

## COMMUNICATIONS TO THE EDITOR

## OPTICAL ROTATION AND ATOMIC DIMENSION. IX. HALOGENO-TETRA-ACETYL DERIVATIVES OF MANNOSE. THEIR CONFIGURATIONAL PECULIARITIES

Sir:

In continuation of my investigations on Optical Rotation and Atomic Dimension [last publication, VIII, THIS JOURNAL, 51, 1820 (1929)], there have been prepared the pure crystalline substances  $\alpha$ -fluorotetraacetylmannose and  $\alpha$ -iodotetraacetylmannose and their specific rotations measured. Further, we have revised the value for crystalline  $\alpha$ -bromotetraacetylmannose as first measured by Micheel [*Ber.*, 63, 390 (1930)] and later by Levene and Tipson [*J. Biol. Chem.*, 90, 93 (1931)]. As I prepared several years ago crystalline  $\alpha$ -chlorotetraacetylmannose and measured its rotation, a series of values is available for comparison with the atomic dimension values.

It has been established in my former investigations on this subject that for all the investigated halogen derivatives of the monosaccharides (glucose, fructose, xylose and arabinose) the differences in specific rotation, Cl-F, Br-Cl and I-Br, are proportional to the corresponding differences in atomic diameters. These differences in the specific rotations have the same ratio to each other as the corresponding differences in the atomic diameters, namely, 41:17:21. By using the values for the neutral atomic diameters of Goldschmidt [see Wherry, *Am. Mineralogist*, 14, 54 (1929)], the proportionality existing between the differences of specific rotation and atomic diameter values holds very accurately for the derivatives of these four monosaccharides. However, the values for the mannose derivatives give the ratio 41:25:35. These experimental results point to the explanation that for the mannose derivatives the halogens on the one hand and the atoms of the second carbon on the other influence each other, as will be discussed in detail in the forthcoming paper. The results of Freudenberg [*Naturwissenschaften*, 18, 393 (1930)] and Haworth [*J. Chem. Soc.*, 1395 (1930)] are of interest in this connection. They found for the structure of some mannose derivatives that even ring formation occurs between the adjacent groups of the first and second carbon atoms. An explanation of the different behavior of the mannose derivatives in comparison with the other monosaccharide derivatives could be obtained by model studies (detailed in the forthcoming article) which show that for the  $\alpha$ -halogen derivatives of mannose the acetyl group of the second carbon is directed through its CH<sub>3</sub> group to the halogens of the first carbon with a resulting influence; whereas for the  $\alpha$ -halogen derivatives of glucose, arabinose and xylose, the acetyl group of the second carbon is directed through its CH<sub>3</sub> group to the ring or another oxygen atom and also that the detailed structure of the halogen derivatives of fructose ( $\beta$ -derivatives) does not show a similar influence on the halogen atoms.

If we consider the consequences of this explanation it is seen that for the  $\alpha$ - and  $\beta$ -mannose pentaacetates the acetyl group of the second carbon atom has a different position for the  $\alpha$ -compound in comparison with the  $\beta$ -derivative, as its  $\text{CH}_3$  group is directed by the respective places of the oxygen atoms of the first carbon acetyl group, whereas such a difference does not exist (or is of another nature) for the other discussed monosaccharides. Hence the testing of the principle of optical superposition in the mannose and rhamnose series should be taken up with caution, taking into account these configurational peculiarities.

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#### THE VARIATION OF ELECTRIC MOMENT WITH TEMPERATURE

Sir:

Because of the uncertainty which has recently arisen in regard to the possible temperature variation of the moments of molecules in which two dipoles may rotate relative to one another, it has seemed of immediate importance to investigate this effect in such molecules. Ethyl acetate, the moment of which should depend, to a considerable extent, upon the position of the moment of the  $\text{O}-\text{C}_2\text{H}_5$  bond relative to that of the  $\text{C}=\text{O}$  group, is found to show no significant variation of moment with temperature between  $-70$  and  $+30^\circ$  when measured in dilute solution in heptane. The moment of ethylene chloride in solution in heptane is found to increase uniformly from  $1.07 \times 10^{-18}$  at  $-70^\circ$  to  $1.41 \times 10^{-18}$  at  $+30^\circ$  in satisfactory agreement with the measurements of Meyer [*Z. physik. Chem.*, [B] 8, 27 (1930)]. In similar fashion the moment of ethylene chlorobromide in heptane solution is found to increase from  $0.92 \times 10^{-18}$  at  $-50^\circ$  to  $1.19 \times 10^{-18}$  at  $+30^\circ$ . This change is in accord with Meyer's idea that the mutual potential energies of the doublets in the two halves of the molecule cause these halves to occupy such positions relative to one another that the moments are partially canceled. The increase in rotational energy with rising temperature tends to overcome this effect of the mutual potential energies and so increase the moment.

Diethyl succinate which was found to have a moment lower than those of the other dicarboxylic acid esters and, apparently, increasing with temperature [Smyth and Walls, *THIS JOURNAL*, 53, 527 (1931)], has been measured over a wide range of temperature in solution in kerosene. The moment increases regularly from  $2.01 \times 10^{-18}$  at  $0^\circ$  to  $2.47 \times 10^{-18}$  at  $180^\circ$ , the latter value being practically identical with the moments of the higher members of the series. The tendency of the succinate molecule to bend in such a way that the doublets partially oppose and cancel one