Thermochemistry of nine diazenes (azo compounds)

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Enthalpies of combustion of five diazenes and enthalpies of vaporization of nine diazenes have been measured. The experimental results yield values of the enthalpies of formation for the condensed and gaseous states of these compounds: di-*n*-propyldiazene; di-*i*-propyldiazene; di-*t*-butyl(1,1,3,3-tetramethylbutyl)diazene; di(1,1,3,3-tetramethylbutyl)diazene; 1,1,3,3-tetramethylbutyl)diazene; 1,1,4,4-tetramethyltetra-methylenediazene; 2,3-diazabicyclo[2.2.1]heptene-2; and 1,4-dimethyl-2.3-diazabicyclo-[2.2.2]-octene-2.

1. Introduction

Diazenes, characterized by the azo group, -N=N-, are widely used to produce free radicals because they decompose on irradiation with ultraviolet light or on heating in the gas phase or in solution.[†] Their decomposition is represented by the net reaction:

$$\mathbf{R} - \mathbf{N} = \mathbf{N} - \mathbf{R}' \rightarrow \mathbf{R} \cdot + \mathbf{N}_2 + \mathbf{R}'$$

Although the energy associated with this reaction is important, few enthalpies of formation of diazenes have been measured. Prior to 1973, most such values were estimated from the work of Coates and Sutton⁽³⁾ on di-*i*-propyldiazene (azo-*i*-propane). However, a recent investigation⁽⁴⁾ reveals that this early result is in error by about 10 kcal_{th} mol⁻¹.[‡]

The aim of the present study was to obtain reliable thermochemical data on nine diazenes, including reinvestigation of one of the recently measured compounds.⁽⁴⁾

Table 1 lists the compounds prepared for this investigation. These include five for which new experimental enthalpies of combustion and vaporization have been obtained and four others for which enthalpies of combustion were measured previously, but for which we report new direct experimental values of enthalpies of vaporization.

 $[\]dagger$ A bibliography on the decomposition of diazenes is too extensive to include here. However, two leading references are given.^(1, 2)

 $[\]ddagger$ Throughout this paper cal_{th} = 4.184 J; Torr = (101.325/760) kPa.

No.	Molecular formula	Chemical structure	Name
1	$C_6H_{14}N_2$		di-n-propyldiazene
2	$C_6H_{14}N_2$	N	di- <i>i</i> -propyldiazene
3	$C_8H_{18}N_2$	$X_N^N X$	di-t-butyldiazene
4	$C_{12}H_{26}N_2$	$X \to \mathbb{N}_{\mathbb{N}^{2}} \to \mathbb{N}_{X}$	<i>i</i> -butyl(1,1,3,3-tetramethylbutyl)diazene
5	$C_{16}H_{34}N_2$	$X \to X \to X$	di(1,1,3,3-tetramethylbutyl)diazene
6	$C_7H_{14}N_2$	$\bigvee_{N=N}$	1,1,3,3-tetramethyltrimethylenediazene
7	$C_8H_{16}N_2$	X Z Z Z	1,1,4,4-tetramethyltetramethylenediazene
8	C₅H ₈ N₂	N N	2,3-diazabicyclo[2.2.1]heptene-2
9	C ₈ H ₁₄ N ₂	N N	1,4-dimethyl-2,3-diazabicyclo[2.2.2]- octene-2

TABLE 1. Identification of the nine diazenes investigated

2. Experimental

SYNTHESIS AND PURIFICATION OF FIVE DIAZENES

Compound 3 was synthesized by sodium hypochlorite oxidation of di-t-butylsulfamide⁽⁵⁾ and was purified by distillation in a spinning band column. The center cut used in this work had a normal boiling temperature of 382 K and showed no impurities by g.l.c., under conditions where about 0.1 per cent of impurity could have been detected.

Compound 4 was prepared by *t*-butylhypochlorite oxidation of the unsymmetrical sulfamide⁽⁶⁾ and was purified by distillation in a spinning band column at reduced pressure (boiling temperature: 335 K at 9 Torr). Elemental analysis gave 72.83 mass per cent of C (theoretical: 72.66) and 13.12 mass per cent of H (theoretical: 13.21). Analysis by g.l.c. revealed 0.23 mole per cent of ethyl acetate.

Compound 5 was synthesized⁽⁷⁾ in the same manner as Compound 4. After distillation at reduced pressure (boiling temperature: 363 K at 2 Torr), it was recrystallized from methanol at 195 K and then zone refined at 275 K. Analysis by g.l.c. showed 0.03 mole per cent of an unidentified impurity and (0.15 ± 0.05) mole per cent each of 2,2,4-trimethylpentane and 2,4,4-trimethyl-1-pentene.

Attempts to prepare Compound 6 by the published procedure⁽⁸⁾ were unsuccessful. Therefore, a new synthesis was devised, as follows:



Although the last step gave low yields, the starting materials are readily available in quantity and it was possible to prepare Compound 6 in gram lots. After distillation (boiling temperature: 348 K at 63 Torr), this diazene was purified by recrystallizing it twice from pentane under nitrogen at 195 K. Analysis by g.l.c. indicated no impurities, the sensitivity being 0.03 per cent of the main peak.

Compound 7 was prepared[†] in 12 per cent yield by oxidation⁽⁹⁾ of 2,5-dimethyl-2,5-diaminohexane (Aldrich Chemical Company) with iodine pentafluoride. The material was purified by distillation in a spinning band column (boiling temperature: 335 K at 12 Torr).⁽¹⁰⁾ A proton n.m.r. spectrum of the sample used in the combustion experiments showed no extraneous peaks, with a sensitivity of 1 per cent of the largest peak. Analysis by g.l.c. also indicated no impurities, with a sensitivity of 0.3 per cent. Elemental analysis yielded 68.75 mass per cent of C (theoretical: 68.52) and 11.60 mass per cent of H (theoretical: 11.50). However, it should be noted that during some of the vaporization measurements (see below), a small amount of a yellow material of lower volatility collected at a joint some distance away from the calorimeter outlet. It is not known whether this is an impurity or a decomposition product formed during the vaporization experiments.

