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# Gas phase enthalpies of formation, isomerization, and disproportionation of mono- through tetra-substituted tetrahedranes: A G4(MP2)/G4 theoretical study

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## ABSTRACT

Gas phase standard state (298.15 K, 1 atm) enthalpies of formation ( $\Delta_f H^\circ_{(g)}$ ), enthalpies of disproportionation to two corresponding acetylene molecules ( $\Delta_{rxn} H^\circ_{(g),Td \rightarrow acet}$ ), and enthalpies of isomerization from a tetrahedrane geometry to a 1,3-cyclobutadiene structure ( $\Delta_{isom} H^\circ_{(g),Td \rightarrow CBD}$ ) were calculated for the mono- through tetra-substituted hydro, fluoro, chloro, bromo, methyl, ethynyl, and cyano carbon tetrahedrane derivatives at the G4(MP2) and G4 levels of theory. All derivatives have endothermic  $\Delta_f H^\circ_{(g)}$  indicative of the cage strain in these systems. In all cases,  $\Delta_{rxn} H^\circ_{(g),Td \rightarrow acet}$  and  $\Delta_{isom} H^\circ_{(g),Td \rightarrow CBD}$  are predicted to be substantially exothermic. High quality linear regression fits within a homologous series were obtained between the number of substituents and the G4(MP2)/G4 estimated  $\Delta_f H^\circ_{(g)}$ . Via calculations on lower homolog members, this strategy was employed to allow extrapolated G4 and/or G4(MP2)  $\Delta_f H^\circ_{(g)}$  (as well as some  $\Delta_{rxn} H^\circ_{(g),Td \rightarrow acet}$  and  $\Delta_{isom} H^\circ_{(g),Td \rightarrow CBD}$ ) to be obtained for the higher homolog t-butyl, trifluoromethyl, and trimethylsilyl carbon tetrahedrane derivatives.

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Tetrahedrane (Fig. 1) has long captured the imagination of theoreticians and experimentalists [1]. Although synthesis of the parent carbon tetrahedrane has not yet been achieved, a number of its substituted derivatives have been prepared [2–10]. While much theoretical work has focused on the parent system (see, e.g., Refs. [11–23] and references therein), less computational effort has been undertaken on substituted tetrahedranes [24–32]. Continued theoretical interest in the tetrahedranes is important because advances in computing power and model chemistries (particularly composite methods) are facilitating increasingly accurate thermodynamic studies on these compounds. In concert, synthetic chemists are illustrating that the successful isolation of many tetrahedrane derivatives are likely within practical reach.

Our initial theoretical efforts focused on the mono- through tetra-substituted hydro (i.e., parent system), fluoro, chloro, bromo, methyl, ethynyl, and cyano carbon tetrahedrane derivatives. These substituents encompass a range of electron-withdrawing and releasing abilities and impart minimal conformational complexity. The G4 [33] and G4(MP2) [34] composite methods were employed using Gaussian 09 [35]. All calculations were conducted in the gas phase (1 atm) at 298.15 K. Geometries were visualized using

Gabedit v.2.2.12 [36] and Avogadro v.1.01 (<http://avogadro.openmolecules.net/>). Except where noted otherwise, all compounds converged absent imaginary frequencies.

Gas phase (298.15 K, 1 atm) enthalpies of formation ( $\Delta_f H^\circ_{(g)}$ ) were calculated using the atomization approach [37–40] (Table 1). Prior work has established that G4(MP2)/G4 atomization  $\Delta_f H^\circ_{(g)}$  are expected to be at effective chemical accuracy [33,34,29,39–46]. None of these compounds have been synthesized; thus, no experimental  $\Delta_f H^\circ_{(g)}$  are available for comparison. Excellent agreement between the G4(MP2) and G4  $\Delta_f H^\circ_{(g)}$  estimates was obtained, yielding a mean signed deviation (MSD) of 1.6 kJ/mol (G4–G4(MP2)), mean absolute deviation (MAD) of 3.3 kJ/mol, and a root mean squared deviation (RMSD) of 4.4 kJ/mol. Neither the G4(MP2) nor G4 methods converged on a tetrafluorotetrahedrane structure absent imaginary frequencies. Instead, both methods yielded a final geometry with two imaginary frequencies. A Gaussian-3 (G3) [47–49] calculation on this compound gave the desired tetrahedrane structure with no imaginary frequencies, and a corresponding atomization  $\Delta_f H^\circ_{(g)}$  at this level of 70.2 kJ/mol.

Linearly regressing the number of fluorine substituents ( $n = 1–3$ ) against the G4(MP2) and G4  $\Delta_f H^\circ_{(g)}$  estimates provides high quality fits (G4(MP2):  $r^2 = 0.9994$ ,  $m = 516.7$ ,  $b = -114.6$ ; G4:  $r^2 = 0.9994$ ,  $m = 520.5$ ,  $b = -115.4$ ; values in kJ/mol). Extrapolating

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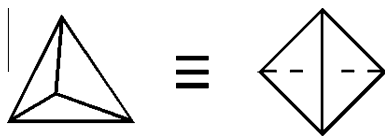


Fig. 1. Three- and two-dimensional representations of tetrahedrane.

Table 1

G4(MP2) and G4 estimated gas phase standard state (298.15 K, 1 atm) enthalpies of formation ( $\Delta_f H^\circ_{(g)}$ ) using the atomization approach for various mono- through tetra-substituted carbon tetrahedrane derivatives. Values are in kJ/mol.

