in ammonia in solution and in ethylenimine in the gas phase.

Acknowledgment.—We wish to express our gratitude to our colleagues including Drs. Turner, Pigford and Sager for many helpful discussions during the progress of our work.

[CONTRIBUTION FROM THE RICHARDSON CHEMICAL LABORATORY, TULANE UNIVERSITY]

The Heats of Combustion of Cyclopentyl and Cyclohexyl Azides

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The ΔH's of combustion at 298.1°K. of cyclopentyl and cyclohexyl azides were found to be 820.48 ± 0.33 and 965.96 ± 0.21 kcal. per mole, respectively. From these the enthalpies of formation from the elements and from the gaseous atoms have been calculated. The resonance energy of the azido group has been estimated.

In continuation of a study of the physical properties of organic azides in this Laboratory, the heats of combustion of cyclopentyl and cyclohexyl azides have been measured. The only other recorded heats of combustion of organic azides have been those of 2-triazoethanol,[1] hydrazoic acid,[2] triazoethyl acetate and phenyl azide.[3] Since the structural properties of the azido group are of interest the resonance energy has been estimated.

Experimental

Preparation and Purification of Materials.—Both azides were prepared by the method of replacing the bromine of the mono-substituted cyclic bromide with the azido group by reaction with sodium azide. The procedure used in the preparation was that of Boyer[4] and is essentially as follows. To a solution of the bromide (0.24 mole) in 200 ml. of ethanol was added a solution of sodium azide (0.48 mole) and 10 g. of sodium acetate in 100 ml. of water, and the resulting mixture heated at reflux temperature for 12 hours. Addition of 500 ml. of water caused two layers to form; these were separated and the bottom layer was extracted with ether. The ether extracts were added to the top oily layer and the solution dried over sodium sulfate, which was then removed by filtration. Distillation of the ether left an oily residue. Distillation at reduced pressure, in an atmosphere of nitrogen, of the cyclopentyl and cyclohexyl azides gave excellent yields at 51–52° (20 mm.) and 64–65° (21 mm.), respectively.

The samples used in this investigation had been purified by triple distillation at reduced pressure. A nearly constant refractive index (±0.0001) for successive constant boiling fractions was considered evidence for the purity of the compounds. The refractive index for the sodium-D line at 25° was 1.4690 for cyclohexyl azide and 1.4615 for cyclopentyl azide. The densities at 25° were 0.98546 g./ml. and 0.9789 g./ml. for cyclohexyl azide and cyclopentyl azide, respectively. The heat capacities of the liquids, as measured by the method of mixtures, were found to be 19.4 abs. j./g. for cyclopentyl azide and 19.2 abs. j./g. for cyclohexyl azide, with an estimated error of ±1.2 abs. j./g. The heat of combustion was a more sensitive criterion of purity of the compounds than the boiling points or refractive indices.

The constant temperature jacket calorimeter used in this work consisted of a Parr Adiabatic Oxygen Bomb Calorimeter, which has been previously described,[1] with appropriate modifications for isothermal measurements. The major change involved the installation of a thermal regulator and heating unit, and insulation between the bucket well and the walls by filling with vermiculite. A coil of twenty-gage nichrome wire, wound on a glass tube and coated with glyptal, comprised the electrical heater. The temperature was controlled by an American Instrument Company Supersensitive Mercury Relay and an Aminco Rectran Rectifier–Transformer. With these changes, the jacket was maintained at constant temperature to ±0.002°.

Temperature changes were measured with a calorimetric-type platinum resistance thermometer constructed and calibrated by the Leeds and Northrup Company, and checked by comparison with standard research platinum thermometers certified by the National Bureau of Standards. The thermometer, of the four-lead cable type, was used in conjunction with a Leeds and Northrup G-2 Mueller Bridge and a high sensitivity galvanometer.

The rating-period procedure of White[5] with modifications recommended by Prosen[6] was employed in order to obtain the correct resistance change.

The spherical glass bulbs into which the samples were placed for ignition were prepared from 4 mm. soft glass tubing according to the procedure of Coops.[7] The bulbs averaged 11 mm. in diameter and, with a 20-mm. capillary neck, weighed between 75 and 150 mg. With both liquids it was found that carbon-free combustion was obtained with completely filled bulbs at a pressure of 35 atmospheres of oxygen.

