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Measurement of the Strain Energy of a Transient Bridgehead Imine, 4-Azahomoadamant-3-ene, by Photoacoustic Calorimetry

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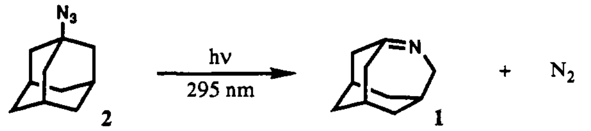
Understanding the energetic cost of twisting and other distortions of π-bonds is fundamentally interesting and provides important insight into double bond stereoisomerization processes. Compounds with highly distorted double bonds are potentially the most important sources of these thermochemical data.[1] Photoacoustic calorimetry (PAC)[2] is uniquely capable of directly measuring the enthalpy changes for the photochemical reactions of such compounds.[2,3] We report herein the use of PAC to achieve the first experimental measurement of ΔH_f of a transient bridgehead imine, 4-azahomoadamant-3-ene (**1**), produced by photolysis of 1-azidoadamantane (**2**).



The PAC experiment is conceptually quite simple. A low-energy laser pulse is used to initiate the reaction of interest. The ensuing heat release causes an expansion of the irradiated volume. This generates a pressure pulse that is detected by a piezoelectric transducer. In general, one observes the lump-sum heat release for all processes that occur much faster than the transducer frequency (≤ca. 1 ns for a 1-MHz transducer) and can obtain both energetic and kinetic information for processes that occur on the 10-ns to 10-μs time scale.[2]

It is important to appreciate that in addition to the thermal expansion (ΔV_{th}), the intrinsic volume change of the system (ΔV_{chem}) also contributes to the PAC signal.[2] In organic solvents the former usually dominates, but the latter can be significant.[4]

These components can be separated by studying the dependence of the PAC signal on the thermal expansivity of the solution, X_s,[4,5] since $\Delta V_{th} = E_{th}X_s$, where E_{th} is the amount of heat released. If the chemistry of interest is rapid on the transducer time scale, one can simply compare the signal amplitude to that of a calorimetric reference that rapidly returns all of the absorbed light energy, $E_{h\nu}$, as heat. The ratio, f, of these signal amplitudes is given by[4]

$$f = (E_{th}/E_{h\nu}) + (\Delta V_{chem}/E_{h\nu}X_s) \qquad (1)$$

Thus, by plotting f vs $1/X_s$, one can obtain E_{th} and ΔV_{chem}, provided that these remain constant for the series of solvents used.

If nonradiative decay is the only mechanism that competes with the reaction of interest,

$$\Delta H_{rxn} = (E_{h\nu} - E_{th})/\Phi \qquad (2)$$

and

$$\Delta V_{rxn} = \Delta V_{chem}/\Phi \qquad (3)$$

where Φ is the reaction quantum yield.

The conversion of **2** to **1** is ideally suited to study by PAC. In general, direct photolysis of alkyl azides produces imines cleanly[6,7] and efficiently.[8] A variety of strained bridgehead imines have been generated by photolysis of bridgehead azides.[1a,7,9,10] In particular, **1** has been generated from **2** and observed by matrix-isolation vibrational and electronic spectroscopy.[9,11,12] At ambient temperature in solution, the imine can be trapped with alcohols or other reagents; in the absence of traps, it dimerizes quantitatively in a formal [2 + 2] head-to-tail fashion.[13]

Our experimental setup is similar to those previously described.[2b,14] A solution of 1-adamantyl azide[15] in an alkane solvent was irradiated with a 500-ps, 295-nm, 8-μJ laser pulse and the acoustic signal detected with a 0.3- or 2.25-MHz transducer. The normalized signal amplitudes were independent of azide concentration, (0.01–0.04 M) and light intensity (1–8 μJ). The signal frequency was identical to that of the reference compound, *o*-hydroxybenzophenone, which is known to relax nonradiatively in <1 ns.[2] Thus no heat deposition is occurring on a time scale of about 10 ns to 50 μs. This is consistent with our expectation that the imine would be formed rapidly and be stable on the time scale of the PAC experiment.

There is good evidence that alkyl group migration is concerted with nitrogen loss in acyclic alkyl azides,[6] although the intermediacy of a singlet nitrene cannot be ruled out, at least in the bridgehead systems.[1a,7b] If such a species is involved, our PAC results require that it rearrange to the imine within ca. 1 ns. Moreover, that the imine is stable on our time scale is also reasonable. We estimate [**1**] ≤ 10^{-6} M, so dimerization occurs too slowly to be detected.

