4. X-ray patterns of polyvinyl alcohol and polyvinyl acetate have been described.

5. Some reactions of polyvinyl alcohol with boric acid, ethyl oxalate, and bromine water have been investigated.

URBANA, ILLINOIS RECEIVED FEBRUARY 23, 1938

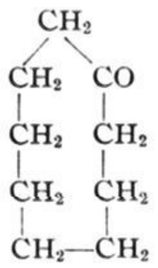
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

The Possible Asymmetry of a Monosubstituted Cyclononane[1]

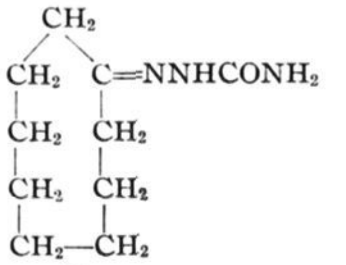
BY C. S. MARVEL AND DUDLEY B. GLASS

Construction of a model of a monosubstituted cyclononane using the atomic models developed by Stuart[2] has shown that two arrangements of the atoms are possible and that one of these models is a non-superimposable mirror image of the other (Fig. 1). Consequently it has seemed worth while to prepare a monosubstituted cyclononane and attempt its resolution.

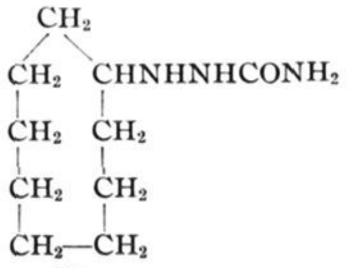
Cyclononanone (I) was prepared from the thorium salt of sebacic acid by the procedure of Ruzicka and Brugger.[3] It was then converted to the semicarbazone (II) for final purification and the pure semicarbazone was reduced to 1-cyclononylsemicarbazide (III).



I



II



III

The salts of this base with Reychler's *d*-camphorsulfonic acid and with *d*-α-bromocamphor-π-sulfonic acid were prepared and submitted to fractional crystallization. No evidence of resolution was obtained.

Our experiments on this cyclononane derivative furnish evidence that these rigid models of molecules do not present a true picture of the flexibility of the molecules themselves. It is of interest to note that the cyclohexane molecule constructed from the Stuart atomic models cannot be easily shifted from the "boat" to the "chair" form. This shift must actually occur easily in the cyclohexane molecule.[4]

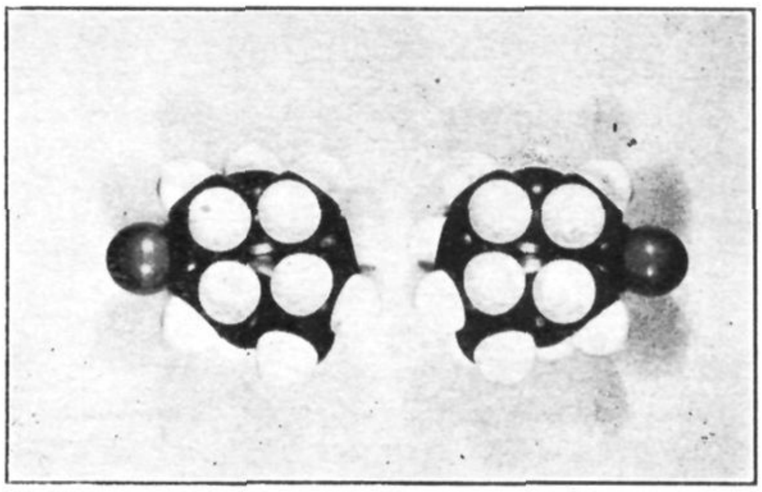


Fig. 1.

In connection with this work some new derivatives of cycloöctane have been prepared in order to develop methods of procedure with these homologs before carrying out reactions with the difficultly obtainable cyclononane derivatives.

Experimental

Cycloöctanone semicarbazone, m. p. 168–169°, was prepared from thorium azelate by the method of Ruzicka and Brugger.[5]

Anal. Calcd. for $C_9H_{17}ON_3$: N, 22.95. Found: N, 22.99.

Cyclononanone semicarbazone, m. p. 178–179°, was obtained in a similar manner from thorium sebacate. Ruzicka and Brugger[3] report that this compound melts at 178° and Ziegler and Aurnhammer[6] report the melting point as 184°. An analysis of our product indicated that it was very pure.