Allowance for some impurity in the above compounds, in appropriate amount for each, is made in propagating the errors to obtain the overall uncertainty in the final thermochemical values.

ENTHALPY OF COMBUSTION OF FIVE DIAZENES

The calorimeter assembly for the bomb combustion experiments was of the Hubbard-Argonne National Laboratory Design, CT-3986, which had been assembled at Rice

[†] Thanks are due to Professor N. A. Porter, Duke University, for supplying several grams of Compound 7 in the initial stages of this work.

University some years ago by John L. Margrave^(4, 11) and associates. For the present experiments, the bomb was not rotated. The combustion bomb for these experiments was Parr Model 1002, having an internal volume of 380 cm³.

The temperature of the water jacket was maintained constant to 0.001 K with an automatic controller (Bayley Instrument Model 123), at the final temperature of the experiment. The temperature of the calorimeter was measured to 0.0001 K with a quartz-crystal thermometer (Hewlett-Packard Model 2801A, with Probe 2850D) with direct readout.⁽⁴⁾ The output of this thermometer was converted by means of an interface into a form usable by a teleprinter (Teletype Model ASR 33) to provide a digital time-temperature record of each experiment.⁽⁴⁾

For our measurements, the thermometric system was calibrated to the IPTS-68,⁽¹²⁾ using the triple points of water, 273.16 K, and of phenoxybenzene (diphenylether), 300.02 K. For water, a triple-point cell ready to use was purchased (Jarrett Instrument Company). For phenoxybenzene, a triple-point cell was made of the same design as the one for water, using vigorously cleaned Pyrex glass.⁽¹³⁾ The phenoxybenzene was purified, from material (Fisher Scientific Company) labelled "reagent grade", by successive crystallizations until the liquid residue showed no evidence of impurity when examined by g.l.c. Prior to sealing, the phenoxybenzene was degassed in its triple-point cell under vacuum by successive freezing and melting.

The amount of reaction in each experiment was determined from the mass of sample placed in the bomb. The sample was weighed to 0.00001 g on a semimicro balance (Mettler Model B6), which was calibrated with Class S metric weights (Fisher Scientific Company) having a certificate traceable to the National Bureau of Standards. Correction to vacuum was made. Conversion of masses to amounts of substance was done using the atomic weights⁽¹⁴⁾ of 1973: C, 12.011; H, 1.0079; N, 14.0067.

The oxygen used for combustion was purified by passing it over copper oxide at 875 K, any products of combustion being absorbed in ascarite and magnesium perchlorate before the oxygen entered the bomb. The gas produced in the combustion was examined for the presence of carbon monoxide by passage through carbon monoxide detector tubes (Bacharach Instrument Company). No significant amount of carbon monoxide was found. The small amount of nitric acid formed in the experiments was determined and corrected for in the standard manner, as prescribed in the certificate for the standard benzoic acid.

In each experiment, the reaction temperature was taken as the final temperature (either 303.15 or 298.15 K), the temperature rise being near 2 K in each case. The mass of water placed in the calorimeter can to constitute, with the bomb, thermometer, stirrer, *etc.*, the standard calorimeter system, was 3020.75 g. Also, in each combustion experiment, 1.0 cm³ of water was placed in the bomb at the start.

The energy equivalent of the standard calorimeter system was determined using standard benzoic acid, National Bureau of Standards No. 39i, which was certified to have a specific energy of combustion at 298.15 K of (26434 ± 3) J g⁻¹ under specified conditions. In this investigation, three standard calorimeter systems were used: I, for a reaction temperature of 303.15 K; II, for the same system at the same temperature but with the ignition system having been modified slightly; and III, for the same system as II but for a reaction temperature of 298.15 K.

For combustion, the samples of the diazenes were enclosed in polyester (Mylar) bags. Each bag was carefully adjusted as to position in the platinum crucible, which had a mass of 16.038 g. The Mylar was kept at constant humidity and handled in the same way in all experiments.

The pressure of the oxygen introduced into the bomb at the start was adjusted so that it would be near 3.2 MPa at the final temperature of the experiment.

For ignition, a cotton thread was tied to the polyester bag and a platinum wire appropriately affixed to the head of the bomb. The ignition energy was supplied electrically by a pulse counter circuit driven by the quartz thermometer, which was preset to charge and fire at the proper time. The quantity of the electrical ignition energy was calculated from the potential drop across the capacitor and its capacitance, $375 \ \mu\text{F}$. Observations of temperature were recorded at intervals of about 15 s during the initial period, the reaction period, and the final period.

The method for reducing the experimental observations is as follows. The recorded observations of temperature were processed with a computer program prepared by D. W. Bonnell.⁽¹⁵⁾ This program fits straight lines to the initial and the final rating periods and computes the corrected temperature rise, Δt_c . A computer program⁽¹⁵⁾ was used to calculate the energy of the actual combustion process, in accordance with the methods described by Coops, Jessup, van Nes, Hubbard, Scott, Waddington, and Prosen.⁽¹⁶⁾

Table 2 gives the results of five experiments to determine the energy equivalent of the standard calorimeter system I, for a final temperature of 303.15 K, with a temperature rise of 2 K. The difference between the energy equivalent ε of the calorimeter

m _{вA} /g	$\Delta t/\mathrm{K}$	$\Delta t_{\rm c}/{\rm K}$	Δε/J K ⁻¹	$q_{ m cf}/{ m J}$	$q_{ m n}/{ m J}$	$q_{\rm i}/{ m J}$	ε _s /J K ⁻¹
1.14437 to 1.17469	1.99636 to 2.04641	1.98252 to 2.03492	19.75 to 19.80	54.59 to 57.60	19.41 to 42.17	1.88	15265.49 to 15272.22
				Standa	urd deviation	Mean: of the mean:	15268.37 ±1.10

