

electron density in the nitro group. The asymmetric NO₂ stretch is overestimated by 199 cm⁻¹ in CH₂NO₂ compared to 130 cm⁻¹ in CH₃NO₂. For both NO₂ stretches the error is due to neglecting a low-lying configuration, which contains two electrons in an orbital which is N-O antibonding.

The isotope frequency shifts were calculated with the 6-31G* force constants and are reported in Table VIII. One can clearly see that the calculated shifts support the present assignment. The CN stretch, which was previously thought to be much higher, has only a small isotope shift for ¹³C and ¹⁵N. For a pure C-N mode with a frequency of 986 cm⁻¹ the isotope shift for ¹³C and ¹⁵N would be 21 and 15 cm⁻¹, respectively. The calculated and observed shifts are less due to coupling with the hydrogens and oxygens. In fact, the isotope shift with deuterium is calculated to be 65 cm⁻¹ for the CN stretch (observed 81 cm⁻¹), which also suggests coupling. The observed isotope shifts have been reported where it was clear that the new band was shifted from one which was identifiable in the normal isotope spectrum. The MNDO isotope shifts are also presented in Table VIII. Although the agreement is not as good as the 6-31G* scaled results, the trends are generally the same. One exception is the shifts for the B₁ wags. The 6-31G* scaled results show a considerable shift as a result of substituting ¹⁵N for ¹⁴N for the first (higher frequency) wag

as compared to the second wag while MNDO results predicts the opposite effect. This clearly shows that MNDO predicts CH₂ wag > NO₂ wag in contradiction to the 6-31G* scaled results. Unfortunately the lower frequency wag was not observed in the experimental spectrum.

Conclusion

Ab initio results predict that the methyl group tilt is controlled by CH₃ donation into a vacant nitrogen orbital in the LUMO and that the rotational barrier is extremely small. The CH₂NO₂ radical is predicted to be of C_{2v} symmetry at the UMP2/3-21G level. The UHF solution, on the other hand, contains an internal instability which when removed leads to a broken symmetry solution in C_s symmetry, and which is further stabilized by a geometric distortion of the NO₂ group. Comparing vibrational frequencies calculated with several wave functions, it is found that scaled 6-31G* frequencies can be used to assign the character of CH₂NO₂ frequencies. Although not of quantitative quality, the MNDO frequencies may be of sufficient accuracy to help interpret and assign vibrational frequencies.

Acknowledgment. The author is grateful to Auburn University for a Grant in Aid and to the Auburn University Computer Center for a generous allotment of computer time.

Ab Initio Heats of Formation of Medium-Sized Hydrocarbons. 2. Use of Second-Order Correlation Energies

Raymond L. Disch,* Jerome M. Schulman, and Michael L. Sabio

Contribution from the Department of Chemistry, City University of New York, Queens College, Flushing, New York 11367. Received August 6, 1984

Abstract: The heats of formation of 15 representative strained and unstrained hydrocarbons have been calculated by ab initio molecular orbital theory with the 6-31G* basis set. It is shown that RMP2 energies computed at SCF geometries in conjunction with homodesmotic reactions furnish heats of formation within 3 kcal/mol of experiment; the root-mean-square (rms) error is 1.3 kcal/mol. An exception is benzene, for which homodesmotic cycles using single- and double-bonded carbons are probably inadequate. Calculations are also reported for isodesmotic reactions, the rms error being 2.1 kcal/mol. Heats of formation calculated at the 6-31G*(SCF) level are in error to a substantially greater degree.

In the first paper of this series¹ we investigated the possibility of using ab initio molecular orbital theory to calculate accurate heats of formation of the medium-sized hydrocarbons cyclohexane, adamantane, cubane, and dodecahedrane. The highest level of calculation employed 6-31G* (SCF) energies² and homodesmotic reactions³ of the molecules of interest. While the deviations of the calculated $\Delta H_f(298\text{ K})$ from the experimental values for the relatively unstrained hydrocarbons cyclohexane and adamantane were reasonably good (0.7 and 2.1–2.8 kcal/mol, respectively), the calculated $\Delta H_f(298\text{ K})$ for cubane with three different thermochemical cycles were 9 to 16 kcal/mol in error. This persistent and appreciable error is disturbing in view of the importance of the application of ab initio calculation to the thermochemistry of highly strained systems, whose preparation in

quantity is often difficult or impossible. The present work describes a systematic study of the heats of formation of a number of representative strained and unstrained hydrocarbons with 6-31G* SCF and RMP2⁴ energies in conjunction with both isodesmotic⁵ and homodesmotic³ reactions. With the exception of benzene, heats of formation calculated from RMP2 ab initio energies are in excellent agreement with experiment, even for highly strained systems such as cubane.

