The experimental value obtained by unimolecular film measurements[2] is 34 sq. Å., with a possible error certainly not greater than 2 sq. Å., so that the first and last structures are decisively eliminated. The elimination of the 8:14 structure is supported by the crystallographic structure of Bernal.[3]

[2] Danielli, Marrian and Haslewood, *Biochem. J.*, **27**, 311 (1933).

[3] Bernal, *Chem. Ind.*, **51**, 259 (1932).

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DIAMAGNETISM OF NITROSO COMPOUNDS

Sir:

Because organic nitroso compounds display certain anomalous properties, such as intense color and a marked tendency to form double molecules, G. N. Lewis[1] suggested that the explanation of their unusual behavior might be related to the cause of the peculiar properties of O_2 and NO, the former being paramagnetic and the latter showing little unsaturation, although it is an odd molecule. Pauling[2] proposed a structure for oxygen and nitric oxide involving the three-electron bond, which, therefore, in view of the above, led him to ascribe a similar triplet structure, $-\underset{\cdot}{\dot{N}}\,\underset{\cdot}{\dot{:}}\,\underset{\cdot}{\dot{O}}:$, to the nitroso group instead of the singlet configuration, $-\ddot{N}::\ddot{O}:$.

I have measured the magnetic susceptibilities of nitrosyl chloride (NOCl), of nitrosobenzene (C_6H_5NO), and of *p*-nitrosodimethylaniline ($(CH_3)_2NC_6H_4NO$), the first as a liquid, the second both as a solid and as a solute in benzene and toluene, the third as a solute in toluene. The Gouy[3] method was used. All three compounds were found to be diamagnetic, a result which cannot be accounted for by the presence of any reasonable amounts of impurities, since the paramagnetism which would be exhibited if the molecules were in the triplet state would be too large to be so masked.

Likewise the result is not explicable on the basis of the formation of double molecules. The solutions were highly colored, a property which is definitely correlated with the monomeric state. Furthermore, investigation of toluene solutions of *p*-nitrosodimethylaniline, 1 to 7% by weight, with a Klett colorimeter showed that the depth of color was proportional to the concentration, indicating at least a high degree of dissociation into single molecules. Freezing point studies[4] on nitrosobenzene in benzene lead to the same result.

The conclusion is that these compounds, at least, are in singlet states,[5] which indicates that they do not have the similarity to oxygen previously suggested. Since at the present time there seems to be no theoretical basis for choosing between the singlet and triplet configurations for the ground state of this type of molecule, it is perhaps not worth while discussing reasons for the above experimental results. However, it is true that for each of the above compounds several singlet structures could be drawn which on the basis of energy data[6] are known to contribute to the stability of related molecules through resonance and which have no triplet analogs. Such resonance would certainly tend to stabilize the singlet configuration but whether this is the determining factor cannot be stated.

I should like to thank Professor Linus Pauling for suggesting this investigation.

[1] G. N. Lewis, "Valence and the Structure of Atoms and Molecules," Chemical Catalog Co., Inc., New York, 1923, p. 128.

[2] Linus Pauling, THIS JOURNAL, **53**, 3225 (1931).

[3] E. C. Stoner, "Magnetism and Atomic Structure," p. 40.

[4] K. Auwers, *Z. physik. Chem.*, **32**, 52 (1900).

[5] Linus Pauling, THIS JOURNAL, **53**, 1392 (1931).

[6] Linus Pauling and J. Sherman, *J. Chem. Physics*, **1**, 606 (1933).

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MUTAROTATION OF β-*d*-RIBOSE AND β-*l*-RIBOSE

Sir:

Owing to the importance of the little known sugar, ribose, not only in its structural relation to other sugars but also in its physiological relation to animal and plant life, since it appears to be of almost universal occurrence in tissues bearing upon the regeneration of life, Phelps and Bates a number of years ago undertook the preparation of a quantity of this sugar in order to study its properties and the improvement of the existing methods of production. One of us (Isbell) has been engaged for some time in the study of the composition of sugar solutions and in the investigation of the isomeric changes which follow solution in water, and has developed a method for determining the composition of the solutions by oxidation with bromine water. Since mutarotation of ribose is not reported in the literature

[Van Ekenstein and Blanksma, *Chem. Weekblad,* **6**, 374 (1909); also Levene, "Nucleic Acids," A. C. S. Monograph No. 56, p. 131, 1931], it seemed desirable to apply the methods [*Bur. Standards J. Res.*, **8**, 615 (1932); **10**, 337 (1933)] which had been developed for the study of other sugars to the investigation of *d*- and *l*-ribose.

