rearrangement and the [1,2] shift are in strong competition with dissociation. A supra [1.3] rearrangement does not appear to be possible, either as a direct shift from one terminal carbon to the other or as two [1.2] shifts. In the first case. a [1,3] supra transition structure does not exist because a diradical state is lower in energy than the closed-shell singlet. In the latter case, the topomerization via successive [1.2] shifts is unlikely because the intermediate diradical can close to give cyclopropane more easily than undergo a further [1.2] shift.[31,33]

Acknowledgment. We wish to express our gratitude to NATO (Grant RG096.81) and to the donors of the Petroleum Research Fund, administered by the American Chemical Society. for support of this work. G.T. acknowledges a computational grant from CSI-Piemonte (Torino, Italy).

Registry No. Propene, 115-07-1.

Ab Initio Heats of Formation of Medium-Sized Hydrocarbons. The Heat of Formation of Dodecahedrane

Jerome M. Schulman* and Raymond L. Disch

Contribution from the Department of Chemistry, City University of New York. Queens College. Flushing, New York 11367. *Received August 8. 1983*

Abstract: The use of ab initio molecular orbital calculations to predict accurate geometries and heats of formation has been studied for cyclohexane, cubane, adamantane, and dodecahedrane at the SCF level with use of the basis sets STO-3G. 4-31G, and 6-31G*. Good agreement with experiment is obtained for geometries in all cases. In the 6-31G* basis set, heats of formation of cyclohexane, adamantane, and cubane are in error by 0.5, 2.1, and 9.9 kcal/mol, respectively; for dodecahedrane, the heat of formation is predicted to be −5.0 kcal/mol. This work has been somewhat hampered by the unreliability of experimental thermochemical data.

Ab initio molecular orbital theory at the SCF level has been shown to be capable of the accurate prediction of geometry and thermochemistry for small hydrocarbons (C_1–C_7). These predictions require full geometry optimization at basis set levels of split valence or double-ζ (with d orbitals on all carbon atoms if there is appreciable strain energy)[2] and the construction of isodesmic[3] or preferably homodesmic[4] thermochemical processes. All this notwithstanding. the application of these methods to hydrocarbons through C_7 will soon become routine.

The present work attempts to assess the feasibility of applying these methods to the larger systems cubane, adamantane. and dodecahedrane. The latter is of particular interest. because semiempirical molecular orbital[5] and molecular mechanics[6] methods yield substantially different ΔH_f^{298} values. One conclusion of this study is that the accuracy of calculated heats of formation is strongly dependent upon the quality of available zero-point energies. heat capacity data, and experimental heats of formation for species involved in a homodesmic reaction.

Methods

The ab initio calculations were performed by optimized programs developed by us (The Queens College Quantum Chemistry Package). The basis sets employed are STO-3G.[7a] 4-31G.[7b] and 6-31G*.[7c] For dodecahedrane. the 6-31G* energy was estimated by a procedure described below.

The ΔH_f^{298} for cubane. adamantane, and dodecahedrane are calculated from several homodesmic reactions. Heats of reaction at 0 K are computed from the ab initio energy differences corrected for zero-point energies. In the absence of experimentally determined vibrational frequencies by which the latter could be calculated, values obtained from molecular mechanics are used. Enthalpies are converted from 0 K to 298 K according to the equations of Hehre et al.[3] In the final step, the desired ΔH_f^{298} is obtained from these heats of reaction corrected to 298 K and the experimental ΔH_f^{298}.

Results

Table I contains the ab initio and zero-point energies for ethane, propane. isobutane, cyclobutane. cyclohexane, cubane. adamantane. and dodecahedrane; their ΔH_f^{298} and enthalpy corrections from 0 K to 298 K are also included. All species are treated as ideal gases. The ab initio energy for each basis set corresponds to the geometry optimized in that basis with the sole exception of the 6-31G* energy of dodecahedrane, which is estimated as the sum of the 4-31G energy and a correction of 0.05645 au per carbon atom—one-fifth of the difference between the energies of planar cyclopentane in the two basis sets. This correction, nearly identical with that recommended by Hehre and Pople,[1d] is probably suitable for molecules with little angle strain. When applied to adamantane, it furnishes a 6-31G* estimate of the energy only 1.3 kcal/mol too high, whereas for cubane the error is 8.4 kcal/mol.

