with rapid intramolecular conformational equilibria averaging the magnetic environments of all six methylenic hydrogen atoms.

The geometry of the three individual ferrocene moieties is normal[17] (Tables III and IV), with $\phi$ (dihedral angle between the two five-membered rings) values ranging from 2.6 to 4.6°. The relative rotational orientation angles, $\omega$,[17] are 19° for ferrocene 1, 11.5° for ferrocene 2, and 24.5° for ferrocene 3; the analogous angles measured between the $CH_2$ substitutents of the rings are 53, 61.5, and 24.5°, respectively.

Previous studies of polyferrocene units by X-ray diffraction methods have been reported.[2,18] In the only other $[1^n]$ferrocenophane to be structurally characterized, 1,12-dimethyl[1.1]ferrocenophane,[2] the molecule was found to be twisted by 31° from the idealized conformation (I) in order to relieve hydrogen–hydrogen interactions of the type $H_\alpha$–$H_{\alpha'}$. The resultant proton–proton contact distance between nearest $\alpha$ hydrogen atoms of the same ligand was increased to 2.0 Å. A point not emphasized by the authors is that the analogous distance between $\alpha$ protons on *different* ligands must also be close to 2.0 Å, and that a greater degree of twist would thus diminish the intraligand interactions only at the expense of increasing interligand repulsions. It therefore appears that the minimization of intramolecular nonbonded hydrogen contacts is the most important factor controlling the molecular conformation of the $[1^n]$ferrocenophanes, at least for small values of $n$.

**Intermolecular Geometry and Crystal Packing.** The packing of four trimeric molecules in the unit cell is illustrated in Figure 3. It is evident from the figure that the crystal lattice is composed of "layers" of relatively flat ferrocenophanes stacked approximately along $a$. The crystals were observed to be readily cleaved perpendicular to this direction, which appears to be a macroscopic consequence of the layered packing of the molecules in the lattice.

**Acknowledgments.** We are grateful to the donors of the Petroleum Research Fund for their support of this work under PRF Grant. No. 3799-A3, to the Alfred P. Sloan Foundation for a Research Fellowship to S. J. L. (1968–1970), and to Professor C. Levinthal for making the ADAGE computer available to us.

---

(17) See, for example, M. R. Churchill and J. Wormald, *Inorg. Chem.*, **8**, 716 (1969), Table VIII.

(18) M. R. Churchill and J. Wormald, *ibid.*, **8**, 1970 (1969), and references cited therein.

---

# Enthalpies of Formation of Globular Molecules. I. Adamantane and Hexamethylenetetramine[1]

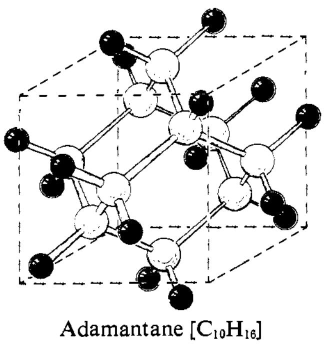
**Margret Månsson, Naomi Rapport, and Edgar F. Westrum, Jr.**[2]

*Contribution from the Department of Chemistry, University of Michigan, Ann Arbor, Michigan 48104.*

*Received February 23, 1970*

**Abstract:** Enthalpies of combustion at 298.15°K have been measured for crystalline adamantane (tricyclo-[3.3.1.1$^{3,7}$]decane) and hexamethylenetetramine (1,3,5,7-tetraazatricyclo[3.3.1.1$^{3,7}$]decane). The derived enthalpies of formation for the two compounds in the crystalline state, $\Delta H_f°$(c), at 298.15°K are $-47.14 \pm 0.19$ and $+29.65 \pm 0.18$ kcal/mol, respectively. Use of adjuvant data for both compounds permits evaluation of corresponding enthalpy values, $\Delta H_f°$(g), at 298.15°K for the gaseous compounds as $-32.96 \pm 0.19$ and $47.6 \pm 0.7$ kcal/mol. The strain energies of both compounds are discussed.