An ordinary 2-cc. hypodermic syringe with a number 22 needle into which was fitted a fine glass capillary was used for filling the bulbs. After the bulb was filled with the freshly distilled azide it was placed in crushed Dry Ice and the vapors in the neck removed by placing a small warmed coil of copper around it. The tip of the neck was then sealed with a micro-burner flame.

The preparation for ignition and the determination of the nitric acid formed were performed as described previously.[1] Ten milliliters of water were placed in the bomb with the sample.

Calibration.—The energy equivalent of the calorimeter was determined by burning Bureau of Standards benzoic acid (Standard sample 39 g.). For its isothermal heat of combustion per gram under standard conditions at 25° the value of 26,433.8 abs. j./g. mass (weight *in vacuo*) was reported with an estimated uncertainty of 2.6 j./g. This value was converted[8] to the bomb conditions used throughout this investigation and found to be 26,434.6 abs. j./g.

In a series of calibration determinations, the mean energy equivalent for the system was 19,705.5 ± 3.5 joules per ohm. Since the amount of water in the bucket (m_w) varied from one experiment to another, it was not included in the standard calorimeter system.

Results and Calculations

All weights were corrected to "*in vacuo*." The data are referred to a standard temperature of 25°.

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[6] E. J. Prosen, "Determination of Heats of Combustion Using a Bomb Calorimeter," National Bureau of Standards Report No. 1119, August 6, 1951; U. S. Department of Commerce.

[7] J. Coops, D. Mulder, J. W. Dienske and J. Smittenberg, *Rec. trav. chim.*, **66**, 153 (1947).

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TABLE I

Trial	Wt. sample, g.	Wt. water, g.	ΔR, ohms	Total heat evolved, abs. j.	Ignition energy, abs. j.	Nitric acid formation, abs. j.	$-\Delta U_B$, kj./mole	Washburn cor., abs. j.	$-\Delta U°$ at final temp., kj./mole	$-\Delta U°$ (298°K.), kcal./mole
					Cyclopentyl azide					
1	0.5517	2005.11	0.1671	17,214.9	103.8	69.4	3433.39	13.72	3430.64	819.99
2	.7236	2002.02	.2194	22,554.4	101.1	83.0	3436.11	23.06	3432.56	820.45
3	.6101	2003.12	.1849	19,032.0	105.1	76.2	3434.61	15.07	3431.86	820.28
4	.4889	1999.22	.1483	15,245.3	95.7	59.2	3430.76	10.67	3428.32	819.44
									Av.	820.04 ± 0.33
					Cyclohexyl azide					
1	0.7636	1997.67	0.2419	24,828.9	106.4	81.2	4039.81	19.20	4036.67	964.92
2	.7153	2003.89	.2261	23,261.9	82.3	78.6	4042.42	18.10	4039.27	965.55
3	.6529	1997.26	.2071	21,248.0	85.7	81.6	4041.80	16.48	4038.65	965.40
4	.6780	2000.67	.2146	22,049.8	79.6	83.0	4041.47	16.87	4038.36	965.33
5	.5046	1996.24	.1600	16,419.4	72.9	61.1	4040.30	12.57	4037.17	965.04
6	.7397	1998.61	.2342	24,044.5	86.3	83.3	4040.69	20.19	4037.28	965.07
									Av.	965.22 ± 0.21

The atomic weights used were those reported by Wichers.[9] The energy unit used is the calorie, which is defined as equal to 4.1840 absolute joules.

The observed heat of combustion, $-\Delta U_B$, under the conditions of the bomb process in each experiment was reduced to the value of $-\Delta U°$ (298°K.), the decrease in intrinsic energy accompanying the reactions

$$C_5H_9N_3(l) + 29/4O_2(g) \longrightarrow 5CO_2(g) + 3/2N_2(g) + 9/2H_2O(l) \quad (1)$$

$$C_6H_{11}N_3(l) + 35/4O_2(g) \longrightarrow 6CO_2(g) + 3/2N_2(g) + 11/2H_2O(l) \quad (2)$$

with each of the reactants and products in its thermodynamic standard state. This was done in accordance with the Washburn[10] procedure, modified by Prosen[6] so as to apply to nitrogen containing compounds, and to the energy content of the gases at zero pressure.

