Research Article

Journal of Physical Organic Chemistry

Received: 1 January 2008, Revised: 11 February 2008, Accepted: 12 February 2008,

(www.interscience.wiley.com) DOI 10.1002/poc.1360

Hexacyclo[7.1.0.0^{1,3}.0^{3,5}.0^{5,7}.0^{7,9}]decane, or pentagramane: high-level computational studies on a novel hydrocarbon

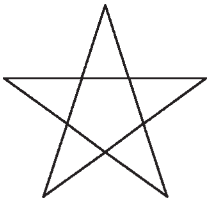
David W. Ball[a]*

A novel hydrocarbon whose line diagram is that of the classic pentagram is described. High-level computational studies have been performed to determine its structure, vibrational frequencies, NMR spectra, and thermochemistry. Copyright © 2008 John Wiley & Sons, Ltd.

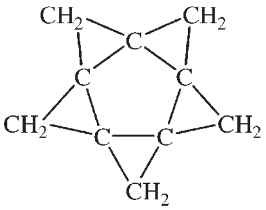
Keywords: pentagramane; cyclic triangulanes; G2 calculations; G3 calculations

INTRODUCTION

A shape familiar to most of us is the five-pointed star, or pentagram:



A search of the literature suggests that, to date, no one has mentioned that this shape also defines a hydrocarbon, *viz*.:



1

The formula for this hydrocarbon is $C_{10}H_{10}$. It can be considered from different perspectives: as a cyclopentane ring with five methylene groups as substituents, or as five cyclopropane rings bonded by five spiro carbons. In either case, should such a hydrocarbon be isolated, it would undoubtedly be a high-energy substance because of the presumed large amount of ring strain in the molecule. Spiropentane itself, *spiro*-C_5H_8, has a strain energy of about 262 kJ mol^{-1},[1] making its enthalpy of combustion higher in magnitude, by about 110 kJ mol^{-1}, than its straight-chain diene isomer 1,3-pentadiene.[2] With two and a half spiropentane molecules constrained to a ring, we expect that this $C_{10}H_{10}$ isomer will likely have a higher specific combustion energy.

As mentioned, a literature search found no connection between the title molecule and the pentagram. However, the molecule itself has been mentioned in a few previous studies. Zefirov *et al*.[3] referenced molecule **1** in a footnote of a study on cyclosubstituted triangulanes (the general name for *spiro*-fused polycyclopropane molecules). They quoted some force field calculations using PC Model that predicted its enthalpy of formation to be 191.9 kcal mol^{-1} (802.9 kJ mol^{-1}). They followed up with another study of triangulanes,[4] repeating this information (although in the second paper, the enthalpy of formation is listed as 191.1 kcal mol^{-1}; the reported strain energy and strain per methylene group are the same). However, neither paper mentions the connection between the molecule and its highly recognizable line diagram.

Although a 'triangulane' nomenclature has already been introduced into the literature, we would like to propose a common name of 'pentagramane' for this particular compound, as this name succinctly conveys the structure of the molecule's line diagram. Its IUPAC name is hexacyclo[7.1.0.0^{1,3}.0^{3,5}.0^{5,7}.0^{7,9}]-decane. Here, we present results of calculations on the minimum-energy geometry, expected vibrational and NMR spectra, and enthalpies of formation and combustion of pentagramane.

COMPUTATIONAL DETAILS

All calculations were performed using the Gaussian03 program.[5] The calculations were performed on an Itanium Linux cluster located at the Ohio Supercomputer Center in Columbus, Ohio. The calculational methods used were the G2[6] and G3[7] compound methods, which use relatively low-level calculations to find an optimized geometry and then calculate high-level corrections to determine a precise energy. The methods were applied as predefined in the Gaussian03 program. The vibrational spectra were plotted using the SWizard program.[8]

---

* Department of Chemistry, Cleveland State University, 2121 Euclid Avenue, Cleveland, OH 44115, USA.
E-mail: d.ball@csuohio.edu

a David W. Ball
Department of Chemistry, Cleveland State University, 2121 Euclid Avenue, Cleveland, Ohio 44115, USA