To evaluate the accuracy of our measurement of ΔH_f of imine **1**, we also studied two acyclic tertiary azides, $Et_3C{-}N_3$ (**3**) and

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(1) Recent reviews on bridgehead olefins: (a) Warner, P. M. *Chem. Rev.* **1989**, *89*, 1067–1093. (b) Borden, W. T. *Chem. Rev.* **1989**, *89*, 1095–1109. Luef, W.; Keese, R. In *Topics in Stereochemistry*; Eliel, E. L., Wilen, S. H., Eds.; Wiley: New York, 1991; Vol. 20, pp 231–318.

(2) (a) Braslavsky, S. E.; Heibel, G. E. *Chem. Rev.* **1992**, *92*, 1381–1410. (b) Peters, K.S.; Snyder, G. J. *Science* **1988**, *241*, 1053–1057.

(3) PAC has provided the strain energies of *trans*-cycloalkenes. Goodman, J. L.; Peters, K. S.; Misawa, H.; Caldwell, R. A. *J. Am. Chem. Soc.* **1986**, *108*, 6803–6805. Brennan, C. M.; Caldwell, R. A. *Photochem. Photobiol.* **1991**, *53*, 165–168.

(4) (a) Morais, J.; Ma, J.; Zimmt, M. B. *J. Phys. Chem.* **1991**, *95*, 3885–3888. See also: (b) Hung, R. R.; Grabowski, J. J. *J. Am. Chem. Soc.* **1992**, *114*, 351–353.

(5) $X_s = \beta(MW)/C_p\rho$, where β is the thermal expansion coefficient, MW the molecular weight, C_p the molar heat capacity, and ρ the density.

(6) (a) Kyba, E. P.; Abramovitch, R. A. *J. Am. Chem. Soc.* **1980**, *102*, 735–740. Abramovitch, R. A.; Kyba, E. P. In *The Chemistry of the Azido Group*; Patai, S., Ed.; Wiley: New York, 1971; Chapter 5, pp 221–329, esp. pp 297–308.

(7) (a) Kyba, E. P. In *Azides and Nitrenes*; Scriven, E. F. V., Ed.; Academic: New York, 1984; Chapter 1, pp 1–34. (b) Wentrup, C. Reference 7a, Chapter 8, pp 395–432.

(8) Lewis, F. D.; Saunders, W. H., Jr. *J. Am. Chem. Soc.* **1968**, *90*, 7031–7033.

(9) Michl, J.; Radziszewski, J. G.; Downing, J. W.; Kopecky, J.; Kaszynski, P.; Miller, R.D. *Pure Appl. Chem.* **1987**, *59*, 1613–1626.

(10) Eguchi, S.; Okano, T.; Takeuchi, H. *Heterocycles* **1987**, *26*, 3265–3284.

(11) Radziszewski, J. G; Downing, J. W.; Jawdosiuk, M.; Kovacic, P.; Michl, J. *J. Am. Chem. Soc.* **1985**, *107*, 594–603. Michl J.; Radziszewski, G. J.; Downing, J. W.; Wiberg, K. B.; Walker, F. H.; Miller, R. D.; Kovacic, P.; Jawdosiuk, M.; Bonacic-Koutecky, V. *Pure Appl. Chem.* **1983**, *55*, 315–321.

(12) Dunkin, I. R.; Shields, C. J.; Quast, H.; Seiferling, B. *Tetrahedron Lett.* **1983**, *24*, 3887–3890.

(13) Quast, H.; Eckert, P. *Liebigs Ann. Chem.* **1974**, 1727–1741.

(14) The frequency-doubled output of a nitrogen-pumped dye laser (Laser Photonics LN1000, LN107, L-2X) is focused to a beam diameter of ca. 1 mm and directed through the sample, which typically has an absorbance of 0.1–0.5. Transmitted and reference light energies are measured with pyroelectric probes. The output from a home-made 0.3-MHz PZT or a commercial 2.25-MHz (Panametrics A-106S) transducer, clamped to the side of the sample cuvette, is amplified (Panametrics 5676 pre-amp) and digitized at 10 ns per point with a 150-MHz oscilloscope (LeCroy 9430). The data from 100–250 laser shots are averaged before analysis. More details will be published later.