TABLE 2. Results of five experiments to determine the energy equivalent ε_s of the standard calorimeter system I, at a final temperature of 303.15 K, with a temperature rise of 2 K

system in the actual experiment and that of the standard calorimeter system, ε_s , used as a reference is $\Delta \varepsilon = \varepsilon - \varepsilon_s$. This difference includes the heat capacities of the sample to be burned, the polyester (Mylar) bag, the cotton fuse, and, when used, the auxiliary combustible, as paraffin oil. The other symbols are identified as follows: Δt , the temperature rise; Δt_c , the corrected temperature rise; q_{cf} , the energy of combustion of the cotton used as fuse; q_n , the energy of formation of nitric acid; q_i , the electrical energy of ignition.

Table 3 gives the results of six experiments to determine the energy equivalent of the standard calorimeter system II, for a final temperature of 303.15 K, with a temperature rise of 2 K. This calorimeter system is the same as standard calorimeter system I except for a minor modification of the ignition arrangement.

$m_{\rm BA}/{ m g}$	$\Delta t/\mathbf{K}$	$\Delta t_{\rm c}/{\rm K}$	Δε/J K ⁻¹	$q_{ m cf}/{ m J}$	$q_{ m n}/{ m J}$	$q_{\rm i}/{ m J}$	<i>ε</i> ₅/J K ^{~1}
1.13846 to 1.15130	1.98217 to 2.00713	1.97264 to 1.99633	19.70 to 19.62	55.35 to 64.14	0.36 to 7.28	1.88	15253.66 to 15262.79
				Standard	deviation of	Mean: the mean:	15258.78 ±1.25

TABLE 3. Results of six experiments to determine the energy equivalent ε_s of the standard calorimeter system II, for a final temperature of 303.15 K, with a temperature rise of 2 K

Table 4 gives the results of five experiments to determine the energy equivalent of the standard calorimeter system III, for a final temperature of 298.15 K, with a temperature rise of 2 K. This calorimeter system is the same as the standard calorimeter system II except that the final temperature is 298.15 K. In these experiments, the values of the "heat leak constant", k, and the constant contribution from stirring,

TABLE 4. Results of five experiments to determine the energy equivalent ε_s of the standard calorimeter system III, for a final temperature of 298.15 K, with a temperature rise of 2 K

m _{вA} /g	$\Delta t/\mathbf{K}$	$\Delta t_{\rm c}/{\rm K}$	Δε/J Κ-1	$q_{ m cf}/{ m J}$	$q_{ m n}/{ m J}$	q_{i}/J	ε _s /J K ^{−1}
1.14432 to 1.15555	1.99640 to 2.01277	1.98521 to 2.00406	19.43 to 19.54	59.90 to 68.45	0.53 to 4.36	1.51	15252.84 to 15257.21
				Standard o	deviation of	Mean: the mean:	15254.99 ±0.89

etc., u, ranged from 3.29 to 3.33 s⁻¹ for $10^5 k$ and from -0.89 to 1.99 K min⁻¹ for $10^4 u$.^(16c,e)

Table 5 gives the results of seven experiments designed to determine the energy of combustion of the cotton used in the ignition process. The mass of cotton in each experiment was about ten times that used in a regular combustion experiment. To simulate the actual combustion experiments, a quantity of standard benzoic acid sufficient to provide a temperature rise of 2 K was used. The standard calorimeter

TABLE 5. Results of seven experiments to determine the energy of combustion of the cotton fuse used, at 298.15 K

m _{of} /g	$\Delta t/\mathbf{K}$	$\Delta t_{\rm o}/{ m K}$	ε/J K ⁻¹	$q_{\mathrm{BA}}/\mathrm{J}$	$q_{ m n}/{ m J}$	$q_{\rm i}/{ m J}$	$q_{\rm of}/{ m J}~{ m g}^{-1}$
0.03327 to 0.04353	1.97724 to 1.99591	1.96542 to 1.98866	15274.5	29442.26 to 29796.69	1.13 to 4.18	1.51	16977.3 to 17351.1
				Standard	deviation of	Mean: the mean:	17168 ±52

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system III was used in these experiments. The energy due to the combustion of the cotton was calculated as

$$q_{\rm cf} = \Delta t_{\rm c} \varepsilon - q_{\rm n} - q_{\rm i} - q_{\rm BA},$$

where q_{BA} is the energy of combustion of the benzoic acid.

Table 6 gives the results of five experiments to determine the energy of combustion of the polyester, Mylar, used to contain the diazenes for combustion. The mass of polyester in each experiment was about ten times that in a regular combustion experiment. To simulate the actual combustion experiments, a quantity of standard

TABLE 6. Results of five experiments to determine the energy of the combustion at 298.15 K of the polyester, Mylar, used to contain the diazenes for combustion

$m_{ m m}/{ m g}$	$\Delta t/K$	$\Delta t_{\rm c}/{\rm K}$	ε/J K ⁻¹	$q_{\mathrm{BA}}/\mathrm{J}$	$q_{\rm cf}/{ m J}$	$q_{ m n}/{ m J}$	$q_{\rm l}/{ m J}$	$q_{\rm m}/{ m J~g^{-1}}$
0.53715 to 0.57868	2.00084 to 2.07191	1.99256 to 2.06677	15274.5 to 15274.7	18081.83 to 18264.16	61.67 to 70.46	2.18 to 3.77	1.51	22860.5 to 22880.2
				Sta	andard de	viation of	Mean: the mean:	22873.0 ±3.6

benzoic acid sufficient to provide a temperature rise of 2 K was used. The standard calorimeter system III was used in these experiments. The energy due to the combustion of the polyester, Mylar, was calculated as

$$q_{\rm m} = \Delta t_{\rm c} \varepsilon - q_{\rm n} - q_{\rm i} - q_{\rm cf} - q_{\rm BA}.$$