Few "globular"[3] molecules approach geometrical or force-field sphericity to the extent of adamantane ($C_{10}H_{16}$, tricyclo[3.3.1.1$^{3,7}$] decane), which is the simplest saturated polycyclic hydrocarbon possessing the cage-like skeleton characteristic of the crystalline lattice of diamond. This substance undergoes an apparently first-order transition at 208.62°K[4] from a body-centered tetragonal lattice to a face-centered cubic array.[5] The nature of the transition, with its accompanying entropy increment of 3.87 cal/(mol °K), has been further delineated by additional analysis of crystallographic data[6,7] and by nuclear magnetic resonance[8,9] as involving rotational reorientation of the molecules. Moreover, higher temperature thermal data[10] through



Adamantane [$C_{10}H_{16}$]

---

(1) Supported in part by the Division of Research of the United States Atomic Energy Commission.

(2) To whom correspondence concerning this work should be addressed.

(3) J. Timmermans, *J. Phys. Chem. Solids*, 18, 1 (1961).

(4) S. S. Chang and E. F. Westrum, Jr., *J. Phys. Chem.*, **64**, 1547 (1960).

(5) C. E. Nordman and D. L. Schmitkons, *Acta Crystallogr.*, **18**, 764 (1965).

(6) J. Donohue and S. Goodman, *ibid.*, **22**, 352 (1967).

(7) B. W. Lucas, Thesis, Queen Mary College, London, 1965.

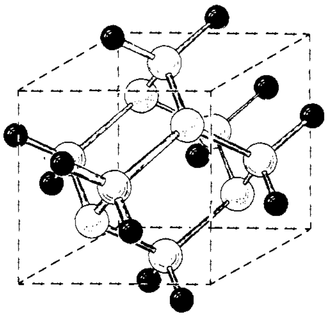
(8) D. W. McCall and D. C. Douglass, *J. Chem. Phys.*, **33**, 777 (1960).

(9) H. A. Resing, *ibid.*, **43**, 1828 (1965).

(10) H. L. Girdhar, E. F. Westrum, Jr., and E. Morawetz, submitted for publication.

fusion have confirmed the plastically crystalline nature of the phase, stable at 300°K, and have been supplemented by the compressibility studies of Pistorius and Resing.[11]

The presence of a similar transition in the closely related substance, hexamethylenetetramine, or urotropine ($C_6N_4H_{12}$, 1,3,5,7-tetrazatricyclo[3.3.1.1$^{3,7}$]decane) was not detectable by thermal measurements,[10] although nmr measurements[12] on this material indicate behavior rather similar at 360°K to that in adamantane at 140°K.[8] To complete the chemical thermodynamic studies on these materials, it was desirable to supplement the thermal data with thermochemical studies in order to obtain the enthalpies of formation and to investigate and interpret the strain energies for this pair of rather interesting compounds.



Hexamethylenetetramine [$C_6N_4H_{12}$]

Although an earlier value of the enthalpy of combustion for adamantane[13] and several values for hexamethylenetetramine have been reported,[14] the former was poorly established, and the latest value for hexamethylenetetramine disagreed by tens of kilocalories from a previous determination. Thus, the importance of having a new determination on both materials with modern precision calorimetry and of high purity samples for theoretical arguments was apparent.

## Experimental Section

**Preparation and Characterization of the Compounds.** Adamantane was prepared by the method of Schleyer.[15] Its characterization has been reported previously.[4,10] Hexamethylenetetramine was obtained from Eastman Kodak Co. and purified and characterized as described earlier.[4] The high-temperature properties of both materials have been studied subsequent to further purification by zone melting. The properties of the least pure fraction indicate the absence of significant contamination.

**Calorimeter.** The rotating bomb calorimeter used in this investigation is patterned upon those developed by Hubbard, *et al.*, of the U. S. Bureau of Mines, Petroleum Research Center, Bartlesville, Okla., and was largely machined and fabricated from drawings supplied through the courtesy of Dr. John P. McCullough, formerly of that laboratory. The bomb (laboratory designation MM-Pt-I) lined with 0.50-mm thick platinum has a volume of 0.3452 l. The general constructional features have already been described,[16] and details of the rotational mechanism are contained in a subsequent publication.[17] Temperatures of both bath and calorimeter were measured with 25-ohm stainless-steel-sheathed, platinum-resistance thermometers, using a G-2 Müller bridge.