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(1) The concept that a monosubstituted cyclononane might exist in two optically active forms arose during a discussion between the late W. H. Carothers, J. B. Conant, B. S. Garvey, John R. Johnson and one of the authors on the evening of December 31, 1935, during the sixth National Organic Chemistry Symposium at Rochester, N. Y.—C. S. M.

(2) Stuart, *Z. physik. Chem.*, **B27**, 350 (1934).

(3) Ruzicka and Brugger, *Helv. Chim. Acta*, **9**, 389 (1926).

(4) Professor W. H. Mills first pointed out this weakness of the Stuart models to us. He also predicted that the resolution of a monosubstituted cyclononane would not be accomplished.

(5) Ruzicka and Brugger, *Helv. Chim. Acta*, **9**, 339 (1926).

(6) Ziegler and Aurnhammer, *Ann.*, **513**, 43 (1934).

Anal. Calcd. for $C_{10}H_{19}ON_3$: N, 21.30. Found: N, 21.31.

1-Cycloöctylsemicarbazide and 1-Cyclononylsemicarbazide.—The semicarbazones were reduced to semicarbazides by a method similar to that which has been used by Poth and Bailey[7] for the catalytic reduction of semicarbazones. To a solution of 1.83 g. of cycloöctanone semicarbazone in 30 cc. of 50% methanol was added 1.25 cc. of concentrated hydrochloric acid and 0.04 g. of platinum oxide catalyst.[8] The reduction was carried out in the usual hydrogenation outfit under a hydrogen pressure of about forty-five pounds (3 atm.). Reduction was complete in fifteen minutes. The solution was filtered to remove the catalyst and the solvent was evaporated under reduced pressure. The residue was dissolved in 60 cc. of a 25% solution of ethanol in water and the free base was liberated by the addition of concentrated aqueous ammonia. The solution was heated to boiling and then allowed to cool. The free base crystallized in large, shiny plates. The yield was 1.5 g. (81%). After two recrystallizations from dilute ethanol the 1-cycloöctylsemicarbazide melted at 183°.

Anal. Calcd. for $C_9H_{19}ON_3$: N, 22.69. Found: N, 22.80.

In a similar manner reduction of 1.05 g. of cyclononanone semicarbazone dissolved in 80 cc. of cold (−10°) 50% methanol containing 0.6 cc. of concentrated hydrochloric acid in the presence of 0.05 g. of platinum oxide catalyst[8] was complete in two hours. The yield was 0.96 (91%) of 1-cyclononylsemicarbazide, m. p. 156°.

Anal. Calcd. for $C_{10}H_{21}ON_3$: N, 21.09. Found: N, 21.03.

1-Cycloöctylsemicarbazide *d*-Camphor-10-sulfonate.—A mixture of 1 g. of cycloöctylsemicarbazide and 1.26 g. of *d*-camphor-10-sulfonic acid in 100 cc. of dry ethyl acetate was heated to boiling. The desired salt separated from the solution. The mixture was cooled and the salt was collected on a suction filter and washed with ethyl acetate. It was then dissolved in 20 cc. of a hot mixture of *n*-propyl acetate (88%) and *n*-propyl alcohol (12%). On allowing this solution to stand at 7° for forty-eight hours, the salt separated. The yield was 2.04 g. (90%) of a product, m. p. 169–170°, $[\alpha]^{27}_D$ 26.4 ± 1° (*c* 0.8, chloroform).

Anal. Calcd. for $C_{19}H_{35}O_5N_3S$: C, 54.65; H, 8.45; N, 10.06. Found: C, 54.75; H, 8.23; N, 10.24.

1-Cyclononylsemicarbazide *d*-Camphor-10-sulfonate.—A solution of 0.8 g. of 1-cyclononylsemicarbazide and 0.93 g. of *d*-camphor-10-sulfonic acid in 20 cc. of *n*-propyl acetate was allowed to stand about fifty hours at 7°. On filtering the solution 1.58 g. (91%) of the salt (fraction A) was obtained. This fraction melted at 95–115°; $[\alpha]^{28}_D$ 19.1 ± 0.5° (*c* 1.47, methanol).

Anal. Calcd. for $C_{20}H_{37}O_5N_3S$: C, 55.65; H, 8.64; N, 9.74. Found: C, 55.64; H, 8.36; N, 9.80.

