

199. Infrared Spectra of Carbohydrate Nitrates and Sulphonates.

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Characteristic infrared absorption bands of the nitrate group present in carbohydrate nitrate esters, mainly derivatives of D-glucose, D-mannose, D-galactose, and D-altrose, have been studied; they enable the nitrate group to be identified in the presence of other groups such as acetyl and methane- and toluene-*p*-sulphonyl, and aromatic rings. The results are compared with those obtained elsewhere for simple aliphatic nitrates. The spectra of eleven of the above D-glucose compounds which contained a sulphonate ester group, together with that of one other toluene-*p*-sulphonate of D-glucose, have been examined for absorption bands characteristic of the sulphonyl groups.

MOST of the data on the infrared spectra of covalent nitrates are provided by Brown.¹ Since Bellamy² summarised the position, Brand and Cawthon³ have studied the vibrational spectrum of methyl nitrate, Rossmly⁴ has published measurements of three diol nitrates, and Krimm and Liang⁵ have analysed the spectrum of polyvinyl nitrate. These later studies disclose only one compound, ethylene glycol dinitrate,⁴ whose group frequencies exceed the normal ranges given by Brown¹ and there by not more than 4 cm.⁻¹.

It is certain that the two strong infrared bands in covalent nitrates near 1640 and 1280 cm.⁻¹ correspond to the asymmetric and symmetric stretching frequencies of the NO₂ grouping. In addition, there is a strong band near 860 cm.⁻¹ and weaker ones are found near 760 and 700 cm.⁻¹. The 860 cm.⁻¹ band is due to the O-NO₂ stretching vibration and that near 760 cm.⁻¹ to the NO₂ out-of-plane rocking.^{1,3,5} There is less certainty about the origin of the 700 cm.⁻¹ band, which is absent in methyl nitrate. It has been variously assigned to NO₂ bending,^{1,5} to the overtone of the 351 cm.⁻¹ C-O-N bending vibration,⁶ and much earlier to NO₂ planar rocking (along with a band near 660 cm.⁻¹).⁷

In the compounds now studied other groups beside the nitrate give rise to absorption bands in the 760 and the 700 cm.⁻¹ region (see below), so that the diagnostic value of the two nitrate bands at these frequencies is much less than in the simpler nitrates. For example, in ethyl nitrate,⁸ ethylene glycol mono- and di-nitrate,⁴ diethylene glycol mono-⁴ and di-nitrate,⁹ triethylene glycol dinitrate and glycerol trinitrate,⁹ and polyvinyl nitrate⁵ there are only two distinctive bands between 800 and 670 cm.⁻¹, but in most of the sugar nitrates there are usually at least three or four of roughly the same intensity.

Table I lists the bands occurring in or near the five characteristic regions given by Brown.¹ Of these, bands I, II, and III are easier to identify by reason of their high intensity and singularity than bands IV and V. Each band with its characteristic features is discussed separately below.

Band I.—Brown¹ assigned the range 1652—1626 cm.⁻¹ to this band. The nitrates examined here had one, occasionally two, and less often more, very strong bands at 1667—1613 cm.⁻¹ [1645 ± 13],* with forty-nine compounds absorbing in the narrower range of 1667—1629 cm.⁻¹. One compound (33) which absorbed here had an additional strong band at 1681 cm.⁻¹. The multiplicity of bands bore no relation to the number of nitrate groups in the molecule. Where there is more than one band the probable cause is

* Arithmetic mean, followed by standard deviation, is given in square brackets.

¹ Brown, *J. Amer. Chem. Soc.*, 1955, **77**, 6341.

² Bellamy, "The Infra-Red Spectra of Complex Molecules," Methuen, London, 1958.

³ Brand and Cawthon, *J. Amer. Chem. Soc.*, 1955, **77**, 319.

⁴ Rossmly, *Chem. Ber.*, 1955, **88**, 1969.

⁵ Krimm and Liang, *J. Appl. Phys.*, 1958, **29**, 1407.

⁶ Suggestion by Brand and Cawthon quoted by Brown.¹

⁷ Lecomte and Mathieu, *J. Chim. phys.*, 1942, **39**, 57.