Substituent	No.	G4(MP2)	G4
–H	tetra-	532.4	536.4
–CH <sub>3</sub>	mono-	498.0	501.0
–CH <sub>3</sub>	di-	464.5	466.2
–CH <sub>3</sub>	tri-	431.8	432.2
–CH <sub>3</sub>	tetra-	400.2	399.1
–C≡CH	mono-	769.9	772.9
–C≡CH	di-	1009.5	1011.3
–C≡CH	tri-	1250.2	1250.9
–C≡CH	tetra-	1490.9	1490.7
–C≡N	mono-	668.2	668.5
–C≡N	di-	821.5	818.4
–C≡N	tri-	988.4	982.1
–C≡N	tetra-	1166.1	1156.7
–F	mono-	403.7	406.7
–F	di-	284.2	286.4
–F	tri-	174.5	175.9
–F	tetra-	n/a <sup>a</sup>	n/a <sup>a</sup>
–Cl	mono-	529.7	535.2
–Cl	di-	529.0	535.9
–Cl	tri-	529.7	538.1
–Cl	tetra-	531.2	541.0
–Br	mono-	582.4	585.8
–Br	di-	632.9	635.2
–Br	tri-	683.2	684.3
–Br	tetra-	732.5	732.0

<sup>a</sup> Tetrahedrane structure converged with two imaginary frequencies.

these regressions to the  $n = 4$  (i.e., tetrafluoro-) member of the homologous series yields predicted G4(MP2) and G4  $\Delta_f H^\circ_{(g)}$  estimates of 58.3 and 58.9 kJ/mol, respectively. In light of the higher atomization  $\Delta_f H^\circ_{(g)}$  predictive ability of the G4(MP2) and G4 methods versus the G3 level, and the high quality regression fits obtained over the mono- through trifluorinated range, we recommend the predicted G4(MP2)/G4  $\Delta_f H^\circ_{(g)}$  estimates over the G3 atomization estimate. To ensure there are likely no discontinuities in the linear relationship between the number of fluorine substituents and the predicted G4(MP2)/G4  $\Delta_f H^\circ_{(g)}$  for the fluorinated tetrahedranes, we also conducted G3 calculations on the mono-through trifluorinated tetrahedranes, resulting in G3 atomization  $\Delta_f H^\circ_{(g)}$  estimates of 411.7 and 174.6 kJ/mol, respectively, for the mono- and tri-substituted derivatives (the difluorotetrahedrane would not converge at the G3 level despite several attempts). There is a high quality fit ( $r^2 = 0.9991$ ,  $m = -114.5$ ,  $b = 524.2$ ; values in kJ/mol) between the number of fluorine substituents and the G3 atomization  $\Delta_f H^\circ_{(g)}$  across the mono-, tri-, and tetrafluorinated range, further suggesting the linear regression extrapolation of the  $n = 1-3$  G4(MP2)/G4  $\Delta_f H^\circ_{(g)}$  data to the  $n = 4$  homolog is valid.

With the exception of the chlorinated derivatives (for which there is negligible predicted variation in  $\Delta_f H^\circ_{(g)}$  with increasing chlorination), similarly strong linear regressions were obtained between the number of substituents and the G4(MP2)/G4  $\Delta_f H^\circ_{(g)}$  estimates within each homologous series for the other tetrahedrane

derivatives (values in kJ/mol): methyl, G4(MP2) ( $r^2 = 0.998$ ,  $m = -32.6$ ,  $b = 530.2$ ), G4 ( $r^2 = 0.99990$ ,  $m = -34.0$ ,  $b = 534.5$ ); ethynyl, G4(MP2) ( $r^2 = 0.9999987$ ,  $m = 240.4$ ,  $b = 529.2$ ), G4 ( $r^2 = 0.9999981$ ,  $m = 239.3$ ,  $b = 533.2$ ); cyano, G4(MP2) ( $r^2 = 0.9989$ ,  $m = 166.1$ ,  $b = 495.9$ ), G4 ( $r^2 = 0.9988$ ,  $m = 162.8$ ,  $b = 499.4$ ); and bromo, G4(MP2) ( $r^2 = 0.99997$ ,  $m = 50.1$ ,  $b = 532.6$ ), G4 ( $r^2 = 0.99993$ ,  $m = 48.8$ ,  $b = 537.4$ ).

To determine if the G3 convergence on a tetrafluorotetrahedrane geometry with no imaginary frequencies was anomalous, a further suite of calculations at varying levels of theory was undertaken. The two closely spaced G4(MP2) and G4 imaginary frequencies for this compound occur at  $-69.8$  and  $-67.6 \text{ cm}^{-1}$  and correspond to molecular vibrations that alternately elongate and compress adjacent carbons. If the imaginary frequencies are ignored, the calculated  $\Delta_f H^\circ_{(g)}$  are 69.0 (G4(MP2)) and 69.7 (G4) kJ/mol, or about 11 kJ/mol above the mono- through tri-fluorotetrahedrane regression predicted  $\Delta_f H^\circ_{(g)}$  for tetrafluorotetrahedrane at these two levels of theory. Slightly changing the bond angles and distances in the directions of the imaginary nodes and reoptimizing at these levels of theory leads to a cage-opened  $\text{C}_4\text{F}_4$  product  $\sim 200$  kJ/mol lower in free energy than the tetrahedrane structure and having a geometry analogous to the biradical-like species **6** found as a local minimum along the reaction coordinate for the conversion of the parent  $\text{C}_4\text{H}_4$  tetrahedrane to cyclobutadiene [50].

Additional geometry optimizations and corresponding frequency calculations were conducted using the M062X [51], PBE0D3 [52–56], B97D3 [57,55,56], B2PLYPD3 [58,55,56], and MP2 [59–63] methods each with the AUG-cc-pVTZ [64,65] and QZVP [66,67] basis sets, as well as calculations using the rest of the Gn methods (G1 [68], G2 [69], G2MP2 [70], G3MP2 [71], G3B3 [72], and G3MP2B3 [72]). With the converged G3 tetrafluorotetrahedrane geometry absent any imaginary frequencies used as the starting geometry, the G1, G2, G2MP2, and G3MP2 methods yielded a final cage-opened  $\text{C}_4\text{F}_4$  product as described above, while all other levels of theory considered gave a tetrafluorotetrahedrane geometry in return – except having two imaginary frequencies analogous to the G4(MP2) and G4 methods. Consequently, it appears unlikely that tetrafluorotetrahedrane is a minimum on the  $\text{C}_4\text{F}_4$  potential energy surface. While the G3 result is suggestive of a possible minimum, and thereby warrants a postulated  $\Delta_f H^\circ_{(g)}$  for tetrafluorotetrahedrane and consideration of its potential reactivity, the fact this method appears to stand alone in predicting the structure as a potential energy minima necessitates caution in the use of any associated data.