A solution of 1.4 g. of this salt (fraction A) in 45 cc. of *n*-propyl acetate was allowed to stand for forty-eight hours at 7°. The crystals (fraction B) which separated were collected on a filter and then allowed to stand for four days at room temperature with 20 cc. of *n*-propyl acetate. This solution was filtered to obtain a crop of crystals (fraction C) which melted at 97–112°; $[\alpha]^{28}_D$ 19.9 ± 0.5° (*c* 2.1, methanol).

Anal. Calcd. for $C_{20}H_{37}O_5N_3S$: C, 55.65; H, 8.64; N, 9.74. Found: C, 55.71; H, 8.39; N, 9.46.

The methanol solution used for determining the rotation was evaporated to dryness by a current of air at room temperature and the residue was dissolved in dilute ethanol. Addition of concentrated ammonium hydroxide precipitated 1-cyclononylsemicarbazide which showed no rotation in methanol solution.

The mother liquors from fraction B were evaporated under reduced pressure to a volume of about 20 cc. This solution was allowed to stand for about seventy-two hours at 7° and the salt which crystallized was filtered off. This salt melted at 95–110°; $[\alpha]^{28}_D$ 19.8 ± 0.5° (*c* 1.7, methanol).

Anal. Calcd. for $C_{20}H_{37}O_5N_3S$: C, 55.65; H, 8.64. Found: C, 55.85; H, 8.71.

The mother liquors from which this salt was isolated were evaporated to dryness, the residue dissolved in dilute ethanol and the free base liberated by the addition of ammonium hydroxide. The free base showed no optical activity in methanol solution.

1-Cyclononylsemicarbazide *d*-α-Bromocamphor-π-sulfonate.—To a solution of 1.22 g. of *d*-α-bromocamphor-π-sulfonic acid in 20 cc. of water was added a suspension of 0.78 g. of 1-cyclononylsemicarbazide in 30 cc. of water. The mixture was warmed on the water-bath for about thirty minutes and then allowed to stand at room temperature for about twenty-four hours. The salt crystallized and was collected on a suction filter. The yield was 1.7 g. (85%) of a product (fraction A), m. p. 106–111°; $[\alpha]^{29}_D$ 56.4 ± 0.5° (*c* 2.374, methanol).

Anal. Calcd. for $C_{20}H_{36}O_5N_3SBr$: C, 47.05; H, 7.11. Found: C, 46.92; H, 7.26.

The mother liquor from which this crop of crystals had separated was made alkaline with ammonium hydroxide solution and the free base (m. p. 152–153°) was dissolved in methanol. This solution possessed no optical activity.

A solution of 1.4 g. of the salt obtained above (fraction A) was dissolved in 200 cc. of water. There was a slight trace of insoluble material which was removed by filtration. The solution was then evaporated slowly by means of a gentle current of air until the volume was 100 cc. On filtering this solution 0.68 g. of salt (fraction B) was obtained. This fraction was dissolved in 100 cc. of water and the solution concentrated as before to 60 cc. The salt which crystallized was collected on a filter. This fraction (C) weighed 0.27 g.; m. p. 106–111°; $[\alpha]^{29}_D$ 56.4 ± 0.5° (*c* 2.156, methanol).

Anal. Calcd. for $C_{20}H_{36}O_5N_3SBr$: C, 47.05; H, 7.11; N, 8.23. Found: C, 46.98; H, 7.19; N, 8.34.

The free base obtained from this salt showed no optical activity in methanol solution.

The mother liquors from fraction C were concentrated to 15 cc. and the salt which had separated was collected on a filter. This fraction (D) weighed 0.30 g.; m. p. 106–111°; $[\alpha]^{29}_D$ 58.3 ± 0.5° (*c* 1.122, methanol).

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[7] Poth and Bailey, THIS JOURNAL, **45**, 3001 (1923).

[8] Adams, Voorhees and Shriner, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1932, pp. 452, 453.

The mother liquors from fraction B were concentrated to 60 cc. and 0.25 g. of salt (fraction E) obtained; m. p. 106–112°, $[\alpha]^{29}\text{D}$ 57.5 ± 0.5° (*c* 1.895, methanol).

The mother liquors from fraction E were concentrated to 30 cc. and 0.20 g. of salt (fraction F) obtained; m. p. 106–112°; $[\alpha]^{29}\text{D}$ 57.9 ± 0.5° (*c* 1.425, methanol).