The results of a series of combustion experiments on cyclopentyl and cyclohexyl azides are given in Table I. These experiments were performed in the same manner as those of calibration. The average values of $-\Delta U°$ (298°K.) for cyclopentyl and cyclohexyl azides are 820.04 and 965.22 kcal./mole, respectively. The standard error of the mean, defined by $\{d^2/n(n-1)\}^{1/2}$ where d is the deviation of an individual measurement from the mean and n is the number of measurements, was found to be 0.22 kcal. for cyclopentyl azide and 0.10 kcal. for cyclohexyl azide.

Since this value ($-\Delta U°$ (298°K.)) is the thermodynamic quantity ΔE, the formula $\Delta H = \Delta E + \Delta nRT$ was used to obtain the enthalpy for the reaction. The values of ΔH for cyclopentyl and cyclohexyl azides are -820.48 and -965.96 kcal./mole, respectively.

Discussion

The enthalpies of formation, at 298°K., of the compounds from their elements were calculated with the use of the data from Rossini[11]

$$5C(gr) + 9/2H_2(g) + 3/2N_2(g) \longrightarrow C_5H_9N_3(l) \quad (3)$$
$$\Delta H^0_f\,(298°K.) = +42.79 \text{ kcal.}$$

$$6C(gr) + 11/2H_2(g) + 3/2N_2(g) \longrightarrow C_6H_{11}N_3(l) \quad (4)$$
$$\Delta H^0_f\,(298°K.) = +25.90 \text{ kcal.}$$

The enthalpies of formation of the gaseous azides from the gaseous elements in the atomic state were found to be

$$5C(g) + 9H(g) + 3N(g) \longrightarrow C_5H_9N_3(g)$$
$$\Delta H^0_f\,(298°K.) = -1612.1 \text{ kcal.} \quad (5)$$

$$6C(g) + 11H(g) + 3N(g) \longrightarrow C_6H_{11}N_3(g)$$
$$\Delta H^0_f\,(298°K.) = -1903.9 \text{ kcal.} \quad (6)$$

(L(C) = 171.698 kcal.; $D(N_2)$ = 225.089 kcal.). Approximate values of the heats of vaporization of cyclopentyl azide (10.0 kcal.) and cyclohexyl azide (11.0 kcal.) were made by use of an empirically derived equation of Hildebrand,[12] which relates surface tension to the heat of vaporization. The surface tensions, measured by the capillary rise techniques, were 32.5 dynes/cm. for cyclopentyl azide and 29.5 dynes/cm. for cyclohexyl azide at 25°.

For the covalent azides, it has been established that the structures I and II contribute the only significant resonance effect

$$\text{(I)}\ \mathrm{R{-}N{=}N\overset{\rightarrow}{=}N} \qquad \text{(II)}\ \mathrm{R{-}N{\leftarrow}N{\equiv}N}$$

The structures used as the reference for the resonance energy calculations were methane, methylamine and *trans*-azobenzene. The bond energies, evaluated after Pauling[13] at 25° were those tabulated in Table II.

TABLE II

Parent compound	Bond	Bond energy,[a] kcal.
Methane	(C-H)	99.5
Ammonia	(N-H)	93.4
Methylamine	(C-N)	66.0
trans-Azobenzene	(N=N)	103.5

[a] L(C) = 171.698; $D(N_2)$ = 225.089.

The heats of formation of gaseous cyclopentane and cyclohexane from the atoms in the gaseous

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state were calculated from data given by Rossini[14] and were found to be −1397.6 and −1685.6 kcal./mole, respectively.

