

The Influence of Pressure on the Infrared Spectra of Hydrogen-Bonded Solids. IV* Miscellaneous Compounds

Sefton D. Hamann and Max Linton

Applied Chemistry Laboratories, CSIRO,
P.O. Box 4331, Melbourne, Vic. 3001.

Abstract

Measurements have been made of the influence of pressure on the stretching and bending frequencies of hydrogen bonds in a further series of 15 solid compounds. Two exceptions have been found to the general rule that an increase of pressure decreases the X-H stretching frequencies of weak and medium-strength X-H...Y bonds. Possible explanations are offered of the exceptions.

In earlier papers in this series¹⁻³ we reported measurements of the influence of pressure on the infrared vibrational spectra of polycrystalline solids containing the hydrogen-bond systems O-H...O, N-H...N, N-H...O, N-H...Cl, F-H-F and Cl-H-Cl. The present note concerns a few additional compounds which have O-H...O, O-H...N, N-H...N, and N-H...O bonds.

The compounds are listed in Table 1. The first eleven, which are disubstituted derivatives of benzene, have been shown by Bridgman⁴ to be free of high-pressure phase transitions below 40 kbar (1 kbar = 10^8 Pa \equiv 986.92 atm). The spectra of all the compounds except compound 15 (which gave evidence of a phase transition) changed smoothly with increasing pressure, and Table 1 shows the frequency shifts that occurred for the hydrogen-bond stretching and bending bands between 0 and 40 kbar. The assignments are those of Varsányi⁵ for compounds 1-9 and 11; of Newman and Badger⁶ for compound 12; of Marzocchi and Castellucci⁷ for compound 15, and our own for compounds 10, 13 and 14. Table 1 also shows the lengths *R* of the hydrogen bonds, where these have been measured.

The hydrogen bonds of the compounds in Table 1 are either weak or of medium strength and, for the reasons outlined earlier,¹⁻³ we expected their stretching frequencies to decrease and their bending frequencies to increase with increasing pressure. Wherever changes occurred they were in agreement with those expectations, except in the case of the stretching frequencies of compounds 4, 5 and 9. It is doubtful

* Part III, *Aust. J. Chem.*, 1976, 29, 1641.

¹ Hamann, S. D., and Linton, M., *Aust. J. Chem.*, 1975, 28, 2567.

² Hamann, S. D., and Linton, M., *Aust. J. Chem.*, 1976, 29, 479.

³ Hamann, S. D., and Linton, M., *Aust. J. Chem.*, 1976, 29, 1641.

⁴ Bridgman, P. W., *Proc. Am. Acad. Arts Sci.*, 1948, 76, 71.

⁵ Varsányi, G., 'Assignments for Vibrational Spectra of Seven Hundred Benzene Derivatives' (Adam Hilger: London 1974).

⁶ Newman, R., and Badger, R. M., *J. Am. Chem. Soc.*, 1952, 74, 3545.

⁷ Marzocchi, M. P., and Castellucci, E., *J. Mol. Struct.*, 1971, 9, 129.

whether the increase of 1 cm^{-1} for the 3455-cm^{-1} band of compound 9 is significant, and that band may in any case arise from an N-H group which is not hydrogen-bonded, but the increases of frequency for compounds 4 and 5 were unmistakable and certainly related to hydrogen-bonded groups.

Table 1. The effects of pressure on the vibrational frequencies of hydrogen bonds

The ν are wavenumbers in cm^{-1} and the $\Delta\nu$ are the changes of wavenumber that occurred between 0 and 40 kbar. R denotes the $\text{X}\cdots\text{Y}$ distance in Å in the hydrogen-bonded system $\text{X-H}\cdots\text{Y}$