⁸ Jander and Haszeldine, *J.*, 1954, 919.

⁹ Pristera, *Analyt. Chem.*, 1953, **25**, 844.

TABLE I.^a Absorption frequencies of nitrates.

No.	Compound †	I ^b	II ^b	III ^b	IV ^c	V ^c
<i>Methyl α-D-glucosides.</i>						
(1) 4,6-O-Ethylidene derivatives						
1	2,3-Dinitrate	1650	1277	843 833	749 743	707 700 690
2	2-Nitrate	1645	1285	869	752	715 690
3	3-O-Methyl- 2-nitrate	1653	1279	848	742	716
4	2-Nitrate 3-tos	1661	1279	848 *	745	709
5	3-Nitrate	1629	1267	840 855	746	700 * 701
6	3-Nitrate 2-tos	1650	1274	837 br	752 742	695 * 700 * 691
(2) 4,6-O-Propylidene derivatives						
7	2,3-Dinitrate	1653	1274	861 * 842	749 745	709 704 *
8	3-Nitrate	1634	1269	852 * 848	758 * 744	702
9	2-O-Methyl- 3-nitrate	1639	1276	855	749	697
10	3-Nitrate 2-tos	1664	1269	833	741	701
(3) 4,6-O-Benzylidene derivatives						
11	2,3-Dinitrate	1664 1645	1277 1269	857 844 833	752 ^b 742 768	715 703 697 ^d
12	3-O-Methyl- 2-nitrate	1650 1634	1284	861	746 ^d 743 * ^d	715 694 ^d
13	3-Mes 2-nitrate	1658	1276	840 br	752 ^d 741	709 697 ^d
14	2-Nitrate 3-tos	1656	1276	835 br	761 ^d br 745	707 695 ^d
15	3-Nitrate	1642	1274	846	758 745	700 ^d 695 *
16	2-O-Methyl- 3-nitrate	1639	1269	849	758 * 746 ^d	695 ^d 685 *
17	2-Acetate 3-nitrate	1653 1631	1280	855	747	702 ^d 695
18	2-Mes 3-nitrate	1645	1271	846 br	768 752 ^d	697 ^d 685
19	3-Nitrate 2-tos	1647	1274	855 * 844 br	755 * 746	700 ^d 694 *
(4) Various						
20	4,6-O- <i>p</i> -Nitrobenzylidene- 2,3-di-nitrate ^e	1661	1276	840 br	738	704
21	2,3,4-Triacetate 6-nitrate	1639	1279	878 848 w	755	715
22	2,3,4,6-Tetranitrate ^f	1661	1277	833 br	745	706
<i>Methyl β-D-glucosides.</i>						
(1) Various						
23	3-Nitrate	1621	1277	866	746	713 704 *
24	6-O-Trityl- 3-nitrate ^g	1642	1277	848 br w	746 ^d br	702 ^d br
25	2,4,6-Triacetate 3-nitrate ^h	1667	1276	828	741 vw	704 690
26	2,3,4-Triacetate 6-nitrate ^j	1645	1276	840 w	749	704 br
27	6-Nitrate 2,3,4-tritos *	1639	1279	866 w 840 *	754 * 744	702
28	2,3-Di-O-methyl- 6-nitrate 4-tos	1637	1272	840 * 833 br	749	702 685 *
29	2,3,4-Tri-O-methyl- 6-nitrate ^j	1639	1282	871	752	709 vw
30	3,6-Dinitrate ^g	1664 1639	1274	853 * 846	746	704

TABLE I. (Continued.)

