

# What causes the nonclassical structure of 2-norbornyl ion?

Ruchit A. Patel and Allan L.L. East

**Abstract:** A recent publication of a general carbocation rearrangement mechanism highlighted protonated cyclopropane (PCP<sup>+</sup>) intermediates, whose structures are meso between the nonclassical hypotheses of edge-PCP<sup>+</sup> and corner-PCP<sup>+</sup>. Unlike the nonclassical structures, which possess 3-centre–2-electron bonds, the meso-PCP<sup>+</sup> structures appear as closed classical structures. The 2-norbornyl ion, however, is known to have a nonclassical corner-PCP<sup>+</sup> structure, and here we explore (using computational chemistry) the reasons why. The main reasons are due to the three 5-membered carbon rings, whose ring strain resist relaxation to a meso-PCP<sup>+</sup> structure, but an additional reason is the trisubstitution on one side of the PCP<sup>+</sup> face, which causes unfavourable C–C bond eclipsing.

*Key words:* carbocation, carbenium, nonclassical, norbornyl.

**Résumé :** Dans une récente publication portant sur un mécanisme général de réarrangement de carbocations, on a mis en évidence des intermédiaires protonés du cyclopropane (CPP<sup>+</sup>), dont les structures sont méso entre des structures de type arête-CPP<sup>+</sup> et sommet-CPP<sup>+</sup> proposées par des hypothèses non classiques. Contrairement aux structures non classiques, qui possèdent des liaisons tricentriques à deux électrons, les structures de type méso-CPP<sup>+</sup> semblent plus près des structures classiques. Toutefois, on sait que l'ion 2-norbornyl possède une structure non classique de type sommet-CPP<sup>+</sup>, et nous en avons cherché les raisons dans le cadre des présents travaux (par des méthodes de chimie computationnelle). Les principales raisons concernent les trois cycles carbonés à 5 membres, dont la tension de cycle résiste à la relaxation de la structure de type méso-CPP<sup>+</sup>; cependant, une autre raison concerne la trisubstitution d'un côté de la face de l'ion CPP<sup>+</sup>, ce qui produit une éclipse défavorable des liaisons C–C. [Traduit par la Rédaction]

*Mots-clés :* carbocation, carbénium, non classique, norbornyl.

## Introduction

Olah popularized the notion of 3-centre–2-electron (3c–2e) nonclassical bonds in carbocation intermediates.<sup>1–3</sup> Cases of CHH (e.g., CH<sub>5</sub><sup>+</sup>),<sup>4</sup> CCH (e.g., 2-butyl),<sup>5</sup> and CCC (e.g., 2-norbornyl)<sup>6–9</sup> 3c–2e bonds are known experimentally.

Here, the CCC 3c–2e bonds (“protonated cyclopropane” units or PCP<sup>+</sup>), are scrutinized. The 2-norbornyl cation is one of a few known cases of a nonclassical protonated cyclopropane.<sup>3</sup> Most computational geometry optimization studies of acyclic alkyl ions<sup>10–15</sup> instead produce “closed” pseudoclassical structures we term meso-PCP<sup>+</sup> (for being mesomeric between nonclassical edge-PCP<sup>+</sup> or corner-PCP<sup>+</sup> forms, Fig. 1). Our group recently published the results of a large study of hexyl ion rearrangements in which it is suggested that nonclassical CCC 3c–2e structures are more the exception than the norm.<sup>16</sup> In this study, we set out to employ computational chemistry methods to learn what causes the 2-norbornyl ion to prefer a nonclassical structure.

## Computational methods

Computations employed Gaussian09.<sup>17</sup> Most geometry optimizations were performed with B3LYP/cc-pVDZ, a standard density functional theory and basis set. Some of the smaller systems were also optimized with the (frozen-core) coupled-cluster method CCSD/cc-pVDZ. Effects of larger Dunning basis sets<sup>18,19</sup> and the (T) coupled-cluster correction<sup>20</sup> were explored with single-point runs. Only electronic energies are reported, because, in some cases, the harmonic-oscillator zero-point vibrational energy (ZPVE) for the

mode of interest (meso-PCP<sup>+</sup> → corner-PCP<sup>+</sup>) would be a significant overestimate of the true ZPVE compared to the small barrier separating these two structures. Eight carbocations (cyclic and acyclic) in addition to 2-norbornyl cation were examined (Fig. 2).