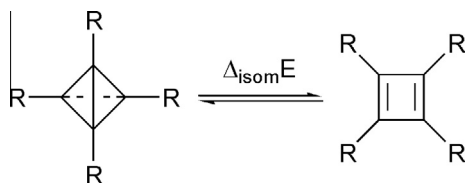
Increasing methyl and fluoro substitution is predicted to increase the thermodynamic stabilities of these substituted carbon tetrahedranes, versus increasing ethynyl, cyano, and bromo substitution decreasing the thermodynamic stability, and (as mentioned previously) no expected effect due to increasing chlorine substitution. All derivatives have endothermic  $\Delta_f H^\circ_{(g)}$  (ranging from about +60 to +1500 kJ/mol), indicative of the cage strain in these systems. Our G4(MP2)/G4  $\Delta_f H^\circ_{(g)}$  of 400.2/399.1 kJ/mol for tetramethyltetrahedrane is in modest agreement with the value of 429.7 kJ/mol reported by Balci et al. [25] at the B3LYP/6-311+G(d)//B3LYP/6-31G(d)+ZPC/6-31G(d) level using isodesmic reactions. A substantial number of prior theoretical works have estimated the  $\Delta_f H^\circ_{(g)}$  of the parent tetrahedrane at various levels of theory. This literature is summarized in Table 2, and our G4(MP2)/G4  $\Delta_f H^\circ_{(g)}$  estimates for this compound are in excellent agreement with other high level calculations.

Tetrahedranes may disproportionate to two acetylenes, or may isomerize (Fig. 2) to a corresponding 1,3-cyclobutadiene. For each of the mono- through tetra-substituted carbon tetrahedrane derivatives discussed above, the enthalpies of these respective reactions were calculated at the G4(MP2) and G4 levels (Tables 3

**Table 2**

Prior theoretical estimates for the enthalpy of formation ( $\Delta_f H^\circ_{(g)}$ ) of the parent carbon tetrahedrane. Values are in kJ/mol.

Level of theory	$\Delta_f H^\circ_{(g)}$	Ref.	Comments
BP/6-31G*	485.3	[16]	Homodesmotic reaction set
SCF/6-31G*	518.4	[73]	
BLYP/6-31G*	523.4	[16]	
MINDO/3	528.4	[50]	
G2	535.1	[18]	
B3LYP/aug-cc-pVDZ	535.6	[27]	Isodesmotic reaction set 2
CBS-Q	537.2	[21]	
SCF/4-31G	541.0	[11]	
RMP2/6-31G*	553.5	[73]	
SCF/6-31G*	555.2	[15]	
RMP2/6-31G*	555.2	[73]	Isodesmotic reaction set 1
SCF/DZ+D	560.7	[12]	
SCF/4-31G	572.8	[11]	
SCF/6-31G*	587.4	[73]	
SCF/6-31G*	591.2	[74]	
B3LYP/6-31G*	600.0	[16]	Isodesmotic reaction set 2
SVWN/6-31G*	609.6	[16]	
SCF(MO)	611.3	[75]	
SCF/6-31G*	651.0	[15]	
SCF/6-31G	661.9	[15]	
AM1	666.5	[15]	Isodesmotic reaction set 1
SCF/4-21G	693.7	[15]	
SCF/4-31G	697.1	[74]	
SCF/6-31G	705.4	[15]	
SCF/4-21G	720.1	[15]	
tight-binding MD	771.9	[22]	



**Fig. 2.** General isomerization reaction for tetra-substituted tetrahedranes to the corresponding cyclobutadienes.

and 4). In all cases, the enthalpies of disproportionation to two corresponding acetylene molecules ( $\Delta_{rxn} H^\circ_{(g),Td \rightarrow acet}$ ) and enthalpies of isomerization to a 1,3-cyclobutadiene structure ( $\Delta_{isom} H^\circ_{(g),Td \rightarrow CBD}$ ) are predicted to be substantially exothermic. Increasing exothermicity with increasing substitution is predicted for all compounds and both  $\Delta_{rxn} H^\circ_{(g),Td \rightarrow acet}$  and  $\Delta_{isom} H^\circ_{(g),Td \rightarrow CBD}$ , with the exception of the acetylene disproportionations for the halogen derivatives. Negligible variation in  $\Delta_{rxn} H^\circ_{(g),Td \rightarrow acet}$  is expected with increasing chlorination and no clear trend for fluorination, whereas increasing bromination is estimated to modestly decrease the reaction exothermicity. For the disubstituted derivatives, disproportionation to two acetylenes can proceed via two pathways, leading either to (a) the parent unsubstituted acetylene ( $HC \equiv CH$ ) and a disubstituted acetylene ( $RC \equiv CR$ ) or (b) two monosubstituted acetylenes ( $HC \equiv CR$ ). Similarly, isomerization to a 1,3-cyclobutadiene from a disubstituted tetrahedrane can result in (a) a cis-disubstituted 1,3-cyclobutadiene or (b) a trans-disubstituted 1,3-cyclobutadiene. For most derivatives, these competing pathways are expected to be effectively isoenergetic (i.e.,  $\Delta \Delta H^\circ_{(g)} \leq 10\text{--}15$  kJ/mol; or within the likely accuracy of the computational method).

The tetrafluoro-1,3-cyclobutadiene yields one imaginary frequency with both the G4(MP2) and G4 methods, preventing us from using the linear regression derived G4(MP2)/G4  $\Delta_f H^\circ_{(g)}$  estimates for the tetrafluorotetrahedrane, coupled with corresponding atomization  $\Delta_f H^\circ_{(g)}$  estimates at these levels for the tetrafluoro-1,3-cyclobutadiene, in order to obtain indirect  $\Delta_{isom} H^\circ_{(g),Td \rightarrow CBD}$  at

**Table 3**

G4(MP2) and G4 estimated gas phase standard state (298.15 K, 1 atm) enthalpies of disproportionation to two corresponding acetylene molecules ( $\Delta_{rxn} H^\circ_{(g),Td \rightarrow acet}$ ) for various mono- through tetra-substituted carbon tetrahedrane derivatives. Values are in kJ/mol.