Measurements taken at 20 and at 1° show that both *d*-ribose and *l*-ribose exhibit a very remarkable mutarotation. The mutarotation takes place rapidly and direction of the change reverses after a few minutes, so that the initial and final rotations are not greatly different. On account of the rapidity with which the reaction takes place the mutarotation can be best observed at low temperatures.

A 2.0236-g. sample of *d*-ribose (m. p. 87°) dissolved in 45.223 g. of water at 1° gave $[\alpha]^1_D$ −23.1°, 1.5 minutes after solution; −21.3°, five minutes; −19.5°, ten minutes; −18.8° (minimum), twenty minutes; −19.1°, thirty minutes; −21.2°, sixty minutes; −23.1°, one hundred and twenty minutes; −23.7°, three hundred minutes. A 1.9941-g. sample of *l*-ribose (m. p. 87°) dissolved in 45.223 g. of water at 1° gave $[\alpha]^1_D$ +23.2°, two minutes; +21.5°, five minutes; +19.9°, ten minutes; +18.7° (minimum), twenty minutes; +19.4°, thirty minutes; +21.5°, sixty minutes; +23.2°, one hundred and twenty minutes; +24.3°, three hundred minutes; +24.0°, twenty-eight hours.

The complex character of the mutarotation curves shows that crystalline *d*-ribose and also *l*-ribose in water solution establish equilibrium with at least three isomers. One of the isomers is less levorotatory than the crystalline *d*-sugar and the other is more levorotatory. The mutarotation resembles that of the labile calcium chloride compound of mannose reported by Dale [THIS JOURNAL, **51**, 2225 (1929)] which Isbell has shown [*ibid.*, **55**, 2166 (1933)] gives γ-mannonic lactone when oxidized with bromine water in the presence of barium carbonate, and which probably has a 1,4 ring structure.

Oxidation of *d*- and *l*-ribose by the barium carbonate–bromine method shows that they are oxidized rapidly at first and then more slowly. The decrease in reaction rate is presumably caused by a less readily oxidized substance formed by the mutarotation reaction.

Since the rotation of *d*-ribose changes initially from a negative to a less negative value, in accordance with the usual nomenclature, the crystalline sugar will be tentatively designated as *β*-*d*-ribose and its mirror image as *β*-*l*-ribose. The similarity of *β*-*d*- and *β*-*l*-ribose to the labile calcium chloride compound of mannose suggests that these substances may have furanose structures which on solution in water change spontaneously into the corresponding pyranose forms. However, no definite classification of structures is possible until further experiments are completed.

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THE ASSUMED NON-IDENTITY OF COTTON AND WOOD CELLULOSE

Sir:

On the basis of methylation experiments carried out on cotton and α-celluloses prepared from five different woods, D. J. Bell [*Biochem, J.*, **26**, 590-597 (1932); **26**, 598-608 (1932); **26**, 609-614 (1932)] has questioned the identity of the chemical structure of cotton and wood cellulose. He found that a maximum methoxyl content of 36.3–39.0% was attained with the wood α-celluloses as contrasted with a theoretical value of 45.6%. Bell ascribes this resistance to methylation shown by the wood α-celluloses to the presence of a so-called "resistant portion." These results have been regarded by Irvine as having a marked bearing on the conclusions drawn by other authors with respect to chain length.

In an attempt to duplicate these results with rayon pulps from spruce, beech and maple wood it was not found possible to confirm the work of Bell with respect to the presence in the cellulose of a portion resistant to methylation. The following results were obtained.

Source of α-cellulose	No. of methylations	OMe, %
Spruce	9	44.24
Beech	5	43.08
Maple	5	43.72

The methoxyl values given above are not maximum figures since the reaction has given as yet no indication of an end-point and the methylations are therefore being continued in order to arrive, as closely as possible, at the theoretical value of 45.6% OMe.

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