## Results and discussion

### C<sub>s</sub>-symmetry corner-PCP<sup>+</sup> structures

The nine carbocations were first optimized within C<sub>s</sub> symmetry, which maintains a nonclassical corner-PCP<sup>+</sup> structure. Only 2-norbornyl 111cap) was found to have a local minimum in C<sub>s</sub> (at the two levels of theory chosen); all others produced one or two imaginary *a*′-symmetry vibrational frequencies (Table 1). At these levels of theory, 2-norbornyl is indeed unique for having a C<sub>s</sub>-symmetry corner-PCP<sup>+</sup> minimum.

Insight into the unique stability of 2-norbornyl can be had from comparing frequencies of common normal modes among the carbocations in Table 1. Consider first the shift and internal-rotation modes ( $\omega_{\text{shift}}$  and  $\omega_{\text{rot}}$ ). The 000 and 001 molecules are in a class by themselves, because they have no substituents on the two base carbons of the PCP<sup>+</sup> unit; they are thus closed primary cations. In these cases, the imaginary frequency is for internal rotation ( $\omega_{\text{rot}}$ ), whereas the shift mode ( $\omega_{\text{shift}}$ ) has positive curvature. The stability in the shift mode indicates significant reluctance by both base carbons to lose the bridgehead carbon and gain positive partial charge (owing to lack of charge-stabilizing subalkyl substituents). The situation is different for the closed secondary cases, where  $\omega_{\text{rot}}$  becomes positive and  $\omega_{\text{shift}}$  (in five of the seven cases with

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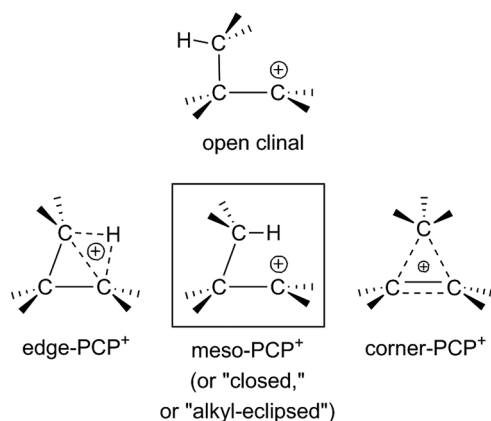
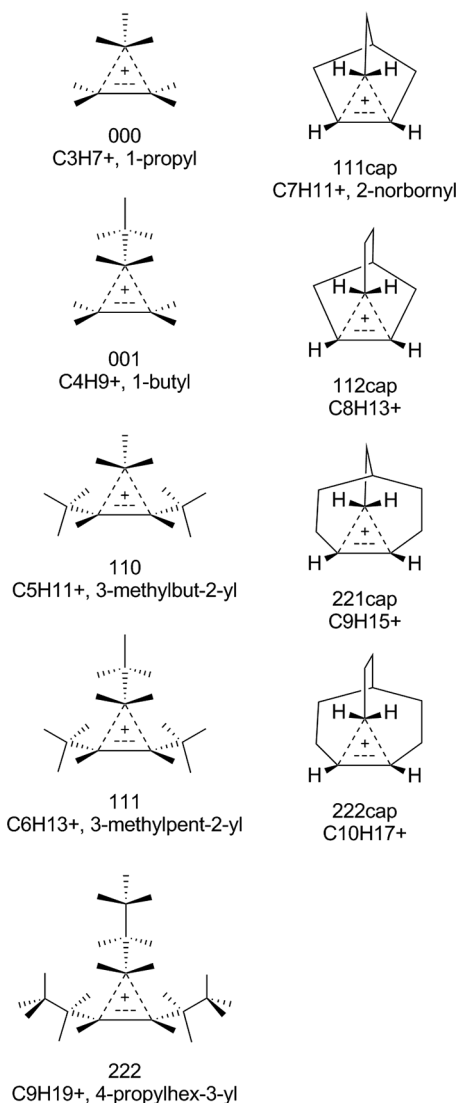
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Fig. 1. Structure definitions.

