[CONTRIBUTION FROM THE BUREAU OF MINES, UNITED STATES DEPARTMENT OF COMMERCE]

STEREO-ISOMERIC FORMS OF BIS(TRIMETHYLETHYLENE NITROSATE)[1]

BY C. A. TAYLOR[2] AND WM. H. RINKENBACH[3]

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While carrying out a program of work on initiators suggested by Dr. C. E. Munroe, Chairman of the Committee on Explosives Investigations of the National Research Council, bimolecular amylene nitrosate was prepared. Certain characteristics of this compound were observed which do not appear to have been recorded by Guthrie,[4] Wallach,[5] Denjanow,[6] Schmidt,[7] or Cusmano.[8]

Preparation

The compound was prepared by three methods, as follows.

1. Nitrogen dioxide formed by heating dry lead nitrate was passed through amylene the crystalline deposit washed with 96% ethyl alcohol, and portions were recrystallized from benzene and ether. After drying, each melted at 86.5° with decomposition. After storage in a desiccator over sulfuric acid for two weeks, the second melted and decomposed at 88.8°, this checking Wallach's value of 89°.

2. Oxides of nitrogen from arsenious oxide and nitric acid (d., 1.42 were passed through a mixture of 25 cc. of amylene with 50 cc. of glacial acetic acid. Crystals separated after several hours. These were drained and washed with small portions of cold water, 95% ethyl alcohol, and ether. The weight of dry product was 5.2 g. It softened and melted with decomposition over the range 81–85°. The material was dissolved in boiling benzene, the solution filtered, and the solute allowed to crystallize with partial evaporation of the benzene. The crystals were washed with small portions of ether and dried.

The microscope showed that these crystals consisted of a mixture of minute, colorless, monoclinic or triclinic needles with prism or pinacoidal faces well developed, and pseudo-cubes probably of the triclinic system with well-developed pyramids, triclinic prisms, and basal pinacoids. The

[1] Published with approval of the Director, U. S. Bureau of Mines.

[2] Explosives chemist, Pittsburgh Experiment Station, U. S. Bureau of Mines.

[3] Assistant explosives chemist, Pittsburgh Experiment Station, U. S. Bureau of Mines.

[4] Guthrie, *J. Chem. Soc.*, **13**, 45, 129 (1861); *Ann.*, **116**, 234 (1860); **119**, 83 (1861).

[5] Wallach, *Ann.*, **241**, 288 (1887); **245**, 241 (1888); **248**, 161 (1888); **262**, 324 (1891).

[6] Denjanow, *Ann. Inst. Agron. Moscou*, [4] **4**, 155 (1898); *Chem. Centr.*, **70**, I, 1064 (1899).

[7] Schmidt, *Ber.*, **35**, 2323, 2336, 3721 (1902).

[8] Cusmano, *Gazz. chim. ital.*, **40**, II, 525 (1910). *Atti. accad. Lincei*, **22**, I, 225 (1912).

pseudo-cubes were much the larger, and when separated and rinsed with ether, melted with decomposition at 93.5–94°, while the residue of needle-like crystals which contained some small pseudo-cubes melted at 91° with decomposition; the refractive indices of both forms were 1.515 and 1.620.

3. A mixture of 25 cc. of amylene, 25 cc. of glacial acetic acid, and 37 cc. of amyl nitrite was cooled with ice and treated with 20 cc. of nitric acid (d., 1.39) in small portions during stirring. The reaction became violent when not checked by cooling.

The solid product was washed with water, 95% ethyl alcohol, and ether and dried. The microscope showed that it consisted of colorless, irregular plates or aggregates of the needle form. No needles or pseudo-cubes could be found. It melted with decomposition at 85–86° and its refractive indices were 1.515 and 1.620.

The third experiment was repeated. The yield was 9.98 g. of colorless plates with the same refractive indices, and melting at 90.3° with decomposition. These were dissolved in 3 liters of ether at room temperature, filtered, and evaporated to dryness at room temperature. The needles deposited were dried in a vacuum desiccator over sulfuric acid. Determinations of decomposition points gave 91.9°, 90.4°, 88.8° and 89.2°. Values of 89.6° and 90.3° were obtained, after further storage in the desiccator for two weeks.

The products obtained in Expts. 1 and 2 were used to prove the possibility of converting one crystal form into the other by means of solvents, and the results are given in Table I.