Substituent	No.	G4(MP2)	G4
—H	tetra-	−78.4	−79.6
—CH <sub>3</sub>	mono-	−86.6	−87.5
—CH <sub>3</sub>	di-	−89.8 <sup>a</sup> /−95.7	−89.9/−95.9
—CH <sub>3</sub>	tri-	−99.7	−99.2
—CH <sub>3</sub>	tetra-	−104.8	−103.3
—C≡CH	mono-	−84.6	−85.2
—C≡CH	di-	−100.3/−92.9	−98.2/−92.6
—C≡CH	tri-	−109.7	−106.9
—C≡CH	tetra-	−126.5	−121.3
—C≡N	mono-	−67.8	−68.2
—C≡N	di-	−61.4/−74.7	−61.3/−74.5
—C≡N	tri-	−81.9	−81.4
—C≡N	tetra-	−99.9	−99.4
—F	mono-	−70.6	−71.6
—F	di-	−50.3/−72.1	−51.0/−72.9
—F	tri-	−61.6	−62.1
—F	tetra-	n/a <sup>b</sup>	n/a <sup>b</sup>
—Cl	mono-	−78.9	−79.4
—Cl	di-	−76.6/−81.4	−77.0/−81.2
—Cl	tri-	−80.6	−80.2
—Cl	tetra-	−80.5	−79.9
—Br	mono-	−74.6	−74.9
—Br	di-	−70.9/−71.2	−70.6/−70.3
—Br	tri-	−67.4	−65.6
—Br	tetra-	−62.5	−59.4

<sup>a</sup> For disubstituted tetrahedranes, disproportionation to two acetylene compounds can produce either (a) the parent unsubstituted acetylene ( $HC \equiv CH$ ) and a disubstituted acetylene ( $RC \equiv CR$ ) or (b) two monosubstituted acetylenes ( $HC \equiv CR$ ). The value on the left of the “/” represents path (a); the value on the right of the “/” represents path (b).

<sup>b</sup> Tetrahedrane structure converged with two imaginary frequencies.

these two levels of theory. Difluoroacetylene does converge absent imaginary frequencies at both the G4(MP2) and G4 levels, giving atomization  $\Delta_f H^\circ_{(g)}$  estimates of 6.9 and 7.0 kJ/mol, respectively. Applying these difluoroacetylene  $\Delta_f H^\circ_{(g)}$  estimates to the corresponding G4(MP2)/G4 regression predicted  $\Delta_f H^\circ_{(g)}$  of 58.3 and 58.9 kJ/mol, respectively, results in G4(MP2) and G4 estimated  $\Delta_{rxn} H^\circ_{(g),Td \rightarrow acet}$  for tetrafluorotetrahedrane of −44.5 and −44.9 kJ/mol, respectively. These indirect G4(MP2)/G4  $\Delta_{rxn} H^\circ_{(g),Td \rightarrow acet}$  estimates are likely more accurate than the corresponding G3 estimate of −70.5 kJ/mol.

The high quality linear regression fits discussed above between the number of substituents and the G4(MP2)/G4 estimated  $\Delta_f H^\circ_{(g)}$  within a homologous series allows for reasonable confidence in using such regression approaches to estimate the  $\Delta_f H^\circ_{(g)}$  of higher substituted tetrahedrane homologs where only the  $\Delta_f H^\circ_{(g)}$  of less substituted members are known. As further validation of this approach, we used the  $n = 1\text{--}3$  G4(MP2)/G4  $\Delta_f H^\circ_{(g)}$  regression trends for the methyl, ethynyl, cyano, and bromo substituted tetrahedranes to predict the  $\Delta_f H^\circ_{(g)}$  of the corresponding  $n = 4$  member, and then compared this extrapolated  $\Delta_f H^\circ_{(g)}$  to the calculated G4(MP2)/G4  $\Delta_f H^\circ_{(g)}$  for the tetrasubstituted homolog. Estimated/actual  $\Delta_f H^\circ_{(g)}$  values were as follows (presented as G4(MP2) [G4]; values in kJ/mol): methyl, 398.6/400.2 [397.7/399.1]; ethynyl, 1490.2/1490.9 [1489.7/1490.7]; cyano, 1146.2/1166.1 [1136.6/1156.7]; and bromo, 733.6/732.5 [733.6/732.0]. The  $\Delta_f H^\circ_{(g)}$  using this validation approach are on the order of 1 kJ/mol for the methyl, ethynyl, and bromo derivatives, and about 20 kJ/mol for the tetracyanotetrahedrane. We then applied this concept to the corresponding t-butyl, trifluoromethyl, and trimethylsilyl carbon



**Table 4**

G4(MP2) and G4 estimated gas phase standard state (298.15 K, 1 atm) enthalpies of isomerization from a tetrahedrane geometry (Td) to a 1,3-cyclobutadiene (CBD) structure ( $\Delta_{\text{isom}}H^\circ_{(\text{g}),\text{Td} \rightarrow \text{CBD}}$ ) for various mono- through tetra-substituted carbon tetrahedrane derivatives. Values are in kJ/mol.

Substituent	No.	G4(MP2)	G4
—H	tetra-	−109.0	−107.3
—CH <sub>3</sub>	mono-	−119.0	−117.2
—CH <sub>3</sub>	di-	−127.4 <sup>a</sup> /−130.2	−125.2/−127.9
—CH <sub>3</sub>	tri-	−137.0	−134.1
—CH <sub>3</sub>	tetra-	−145.6	−142.2
—C≡CH	mono-	−126.4	−124.1
—C≡CH	di-	−144.3/−143.5	−141.0/−140.0
—C≡CH	tri-	−164.3	−159.8
—C≡CH	tetra-	−184.3	−179.0
—C≡N	mono-	−120.2	−118.0
—C≡N	di-	−133.7/−136.7	−131.0/−133.9
—C≡N	tri-	−151.0	−147.7
—C≡N	tetra-	−169.4	−165.7
—F	mono-	−173.7	−172.2
—F	di-	−230.4/−241.7	−228.8/−240.4
—F	tri-	−284.1	−282.4
—F	tetra-	n/a <sup>b</sup>	n/a <sup>b</sup>
—Cl	mono-	−147.3	−145.6
—Cl	di-	−181.9/−183.7	−180.3/−182.0
—Cl	tri-	−214.7	−213.2
—Cl	tetra-	−244.4	−243.5
—Br	mono-	−140.3	−138.8
—Br	di-	−168.3/−169.1	−166.9/−167.5
—Br	tri-	−195.3	−193.8
—Br	tetra-	−219.2	−217.7

<sup>a</sup> For disubstituted tetrahedranes, isomerization to a 1,3-cyclobutadiene can result in (a) a cis-disubstituted 1,3-cyclobutadiene or (b) a trans-disubstituted 1,3-cyclobutadiene. The value on the left of the “/” represents path (a); the value on the right of the “/” represents path (b).