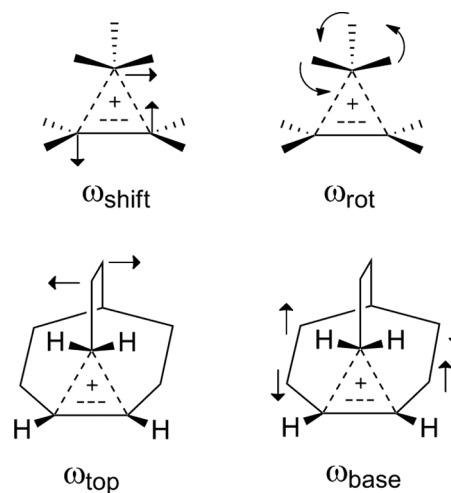
Fig. 2. Carbocations in this study (hypothetical  $C_s$ -symmetry corner-PCP<sup>+</sup> forms). PCP = protonated cyclopropane.

B3LYP) becomes imaginary. Here, the instability in the shift mode denotes an energetic preference to localize the 3c–2e bond into a 2c–2e bond, the benefit apparently outweighing the penalty of partial localization of charge on a substituent-stabilized base carbon.

Table 1. The important low-frequency ( $\omega$ ,  $\text{cm}^{-1}$ )  $a''$ -symmetry harmonic vibrational modes of optimized hypothetical  $C_s$ -symmetry corner-PCP<sup>+</sup> structures.

Cation (substituents)	B3LYP/cc-pVDZ				CCSD/cc-pVDZ			
	$\omega_{\text{shift}}$	$\omega_{\text{rot}}$	$\omega_{\text{top}}$	$\omega_{\text{base}}$	$\omega_{\text{shift}}$	$\omega_{\text{rot}}$	$\omega_{\text{top}}$	$\omega_{\text{base}}$
<b>Closed primary carbocations</b>								
000	311	(63i)			321	(100i)		
001	317	(84i)			328	(106i)		
<b>Closed secondary carbocations</b>								
110	(186i)	125			(134i)	147		
111	(115i)	79			(95i)	131		
222	(166i)	39, 81			(133i)	45, 130		
111cap	138				190			
112cap	89		(204i)		160		(214i)	
221cap	(166i)			(105i)	(45i)			(124i)
222cap	(126i)		(235i)	85	54		(224i)	161

Note: Definitions of the normal modes appear in Fig. 3. Values in italic typeface are imaginary frequencies.

Fig. 3. Normal mode definitions. The rot mode does not exist in the cyclic (capped) ions. The top and base twist modes exist if ethylene connections (from the PCP<sup>+</sup> unit to the CH cap) are present. PCP = protonated cyclopropane.

Unlike the other five closed-secondary carbocations in Table 1, the 111cap and 112cap species produced shift modes of positive curvature (B3LYP). When compared with these other five carbocations, the only conclusion possible is that this is due to the cyclopentyl base. In animations, the shift mode contains a not insignificant component of base-carbon oscillation (see Fig. 3), and it seems that when these two base carbons are contained in 5-membered rings, ring strain does not allow this motion to be a relaxing one.

The CCSD  $\omega_{\text{shift}}$  frequencies are consistently less imaginary/more positive than the B3LYP values: by  $\sim 10 \text{ cm}^{-1}$  for the closed primary ions,  $20\text{--}50 \text{ cm}^{-1}$  for most of the closed secondary ions, and by  $120\text{--}180 \text{ cm}^{-1}$  for the cyclic secondary ions having a cycloheptyl base. This indicates that CCSD favours the nonclassical structures to a greater degree than B3LYP does. It is peculiar that the largest effect is for cases that lie between the no-strain acyclic species and the significantly strained cyclopentyl-base cases. The effect for the cycloheptyl-base cases was so large that it produced a qualitative disagreement with B3LYP, allowing one of these two cases (222cap) to produce a positive  $\omega_{\text{shift}}$  value. CCSD predicts that this ion, with a 7-membered-ring base, obtains sufficient stability with the 3c–2e bond that no relaxation benefit is available via distortion with the shift mode.