(15) Azide **2** was prepared by the procedure of Prakash, G. K. S.; Stephenson, M. A.; Shih, J. G.; Olah, G. A. *J. Org. Chem.* **1986**, *51*, 3215–3217; azides **3** and **4** by that of ref 11.

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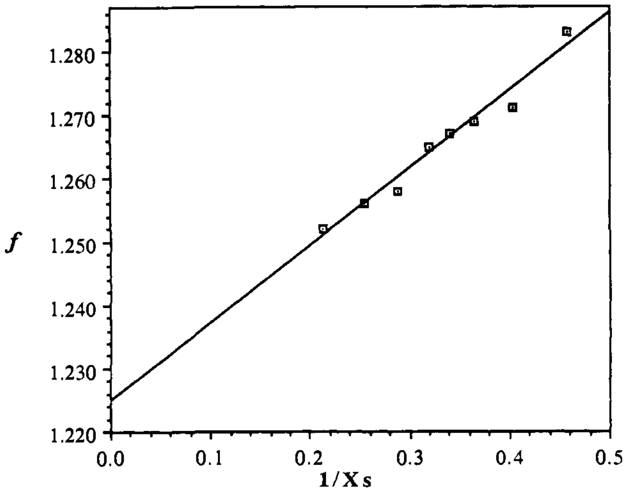

Figure 1. Plot of f versus $1/X_s$ (kcal/mL) for photolysis of 1-azidoadamantane. The solvents used were *n*-alkanes pentane through decane, dodecane, and hexadecane. Slope = 0.122 ± 0.018 mL/kcal; intercept = 1.225 ± 0.006.

Table I[a]

azide	ΔV_{chem}[b]	E_{th}[c]	Φ[d]	ΔV_{rxn}[b]	ΔH_{rxn}[c]
2	11.8 ± 1.8	118.8 ± 0.6	0.96[e] ± 0.06	12.3 ± 2.0	−22.7 ± 1.6
3	17.2 ± 1.8	149.9 ± 0.6	0.94 ± 0.08	18.3 ± 2.4	−56.3 ± 4.8
4	12.5 ± 2.2	149.7 ± 0.8	0.99 ± 0.08	12.6 ± 2.4	−53.2 ± 4.4

[a] Error limits are 2σ. [b] In mL/mol. [c] In kcal/mol. [d] In pentane. Average of 2–4 measurements. [e] Solvent: 5% ethanol in pentane.[17]

$PhC(Me_2)-N_3$ (**4**),[15] that form unstrained imines whose heats of formation can be calculated with reasonable accuracy.

In order to determine ΔH_f for the imines, three pieces of information are required: E_{th}, Φ, and ΔH_f of the azides. The ratios of the azide and reference signal amplitudes, f, were measured in a series of alkane solvents having known X_s values.[16] In Figure 1, the f values for adamantyl azide, **2**, are plotted vs $1/X_s$ according to eq 1. The slope and intercept and the photon energy ($E_{h\nu}$) of 97.0 kcal/mol give E_{th} = 118.8 kcal/mol and ΔV_{chem} = 11.8 mL/mol. The results for all the azides are summarized in Table I.

The quantum yields for the azide-to-imine conversions, Φ, were measured in pentane (Table I).[18] We were unable to detect fluorescence from any of the azides. Thus, assuming that $1 - \Phi$ corresponds to nonradiative decay, eqs 2 and 3 give ΔH and ΔV for the reactions (Table I).

To calculate ΔH_f of the imines, ΔH_f of the azides are required. Unfortunately, the existing literature values are sparse and unreliable.[20] We therefore obtained these values by measuring the Pd/C-catalyzed heats of hydrogenation.[21,22] This reaction cleanly produces the amine and N_2. Table II lists ΔH_{hydrog} of the azides, ΔH_f of the amines, and ΔH_f of the azides. Heats of formation of the imines derived from the PAC ΔH_{rxn} and ΔH_f(azide) are also included in Table II.

