

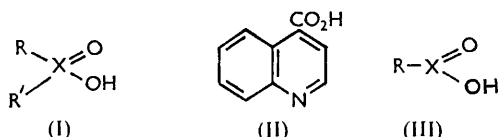
178. Infrared Spectra and Hydrogen Bonding in Compounds containing X(:O)·OH Groups.

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A well-defined absorption pattern, consisting of a characteristic trio of very broad bands in the regions 2800—2400 (*A*), 2350—1900 (*B*), and 1720—1600 cm^{-1} (*C*), appears to provide a reliable criterion for the presence of the structural grouping X(:O)·OH, and to be largely independent of the nature of the central atom X. Examples are cited for X = P, As, S, and Se and, less commonly, C. These bands are undoubtedly associated with vibrations of the OH groups under conditions of strong hydrogen bonding; it is suggested that *A* and *B* correspond to ν OH and *C* to δ OH vibrations. Band *C* is variable in intensity, and is sometimes weak when two OH groups are attached to X, as in organic phosphonic and arsonic acids.

In certain cases these characteristic bands are not observed despite the presence of X(:O)·OH groups, *e.g.*, in the spectra of most carboxylic acids, presumably owing to the occurrence of different patterns of hydrogen bonding.

THE infrared spectra between 4000 and 1500 cm^{-1} of dibenzyl hydrogen phosphate (I; X = P, R = R' = O-CH₂Ph), diphenylphosphinic acid (I; X = P, R = R' = Ph), methylphenylarsinic acid (I; X = As, R = Me, R' = Ph), cinchoninic acid (II), and phenylarsonic acid (I; X = As, R = Ph, R' = OH) are shown in Fig. 1. The relative



widths of the bands are emphasised by adopting the unusual convention of plotting the spectra on a uniform scale of cm^{-1} throughout.

We draw attention to the characteristic trio of very broad absorption bands near 2600, 2200, and 1700 cm^{-1} (subsequently referred to as *A*, *B*, *C*, respectively), each extending over approximately 250 cm^{-1} , which occur strongly in all the spectra except that of the arsonic acid, where band *C* is weaker than *A* and *B*. The same pattern of bands has been observed in the spectra of other phosphinic (I; X = P, R and R' = alkyl or aryl) and arsinic acids (I; X = As, R and R' = alkyl or aryl) studied during the present work. *iso*Nicotinic, quinaldinic, and cinchoninic acids are unusual examples of carboxylic acids which also show the *A*, *B*, *C* pattern of absorption bands. Amino-acids containing more basic nitrogen atoms occur usually in the zwitterionic form, but in the above examples a relatively sharp carbonyl absorption band occurs near 1700 cm^{-1} superimposed on the broad band *C*, indicating that the carboxyl group persists as such, although it is strongly hydrogen bonded, probably with the nitrogen atom of another molecule. Analogous spectroscopic phenomena have been briefly reported for polycyclic derivatives of cinchoninic acid.^{1,2} In this region carboxylic acids which do not contain nitrogen atoms usually give a quite different spectrum, associated with dimeric hydrogen bonded units.³

The pattern *A*, *B*, *C* of absorption bands has been observed previously in the spectra of other phosphinic acids⁴ (I; X = P, R = H, R' = alkyl or aryl), disubstituted phosphates⁴⁻⁷

¹ Braunholtz and Mann, *J.*, 1958, 3368.

² *Idem*, *J.*, 1958, 3377.

³ Bratož, Hadži, and Sheppard, *Spectrochim. Acta*, 1956, 8, 249.

⁴ Daasch and Smith, *Analyt. Chem.*, 1951, 23, 853.

⁵ Bellamy and Beecher, *J.*, 1952, 1701.

⁶ Bellamy and Beecher, *J.*, 1953, 728.

⁷ Maarsen, Smit, and Matze, *Rec. Trav. chim.*, 1957, 76, 713.

