Raman spectrum of liquid heavy water and of ice.

The empirical treatment of the perturbing potentials as modified Morse functions leads to an estimate of the energy of the hydrogen bond in water as about 3 kcal. per mole per bond.

The essential agreement of the results of this analysis with X-ray data on liquid water is discussed and the usefulness of Raman spectra as tools for further studies of associated liquids is suggested.

STANFORD UNIVERSITY, CALIF.

NOTES

The Molecular Structures of the 2,3-Epoxybutanes: a Correction

BY L. O. BROCKWAY AND PAUL C. CROSS

In the recently published report of the electron diffraction investigation of the 2,3-epoxybutanes[1] it was incorrectly stated that the identification of the geometric isomers was the same as that found in the chemical[2] investigation. Because of this misapprehension the electron diffraction investigation has been repeated and extended, and the consideration of new molecular models has led to the assignment supported by the chemical investigation.

The original preparations were refractionated and samples were taken having the boiling point ranges, 52.9–53.7 and 59.3–59.9°, respectively, at 746 mm. For each substance the new electron diffraction photographs have a lighter background, the diffraction pattern is more distinct and measurements of the ring diameters are more reliable than on the earlier photographs. The same characteristic features appear as before, however; and although the photographs of the two substances again look very much alike, the chief distinguishing feature is still observed, i. e., photographs of the low boiling modification show a well-defined shoulder on the inside of the second strong maximum near $s = 10$ (see Fig. 1, reference 1).

(1) L. O. Brockway and Paul C. Cross. THIS JOURNAL, 58, 2407 (1936).

(2) C. E. Wilson and H. J. Lucas, ibid., 58, 2396 (1936).

In the models previously considered it was assumed that the strain introduced in the bond angles on each of the central carbon atoms by the formation of the three-membered ring was distributed only among the angles involving the carbon–oxygen bond. Of the six angles between the four bonds the angle in the ring is 57°26′, the other two strained angles are 125°10′, and the three remaining angles have the value 109°28′. It seems probable that the strain is more widely distributed; and accordingly new curves have been calculated on the basis of
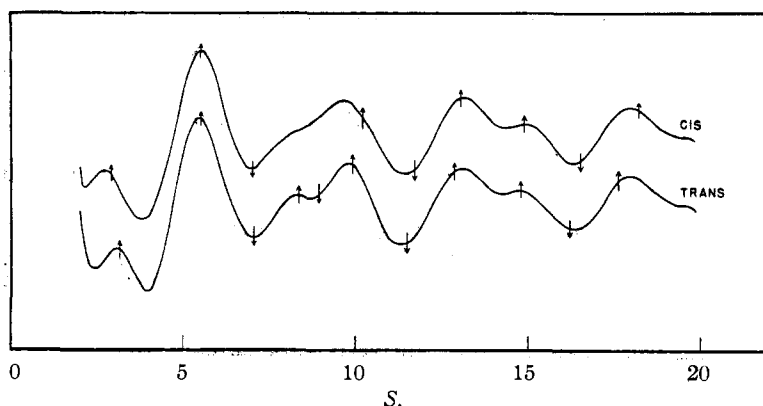

Fig. 1.—Theoretical electron scattering curves for models of the cis and trans 2,3-epoxybutanes in which five bond angles on each of the central carbon atoms divide equally the strain due to the formation of the three membered ring. The arrows represent maxima and minima observed on the photographs.

models in which the strain of the small angle is divided among four other angles and also on models in which all five of the other angles divide the strain. These curves are very similar, and the pair corresponding to a small angle of 57°26′ and five equal angles of 117°20′ is reproduced in Fig. 1. It will be observed that the inner

shoulder on the second strong maximum now appears in the curve for the trans form, and accordingly the modification which boils at 53.5° (746 mm.) has the trans configuration. It may be mentioned that the new photographs from each of the compounds show the inner maximum (near $s = 3$) with that for the trans form having a slightly greater s value in agreement with the curves. That this identification is not based on more extensive data is due to the fact that the two expressions for electron scattering by the cis and trans forms show only slight differences. In the chemical investigation[2] the trans form was identified as that one which was obtained in an optically active state and this choice is now supported by the electron diffraction result. The cis form is that boiling at 59.6° (746 mm.).