<sup>b</sup> Tetrahedrane structure converged with two imaginary frequencies.

tetrahedrane derivatives (Table 5). Namely, due to computational expense, G4(MP2) and G4 calculations could only be completed, and atomization  $\Delta_f H^\circ_{(\text{g})}$  estimates obtained, on the lower homolog members at each level of theory. Extrapolations of the linear relationship between the number of substituents and  $\Delta_f H^\circ_{(\text{g})}$  within each homologous series allows reasonable quality  $\Delta_f H^\circ_{(\text{g})}$  estimates to be obtained for all derivatives at one or both levels of theory.

The  $\Delta_f H^\circ_{(\text{g})}$  of the t-butyl, trifluoromethyl, and trimethylsilyl substituted tetrahedranes all decline with increasing substitution. The tetra-t-butyltetrahedrane has only a modestly endothermic  $\Delta_f H^\circ_{(\text{g})}$  (29.2 kJ/mol at the extrapolated G4(MP2) level), consistent with the successful synthesis by Maier et al. [2] and our previous study showing a collective reference level DFT (B3LYP, mPW3LYP, and X3LYP) and MP2 tetrahedrane to 1,3-cyclobutadiene isomerization energy ( $\Delta_{\text{isom}}E^\circ_{(\text{g}),\text{Td} \rightarrow \text{CBD}}$ ) range of −1.2 to 2.0 kJ/mol (i.e., the tetra-t-butyltetrahedrane and tetra-t-butyl-1,3-cyclobutadiene are approximately isoenergetic) [30]. Our G4 (MP2)  $\Delta_f H^\circ_{(\text{g})}$  of 29.2 kJ/mol for tetra-t-butyltetrahedrane differs substantially from the value of 133.5 kJ/mol reported by Balcı et al. [25] at the B3LYP/6-311+G(d)//B3LYP/6-31G(d)+ZPC/6-31G(d) level using isodesmic reactions, but our value is in remarkable agreement with the experimental estimate of 25.9 kJ/mol [76]. In comparison, all trifluoromethyl derivatives and the tri- and tetrakis(trimethylsilyl) tetrahedranes are expected to have exothermic  $\Delta_f H^\circ_{(\text{g})}$ , again consistent with the successful synthesis of tetrakis(trimethylsilyl) tetrahedrane by Maier's group [4] and with the corresponding estimated reference level DFT/MP2  $\Delta_{\text{isom}}E^\circ_{(\text{g}),\text{Td} \rightarrow \text{CBD}}$  for this compound of 19.6–32.3 kJ/mol [30] that suggests the tetrakis(trimethylsilyl) tetrahedrane is more thermodynamically stable than the tetrakis(trimethylsilyl)-1,3-cyclobutadiene.

Tri-t-butyl-mono(trimethylsilyl) tetrahedrane has also been synthesized [10]. In our prior work [30], we showed that – in the absence of access to the more computationally expensive composite methods – the B3LYP [77–79], mPW3LYP [80], and X3LYP [81] density functionals, as well as the MP2 [59–63] model chemistry, appear to best estimate  $\Delta_{\text{isom}}E^\circ_{(\text{g}),\text{Td} \rightarrow \text{CBD}}$ . Calculations at the x/TZVP//B3LYP/6-31G(d) [77–79,82–92] (x = B3LYP, mPW3LYP, X3LYP, MP2, B2PLYPD, and mPW2PLYPD) level on tri-t-butyl-mono(trimethylsilyl) tetrahedrane and tri-t-butyl-mono(trimethylsilyl)-1,3-cyclobutadiene yield the following  $\Delta_{\text{isom}}E^\circ_{(\text{g}),\text{Td} \rightarrow \text{CBD}}$  estimates (values in kJ/mol): B3LYP, −2.5; mPW3LYP, −4.0; X3LYP, −2.9; and MP2, 0.3. The B2PLYPD [58,93] and mPW2PLYPD [93,94] functionals give systematically lower  $\Delta_{\text{isom}}E^\circ_{(\text{g}),\text{Td} \rightarrow \text{CBD}}$  estimates of −17.9 and −14.0 kJ/mol, respectively, as expected [30]. Consequently, consistent with the successful synthesis of tri-t-butyl-mono(trimethylsilyl) tetrahedrane, we find that this compound is approximately isoenergetic with its isomer tri-t-butyl-mono(trimethylsilyl)-1,3-cyclobutadiene.

Increasing substitution among the t-butyl and trimethylsilyl tetrahedranes has only a modest influence on the expected  $\Delta_{\text{rxn}}H^\circ_{(\text{g}),\text{Td} \rightarrow \text{acet}}$  (increasing by about 5–7 kJ/mol per substituent), and all mono- through tetra-substituted derivatives are expected to have substantially exothermic disproportionation enthalpies. In contrast, increasing trifluoromethylation significantly increases the  $\Delta_{\text{rxn}}H^\circ_{(\text{g}),\text{Td} \rightarrow \text{acet}}$  such that the tri(trifluoromethyl) tetrahedrane disproportionation is predicted to be approximately isoenergetic, while the tetrakis(trifluoromethyl) tetrahedrane disproportionation is expected to be modestly endothermic. t-Butyl, trifluoromethyl, and trimethylsilyl substituted tetrahedrane  $\Delta_{\text{rxn}}H^\circ_{(\text{g}),\text{Td} \rightarrow \text{acet}}$  are expected to be strongly exothermic for the mono- and di-substituted homologs (and for the tri(trifluoromethyl) derivative). Projecting the mono- and di-(trimethylsilyl)  $\Delta_{\text{isom}}H^\circ_{(\text{g}),\text{Td} \rightarrow \text{CBD}}$  trend yields estimated  $\Delta_{\text{isom}}H^\circ_{(\text{g}),\text{Td} \rightarrow \text{CBD}}$  of −19.8 and 11.4 kJ/mol for the tri- and tetra-substituted members, respectively, in good agreement with our prior reference level DFT/MP2  $\Delta_{\text{isom}}E^\circ_{(\text{g}),\text{Td} \rightarrow \text{CBD}}$  of 19.6 to 32.3 kJ/mol [30] for tetrakis(trimethylsilyl) tetrahedrane.

