

These data correspond to values of  $\alpha$  of 1.06 and 1.03, again indicating that exchange is complete before chlorination takes place.

While these experiments are of a preliminary nature they do indicate that in the present favorable case there is no indication but that the velocity of the exchange reaction is far greater than that of the chlorination. As an investigation of chlorination reactions the method seems to hold little promise. It is, of course, not impossible that the  $\text{Br}_2\text{-Br}^-$  or the  $\text{I}_2\text{-I}^-$  exchanges might be sufficiently slow so that significant measures of rates of halogenation could be obtained in these cases.

The author wishes to express his indebtedness to Prof. Ernest C. Pollard of the Sloane Physics Laboratory in Yale University through whose kindness the radioactive samples were made available.

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### Crystal Form of Sucrose Octaacetate

By C. D. WEST

When an acetone solution of sucrose octaacetate<sup>1</sup> is allowed to stand at room temperature for several weeks, well-formed prisms of m. p. 84.5°, density 1.335, develop which are suitable for goniometric measurement. The expectation that this optically active molecule would crystallize in one of the enantiomorphous symmetry classes is confirmed by the finding of orthorhombic bisphenoidal symmetry (point group V), as shown by the accompanying orthogonal projection.

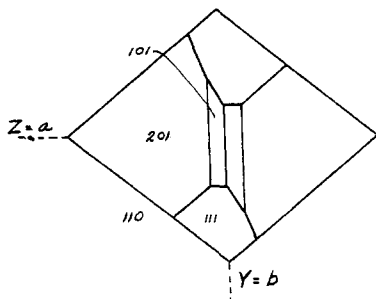


Fig. 1.—End faces and optical orientation.

The elements as calculated for a single crystal, the best of several measured, are set out in the table.

(1) From Niacet Chemicals Corporation, Niagara Falls, N. Y.

TABLE I

TWO CIRCLE ANGLES OF SUCROSE OCTAACETATE  
 $a:b:c = 1.2156:1:0.4605$ ;  $p_0:q_0:r_0 = 0.3789:0.4605:1$

hkl	Faces	Measured		Mean		Calculated	
		$\varphi$	$\rho$	$\varphi$	$\rho$	$\varphi$	$\rho$
110	4	39°27'	90°0'	39°26½'	90°0'		
101	2	90 0	20 16	90 0	20 45		
201	2	90 0	37 10	90 0	37 9		
111	2	39 26	30 48	39 26½	30 48½		

Cleavage planes are absent, and doubly terminated prisms were not noted. Crystals from ethanol solution have the same melting point and show the same faces. Optically the crystals are biaxial negative with the orientation  $\alpha//c$ ,  $\beta//b$ ,  $\gamma//a$ ; the refractive indices are identical with Brandt's published values, namely,  $\alpha = 1.470$ ,  $\beta = 1.488$ ,  $\gamma = 1.500$ , all  $\pm 0.002$  (2). Dispersion of the optic axes was not observed. The present crystals are thus identified with the stable, unsolvated form of sucrose octaacetate of m. p. 89° in the pure state.<sup>2</sup>

For the glassy form of this material the reported constants  $n_{20D} = 1.4660$ ,  $d = 1.283$  yield the specific refraction  $\frac{n^2 - 1}{n^2 + 2} \cdot \frac{1}{d} = 0.2164$ . The same constant for the crystals, as calculated from the average refractive index 1.486, is 0.2150.

The writer is indebted to Dr. Harry Berman for the opportunity to make the foregoing angle measurements at the Harvard Mineralogical Laboratories.

(2) In Linstead, Rutenberg, Dauben and Evans, *THIS JOURNAL*, **62**, 3260 (1940).

(3) Cox, Ferguson and Dodds, *Ind. Eng. Chem.*, **25**, 968 (1933).