No.	Compound †	I ^b	II ^b	III ^b	IV ^c	V ^c
31	2,3-Dinitrate ^t	1661 1642	1269	840 br	749 740 *	705 690
32	2,3-Di-O-methyl- 4,6-dinitrate ^k	1634	1280	870 839	753 746 *	708 704 *
33	3-O-Methyl- 2,4,6-trinitrate ^m	1656 1684	1276	840 br	746	704 br
34	2,3,4,6-Tetranitrate ⁿ	1661 1631	1276	840 br	752 740	712 690
(2) 4,6-O-Ethylidene derivatives						
35	2,3-Dinitrate	1661	1284 1272	848 * 836	744	694
36	2-Nitrate	1637	1277	846	744	716 701
37	3-Nitrate	1652	1282	848 * 838 br	745	692 s
38	2-Acetate 3-nitrate	1645	1272	845 840 *	746	705 703 *
<i>D-Glucofuranoses.</i>						
39	1,2-O-Cyclohexylidene 3-nitrate	1637	1269	851 843 *	749	709 vw
40	3,5-O-Benzylidene-1,2-O-isopropylidene 6-nitrate	1631	1280	878 862	758 ^d 741	700 ^d 692 *
<i>Methyl α-D-mannosides</i>						
(1) 4,6-O-Ethylidene derivatives						
41	2,3-Dinitrate	1650	1293 1269	848 br 827	746	692
42	2-O-Methyl- 3-nitrate	1636	1282	853	750	—
(2) Various						
43	4,6-O-Benzylidene- 2,3-dinitrate	1647	1293 1276	867 846 856 839	752 746 *	704 ^d 695
44	2-O-Methyl- 3-nitrate	1637	1279	851	748	715
<i>Methyl α-D-galactosides.</i>						
45	2,3-Di-O-methyl- 4,6-dinitrate ^p	1639	1277 1269	855 * 845	752 745	—
46	2,6-Diacetate 3,4-dinitrate	1645 1634	1285 1269	862 840 * 846 833 *	752	709
47	1,2 : 3,4-Di-O-isopropylidene-D-galactose. 6-Nitrate	1623	1272	853	759	704
48	1,3 : 2,4-Di-O-ethylidene-D-sorbitols. 6-Nitrate	1618	1272	858 844	759 753 755	685
49	5,6-Dinitrate	1658 1639	1284	848	751 * 742	685
50	6-Nitrate 5-tos	1645	1279	864 * 861	759 752	701
<i>Various.</i>						
51	Methyl 4,6-O-benzylidene-α-D-altroside 3-nitrate 2-tos	1642	1276	848 br 839 836 *	755 ^d 742	702 * 695 ^d
52	1,3-O-Benzylidene glycerol 2-nitrate	1613	1290	862 w 856 * w	746 ^d 741 ^d	707 * 695 ^d
53	Cellulose trinitrate ^q	1656 br	1276 br	840 v br	746 br	690 br

* Shoulder; br = broad; v = very; w = weak. † tos = toluene-*p*-sulphonate; mes = methanesulphonate.

^a In several spectra where bands I and II had shoulders, only the frequency of the main band is listed. ^b All bands strong except where indicated. ^c All bands weak—medium except where indicated. ^d Medium-strong band assigned to monosubstituted benzene ring. ^e Oldham, *J. Soc. Chem. Ind.*, 1934, 53, 236r. ^f Film, from ether. ^g Dewar and Fort, *J.*, 1944, 492. ^h Fort, Ph.D. Thesis, St. Andrews, 1943. ⁱ Oldham, *J.*, 1925, 127, 2840. ^k Oldham and Rutherford, *J. Amer. Chem. Soc.*, 1932, 54, 366. ^l Bell and Syngé, *J.*, 1937, 1711. ^m Dewar and Fort, *J.*, 1944, 496. ⁿ Dewar, Fort, and McArthur, *J.*, 1944, 499. ^p Robertson and Lamb, *J.*, 1934, 1321. ^q Film.

vibrational interaction of groups within the unit cell of the crystal, or interaction between a group vibration and a lattice vibration, rather than rotational isomerism which is unlikely in the crystalline solid. This is supported by additional measurements on methyl 4,6-*O*-benzylidene-3-*O*-methyl- α -D-glucoside 2-nitrate (12) in Nujol and in chloroform solution. The former spectrum, like that in potassium bromide, showed two bands, whereas the spectrum measured in solution showed only one, at an intermediate frequency (the same compound showed similar behaviour with respect to band II).