Both the t-butyl and trifluoromethyl derivatives show no significant  $\Delta_{\text{isom}}H^\circ_{(\text{g}),\text{Td} \rightarrow \text{CBD}}$  trends over their respective available G4 (MP2)/G4 datasets. We expect the tetra-t-butyltetrahedrane  $\Delta_{\text{isom}}H^\circ_{(\text{g}),\text{Td} \rightarrow \text{CBD}}$  to be approximately isoenergetic [30] due to steric congestion on the 1,3-cyclobutadiene system, but do not expect a similarly isoenergetic  $\Delta_{\text{isom}}H^\circ_{(\text{g}),\text{Td} \rightarrow \text{CBD}}$  for tetrakis(trifluoromethyl) tetrahedrane due to the absence of steric bulk in the trifluoromethyl groups. Attempts to estimate  $\Delta_{\text{isom}}H^\circ_{(\text{g}),\text{Td} \rightarrow \text{CBD}}$  for tetrakis(trifluoromethyl) tetrahedrane obtained a converged tetrakis(trifluoromethyl)-1,3-cyclobutadiene structure with two imaginary frequencies at the B3LYP/6-31G(d) level, precluding any subsequent thermodynamic analysis. However, the minimum C—F...F—C distance between adjacent trifluoromethyl groups on this tetrakis(trifluoromethyl)-1,3-cyclobutadiene structure was 2.714 Å (B3LYP/6-31G(d)), which is longer than the C—H...H—C distance (2.671 Å) between adjacent methyl groups on tetramethyl-1,3-cyclobutadiene at the G4 level of theory. Thus, we do not expect the  $\Delta_{\text{isom}}H^\circ_{(\text{g}),\text{Td} \rightarrow \text{CBD}}$  for tetrakis(trifluoromethyl) tetrahedrane to be significantly different from that of the mono-through tri-substituted homologs (−113 to −120 kJ/mol).

Analogous calculations were performed for tri-t-butyltetrahedrane to investigate whether the steric influence that renders  $\Delta_{\text{isom}}H^\circ_{(\text{g}),\text{Td} \rightarrow \text{CBD}}$  isoenergetic for the tetra-t-butyl derivative also operates with three t-butyl substituents. As evidenced by the negligible change in  $\Delta_{\text{isom}}H^\circ_{(\text{g}),\text{Td} \rightarrow \text{CBD}}$  when moving from the mono- to di-t-butyl derivatives, the t-butyl effect is absent at these homologs. Calculations at the x/TZVP//B3LYP/6-31G(d) (x = B3LYP,

**Table 5**

G4(MP2) and G4 estimated gas phase standard state (298.15 K, 1 atm) enthalpies of formation ( $\Delta_f H^\circ_{(g)}$ ), enthalpies of disproportionation to two corresponding acetylene molecules ( $\Delta_{rxn} H^\circ_{(g),Td \rightarrow acet}$ ), and enthalpies of isomerization from a tetrahedrane geometry (Td) to a 1,3-cyclobutadiene (CBD) structure ( $\Delta_{isom} H^\circ_{(g),Td \rightarrow CBD}$ ) for the t-butyl, trifluoromethyl, and trimethylsilyl mono- through tetra-substituted carbon tetrahedrane derivatives. Values are in kJ/mol.

	C(CH <sub>3</sub> ) <sub>3</sub>		CF <sub>3</sub>		Si(CH <sub>3</sub> ) <sub>3</sub>	
	G4(MP2)	G4	G4(MP2)	G4	G4(MP2)	G4
$\Delta_f H^\circ_{(g)}$						
mono-	408.4	411.1	−143.0	−142.6	333.8	336.2
di-	282.0	c/e <sup>a</sup>	−808.4	−811.6	130.9	c/e
tri-	155.6 <sup>b</sup>	c/e	−1466.0	−1480.6 <sup>b</sup>	−72.0 <sup>b</sup>	c/e
tetra-	29.2 <sup>b</sup>	c/e	−2128.8 <sup>b</sup>	−2149.5 <sup>b</sup>	−274.9 <sup>b</sup>	c/e
$\Delta_{rxn} H^\circ_{(g),Td \rightarrow acet}$						
mono-	−76.2	−76.6	−51.5	−51.3	−75.4	−76.6
di-	−70.5 <sup>c</sup> /−71.6	n/a	−24.8/−34.7	−22.8/−33.0	n/c <sup>d</sup> /−68.0	n/a
tri-	−65.9 <sup>e</sup>	n/a	−15.8	−4.5 <sup>f</sup>	n/a <sup>g</sup>	n/a
tetra-	−60.2 <sup>h</sup>	n/a	8.4 <sup>i</sup>	23.9 <sup>j</sup>	n/a <sup>g</sup>	n/a
$\Delta_{isom} H^\circ_{(g),Td \rightarrow CBD}$						
mono-	−115.3	−113.4	−113.0	−111.5	−82.2	−80.9
di-	−110.0 <sup>k</sup> /−120.8	n/a	−116.6/−120.0	−115.2/−118.2	−54.5/−51.0	n/a
tri-	n/a	n/a	−115.4	n/a	n/a	n/a
tetra-	n/a	n/a	n/a	n/a	n/a	n/a

<sup>a</sup> Not completed due to computational expense.

<sup>b</sup> Estimated via extrapolation of the G4(MP2) and G4  $\Delta_f H^\circ_{(g)}$  trends from lower homologs.

<sup>c</sup> For disubstituted tetrahedranes, disproportionation to two acetylene compounds can produce either (a) the parent unsubstituted acetylene (HC≡CH) and a disubstituted acetylene (RC≡CR) or (b) two monosubstituted acetylenes (HC≡CR). The value on the left of the “/” represents path (a); the value on the right of the “/” represents path (b).

<sup>d</sup> Calculation for the di(trimethylsilyl) acetylene failed to converge.

<sup>e</sup>  $\Delta_{rxn} H^\circ_{(g),Td \rightarrow acet}$  obtained using G4(MP2) atomization  $\Delta_f H^\circ_{(g)}$  of 105.2 and −15.5 kJ/mol, respectively, for the mono- and di-t-butylacetylenes and the regression estimated  $\Delta_f H^\circ_{(g)}$  of 155.6 kJ/mol for the tri-t-butyltetrahedrane.

