TABLE I

THE ENTROPY OF CYCLOPENTANE IN THE IDEAL GAS STATE

	Cal./deg./mole 230°K.	260°K.	323.2°K.
Calorimetric	65.26 ± 0.15	67.50 ± 0.15	71.2 ± 0.5
Translational + Rotational (σ = 10)	57.18	58.15	59.85
Vibrational	3.90	4.89	7.69
Total, D_{5h} (σ = 10)	61.08	63.04	67.54
Total, C_2 (σ = 2)	64.27	66.23	70.73
Total, C_s (σ = 1)	65.65	67.61	72.11
Total vibrational with γ_1 changed to 56 and γ_2 to 88	8.08	9.13	12.05
Total, D_{5h} (σ = 10) γ_1 = 56, γ_2 = 88 cm.$^{-1}$	65.26	67.28	71.90

179 (1936)] applied to his data and those of Kohlrausch and Seka [*Ber.*, **69**, 729 (1936)], namely

Ring: $\omega_1 = 886$; $\omega_2 = 1050$; $\omega_3 = 1050$; $\omega_4 = 1216$; $\omega_5 = 1216$; $\omega_6 = 967$; $\omega_7 = 967$; $\gamma_1 = 165$; $\gamma_2 = 285$; CH_2 internal: $^{10}\nu = 2900$; $^5\delta = 1446$; CH_2 waving: $^5\delta_1 = 772$; $^5\delta_2 = 1028$; $^5\delta_3 = 1283$

As can be seen, the experimental data fit best the value of $\sigma = 1$, corresponding to the C_s configuration. In order to get an idea of what revision in the frequency assignment would be necessary to get agreement for $\sigma = 10$, in the last two lines of Table I we have compared the experimental values with those calculated using the above frequency assignment except with $\gamma_1 = 56$ cm.$^{-1}$ and $\gamma_2 = 88$ cm.$^{-1}$ and taking $\sigma = 10$. These frequencies were chosen to give agreement at the lowest temperature. Inasmuch as the lowest of the frequencies in benzene is 406 cm.$^{-1}$, these values of γ are quite unlikely. Further, they give a poor fit with the calorimetric data at the higher temperatures. At present the indication is that the cyclopentane ring has the non-planar configuration C_s.

Inasmuch as strong hydrogen repulsions have been indicated in other compounds [Aston and Kennedy, THIS JOURNAL, **62**, 2567 (1940)], it is suggested that it is this repulsive action on the carbon tetrahedra that pushes one (or two) atoms out of the plane. We have also made similar comparisons on methylcyclopentane based on data of Huffman, Parks and Barmore [*ibid.*, **53**, 3876 (1931)] down to 90°K., which lead to the same conclusion. With cyclohexane, by the same method and taking $\gamma_1 = 377$, $\gamma_2 = \gamma_3 = 250$, we have found a configuration with $\sigma = 6$ as is to be expected. [It should be noted that Langseth and Bak, *J. Chem. Phys.*, **8**, 403 (1940), consider that the spectroscopic evidence points to a planar configuration ($\sigma = 12$), with little justification, however.]

Our results are in agreement with those of Beach from the electron diffraction by tetrahydrofuran which lead also to the adoption of a non-planar configuration [Beach, private discussions and *J. Chem. Phys.*, **9**, 54 (1941)].

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ON THE LUMINESCENT OXIDATION OF LUCIFERIN

Sir:

Bioluminescence, the result of the oxidation of luciferin by luciferase and oxygen, has been the subject of numerous studies from this Laboratory.[1] The following observations are reported since they throw some light on the nature of the luminescent reaction and the structure of the luciferin molecule. Application of ultramicro analysis[2] to the highly purified extracts of *Cypridina* luciferin[3] shows that carbon, hydrogen and oxygen are the only constituents (tests for nitrogen, sulfur, halogen and ash were all negative). Deduction from available evidence (conditions of benzoylation[3]; irreversible inhibition by cyanide[4]; irreversible step in the luminescent oxidation[5]) lead us to the conclusion that luciferin contains a keto-hydroxy side chain which is oxidatively degraded in the luminescent reaction. Evidence for a keto group was derived from the fact that the addition of hydroxylamine acetate gave a microcrystalline precipitate which is inactive toward luciferase, but on acid hydrolysis gave light with the enzyme. If our deduction as to the nature of the side chain and its role in the luminescent reaction is correct, the irreversible step[5] in the luminescent reaction may be formulated as