Three compounds (41, 43, and 51), containing an axial nitrate group, absorbed within the same frequency range as the remainder with equatorial groups.

For the pyranose secondary mononitrates the band frequency generally increases with increasing size of adjacent groups. This is in line with the fact that in primary nitrates, where the group is relatively isolated from the rest of the molecule and substitution within the pyranose ring would have little effect, the mean frequency is lower than in either type of secondary nitrate (see Table 2).

TABLE 2. Frequency ranges of bands I and II in pyranose mononitrates

Position of nitrate group	No. of compounds	Band I (cm. ⁻¹)	Band II (cm. ⁻¹)
6-	6	1645—1623	1282—1272
		[1637 \pm 7]	[1277 \pm 4]
2-	7	1661—1634	1285—1276
(equatorial)		[1649 \pm 10]	[1279 \pm 4]
3-	19	1667—1621	1282—1267
(equatorial)		[1643 \pm 11]	[1274 \pm 5]

Band II.—This band occurred in the range 1286—1272 cm.⁻¹ in alkyl nitrates.¹ All but one of the compounds examined had one, sometimes two, bands between 1285 and 1267 cm.⁻¹ [1277 \pm 6], while two derivatives of methyl α -D-mannoside (41 and 43) had an additional band at 1293 cm.⁻¹. The one exception was a glycerol derivative (52) which had no band in the above range, but had a very strong one at 1290 cm.⁻¹. There were no marked differences between the various types of nitrate group, as shown in Table 2. In all cases, band II was approximately as intense as band I, and both were amongst the strongest bands in each spectrum.

Band III.—This was assigned the range 872—841 cm.⁻¹ in alkyl nitrates.¹ Many of the compounds studied should have other absorption bands in this region. These include the type 2*a* absorption¹⁰ for derivatives of the α -anomers of D-glucose at 843 \pm 4 cm.⁻¹, of D-mannose at 833 \pm 8 cm.⁻¹, and D-galactose at 825 \pm 11 cm.⁻¹; type 2*c* absorption¹⁰ for derivatives of D-mannose at 876 \pm 9 cm.⁻¹ and D-galactose at 871 \pm 7 cm.⁻¹; type C absorption¹¹ for compounds containing a furanose ring at 858 \pm 7 cm.⁻¹; and the out-of-plane CH deformation vibration² of a 1,4-disubstituted benzene ring at 860—800 cm.⁻¹.

All spectra studied showed one or more bands between 871 and 833 cm.⁻¹, with one exception only (compound 25) where the nearest band was at 828 cm.⁻¹. Table I mentions only the band or bands which are much stronger than the rest within this range. [Three spectra each had an additional band just outside this range—one at 827 cm.⁻¹ (compound 41) and two at 878 cm.⁻¹ (compounds 21 and 40)—which was stronger than any inside and should therefore be considered as a possibility.] This band was often broad, particularly for the polynitrates, and was generally as intense as, or only slightly weaker than, bands I and II. However, for five compounds (21, 24, 26, 27, and 52) it was significantly weaker, and in one of these (52) had only one-tenth of the intensity of bands I or II. The arithmetic mean has not been calculated for this band because many spectra showed several bands in this range, as expected from the complicating factors mentioned above. Similar difficulties and considerations apply to bands IV and V below.

Band IV.—This band was found between 761 and 745 cm.⁻¹ by Brown.¹ In many of

¹⁰ Barker, Bourne, Stephens, and Whiffen, *J.*, 1954, 3468.

¹¹ Barker and Stephens, *J.*, 1954, 4550.

the sugar nitrates examined there were interfering absorption bands from type 3 absorption¹⁰ for derivatives of D-glucose at 753 ± 17 cm.⁻¹ and D-galactose at 752 ± 20 cm.⁻¹, and from the out-of-plane CH vibration² for a monosubstituted benzene ring at 770—730 cm.⁻¹.

There was at least one band between 759 and 738 cm.⁻¹ in all the compounds studied. They were all weak-medium except for one toluene-*p*-sulphonate (4) and the benzylidene compounds where the strong CH vibration (referred to above) came within this range.