<sup>f</sup>  $\Delta_{rxn} H^\circ_{(g),Td \rightarrow acet}$  obtained using G4 atomization  $\Delta_f H^\circ_{(g)}$  of −422.3 and −1062.8 kJ/mol, respectively, for the mono- and di-(trifluoromethyl) acetylenes and the regression estimated  $\Delta_f H^\circ_{(g)}$  of −1480.6 kJ/mol for the tri(trifluoromethyl) tetrahedrane.

<sup>g</sup> Calculation for the di(trimethylsilyl) acetylene failed to converge.

<sup>h</sup>  $\Delta_{rxn} H^\circ_{(g),Td \rightarrow acet}$  obtained using G4(MP2) atomization  $\Delta_f H^\circ_{(g)}$  of −15.5 kJ/mol for the di-t-butylacetylene and the regression estimated  $\Delta_f H^\circ_{(g)}$  of 29.2 kJ/mol for the tetra-t-butyltetrahedrane.

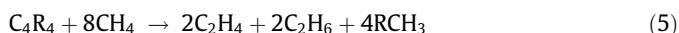
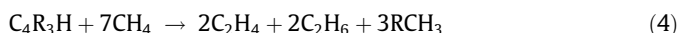
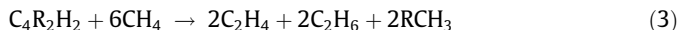
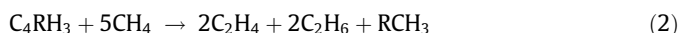
<sup>i</sup>  $\Delta_{rxn} H^\circ_{(g),Td \rightarrow acet}$  obtained using G4(MP2) atomization  $\Delta_f H^\circ_{(g)}$  of −1060.2 kJ/mol for the di(trifluoromethyl) acetylene and the regression estimated  $\Delta_f H^\circ_{(g)}$  of −2128.8 kJ/mol for the tetra-t-butyltetrahedrane.

<sup>j</sup>  $\Delta_{rxn} H^\circ_{(g),Td \rightarrow acet}$  obtained using G4 atomization  $\Delta_f H^\circ_{(g)}$  of −1062.8 kJ/mol for the di(trifluoromethyl) acetylene and the regression estimated  $\Delta_f H^\circ_{(g)}$  of −2149.5 kJ/mol for the tetra(trifluoromethyl) tetrahedrane.

<sup>k</sup> For disubstituted tetrahedranes, isomerization to a 1,3-cyclobutadiene can result in (a) a cis-disubstituted 1,3-cyclobutadiene or (b) a trans-disubstituted 1,3-cyclobutadiene. The value on the left of the “/” represents path (a); the value on the right of the “/” represents path (b).

mPW3LYP, X3LYP, and MP2) level of theory for tri-t-butyltetrahedrane and tri-t-butyl-1,3-cyclobutadiene yield the following  $\Delta_{isom} E^\circ_{(g),Td \rightarrow CBD}$  (values in kJ/mol): B3LYP, −83.4; mPW3LYP, −83.9; X3LYP, −83.2; and MP2, −78.0. When compared to the tetra-t-butyl  $\Delta_{isom} E^\circ_{(g),Td \rightarrow CBD}$  of −1.3, −2.0, −1.2, and −1.7 kJ/mol [30] at these four levels of theory, respectively, and the mono- and di-t-butyl G4(MP2)  $\Delta_{isom} H^\circ_{(g),Td \rightarrow CBD}$  of −115.3 and −110.0/−120.8 kJ/mol, respectively, we see that the t-butyl effect is modestly in effect on the tri-t-butyl derivative, reducing the exothermicity of the tetrahedrane to 1,3-cyclobutadiene isomerization by about 35 kJ/mol compared to the lower homologs.

The unsatisfying agreement between our calculated G4(MP2) and G4 atomization based  $\Delta_f H^\circ_{(g)}$  for tetramethyltetrahedrane (400.2 and 399.1 kJ/mol, respectively) and G4(MP2) atomization/regression based  $\Delta_f H^\circ_{(g)}$  for tetra-t-butyltetrahedrane (29.2 kJ/mol) with the corresponding  $\Delta_f H^\circ_{(g)}$  at the B3LYP/6-311+G(d)//B3LYP/6-31G(d)+ZPC/6-31G(d) level using isodesmic reactions reported by Balci et al. [25] (429.7 and 133.5 kJ/mol) led us to re-examine the isodesmic approach from Ref. [25] at the G4(MP2) and G4 levels on all compounds for which we had applied the atomization method. In their work, Balci et al. [25] applied the following general isodesmic reactions for estimating the  $\Delta_f H^\circ_{(g)}$  of the parent tetrahedrane and any mono- through tetra-substituted derivative:



While isodesmic approaches offer great utility in computational thermochemistry, one of the underacknowledged problems with the method is that experimental  $\Delta_f H^\circ_{(g)}$  used in the equations are not exact values without error. Depending on the construction method for the isodesmic reaction, experimental  $\Delta_f H^\circ_{(g)}$  uncertainty can meet or exceed any computational uncertainty – particularly at high levels of theory such as G4. In Eqs. (1)–(5) above, experimental  $\Delta_f H^\circ_{(g)}$  are required for CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, CH<sub>3</sub>C≡CH, CH<sub>3</sub>C≡N, CH<sub>3</sub>F, CH<sub>3</sub>Cl, CH<sub>3</sub>Br, neopentane, CH<sub>3</sub>CF<sub>3</sub>, and tetramethylsilane. High-quality reviewed experimental  $\Delta_f H^\circ_{(g)}$  data are available for methane (−74.9 [95] and −74.6 ± 0.3 kJ/mol [96]), ethene (52.5 [95] and 52.4 ± 0.5 kJ/mol [96]), ethane (−84.0 ± 0.4 kJ/mol [96]), fluoromethane (−234.3 kJ/mol [95]), and chloromethane (−83.7 [95] and −81.9 ± 1.5 kJ/mol [96]) in the NIST database [97], along with what appear to be solid experimental  $\Delta_f H^\circ_{(g)}$  for propyne (185.4 ± 0.9 kJ/mol [98]), bromomethane (−37.5 ± 1.5 [99], −38.0 ± 1.3 [100], and −34.3 ± 0.8 kJ/mol [101]), neopentane (−166.0 ± 1.0 [102], −168.5 ± 1.0 [103], and −167.9 ± 0.6 kJ/mol [104]), and 1,1,1-trifluoroethane (−749 ± 2 [105] and −748.7 ± 3.2 kJ/mol [106,107]). On the other hand, wide variability exists for the exper-

**Table 6**

G4(MP2) and G4 estimated gas phase standard state (298.15 K, 1 atm) enthalpies of formation ( $\Delta_f H^\circ_{(g)}$ ) using isodesmic reaction Eqs. (1)–(5) for various mono- through tetra-substituted carbon tetrahedrane derivatives. Values are in kJ/mol.