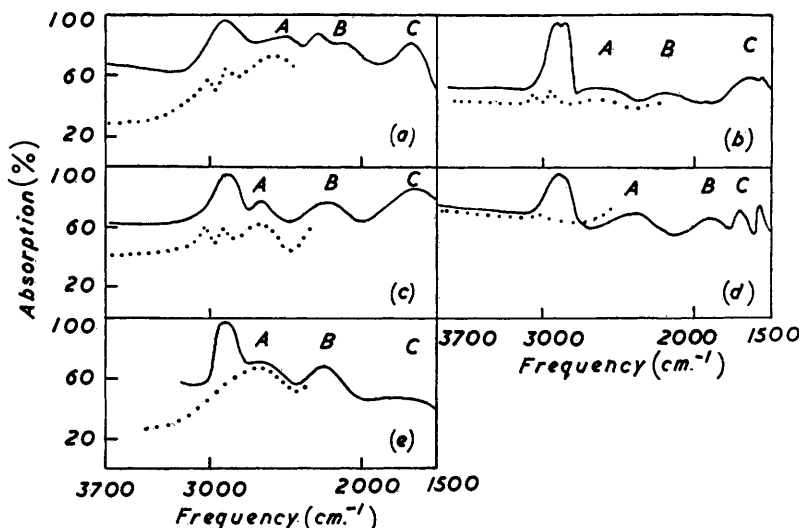
(I; X = P, R and R' = OAlkyl or OAryl), and seleninic acids⁸ (III; X = Se, R = aryl); the bands are also present in the spectra of sulphinic acids^{9,10} (III; X = S, R = aryl) although band C is very weak in this case. Other examples are to be found in published spectra of a variety of inorganic acid salts, such as those containing HPO_4^{2-} , H_2PO_4^- , and H_2AsO_4^- anions.¹¹⁻¹³

Experimental data obtained in the present and previous work are given in the Table. An examination of these leads to the following generalisations:

(1) The presence of the complete trio of bands (A, B, C) appears always to indicate the presence of the structural group X(:O)·OH. The Table gives examples for X = P, As, S, Se, and C.

(2) The presence of the group X(:O)·OH does not, however, necessarily produce in the spectrum any or all of the bands A, B, and C. Thus, the bands are not shown by dimeric carboxylic acids,³ liquid nitric or sulphuric and solid perchloric acids,¹⁴ seleninic acid,⁸ and phenylstibonic acid; the spectra of all these compounds have less broad OH absorption bands at somewhat higher frequencies.

FIG. 1. The infrared spectra, in the region 3700—1500 cm^{-1} , of (a) dibenzyl hydrogen phosphate (I; X = P, R = R' = $\text{O-CH}_2\text{Ph}$), (b) diphenylphosphinic acid (I; X = P, R = R' = Ph), (c) methylphenylarsinic acid (I; X = As, R = Me, R' = Ph), (d) cinchoninic acid (II), and (e) phenylarsonic acid (I; X = As, R = Ph, R' = OH).



The use of a Nujol mull is denoted by (—), and of a hexachlorobutadiene mull by (.....).

(3) Among the organic derivatives band C is usually missing or ill-defined in comparison with A and B when a second hydroxyl group is attached to X. This behaviour is shown, for example, by the phosphonic and arsonic acid (I; X = P or As, R = OH, R' = alkyl or aryl; Fig. 1) and the dihydrogen phosphates⁵ (I; X = P, R = OH; R' = OAlkyl or OAryl). Inorganic ions behave less regularly in this respect, for H_2PO_4^- and H_2AsO_4^- (Fig. 2) show band C strongly, whereas it appears to be weak in the spectrum¹¹ of HSO_4^- . It is probable that the detailed hydrogen-bonding pattern, as influenced by the second hydroxyl group, is responsible for these differences.

⁸ Detoni and Hadži, *J. Chim. phys.*, 1956, **53**, 760.

⁹ Guryanova and Syrkin, *Zhur. fiz. Khim.*, 1949, **23**, 105.

¹⁰ Detoni and Hadži, *J.*, 1955, 3163.