The enthalpy of formation was determined using several different chemical reactions, each of which has its strengths and drawbacks. The first was the reverse atomization reaction:

$$10C(g) + 10H(g) \rightarrow C_{10}H_{10}(g) \qquad (1)$$

Atomization reactions are used because of the perceived accuracy of computational chemistry programs to determine absolute energies of atoms. However, they ignore any errors introduced by chemical bonding. To determine the enthalpy of formation of pentagramane, we correct the energy change of reaction (1) for the enthalpies of formation of the atoms, taken from the NIST Chemistry Webbook website,[9] to get a true formation reaction whose enthalpy change is $\Delta H_f[C_{10}H_{10}]$. Next, we consider the reaction of five cyclopropane molecules combining to make pentagramane and methane:

$$5C_3H_6(g) \rightarrow C_{10}H_{10}(g) + 5CH_4(g) \qquad (2)$$

This reaction preserves the number of cyclopropane rings in both products and reactants, but suffers from having no *spiro*-bonded carbons. To rectify that, we need to use spiropentane, C_5H_8, as a reactant. We do this in two different reactions:

$$2C_5H_8(g) \rightarrow C_{10}H_{10}(g) + 3H_2(g) \qquad (3)$$

$$5C_5H_8(g) \rightarrow C_{10}H_{10}(g) + 5C_3H_6(g) \qquad (4)$$

where the C_3H_6 product in reaction (4) is also cyclopropane. Reaction (4) may be the most accurate because it is closest to a true isodesmic reaction. However, it also has the greatest number of highly strained molecules, so if any one species is calculated inaccurately, the calculated enthalpy of formation of pentagramane may be inaccurate in turn. Hence, we will use all four reactions for comparison. The $\Delta H_f[C_{10}H_{10}]$ is determined by calculating the energies of all species in reactions (2)–(4) and then equating the energy difference to the differences in the enthalpies of formation of the products and reactants. Known ΔH_f data were determined using the NIST Chemistry Webbook.[2]

The enthalpies of combustion are determined using the following reaction:

$$C_{10}H_{10}(g) + 25/2\,O_2(g) \rightarrow 10CO_2(g) + 5H_2O(l) \qquad (5)$$

The specific enthalpy of combustion is determined by dividing the molar enthalpy of combustion by the molar mass of $C_{10}H_{10}$, which is 130.18 g mol^{-1}.

Carbon and proton NMR shifts are both referenced to tetramethylsilane, TMS. The shifts were calculated using a MP2(full)/6-31G(d) calculation, since this is the ultimate method that GX theories use to determine a minimum-energy geometry.

RESULTS AND DISCUSSION

Optimized geometry

Figure 1 shows top and side views of the minimum-energy geometry of pentagramane. The inside ring is almost a regular pentagon, and the side view of the molecule shows that this pentagon is essentially planar. Four of the five methylene groups adopt alternating axial-type positions about the planar pentagonal ring, while the fifth methylene group adopts an equatorial-like orientation. These positions doubtless minimize steric hindrance in the minimum-energy structure. Notice that the equatorial methylene group is slightly twisted, as if the proximal methylene groups on both sides are attracting the hydrogen atom. A list of representative bonding parameters is listed in Table 1. The numbers in Table 1 show that the central pentagon is not a perfect regular polygon, and that while similar in geometry the cyclopropane rings are slightly different in structure, although these differences may be caused by inherent imperfections in the numerical method used to determine the final minimum-energy geometry (which in the G2 and G3 compound methods is a MP2(full)/6-31G(d) calculation). The dihedral angles in the

