Following Hope and Robinson's directions[5] for the preparation of anhydrocotarninenitromethane picrate, anhydrocotarninenitromethane was dissolved in aqueous acetic acid and an aqueous solution of picric acid was added. A solid picrate resulted which melted at 134–136°, when the melting point was taken with rapid heating, and sintered at 140° with melting at 142–144°, when the temperature was raised slowly. When mixed with cotarnine picrate, the melting point was 143–144°. A sample was submitted for analysis after two recrystallizations from absolute ethanol; yellow needles, m. p. 143–144°.

Anal. Calcd. for cotarnine picrate, $C_{18}H_{16}N_4O_{10}$: C, 48.22; H, 3.60; N, 12.50. Found: C, 48.35; H, 3.66; N, 12.14.

Summary

The elimination of nitromethane from 2-methyl-1-nitromethyl-1,2,3,4-tetrahydroisoquinoline and anhydrocotarninenitromethane and of phenylnitromethane from 2-methyl-1-(α-nitrobenzyl)-1,2,3,4-tetrahydroisoquinoline has been observed in the presence of picric acid.

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

Equilibrium Ratio of Rotational Isomers of *n*-Pentane: with Special Reference to its Difference from that of 1,2-Dichloroethane

BY SAN-ICHIRO MIZUSHIMA AND HIROATSU OKAZAKI

As shown in our preceding papers on the Raman effect, infrared absorption, dipole moment, and electron diffraction,[1] the molecules of 1,2-dichloroethane $ClH_2C–CH_2Cl$ in the gaseous and liquid states consist of the *trans* and the gauche forms, where the former is the configuration in which the two chlorine atoms are at the farthest distance apart and the latter differs from the former in an internal rotation by ±120° about the C–C bond as axis.

We determined also the equilibrium ratio of these two "rotational isomers" in the gaseous state by the measurement of dielectric constant and of the intensity ratio of two Raman lines or of two infrared absorption lines, one assigned to the *trans* form and the other to the gauche form.[1] From this equilibrium ratio the energy of the gauche molecule was found to be greater than that of the *trans* molecule by an amount of $\Delta E = 1.20$ kcal./mole. The intensity measurement made for the liquid spectra tells us that the situation is quite different in the liquid state. The relative number of molecules in the gauche form was found much larger than was expected from the value of ΔE stated above.[1a] This was explained[2] as due to the electrostatic interaction between the molecules in the liquid state: *i. e.*—while the *trans* molecule has no dipole moment, the gauche molecule has a considerable one and in consequence the energy of the gauche molecule is lowered by the electrostatic interaction to approach to that of the *trans* molecule.[3] If this explanation be appropriate, we expect for a non-polar substance that the value of ΔE in the liquid state will not be much different from that in the gaseous state. It would, therefore, be very interesting to measure the intensity change of the Raman spectrum of a non-polar liquid with temperature. With this object in view we have measured the Raman spectrum of *n*-pentane at 32° and at −72°.

For *n*-pentane there can be considered three rotational isomers of skeleton: the first one corresponding to the planar, zigzag form (four consecutive carbon atoms forming the *trans* configuration), the second one containing one gauche structure, and the third one containing two gauche structures. Of these three forms the first one is the most stable and the third one the most unstable, since in the first form all the movable groups (*i. e.*, CH_3– or CH_2–groups) are at the farthest distance apart.

The identification of the Raman lines to be assigned to the first form can at once be made from

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[1] The former part of this series of researches is summarized in: Mizushima and Morino, *Bull. Chem. Soc. Japan*, **17**, 94 (1942), (see also Mizushima, Morino and Takeda, *J. Chem. Phys.*, **9**, 826 (1941)) and the latter part is published in Mizushima, Morino, Watanabe, Simanouti, Yamaguchi, *etc.*, *Sci. Papers Inst. Phys. Chem. Research, Tokyo*, **39**, 387, 396, 401 (1942), **40**, 87, 100, 417, 425, 467 (1943), **42**, *Chem.*, 1, 5, 27 (1944), **42**, *Chem.*, 51 (1946).

[1a] *Cf.* Gerding and Meerman, *Rec. trav. chim. pays-bas*, **61**, 523 (1942). This paper is not available to the authors.

[2] Watanabe, Mizushima, and Masiko, *Sci. Papers Inst. Phys. Chem. Research, Tokyo*, **40**, 425 (1943).

[3] If we assume the same model of dielectrics as that of Onsager (THIS JOURNAL, **58**, 1486 (1936)) and consider a small cavity of radius a in the continuous medium of dielectric constant ϵ, a dipole of moment μ situated at the center of this spherical cavity will cause dielectric polarization in the continuous medium, which in turn exerts a field R (reaction field) upon the original dipole.

$$R = \frac{2(\epsilon - 1)}{2\epsilon + 1}\frac{\mu}{a^3}$$

Let us further assume that the gauche molecule can be represented by a sphere of radius a, at whose center the total permanent moment is located. The gauche molecule in the liquid state will then acquire an excess of electrostatic energy by an amount of

$$\Delta E' = \int_0^{\mu} -R\,d\mu = -\frac{(\epsilon - 1)}{2\epsilon + 1}\frac{\mu^2}{a^3}$$

as compared with that in the gaseous state (*i. e.*, of the free molecule). The corresponding energy change of the *trans* molecule with no moment is negligible. Introducing the moment value of the gauche molecule (2.55 D) into μ of the above equation, we see that the value of $\Delta E'$ is almost equal to the value of ΔE, and therefore, the energy of the gauche molecule approaches to that of the *trans* molecule in the liquid state (see footnote (2)).