With the above values, the calculated heats of formation from the atoms were obtained as

$$\Delta H_f(298^\circ\text{K.})\ \text{cyclopentane(g)} - \text{B(C–H)} + \text{B(C–N)} + 2\text{B(N=N)} \quad (7)$$
$$= \Delta H_f \text{ of structure I for cyclopentyl azide}$$

$$\Delta H_f(298^\circ\text{K.})\ \text{cyclohexane(g)} - \text{B(C–H)} + \text{B(C–N)} + 2\text{B(N=N)} \quad (8)$$
$$= \Delta H_f \text{ of structure I for cyclohexyl azide}$$

The structure II was not used as a reference for the stabilization energy calculation; as shown by Sidgwick,[15] there is no nitrogen–nitrogen triple bond value that can be used without ambiguity.

On the basis of equations 7 and 8 the calculated heats of formation were −1571.1 and −1859.1 kcal., respectively. Comparison of these values with those observed leads to a resonance energy of 41.0 kcal. for cyclopentyl azide and 44.8 kcal. for cyclohexyl azide.

Acknowledgment.—One of us (TFF) wishes to acknowledge his indebtedness to the Research Corporation for a grant which made this and continuing investigations possible.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY, FACULTY OF SCIENCE, TOKYO UNIVERSITY]

Near Infrared Spectra of Compounds with Two Peptide Bonds and the Configuration of a Polypeptide Chain V

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The near infrared spectra of acetylpiperidine α-carboxylic acid N-methylamide have been measured in carbon tetrachloride and chloroform solutions. A considerable difference in the behavior of the NH bands has been found between this substance and acetylproline N-methylamide. This has been explained as arising from the different steric effects of the five-membered and six-membered rings on the internal rotation of these two substances. The piperidine ring affects the internal rotation in such a way that the internal hydrogen bond N–H...O of acetylpiperidine α-carboxylic acid N-methylamide becomes much weaker than that of acetylproline N-methylamide. *Intermolecular* hydrogen bonding in these two substances has also been discussed.

In this series of researches the near infrared spectra of various acetylaminoacid N-methylamides, $CH_3CONHCHRCONHCH_3$, have been measured in carbon tetrachloride and chloroform solutions.[1–5] From the experimental results it was concluded that there is in general an equilibrium of three molecular configurations: extended, folded and associated configurations shown in Fig. 1, A, B and C, respectively. These configurations correspond to the stable positions of internal rotation about the four single bonds I, II, III and IV shown in Fig. 1A.[6] In the case of acetylproline N-methylamide in carbon tetrachloride the molecules exist only in the folded configuration shown in Fig. 1D,[3] which is partly converted to another form such as shown in Fig. 1E in chloroform in which the internal hydrogen bonding is reduced.[5] The interesting behavior of this substance different from that of other acetylaminoacid N-methylamide arises from the facts that the molecule has only one N–H bond and that owing to the ring formation, the C–N (I) and C–C (III) bonds cannot form the *trans* configuration. It would, therefore, be interesting to make a similar research on acetylpiperidine α-carboxylic acid N-methylamide which has six-membered rings instead of five (Fig. 1F), as the two rings affect the internal rotations quite differently. Such a study will make a further contribution to the determination of the configurations of aminoacid residues building up a polypeptide chain.

Experimental

Fourteen grams of acetylpiperidine α-carboxylic acid ethyl ester was dissolved in 35 cc. of methanol cooled at −50° by a mixture of Dry Ice and ethanol. To this solution was added 10 g. of methylamine cooled by the same cryogen and the reaction product was allowed to stand for two weeks. After removal of remaining methylamine and solvent, colorless crystal of acetylpiperidine α-carboxylic acid N-methylamide was obtained. This was recrystallized from chloroform and was used in the measurement, m.p. 107–108°.

Anal. Calcd. for $C_9H_{16}O_2N_2$: C, 58.67; H, 8.71; N, 15.21. Found: C, 58.36; H, 8.59; N, 15.05.

The infrared absorption measurement was made, using the LiF prism in the reflection monochromator constructed in our laboratory.

Results and Discussions

A. Intramolecular and Intermolecular Hydrogen Bonds of Acetylpiperidine α-Carboxylic Acid N-Methylamide.

—The results of the absorption measurements in the 3 μ region are shown in Figs. 2 and 3, each of which consists of two parts, one referring to the molar absorption coefficient *versus* wave length and the other to the dependence of the absorption coefficient on the concentration of the solution.

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