INFRA-RED AND ^{35}Cl NUCLEAR QUADRUPOLE RESONANCE STUDIES OF HYDROGEN BONDED ADDUCTS OF 2-CHLOROBENZOIC ACID DERIVATIVES

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Dedicated to Professor Otto Exner on the occasion of his 65th birthday.

The IR and ^{35}Cl NQR spectra of several solid hydrogen bonded adducts of *o*-chlorobenzoic acids and amines were studied over the broad ΔpK_a range. Both IR and NQR spectra yield the indication of the existence of an inversion (critical) ΔpK_a range where the proton transfer takes place. The critical point is distinguished by a deep minimum of the position of the gravity centre of the broad protonic band. The mechanism of the transmittance of the charge distribution within the hydrogen bridge on the electric field gradient in the position of quadrupole Cl nuclei attached to the phenyl ring is analysed.

The studies of hydrogen bonded complexes formed by carboxylic acids and nitrogen bases in condensed phases seem to indicate[1,2] that there exists some ΔpK_a range where the proton transfer (PT) takes place followed by the formation of ion pairs. In numerous liquid systems one observes within an appropriate ΔpK_a range the PT equilibrium[3−5].

$$\text{—O—H····N} \quad \rightleftharpoons \quad \text{—O}^{(-)}\text{···H—N}^{(+)}\text{—}$$
$$\text{(HB)} \qquad\qquad \text{(PT)}$$
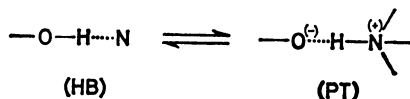
This inversion ΔpK_a range, called critical[2,6], is characterized by a number of anomalies such as: (i) unusual broadening of protonic IR absorption bands[7−9]; (ii) remarkable increase of their intensities[10,11]; (iii) the shift of the gravity centre of "continua" to extremely[12−14] low frequencies, sometimes below $1\,000\,\text{cm}^{-1}$; (iv) very high values of chemical shifts in NMR of bridge active protons[15,16]; (v)

particularly low values of the isotopic ratio $\nu(OH)/\nu(OD)$ (ref.[17]) and finally a step-wise change of the charge distribution visible in the value of the hydrogen bond dipole moment[18].

The [35]Cl NQR studies of crystalline hydrogen bonded complexes performed so far[19-21] showed that the NQR frequencies observed for Cl nuclei in proton-donor molecules undergo a marked drop after complexation with bases. It was found out that the shape of the plot NQR frequency versus ΔpK_a is to large extent similar to that of $\Delta\mu$ (the increase of the dipole moment) versus ΔpK_a in the solution. It means that the NQR frequencies observed on Cl atoms in proton-donor molecules are formally the linear functions of the proton transfer degree. It is worth noticing that the Cl atoms do not participate directly in the hydrogen bond formation and play only a role of probes sensitive to the charge distribution in the hydrogen bridge. The mechanism of the transmittance of the change in the charge distribution within the bridge on the electric field gradient in the position of a resonating nucleus is not understood, but it seems that the direct inductive effect causing the polarization of the C—Cl bond is dominating (the internal Stark effect[22]).

In the present paper we would like to present the results of studies on the relation-ships between the position of the gravity centre of the broad protonic bands, ν_{cg}, as well as [35]Cl NQR frequencies and ΔpK_a value for a large group of complexes com-posed of benzoic acids in the solid state. The results of such complementary studies should answer the question to what extent the critical point seen in anomalies in IR spectra can be correlated with the degree of the charge transfer.

EXPERIMENTAL

The adducts of 2-chloro-4-nitro-, 2-chloro-5-nitro-, 2,6-dichloro-3-nitro- and 2-chloro-3,5-di-nitrobenzoic acids with amines were prepared by precipitation from equimolar solutions of the components in acetonitrile. The composition of adducts was controlled by analysis of Cl. The ΔpK_a value changed within the range $-2\cdot4$ to $10\cdot4$. The NQR spectra were recorded at liquid nitrogen temperature by means of a pulse ISSh-1-13M spectrometer. The great majority of adducts showed single [35]Cl resonance line. In a few cases where more than one resonance lines were observed the averaged frequencies were taken for the analysis.

The IR spectra were recorded on a Perkin–Elmer 180 spectrophotometer by using the KBr pellets. The gravity centres of broad bands corresponding to protonic vibrations (either ν_{OH} or ν_{NH^+}) were estimated by a numerical integration ($\nu_{cg} = \int\nu A(\nu)\,d\nu/\int A(\nu)\,d\nu$).

RESULTS AND DISCUSSION

The behaviour of the adducts investigated in this paper is consistent with that ob-served so far in studies of the charge distribution in hydrogen bridges by using both the dipole moment technique in solutions[18] and NQR application to solid com-plexes[20]. The hydrogen bond formation leads in all known cases of intermolecular

interactions to the charge displacement expressed by a $\Delta\mu$ vector directed from the proton acceptor B to proton donor AH group.

$$A—\overset{\overleftarrow{\Delta\mu}}{H}\cdots\cdots B$$
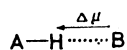
The sense of $\Delta\mu$ implies that in such complexes as chlorophenols with amines, chloro-acetic acid with amines and chlorobenzoic acids with amines the hydrogen bond formation always causes the lowering of the ^{35}Cl NQR frequency.