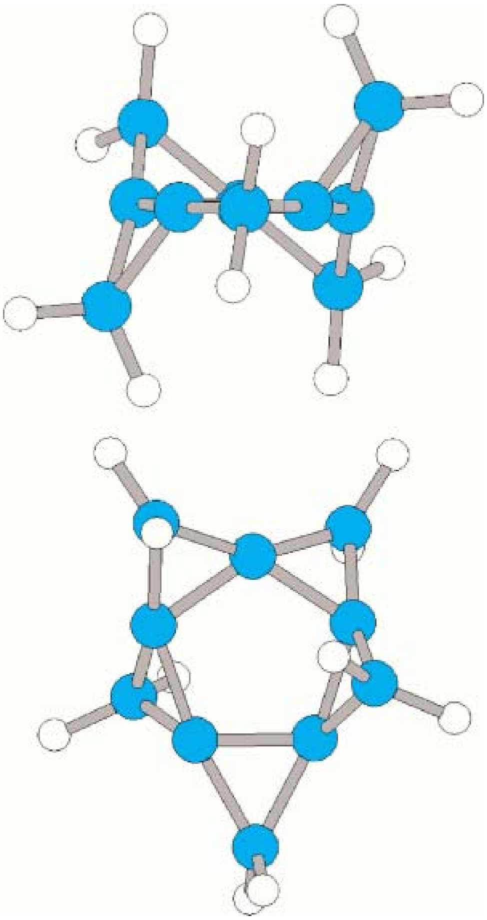


Figure 1. Side and top views of the minimum-energy geometry of pentagramane

Table 1. A list of representative bonding parameters for pentagramane. (All distances in Å, all angles in degrees)

Parameter	Value
r(C–H)	1.080
r(C–C[methylene, ax])	1.528
r(C–C[methylene, eq])	1.507
r(C–C[cyclopentane])	1.501, 1.474, 1.462
α(C–C–C[methylene])	58.1, 58.9, 60.0
α(C–C–C[cyclopentane])	105.1, 109.0, 111.7
α(H–C–H)	114.0 (ax), 114.2 (eq)
δ(C–C–C–C[methylene])	60.2, 59.3, 60.9, 66.9, 11.7
δ(C–C–C–C[cyclopentane])	1.1, 2.8, 3.6

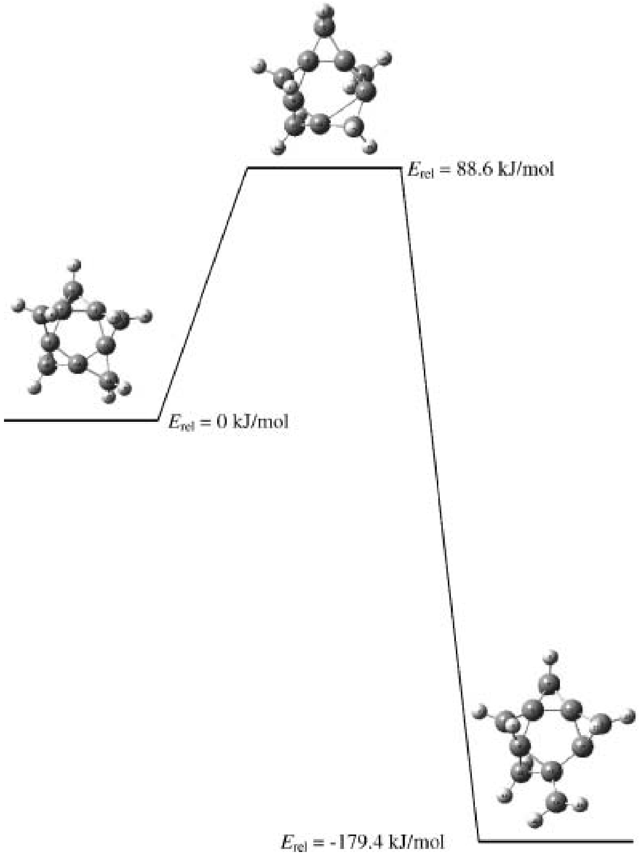


Figure 2. Relative energies of pentagramane, transition state to reaction product, and reaction product

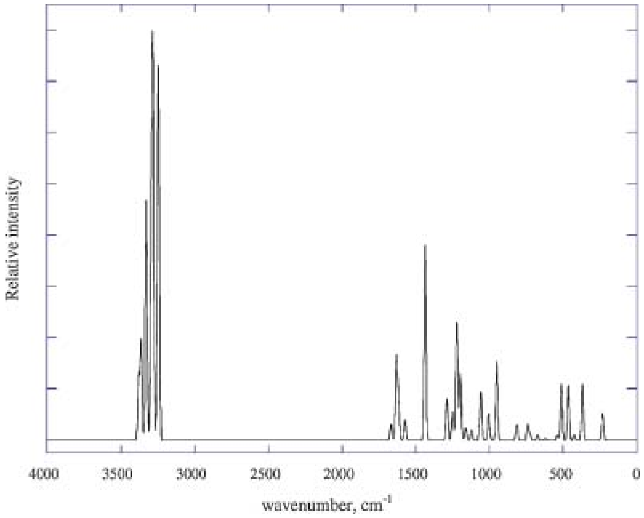


Figure 3. Predicted infrared absorption spectrum of pentagramane

cyclopentane ring range from 1.1 to 3.6°, indicating that this central ring is very close to planar. Cyclopentane itself is known to be puckered by 7–42°, varying based on the value of the pseudorotation phase angle.[9] Although this is a rather wide range of pucker, it is still definitely larger than the pucker found in the central ring of pentagramane.