(1) E. N. Harvey, "Living Light, Princeton, 1940."
(2) D. G. Foulke and F. Schneider, *Ind. Eng. Chem., Anal. Ed.*, **10**, 104 (1938).
(3) R. S. Anderson, *J. Gen. Physiol.*, **19**, 301 (1935).
(4) A. C. Giese and A. M. Chase, *J. Cellular Comp. Physiol.*, **16**, 237 (1940).
(5) R. S. Anderson, *ibid.*, **8**, 26 (1936).

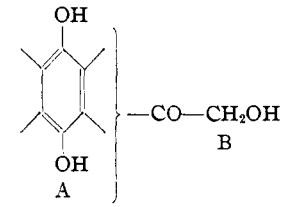
$$R{-}CO{-}CH_2{-}OH \xrightarrow{\text{luciferase}} R{-}COOH$$

Then the original material might be regenerated by the following series of reactions

$$R{-}COOH \xrightarrow{SOCl_2} R{-}COCl \xrightarrow{CH_2N_2}$$

$$R{-}CO{-}CHN_2 \xrightarrow{\text{dil. } H_2SO_4} R{-}CO{-}CH_2OH$$

We have carried out this series of operations starting with luciferase-oxidized luciferin. Since a trace of active luciferin remained in the starting material, tests with untreated fractions were run parallel to those with chemically treated fraction. The test consisted essentially of adding hydrosulfide to the test substance followed by luciferase and bubbling air through solution. The untreated fraction gave a constant dim light while a flash of much greater intensity followed by dimmed luminescence was observed in case of the treated fraction. The whole series of experiments was repeated with the same results. Interpretation of these observations and also the earlier ones, strongly suggests the validity of our hypothesis. Therefore, we propose the following partial structure for luciferin



Oxidation of A comprises the reversible oxidation of luciferin by oxygen.[5,6] The degradation of B forms the irreversible step in the luminescent reaction. The supply of *Cypridina* is extremely limited and the ease of auto-oxidation of luciferin renders chemical purification difficult. Therefore, we are attempting to confirm these observations and to determine the complete structure of the luciferin molecule by a synthetic approach.

We wish to thank Dr. E. N. Harvey for many stimulating discussions concerning this work. We are indebted to Dr. Aurin M. Chase for his many helpful suggestions and also for the samples of purified luciferin.

(6) A. M. Chase, *J. Cellular Comp. Physiol.*, **15**, 159 (1940).

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NEW BOOKS

Physical Chemistry for Colleges. By E. B. MILLARD, Professor of Physical Chemistry, Massachusetts Institute of Technology. Fifth Edition. McGraw-Hill Book Co., Inc., 330 West 42nd Street, New York, N. Y., 1941. ix + 600 pp. 70 figs. 16.5 × 23.5 cm. Price, $3.75.

The fifth edition of this well-known and widely used book has received painstaking revision, but the topics treated and the general arrangement of subject material remain essentially unchanged. In many instances the explanatory matter has been reorganized and revised to conform with the newer concepts; the derivations of some of the equations have been improved; the thermodynamic treatment has been expanded and the chapter on thermochemistry has been completely rewritten. New problems have been added and in all the book has been expanded by some seventy-six pages. It is certain that those who have been using this book as a text will appreciate the improvements which have been made.

F. E. BARTELL

Laboratory Manual of Elementary Organic Chemistry. By GEORGE HOLMES RICHTER, Assistant Professor of Organic Chemistry, The Rice Institute. John Wiley and Sons, Inc., 440 Fourth Avenue, New York, N. Y., 1940. 128 pp. Price, $1.25.

It is the author's stated purpose to provide a series of experiments which will be of special interest to students specializing in the biological sciences. It is in the accomplishment of this aim that this book differs from the usual organic laboratory manual. The major objective of each experiment is the illustration of an organic chemical reaction or principle, and this is accomplished in most cases by the use of compounds and reactions which are of importance to biology or medicine. In a short discussion following each of these exercises this relationship and the uses of the substances involved are pointed out.

The experiments appear to be carefully written with appropriate attention given to details of manipulations and safety.

The manual is quite suitable for a general organic chem-