Anal. Calcd. for $C_{20}H_{36}O_5N_3SBr$: C, 47.05; H, 7.11; N, 8.23. Found: C, 46.78; H, 7.19; N, 8.24.

The mother liquors from fraction F were evaporated to dryness and the residue taken up in dilute ethanol. The free 1-cyclononylsemicarbazide thus obtained showed no rotation in a methanol solution.

While the various fractions of salt showed slight differences in specific rotation, no evidence of activity in the free base was detected. This indicated that the variations in rotation of the various portions of the salt might well be due to differences in the concentrations used in determining their rotations. Fractions C and D seemed most likely to be pure and yet their specific rotations differed by 1.9°. If it is assumed that this difference is due to a dilution effect and all rotations are recalculated using a factor to offset dilution, the following values for $[\alpha]^{29}\text{D}$ (*c* 2, methanol) are obtained:

Fraction A, 57.1 ± 0.5°; Fraction C, 56.7 ± 0.5°; Fraction D, 56.7 ± 0.5°; Fraction E, 57.3 ± 0.5°; Fraction F, 56.9 ± 0.5°.

Summary

1. 1-Cycloöctylsemicarbazide and 1-cyclononylsemicarbazide have been described.
2. The *d*-camphor-10-sulfonate and the *d*-α-bromocamphor-π-sulfonate of 1-cyclononylsemicarbazide were fractionally crystallized but no evidence of resolution was obtained.

URBANA, ILLINOIS RECEIVED MARCH 7, 1938

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

Amorphous Carbon Resistance Thermometer-Heaters for Magnetic and Calorimetric Investigations at Temperatures below 1°K.

BY W. F. GIAUQUE, J. W. STOUT AND C. W. CLARK

In various magnetic and calorimetric experiments in the region below 1°K. previously reported from this Laboratory magnetic susceptibility has been used to measure temperature. At the same time Giauque and MacDougall[1] pointed out that magnetic susceptibility is not appreciably useful for the purpose of denoting temperatures in the presence of any considerable magnetic field. Since in practice it is necessary to perform experiments at temperatures below 1°A. in a thermally isolated system, the only type of susceptibility which can be measured conveniently is the adiabatic susceptibility. The adiabatic differential susceptibility, $(\partial\mathbf{I}/\partial\mathbf{H})_S$, is of considerable importance in the application of thermodynamics to magnetic phenomena. **I, H** and S refer to the intensity of magnetization, field strength and entropy, respectively.

We recall[1a] that in an ideal paramagnetic system, at a temperature where the heat capacity due to the vibrations of the solid has approached zero, $(\partial\mathbf{I}/\partial\mathbf{H})_S$ is zero under all conditions. The reason for this is that the intensity of magnetization and entropy both depend on the magneton distribution among the various quantum states; thus constant S is equivalent to constant **I**. It is of interest to note that only the existence of magnetic interactions leading to non-ideal paramagnetism, and a resultant heat capacity, has made it possible for the various experimenters to use magnetic susceptibility as a measure of temperature below 1°A.

At high fields the interionic magnetic interactions become nearly negligible in comparison with the applied field and the value of $(\partial\mathbf{I}/\partial\mathbf{H})_S$ does approach zero. This is shown experimentally by the curves in Fig. 1. The data used in plotting these curves have been taken from the work of Giauque and MacDougall.[2] The values of the adiabatic differential susceptibility are given as a function of magnetic field strength along constant entropy paths. Not only does Fig. 1 show that the quantity $(\partial\mathbf{I}/\partial\mathbf{H})_S$ drops to values too low to be of use in denoting temperature but it also shows that a given value of $(\partial\mathbf{I}/\partial\mathbf{H})_S$ does not uniquely determine a given value of temperature. Giauque and MacDougall[2] have also shown that data such as are illustrated in Fig. 1 may be used in combination with well-known thermodynamic equations to calculate the change of thermodynamic temperature along such an adiabatic path and thus one may know the temperature corresponding to any value of mag-

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[1] (a) Giauque and MacDougall, THIS JOURNAL, **57**, 1175 (1935); (b) Giauque, *Ind. Eng. Chem.*, **28**, 743 (1936); (c) Proc. VIIth Inter. Congress Refrig., (1936).

[2] Giauque and MacDougall, THIS JOURNAL, **60**, 376 (1938).