**Table 2.** Structure parameters  $\theta$  and  $\Phi$  (see Fig. 4) ( $^\circ$ ) and stabilization energies ( $\Delta E$ , kJ mol $^{-1}$ ) of meso-PCP $^+$  structures.

Cation	$\theta$ (B3LYP)	$\Delta E$ (B3LYP)	$\Phi$ (B3LYP)	$\theta$ (CCSD)	$\Delta E$ (CCSD)	$\Phi$ (CCSD)
000	71.4	0.39	0	71.2	0.85	0
001	73.2	1.02	-15	73.0	1.80	-11
110	88.0	2.45	-53	76.1	0.60	-24
111	79.7	1.08	-26	76.8	0.98	-19
222	82.1	3.65	-21	78.1	2.71	-18

Note: PCP = protonated cyclopropane.

Despite the ability of cyclopentyl bases and (or) CCSD to benefit  $C_s$ -symmetry structures (relative to  $\omega_{\text{shift}}$ -distorted ones), in the cyclic cases there are other modes that succeed in causing distortions away from  $C_s$  symmetry, because of the ethylene bridges (from PCP $^+$  face to CH cap) that prefer to twist out of  $C_s$  symmetry to avoid eclipsed CH bonds. When the top arm is increased from  $\text{CH}_2$  to  $\text{CH}_2\text{CH}_2$  (112cap or 222cap), the created top twist mode ( $\omega_{\text{top}}$ ) gives an imaginary frequency. When the base arms are similarly increased in length, the created base antisymmetric twist mode ( $\omega_{\text{base}}$ ) gives an imaginary frequency for 221cap, but not for 222cap. This gives further insight into the unique stability of corner-PCP $^+$  in the case of 2-norbornyl ion: the methylene connections eliminate the possibility of twist modes that would cause loss of  $C_s$  symmetry. This aspect, together with the rigidity of the cyclopentyl base preventing shift distortion, explains why 2-norbornyl is unique as the only stable  $C_s$ -symmetry nonclassical PCP $^+$  among the nine cations tested, according to data in Table 1.

Three questions could still be posed: (i) Could some of these molecules with positive  $\omega_{\text{shift}}$  values distort into  $C_1$  symmetry via other modes but maintain corner-PCP $^+$  structures? (ii) Could even higher levels of theory turn some of the Table 1 ions into all-positive-frequency  $C_s$ -symmetry corner-PCP $^+$  ions? (iii) Could other carbocations (beyond those in Fig. 2 and Table 1) produce  $C_s$ -symmetry corner-PCP $^+$  ions? These questions are addressed in turn in the following.

#### Possible $C_1$ -symmetry corner-PCP $^+$ structures

The eight carbocations showing imaginary frequencies when in  $C_s$  were next distorted and relaxed in  $C_1$  symmetry to search for  $C_1$ -symmetry corner-PCP $^+$  structures, but also (in the cases where meso-PCP $^+$  minima were found) to compute the meso stabilization energy  $\Delta E = E(\text{corner-PCP}^+) - E(\text{meso-PCP}^+)$ .

To isolate the ring strain effects, the trends for the acyclic compounds were first analyzed (Table 2 and Fig. 4). For all five cases, minimizations produced meso-PCP $^+$  structures. Generally, as substituents are added to the PCP $^+$  moiety, the  $\theta_{\alpha,\beta,\gamma}$  angle in the meso-PCP $^+$  structure increasingly distorts, from corner-PCP $^+$  values of  $67.0^\circ$ – $68.5^\circ$  to values beyond  $70^\circ$  (note Et > Me > H). With this increased distortion come increases in  $\Delta E$ ,  $\Phi_{\alpha,\beta,\gamma,\delta}$  (dihedral distortion from zero, owing to increased steric repulsion of the eclipsed  $\text{C}_\beta\text{C}_\gamma$  orientation), and  $|\omega_{\text{imag}}|$  (the magnitude of the imaginary frequency at the corner-PCP $^+$  saddle point). Also worth pointing out at this juncture are the differences between CCSD and the presumably inferior B3LYP. For the closed primary carbocations (000 and 001), CCSD relative to B3LYP predicts higher stabilizations (and nearly equal distortions), but for the closed secondary carbocations (110, 111, 222), CCSD relative to B3LYP predicts smaller stabilizations (and smaller distortions).