In two such compounds (14 and 18) there was only one band (strong) and in another (12) there were two bands only, both strong. If these strong bands in the two compounds are attributable solely to the CH out-of-plane vibration (which can occasionally split into two components²) then the range of band IV has to be extended to include the nearest (weak) absorption which was at 768 cm.⁻¹.

Band V.—Brown¹ found a band between 711 and 690 cm.⁻¹ in the compounds he studied. In the present investigation there was at least one band, and in benzylidene derivatives at least two, in the range 716—685 cm.⁻¹ in all but two compounds (42 and 45). In compounds where there was more than one band of comparable intensity (weak-medium) there was no indication which was the nitrate band, but in benzylidene derivatives the strongest band always occurred between 710 and 690 cm.⁻¹ and has been assigned to the intense out-of-plane ring vibration which occurs in this narrower range.²

Comparison of the above results with Brown's¹ (where the measurements were mostly done on liquid samples) has shown that both limits of bands I, II, and V have to be extended, while bands III and IV certainly require extension towards lower frequencies and possibly at the upper limit too. The extension of the upper limit of band I and of the lower limit of band III bears out Brown's observation¹ from a limited number of compounds that such extensions are necessary for polyol nitrates.

This study has shown that a nitrate group in complex carbohydrate derivatives can be readily identified, principally from bands I and II which are very characteristic and do not suffer from interference by such groups as nitro, acetate, sulphonate, or aromatic rings (see below). Band III is useful for confirmation, but bands IV and V are of very doubtful value. Bands I and II of the nitrate group were as intense as the C=O stretching band of the acetate group.

The spectra of eleven nitrates which also contained a sulphonate group, together with that of another toluenesulphonyl derivative, were found to have bands characteristic of the SO₂ grouping. In the few covalent sulphonates examined previously,¹² these bands were found at 1420—1330 and 1200—1145 cm.⁻¹ and correspond to the SO₂ asymmetric and symmetric stretching frequencies. Five esters of toluene-*p*-sulphonic acid absorbed in the narrower ranges¹³ of 1375—1350 cm.⁻¹ and 1192—1170 cm.⁻¹. In nearly all the sulphonates examined here, there were two bands (usually intense) in each of the two regions 1372—1337 and 1194—1168 cm.⁻¹.

Table 3 lists five absorption regions in the toluene-*p*-sulphonates. These are the aromatic ring vibration² near 1600 cm.⁻¹; the two SO₂ vibrations already mentioned; a band near 810 cm.⁻¹ which is most likely the out-of-plane CH deformation mode² in a 1,4-substituted benzene ring; and a band near 670 cm.⁻¹ which was very much weaker in the two methanesulphonyl derivatives examined. The presence of the aromatic ring must therefore greatly enhance the intensity of the last-named band.

Of the other regions listed in Table 3, the two methanesulphonyl derivatives absorbed strongly in those corresponding to the SO₂ stretching vibrations, but not at all in the two regions near 1600 and 810 cm.⁻¹. The 1600 cm.⁻¹ region is the best for differentiating between a toluene-*p*- and a methane-sulphonate. [Compounds not containing a toluene-*p*-sulphonyl group may absorb near 810 cm.⁻¹, *e.g.*, two sorbitol nitrates (48 and 49) had medium bands at 815—810 cm.⁻¹.]

¹² Colthup, *J. Opt. Soc. Amer.*, 1950, **40**, 397.

¹³ Tipson, *J. Amer. Chem. Soc.*, 1952, **74**, 1354.

As noted,¹⁴ most benzylidene derivatives do not absorb near 1600 cm.⁻¹ and this group did not interfere with the recognition of the toluene-*p*-sulphonate band here. Nor, in any of the compounds examined, did the nitrate band I obscure this sulphonate band. There was little or no absorption near 1500 cm.⁻¹ as generally found in aromatic compounds.