Table 7 gives the results of five experiments to determine the energy of combustion of the paraffin oil that was used as an auxiliary combustible for Compound 7. This

 TABLE 7. Results of five experiments to determine the energy of combustion, at 298.15 K, of the paraffin oil used as an auxiliary combustible for Compound 7

m _{oil} /g	$\Delta t/\mathbf{K}$	$\Delta t_{\rm c}/{\rm K}$	ε/J K ⁻¹	$q_{ m m}/{ m J}$	$q_{ m cf}/{ m J}$	$q_{ m n}/{ m J}$	<i>q</i> 1/J	$q_{\rm oil}/{ m J~g^{-1}}$
0.62713 to 0.69557	1.98773 to 2.18906	1.98004 to 2.18717	15274.6 to 15275.0	1197.96 to 1293.82	59.16 to 71.71	1.42 to 2.47	1.51	46050.0 to 46088.6
				St	tandard de	viation of	Mean: the mean:	46069.7 ±7.7

paraffin oil, TKL-66, was obtained through the courtesy of W. D. Good.[†] A quantity of oil sufficient to provide a temperature rise of 2 K was used. The energy of combustion of the paraffin oil under the conditions of the bomb process was calculated as

$$q_{\rm oil} = \Delta t_{\rm c} \varepsilon - q_{\rm n} - q_{\rm i} - q_{\rm cf} - q_{\rm m}$$

The Washburn correction was applied to q_{oil} to obtain q_{oil}° .

† U.S. Energy Research and Development Administration Laboratory (formerly U.S. Bureau of Mines Laboratory), Bartlesville, Oklahoma.

Tables 8, 9, 10, 11, and 12 give the results of the calorimetric combustion experiments for five diazenes. The values of k and u given in these tables serve to indicate how the calorimeter is operating.^(16c,e) Table 8 gives the results for Compound 3, $C_8H_{18}N_2$, di-t-butyldiazene, the molar mass of which was taken as 142.2461 g mol⁻¹. Table 9 gives the results for Compound 4, C₁₂H₂₆N₂, t-butyl(1,1,3,3-tetramethylbutyl) diazene, the molar mass of which was taken as 198.3520 g mol⁻¹. The column headed q_{im} in this table gives the correction for an impurity of 0.23 mole per cent of ethylacetate in this sample. Table 10 gives the results for Compound 5, $C_{16}H_{34}N_2$, di(1,1,3,3-tetramethylbutyl)diazene, the molar mass of which was taken as 254.4614 g mol^{-1} . The column headed q_{im} in this table gives the correction for an impurity of 0.15 mol per cent of 2,2,4-trimethylpentane and 0.15 mol per cent of 2,4,4-trimethyl-1pentene. Table 11 gives the results for Compound 6, C7H14N2, 1,1,3,3-tetramethyltrimethylenediazene, the molar mass of which was taken as $126.2030 \text{ g mol}^{-1}$. For this compound, six experiments were performed with the standard calorimeter system I at 303.15 K and two experiments with the standard calorimeter system III at 298.15 K. The values obtained at 298.15 K for the latter experiments were converted to corresponding values at 303.15 K, and all eight experiments were given equal weight in arriving at the mean and the standard deviation. The two latter experiments at 298.15 K were performed to ensure that the material burned in the first six experiments, which began at 301 K, was solid. The accord of the experiments indicates that, within the limits of uncertainty, the material was in the solid state. From observations made by Månsson,⁽¹⁷⁾ the enthalpy of fusion of this compound is (16.0 ± 0.3) kJ mol⁻¹. Table 12 gives the results for Compound 7, C₈H₁₆N₂, 1,1,4,4-tetramethyltetramethylenediazene, the molar mass of which was taken as $140.2301 \text{ g mol}^{-1}$.

Table 13 gives the values for the standard enthalpies of combustion at 298.15 K for the five diazenes measured in this investigation. The difference between $-\Delta E_c$ at 298.15 K or 303.15 K and $-\Delta E_c^{\circ}$ for the same compound at the same temperature is the Washburn correction to the standard states.^(16b,e) For conversion to 298.15 K, the heat capacities of the diazenes were estimated. For Compound 7, the Washburn correction includes that of the oil as well as that of the sample.

The last column gives the value of $-\Delta H_{c}^{\circ}$ at 298.15 K for each compound, together with the overall uncertainty interval,⁽¹⁸⁾ which was taken as twice the propagated standard deviation for four components. The standard deviation for three of the four components was taken as follows: for the certified value of the standard benzoic acid, ± 0.004 per cent; for the determination of the energy equivalent, as given in tables 2, 3, and 4, for systems I, II, and III; for the combustion experiments, as given in tables 8, 9, 10, 11, and 12, for the respective compounds. The fourth component has to do with the purity of the samples. In two cases, Compound 4 and Compound 5, correction was made, as already reported, for a small amount of known impurity in each case. For Compound 5, about 0.03 mole per cent of an unknown impurity was present. It was estimated that undetected unknown impurities in these compounds would not cause an error of as much as ± 0.03 per cent in the value of the energy of combustion. Accordingly, by subjective judgment, a standard deviation was arbitrarily assigned for unknown impurities in Compounds 3, 4, and 6 of ± 0.03 per cent and in Compounds 5 and 7 of ± 0.04 per cent. The propagated standard deviation thus