our previous observation[4] on the change of Raman spectrum on solidification, since the solid consists only of the molecules of the first form. Thus the Raman line observed at 865 cm.$^{-1}$ is assigned to the first form and that observed at 838 cm.$^{-1}$ to the second form or to the third. The intensity ratio of these two lines was obtained from the microphotometer tracings of the Raman spectra photographed at the two temperatures, and was found as

$$I(838)/I(865) = 1.21 \text{ at } 305°\text{K.}$$
$$= 0.77 \text{ at } 201°\text{K.}$$

Then the energy difference ΔE between the first form and another can at once be calculated from:[4a]

$$\frac{1.21}{0.77} = e^{-\frac{\Delta E}{R}\left(\frac{1}{305} - \frac{1}{201}\right)}$$

and we have

$$\Delta E = 0.53 \text{ kcal./mole}^{4b}$$

Similarly from a pair of lines at 865 and at 764 cm.$^{-1}$ we obtain a value of $\Delta E = 0.70$ kcal./mole which is somewhat larger than the preceding one. The difference may merely be due to the experimental error, but we cannot deny the possibility that the line at 764 cm.$^{-1}$ belongs to the rotational isomer different from what we stated above with regard to the line at 838 cm.$^{-1}$: *i. e.*, we may assign the line at 764 cm.$^{-1}$ to the third molecular form which is more unstable than the second one. We are not, however, sure whether this assignment is appropriate, since the number of lines seems to be too small to account for the coexistence of three molecular forms.[5]

TABLE I

OBSERVED INTENSITY RATIO OF PAIRS OF LINES AT ν AND 865 CM.$^{-1}$

ν	$I(\nu)/I(865)$ at 201° K.	at 305° K.	ΔE kcal./mole
764	0.27	0.49	0.70
838	.77	1.21	.53

We have not yet observed the temperature dependence of the intensity ratio in the gaseous state, the accurate determination of which would be considerably difficult, but we have reason to believe that the values of ΔE obtained above are not much different from that of a free molecule, since these values are of the magnitude which would be expected from the steric repulsion between the moving groups about the C–C bond as axis.[6]

In any case we are sure that on liquefaction the energy difference between the rotational isomers of *n*-pentane does not change so much as in the case of dichloroethane and it is, therefore, reasonable that we explained the difference in the spectral intensity between the gaseous and liquid dichloroethane mainly by the electrostatic interaction between polar molecules.

Summary

The relative intensity of the Raman lines of *n*-pentane was measured at 32° and at −72° and from this experimental result the energy difference between the rotational isomers was calculated as 0.5 kcal./mole.

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[4] Mizushima and Simanouti, THIS JOURNAL, **71**, 1320 (1949).

[4a] See Langseth and Bernstein, *J. Chem. Phys.*, **8**, 410 (1940).

[4b] After the manuscript was submitted to the Editorial Board, Sheppard and Szasz (*J. Chem. Phys.*, **17**, 86 (1949)) reported the value of ΔE in excellent agreement with ours.

[5] The number of Raman lines observed for *n*-pentane is not larger than that observed for *n*-butane (see footnote (4)). It seems, therefore, probable to consider the coexistence of only two molecular forms for *n*-pentane as for *n*-butane. However, some Raman lines of *n*-pentane may escape detection because of their weak intensity and, therefore, we cannot deny the possibility of the coexistence of three molecular forms.

[6] The value of ΔE obtained by Pitzer (0.8 kcal./mole) in his calculation of entropies of *n*-butane and *n*-heptane is not much different from that obtained in the present experiment; see Pitzer, *Chem. Rev.*, **27**, 39 (1940), *J. Chem. Phys.*, **8**, 711 (1940).

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[CONTRIBUTION FROM (a) THE WELLCOME RESEARCH LABORATORIES AND (b) CHEMICAL INSTITUTE, UNIVERSITY OF MUNICH, GERMANY]

The Synthesis of Pterorhodin (Rhodopterin)[1,1a]

BY PETER B. RUSSELL,[a] ROBERT PURRMANN,[b] WERNER SCHMITT[b] AND GEORGE H. HITCHINGS[a]

Pterorhodin is a violet-red substance which is formed during autoxidation of acid solutions of crude butterfly wing pigments,[2] and xanthopterin[3] and erythropterin[3] of natural origin. Both Schöpf[5] and Hopkins[3] suggested that it was formed from erythropterin, but the proportion of pterorhodin obtainable from this source diminishes with increasing purity of the erythropterin.[6] Moreover, xanthopterin is not the precursor since synthetic xanthopterin fails to yield the substance.[4,7]

A structural formula for pterorhodin (I) was suggested by Purrmann and Maas[4] primarily on the basis of degradative experiments in which leucopterin (II) and xanthopterin-7-carboxylic acid (III) were obtained as the products of oxida-

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[1] Presented in part at the 115th meeting of the American Chemical Society at San Francisco, California, March 30, 1949.

[1a] Pterorhodin has been named first lepidoporphyrin,[2] then rhodopterin[3] by Hopkins, but Purrmann's proposal,[4] pterorhodin, is perhaps preferable since the substance is not a primary butterfly wing pigment.

[2] Hopkins, *Trans. Roy. Soc.* (*London*), **B186**, 661 (1895).

[3] Hopkins, *Proc. Roy. Soc.* (*London*), **B130**, 359 (1942).

[4] Purrmann and Maas, *Ann.*, **556**, 186 (1944).

[5] Schöpf and Becker, *ibid.*, **507**, 266 (1933).

[6] Purrmann and Eulitz, *ibid.*, **559**, 169 (1948).

[7] A. R. Todd, personal communication.