Accepting the chemical identification of the isomers, we see that the electron diffraction study offers proof that bending the carbon–oxygen bond in forming the three-membered ring also bends the other bonds from their "natural" or unstrained positions, since the model in which the bending effect is confined to the one bond leads to the wrong identification of the isomers.

The interatomic distances previously reported are still to be accepted since the new photographs and curves lead to the same dimensions for the molecules.

PASADENA, CALIF.   RECEIVED MARCH 29, 1937

Improved Preparation of Pentaacetyl-keto-fructose

BY FRANCIS B. CRAMER AND EUGENE PACSU

Pentaacetyl-keto-fructose, formerly designated as α-pentaacetylfructose, was first prepared by Hudson and Brauns[1] by the action of zinc chloride and acetic anhydride on fructose. The yield was less than 8% of the theoretical. Acetylation of fructose with acetic anhydride and pyridine gave rise to the same compound in less than 5% yield. When tetraacetylfructose is prepared by the improved method of Pacsu and Rich,[2] and this converted into the keto-pentaacetate by the procedure of Hudson and Brauns,[1] the yield, calculated on fructose, is increased to 36%. A procedure has now been worked out by which the keto-penta-

(1) Hudson and Brauns, THIS JOURNAL, 37, 2736 (1915).
(2) Pacsu and Rich, ibid., 55, 3018 (1933).

acetate may be obtained in about 50% yield by the direct acetylation of fructose without the isolation of an intermediate compound. The production of a good yield of pentaacetyl-keto-fructose appears to take place under conditions which facilitate the preliminary formation of a large amount of β-tetraacetylfructose. As amply demonstrated by Hudson and Brauns,[1] the keto-pentaacetate, once formed, is unaffected when heated with zinc chloride and acetic anhydride in the concentrations used in our experiments.

Experimental

Preparation of Pentaacetyl-keto-fructose.—Ten grams of finely powdered fructose was added in one portion to a solution of 1 g. of fused zinc chloride in 100 cc. of distilled acetic anhydride cooled in an ice-bath. The mixture was stirred vigorously at 0° for four hours, during which time most of the sugar dissolved. The temperature was then kept at 20–25° for one hour and finally at 50° for two hours. The cooled solution was stirred with an equal volume of water for one and one-half hours, further diluted, and neutralized with an excess of sodium bicarbonate. The chloroform solution of the gummy precipitate was united with the chloroform extracts of the water solution, then dried with calcium chloride, filtered, and evaporated to a sirup in vacuo. The sirup was dissolved in about 50 cc. of absolute ether, and the solution on standing overnight in the ice-box deposited 10.3 g. of crystalline pentaacetyl-keto-fructose, having $[\alpha]^{20}$D 33.5° in chloroform solution.

When half the above amount of acetic anhydride was used, the yield of the crystalline pentaacetate was 9 g. (42%). The keto-acetate was prepared more rapidly by stirring 10 g. of fructose with 50 cc. of acetic anhydride, and 1 g. of zinc chloride for one hour at room temperature and one hour at 50°. The yield was 7.5 g., or 35%. When 10 g. of fructose was stirred with the same acetylating solution at 50° for one hour and the reaction mixture worked up immediately, the yield was only 6 g., or 28%.

FRICK CHEMICAL LABORATORY
PRINCETON UNIVERSITY
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Physical Constants of Morpholine

BY V. H. DERMER AND O. C. DERMER

In preparing to study morpholine as an ionizing solvent, we have investigated its purification and measured some of its physical constants. Since the first shipment of morpholine we obtained apparently contained esters, we resorted to chemical purification through the acid oxalate. Later lots proved to be of extraordinary purity, requiring only to be dried over metallic sodium.

Table I gives the results of our measurements and calculations.