With these general trends in hand, the results for the capped (cyclic) species are now presented.

The species 112cap differs from 2-norbornyl by having one extra methylene group in the “top arm” (Fig. 2), which introduces to the  $C_s$ -symmetry PCP $^+$  form an imaginary frequency for top-arm twisting ( $\omega_{\text{top}}$ ). However, its  $\omega_{\text{shift}}$  is positive (Table 1), and hence there was the prospect of a  $C_1$ -symmetry corner-PCP $^+$  minimum. However, relaxation led to a meso-PCP $^+$  structure. The  $C_s$ -symmetry PCP $^+$  structure is a high-energy transition state (TS) for flipping the top-

arm chirality, which happens to also result in the 1,2-subalkyl shift. There is a lower energy  $C_1$ -symmetry corner-PCP $^+$  stationary point, but it is due to a TS (for a lower-energy 1,2-subalkyl shift that follows  $\omega_{\text{shift}}$  rather than  $\omega_{\text{top}}$  and thus avoids the top-arm flip) (Fig. 5).

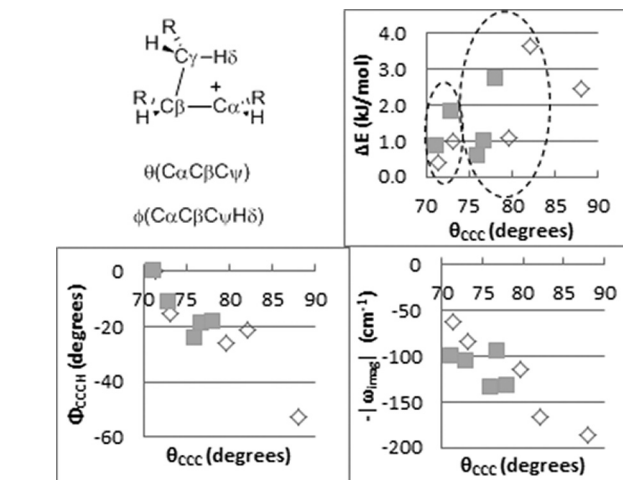
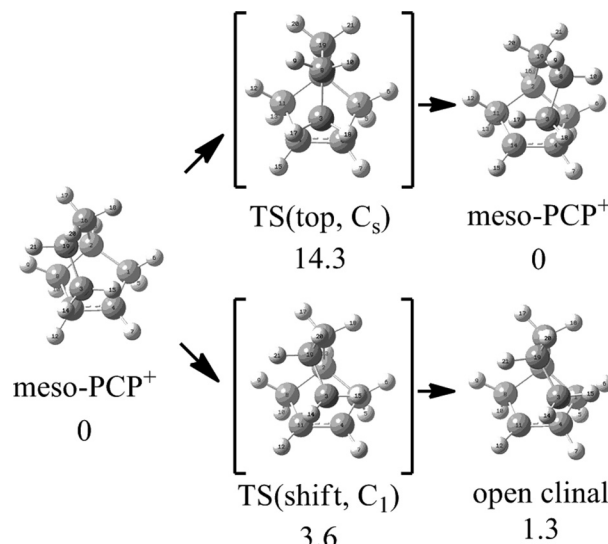


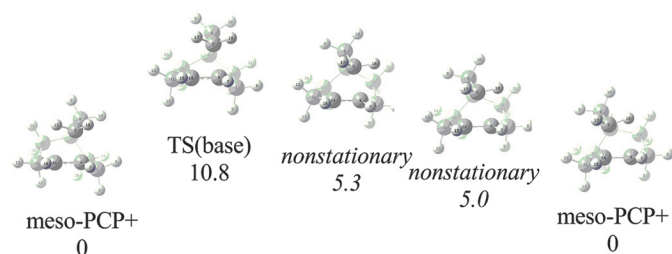
Fig. 5. B3LYP/cc-pVDZ results for cation 112cap. Numbers are relative energies (kJ mol $^{-1}$ ).