Compound	R	Hydrogen bond	Stretching vibrations			Bending vibrations		
			ν	$\Delta\nu$	Assignment	ν	$\Delta\nu$	Assignment
1 <i>o</i> -Nitrophenol			3238	-16	O-H str.	1173	+2	OH i.p. bend
						1260	+24	OH i.p. bend
2 <i>m</i> -Nitrophenol			3375	-45	O-H str.	1163	+13	OH i.p. bend
						1213	+8	OH i.p. bend
3 <i>p</i> -Nitrophenol			3350	-23	O-H str.	595	+10	OH o.p. bend
						1200	0	OH i.p. bend
4 <i>o</i> -Aminophenol			3295	+8	N-H str.	883	+7	OH o.p. bend
			3365	+5	N-H str.	1071	+2	NH ₂ rock
						1215	+18	OH i.p. bend
5 <i>m</i> -Aminophenol	2.75 ^B	O-H \cdots N	3287	0	N-H str.	900	+15	OH o.p. bend
	3.05	N-H \cdots O	3351	+4	N-H str.	1180	+7	OH i.p. bend
						1260	+21	OH i.p. bend
6 <i>p</i> -Aminophenol	2.83 ^C	O-H \cdots N	3270	-10	N-H str.	973	+47	OH o.p. bend
	3.13, 3.18	N-H \cdots O	3325	0	N-H str.	1095	+10	NH ₂ rock
						1230	0	OH i.p. bend
7 <i>o</i> -Aminobenzoic acid	2.54 ^D	O-H \cdots O	3230	-70	N-H str.	929	+16	OH o.p. bend
	2.61-2.87	N-H \cdots O	3315	-15	N-H str.	1070	0	NH ₂ rock
	2.87	N-H \cdots N				1373	+13	OH i.p. bend
8 <i>m</i> -Aminobenzoic acid (zwitterion)			3000 ^K	-10 ^K	N ⁺ -H str.			
9 <i>p</i> -Aminobenzoic acid	2.61, ^E 2.64	O-H \cdots O	3217	-8	O-H str.	540	+4	NH ₂ wag
	2.98	N-H \cdots O	3359	-7	N-H str.	890	+32	OH o.p. bend
			3455	+1	N-H str.	1420	+5	OH i.p. bend
						1620	+4	NH ₂ def.
10 <i>o</i> -Methylbenzoic acid	2.63 ^F	O-H \cdots O	3065	-30	O-H str.	910	+35	OH o.p. bend
11 <i>o</i> -Phenylene-diamine			3197	-10	N-H str.	1055	0	NH ₂ rock
			3280	0	N-H str.	1635	0	NH ₂ def.
			3370	0	N-H str.			
12 Cyanuric acid	2.78, ^G 2.81	N-H \cdots O	3080	-25	N-H str.	805	+15	NH o.p. bend
			3200	-30	N-H str.	1400	+2	NH i.p. bend
13 Chloranilic acid	2.77 ^H	O-H \cdots O	3230	-80	O-H str.	852	+20	OH o.p. bend
						1265	+15	OH i.p. bend
14 D-Tartaric acid	2.63-2.91 ^I	O-H \cdots O	3390	-62	O-H str.	940	+60	OH o.p. bend
						1255	+28	OH i.p. bend
15 Pentaerythritol ^A	2.74 ^J	O-H \cdots O	3320	-70	O-H str.	660	+63	OH o.p. bend
						1410	+33	OH i.p. bend

^A The spectra suggest that pentaerythritol undergoes a high-pressure phase transformation; this will be discussed elsewhere.

^B De Rango, C., Brunie, S., Tsoucaris, G., Declercq, J. P., and Germain, G., *Cryst. Struct. Commun.*, 1974, 3, 485.

^C Brown, C. J., *Acta Crystallogr.*, 1951, 4, 100.

^D Brown, C. J., *Proc. R. Soc. London, Ser. A*, 1968, 302, 185.

^E Lai, F. T., and Marsh, E., *Acta Crystallogr.*, 1967, 22, 885.

^F Katayama, C., Furusaki, A., and Nitta, I., *Bull. Chem. Soc. Jpn*, 1967, 40, 1293.

^G Verschoor, G. C., and Keulen, E., *Acta Crystallogr., Sect. B*, 1971, 27, 134.

^H Andersen, E. K., *Acta Crystallogr.*, 1967, 22, 188.

^I Okaya, Y., Stemple, N. R., and Kay, M. I., *Acta Crystallogr.*, 1966, 21, 237.

^J Hvorslev, J., *Acta Crystallogr.*, 1958, 11, 383.

^K This band is very broad and it is difficult to determine the position of its maximum; the values of ν and $\Delta\nu$ are approximate values.

Although we are not sure of the exact reasons for these exceptions to the general rule, we can suggest two possible explanations. First, there is an implicit assumption in our simple theoretical model¹ that an increase of pressure causes a decrease of the $\text{X}\cdots\text{Y}$ distance in a solid with $\text{X-H}\cdots\text{Y}$ bonds. That seems a generally plausible

assumption, but it is not necessarily valid in all cases. Although there is a thermodynamic requirement that the total volume of a stable solid decrease with increasing pressure, there is no theoretical requirement that *all* the interatomic distances should decrease, and quite simple solids such as hexagonal selenium and tellurium have been found to expand along one of their axes when they are compressed, the expansion in that direction being counterbalanced by much larger contractions along the other axes.⁸ It is known that hydrogen-bonded solids have highly anisotropic compressibilities—for instance compounds 14 and 15 of Table 1 are many times less compressible in the planes of their hydrogen bonds than at right angles to those planes⁹—and there may well be cases where the $X \cdots Y$ distance actually increases with increasing pressure. Unfortunately nothing is known about the compressional anisotropy of compounds 4 and 5, but it may be significant that the three aminophenols are the least compressible, in the range 0–40 kbar, of all but one of the 54 non-ionic disubstituted derivatives of benzene that Bridgman⁴ examined. The second possible explanation is that compression may cause bending and consequent weakening of the hydrogen bonds (the $N-H \cdots O$ bonds in *m*-aminophenol are already considerably bent at normal pressure¹⁰).

To decide between these possibilities, and others, would require a high-pressure X-ray diffraction study of the aminophenols.

Manuscript received 24 February 1976

⁸ Vereshchagin, L. F., Kabalkina, S. S., and Shulenin, B. M., *Sov. Phys.—Dokl.*, 1966, **10**, 1053.

⁹ Kabalkina, S. S., *Sov. Phys.—Solid State*, 1963, **4**, 2288.

¹⁰ De Rango, C., Brunie, S., Tsoucaris, G., Declercq, J. P., and Germain, G., *Cryst. Struct. Commun.*, 1974, **3**, 485.