Table II contains the optimized geometric parameters for cyclohexane, cubane, adamantane, and dodecahedrane. The geometries in the various basis sets are very similar and in good agreement with experimental values. For cubane, the calculated geometries compare well with previous STO-3G and 4-31G values.[8a,b] as well as recent "double-ζ + d" results.[8c]

Table III contains the calculated values of ΔH_f^{298} for cyclohexane, cubane. adamantane, and dodecahedrane in the STO-3G, 4-31G, and 6-31G* basis sets, which were obtained from the seven

---

(1) For recent examples, see: (a) Wiberg, K. B.; Wendoloski, J. J. *J. Am. Chem. Soc.* **1982**, *104*, 5679. (b) Wilberg, K. B. *Ibid.* **1983**, *105*, 1227. (c) Schulman, J. M.; Disch. R. L.; Sabio, M. L. *Ibid.* **1982**, *104*, 3785. (d) Hehre, W. J.; Pople, J. A. *Ibid.* **1975**, *97*, 6941.

(2) Binkley, J. S.; Pople, J. A. *Chem. Phys. Lett.* **1975**, *36*, 1.

(3) Hehre, W. J.; Ditchfield, R.; Radom, L.; Pople, J. A. *J. Am. Chem. Soc.* **1970**, *92*, 4796.

(4) (a) George, P.; Trachtman, M.; Beck, C. W.; Brett, A. M. *Tetrahedron*, **1976**, *32*, 317. (b) George, P.; Trachtman, M.; Brett, A. M.; Bock, C. W. *J. Chem. Soc., Perkin Trans. 2* **1977**, 1036. We suggest use of the term "homodesmic" to replace "homodesmotic".

(5) Schulman, J. M.; Disch, R. L. *J. Am. Chem. Soc.* **1978**, *100*, 5677.

(6) (a) Engler, E. M.; Andose, J. D.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1973**, *95*, 8005. (b) Allinger, N. L. *Ibid.* **1977**, *99*, 8127.

(7) (a) Hehre, W. J.; Stewart, R. F.; Pople, J. A. *J. Chem. Phys.* **1969**, *51*, 2657. (b) Ditchfield, R.: Hehre, W. J.; Pople, J. A. *Ibid.* **1971**. *54*, 724. (c) Hariharan, P. C.; Pople, J. A. *Chem. Phys. Lett.* **1972**, *16*, 217.

0002-7863/84/1506-1202$01.50/0

Table I. Energies Employed in the Present Study[a]

	ab initio energy					
molecule	STO-3G	4-31G	6-31G*	zero-point energy	$H_{298\,\mathrm{K}} - H_{0\,\mathrm{K}}$	ΔH_f^{298}
ethane	−78.30618[b]	−79.11593[b]	−79.22876[b]	45.27[g]	2.86[k]	−20.04[l]
propane	−116.88580[c]	−118.09381[e]	−118.26365[e]	62.52[g]	3.51[k]	−25.02[l]
isobutane	−155.46683	−157.07260	−157.29897	79.61[h]	4.28[k]	−32.07[l]
cyclobutane	−154.27390[d]	−155.86681[e]	−156.09703[e]	67.07[g]	3.22[g]	6.78[m]
cyclohexane	−231.48268	−233.86680[e]	−234.20799	103.37[h]	4.24[k]	−29.5[m]
cubane	−303.78139	−306.92890	−307.39383	80.66[i]	3.54[i]	148.7[n]
adamantane	−383.51533	−387.46002	−388.02653	148.59[h]	5.04[h]	−32.51[o]
dodecahedrane	−760.13797	−767.93349	(−769.06249)[f]	214.55[j]	6.67[j]	