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The species 221cap differs from 2-norbornyl by having extra methylene groups in the base arms (Fig. 2), which introduces to the  $C_s$ -symmetry PCP $^+$  form two imaginary frequencies: one for base-arm twisting ( $\omega_{\text{base}}$ ), but also one for the shift proper ( $\omega_{\text{shift}}$ ). Hence, there was little prospect in finding a  $C_1$ -symmetry corner-PCP $^+$  minimum. So far we have found only one energy-unique minimum with B3LYP, a chiral meso-PCP $^+$  structure, and one  $C_1$ -symmetry transition state connecting the enantiomers. The path is asynchronous, in that the TS occurs during the base-twist mo-

**Fig. 6.** B3LYP/cc-pVDZ results for cation 221cap. Numbers are relative energies ( $\text{kJ mol}^{-1}$ ).



**Table 3.** B3LYP/cc-pVDZ relative energies for six elementary rearrangements among PCP<sup>+</sup> conformers of 222cap carbocation.

Structure	Relative energy ( $\text{kJ mol}^{-1}$ )					
	AE shift	AB base	BC shift	CE base	BD top	AC top
min	0.0	0.0	1.1	1.9	1.1	0.0
TS	4.3	4.6	5.1	5.8	22.5	26.7
min	3.1	1.1	1.9	3.1	2.9	1.9

**Note:** The path labels refer to the conformers connected and the connecting mode of Fig. 3, e.g. “AE shift” is the path from conformer A to conformer E via  $\omega_{\text{shift}}$ . Two of the six paths are explicitly shown in Fig. 7. See text for additional description of the paths.

tion, leaving the 1,2-subalkyl shift motion as an afterthought during energy descent (Fig. 6).

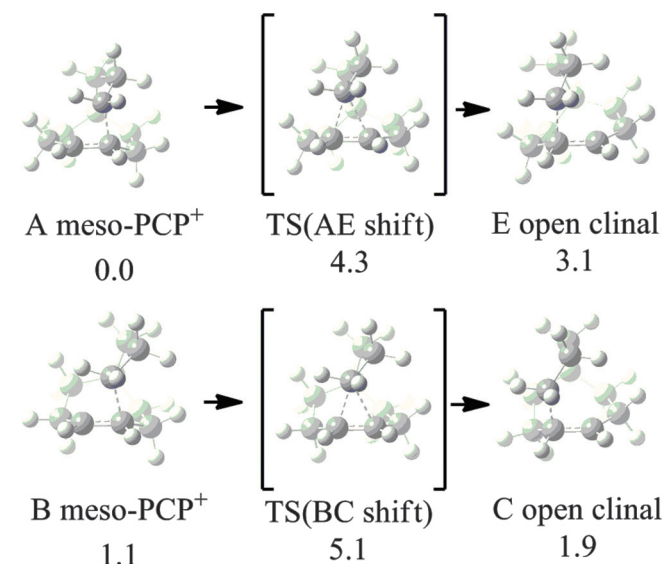
The species 222cap differs from 2-norbornyl by having extra methylene groups in all three arms. This introduces an imaginary frequency for top-arm twisting ( $\omega_{\text{top}}$ ), and at B3LYP (but not CCSD) another imaginary frequency ( $\omega_{\text{shift}}$ ). In searches for energy minima at the B3LYP level of theory we found 4 energy-unique pairs of enantiomeric PCP<sup>+</sup> intermediates, connected by 6 energy-unique pairs of enantiomeric transition states. None of the 4 intermediates have nonclassical corner-PCP<sup>+</sup> structures: two are meso-PCP<sup>+</sup> while two others are open clinal structures. If one labels the intermediates according to their top-arm torsional distortion (+ or -), their base-loop distortion (+ or -), and the shift distortion (L or R); then the four energy-unique intermediates are A (++L = --R), B (+-L = +-R), C (-+L = +-R), and DE<sup>21</sup> (-L = ++R); and the six energy-unique TSs are of two shift, two top flip, and two base flip type: AE Shift (++L to +-R), BC Shift (+-L to +-R), AB Base (++L to +-L), CE Base (-+L to --L), BD Top (++L to --L), and AC Top (+-L to --L). Table 3 presents the energies of these six elementary rearrangement steps. Only the shift steps traverse nonclassical corner-PCP<sup>+</sup> structures, such structures being TSs (Fig. 7).