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## NEW COMPOUNDS

### Derivatives of Piperazine. XIX. Reactions with Aryl Sulfonyl Chlorides and Aryl Sulfonic Acids

**N,N'-Bis-(arylsulfonyl)-piperazines.**<sup>1</sup>—The benzene, *p*-toluene, *p*-bromobenzene, and 2-nitrotoluene sulfonyl derivatives were prepared by adding with stirring a hot ethanolic solution of 0.1 mole of the appropriate sulfonyl chloride to an ethanolic solution of 0.05 mole (9.7 g.) of piperazine hexahydrate which contained a suspension of 6 g. of anhydrous sodium carbonate. The *o*-toluenesulfonyl derivative was prepared by gently refluxing 34 g. of *o*-toluenesulfonamide, 65 g. of ethylene bromide, and 30

(1) The melting points of N,N'-bis-(benzenesulfonyl)-piperazine<sup>1</sup> and N,N'-bis-(*p*-toluenesulfonyl)-piperazine<sup>2</sup> have been reported in the literature as being 282–283 and 286°, respectively, values which are lower than those which we have found for these compounds.

TABLE I<sup>a</sup>  
 N,N'-BIS-(ARYLSULFONYL)-PIPERAZINES AND N,N'-PIPERAZINIUM BIS-(ARYLSULFONATES)

R	M. p., °C. (cor.)	Yield, %	Formula	Analyses, %			
				Nitrogen		Sulfur	
				Calcd.	Found	Calcd.	Found
N,N'-Bis-(R-sulfonyl)-piperazine							
Benzene	291.3-291.7	83	C <sub>16</sub> H <sub>18</sub> N <sub>2</sub> O <sub>4</sub> S <sub>2</sub>	7.65	7.56		
<i>p</i> -Toluene	298.4-298.6	35	C <sub>15</sub> H <sub>22</sub> N <sub>2</sub> O <sub>4</sub> S <sub>2</sub>	7.11	7.01		
<i>o</i> -Toluene	209.0-209.4	23	C <sub>15</sub> H <sub>22</sub> N <sub>2</sub> O <sub>4</sub> S <sub>2</sub>	7.11	7.15	16.26	16.25
<i>p</i> -Bromobenzene	Not below 300	25	C <sub>16</sub> H <sub>14</sub> Br <sub>2</sub> N <sub>2</sub> O <sub>4</sub> S <sub>2</sub>	5.35	5.55	12.23	12.47
2-Nitrotoluene	278.0-278.3	51	C <sub>15</sub> H <sub>20</sub> N <sub>2</sub> O <sub>5</sub> S <sub>2</sub>	11.57	11.52	13.24	12.95
N,N'-Piperazinium Bis-(R-sulfonate)							
Benzene	Not below 300	57	C <sub>16</sub> H <sub>22</sub> N <sub>2</sub> O <sub>6</sub> S <sub>2</sub>	6.96	6.84	15.94	15.88
<i>p</i> -Toluene	Not below 300	80	C <sub>15</sub> H <sub>26</sub> N <sub>2</sub> O <sub>6</sub> S <sub>2</sub>	6.51	6.53	14.67	14.45
4-Nitrochlorobenzene	Not below 300	68	C <sub>16</sub> H <sub>13</sub> Cl <sub>2</sub> N <sub>2</sub> O <sub>10</sub> S <sub>2</sub>	9.98	9.98	11.43	11.27
2,5-Dichlorobenzene	Not below 300	62	C <sub>16</sub> H <sub>13</sub> Cl <sub>4</sub> N <sub>2</sub> O <sub>6</sub> S <sub>2</sub>	5.19	5.04	11.87	11.68

<sup>a</sup> Previous preparations of symmetrical sulfonyl derivatives have been carried out by Marckwald and von Droste-Huelshoff, *Ber.* **31**, 3261 (1898); Peacock and Dutta, *J. Chem. Soc.*, 1303 (1934); Kermack and Tebrich, *ibid.*, 202 (1940); Gough and King, *J. Chem. Soc.*, 2426 (1928), prepared a piperazinium sulfonate.

g. of anhydrous potassium carbonate for seven hours. In all cases the resulting amorphous white material was washed several times with hot water and ethanol before being recrystallized twice from hot nitrobenzene. The crystals were then filtered out and washed with hot water, hot ethanol, and ether to remove the last traces of the nitrobenzene. These compounds were insoluble in water, ethanol, and ether, but could be recrystallized from glacial acetic acid, acetamide or pyridine.