[a] Ab initio energies in hartrees; 1 hartree = 627.5 kcal/mol. Other energies in kcal/mol.
[b] Reference 1a.
[c] Reference 3.
[d] Reference 1d.
[e] Reference 1b.
[f] Estimated as described in the text.
[g] Calculated from the experimental frequencies given by Shimanouchi: Shimanouchi, T. "Tables of Molecular Vibrational Frequencies"; U.S. Government Printing Office, Washington, DC; NSRDS-NBS 6, 11, 17.
[h] Calculated from the force field frequencies given by Snyder et al.: Snyder, R. G.; Schachtschneider, J. H. *Spectrochim. Acta* **1965**, *21*, 169.
[i] Calculated from the experimental frequencies given by Della et al.: Della, E. W.; McCoy, E. F.; Patney, H. K.; Jones, G. L.; Miller, F. A. *J. Am. Chem. Soc.* **1979**, *101*, 7441.
[j] From the experimental frequencies of Ternansky et al.: Ternansky, R. J.; Balogh, D. W.; Paquette, L. A. *J. Am. Chem. Soc.* **1982**, *104*, 4503) and the calculated frequencies of Ermer (Ermer, O. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 411).
[k] Rossini, F. D.; Pitzer, K. S.; Arnett, R. L.; Braun, R. M.; Pimentel, G. C. "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds"; Carnegie Press: Pittsburgh, 1953.
[l] Pittam, D. A.; Pilcher, G. *J. Chem. Soc., Faraday Trans.* **1972**, *168*, 2224.
[m] Reference 11.
[n] Kybett, B. D.; Carroll, S.; Natalis, P.; Bonnell, D. W.; Margrave, J. L.; Franklin, J. L. *J. Am. Chem. Soc.* **1966**, *88*, 626.
[o] Reference 12.

Table II. Optimized Geometries of Cyclohexane, Cubane, Adamantane, and Dodecahedrane (Bond Lengths in Angstroms and Angles in Degrees)

molecule	parameter	STO-3G	4-31G	6-31G*	obsd	ref
cyclohexane	r(CC)	1.544	1.534[a]	1.531	1.536 ± 0.002	*b*
	$r(\mathrm{CH_e})$	1.088	1.086	1.087	1.121 ± 0.004 (av)	
	$r(\mathrm{CH_a})$	1.089	1.088	1.089		
	$\angle$(CCC)	111.4	111.4	111.5	111.4 ± 0.2	
	$\angle(\mathrm{CCH_e})$	109.8	110.1	109.9		
	$\angle(\mathrm{CCH_a})$	109.2	109.1	109.3		
	$\angle(\mathrm{H_aCH_e})$	107.4	106.9	106.8	107.5 ± 1.5	
	$\angle$(CCCC)	55.0	55.0	54.5	54.9 ± 0.4	
cubane	r(CC)	1.562	1.573	1.557	1.549–1.553	*c*
	r(CH)	1.087	1.075	1.079	1.01–1.11	
adamantane[d]	r(CC)	1.548	1.546	1.539	1.540 ± 0.004	*e*
	$r(\mathrm{CH_s})$	1.088	1.086	1.087	1.12 ± 0.004 (av)	
	$r(\mathrm{CH_t})$	1.090	1.084	1.088		
	$\angle\mathrm{C_tC_sC_t}$	109.6	109.6	109.5	108.8 ± 1.0	
	$\angle\mathrm{C_sC_tC_s}$	109.4	109.4	109.5	109.8 ± 0.5	
	$\angle\mathrm{H_sC_sH_s}$	107.6	107.3	107.3	116.9 ± 6.0	
	$\angle\mathrm{H_sC_sC_t}$	109.9	110.0	110.0		
dodecahedrane	r(CC)	1.553	1.547	(1.546)	(1.546)[f]	
	r(CH)	1.087	1.083	(1.084)	(0.98)	

[a] Reference 1b.
[b] Bastiansen, O.; Fernholt, L.; Seip, H. M. *J. Mol. Struct.* **1973**, *18*, 163.
[c] Fleischer, E. B. *J. Am. Chem. Soc.* **1964**, *86*, 3889.
[d] The subscripts s and t refer to secondary and tertiary carbons, respectively, and to their attached hydrogens. T_d symmetry was assumed.
[e] Hargittai, I. *Chem. Commun.* **1971**, 1499.
[f] Bond lengths found for 1,16-dimethyldodecahedrane: Paquette, L. A.; Balogh, D. W.; Usha, R.; Kountz, D.; Christoph, G. G. *Science (Washington, DC)* **1981**, *211*, 575. Paquette, L. A.; Balogh, D. W. *J. Am. Chem. Soc.* **1982**, *104*, 774.