In order to get an idea of the kinetic stability of the minimum-energy geometry, we calculated the energy involved in the rearrangement of pentagramane through a transition state **2** to a structure **3** that represents a reasonable rearrangement product of the pentagram structure. We assumed that a C—C bond in a cyclopropane group in the pentagramane structure was most likely to break. We then optimized that geometry and used it, along with the optimized geometry of pentagramane itself, to find a maximum-energy transition state geometry using the OPT = QST3 function in the Gaussian03 program. Such a first-order transition state would be expected to have one imaginary vibrational frequency. Figure 2 shows the results, along with the relative energies of the three structures (also shown). The three structures are oriented so that the same atoms are in the same relative orientation, clearly showing structural differences in the bond breaking process and the ultimate product, on the lower right of each molecule. The relative energies listed show that pentagramane has a *ca.* 88 kJ mol^{-1} barrier to overcome to undergo what we would argue is the most expected bond-breaking process, that is, the opening of a cyclopropane ring. We confirmed the transition-state status of the middle structure by calculating its vibrational frequencies, which show one imaginary frequency at 404*i* cm^{-1}. Animation of this vibration showed a C—C stretch involving the two carbon atoms in the lower right of pentagon in concert with the attached CH_2 wagging toward the left, exactly as one might expect in going from pentagram on the left and the biradical product on the right. Although different geometries having the formula $C_{10}H_{10}$ are more thermodynamically stable than the pentagram (which is not surprising; see energy determinations below), from these calculations we can conclude that pentagramane has a reasonable probability of kinetic stability if isolated.

Predicted spectra

Figure 3 shows the predicted vibrational spectrum of pentagramane. The molecule has 54 fundamental vibrations, and since the molecule was optimized without constraining symmetry, all 54 vibrations are infrared active. Because of the lack of symmetry in the molecule (it is very nearly of C_2 symmetry, with the C_2 axis going through the carbon atom of the equatorial methylene group), many of the vibrations that would have similar approximate descriptions are near degenerate. With the 15-wavenumber half width used to plot Fig. 3, overlapping absorptions decrease the number of distinct peaks seen in the predicted spectrum to about 25. The actual spectrum may be more complicated by combination bands, Fermi resonances, overtones, etc. A list of all 54 fundamental vibrations, their intensities, and the motion vectors of the atoms can be obtained by the author upon request.

Table 2 lists the ^{1}H and ^{13}C NMR isotropic magnetic field shifts expected for pentagramane, with respect to TMS. Figure 4 shows the numbering of the atoms used in Table 3; carbon #6 is eclipsed by hydrogen #8, while hydrogen #16 is blocked by hydrogen #15 and hydrogen #3 is hidden by carbon #2. The line diagram of pentagramane is misleading: it suggests two types of carbon atoms and one type of hydrogen atom, yielding simple NMR spectra. However, because of the three-dimensional structure of the molecule, several different environments of carbon and hydrogen are actually present. There are some degeneracies that can be explained in terms of the position of the atoms with respect to the unique equatorial methylene group in the molecule. For both ^{1}H and ^{13}C NMR spectra, the methylene group

Table 2. Predicted NMR shifts for pentagramane (in ppm *versus* TMS). See Figure 4 for atom numbering

Atom(s)	Shift	Position relative to equatorial CH_2
H12, H19	0.95	Methylene group adjacent to equatorial CH_2
H11, H20	1.85	Methylene group adjacent to equatorial CH_2
H3, H8	2.62	Methylene group distal to equatorial CH_2
H4, H7	2.87	Methylene group distal to equatorial CH_2
H15, H16	5.08	Equatorial CH_2 group
C10, C18	23.09	Methylene groups adjacent to equatorial CH_2
C2, C6	35.14	Methylene groups distal to equatorial CH_2
C1, C9	45.87	Cyclopentanic, intermediate from equatorial CH_2
C13, C17	50.27	Cyclopentanic, adjacent to equatorial CH_2
C5	54.22	Cyclopentanic, farthest from equatorial CH_2
C14	72.10	Equatorial CH_2