Methods

All RMP2 calculations were performed at 6-31G*(SCF)-optimized geometries with the frozen-core approximation,^{5c} which excludes correlation contributions from carbon 1s-like molecular orbitals. The calculations were performed with optimized programs developed by us (The Queens College Quantum Chemistry Package). Heats of reaction at 0 K are computed from the ab initio energy differences corrected for

(1) Paper I of this series: Schulman, J. M.; Disch, R. L. *J. Am. Chem. Soc.* **1984**, *106*, 1202.

(2) Hariharan, P. C.; Pople, J. A. *Chem. Phys. Lett.* **1972**, *16*, 217.

(3) (a) George, P.; Trachtman, M.; Bock, 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.

(4) (a) Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618. (b) Schulman, J. M.; Kaufman, D. N. *J. Chem. Phys.* **1970**, *52*, 3662. (c) Pople, J. A.; Binkley, J. S.; Seeger, P. *Int. J. Quantum Chem. Symp.* **1976**, *10*, 1.

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

Table I. Energies Used in the Present Study^a

molecule	6-31G*(SCF)	6-31G*(RMP2)	zero-point energy ^k	H(298) - H(0)	$\Delta H_f(298)^u$
methane	-40.1952 ^b	-40.3324	27.1	2.4 ^p	-17.8 ^v
ethane	-79.2288 ^b	-79.4945	45.3	2.9 ^p	-20.0 ^v
ethylene	-78.0317 ^b	-78.2844	30.9	2.5 ^p	12.5
propane	-118.2637 ^b	-118.6600	62.5	3.5 ^p	-25.0 ^v
propene	-117.0715 ^b	-117.4545	48.6	3.2 ^p	4.9
cyclopropane	-117.0589 ^b	-117.4482	49.4	2.7 ^q	12.7
cyclopropene	-115.8231 ^b	-116.2039	34.2	2.5 ^q	66.2
isobutane	-157.2990 ^c	-157.8281	79.6	4.3 ^c	-32.1 ^v
trans-2-butene	-156.1104 ^d	-156.6247	65.5 ^l	4.2 ^l	-3.0
cyclobutane	-156.0970 ^c	-156.6174	67.1 ^c	3.2 ^c	6.8
cyclobutene	-154.8996 ^d	-155.4091	53.1 ^l	3.1 ^l	37.5
tetrahydrane	-153.5979 ^c	-154.1067	34.3 ^e	3.0 ^r	
1,3-cyclobutadiene	-153.6412 ^f	-154.1438	35.3 ^m	2.9 ^r	
1,3-butadiene	-154.9197 ^f	-155.4212	51.4 ^l	3.6 ^l	26.1
bicyclobutane	-154.8718 ^d	-155.3889	51.7 ^d	3.0 ^s	51.9
cyclohexane	-234.2080 ^c	-234.9916	103.4 ^c	4.2 ^c	-29.5
benzene	-230.7031 ^f	-231.4564	61.2	3.4 ^p	19.8
1,3,5-cycloheptatriene	-269.6817 ^g	-270.5642	77.4 ⁿ	4.3 ⁿ	43.9
cyclooctatetraene	-307.5239 ^h	-308.5236	81.8 ^o	4.5 ^s	71.1
cubane	-307.3938 ^c	-308.4133	80.7 ^c	3.5 ^c	148.7
adamantane	-388.0265 ^c	-389.3296 ^l	148.6 ^c	5.0 ^c	-32.5 ^c
dodecahedrane	-769.0472 ^l		214.6 ^c	6.7 ^c	