			TABLE 8. di-	. Results oi <i>t</i> -butyldiaz	f six exper ene, using	iments on th the standard	ie enthalpy 1 calorimete	of combu	stion of (II, at 303	Jompoune .15 K	d 3,	
	m _{sample} /g	10 ⁵ k/s ⁻	¹ $10^4 u/K min$	-1 Δ <i>ι</i>	/K 1	Δſ _c /K ε,	/J K - 1	$q_{ m m}/J$	$q_{\rm cr}/{ m J}$	$q_{n/J}$	q ₁ /J	$-\Delta E_{\rm c}(303.15 {\rm K})/{\rm kJ} {\rm mol}^{-1}$
	0.65666 to 0.79029	3.26 to 3.39	-1.439 to 0.861	2.1.2	0945 1 to 4130 2	.79909 1 to .13738 1	5279.53 to 5280.12	1209.93 to 1363.26	61.38 to 67.93	53.75 to 62.17	1.8	5637.07 3 to 5640.55
Mean:	0.70298	I	Ι	1.9	2390 1	.91684 1	5279.73	1297.43	65.16 ⁵⁴⁰⁰	57.43	1.85	5638.79
			TABLE 9. <i>t</i> -butyl(1,1,3,3-	. Results of tetramethy	f six exper Ibutyl)diaz	iments on th zene, using ti	e enthalpy o	of combu	stion of C	Compound III, at 2	ation of d 4, 98.15 K	the mean: ±0.00
	msample/g	$10^{5}k/s^{-1}$	$10^4 u/K \min^{-1}$	Δι/Κ	$\Delta t_{\rm o}/{ m K}$	ε/J K - 1	q_{m}/J	q _{et} /J	$q_{ m n}/J$	$q_{\rm in}/J$	q ₁ /J	$-\Delta E_{\rm o}(298.15 \text{ K})/\text{kJ mol}^{-1}$
	0.68746 to 0.71239	3.28 to 3.32	1.14 to 3.00	1.96983 to 2.03528	1.95996 to 2.02930	15275.46 to 15275.59	1241.18 to 1287.55	58.89 to 68.20	51.82 to 55.79	26.62 to 27.58	1.55	8250.98 to 8257.93
Mean:	0.69856	l	Į	1.99922	1.99188	15275.50	1263.55	64.51	53.97 Stane	27.06 darđ đevi	1.55 ation of	8254.38 the mean · +1 13
			TABLE 10 di(1,1,3,3-tc	Results o	f five expe outyl)diaze	riments on t ne, using th	he enthalpy e standard c	/ of combi calorimete	ustion of t system	Compour L, at 303.	ation of ad 5, 15 K	111c IIIcall : 1.1.2
	$m_{\rm sample}/g$	10 ⁵ k/s ⁻¹	$10^4 u/K min^{-1}$	Δι/Κ	$\Delta t_{\rm e}/{\rm K}$	ε/J K - 1	$q_{ m m}/J$	$q_{ m im}/J$	$q_{ m or}/J$	$q_{ m n}/J$	q_i/J	$-\Delta E_{\rm c}(303.15 {\rm K})/{\rm kJ} {\rm mol}^{-1}$
Mean:	0.67816 to 0.69418 0.68517	3.26 to 3.46	4.04 to 5.27	2.00250 to 2.04606 2.02151	1.98917 to 2.03349 2.00947	15289.30 to 15289.38 15289.36	1281.38 to 1383.47 1319.49	25.14 to 25.80 25.43	55.85 to 63.65 59.07 Star	48.29 to 50.11 48.93 ndard dev	1.88 1.88 1.88 riation o	10871.8 to 10878.5 10875.7 f the mean: ±1.2

