lie at the apices of a trigonal prism and the remaining two beyond the centres of two of the three prism faces. This corresponds to a 9-coordination with one of the coordination sites unoccupied. The Pb—Br distances range from 2.94 Å to 3.47 Å, the mean value being 3.20 Å. The Pb—O bond distance is 2.59 Å.

A full report of the structure determination will soon be published in this journal.

This work has been supported financially by the *Swedish Natural Science Research Council*, Contract No. 2318.

1. *The International Tables for X-ray Crystallography*, 2nd. Ed., Kynoch Press, Birmingham 1952, Vol. I.

Received September 4, 1970.

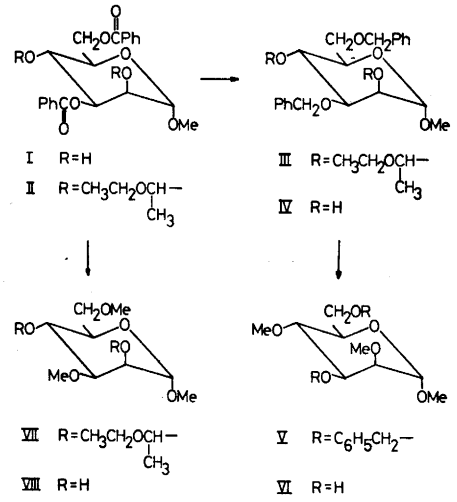
Synthesis of 2,4- and 3,6-Di-*O*-methyl-D-mannose

GUNNEL ALFREDSSON, PER J. GAREGG and BENGT LINDBERG

Institutionen för organisk kemi, Stockholms Universitet, Stockholm, Sweden

Methyl 3,6-di-*O*-benzoyl-α-D-mannopyranoside is readily prepared by partial benzoylation of methyl α-D-mannopyranoside [1] and should provide a convenient starting material for the syntheses of 2,4- and 3,6-di-*O*-methyl-D-mannose. These substances, which were needed in connection with methylation analysis of polysaccharides, containing D-mannose residues, had not previously been synthesized at the outset of the present work. Recently, however, Bhattacharjee and Gorin [2] reported the synthesis of the pure 2,4-dimethyl ether and of the 3,6-isomer, contaminated with other ethers. Another synthesis of the 2,4-dimethyl ether was reported by Murty and Siddiqui [3] and methyl 3,6-di-*O*-methyl-α-D-mannopyranoside was obtained, by Handa and Montgomery,[4] as one of several products on partial methylation of methyl α-D-mannopyranoside.

Methyl 3,6-di-*O*-benzoyl-α-D-mannopyranoside (I) was converted, by treatment with ethyl vinyl ether and an acidic catalyst, into the 2,4-di-*O*-(1′-ethoxyethyl) derivative (II) which provided the starting material for both syntheses. Syrupy II (a mixture of stereoisomers) was debenzoylated and then benzylated to give III. Removal of the 1′-ethoxyethyl groups by mild acid hydrolysis yielded IV, which upon methylation and subsequent removal of the benzyl groups by catalytical hydrogenation of the intermediate V, gave methyl 2,4-di-*O*-methyl-α-D-mannopyranoside, VI. Acid hydrolysis of VI yielded the crystalline 2,4-di-*O*-methyl-D-mannose. The total yield from I was 26 %.



Methyl 3,6-di-*O*-benzoyl-2,4-di-*O*-(1′-ethoxyethyl)-α-D-mannopyranoside (II) on debenzoylation and subsequent methylation yielded VII. This on mild acid hydrolysis yielded methyl 3,6-di-*O*-methyl-α-D-mannopyranoside, VIII, in a total yield from I of 50 %. Part of the amorphous VIII was converted into the crystalline 2,4-di-*p*-nitrobenzoate. 3,6-Di-*O*-methyl-D-mannose was prepared by acid hydrolysis of VIII.

The syntheses were followed by TLC and most of the products characterized by NMR. The structures of the 2,4- and 3,6-di-*O*-methyl-D-mannose were confirmed by converting them into the alditol ace-

tates, which gave the expected mass spectra.[5] The retention times of the alditol acetates, relative to that of 1,5-di-*O*-acetyl-2,3,4,6-tetra-*O*-methyl-D-glucitol, on an ECNSS-M column, were determined.