¹¹ Miller and Wilkins, *Analyt. Chem.*, 1952, **24**, 1253.

¹² Corbridge and Lowe, *J.*, 1954, 493.

¹³ *Idem*, *J.*, 1954, 4555.

¹⁴ Bethell and Sheppard, unpublished work.

(4) The trio of bands seems to be relatively independent of the other substituents on X, except when there is another hydroxyl group, as noted in (3).

Characteristic OH absorption bands in the infrared spectra of compounds containing the group X(:O)·OH.

Compound	Position of OH bands (cm. ⁻¹)			Compound	Position of OH bands (cm. ⁻¹)		
	A	B	C		A	B	C
(a) X carries one hydroxyl group.				(b) X carries two hydroxyl groups.			
(I; X = P)				(I; X = P, R = OH).			
R = H, R' = Ph ⁴	2680	2300 *	1670 *	R' = <i>cyclo</i> Hexyl ⁵	2667	2273	—
R = H, R' = <i>p</i> -C ₆ H ₄ Me ⁴	2640	2300 *	1670 *	R' = Bu ⁿ ⁴	2550,	2300	—
R = H, R' = <i>p</i> -C ₆ H ₄ Et ⁴	2640	2300 *	1680 *		2800		
R = H, R' = C ₁₀ H ₇ † ⁴	2550	2300 *	1650 *	R' = Ph ⁴	2690	2300	—
R = R' = Ph	2600	2200	1660	R' = <i>p</i> -C ₆ H ₄ Cl ⁴	†	2300	—
R = Ph, R' = <i>m</i> -C ₆ H ₄ ·OMe	2590	2260,	1720	R' = O-C ₁₈ H ₃₇ ⁶	2700,	2240	—
		2150			2500		
R = Ph, R' = <i>o</i> -C ₆ H ₄ ·OMe	2650	2150	1600	R' = OPh [§] 5	2667	2222	—
R = OMe, R' = OEt ⁴	2650	2300 *	1720 *	R' = O-C ₆ H ₄ ·C ₈ H ₁₇ - <i>p</i> ⁶	2660	2220	—
R = R' = OPrl ⁷	2665	†	1712				
R = R' = OBu ⁿ ⁶	2600	2280	1665	(I; X = As, R = OH).			
R = R' = OBu ^l ⁶	2580	2160	1665	R' = Ph	2680	2280	1650 †
R = R' = O-C ₅ H ₁₁ ⁿ ⁶	2590	2290	1665	R' = <i>p</i> -C ₆ H ₄ Me	2720	2290	1750 †
R = R' = O-C ₅ H ₁₁ ^l ⁶	2600	2220	1665	R' = <i>o</i> -C ₆ H ₄ Me	2800	2340	—
R = R' = O-CH ₂ Ph (see also ref. 6)	2520	2280,	1675	R' = <i>p</i> -C ₆ H ₄ Cl	2800	2340	1650 †
		2150		R' = <i>o</i> -C ₆ H ₄ Br	2750	2320,	1620 †
R = R' = OPh (see also ref. 5)	2600	2100	1675			2180	
R = R' = O-C ₆ H ₄ ·NO ₂ - <i>p</i> ⁵	2632	2353,	1667	(c) Inorganic compounds ¹¹			
		1923		K ₂ HPO ₄ [*]	2860	2380	1850
R = R' = O-C ₆ H ₄ ·OMe- <i>o</i> ⁵	2632	2000	1639	BaHPO ₄ [*]	2700	2440,	1720
R = R' = O-C ₆ H ₂ Cl ₃ - 2 : 4 : 6 ⁵	2703	2353,	1709			2330	
		2174,		KHSO ₄ [*]	2860	2330	1640 †
		1942		KH ₂ PO ₄ [*]	~2800	2330	1640
(I; X = As)				(NH ₄)H ₂ PO ₄ [*]	2860	2330	1640
R = Me, R' = Ph	2700	2240	1675	KH ₂ AsO ₄ (see also ref. 11)	2700	2300	1700
R = Ph, R' = CH ₂ Ph	2680	2340	1700				
R = Ph, R' = <i>m</i> -C ₆ H ₄ ·NO ₂	2670	2370,	1705	(d) Compounds containing X(:O)·OH groups with exceptional OH frequencies.			
		2260		Carboxylic acids (dimeric) ³	ca. 3000		
(III; X = S) ¹⁰				(I; X = Sb, R = OH, R' = Ph)	3200		
R = Ph	2790 *	2340 *	1650 *	HNO ₃ (liquid) ¹⁴	ca. 3300,	3000,	2700
R = <i>p</i> -C ₆ H ₄ Me	2790 *	2340 *	1650 *	H ₂ SO ₄ (liquid) ¹⁴	ca. 2900		
R = 2-C ₁₀ H ₇	2790 *	2340 *	1700 *	HClO ₄ (solid) ¹⁴	ca. 3300		
(III; X = Se) ⁸				NaHCO ₃ ¹¹	ca. (2900),	2500	
R = Ph	2720 *	2270 *	1660 *	KHCO ₃ ¹¹	ca. 2900,	2650	
R = <i>p</i> -C ₆ H ₄ Me	2720 *	2270 *	1660 *	(III; X = Fe) ^a (Lepidocrocite)	3395,	3125	
(III; X = C)				(III; X = Fe) ^a (Goethite)	3095		
<i>iso</i> Nicotinic acid	2400	1972	1700	(III; X = Mn) ^a (Manganite)	2625,	2040	
Quinaldinic acid	2500	1932	1690	(III; X = Al) ^a (Diaspore)	2925,	2340,	2115,
Cinchoninic acid (II)	2370	1900	1715		1985		