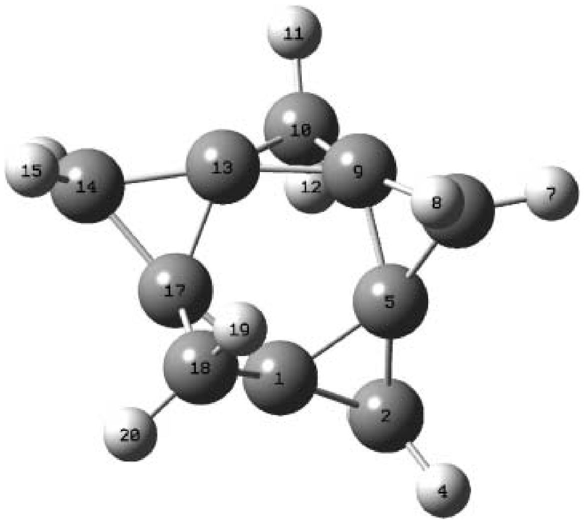


Figure 4. Numbering scheme of atoms in pentagramane for NMR spectrum; see Table 2

Table 3. Enthalpies of formation for pentagramane, in kJ mol^{-1}

Reaction	G2	G3
(1)	1005.3	1004.8
(2)	1011.6	1014.9
(3)	1040.0	1027.7
(4)	1024.7	1029.3

has the resonance farthest downfield, while the two methylene groups adjacent to the equatorial methylene group have resonances farthest upfield. Thus, the ^1H NMR spectrum is predicted to have five resonances, representing the five different types of hydrogen environments in the methylene groups. The ^{13}C NMR spectrum has six resonances, as the cyclopentane carbon atoms have a different environment than the methylene carbon atoms.

Some comparisons to the predicted NMR spectra are cyclopropane (^1H shift = 0.20 ppm)[10] and spiropentane (^1H shift = 0.73 ppm).[11] There is also a report of the synthesis of [5]-triangulane, which has five *spiro*-fused cyclopropane rings, essentially pentagramane without closing into a central five-membered ring.[12] They report ^1H NMR shifts of 0.62–0.86, 1.30, and 1.45–1.60 ppm and ^{13}C shifts of 4.30, 4.74, 10.95, 11.23, 13.81, and 18.71 ppm. While there is some agreement in the ^1H shifts, the reported shifts for the ^{13}C NMR spectra do not even overlap. Either the experimental reports are inaccurate; the method for calculating NMR shifts used here is inaccurate; or the constraining of the five cyclopropane rings into a cycle greatly modifies the local isotropic magnetic field.

Thermodynamics

Table 3 lists the enthalpies of formation of pentagramane as determined by the four reactions listed in the previous section. The enthalpies of formation are remarkably similar, given the differences in the reactions, and also given the number of species and the strain energy in many of the reactants and products in reactions 1, 2, and 4. The values range over 25 kJ mol^{-1} for the G2 and G3 calculations, with reactions 1 and 3 determining the extreme values for the G2 calculations and reactions (1) and (4) determining the extreme values for the G3 calculations. An average value for $\Delta H_f[C_{10}H_{10}]$ of 1020 kJ mol^{-1} appears appropriate to recommend.

With the enthalpies of formation determined for pentagramane, the enthalpies of combustion are straightforward to determine, using Eqn (5). The results are given in Table 4, both in units of kJ mol^{-1} and kJ g^{-1}; these last values are important because for high-energy materials, energy given off per unit mass is an important aspect. Since the calculated enthalpies of formation are close in values, so are the enthalpies of combustion. The magnitudes cluster around ~6380 kJ mol^{-1}, or about 49.0 kJ g^{-1}. For comparison, the NIST Chemistry Webbook[2] lists enthalpies of formation for two hydrocarbons that have the same molecular formula as pentagramane that do not have any aromatic rings. They are 1,4-dicyclopropylbuta-1,3-diyne (ΔH_{comb} = 5867 kJ mol^{-1}) and diisopropenyldiacetylene (ΔH_{comb} = 5808 kJ mol^{-1}). The combustion enthalpy for pentagramane is significantly greater than either of these two isomers.