Experimental. Concentrations were performed at reduced pressure. Melting points are corrected. Optical rotations were determined at room temperature with a Perkin-Elmer 141 polarimeter. NMR spectra, in deuterochloroform, were recorded with a Varian 60 A spectrometer using tetramethylsilane as internal reference. Chemical shifts (δ) are given in ppm downfield from tetramethylsilane. In the section below, only pertinent parts of the NMR spectra are presented. The remainder of the spectra were invariably in accordance with the presumed structures. TLC was performed on silica gel GF_{254} (Merck). Sulphuric acid was used as spray reagent. GLC-MS was run on a Perkin-Elmer 270 instrument. Spectra were recorded at a manifold temperature of 200°, an ionization current of 80 μA and a temperature at the ion source chamber of 80°. Light petroleum refers to a fraction with b.p. 40–60°.

*Methyl 3,6-di-*O*-benzoyl-2,4-di-*O*-(1'-ethoxyethyl)-α-*D*-mannopyranoside (II).* Ethyl vinyl ether (5 ml) and then 0.4 % hydrogen chloride in dichloromethane (1 ml) were added to a solution of the dibenzoate I (4.5 g) in dichloromethane (50 ml). After 20 h at room temperature the solution was neutralized with solid potassium carbonate and then washed with 5 % aqueous potassium carbonate, dried over sodium sulphate and concentrated to a syrup (6.7 g), showing $[\alpha]_D + 53°$(*c*, 0.1, chloroform). TLC (light petroleum-ethyl ether, 2:1) showed a single spot. NMR: Two multiplets, at 8.1 (4H) and 7.5 ppm (6H) were assigned to aromatic protons, a singlet, at 3.44 ppm (3H), to the methoxyl and multiplets at 1.4–0.8 ppm (12H), to the methyl protons of the 1'-*O*-ethoxy-ethyl groups.

*Methyl 3,6-di-*O*-benzyl-α-*D*-mannopyranoside (IV).* A solution of II (5.6 g) in methanol (50 ml) was treated with barium oxide (100 mg) at reflux temperature for 1 h, filtered and concentrated to a syrup (5.3 g). TLC (ethyl acetate) showed a single spot. The syrup (2.4 g), which was not further purified, was treated with benzyl chloride (40 ml) and powdered sodium hydroxide (25 g) under nitrogen with stirring at 130–140° for 2 h. After cooling, methanol (40 ml) was added, the mixture refluxed for 2 h, cooled and poured into water (100 ml). The mixture was extracted with chloroform, the chloroform solution dried over sodium sulphate and concentrated. The crude dibenzyl ether, III, was hydrolyzed in 50 % aqueous acetic acid (100 ml) at 100° for 1 h. Concentration yielded a product which on TLC (toluene-ethyl ether, 1:1) gave a major spot in addition to a minor, tentatively identified as due to dibenzyl ether. Small amounts of slow-moving components were also present. The mixture was separated on a silica gel column, (toluene-ethyl acetate, 1:1), and IV (735 mg) was obtained chromatographically pure. NMR: A multiplet at 7.4 ppm (10H) was assigned to the aromatic protons, singlets at 4.73 ppm (2H) and 4.67 ppm (2H) to the benzylic protons and a singlet at 3.42 ppm (3H) to the methoxyl protons.

*Methyl 2,4-di-*O*-methyl-α-*D*-mannopyranoside (VI).* Syrupy IV (675 mg) was methylated in methyl sulphoxide (10 ml) under nitrogen with methylsulphinyl sodium (from 250 mg sodium hydride in 10 ml methyl sulphoxide) and methyl iodide (10 ml) essentially as described by Hakomori.[6] The resulting solution was poured into water (50 ml) and the mixture extracted with light petroleum. The combined extracts were dried over sodium sulphate and concentrated. The syrupy product (V), in ethanol (20 ml) was hydrogenated at room temperature and atmospheric pressure, using as catalyst 10 % palladium on carbon[7] (4 g). Filtration and concentration yielded chromatographically pure VI (241 mg, TLC; ethyl acetate-methanol, 10:1). NMR: Singlets at 3.48 (3H), 3.45 (3H), and 3.30 (3H) were assigned to the methoxyl protons.