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mssmall 10^{4} k/s ⁻¹ 0^{4} /k δ_{1} /k δ_{1}/k <													E(T)/bI mol	
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$		m _{sample} /g	10 ⁵ k/s ⁻¹	$10^4 u/K min^{-1}$	Δt/K	Δſ _e /Κ	ε/J K⁻¹	$q_{ m m}/J$	q _{et} /J	q_n/J	q ₁ /J	T = 298	15 K T = 3	03.15 K
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		0.60925	3.15	3.92	1.61062	1.58801	15288.39	1179.27	58.62	57.93			472	7.22
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		to	to	to	to	to	to	to	to	to	1.88			to
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		0.80462	3.37	5.87	2.07194	2.06196	15289.25	1368.49	64.66	72.09			473	1.43
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		0.73276	3.33	1.29	1.90402	1.89118	15275.68	1319.60	62.16	66.13	1.88	4725.3	85 472	5.78
Mean: 0.42361 1.96210 5423.80 Mean: 0.42361 -1.96210 1.94369 15275.32 11958.11 1236.41 6.1.93 50.21 1.51 5420.99 Maampely 10.4 Vetramethyltetramethyle 0.410 0.411 0.41 0.41 298.15 K/s ⁻¹ Maampely 10 ⁵ k/s ⁻¹ 10 ⁴ u/k min ⁻¹ Δr/k ε/J K ⁻¹ 0°0.1/J 0.41 0.41 298.15 K/s ⁻¹ Maampely 10 ⁵ k/s ⁻¹ 10 ⁴ u/k min ⁻¹ Δr/k ε/J K ⁻¹ 0°0.1/J qm/J qer/J q/J		0.76658	3.34	0.87	1.98275	1.97500	15275.84	1335.98	61.41	69.84	1.88	4725.(01 472	4.94
Standard deviation of the mean: ± 0.94 TABLE 12. Results of seven experiments on the enthalpy of combustion of Compound 7, CaH ₁₆ N ₂ , 1,1,4,4-tetramethyleteramethylenediazene, using the standard calorimeter system III, at 298.15 K m_{aamole} 10 ⁶ k/s ⁻¹ 10 ⁴ u/K min ⁻¹ $\Delta t/K$ $\Delta t_{c}/K$ e/J q_{o1}/J q_{o1}/J q_{o1}/J q_{o1}/J q_{o1}/J q_{o1}/J $-\Delta E_{c}(298.15 K)/K$ m_{aamole} 10 ⁶ k/s ⁻¹ 10 ⁴ u/K min ⁻¹ $\Delta t/K$ $\Delta t_{c}/K$ e/J K^{-1} q_{00}^{a}/J q_{m}/J q_{o1}/J q_{o1}/J q_{o1}/J $-\Delta E_{c}(298.15 K)/K$ m_{aamole} 10 ⁶ to 108 1.78142 1.76946 15275.53 13890.96 1182.98 58.91 47.24 5420.99 to 5425.45 Mean: 0.42361 - - 1.96210 1.94369 15275.32 11958.11 1236.41 61.93 50.21 151 5425.45 Mean: 0.42361 - - 1.94369 15275.32 11958.11 1236.41 61.93 50.21 1.51										ų	Mean (oi	f 8 experin	nents): 472	8.80
TABLE 12. Results of seven experiments on the enthalpy of combustion of Compound 7, C ₆ H ₁₆ N ₂ , 1,1,4,4-tetramethyltetramethylenediazene, using the standard calorimeter system III, at 298.15 K $m_{sample}[g \ 10^{5}k/s^{-1} \ 10^{4}u/K \ min^{-1} \ \Delta t/K \ min^{-1} \ \Delta t/K \ \Delta t_{o}/K \ s/J \ K^{-1} \ q_{oll}/J \ q_{oll}/J \ q_{ol}/J \ q_{ol}/J \ q_{ol}/J \ q_{ol}/J \ q_{ol}/J \ -\Delta E_{o}(298.15 \ K)/kJ$ 0.40866 3.28 1.08 1.78142 1.76946 15275.07 9736.29 1182.98 58.91 47.24 5420.99 0.40866 3.28 1.08 1.08 1.78142 1.76946 15275.53 13890.96 1287.21 67.45 53.76 1.51 5425.45 5420.99 0.40866 3.28 3.31 3.46 2.08722 2.08174 15275.53 13890.96 1287.21 67.45 53.76 1.51 5425.45 60.10 1.51 5425.45 Mean: 0.42361 1.96210 1.94369 15275.32 11958.11 1236.41 61.93 50.21 1.51 5425.45 5423.14 5423.14										Standar	d deviati	ion of the	mean: ±	0.94
TABLE 12. Results of seven experiments on the enthalpy of combustion of Compound 7, C ₆ H ₁₆ N ₂ , 1,1,4,4-tetramethyltetramethylencdiazene, using the standard calorimeter system III, at 298.15 K <i>m</i> _{sample} [g 10 ⁵ k/s ⁻¹ 10 ⁴ u/K min ⁻¹ $\Delta t/K$ $\Delta t_o K = s/J K^{-1}$ $q_o J = q_o J = -\Delta E_o (298.15 K)/kJ$ 0.40866 3.28 1.08 1.78142 1.76946 15275.07 9736.29 1182.98 58.91 47.24 5420.99 0.40856 3.28 1.08 1.78142 1.76946 15275.53 13890.96 1287.21 67.45 53.76 5420.99 0.40856 3.31 3.46 2.08722 2.08174 15275.53 13890.96 1287.21 61.95 5425.45 Mean: 0.42361 1.96210 1.94369 15275.32 11958.11 1236.41 61.93 50.21 1.51 5425.45 Mean: 0.42361 - 1.96210 1.94369 15275.32 11958.11 1236.41 61.93 50.21 1.51 5425.45														
1,1,4,4-tetramethyleteramethylenediazene, using the standard calorimeter system III, at 298.15 K m_{aamnel} m_{aamnel} m_{aamnel} $1,1,4,4$ -tetramethyleteramethylenediazene, using the standard calorimeter system III, at 298.15 K)/kJ m_{aamnel} 0.40866 3.28 10^4 M_6 $8/J$ q_0°/J q_m/J q_{of}/J q_n/J $-\Delta E_0(298.15 K)/kJ$ 0.40866 3.28 1.08 1.7842 1.76946 15275.07 9736.29 1882.98 58.91 47.24 5420.99 10 0.45858 3.31 3.46 2.08174 15275.53 13890.96 1287.21 67.45 53.76 5425.45 Mean: 0.42361 $$ 1.96210 1.94369 15275.32 11958.11 1236.41 61.93 50.21 1.51 5423.14 Mean: 0.42361 $$ 1.96210 1.94369 15275.32 11958.11 1236.41 61.93 50.21 1.51 5423.14 </td <td></td> <td></td> <td>ΤA</td> <td>ABLE 12. Resu</td> <td>Its of seven</td> <td>i experimen</td> <td>ts on the en</td> <td>thalpv of c</td> <td>ombustio</td> <td>n of Con</td> <td>punouu</td> <td>7. C.H.</td> <td></td> <td></td>			ΤA	ABLE 12. Resu	Its of seven	i experimen	ts on the en	thalpv of c	ombustio	n of Con	punouu	7. C.H.		
m_{tample} $10^4 u/\text{K}$ min ⁻¹ $\Delta t/\text{K}$ $\Delta t_{\rm c}/\text{K}$ e/J $q_{\rm oll}/J$ $q_{\rm cf}/J$ $q_{\rm ol}/J$ $q_{\rm ol}/J$ $-\Delta E_{\rm c}(298.15 \text{ K})/\text{kJ}$ 0.40866 3.28 1.08 1.78142 1.76946 15275.07 9736.29 1182.98 58.91 47.24 5420.99 0.40866 3.28 1.08 1.78142 1.76946 15275.07 9736.29 1182.98 58.91 47.24 5420.99 0.40866 3.28 1.0 to				l,1,4,4-tetramet	thyltetrame	thylenediaz	ene, using th	he standard	l calorime	ter syste	m III, al	t 298.15 K	4	
0.40866 3.28 1.08 1.78142 1.76946 15275.07 9736.29 1182.98 58.91 47.24 5420.99 to to t	!	m _{sample} /g	$10^{5}k/s^{-1}$	$10^4 u/K min^{-1}$	Δr/K	$\Delta t_{\rm c}/{ m K}$	ε/J K−1	$q_{ m oll}^{\circ}/J$	$q_{ m m}/J$	$q_{ m cr}/J$	$q_{ m n}/J$	q_i/J	$-\Delta E_{\rm e}(298.15$	K)/kJ mol ⁻¹
to t		0.40866	3.28	1.08	1.78142	1.76946	15275.07	9736.29	1182.98	58.91	47.24		542	0.99
0.45858 3.31 3.46 2.08722 2.08174 15275.53 13890.96 1287.21 67.45 53.76 5425.45 Mean: 0.42361 1.96210 1.94369 15275.32 11958.11 1236.41 61.93 50.21 1.51 5423.14 Standard deviation of the mean: -40.58		5	5	to	to	to	to	to	to	to	<u>0</u>	1.51	t	0
Mean: 0.42361 1.96210 1.94369 15275.32 11958.11 1236.41 61.93 50.21 1.51 5423.14 5423.14 Standard deviation of the mean: +0.58		0.45858	3.31	3.46	2.08722	2.08174	15275.53	13890.96	1287.21	67.45	53.76		542	25.45
Standard deviation of the mean $z \rightarrow 0.58$	Mean:	0.42361	}	}	1.96210	1.94369	15275.32	11958.11	1236.41	61.93	50.21	1.51	542	23.14
										Stan	dard dev	viation of t	the mean: ±	0.58