**Procedure.** The compounds, including the benzoic acid, were burned as pellets, and the amount of substance was adjusted so that the corrected temperature increase of the calorimeter would be 1.66°. The initial temperature was chosen such that $t_f - \Delta t_{corr}$ (*cf.* ref 18) would be close to the reference temperature, $t_h = 25.00°$. The amount of water added to the bomb was 1.04 ml. The bomb was flushed with oxygen prior to filling and then charged to a pressure equivalent to 30.00 atm at 25°. The bomb was placed in the calorimeter can prior to filling with water and the entire assembly of bomb, calorimeter, and water was adjusted to the same apparent mass for each combustion. Bomb rotation was started at the midtime of the combustion[17] and was continued throughout the experiment. Unmercerized cotton thread was used as a fuse, and this was initiated by a measured discharge of electrical energy through a platinum wire of 0.025-mm diameter. After each experiment, the bomb washings were analyzed for nitric acid. For further details, see ref 16 and 17.

All data reduction and correction of the data to standard state conditions were performed by high-speed digital computer using the program developed by C. H. Shomate of China Lake, Calif., and modified for this laboratory by J. T. S. Andrews.

**Calibrations.** Since the bomb, calorimeter, and contents are always adjusted to the same mass, the energy equivalent of the system is best computed in terms of an $\epsilon^0$(cal)

$$\epsilon(\text{cal}) = \epsilon^0(\text{cal}) - 0.9990m^i(\text{cont})$$

in which $m^i$ is the mass of the contents of the bomb.

Two calibration series were made, using National Bureau of Standards benzoic acid sample 39i as the calibration material. After correcting from certificate conditions to the standard conditions,[19] the energy of combustion of this sample is −6312.97 cal/g. The six calibration runs for the adamantane series yielded $\epsilon^0$(cal) = 3969.92 ± 0.07 cal/°K. The seven calibration runs for the hexamethylenetetramine series yielded a mean value $\epsilon^0$(cal) = 3969.92 ± 0.12 cal/°K. The precision indices are standard deviations of the mean.

Adamantane is sufficiently volatile for a pellet to lose weight on exposure to the atmosphere. Consequently, the pellets of adamantane were sealed into a small envelope made of 100-gauge, Type A Mylar polyester film obtained from E. I. du Pont de Nemours and Co. The envelope was sealed by the radiant heat from a platinum-tipped soldering iron.[20] The energy of combustion, $\Delta E_c°/M$, as a function of humidity for this sample of Mylar film was established to be −5479.30 + 0.2524RH cal/g, in which RH stands for the relative humidity expressed in per cent. The energy of combustion of the cotton fuse was −4108 cal/g.

**Units and Auxiliary Quantities.** The enthalpies of combustion and derived quantities are given in defined thermochemical calories equal to 4.1840 J. The atomic weights used are based on the 1961 table of atomic weights.[21] The ice point was taken as 273.15°K. The values of the parameters used for converting the measured quantities to weights *in vacuo*, to the isothermal process, and to standard states are tabulated in Table I. These values were obtained from the literature; those in parentheses were estimated by analogy with similar materials. Enthalpies of formation, $\Delta H_f$,

**Table I**

| | Density | $C_p$, cal/(g °K) | $(dE/dP)_T$, cal/(g atm) |
|---|---|---|---|
| Adamantane | 1.07 | 0.334 | ($-3.76 \times 10^{-2}$) |
| Hexamethylenetetramine | 1.345 | 0.2596 | ($-3.76 \times 10^{-2}$) |
| Mylar | 1.38 | 0.315 | ($-8 \times 10^{-4}$) |

---

(11) C. W. F. T. Pistorius and H. A. Resing, *Mol. Cryst. Liquid Cryst.*, **5**, 353 (1969).

(12) G. W. Smith, *J. Chem. Phys.*, **36**, 3081 (1962).

(13) S. Landa and V. Macháček, *Collect. Czech. Chem. Commun.*, **5**, 1 (1933); S. Landa, V. Macháček, and J. Mžourek, *Chem. Listy*, **27**, 415, 443 (1933); *Petrol. Z.*, 30, 1 (1934).