Substituent	No.	G4(MP2)	G4
–H	tetra-	537.8	536.3
–CH <sub>3</sub>	mono-	503.2	500.5
–CH <sub>3</sub>	di-	478.7	465.2
–CH <sub>3</sub>	tri-	436.5	430.7
–CH <sub>3</sub>	tetra-	404.7	397.1
–C≡CH	mono-	777.3	773.0
–C≡CH	di-	1018.9	1011.6
–C≡CH	tri-	1261.5	1251.4
–C≡CH	tetra-	1504.1	1491.3
–C≡N	mono-	670.5	665.7
–C≡N	di-	820.8	812.9
–C≡N	tri-	984.7	973.9
–C≡N	tetra-	1159.3	1145.9
–F	mono-	411.1	408.4
–F	di-	293.6	289.8
–F	tri-	186.0	181.0
–F	tetra-	n/a <sup>a</sup>	n/a <sup>a</sup>
–Cl	mono-	536.8	533.8
–Cl	di-	537.8	533.3
–Cl	tri-	540.2	534.2
–Cl	tetra-	543.4	535.8
–Br	mono-	580.2	576.8
–Br	di-	623.0	617.3
–Br	tri-	665.8	657.5
–Br	tetra-	707.4	696.2

<sup>a</sup> Tetrahedrane structure converged with two imaginary frequencies.

imental  $\Delta_f H^\circ_{(g)}$  of acetonitrile (65.9 [108] and  $74.0 \pm 0.4$  kJ/mol [109]). The NIST database quotes an erroneous  $\Delta_f H^\circ_{(g)}$  of  $-286.6$  kJ/mol [95] for tetramethylsilane. The most widely used  $\Delta_f H^\circ_{(g)}$  of this compound is  $-233.2 \pm 3.2$  kJ/mol [110] and is the one we employ, although as noted in their review, Doncaster and Walsh [111] report that the experimental  $\Delta_f H^\circ_{(g)}$  for this compound ranges widely from  $-245.6$  to  $-176.6$  kJ/mol. Our G4 atomization  $\Delta_f H^\circ_{(g)}$  for  $\text{Si}(\text{CH}_3)_4$  is  $-218.6$  kJ/mol. Even small (i.e.,  $\leq 4$  kJ/mol) errors in experimental  $\Delta_f H^\circ_{(g)}$  can be magnified within isodesmic reactions; and thus, caution needs to be exercised in assuming isodesmic  $\Delta_f H^\circ_{(g)}$  have equal or superior accuracy to atomization  $\Delta_f H^\circ_{(g)}$ . For our calculations, we chose to average without bias – where applicable – the available values listed above.

Isodesmic derived  $\Delta_f H^\circ_{(g)}$  for the parent and mono- through tetra-substituted methyl, ethynyl, cyano, fluoro, chloro, and bromo derivatives of tetrahedrane are provided in Table 6. In general, good agreement is found between these values and the atomization  $\Delta_f H^\circ_{(g)}$  in Table 1, particularly at the G4 level. For the parent, methyl, ethynyl, fluoro, and chloro derivatives, the deviations between the G4 atomization and isodesmic  $\Delta_f H^\circ_{(g)}$  never exceed more than several kJ/mol, even for the tetra-substituted tetrahedranes. With the tetracyanotetrahedrane, the disagreement between the two methods increases to 11 kJ/mol and reaches 36 kJ/mol for the tetrabromotetrahedrane. Our G4 isodesmic  $\Delta_f H^\circ_{(g)}$  for tetramethyltetrahedrane (397.1 kJ/mol) is in excellent agreement with our G4 atomization  $\Delta_f H^\circ_{(g)}$  (399.1 kJ/mol), but almost 31 kJ/mol lower than the isodesmic  $\Delta_f H^\circ_{(g)}$  that Balci et al. [25] obtained at the B3LYP/6-311+G(d)//B3LYP/6-31G(d)+ZP C/6-31G(d) level, suggesting the B3LYP/6-311+G(d)//B3LYP/6-31G(d)+ZPC/6-31G(d) calculations were too low a level (even with isodesmic approaches) to reliably model the thermochemistry of substituted tetrahedranes. For the parent tetrahedrane, the B3LYP/6-311+G(d)//B3LYP/6-31G(d)+ZPC/6-31G(d) isodesmic  $\Delta_f H^\circ_{(g)}$  value of Balci et al. [25] (557.3 kJ/mol) is also well above our G4 atomization (536.4 kJ/mol) and isodesmic results (536.3 kJ/mol).

The isodesmic  $\Delta_f H^\circ_{(g)}$  of the t-butyl, trifluoromethyl, and trimethylsilyl tetrahedranes for which G4(MP2) and G4 calculations could be completed are as follows (G4(MP2)/G4): mono-t-butyl, 415.4/411.6 kJ/mol; di-t-butyl, 290.7; mono-trifluoromethyl,  $-135.8/-139.8$  kJ/mol; di-trifluoromethyl,  $-799.5/-805.8$  kJ/mol; tri-trifluoromethyl,  $-1455.3$  kJ/mol; mono-trimethylsilyl, 325.0/321.6 kJ/mol; and di-trimethylsilyl, 107.7 kJ/mol. These values are in good agreement with the corresponding G4(MP2)/G4 atomization  $\Delta_f H^\circ_{(g)}$  in Table 5, especially in light of the high underlying experimental uncertainty for the  $\Delta_f H^\circ_{(g)}$  of  $\text{Si}(\text{CH}_3)_4$ .

Overall, the current study is the first comprehensive high-level investigation into the enthalpies of formation, disproportionation, and isomerization for a suite of mono- through tetra-substituted tetrahedranes having a range of electron-withdrawing, electron-donating, and sterically congested functionalities. In addition to several structure–property trends evident in the G4(MP2) and G4 thermochemical data, comparisons with prior studies reveal that high-level calculations must be employed to obtain reliable thermodynamic results for this class of compounds.

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