Table III. Homodesmic Reactions Used To Obtain Heats of Formation for Cyclohexane, Cubane, Adamantane, and Dodecahedrane; Values of the Heats of Formation (in kcal/mol)

		ΔH_f^{298}			
molecule of interest	homodesmic reaction[a,b]	STO-3G	4-31G	6-31G*	exptl[c]
cyclohexane	(1) 6propane → cyclohexane + 6ethane	−32.8	−29.4	−28.8	−29.5
adamantane	(2) 4isobutane + cyclohexane → adamantane + 6ethane	−39.8	−37.3	−35.3	−32.51
	(3) 4isobutane + 6propane → adamantane + 12ethane	−43.1	−37.2	−34.6	
cubane	(4) 5cyclobutane + 8isobutane + 8ethane → cubane + 20propane	149.9	137.9	139.8	148.7
	(5) 8isobutane → cubane + 12ethane	149.7	138.2	133.2	
	(6) 2adamantane → cubane + 2cyclohexane	164.3	147.7	138.8	
dodecahedrane	(7) 5adamantane → dodecahedrane + 5cyclohexane	−8.1	−3.5	−5.0	

[a] Zero-point energy corrections for reactions 1 → 7 are the following (kcal/mol): −0.13, −1.60, −1.73, −3.33, −12.98, −9.78, and −11.55, respectively.
[b] Corrections to convert heats of reaction from 0 to 298 K for (1) → (7) are the following (kcal/mol): 0.34, 0.84, 1.18, 0.52, 3.62, 1.94, and 2.67, respectively.
[c] References given in Table I.

homodesmic reactions indicated. The zero-point energy corrections to the ab initio heats of reaction were necessary, especially for reactions 5 to 7, where they are −12.98, −9.78, and −11.55 kcal/mol, respectively. However, these values are small compared to the zero-point energies of individual reactants or products. The corrections of the heats of reaction from 0 to 298 K (see footnote *b*, Table III) are smaller than the zero-point corrections: errors inherent in them due to the ideal gas approximation are likely to be negligible.

Reaction 1 furnishes a ΔH_f^{298} for cyclohexane of −32.8, −29.4, and −28.8 kcal/mol at the STO-3G, 4-31G, and 6-31G* levels of approximation. All values are in good agreement with the experimental result, −29.5 kcal/mol. Reactions 2 and 3 furnish ΔH_f^{298} for adamantane: values at the 6-31G* level differ respectively by −2.8 and −2.1 kcal/mol from experiment, and the difference between them is due to the error in the calculated heat of formation of cyclohexane, because (3) − (2) = (1).

Reactions 4 to 6 are used to obtain ΔH_f^{298} for cubane: the eight methine hydrogen atoms are obtained from eight isobutanes in (4) and (5) and from two admantanes in (6). In reaction 4 the independent four-membered rings are balanced by using five cyclobutanes. This reaction uses a large number of small molecules—41 in all—in the production of one cubane, thus magnifying the errors in their zero-point energies, heat capacities, and heats of formation. The calculated ΔH_f^{298} of cubane at the 6-31G* level is 139.8, 133.2, and 138.8 kcal/mol from reactions 4, 5, and 6, respectively: the experimental value is 148.7 kcal/mol. For cubane, the errors in the calculated heats of formation are appreciably larger than those for adamantane, the best results being obtained from reaction 4. It may be noted that because (5) − (6) = 2(2), the difference in the heat of formation of cubane between (5) and (6) is, apart from round-off, twice the error in the heat of formation of adamantane obtained from (2).

The ΔH_f^{298} of dodecahedrane is obtained from reaction 7, which has the virtue of using only 11 molecules, the 20 CH moieties being obtained from 5 molecules of adamantane. The heat of formation of dodecahedrane is found to be −8.1, −3.5, and −5.0 kcal/mol for the STO-3G, 4-31G, and 6-31G* basis sets, respectively. The latter value relies upon an estimated 6-31G* energy of dodecahedrane (see above) which is most probably a few kcal/mol too high.

Recent estimates of the heat of formation of dodecahedrane include the following: 62.3 (MINDO/3),[5] −0.22 (molecular mechanics),[6a] 22.5 (molecular mechanics, MM2),[6b] and −46.9 kcal/mol (MNDO, this work). Our ab initio results are in best agreement with the value of Engler et al.[6a] The larger MM2 value of 22.5 kcal/mol is not surprising in view of the overestimate by this method of the heat of formation of perhydroquinacene by 2.38 kcal/mol.[9] Nor is the MINDO/3 result surprising, because this method overestimates the heat of formation of adamantane by 35.1 kcal/mol.