*2,4-Di-*O*-methyl-*D*-mannose.* Hydrolysis of VI in 0.25 M sulphuric acid at 100° overnight afforded, in almost quantitative yield, 2,4-di-*O*-methyl-D-mannose. It showed m.p. 120–123°, $[\alpha]_D + 12°$(*c*, 0.2, water), in good agreement with published values.[2,3]

*Methyl 3,6-di-*O*-methyl-α-*D*-mannopyranoside (VIII).* II (6.7 g) was debenzoylated as described above and the product, in dry dioxane (200 ml), treated under stirring with methyl sulphate (15 ml) and powdered sodium hydroxide (25 g) at 60° overnight. The filtered solution was concentrated to a syrup (4.60 g) which, without further purification, was hydrolyzed in 50 % aqueous acetic acid (100 ml) at 100° for 1 h. Concentration afforded crude, syrupy VIII, which was purified by chromatography on a silica gel column (ethyl acetate-methanol. 10:1). VIII (1.38 g) was obtained as a chromatographically pure syrup (TLC; ethyl acetate-methanol, 10:1). A derivative, methyl 3,6-di-*O*-methyl-2,4-di-*O*-*p*-nitrobenzoyl-α-D-mannopyranoside showed m.p. 51–54° and $[\alpha]_D - 88°$ (*c*, 0.6, chloroform) (Found: C 53.2; H 4.77; N 5.43. $C_{23}H_{24}N_2O_{10}$ requires: C 53.1; H 4.65; N 5.38).

3,6-Di-O-methyl-D-mannose was prepared from VIII by acid hydrolysis as described above. The substance, which did not crystallise, showed $[\alpha]_D+4°$ (*c*, 0.8, water) in agreement with a previously determined value.[4]

GLC-MS. The 2,4- and 3,6-di-*O*-methyl-D-mannoses were converted into the corresponding alditol acetates, which were chromatographically homogeneous on GLC. The retention times, on an ECNSS-M-column, relative to that of 1,5-di-*O*-acetyl-2,3,4,6-tetra-*O*-methyl-D-glucitol,[5] were 5.44 and 4.15, respectively. The fragmentation patterns on MS were indistinguishable from those of other, authentic 2,4- and 3,6-di-*O*-methyl hexitol acetates,[8] respectively.

Acknowledgement. The authors are indebted to *Statens Naturvetenskapliga Forskningsråd* for financial support.

1. Williams, J. M. and Richardsson, A. C. *Tetrahedron* **23** (1967) 1369.
2. Bhattacharjee, S. S. and Gorin, P. A. J. *Can. J. Chem.* **47** (1969) 1207.
3. Murty, V. L. N. and Siddiqui, I. R. *Carbohyd. Res.* **10** (1969) 477.
4. Handa, N. and Montgomery, R. *Carbohyd. Res.* **11** (1969) 467.
5. Björndal, H., Lindberg, B. and Svensson, S. *Carbohyd. Res.* **5** (1967) 433.
6. Hakomori, S. *J. Biochem. (Tokyo)* **55** (1964) 205.
7. Mozingo, R. *Org. Syn. Coll. Vol.* **3** (1955) 685.
8. Björndal, H., Lindberg, B. and Svensson, S. *Acta Chem. Scand.* **21** (1967) 1801.

Received September 8, 1970.

The Valence Electron Density Distribution of Strained Single Bonds in the Iterative Extended Hückel Approach

IV. A Comment on the Choice of Slater Exponents in the Calculations of Electron Densities

OLLE MÅRTENSSON

Quantum Chemistry Group, Uppsala University, Box 518, S-751 20 Uppsala, Sweden*

Slater orbitals are often used in molecular calculations. In these cases orbital exponents obtained by the so-called Slater's rules (see for instance Ref. 1) are generally applied, although these values were originally created for atomic purposes. For hydrogen the difference between the so obtained "atomic" and suggested "molecular" values is not negligible, Slater's rules giving 1.0 as compared to 1.2 obtained by minimizing the energy of the hydrogen molecule.[2] As regards the electron density distribution, a greater value of the exponent of the hydrogen orbitals will concentrate the charge somewhat more at the hydrogen atoms.

In order to ensure that the principal results obtained earlier by using the value 1.0[3] for the hydrogen Slater exponent are not violated by a change to 1.2, some recalculations have been made applying the suggested value 1.2 in the calculations of the eigenvectors as well as in the evaluation of the density function. From Figs. 1, 2, and 3 we see that the general picture of the valence electron density distribution of methane in its normal state and under deformation (at angles of 120° and 60°, respectively, mutually between the symmetrically moved three interatomic vectors, *i.e.* 90° and 140°, respectively, between the moving vectors and the fixed one) is essentially the same as in the preceding calculations, the difference being merely a higher charge at the sites of the hydrogen atoms. (It should be pointed out that the levels are not exactly the same in the two

* Sponsored in part by *King Gustaf VI Adolf's 80-Year Fund for Swedish Culture, Knut and Alice Wallenberg's Foundation* and in part by the *Swedish Natural Science Research Council.*