TABLE I

TRANSFORMATION OF CRYSTAL FORMS

Crystal form	Solvent	Soln. temp.	Evap. at temp. of	To	Solids resulting Fract. 1	Fract. 2
Plates	Ether	Boiling	Room	Half	Need. 87.6°	
Plates	Ether	Boiling	Boiling	Dryness	Cubes	Needles
Plates	Benzene	Room	Room	Tenth	Cubes, 94–5°	Needles
Needles	Benzene	Room	Room	Dryness	Cubes[a]	
Cubes	Ether	Boiling	Room	Dryness	Cubes	Needles, 89.5°, 88.5°
Cubes	Ether	Boiling	Boiling	Dryness	Cubes, Needles	Mixture A
Mixt. A	Ether	Boiling	Boiling	Dryness	Needles, Cubes	Mixture B
Mixt. B	Ether	Boiling	Boiling	Dryness	Needles only	
Needles	Benzene	Boiling	Room	Dryness	Cubes, 98.5°, Needles	Mixture C
Needles	Benzene	Boiling	Room	Dryness	Cubes	Needles

[a] These cubes melted at 94.3° and 93.2° and after recrystallization from C_6H_6 melted at 96.3° and 97.2° with decomposition.

The information in Table I proves the transformation of either form to the other and confirms Wallach's observation of the existence of two forms.

Determinations of Molecular Weights

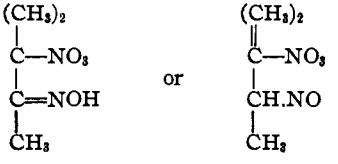
Determinations of molecular weights with benzene and nitrobenzene as solvents for both crystal forms were carried out with the following results: Needles, 325, 325, 351, 315, 351, av. 332; pseudo-cubes, 336, 336, 332, av. 335. As the molecular weight of unimolecular amylene nitrosate is 162.1, this shows that both crystal forms are bimolecular. Schmidt had already found this to be true of the needles.

A solution of each crystal form in benzene was tested with a polariscope and found to be optically inactive. Either form can exist in cold benzene, for crystals were frozen out of such a solution, and filtered off. A few small cubes were found, but the remainder of the material consisted of needle aggregates.

From these results we must conclude that bis(trimethylethylene nitrosate) exists in two solid, optically inactive, stereo-isomeric forms which are transformable, bimolecular forms of amylene nitrosate.

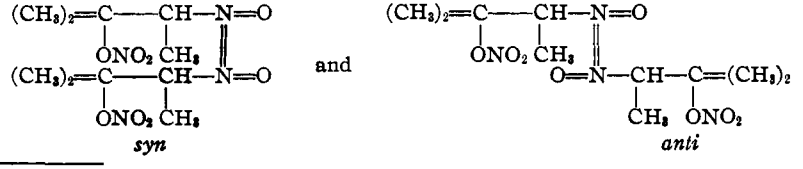
Structure

Wallach studied the structure of solid amylene nitrosate but did not discover that it is bimolecular. He showed that it has the structure



Schmidt isolated amylene nitrosate as a greenish-blue liquid giving the Liebermann nitroso reaction, and found the solid form to be bimolecular and easily dissociated when its solutions are heated. These facts are in accordance with those found by Bamberger and Seligman,[9] Behrend and König,[10] and Harries,[11] in the study of nitroso-butane, bis(nitrosylbenzyl), and nitroso-*iso*propyl-acetone and indicate a linkage between the nitroso nitrogens in the bimolecular form.

As two modifications of the bimolecular form exist, these can be represented graphically as having the probable structures



[9] **Bamberger and Seligman,** *Ber.*, **36,** 685 (1903).

[10] Behrend and König, *Ann.*, **263,** 212 (1891).

[11] Harries, *Ber.*, **36,** 1069 (1903).

Of these, it is probable that the *syn* form represents the needle-like crystals, and the *anti* form represents the pseudo-cubes. Hantzsch[12] showed that the *syn* compounds are, as a rule, of lower melting point and less stable than the *anti* type, into which they have a tendency to be transformed.

Properties

Both forms are insoluble in water, slightly soluble in cold alcohol, and fairly soluble in ether, carbon disulfide, acetone, benzene, chloroform, nitrobenzene and hot alcohol. The pseudo-cubes appear to be less soluble in ether than the needle form. The substance burns with a clear, yellow flame, but is not sensitive to percussion and can be only partly detonated by mercury fulminate. When brought in contact with concd. sulfuric acid it is violently decomposed with the evolution of fumes. Both forms are easily decomposed by heating, and on being stored in a desiccator over sulfuric acid for several months gradually decompose with the liberation of gas and the formation of an oily residue, but the pseudo-cubes are more stable in this respect than the needles. When either form is dissolved, a light blue coloration is frequently developed, and this becomes more intense as the temperature is raised. The melting points of the needles ranged from 86 to 90.4°, and of the pseudo-cubes from 93.2 to 98.5°; decomposition ensued in all cases.

Acknowledgment

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Summary

Bis(trimethylethylene nitrosate), solid amylene nitrosate, has been found to exist in two optically inactive crystal forms, needles and pseudo-cubes, having different melting points. Transformation from one form to the other can be brought about by the action of heat and solvents, and this is reversible.

Both forms are relatively unstable, the needles being more so than the cubes.

Stereo-isomeric structures probably representing these forms have been given.

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[12] Hantzsch, *Ber.*, **27**, 1702 (1894); **28**, 676, 1734 (1895).