Table 4. Enthalpies of formation of pentagramane

	Reaction	G2	G3
In kJ mol^{-1}			
	(1)	−6369.6	−6369.1
	(2)	−6375.9	−6379.2
	(3)	−6404.3	−6392.0
	(4)	−6389.0	−6393.6
In kJ g^{-1}			
	(1)	−48.9	−48.9
	(2)	−49.0	−49.0
	(3)	−49.2	−48.9
	(4)	−49.1	−49.1

A specific enthalpy of combustion of 49 kJ g^{-1} is high for a hydrocarbon: the specific enthalpy of combustion for methane is 55.7 kJ g^{-1}, and drops rather quickly to 51.9 kJ g^{-1} for ethane and approaches an asymptotic value of ~48.0 kJ g^{-1} for larger, saturated hydrocarbons.[2] The title hydrocarbon is not saturated (indeed, it has a degree of unsaturation of 6), so it would form six less water molecules upon combustion than its saturated counterpart. Thus, its expected enthalpy of combustion should be lower by 6 × 283.85 kJ mol^{-1} lower in magnitude, or about −4677 kJ mol^{-1} or 35.9 kJ g^{-1}. The fact that the enthalpy of combustion of pentagramane is so large in magnitude is doubtless due to its strain energy.

What is the strain energy of pentagramane? Ideally, the strain energy of $C_{10}H_{10}$ would be determined by calculating the energy of the reaction:

$$C_{10}H_{10} + 6H_2 \rightarrow C_{10}H_{22} \qquad (6)$$

where in reaction (6) the formula $C_{10}H_{22}$ refers to one of many possible saturated hydrocarbon isomers, depending on which ring bonds of $C_{10}H_{10}$ are broken upon hydrogenation. The calculated energy of reaction (6) would be compared to the expected value of reaction (6) based on average C—H and C—C bond energies, with the difference being attributed to angle strain. An ideal product would be 2,3,4,5-tetramethylhexane, which is the product that would be formed if hydrogenation were to occur at similar bonds in the cyclopropane rings, ultimately yielding pentamethylcyclopentane, then breaking the cyclopentane ring at one point. However, thermodynamic data on this molecule are unavailable. The only tetramethyl derivative of hexane for which thermodynamic data are available is 2,2,5,5-tetramethylhexane, for which the NIST Chemistry Webbook website[2] lists −258 kJ mol^{-1} for the gas phase molecule. However, inspection of the structure of pentagramane shows that it is not possible to hydrogenate a set of C—C bonds in $C_{10}H_{10}$ to generate this particular isomer of $C_{10}H_{22}$.

We can estimate the strain energy of pentagramane in several ways. First, the molecule can be considered as 2½ spiropentane molecules. If we assume that the strain energy will be a minimum 2½ times the strain energy of spiropentane,[1] we have 2.5 × 262 kJ mol^{-1} = 655 kJ mol^{-1} for pentagramane. Second, let us consider the total strain energy of pentagramane as the strain energy of planar cyclopentane plus the strain energy of five cyclopropane rings. Planar cyclopentane is estimated to have a strain energy of about 40 kJ mol^{-1} (it actually has a strain energy of *ca.* 31 kJ mol^{-1} because cyclopentane is not planar), while cyclopropane has a strain energy of about 117.6 kJ mol^{-1}.[1] Hence, we have for the strain energy of pentagramane as 40 + 5(117.6) = 628 kJ mol^{-1}, in the same ballpark as the spiropentane-based estimate. Thus, even without doing detailed calculations, we can estimate that the strain energy of pentagramane should be at least about 600 kJ mol^{-1}. This rivals the strain energy of cubane (C_8H_8), which has been estimated at about 657 kJ mol^{-1} (157 kcal mol^{-1}).[13] These estimated strain energies allow us to estimate a strain energy per cyclopropane unit of about 126–131 kJ mol^{-1}, significantly smaller than the 42.9 kcal mol^{-1} (179.5 kJ mol^{-1}) suggested by Zefirov *et al.*[3,4]