^a Ab initio energies in hartrees; 1 hartree = 627.5 kcal/mol. Other energies are in kcal/mol. ^b Whiteside, R. A.; Frisch, M. J.; Binkley, J. S.; DeFrees, D. J.; Schlegel, H. B.; Raghavachari, K.; Pople, J. A. "Carnegie-Mellon Quantum Chemistry Archive", 2nd ed.; Carnegie-Mellon University, 1981. ^c Reference 1. ^d Wiberg, K. B.; Bonnevill, G.; Dempsey, R. *Isr. J. Chem.* **1983**, *23*, 85. ^e Private communication from L. Schaad. Zero-point energy from the 6-31G*(RMP2) frequencies, scaled by 0.9. ^f Hess, B. A., Jr.; Schaad, L. J. *J. Am. Chem. Soc.* **1983**, *105*, 7500. ^g J. M. Schulman, R. L. Disch, and M. L. Sabio, *J. Am. Chem. Soc.* **1984**, *106*, 7696. ^h The cyclooctatetraene 6-31G*(SCF) parameters are as follows: C=C, 1.323 Å, C—C, 1.477 Å, CH, 1.079 Å; \angle CCC, 126.5°; \angle HC=C, 118.1°; \angle HC—C, 115.3°. ⁱ The dodecahedrane 6-31G*(SCF) parameters are as follows: CC, 1.546 Å; CH, 1.085 Å. ^j Derived from experiment as described in the text. ^k Cited in ref 5, unless otherwise noted. ^l Cited in ref 3b. Enthalpy changes calculated from the $\Delta\Delta H_f$ in this paper. ^m From the 6-31G*(RMP2) frequencies, scaled by 0.9: Hess, B. A., Jr.; Carsky, P.; Schaad, L. J. *J. Am. Chem. Soc.* **1983**, *105*, 695. ⁿ Calculated from the experimental frequencies cited by Paulick et al.: Paulick, W.; Jung, C. W.; Kempka, U.; Suhnel, J.; Gustav, K. *J. Mol. Struct.* **1981**, *85*, 235. ^o Calculated from the empirical formula of Schulman and Disch: (Schulman, J. M.; Disch, R. L. *Chem. Phys. Lett.* **1985**, *113*, 291. ^p 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. ^q Calculated from the $\Delta\Delta H_f$ value of footnote d. ^r Calculated from the 6-31G*(RMP2) frequencies of footnotes l and e. ^s Calculated from the frequencies of Wiberg and Peters (Wiberg, K. B.; Peters, K. S. *Spectrochim. Acta* **1977**, *33A*, 261). ^t From the group equivalents of Franklin (Franklin, J. L. *Ind. Eng. Chem.* **1949**, *10*, 1070). ^u Unless otherwise noted: Cox, J. D.; Pilcher, G. "Thermochemistry of Organic and Organometallic Compounds"; Academic Press: New York, 1970. ^v Pittam, D. A.; Pilcher, G. *J. Chem. Soc., Faraday Trans.* **1972**, *168*, 2224.

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 to 298 K according to the equations of Hehre et al.⁵ In the final step, the desired $\Delta H_f(298\text{ K})$ is obtained from the ab initio heat of reaction corrected to 298 K and the experimental $\Delta H_f(298\text{ K})$'s.

Results

Table I contains the ab initio and zero-point energies, the enthalpy corrections from 0 to 298 K, and the heats of formation for 22 hydrocarbons; all species are treated as ideal gases. 6-31G*(RMP2) energies for adamantane and dodecahedrane were not calculated, but an estimated RMP2 energy for adamantane was obtained by using its known $\Delta H_f(298\text{ K})$, -32.5 kcal/mol, in the homodesmic reaction: 4isobutane + 6propane \rightarrow adamantane + 12ethane. This estimate, -389.3296 au, seems reasonable, since it furnishes accurate heats of formation of adamantane when used in other thermochemical cycles.

Table II contains the homodesmic and isodesmic cycles used to calculate the heats of formation of 15 hydrocarbons. The isodesmic reactions balance all C—C and C=C bonds of the molecule in question by ethanes and ethylenes, respectively, and the CH bonds are balanced by methanes. The homodesmic reactions improve the balance by equating the same numbers of (1) CH₃—, —CH₂—, >CH—, =CH₂, and =CH— groups and (2) bonds between atoms of the same hybridization type. For the homodesmic reactions we have employed ethane, propane, isobutane, propene, 1,3-butadiene, and, in one case, adamantane.

Table III contains the calculated heats of formation of 15 hydrocarbons. For the RMP2 homodesmic reactions, deviations from experiment are less than 3 kcal/mol; the only exception is benzene, for which the homodesmic balance using ethylene and butadiene is probably inadequate, especially in view of the fact that cyclooctatetraene is treated adequately. Excluding benzene, the root-mean-square (rms) deviation of the homodesmic heats

of formation is 1.3 kcal/mol. The isodesmic RMP2 values are less accurate, a deviation of 5.0 kcal/mol occurring for cyclooctatetraene; excluding benzene, the rms deviation is 2.1 kcal/mol. For cubane, which motivated the present study, the homodesmic and isodesmic cycles lead to $\Delta H_f(298\text{ K})$ of 148.7 and 149.5 kcal/mol, in excellent agreement with the experimental value of 148.7 \pm 1 kcal/mol⁶.