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No.	Molecular formula	Compound Structure	State	-Δ <i>E</i> _o /kJ mol ⁻¹ 298.15K 303.15K	ΔE°/kJ mol ⁻¹ 298.15K 303.15K	ΔH°c/kJmol-1 298.15 K
3	$C_8H_{18}N_2$	$\left \right\rangle_{n=n}$	1	5638.79	5636.39	5645.8 ±3.6
4	$C_{12}H_{26}N_2$	\sim	1	8254.38	8251.35	8265.0 ±5.6
5	$C_{16}H_{34}N_2$		1	10875.7	10871.75	10891.9 ±9.4
6	$C_7H_{14}N_2$	$\bigvee_{N=N}$	c	4728.80	4726.66	4733.0 ±3.5
7	$C_8H_{16}N_2$	$\bigvee_{N=N}$	l	5423.14	5419.22	5426.7 ±4.6

TABLE 13. Standard enthalpies of combustion of five diazenes

obtained from the four components was doubled to yield the assigned overall uncertainty interval given in the last column of table 13.

Except for the one case mentioned, Compound 3, no previous data on these diazenes exist for comparison.

ENTHALPY OF VAPORIZATION OF NINE DIAZENES

The measurements of the enthalpies of vaporization were carried out in the Thermochemical Laboratory of the Chemical Center of the University of Lund. For those compounds having a vapor pressure larger than about 0.5 Torr at 298.15 K, the Wadsö calorimeter was used, following the procedure described.⁽¹⁹⁾ For those compounds having a vapor pressure smaller than about 0.5 Torr at 298.15 K, a slightly modified Morawetz calorimeter was used, following the procedure described.⁽²⁰⁾ Compound 7 and Compound 8 were measured in both calorimeters: Compound 7 because of "misbehavior" in the Wadsö calorimeter, when a yellow rather gummy material accumulated at a joint between the plastic tubing and metal tubing some distance away from the calorimeter outlet; Compound 8 because the results from the first series

differed by about 3 kcal_{th} mol⁻¹ from non-calorimetric values extant in the literature.⁽⁴⁾ Compound 8 was run in the Morawetz calorimeter on two successive days, with 5 and 3 experiments, respectively, the results showing a pronounced trend toward successively lower values. After opening the calorimeter, the sample was in the form of a porous loose disk in poor thermal contact with the calorimeter. Because of these observations on Compound 8, only the first four experiments were taken into account.

With the Morawetz calorimeter, it was necessary to take into account a correction, approaching 2 per cent, because of a heater lead error. The correction was established by comparing values for *n*-decane, *n*-dodecane, *n*-tetradecane, and *n*-hexadecane obtained with the present Morawetz calorimeter with the values obtained with the original calorimeter,⁽²¹⁾ which were in accord with other experimental data. The uncertainty arising from this correction was estimated to be ± 0.35 J mol⁻¹ for the compounds measured in the present investigation, and has been appropriately propagated into the overall uncertainty assigned to the values obtained.

Table 14 gives the results of the experiments on the enthalpy of vaporization of nine diazenes, the five diazenes whose synthesis and purification are described in this report and the four diazenes previously reported.⁽⁴⁾ For Compound 7, both the W and M values are given equal weight, while for Compound 8 the W value is given double weight. In each case the assigned uncertainty is the "uncertainty interval", calculated as twice the overall standard deviation of the mean. It is believed that any impurities in these compounds would not have any significant effect within the assigned limits of uncertainty.

Previous data on the enthalpy of vaporization of six of these compounds, obtained by non-calorimetric methods, are summarized as follows, in terms of the difference from the present values: Engel *et al.*,⁽⁴⁾ Compound 1, -0.08, Compound 2, +0.05 and +0.42, Compound 3, +0.13 and -1.5, Compound 7, -0.3, Compound 8, -2.7, and Compound 9, $-0.5 \text{ kcal}_{th} \text{ mol}^{-1}$; Geiseler and Hoffman,⁽²²⁾ Compound 1, +0.29, Compound 2, -0.25; and Steel,⁽²³⁾ Compound 8, -2.6 kcal_{th} mol⁻¹.