CONCLUSIONS

We have presented calculated data on a novel hydrocarbon: hexacyclo[7.1.0.0^{1,3}.0^{3,5}.0^{5,7}.0^{7,9}]decane, which we have given the common name of pentagramane because the line diagram of the molecule resembles the shape of a pentagram (i.e., the five-sided star). Geometry optimizations show that the inner five-membered ring is near planar, with four of the methylene groups in alternating axial positions relative to the ring, and the fifth methylene group in an equatorial-like position. We have determined the predicted vibrational and ^{1}H- and ^{13}C-NMR spectra of the molecule, and find that its enthalpy of formation is considerable, at about 1020 kJ mol^{-1}. Given this high enthalpy of formation, it is not surprising that the enthalpy of combustion is also rather high, with a specific enthalpy of formation of about 49 kJ g^{-1}. This is much higher than expected given the molecular formula, and doubtless due to a high strain energy in the molecule. The strain energy of the molecule has been estimated to be at least 600 kJ mol^{-1}, making it one of the most strained molecules studied.

Will pentagramane ever be synthesized? This is, of course, a problem for the synthetic organic chemist. However, a tantalizing possibility that the answer may be 'yes' can be taken from the work of Zefirov *et al.*[12] In 1990, they reported the synthesis and characterization of cyclopropane chains having three to six *spiro*-fused cyclopropane rings. All it would take would be to join the terminal carbon atoms of [4]-triangulane and include a methylene group between them, or to overlap the terminal carbon atoms of [5]-triangulane and remove a CH_4 moiety to make $C_{10}H_{10}$. We are not suggesting that these are the required synthetic steps, only that these be the net changes needed to make pentagramane. However, if these [*n*]-triangulane molecules are themselves synthesizable, then the formation of pentagramane may be only a few synthetic steps away.

Acknowledgements

A grant of computational time from the Ohio Supercomputer Center in Columbus, Ohio, is appreciated. The author thanks the anonymous reviewers for suggestions, especially in pointing out previous work on the title molecule.

REFERENCES

[1] F. A. Carey, R. J. Sundberg, *Advanced Organic Chemistry*, 4th edn, Springer, New York, **2004**.

[2] NIST Chemistry Webbook, Available online at http://webbook.nist.gov [Accessed 3 December **2007**].
[3] N. S. Zefirov, T. S. Kuznetsova, O. V. Eremenko, O. V. Kokoreva, G. Zatonsky, B. I. Ugrak, *J. Org. Chem.* **1994**, *59*, 4087–4089.
[4] T. S. Kuznetsova, O. V. Yeremenko, O. V. Kokoreva, E. B. Averina, A. N. Zefirov, N. S. Zefirov, *Russ. J. Org. Chem.* **1997**, *33*, 849–857.
[5] Gaussian 03, Revision C.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr, T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, Gaussian, Inc., Wallingford CT, **2004**.
[6] L. A. Curtiss, K. Raghavachari, G. W. Trucks, J. A. Pople, *J. Chem. Phys.* **1991**, *94*, 7221–7330.
[7] L. A. Curtiss, K. Raghavachari, P. C. Redfern, V. Rassolov, J. A. Pople, *J. Chem. Phys.* **1998**, *109*, 7764–7776.
[8] S. I. Gorelsky, SWizard program, version 4.1, http://www.sg-chem.net 2007
[9] W. J. Adams, H. J. Geise, L. S. Bartell, *J. Am. Chem. Soc.* **1970**, *92*, 5013–5019.
[10] K. M. Crecely, V. S. Watts, J. H. Goldstein, *J. Mol. Spectrosc.* **1969**, *30*, 184–191.
[11] D. J. Patel, M. E. H. Howden, J. D. Roberts, *J. Am. Chem. Soc.* **1963**, *85*, 3218–3223.
[12] N. S. Zefirov, S. I. Kozhushkov, T. S. Kuznetsova, O. V. Kokoreva, K. A. Lukin, B. I. Ugrak, S. S. Tratch, *J. Am. Chem. Soc.* **1990**, *112*, 7702–7707.
[13] D. B. Kybett, S. Carroll, P. Natalis, D. W. Bonnell, J. L. Margrave, J. L. Franklin, *J. Am. Chem. Soc.* **1966**, *88*, 626.