The homodesmic cycles at the SCF level yield results of lower accuracy than those of the RMP2 homodesmic and isodesmic cycles; the rms deviation is 4.8 kcal/mol, due primarily to cubane. The isodesmic cycles at the SCF level give even poorer results, especially for the larger molecules cyclohexane, cubane, adamantane, and dodecahedrane, where a significant loss of accuracy is observed; the rms deviation is 10.4 kcal/mol.

Fortunately, an alternative method available at the 6-31G*(SCF) level is the use of ab initio group-equivalents introduced by Wiberg.⁷ It enables 6-31G*(SCF) energies to be converted directly into heats of formation without the need for zero-point energies or enthalpy conversions from 0 to 298 K. The price paid for this simpler procedure is only a moderate loss of accuracy with respect to the more elaborate RMP2 method. The largest errors we have found are 5.6 and 7.2 kcal/mol for cubane and cyclooctatetraene, respectively. When applied to dodecahedrane it gives a $\Delta H_f(298\text{ K})$ of 4.8 kcal/mol, which is similar to the homodesmic 6-31G*(SCF) value, 4.6 kcal/mol.

This work has attempted, in part, to answer the following question: What level of ab initio calculation is required such that homodesmic thermocycles furnish heats of reaction with an accuracy of at worst a few kcal/mol? For nonaromatic hydrocarbons, it is now clear that the desired accuracy is available at

(6) Kybett, K. D.; Carroll, S.; Natalis, P.; Bonnell, D. W.; Margrave, J. L.; Franklin, J. L. *J. Am. Chem. Soc.* **1966**, *88*, 626.

(7) Wiberg, K. B. *J. Comput. Chem.* **1984**, *5*, 187.

Table II. Homodesmic and Isodesmic Reactions Used To Calculate Heats of Formation

molecule of interest	homodesmic reaction
cyclopropane	3propane → cyclopropane + 3ethane
cyclopropene	2propene + propane → cyclopropene + 2ethane + ethylene
<i>trans</i> -2-butene	2propene → <i>trans</i> -2-butene + ethylene
cyclobutane	4propane → cyclobutane + 4ethane
cyclobutene	2propene + 2propane → cyclobutene + 3ethane + ethylene
1,3-cyclobutadiene	2butadiene → 1,3-cyclobutadiene + 2ethylene
bicyclobutane	2propane + 2isobutane → bicyclobutane + 5ethane
tetrahydrane	4isobutane → tetrahydrane + 6ethane
cyclohexane	6propane → cyclohexane + 6ethane
benzene	3 <i>s-trans</i> -1,3-butadiene → benzene + 3ethylene
1,3,5-cycloheptatriene	2 <i>s-trans</i> -1,3-butadiene + propane + 2propene → 1,3,5-cycloheptatriene + 3ethylene + 2ethane
cyclooctatetraene	4 <i>s-trans</i> -1,3-butadiene → cyclooctatetraene + 4ethylene
cubane	8isobutane → cubane + 12ethane
adamantane	4isobutane + cyclohexane → adamantane + 6ethane
dodecahydrane	5adamantane → dodecahydrane + 5cyclohexane

molecule of interest	isodesmic reaction
cyclopropane	3ethane → cyclopropane + 3methane
cyclopropene	ethylene + 2ethane → cyclopropene + 3methane
<i>trans</i> -2-butene	2ethane + ethylene → <i>trans</i> -2-butene + 2methane
cyclobutane	4ethane → cyclobutane + 4methane
cyclobutene	ethylene + 3ethane → cyclobutene + 4methane
1,3-cyclobutadiene	2ethylene + 2ethane → cyclobutadiene + 4methane
bicyclobutane	5ethane → bicyclobutane + 6methane
tetrahydrane	6ethane → tetrahydrane + 8methane
cyclohexane	6ethane → cyclohexane + 6methane
benzene	3ethylene + 3ethane → benzene + 6methane
1,3,5-cycloheptatriene	3ethylene + 4ethane → cycloheptatriene + 7methane
cyclooctatetraene	4ethylene + 4ethane → cyclooctatetraene + 8methane
cubane	12ethane → cubane + 16methane
adamantane	12ethane → adamantane + 14methane
dodecahydrane	30ethane → dodecahydrane + 40methane

the 6-31G*(RMP2) level with use of geometries obtained at the 6-31G*(SCF) level.

