# The stereochemistry of nitrate esters. II. Symmetric stretching frequencies of the nitrato group in nitrate esters of 1,4;3,6-dianhydrohexitols (4,8-dihydroxy-*cis*-2,6-dioxabicyclo[3.3.0]octanes)[1]

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In the infrared spectra of mono- and di-nitrate esters of the 1,4;3,6-dianhydrides of D-mannitol, D-glucitol, and L-iditol in benzene solution (0.04 *M* in nitrato groups), the frequencies of the $\nu_a(NO_2)$ and $\nu(ON)$ bands (singlets) were 1 645 ± 3 and 843 ± 3 $cm^{-1}$, respectively, whereas the $\nu_s(NO_2)$ band occurred at frequencies characteristic of either an *endo* (1 282 ± 1 $cm^{-1}$) or an *exo* (1 274 ± 1 $cm^{-1}$) configuration of the nitrato group; the ratios of the band areas were 1.5:1.0:1.0, respectively.

The stereospecific frequency of the $\nu_s(NO_2)$ band was attributed to non-bonded intramolecular interaction between the nitrato group and vicinal oxy groups on the basis of the spectra run in a series of solvents and the molecular conformations determined by X-ray crystallography. This new stereochemical probe permitted the assignment of the structure, configuration, and conformation in a series of nitrate esters.

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In part I of this series (1) it was shown that, for *cis* and *trans* vicinal dinitrate esters, the frequency of the symmetric vibration of the nitrato group, $\nu_s(NO_2)$, in solution spectra varied with the dihedral angle ($\phi$) between the adjacent C—O bonds. The dependence of $\nu_s(NO_2)$ on $\phi$ has since been confirmed for vicinal dinitrates of homogeneous *gauche* conformation (2). In this paper we report evidence of non-bonded interaction between nitrato groups and vicinal ether oxygen atoms, and a correlation of $\Delta\nu_s(NO_2)$ with $\phi$ which constituted a stereochemical probe for assignment of molecular configuration and conformation.

## EXPERIMENTAL

The dinitrate esters of the 1,4;3,6-dianhydrides of D-mannitol (I), D-glucitol (II), and L-iditol (III) (the 4,8-dihydroxy-*cis*-2,6-dioxabicyclo[3.3.0]octanes) were previously described (3). The mononitrates of the 1,4;3,6-dianhydrohexitols (IV–VII) (Table I) were synthesized by partial nitration of the corresponding parent diols at 5–10° with a nitric acid – acetic anhydride – acetic acid mixture (in the molar proportions of 1:1:10:70, respectively) and purified by chromatography on columns of silica gel (4). The arylsulfonate derivatives IX–XII (Table I) were prepared from the corresponding mononitrates with an excess of arylsulfonyl chloride in pyridine. Compounds VIII, IX, and XI were also synthesized from the parent diols with a 1.3 molar proportion of *p*-toluenesulfonyl chloride in pyridine (5, 6), followed by *O*-nitration of the mono-*p*-toluenesulfonate esters thus obtained. With 1,4;3,6-dianhydro-D-glucitol, the major product was the mononitrate of the *endo*-*p*-toluenesulfonate (IX) (5–8) and was identical with the compound prepared by tosylation of mononitrate V.

The nitrate esters were recrystallized to constant melting points, were shown by thin-layer chromatography (4) to be homogeneous, and gave solid-state infrared spectra indicating the presence of the correct chromophores. The circular dichroism spectra of compounds I–VII were previously reported (9). The structural identification of compounds IV–XII is discussed in the sequel.

Isopropyl ether, tetrahydrofuran, methylal, and pyridine, used as spectral solvents, were purified by standard procedures and fractionally distilled from lithium aluminium hydride or calcium hydride; other solvents were of "spectro grade".

Spectra (600 – 4 000 $cm^{-1}$) were measured on a Perkin–Elmer 21 spectrophotometer (sodium chloride optics in 0.1 mm matched-cavity cells) and on a Leitz double-beam spectrophotometer (75 and 150 lines/mm gratings, 1.0 mm cells with potassium bromide windows). Band positions were determined on the compensated spectra by an average-center method, and relative band areas were measured with a planimeter from the "best" base line drawn through points on the spectral curves at 765, 800, 900, 1 235, and 2 140 $cm^{-1}$. Solutions were examined by thin-layer chromatography before and after the spectra were recorded, and no decomposition or contamination was detected.

## RESULTS AND DISCUSSION

Table II summarizes the frequencies of the nitrato and hydroxyl stretching bands in the dilute solution spectra of 12 nitrate

[1]For part I in this series, see ref. 1.