(14) M. Delépine and M. Badoche, *C. R. Acad. Sci.*, **214**, 777 (1942).

(15) P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **79**, 3292 (1957).

(16) W. N. Hubbard, C. Katz, and G. Waddington, *J. Phys. Chem.*, **58**, 142 (1954).

(17) W. D. Good, D. W. Scott, and G. Waddington, *ibid.*, **60**, 1080 (1956).

(18) W. N. Hubbard, D. W. Scott, and G. Waddington in "Experimental Thermochemistry," F. D. Rossini, Ed., Interscience, New York, N. Y., 1956, p 99.

(19) Reference 18, pp 75–128.

(20) W. D. Good, D. R. Douslin, D. W. Scott, A. George, J. L. Lacina, J. P. Dawson, and G. Waddington, *J. Phys. Chem.*, **63**, 1133 (1959).

(21) A. E. Cameron and E. Wichers, *J. Amer. Chem. Soc.*, **84**, 4175 (1962).

of carbon dioxide(g) and water(l) were taken from ref 22, and are, respectively, −94.051 and −68.315 kcal/mol.

## Results

**Calorimetric Results.** Six combustions were made of adamantane and nine of hexamethylenetetramine. Data from combustions selected as typical for each compound are summarized in Table II. The results of the individual combustion experiments in terms of $-\Delta E_c°/M$ at 298.15°K are summarized as follows: for adamantane, 10551.12, 10551.64, 10551.76, 10551.63, 10551.34, 10551.40, mean value and standard deviation of the mean 10551.48 ± 0.10; for hexamethylenetetramine, 7155.79, 7157.78, 7157.04, 7157.92, 7155.99, 7155.41, 7155.89, 7156.38, 7155.99, mean value 7156.47 ± 0.30.

**Table II.** Typical Combustion Experiments[a]

| | Adamantane | Hexamethylenetetramine |
|---|---|---|
| $m'$ (compound), g | 0.595095 | 0.913295 |
| $\Delta t = t_f - t_i - \Delta t_{corr}$, °K | 1.66020 | 1.66625 |
| $\mathcal{E}$(calor)($-\Delta t$), cal | −6531.90 | −6566.82 |
| $\mathcal{E}$(cont)($-\Delta t$),[b] cal | −7.20 | −6.88 |
| $\Delta E_{ign}$, cal | 0.36 | 0.36 |
| $\Delta E_{dec}^{f}$ ($HNO_3$), cal | 2.10 | 26.68 |
| $\Delta E_{\Sigma}$, cal | 2.55 | 2.67 |
| $-m''\Delta E_c°/M$ (Mylar), cal | 250.80 | 0.00 |
| $-m'''\Delta E_c°/M$ (fuse), cal | 4.21 | 8.44 |
| $m'\Delta E_c°/M$ (compound), cal | −6279.08 | −6535.54 |
| $\Delta E_c°/M$ (compound), cal/g | −10551.40 | −7155.99 |

[a] The symbols correspond to those of ref 18, except as noted. [b] $\mathcal{E}^{i}(\text{cont})(t_i - t_h) + \mathcal{E}^{f}(\text{cont})(t_h - t_f + \Delta t_{corr})$.

The $\Delta E_c°/M$ values refer to the reaction

$$C_{10}H_{16}(c) + 14O_2(g) \longrightarrow 10CO_2(g) + 8H_2O(l)$$

for adamantane and to the following reaction for hexamethylenetetramine.

$$C_6H_{12}N_4(c) + 9O_2(g) \longrightarrow 6CO_2(g) + 6H_2O(l) + 2N(g)$$

**Derived Results.** Table III lists the results derived from the experimental data at 298.15°K, with uncertainties calculated as recommended by Rossini and Deming.[23] The values of $\Delta E_c°$ and $\Delta H_c°$ are for the idealized combustion reactions above. Entropy values for both substances are from Chang and Westrum,[4] and for hydrogen, nitrogen, and graphite, values are from Wagman, *et al.*[22] Data for the vapor pressure and for the sublimation process of adamantane are based on values of Girdhar, Westrum, and Morawetz[10] (see this reference for comparison with other values), and those for hexamethylenetetramine on the vapor pressure measurements of Budurov.[24]