The ΔH_f 's of cyclobutadiene and tetrahydrane are predicted to be 103.7 and 132.3 kcal/mol, respectively. The tetrahydrane value is in good agreement with the RMP2 value of 131.4 kcal/mol obtained from the homodesmic cycle used by us previously:⁸ 2bicyclobutane → tetrahydrane + cyclobutane. The ΔH_f of tetrahydrane is also in good agreement with the CEPA result of Kollmar,⁹ since by including zero-point and enthalpy corrections

(8) Schulman, J. M.; Venanzi, T. J. *J. Am. Chem. Soc.* **1974**, *96*, 4739.

Table III. Calculated Heats of Formation (kcal/mol)^a

molecule of interest	6-31G*(SCF)		6-31G*(RMP2)		exptl ^b
	iso-desmic	homo-desmic	iso-desmic	homo-desmic	
cyclopropane	15.7	12.4	13.3	14.0	12.7
cyclopropene	71.9	68.4	66.7	66.7	66.2
<i>trans</i> -2-butene	-0.2	-2.6	-3.1	-3.3	-3.0
cyclobutane	10.2	5.8	6.2	7.1	6.8
cyclobutene	43.6	39.0	38.2	38.5	37.5
1,3-cyclobutadiene	111.3	106.8	102.2	103.7	
bicyclobutane	60.9	50.5	53.5	53.7	51.9
tetrahydrane	140.4	123.9	132.7	132.3	
cyclohexane	-21.8	-28.3	-29.7	-28.3	-29.5
benzene	22.9	16.0	9.5	11.7	19.8
1,3,5-cycloheptatriene	53.6	45.5	39.8	41.3	43.9
cyclooctatetraene	81.0	71.9	66.1	69.1	71.1
cubane	166.1	133.4	149.5	148.7	148.7
adamantane	-11.2	-35.4	-33.5	-33.7	-32.5
dodecahydrane	72.8	4.6			
rms error ^c	10.4	4.8	2.1	1.3	

^a From the energies given in Table I and the reaction given in Table II. ^b See footnote *u* of Table I. ^c Excludes benzene.

his ΔH_f becomes 133 kcal/mol. Our estimated heat of formation of cyclobutadiene, 103.7 kcal/mol, also agrees well with that of Kollmar, 105 kcal/mol. This result is in accord with Kollmar's finding that cyclobutadiene is slightly more stable than two separated acetylenes. It must be emphasized that unless high levels of calculation are employed, the subtraction of isomer energies in cases such as cyclobutadiene-tetrahydrane, which are nonisodesmic, will lead to poor results; even at the RMP2 level, direct subtraction gives 23 kcal/mol and homodesmic analysis 29.

As a final case, we consider dodecahydrane. The calculated 6-31G*(SCF) energy differs somewhat from our estimated value:¹ the homodesmic SCF heat of formation is now 4.6 kcal/mol. Previous estimates of the heat of formation include -46.9 (MNDO),¹ -0.22 (molecular mechanics),¹⁰ 22.5 (molecular mechanics, MM2),¹¹ and 62.3 kcal/mol (MINDO/3).¹² With use of Franklin's group equivalents,¹³ an unstrained (CH)₂₀ molecule would have a $\Delta H_f(298\text{ K})$ of -21.8 kcal/mol. Thus the strain energy of dodecahydrane is only 26 kcal/mol.

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 thank Prof. L. J. Schaad for communicating results prior to publication.

Registry No. Methane, 74-82-8; ethane, 74-84-0; ethylene, 74-85-1; propane, 74-98-6; propene, 115-07-1; cyclopropane, 75-19-4; cyclopropene, 2781-85-3; isobutane, 75-28-5; *trans*-2-butene, 624-64-6; cyclobutane, 287-23-0; cyclobutene, 822-35-5; tetrahydrane, 157-39-1; 1,3-cyclobutadiene, 1120-53-2; 1,3-butadiene, 106-99-0; bicyclobutane, 157-33-5; cyclohexane, 110-82-7; benzene, 71-43-2; 1,3,5-cycloheptatriene, 544-25-2; cyclooctatetraene, 629-20-9; cubane, 277-10-1; adamantane, 281-23-2; dodecahydrane, 4493-23-6.

(9) Kollmar, H. *J. Am. Chem. Soc.* **1980**, *102*, 2617.

(10) Engler, E. M.; Andose, J. D.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1973**, *95*, 8005.

(11) Allinger, N. L. *J. Am. Chem. Soc.* **1977**, *99*, 8127.

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

(13) Franklin, J. L. *Ind. Eng. Chem.* **1949**, *41*, 1070.