* The position of the centre of these bands has been estimated from published data.

† The original authors do not specify α - or β -naphthyl.

‡ Band doubtful or very weak.

§ Hydrated.

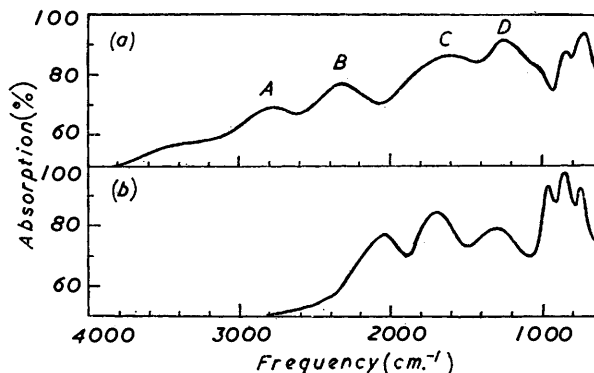
^a Cabannes-Ott, *Compt. rend.*, 1957, **244**, 2491.

The extremely broad bands under consideration are undoubtedly associated with vibrations involving hydroxyl groups which are concerned in very strong hydrogen bonding. Thus they disappear when the hydroxyl group is removed by salt formation,^{8,10-13} and we have observed no such bands in the infrared spectrum of diphenylphosphinodithioic acid.

The higher-frequency bands *A* and *B* have been assigned with consistency to OH bond-stretching vibrations (ν OH) by previous workers; however, conflicting assignments have been proposed for band *C*. Detoni and Hadži⁸ in their study of seleninic acids suggest that *C* is another ν OH band of surprisingly low frequency; Maarsen *et al.*⁷ and Thomas¹⁵ ascribe it on the other hand to an in-plane OH angle deformation vibration (δ OH) of unusually high frequency. In either case strong hydrogen bonding could account qualitatively for the abnormal frequency.