TABLE I

Mononitrate esters of 1,4;3,6-dianhydrohexitols

| | Compound | Melting point (°C) | Elemental analysis* (%) | | |
|---|---|---|---|---|---|
| | | | C | H | N |
| IV | 1,4;3,6-Dianhydro-D-mannitol-2-nitrate | 69.0–70.5 | 37.83 | 4.85 | 7.30 |
| V | 1,4;3,6-Dianhydro-D-glucitol-2-nitrate | 52.0–53.0 | 37.78 | 4.96 | 7.20 |
| VI | 1,4;3,6-Dianhydro-D-glucitol-5-nitrate | 89.5–91.0 | 37.64 | 4.82 | 7.34 |
| VII | 1,4;3,6-Dianhydro-L-iditol-2-nitrate | 55.5–57.0 | 37.80 | 4.96 | 7.28 |
| VIII | 1,4;3,6-Dianhydro-D-mannitol-5-*p*-toluenesulfonate-2-nitrate | 119–120 | 45.33 | 4.37 | 4.19 |
| IX | 1,4;3,6-Dianhydro-D-glucitol-5-*p*-toluenesulfonate-2-nitrate | 74.5–75.5 | 45.29 | 4.30 | 4.13 |
| X | 1,4;3,6-Dianhydro-D-glucitol-2-*p*-toluenesulfonate-5-nitrate | 84.0–85.0 | 44.87 | 4.50 | 3.98 |
| XI | 1,4;3,6-Dianhydro-L-iditol-5-*p*-toluenesulfonate-2-nitrate | 72.5–73.0 | 45.08 | 4.51 | 4.21 |
| XII | 1,4;3,6-Dianhydro-D-glucitol-2-*p*-bromobenzenesulfonate-5-nitrate | 75.0–76.0 | 35.13 | 2.89 | 3.50 |

*Anal. Calcd. for compounds IV–VII ($C_6H_9NO_6$): C, 37.70; H, 4.75; N, 7.33. Calcd. for compounds VIII–XI ($C_{13}H_{15}NO_8S$): C, 45.21; H, 4.39; N, 4.06. Calcd. for compound XII ($C_{12}H_{12}BrNO_8S$): C, 35.14; H, 2.95; N, 3.42 (see also ref. 10).

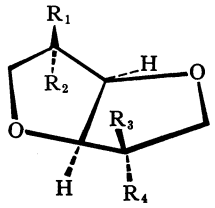
esters of the 1,4;3,6-dianhydrohexitols. In benzene the frequencies of the $\nu_a(NO_2)$ and $\nu$(ON) bands varied within the ranges 1 645 ± 3 and 843 ± 3 $cm^{-1}$, respectively, throughout the series, whereas the $\nu_s(NO_2)$ band occurred at frequencies characteristic of either an *endo* (1 282 ± 1 $cm^{-1}$) or an *exo* (1 274 ± 1 $cm^{-1}$) configuration of the nitrato group. For compounds I to VII the relative band areas were 1.5:1.0:1.0 for $\nu_a(NO_2)$, $\nu_s(NO_2)$, and $\nu$(ON), respectively. Each of the $\nu_s(NO_2)$ bands found for compound II had an area of 0.5 on the same relative scale, in agreement with the presence of "isolated" *endo*- and *exo*-nitrato groups in this molecule. Changing the solvent to acetonitrile, chloroform, isopropyl ether, methylal, or pyridine did not alter the frequencies of the two $\nu_s(NO_2)$ bands for compound II, and the frequencies of the $\nu_s(NO_2)$ bands (singlets) for compounds IV–VII were unchanged in carbon tetrachloride.

On the basis of these spectra and the known absolute configurations of compounds I, II, III, IV, VII, VIII, and XI (established through their syntheses), configurations could be assigned to compounds V, VI, IX, X, and XII (see Tables I and II). These assignments were consistent with the following facts. (*a*) An X-ray diffraction study confirmed the structure and configuration assigned to compound XII (10). (*b*) Because of the enhanced rate of esterification of the *endo*- as compared with the *exo*-hydroxyl group (5–8), treatment of 1,4;3,6-dianhydro-D-glucitol with 1.3 moles of *p*-toluenesulfonyl chloride, followed by complete *O*-nitration of the mixture of monoesters thus obtained, gave the *exo*-mononitrate-*endo*-mono-*p*-toluenesulfonate derivative IX as the major product. Since IX was also obtained directly from mononitrate V, these compounds had *exo*-nitrato groups. It followed, therefore, that mononitrates VI and X had *endo*-nitrato groups. (*c*) The spectra of mononitrates IV–VII in 0.005 *M* solutions in carbon tetrachloride (Table II) showed bands for $\nu$(OH) characteristic of "free" *exo*-hydroxyl groups in VI and VII, and of intramolecularly hydrogen bonded *endo*-hydroxyl groups in IV and V (6–8). (*d*) The mobility of compound V exceeded that of compound VI on silica gel chromatograms, in agreement with the presence of an internal hydrogen bond in the former isomer (8).