TABLE 3. *Absorption frequencies of methane- and toluene-p-sulphonates.*

No.	Compound †					
<i>Methyl α-D-glucosides.</i>						
4	4,6- <i>O</i> -Ethylidene- 2-nitrate 3-tos	1597 w	1364 s	1185 s	812 s	672 s
			1351 s	1168 vs		668 * s
6	4,6- <i>O</i> -Ethylidene- 3-nitrate 2-tos	1603 w	1361 vs	1190 s	812 s	674 s
				1171 vs	808 * s	667 * m
10	4,6- <i>O</i> -Propylidene- 3-nitrate 2-tos	1597 w	1364 s	1190 s	815 m	675 s
			1351 m	1172 s		667 w
14	4,6- <i>O</i> -Benzylidene- 2-nitrate 3-tos	1595 w	1362 s	1186 s	813 m	667 m
			1344 * m	1168 vs		
19	4,6- <i>O</i> -Benzylidene- 3-nitrate 2-tos	1600 w	1362 s	1189 s	815 s	675 w
				1174 vs		668 m
54	4,6- <i>O</i> -Benzylidene- 2-tos ¹⁵	1600 w	1368 s	1194 s	818 m	678 s
			1360 s	1181 vs		670 m
<i>Methyl β-D-glucosides.</i>						
27	6-Nitrate 2,3,4-tritos	1597 w	1370 vs	1189 vs	820 vs	670 * s
			1346 s	1174 vs	807 vs	665 s
28	2,3-Di- <i>O</i> -methyl- 6-nitrate 4-tos	1595 w	1359 s	1185 s		
			1351 * m	1172 vs	811 s	669 s
50	1,3:2,4-Di- <i>O</i> -ethylidene-D-sorbitol 6-nitrate 5-tos	1595 w	1359 s	1190 * m	820 w	
			1351 * m	1183 s	815 m	670 s
				1175 s	813 * w	
51	Methyl 4,6- <i>O</i> -benzylidene-α-D-altroside 3-nitrate 2-tos	1597 w	1372 vs	1188 vs	818 s	670 s
			1353 s	1176 vs	809 s	667 * s br
					807 * s	
<i>Methyl 4,6-<i>O</i>-benzylidene-α-D-glucosides.</i>						
13	2-Nitrate 3-mes	—	1361 s	1182 s	—	670 w
			1348 s	1168 vs		
18	3-Nitrate 2-mes	—	1366 s	1170 vs	—	671 w
			1337 * m			667 * w

* Shoulder; m = medium; s = strong; v = very; w = weak. † tos = toluene-*p*-sulphonate; mes = methanesulphonate.

Other Functional Groups.—(1) *Nitro.* The one nitro-derivative (20) showed strong bands at 1534 and 1348 cm.⁻¹ in addition to the nitrate bands at 1661 and 1276 cm.⁻¹. The former pair, characteristic of nitro-compounds,² did not interfere with the identification of the nitrate group, in agreement with Brown's findings.¹

(2) *Acetate.* Six nitrates also contained one or more acetate groups. The characteristic acetate bands occurred near 1750 and 1220 cm.⁻¹ and were well separated from the nitrate, toluene-*p*-sulphonate and methanesulphonate bands.

EXPERIMENTAL

All but six of the spectra were measured on a Perkin-Elmer Model 21 spectrometer with a sodium chloride prism, by the Sadtler Research Laboratories, Philadelphia, U.S.A. The spectra of compounds 12, 22, 37, 42, 53, and 54 were measured here on a Unicam S.P. 100 spectrometer (with same prism). Except where shown in Table I, the data given there refer to samples measured as pressed discs in potassium bromide.

Details of the preparation of compounds with no reference in Table I can be found in papers on sugar nitrates by Honeyman and his co-workers.¹⁵ The cellulose trinitrate film was prepared by nitration of a very thin viscose film with a mixture of fuming nitric acid, phosphoric acid, and phosphoric anhydride.

¹⁴ Barker, Bourne, and Whiffen, "Methods of Biochemical Analysis," 1956, Vol. III, p. 213.

¹⁵ Honeyman and his co-workers, *J.*, 1952, 2778; 1955, 3660; 1957, 2278; 1958, 537, 2586; *Chem. and Ind.*, 1953, 1035.

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