[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, OREGON STATE COLLEGE]

The Heat of Combustion of *cis*- and *trans*-Decahydronaphthalene[1]

BY GEORGE F. DAVIES AND E. C. GILBERT

In a long series of investigations Seyer and his collaborators[2] have thrown considerable light on the physical and chemical properties of the isomers of decahydronaphthalene. Their success in isolating the *cis* and *trans* forms in a high degree of purity permits a precise determination of the heat of combustion, from which may be estimated the heat of isomerization. Through the courtesy of Professor Seyer, samples of both isomers in their highest purity have been made available to this Laboratory for the present work.

Previous determinations of the heat of combustion of these substances have been reported.[3] There is, however, a spread of 20–60 calories per gram of sample in the values obtained, so the mean reported has little significance.

Apparatus and Procedure.—The calorimeter is essentially that used in earlier work in this Laboratory.[4] The precautions exercised there were continued. However, the entire unit has been reassembled with a new platinum resistance thermometer, and some alterations made. This required a re-determination of the energy equivalent of the calorimeter. For this purpose benzoic acid (Standard Sample 39e, National Bureau of Standards) was used. Seven calibrating runs were made with samples varying in weight from 0.83 to 1.09 g. Corrections were made for the deviation of the bomb from standard dimensions.[5] The energy equivalent thus determined was 2607.31 conventional calories[6] per degree, with a maximum deviation of 0.40 and an average deviation of ±0.22 calorie per degree.

Samples of the decahydronaphthalene were inclosed in small glass ampoules and ignited by iron wire. No additional substances were present. Some difficulty was experienced in obtaining complete combustion. It was found that by using 1.0 ml. of a 1.0 *N* nitric acid in the bomb instead of the customary 1.0 ml. of water the completeness of combustion was improved. Due correction for this nitric acid was made in all the subsequent calculations. For the heat of formation of nitric acid produced in the combustion at 25° and constant volume the value of 13,960 cal. per mole was used. The results are referred to the standard temperature of 25° by using in each instance an initial temperature of 25 ± 0.2°, and calculations involving the heat capacity of the products of the reaction.

The physical constants of the decalin isomers were as supplied by Professor Seyer: *cis*-, f. p. −43.19 ± 0.02°, n^{20}_D 1.48113; *trans*-, f. p. −31.15 ± 0.02°, n^{20}_D 1.4968.

The results of the combustions are shown in Table I. From $-\Delta U_B$, the heat of the bomb reaction, was then calculated in each case in $-\Delta U_R$ the change in energy content per mole, at constant volume, when each substance is at one atmosphere, using the corrections of Washburn.[7] With appropriate correction $-\Delta H_R$ the heat of combustion per mole at standard conditions and at constant pressure was calculated. Using the values of Rossini[8] for the heat of formation of water and carbon dioxide at 25° the standard heat of formation for each isomer was then calculated. The energy of isomerization was then found from the difference in this value for the two isomers. These results are summarized in Table II.

TABLE I

ISOTHERMAL HEAT OF COMBUSTION OF *cis*- AND *trans*-DECAHYDRONAPHTHALENE AT 25°

True mass, g.	Total heat[a] evolved, cal.	Heat from HNO_3, cal.	$-\Delta U_B/m$ cal. g.$^{-1}$	Deviation from mean
		cis		
0.74867	8131.37	6.16	10852.9	+1.6
.69029	7499.74	9.44	10850.9	−0.4
.70161	7624.34	12.20	10849.5	−1.8
.55941	6078.71	9.02	10852.0	+0.7
		cis Mean	10851.3	±1.1
		trans		
0.79086	8573.39	2.90	10836.9	−0.9
.66166	7170.52	1.44	10835.0	−1.0
.72526	7869.13	9.50	10837.0	+1.0
.72863	7898.34	3.64	10835.0	−1.0
		trans Mean	10836.0	±1.0

[a] Corrected for heat of stirring, evaporation, etc., and for the ignition energy.

TABLE II

THERMOCHEMICAL DATA FOR *cis*- AND *trans*-DECALIN AT 25° (CONVENTIONAL KILOCALORIES PER MOLE)

	cis	*trans*
$-\Delta U_B$	1500.1 ± 0.1	1498.0 ± 0.1
$-\Delta U_R$	1499.7 ± .1	1497.6 ± .1
$-\Delta H_R$ (combustion)	1502.4 ± .1	1500.3 ± .1
$-\Delta H_{298.1}$ (formation)	52.75	54.87

Heat of isomerization, *cis* (liquid) → *trans* (liquid). $-\Delta H = 2.12$ kcal./mole.

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(1) Published with the approval of the Monographs Publication Committee, Oregon State College, as Research Paper No. 42, School of Science, Department of Chemistry.