Since the stretching vibrations of the nitrato groups were not significantly altered by substitution at the $\delta$ carbon atom in the adjacent ring, $\Delta\nu_s(NO_2)$ could be attributed to intramolecular interaction of the nitrato group with substituents on the carbon atoms beta to the chromophore. Inter-

TABLE II

Stretching frequencies of 1,4;3,6-dianhydrohexitol nitrates in solution




| Configuration | | $R_1$ (*endo*) | $R_2$ (*exo*) | $R_3$ (*endo*) | $R_4$ (*exo*) | Frequencies ($cm^{-1}$) $\nu$(OH)† | $\nu_a(NO_2)$‡ | $\nu_s(NO_2)$‡ *endo* | $\nu_s(NO_2)$‡ *exo* | $\nu$(ON)‡ |
|---|---|---|---|---|---|---|---|---|---|---|
| I | D-*manno* | $ONO_2$ | H | $ONO_2$ | H | — | 1 647 | 1 282 | — | 841 |
| II | D-*gluco* | $ONO_2$ | H | H | $ONO_2$ | — | 1 647 | 1 283 | 1 274 | 842 |
| III | L-*ido* | H | $ONO_2$ | H | $ONO_2$ | — | 1 647 | — | 1 273 | 841 |
| IV | D-*manno* | $ONO_2$ | H | OH | H | 3 595 | 1 646 | 1 283 | — | 846 |
| V | D-*gluco* | OH | H | H | $ONO_2$ | 3 565 | 1 644 | — | 1 275 | 846 |
| VI | D-*gluco* | $ONO_2$ | H | H | OH | 3 640 | 1 644 | 1 282 | — | 846 |
| VII | L-*ido* | H | $ONO_2$ | H | OH | 3 640 | 1 642 | — | 1 274 | 844 |
| VIII | D-*manno* | $ONO_2$ | H | OTs* | H | — | 1 646 | 1 282 | — | 841 |
| IX | D-*gluco* | OTs* | H | H | $ONO_2$ | — | 1 643 | — | 1 275 | 842 |
| X | D-*gluco* | $ONO_2$ | H | H | OTs* | — | 1 648 | 1 282 | — | 842 |
| XI | L-*ido* | H | $ONO_2$ | H | OTs* | — | 1 646 | — | 1 274 | 841 |
| XII | D-*gluco* | $ONO_2$ | H | H | OBs* | — | 1 648 | 1 283 | — | 843 |

*OTs = *p*-toluenesulfonyloxy; OBs = *p*-bromobenzenesulfonyloxy.
†0.005 *M* solutions in $CCl_4$.
‡0.04 mole of $ONO_2$/l in benzene.

action with neighboring CH bonds, however, was not important, since the $\nu_s(NO_2)$ bands of cyclohexyl and 2,2,6,6-tetradeuteriocyclohexyl nitrates in benzene were identical (1 277 $cm^{-1}$).

Molecular models showed that the *endo*- and *exo*-nitrato groups could assume identical conformations with respect to the vicinal C—O bond in the same ring, but were constrained to two different ranges of conformations with respect to the vicinal C—O bond in the adjacent ring. The dihedral angle ($\phi$) defined by the latter bond and the C—O bond of the nitrato group was either $\phi_{endo} = 0 \pm 30°$ or $\phi_{exo} = 120 \pm 30°$ (cf. ref. 10). The value of $\Delta\nu_s(NO_2)$ was in good agreement in both magnitude (9 $cm^{-1}$) and direction with that observed for *cis*- and *trans*-1,2-acenaphthenediol dinitrates in cyclohexane, where the ranges of the values of $\phi_{cis}$ (~0°) and $\phi_{trans}$ (~120°) were shown to be less than 30° (1). The shift of $\nu_s(NO_2)$ to higher frequency could therefore be attributed to the interaction of the lone-pair electrons of an oxygen atom with the contiguous nitrato group that occurred as $\phi$ approached zero (1, 2).

A test of this proposal and, simultaneously, evidence for the intramolecular origin of $\Delta\nu_s(NO_2)$ were obtained by comparing the data in Table II with the spectra of solutions of the isomeric dinitrates I–III in ethyl ether and tetrahydrofuran. In these solvents the $\nu_a(NO_2)$ and $\nu$(ON) bands were not significantly shifted from their positions in the spectra in benzene, whereas $\nu_s(NO_2)$ now appeared as a singlet band at the *same* frequency (1 272 ± 1 $cm^{-1}$) for *each* of the three isomers. The oxygen atoms of these specific solvents appeared, therefore, to compete successfully with the adjacent ring oxygens in an intermolecular interaction with the *endo*-nitrato groups, thus causing them to rotate away from the adjacent ring and to occupy steric environments essentially identical with those of the *exo*-nitrato groups.

The $\Delta\nu_s(NO_2)$ values observed by Hodosan and Jude (2) for *gauche* vicinal dinitrate esters ($\phi \simeq 60°$) probably originated in similar intramolecular interactions of vicinal oxy and nitrato groups. It is clear from the above, however, that this stereochemical analysis could be applied with safety only to dilute solutions in non-specific solvents; the observed $\Delta\nu_s(NO_2)$ values in condensed-state spectra (11, 12) may have inter- as well as intra-molecular origins.

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