Table II[a,b]

azide	ΔH_{hydrog}	ΔH_f(amine)[c]	ΔH_f(azide)	ΔH_f(imine)	
				expt	calc[c]
2	−80.3 ± 1.6	−28.7,[d] −29.0[e]	51.6 ± 2.6	28.9 ± 3.0	−5.0[f]
3	−80.6 ± 2.0	−40.0	40.6 ± 2.8	−15.7 ± 4.8	−15.1
4	−82.3 ± 1.4	5.9, 4.2[e]	87.4 ± 2.4	34.2 ± 5.0	29.0[g]

[a] In kcal/mol. [b] Error limits are 2σ. [c] Via Benson's group increments[23] unless stated otherwise. [d] From $\Delta H_f°$(adamantane)[24] and group increments. [e] From MM3.[25] [f] Strain-free value. [g] Weighted average of $PhC(CH_3){=}NCH_3$ and $(CH_3)_2C{=}NPh$ formed in a 2.2:1 ratio.[26]

The PAC ΔH_f value for $Et_2C{=}NEt$ (from **3**) is in excellent agreement with that calculated by Benson's group increments.[23] The agreement is acceptable for the imine mixture from azide **4**, given the uncertainty in the calculated value.[27] In addition, the reaction volumes of 12–18 mL/mol are reasonable for these systems, although there is a limited amount of data available for comparison.[4b,28]

The strain energy of **1**, defined as the difference in the measured heat of formation, 28.9 kcal/mol, and the strain-free value derived from group increments (Table II) is 33.9 kcal/mol. Maier and Schleyer have pointed out that the strain associated with the twisted double bond is a useful gauge of reactivity in bridgehead alkenes.[29] They define "olefin strain" as the difference in the strain energies of an olefin and the corresponding alkane.[29] Similarly, using the MM3[25] strain energy of 4-azahomoadamantane (dihydro-**1**), 18.3 kcal/mol, as an approximation of the ring strain, we calculate an "imine strain" of 15.6 kcal/mol for **1**.

Whether the interaction between the N lone pair and the C sp^x orbital[9,11] stabilizes **1** relative to the corresponding bridgehead alkene is unclear, since experimental data for the latter are currently unavailable. Our measured ΔH_f for **1** does provide an important calibration point for molecular mechanics calculations and other computational methods intended to quantitatively model rotational isomerizations of double bonds.

To better quantify the energetics of twisting the C–N double bond, we are currently extending this study to a series of bicyclic azides that give imines with varying amounts of strain.

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Supplementary Material Available: Solvent parameters and f values for azides **2–4** and plots of f vs $1/X_s$ for **3** and **4** (2 pages). Ordering information is given on any current masthead page.

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(16) Riddick, J. A.; Bunger, W. B.; Sakano, T. K. *Organic Solvents*; Wiley: New York, 1986.

(17) Quantum yields for a variety of alkyl azides are independent of solvent (MeOH, Et_2O, alkanes) and wavelength.[8] For **2**, the quantum yields measured in ethanol and in 5% ethanol/95% pentane were identical within experimental error.

(18) Optically opaque solutions of the azide in pentane and valerophenone in ethanol as an actinometer[19] were photolyzed at 300 ± 20 nm to ca. 5% conversion, and the products were analyzed by GC.

(19) Wagner, P. J. *J. Am. Chem. Soc.* **1967**, *89*, 5898–5901.

(20) The existing ΔH_f values for alkyl azides lead to predicted ΔH_{hydrog} of −62 to −72 kcal/mol. Evans, B. L.; Yoffe, A. D.; Gray, P. *Chem. Rev.* **1959**, *59*, 515–568. For a variety of alkyl azides we have found ΔH_{hydrog} = −80 to −86 kcal/mol.[21]

(21) Rogers, D. W.; Wayne, G. S.; Duty, W. C.; Snyder, G. J., manuscript in preparation.

(22) Fang, W.; Rogers, D. W. *J. Org. Chem.* **1992**, *57*, 2294–2297.

(23) Benson, S. W. *Thermochemical Kinetics*, 2nd ed.; Wiley: New York, 1976.

(24) Pedley, J. B.; Naylor, R. D.; Kirby, S. P. *Thermochemical Data of Organic Compounds*, 2nd ed.; Chapman and Hall: New York, 1986.

(25) MM3(92), Allinger, N. L. Obtained from Technical Utilization Corp., 235 Glen Village Ct., Powell, OH 43065.

(26) The ratio of imines was determined by GC and deviates slightly from the published value.[6]

(27) Recent ab initio calculations suggest that 4 kcal of *cis*-imine strain should be added to the calculated value for $Et_2C{=}NEt$ and possibly more for those from **4**. Wiberg, K. B.; Nakaji, D. Y.; Morgan, K. M. *J. Am. Chem. Soc.* **1993**, *115*, 3527–3532.

(28) le Noble, W. J.; Kelm, H. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 841–856.

(29) Maier, W. F.; Schleyer, P.v.R. *J. Am. Chem. Soc.* **1981**, *103*, 1891–1900.