In summary, (i) no nonclassical corner-PCP<sup>+</sup> intermediates were found (in  $C_s$  or  $C_i$  symmetry) for carbocations other than 111cap (2-norbornyl), (ii) in the acyclic carbocations tested, the B3LYP/CCSD meso stabilization energies  $E_{\text{corner}}(C_s, \text{TS}) - E_{\text{meso}}$  were 0.4–3.6  $\text{kJ mol}^{-1}$  (Table 2), and (iii) for the cyclic carbocations tested, the B3LYP stabilization energies  $E_{\text{corner}}(C_i, \text{TS}) - E_{\text{meso}}$  were 3.6–4.6  $\text{kJ mol}^{-1}$  (Figs. 5 and 7, following the subalkyl shift mode without allowing flipping of top or base ethylene bridge chirality).

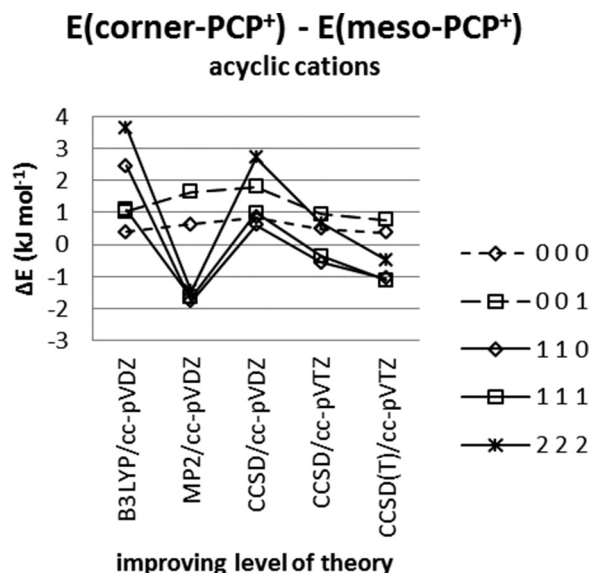
### Higher levels of theory

The computed stabilization energies, for distortion from corner-PCP<sup>+</sup> to meso-PCP<sup>+</sup>, were all less than 5  $\text{kJ mol}^{-1}$ , and in some acyclic cases less than 1  $\text{kJ mol}^{-1}$ . Therefore, we employed higher levels of theory in single-point calculations to test if the lack of corner-PCP<sup>+</sup> structures were due to the B3LYP/cc-pVDZ or CCSD/cc-pVDZ approximations. The results (Fig. 8) were surprising. Although both B3LYP/cc-pVDZ and CCSD/cc-pVDZ predicted positive stabilization in all five cases, CCSD(T)/cc-pVTZ (the best level of theory here<sup>22</sup>) predicted positive stabilization for only the two closed primary cases; for the tree closed secondary cases, it predicted nonclassical corner-PCP<sup>+</sup> to be the structure of the PCP<sup>+</sup>

**Fig. 7.** B3LYP/cc-pVDZ results for cation 222cap. Numbers are relative energies ( $\text{kJ mol}^{-1}$ ).



**Fig. 8.** Computed meso-PCP<sup>+</sup> stabilization energies for five acyclic carbocations. All but the B3LYP/cc-pVDZ data were computed using CCSD/cc-pVDZ geometries. The closed secondary ions (110, 111, 222) were more sensitive to improvements to electron correlation and basis set than the closed primary ions (000, 001). PCP = protonated cyclopropane.



isomer! Improved electron correlation beyond CCSD, and improved basis set coverage beyond cc-pVDZ, both served to further stabilize corner-PCP<sup>+</sup> relative to meso-PCP<sup>+</sup>.