3. Results

To calculate the standard enthalpy of formation for the nine diazenes in the condensed state, we have used the values for the standard enthalpy of combustion, ΔH_{e}° , given in table 13 for Compounds 3, 4, 5, 6, and 7, and those given in table 3 of reference 4 for Compounds 1, 2, 8, and 9. The uncertainties assigned to the latter values have been enlarged according to the procedure for uncertainties described earlier in this report. With the values for the standard enthalpy of combustion, we have used the recommended values for the standard enthalpy of formation for water and for carbon dioxide given in reference 24: H₂O(l), ΔH_{f}° (298.15 K) = -(285.830 ± 0.042) kJ mol⁻¹; CO₂(g), $\Delta H_{f}^{\circ}(298.15 \text{ K}) = -(393.51\pm0.13) \text{ kJ mol}^{-1}$. The assigned uncertainties have been appropriately propagated into the final values to give the uncertainty interval.

To calculate the standard enthalpy of formation in the gaseous state for these nine diazenes, we have used the values for the enthalpy of vaporization given in table 14 and have considered the difference between ΔH_v and ΔH_v° at 298.15 K for these

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No.	Molecular formula	Compound Structure	Process	N	W or M ^a	$\frac{\Delta H_{\star}}{\text{kJ mol}^{-1}}$	$\frac{\Delta H_{\rm v}(298.15 \text{ K})}{\text{kcal}_{\rm th} \text{ mol}^{-1}}$
1	$C_6H_{14}N_2$	N=N_	l = g	4	W	39.88±0.42	9.53±0.10
2	$C_6H_{14}N_2$	N=N	l == g	4	W	35.90±0.42	8.58±0.10
3	$C_8H_{18}N_2$	$\nearrow_{n=n}$	$\mathbf{l} = \mathbf{g}$	5	w	39.08±0.25	9.34±0.06
4	$C_{12}H_{26}N_2$	× _{N=N} ××] = g	5	w	53.60±0.21	12.81±0.05
5	$C_{16}H_{34}N_2$		1 = g	9	М	66.53±0.63	15.90±0.15
6	$C_7H_{14}N_2$	X N=N	c = g	4	W	61.63±0.21	14.73±0.05
7	$C_8H_{16}N_2$	$\bigvee_{N=N}$	l = g	4 5	W M Mean	(50.29±0.25) (49.83±0.46) 50.06±0.42	11.96±0.10
8	$C_5H_8N_2$	NN	c = g	5 4	W M Mean⁵	(55.94±0.29) (53.56±0.96) 55.27±0.63	13.21±0.15
9	$C_8H_{14}N_2$	N N	$\mathbf{c} = \mathbf{g}$	5	М	71.96±0.54	17.20±0.13

TABLE 14. Results of N experiments on the enthalpy of vaporization of each of nine diazenes,
at 298.15 K

 $(cal_{th} = 4.184 J)$

^a Calorimeter used: W, Wadsö; M, Morawetz. ^b The W value is given double weight.

TABLE 15. Values of the standard enthalpy of formation for the condensed state and the gaseous state for the nine diazenes, at 298.15K $(cal_{th} = 4.184 J)$

No. Molecular formula	Compound Structure	State at 298.15	$\frac{\Delta H_{\rm f}^{\circ}(\rm c \ or \ l)}{\rm K \ kJ \ mol^{-1}}$	$\frac{\Delta H_{\rm f}^{\circ}(\rm c \ or \ l)}{\rm kcal_{\rm th} \ mol^{-1}}$	$\frac{\Delta H_{\rm f}^{\circ}({\rm g})}{\rm kJmol^{-1}}$	$\frac{\Delta H_{f}^{\circ}(\mathbf{g})}{\text{kcal}_{\text{th}} \text{ mol}^{-1}}$
1 C ₆ H ₁₄ N ₂	N=N_	1	11.5±3.5	2.74±0.83	51.3±3.5	12.27±0.84
$2 C_{6}H_{14}N_{2}$	N=N_	1	-0.3 ± 3.5	−0.07±0.84	35.6±3.6	8.51±0.85
$3 C_8 H_{18} N_2$	$\nearrow_{n=n}$	ì	-74.7±3.6	-17.85±0.86	-35.6 ± 3.6	-8.51±0.87
4 C ₁₂ H ₂₆ N ₂	× _{n=n} ××	, 1 - \	-172.9±5.6	-41.3 ±1.3	-119.3±5.6	-28.5 ±1.3
5 C ₁₆ H ₃₄ N ₂		, 1 -	-263.3±9.3	-62.9 ±2.2	196.8±9.4	-47.0 ±2.2
6 C ₇ H ₁₄ N ₂	X N=N	с	-22.3±3.5	-5.34±0.84	39.3±3.6	9.39±0.85
7 C ₈ H ₁₆ N ₂	$\bigvee_{N=N}$	1	-8.1±4.6	-1.9 ±1.1	42.0±4.6	10.0 ±1.1
8 C5H8N2	N	c	152.1±2.6	36.35±0.62	207.4±2.7	49.56±0.64
9 C ₈ H ₁₄ N ₂	NNN NNNN	с	20.4±4.4	4.9 ±1.1	92.4±4.4	22.1 ±1.1

compounds to be negligible, within the assigned limits of uncertainty. Table 15 gives the resulting values for the standard enthalpies of formation for the condensed state and for the gaseous state for the nine diazenes.

4. Discussion

The values given in table 14 will be used in connection with other studies on the relation of energy content with molecular structure for these molecules. With regard to the significance of the resulting values for the energies in the gaseous state for these molecules, a separate publication by Engel et al. will appear dealing with strain energies and reactivity of certain diazenes.

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