We have now studied the spectrum of potassium dihydrogen arsenate and its dideuterio-analogue. This pair of compounds was chosen because¹¹ no fundamental frequencies involving As=O or As=O bonds complicate the spectrum above 1000 cm^{-1} . The spectrum of Fig. 2*a* is remarkable for the fact that, apart from a number of relatively shallow dips which define the "separate" bands in the absorption curve, there is almost continuous absorption from about 3000 cm^{-1} to 1000 cm^{-1} . In addition to the bands *A*, *B*, and *C* this spectrum shows another broad band, *D*, near 1300 cm^{-1} which also has its origin in an OH vibration, for it shifts to considerably lower frequencies with deuteration. This band *D* is also discernible in the spectra of a number of organic molecules of the general type discussed here although it is then overlaid by much sharper absorption bands of the alkyl or aryl substituents.

FIG. 2. The infrared spectra of (a) potassium dihydrogen arsenate and (b) potassium dideuterium arsenate: both spectra are compounded from measurements with Nujol and hexachlorobutadiene mulls.



Detoni and Hadži⁸ have previously assigned band *D* in the spectrum of seleninic acids to a δ OH vibration, and as it merges smoothly with band *C* we prefer the assignment of the latter to a δ OH vibration also,^{7,15} and the two higher-frequency bands *A* and *B* to ν OH vibrations. It has been suggested^{5,6} that compounds containing the P(:O)·OH group have δ OH bands in the vicinity of 1030 cm^{-1} ; however, the evidence for this assignment is not clear-cut and has recently been challenged.¹⁵ In most other types of compound hydrogen-bonded δ OH vibrations have been assigned^{16,17} to the general region 1500—1200 cm^{-1} ; a move to higher frequencies is not unexpected for conditions of exceptionally strong hydrogen bonding.

The fact that there are two ν OH and two δ OH absorption bands calls for comment. In the dihydrogen arsenate they agree with the presence of two OH groups in the ion; however, this cannot be the cause of the doubling, since the seleninic acids, with one hydroxyl group per molecule, show all four bands at similar positions.⁸ Blinc and Hadži¹⁸ made the interesting suggestion that the doubling of the ν OH bands is caused by the unusual properties of a double-minimum potential-energy curve which may control the vibration of the hydrogen atoms;¹⁹ however, this suggestion does not seem to explain readily the

¹⁵ Thomas, *Chem. and Ind.*, 1957, 198.

¹⁶ Stuart and Sutherland, *J. Chem. Phys.*, 1956, **24**, 559.

¹⁷ Hadži and Sheppard, *Proc. Roy. Soc.*, 1953, *A*, **216**, 247.

¹⁸ Blinc and Hadži, Proceedings of symposium on hydrogen bonding, Ljubljana, 1957, Pergamon Press (in course of publication); and personal communication.

¹⁹ Kovner and Kapshtal, *Izvest. Akad. Nauk S.S.S.R., Ser. fiz.*, 1953, **17**, 561.

doubling of the δOH bands. Another possibility is that the doubling of both types of vibration frequency is caused by the exceptional coupling between adjacent ions through the strong hydrogen bonds. This explanation would be consistent with the X-ray crystal structures of dibenzyl hydrogen phosphate²⁰ and benzeneseleninic acid,²¹ in which the hydrogen bonds couple the molecules together into spiral-type chains with two-molecule repeating units; on the other hand, a splitting of about 400 cm.^{-1} in each case seems large for intermolecular effects. Finally, it is possible that some of these bands may represent overtones or combination frequencies of the lower-frequency δOH or γOH vibrations³ (thus the *ca.* 2700 cm.^{-1} band might correspond to the overtone of band *D*). Further experimental work is needed to distinguish between these possibilities.

EXPERIMENTAL

Potassium Dideuterium Arsenate.—Dry technical potassium dihydrogen arsenate (*ca.* 250 mg.) was dissolved in deuterium oxide (99.78%; 2 c.c.). The solvent was removed under vacuum, and the procedure was repeated with the solid residue. The dideuterium arsenate so obtained was stringently protected from atmospheric moisture before and during the preparation of the Nujol mull. Complete deuteration was confirmed by the absence of hydroxyl absorption bands from the infrared spectrum.

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²⁰ Dunitz and Rollett, *Acta Cryst.*, 1956, **9**, 327.

²¹ Bryden and McCullough, *ibid.*, 1954, **7**, 833.