At first glance this was alarming, considering that our group recently published results suggesting that corner-PCP<sup>+</sup> structures would be rare as intermediates.<sup>16</sup> Upon careful comparison of the present results for the cation 111 (1,2,3-trimethylPCP<sup>+</sup> or 3-methylpent-2-yl ion) with our previous ones, we discovered that the preference for corner-PCP<sup>+</sup> in the present three cases (110, 111, 222) is due to having all three subalkyl substituents on the *same side* of the PCP<sup>+</sup> face, a higher energy form that we chose here to mimic 2-norbornyl ion. In the lower energy form of 111 in which one methyl group is on the opposite side of the PCP<sup>+</sup> face, meso-PCP<sup>+</sup> is more stable than corner-PCP<sup>+</sup> by 1.6  $\text{kJ mol}^{-1}$  [CCSD(T)/aug-

cc-pVTZ//PBE/6-31G(d,p)].<sup>16</sup> This observation adds a third contributing factor to the unusual stability of the nonclassical corner-PCP<sup>+</sup> 2-norbornyl ion: it forces the three subalkyl groups to be on one side of the PCP<sup>+</sup> face, which slightly destabilizes the meso-PCP<sup>+</sup> structure relative to the corner-PCP<sup>+</sup> version because of eclipsed C–C bonds.

### Other carbocations

Three factors were identified that contribute to the unusual nonclassical 3c–2e CCC bond in 2-norbornyl ion (111cap): (i) the 1,2,3-trisubstitution on the same side of the PCP<sup>+</sup> face, (ii) the short methylene bridges to a common CH cap, which eliminate the possibility of bridge twist modes, and (iii) the rigidity of the cyclopentyl base, which prevents shift distortions (along  $\omega_{\text{shift}}$ ) from contributing to stability. Should carbocations other than 2-norbornyl actually exist with a 3c–2e CCC bond, the most likely candidates would appear to be cyclic versions that hold subalkyl substituents on a common side of the PCP<sup>+</sup> face, with a cyclopentyl base to prevent shift distortions, and a tether to the top carbon that does not introduce strong chiral-flip strain. This is already a significant limitation in possibilities (although one such system, similar to 2-norbornyl but with the methylene in the top arm removed, is known and is indeed nonclassical<sup>23</sup>). In addition, if one considers the possibilities of  $\beta$ -scissions or rearrangements to much more stable tertiary ions, it is hard at present to imagine many more cases of experimentally observable 3c–2e CCC bonds.

### Conclusion

Evidence is presented that the occurrence of CCC 3c–2e bonds in carbocations should be unusual. The occurrence of this nonclassical structure in 2-norbornyl ion was determined to be due to three factors: (i) the 1,2,3-trisubstitution on the same side of the PCP<sup>+</sup> face, (ii) the short methylene bridges to a common CH cap, which eliminate the possibility of bridge twist modes, and (iii) the rigidity of the cyclopentyl base, which prevents shift distortions (along  $\omega_{\text{shift}}$ ) from contributing to stability.

### Supplementary material

Supplementary material is available with the article through the journal Web site at <http://nrcresearchpress.com/doi/suppl/10.1139/cjc-2016-0242>.

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- “DE” represents two nearly identical structures (D and E) separated by only 0.2 kJ mol<sup>-1</sup> in energy and 18° in one CCCC torsional angle.
- The effect of adding diffuse functions to the cc-pVTZ basis set was tested with MP2/aug-cc-pVTZ calculations on ions 000 and 111 and found to have only 0.1 kJ mol<sup>-1</sup> effects on the stabilization energy. Since CCSD(T)/cc-pVTZ does not generally provide reliable 2 kJ mol<sup>-1</sup> accuracy on this type of stability calculation, definitive statements on the most stable form of any of these five acyclic cations in Fig. 8 cannot be made. However, the observed trends (closed-primary versus closed-secondary, effect of same-face versus non-same-face 1,2,3-trisubstitution) should be reliably given by CCSD(T)/cc-pVTZ.
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