**Table III.** Derived Thermochemical Data at 298.15°K[a]

| | Adamantane | Hexamethylenetetramine |
|---|---|---|
| | Crystalline State | |
| $\Delta E_c°$ (c) | −1437.52 ± 0.17 | −1003.26 ± 0.16 |
| $\Delta H_c°$ (c) | −1439.89 ± 0.17 | −1003.85 ± 0.16 |
| $\Delta H_f°$ (c) | −47.14 ± 0.19 | 29.65 ± 0.18 |
| $\Delta S_f°$ (c) | −216.48 ± 0.05 | −247.91 ± 0.05 |
| $\Delta G_f°$ (c) | 17.40 ± 0.19 | 103.56 ± 0.18 |
| | Sublimation Process | |
| $\Delta H_s°$ | 14.18 ± 0.04 | 17.9 ± 0.7[b] |
| $\Delta S_s°$ | 30.2 ± 0.6 | 31.9 ± 2[b] |
| | Ideal Gaseous State | |
| $\Delta H_f°$ (g) | −32.96 ± 0.19 | 47.6 ± 0.7 |
| $\Delta S_f°$ (g) | −186.3 ± 0.6 | −216.0 ± 2 |
| $\Delta G_f°$ (g) | 22.6 ± 0.3 | 112.0 ± 0.9 |

[a] Units: $\Delta H$, $\Delta E$, and $\Delta G$ values are in kcal/mol, $\Delta S$ values are in cal/(mol °K). Uncertainties are the "uncertainty interval," which equals twice the final overall standard deviation of the mean, as recommended by Rossini and Deming.[23] [b] Uncertainty is estimated.

**Discussion.** The value of the enthalpy of combustion $\Delta H_c°$ of adamantane reported herein differs more than 15 kcal/mol from the value reported by Landa, *et al.*[13] In view of the fact that they appear to have burned only a single 0.167-g sample under unspecified conditions, their value will be disregarded. An "unpublished observation" attributed to R. J. Wineman for $\Delta H_c°$ of −1440 kcal/mol has been cited by Fort and Schleyer,[25] but whether this number was ascertained by deduction or by experiment is not evident. For hexamethylenetetramine, the earliest value dates back to the work of Delépine[26] who found, at an unspecified temperature (presumed from the context to be 15°), $\Delta H_c°$ = −1006.3 kcal/mol (when converted to modern units and 298.15°K). Harvey and Baekeland[27] reported a $\Delta H_c°$ value of −1020 kcal/mol at an unspecified temperature. The latest $\Delta H_c°$, that of Delépine and Badoche,[14] was determined at 17° and yields −1003.6 kcal/mol when adjusted to 298.15°K. This is in good accord with the value found in this research, although Baur and Rüetschi[28] asserted (apparently incorrectly) from their own thermochemical results that the more exothermic value reported earlier by Delépine[26] ought to have been as much as 3–4% more exothermic.

The advent of high-speed digital computers has greatly facilitated the evaluation of strain energies by calculations of an empirical nature based on classical mechanical principles. Eleven applications of nonbonded potentials to the calculation of the strain energy of adamantane yielded values of the strain energy from −6.4 to 7.0 kcal/mol.[29]

Although adamantane has traditionally been considered to be a relatively strain-free molecule, the prepublication availability of the data of this paper has provided a firm basis for the evaluation of the strain energy. An extensive treatment by Schleyer, *et al.*,[30] using the value of the enthalpy of formation of this research together with well-known bond-energy and group schemes, as well as modified "skew-separate" and "single conformation" schemes, has derived values for the strain energy of adamantane relative to "strain-free" reference conformers, or to acyclic hydrocarbon refer-

---

(22) D. D. Wagman, W. H. Evans, V. B. Parker, I. Halow, S. M. Bailey, and R. H. Schumm, "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards Technical Note No. 270-3, U. S. Government Printing Office, Washington, D. C., 1968.

(23) F. D. Rossini and W. E. Deming, *J. Wash. Acad. Sci.*, **29**, 416 (1939).