**N,N'-Piperazinium Bis-(arylsulfonates).**—A solution of 0.05 mole (9.7 g.) of piperazine hexahydrate in 50 ml. of water was added to 0.1 mole of the appropriate sulfonic acid dissolved in a minimum quantity of water. If no precipitate formed at once, the solution was concentrated on the steam-bath. The resulting precipitate was filtered off from the solution and was recrystallized twice from the appropriate hot solvent. N,N'-Piperazinium bis-(2,5-dichlorobenzenesulfonate) was recrystallized from water, N,N'-piperazinium bis-(4-nitro-chlorobenzene-2-sulfonate) from 50% ethanol, and the other two compounds from 95% ethanol. In general these piperazinium salts were insoluble in ether, slightly soluble in alcohol, moderately soluble in cold water, and quite soluble in hot water.

A summary of these compounds is shown in Table I.

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#### Pentahydrate of 2-(*p*-Aminobenzenesulfonamido)-thiazole Sodium Salt

Lott and Bergeim<sup>1</sup> report the preparation of 2-(*p*-aminobenzenesulfonamido)-thiazole sodium salt by a method stated to be a modification of that used by Marshall<sup>2</sup> for sodium sulfapyridine.

The necessity for preparation of sulfathiazole sodium salt prompted an investigation of this compound. Using a modification of the Marshall method, we obtained white

plates which formed in clusters. These crystals melted at 55°, and on further heating with loss of water at 100°, recrystallized and melted again at 264.5° with decomposition. The second melting point is in good agreement with that reported by Lott for his sodium sulfathiazole. *Anal.* Calcd. for C<sub>9</sub>H<sub>8</sub>N<sub>2</sub>O<sub>2</sub>Na·5H<sub>2</sub>O: H<sub>2</sub>O, 24.52. Found: H<sub>2</sub>O, 24.55. This pentahydrate (by analysis) was readily soluble in cold water, alcohol and acetone. When an aqueous solution of the salt was added to a copper sulfate solution the characteristic purple precipitate of copper sulfathiazole as described by Lott was formed.

The pentahydrate loses moisture slowly on standing in dry air and yellows in the presence of light. Electrometric *pH* determinations showed aqueous solutions to have the same basicity as solutions of equal molarity prepared from stoichiometric equivalents of standard sodium hydroxide solution and pure sulfathiazole, m. p. 202-202.5° with decomposition.

CIBA PHARMACEUTICAL PRODUCTS, INC.  
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#### α-Naphthylcyclopentanol-1

Fifty grams of α-bromonaphthalene was converted to α-naphthylmagnesium bromide in the usual way.<sup>1</sup> After adding 100 ml. of benzene, the solution was cooled in ice-water and 22 g. of cyclopentanone dissolved in 50 ml. of dry ether was added dropwise. The product was then hydrolyzed and isolated in the customary manner. The carbinol was recrystallized three times from ligroin. It formed clusters of white needles which melted at 74-76°, yield 70%.

*Anal.* Calcd. for C<sub>15</sub>H<sub>16</sub>O: C, 84.8; H, 7.55. Found: C, 84.72; H, 7.68.

(1) Gilman, *et al.*, "Organic Syntheses," Vol. XI, p. 80.

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(1) Lott and Bergeim, *This Journal*, **61**, 3593 (1939).

(2) Marshall, *Science*, **88**, 597 (1938).