(2) Seyer and Walker, THIS JOURNAL, **60**, 2125 (1938); Theses, University of British Columbia.

(3) Roth and Lasse, *Ann.*, **441**, 52 (1925); Hückel, *ibid.*, **451**, 117 (1926).

(4) Hughes, Corruccini and Gilbert, THIS JOURNAL, **61**, 2639, 2925 (1939).

(5) Jessup and Green, *J. Research, Natl. Bur. Standards*, **13**, 496 (1934).

(6) Rossini, *Chem. Rev.*, **18**, 233 (1936).

(7) Washburn, *J. Research, Natl. Bur. Standards*, **10**, 525 (1930).

(8) Rossini, *ibid.*, **22**, 407 (1939).

The *cis* form proves to have a higher heat content than the *trans*, heat being evolved in changing from the former to the latter. The difference is not far from that predicted by the earlier work,[8] but the degree of certainty is very much improved.

There is obviously very little resonance energy in decalin, as may be shown by comparison of the heat of formation from gaseous carbon and atomic hydrogen with the bond energy of 18 C–H bonds and 11 C–C bonds using the values of Pauling.[9]

Bond energy, either form, 2215.0 kcal.; calculated heat of formation in gaseous state from gaseous atoms *cis*- −2215.8; *trans*- −2218.0 kcal. Utilized in these latter calculations is the latent heat of vaporization (10.5 kcal. mole^{-1}) taken from the data of Hertz.[10] The low energy of isomerization moreover ties in with the observation that aluminum chloride at room temperature catalyzes the change *cis* → *trans*.[11]

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Summary

1. The isothermal heats of combustion of *cis*- and *trans*-decahydronaphthalene have been determined at 25°.

2. The standard heat of formation and the heat of isomerization of the two forms have been calculated.

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[9] L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1939.

[10] Hertz, *Z. physik. Chem.*, **101**, 269 (1922).

[11] Zelinskii and Turnova-Pollak, *Ber.*, **65B**, 1299 (1932).

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[CONTRIBUTION FROM THE COBB CHEMICAL LABORATORY, UNIVERSITY OF VIRGINIA]

The Synthesis of Some Iodinated Aromatic Compounds

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The application of iodine compounds to clinical X-ray visualization and chemotherapy[2] has prompted the preparation of a series of aromatic iodine derivatives for biological experimentation.

On the assumption that a high percentage of iodine was desirable in these compounds, preliminary attempts have now been made to prepare derivatives of 2,4,6-triiodoaniline of possible therapeutic value. As the sulfanilamide derivative was considered interesting for this purpose, 2,4,6-triiodoaniline was treated with N-acetylsulfanilyl chloride under various conditions in different solvents, including dry pyridine, pyridine and acetone, dimethylaniline, and quinoline, but only starting material was recovered. The failure of the reaction is assumed to be the result of steric hindrance similar to that of other ortho substituted amines. In like manner, attempts to make 2,4,6-triiodophenylglycine, using formaldehyde and potassium cyanide,[3] ethyl iodoacetate, or ethyl iodoacetate with pyridine in chlorobenzene as a solvent, gave none of the desired compound. Another trial designed to prepare 2,4,6-triiodophenylurea, using nitrourea and 95% ethanol,[4] was also unsuccessful. It was found possible, however, to form 2,4,6-triiodoacetanilide with acetic anhydride and a drop of concentrated sulfuric acid. Like picramide, 2,4,6-triiodoaniline crystallized unchanged from acetic anhydride, and the addition of sulfuric acid was necessary to catalyze the reaction.

More reactive iodinated starting materials were found in 2,4-diiodoaniline[5] and 2,4,6-triiodophenol. N^4-Acetyl-N^1-2,4-diiodophenylsulfanilamide was made in good yield, and the corresponding N^1-2,4-diiodophenylsulfanilamide was obtained readily on hydrolysis with alcoholic hydrogen chloride. 2,4-Diiodophenylglycine could be made in only very low yield by the two methods tried for the formation of 2,4,6-triiodophenylglycine. Better results were obtained from the iodination of phenylglycine by the method of Waters,[5] which yielded reasonable amounts of the desired compound. Difficulties were also encountered in the preparation of 2,4-diiodophenylurea. It was necessary to add pyridine to decompose the nitrourea at room temperature, as

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[1] Smith, Kline and French Research Fellow.

[2] "New and Nonofficial Remedies," American Medical Association, Chicago, Ill., 1940, pp. 226, 289, 300, 302, 304.

[3] Schwalbe, Schulz, and Jochheim, *Ber.*, **41**, 3790 (1908).

[4] Buck and Ferry, THIS JOURNAL, **58**, 854 (1936).

[5] Waters, *J. Chem. Soc.*, 1060 (1933).