The fact that all three basis sets yield rather similar heats of formation suggests that the problem of dodecahedrane is similar to those of cyclohexane and adamantane, which have relatively little angle strain and calculated heats of formation close to experiment. A previous STO-3G calculation[10] furnished a low value for the heat of formation of dodecahedrane; it employed a homodesmic reaction involving 20 isobutanes as the source of the methine groups. Heats of formation of dodecahedrane obtained from this reaction are quite dependent upon basis set and are likely to be less reliable than those of reaction 7.

Discussion

The use of homodesmic reactions for accurate prediction of the thermochemistry of larger organic molecules seems feasible, particularly if they are constructed so as to have small stoichiometric coefficients. This runs counter to the practice of using the simplest molecules containing the moieties of interest, such as group separation reactions.[3,4] However, it is necessary because large stoichiometric coefficients magnify errors in the subsidiary quantities used to evaluate the heat of formation. For example, we have used −32.07 kcal/mol as the experimental heat of formation of isobutane: an older alternative value cited by Cox and Pilcher[11] is −32.41 kcal/mol, which leads to calculated ΔH_f^{298} values of cubane from (5) which are 2.7 kcal/mol larger. Similarly, there is uncertainty in the experimental heat of formation of adamantane, with values ranging from −30.57 to −32.96 kcal/mol.[9] We have chosen the most recent (unpublished) value, −32.51, obtained by Dr. M. Mansson.[12] Perhaps the most important problem is the dearth of accurate vibrational frequencies, particularly for systems which cannot be reliably treated by molecular mechanics.

Despite all of this, the ab initio homodesmic procedure is likely to be useful for highly strained hydrocarbons. A recent application is to the hypothetical [4.4.4.4]fenestrane, where ab initio values of ΔH_f^{298} [1a,13] differ appreciably from the MNDO value.[14]

Acknowledgment. This research was supported in part by Grant No. 663228 from the PSC-CUNY Research Award Program of the City University of New York and a grant of computing time from the City University Committee on Research Computing. We gratefully acknowledge helpful discussions on thermochemical data with Drs. B. Gammon and W. Steele of the United States Department of Energy, Bartlesville, OK, E. F. Westrum, Jr., of the University of Michigan, and Dr. Margaret Mansson of Bofors, Sweden.

Registry No. Cyclohexane, 110-82-7; adamantane, 281-23-2; cubane, 277-10-1; dodecahedrane, 4493-23-6.

---

(8) (a) Bischof, P.; Eaton, P. E.; Gleiter, R.; Heilbronner, E.; Jones, T. B.; Musso, H.; Schmelzer, A.; Stober, R. *Helv. Chim. Acta* **1975**, *61*, 547. (b) Schubert, W.; Yoshimine, M.; Pacansky, J. *J. Phys. Chem.* **1981**, *85*, 1340. (c) Almlof, J.; Jonvik, T. *Chem. Phys. Lett.* **1982**, *92*, 267.

(9) Clark, T.; Knox, T. McO.; McKervey, A.; Mackle, H.; Rooney, J. J. *J. Am. Chem. Soc.* **1979**, *101*, 2404.

(10) Disch, R. L.; Schulman, J. M. *J. Am. Chem. Soc.* **1981**, *103*, 3297.

(11) Cox, J. D.; Pilcher, G. "Thermochemistry of Organic and Organometallic Compounds"; Academic Press; New York, 1970.

(12) Private communication from Dr. M. Mansson. This value is in reasonable agreement with her earlier result, −32.96 kcal/mol: Mansson, M.; Rapport, N.; Westrum, E. F., Jr. *J. Am. Chem. Soc.* **1970**, *92*, 7296.

(13) Schulman, J. M.; Sabio, M. L.; Disch, R. L. *J. Am. Chem. Soc.* **1983**, *105*, 743.

(14) Wurthwein, E.-U.; Chandrasekhar, J.; Jemmis, E. D.; Schleyer, P. v. R. *Tetrahedron Lett.* **1981**, 843; **1982**, 3306.