(24) S. Budurov, *Izv. Khim. Inst. Bulg. Akad. Nauk*, **7**, 281 (1960).

(25) R. C. Fort, Jr., and P. v. R. Schleyer, *Chem. Rev.*, **64**, 277 (1964).

(26) M. Delépine, *C. R. Acad. Sci.*, **123**, 650 (1896).

(27) M. Harvey and L. H. Baekeland, *J. Ind. Eng. Chem.*, **13**, 135 (1921).

(28) E. Baur and W. Rüetschi, *Helv. Chim. Acta*, **24**, 754 (1941).

(29) J. E. Williams, P. J. Stang, and P. v. R. Schleyer, *Annu. Rev. Phys. Chem.*, **19**, 531 (1968).

(30) P. v. R. Schleyer, J. E. Williams, and K. R. Blanchard, *J. Amer. Chem. Soc.*, **92**, 2377 (1970).

ence compounds. The strain energy values range from 2 to 6.5 kcal/mol, with "preferred" ones in the vicinity of 4.7 to 6.5 kcal/mol, depending on the choice of strain-free reference systems. The existence of this amount of strain is rationalized in terms of repulsive $C\cdots C$ interactions in the adamantane skeleton and angle strain.

It is to be noted, however, as pointed out by Nelander and Sunner,[31] that a correction for ring closure should be applied to the strain energy calculation for cyclic and polycyclic molecules when the reference system involves acyclic reference compounds. For example, Schleyer, *et al.*,[30] give single conformation strain values for adamantane (6.5 kcal/mol) and *trans*-decalin (1.8 kcal/mol) relative to acyclic alkanes in *gauche*-free staggered conformation. If these are corrected for ring closure, the single conformation strain energy value for adamantane is reduced to 4.7 kcal/mol relative to an acyclic hydrocarbon and to 4.1 kcal/mol relative to *trans*-decalin.

Moreover, the effect of reducing the calculations for strain energy to a 0°K "vibrationless" basis rather than to the customary 298°K comparison temperature, to exclude the nuclear motion energy differences between the reference model and the molecule under consideration, appears not to be fully established by Schleyer, *et al.*[30] This is especially true for the effect of vibrational contributions differing as much as between those in a rigid molecule and in an acyclic hydrocarbon. A simple Allen-scheme calculation using parameters from Skinner and Pilcher[32] gives, after correction for ring closure, a value of 1.6 kcal/mol for the strain energy in adamantane.

The application of an Allen scheme for the evaluation of possible strain in hexamethylenetetramine is hampered by the scarcity or nonexistence of good data for appropriate reference nitrogen compounds. If such parameters as can presently be reliably evaluated[33] are incorporated in an Allen scheme with the Sunner–Nelander ring closure corrections, the strain energy is equal to ($6\Gamma_{NCN} - 44$) kcal/mol. To establish a value for the N–C–N interaction parameter ($\Gamma_{NCN}$), the enthalpy of formation data on compounds of the type $R_2N$–$CH_2$–$NR_2$ are needed. Even if this parameter were evaluated from experimental data, stabilization or "destabilization" might be involved, as in the oxygen analog O–C–O.[34] The evaluated strain would, therefore, be relative to stabilization in the reference compound selected.

**Acknowledgment.** The authors thank the Division of Research of the United States Atomic Energy Commission for financial support of this research. N. J. R. acknowledges a Research Participation Award from the National Science Foundation and M. M. a fellowship from the Horace H. Rackham School of Graduate Studies. We acknowledge the advice, cooperation, and/or encouragement of J. T. S. Andrews, W. D. Good, J. P. McCullough, Stig Sunner, and Ward Hubbard in this initial bomb calorimetric study at the University of Michigan.

---

(31) B. Nelander and S. Sunner, *J. Chem. Phys.*, **44**, 2476 (1966).

(32) H. A. Skinner and G. Pilcher, *Quart. Rev., Chem. Soc.*, **17**, 264 (1963).

(33) W. D. Good and R. T. Moore, *J. Chem. Eng. Data*, **15**, 150 (1970).

(34) M. Månsson, *J. Chem. Thermodyn.*, **1**, 141 (1969).