that lie somewhat further away, namely, 897 ± 5²¹ and 916 ± 9^{2k} kJ mol⁻¹.¹⁷

The relative energies of benzyl cation (2-C) and tropylium cation (1-C) at a variety of levels of theory are displayed in Table 1. Consistent with previous theoretical and experimental work, tropylium cation is found to be the lower energy isomer.¹⁸ The results in Table 1¹⁴ show that electron correlation effects are very important and the energy difference between 1-C and 2-C is lowered significantly at levels of theory beyond MP2. Basis set effects are much smaller. At our best theoretical level (G2), we find that 1-C is more stable than 2-C by 29 kJ mol⁻¹. This value, in conjunction with our best estimate for the ΔH_f^{298} for 2-C (907 ± 8 kJ mol⁻¹), gives 878 ± 8 kJ mol⁻¹ as the ΔH_f^{298} for 1-C. A very similar value (877 kJ mol⁻¹) is obtained from consideration of the G2 (MP2) energy change for the isodesmic reaction 2,



in conjunction with the experimental ΔH_f^{298} values¹³ for species other than 1-C. Experimental values^{2d,h,k,13} lie in the range 849–866 kJ mol⁻¹ and are often indirect estimates. The discrepancy between theory and experiment of up to 30 kJ mol⁻¹, particularly in the more recent determinations, is sufficiently large that we believe the latter should be reexamined.

The heat of formation for the silabenzyl cation (2-Si) may be estimated through the use of isogyric reactions such as 3 and 4:



Using the G2(MP2) (298 K) energy change for reaction 3 in conjunction with the experimental ΔH_f^{298} values¹³ for all the species involved except for 2-Si, the ΔH_f^{298} of 2-Si is found to be 948 kJ mol⁻¹. Similarly, reaction 4 gives 941 kJ mol⁻¹ for the ΔH_f^{298} of 2-Si.¹⁹ From a set of reactions of this type,¹⁴ we assign a value of 943 ± 12 kJ mol⁻¹ to the heat of formation of 2-Si. There are no direct experimental values, but combining the measured hydride ion affinity of the silabenzyl cation (2-Si) (961 kJ mol⁻¹)^{3b} with the heat of formation of H⁻ (145 kJ mol⁻¹)¹³ and

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(17) Previous semiempirical calculations^{9b,c} yielded higher values (922 kJ mol⁻¹, 933 kJ mol⁻¹), while a low-level ab initio study^{9a} using isodesmic reactions gave 908 kJ mol⁻¹.

(18) Ab initio calculations with the 3-21G basis set including electron correlation find 1-C to be more stable than 2-C by 46 kJ mol⁻¹.^{9d}

Table 2. Comparison of Best Theoretical Thermochemical Data with Experimental Values for 1 and 2 (298 K, kJ mol⁻¹)^a

	theory ^b	expt
ΔH_f^{298} (1-C)	878	853, 859, 866, 849 ^c
ΔH_f^{298} (2-C)	907	910, 897, 916, 899 ^c
<i>E</i> (2-C - 1-C)	29	
ΔH_f^{298} (1-Si)	981	
ΔH_f^{298} (2-Si)	943	
<i>E</i> (2-Si - 1-Si)	-38	

^a See text for details, unless otherwise noted. ^b Theoretical values of ΔH_f^0 , obtained by applying theoretical temperature corrections to the ΔH_f^{298} values, are 898 (1-C), 926 (2-C), 1000 (1-Si), and 962 (2-Si) kJ mol⁻¹. ^c From ref 13.

our predicted heat of formation for silatoluene (127 kJ mol⁻¹)^{14,20} leads also to an estimate for ΔH_f^{298} of 2-Si of 943 kJ mol⁻¹.

The relative stabilities of 1-Si and 2-Si are of great interest, as noted earlier. We find, as for the all-carbon analogues, that electron correlation effects are large whereas basis set effects appear to be small (Table 1). At all ab initio levels of theory, we find the silabenzyl cation (2-Si) to be substantially more stable than the silatropylium cation (1-Si). Our best estimate of the energy difference is 38 kJ mol⁻¹ (G2(MP2)). Substitution by Si thus has the effect of reversing the stability ordering of the two isomers.²¹ We consider it highly unlikely that higher levels of theory would alter this qualitative result. On the basis of our estimate of 943 ± 12 kJ mol⁻¹ for the heat of formation of 2-Si, we propose a ΔH_f^{298} value for 1-Si of 981 ± 12 kJ mol⁻¹.

In summary (Table 2) we find that the tropylium cation lies 29 kJ mol⁻¹ lower in energy than the benzyl cation. Our best predicted ΔH_f^{298} for benzyl cation of 907 ± 8 kJ mol⁻¹ lies close to a recent experimental value of 910 kJ mol⁻¹. However, our proposed ΔH_f^{298} for tropylium cation (1-C) (878 ± 8 kJ mol⁻¹) lies significantly above the current experimental values, suggesting that the latter should be reexamined.

We find that the silabenzyl cation (2-Si) lies 38 kJ mol⁻¹ below the silatropylium cation (1-Si), i.e., substitution by silicon has reversed the stability ordering of the two isomers. Thus, our ab initio results do not support the suggestion based on indirect experimental evidence that the silatropylium cation is more stable than the silabenzyl cation.^{3a} Our best predicted ΔH_f^{298} values are 981 ± 12 kJ mol⁻¹ for the silatropylium cation (1-Si) and 943 ± 12 kJ mol⁻¹ for the silabenzyl cation (2-Si).

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Supplementary Material Available: HF/6-31G(d) frequencies for compounds 1-C, 2-C, 1-Si, and 2-Si (2 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

(19) In the light of uncertainties regarding the experimental ΔH_f^{298} for 2-C, we use our best theoretical estimate of 907 kJ mol⁻¹ in the thermochemical analysis of reaction 4.

(20) The ΔH_f^{298} for silatoluene was obtained from isogyric reactions such as $\text{C}_6\text{H}_5\text{SiH}_3 + \text{CH}_4 \rightarrow \text{C}_6\text{H}_5\text{CH}_3 + \text{SiH}_4$.

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