The results obtained in this paper are summarized in Table I and illustrated in Fig. 1 by using the adducts of 2-chloro-4-nitrobenzoic acid as an example. As it can be seen a remarkable scattering of experimental points has to be emphasized although one can separate two area corresponding to HB and PT states. The average v_{NQR} values for HB and PT adducts differ considerably and the "lattice noises" do not obscure completely the picture. The estimated $\Delta v_{NQR} = v_{PT} - v_{HB}$ values obtained for four series of adducts are equal to $-1\cdot26$ MHz for 2-chloro-4-nitrobenzoic acid, $-1\cdot04$ MHz for 2-chloro-5-nitrobenzoic acid, $-0\cdot96$ MHz for 2-chloro-3,5-di-nitrobenzoic acid and $-0\cdot57$ MHz for 2,6-dichloro-3-nitrobenzoic acid. Therefore, we note a striking difference between the complexes of dichlorobenzoic acid and remaining monochloro derivatives.

Let us assume, which can be justified on basis of the hitherto existing data[20], that the observed shifts of NQR frequencies in complexed proton donors are due to the electric field arising from the dipole moment $\Delta\mu$ of the hydrogen bonding. If the electric field gradient (EFG) tensor posseses the symmetry close to axial ($\eta \leqq 0\cdot2$) and the spin of the quadrupole nucleus equals to 3/2, the shift Δv can be expressed by[24]
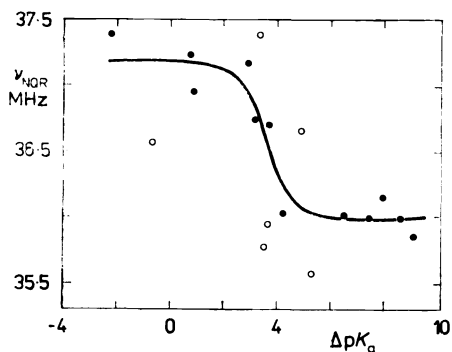
$$\Delta v = \frac{eQ}{2h} R_{zzz}E_z , \tag{1}$$

FIG. 1
v_{NQR} ^{35}Cl plotted versus ΔpK_a for 2-chloro--4-nitrobenzoic acid complexes

TABLE I

^{35}Cl NQR frequencies (ν_{NQR}), average ^{35}Cl NQR frequencies ($\overline{\nu}_{NQR}$), positions of the gravity centres of protonic bands (ν_{cg}) and the proton transfer contributions (x_{PT}) estimated from NQR frequencies

Amine	ΔpK_a	ν_{NQR} MHz	$\overline{\nu}_{NQR}$ MHz	ν_{cg} cm^{-1}	x_{PT}
		2-Chloro-4-nitrobenzoates			
2-Cyanopyridine	−2·22	37·21[a]; 37·56[a]	37·39	1 940	0·00
3-Cyanopyridine	−0·61	36·569	36·57	1 860	0·00
6-Nitroquinoline	0·76	37·21[a]	37·21	1 790	0·00
3-Bromopyridine	0·89	36·926	36·93	1 730	0·00
Quinoline	2·97	37·068	37·07	1 330	0·14
6-Methylquinoline	3·19	36·737	36·74	1 820	0·21
7-Methylquinoline	3·33	37·34[a]	37·34	1 010	0·27
2,6-Dimethylquinoline	3·50	35·768	35·77	660	0·35
4-Methylquinoline	3·63	35·954	35·95	1 160	0·42
3-Methylisoquinoline	3·68	36·702	36·70	1 200	0·45
3,5-Dimethylpyridine	4·18	36·019	36·02	610	0·72
2,4-Dimethylpyridine	4·81	36·651	36·65	1 110	0·92
1-Methylimidazole	5·24	35·561	35·56	1 340	0·97
Morpholine	6·53	36·023	36·02	2 580	1·00
4-Amino-2-methylquinoline	7·46	35·99[a]	35·99	2 260	1·00
Tributylamine	7·97	36·14[a]	36·14	2 650	1·00
Pentylamine	8·67	35·995	36·00	2 710	1·00
Dipropylamine	9·04	35·839	35·84	2 760	1·00
		2-Chloro-5-nitrobenzoates			
2-Cyanopyridine	−2·43	37·014	37·01	2 330	0·00
3-Cyanopyridine	−0·82	37·139	37·14	1 910	0·00
4-Cyanopyridine	−0·31			2 050	0·00
6-Nitroquinoline	0·55	36·621	36·62	1 950	0·00
3-Bromopyridine	0·68	36·862	36·86	2 070	0·00
2-Methoxypyridine	0·89	36·496	36·50	1 952	0·00
8-Methylquinoline	2·74			990	0·09
Quinoline	2·76	36·956	36·96	820	0·09
2,4-Dimethylquinoline	2·95	36·282	36·28	970	0·13
7-Methylquinoline	3·12			1 580	0·18
Isoquinoline	3·23	36·755	36·76	1 650	0·22
2,6-Dimethylquinoline	3·29	35·807; 36·468	36·14	630	0·25
4-Methylquinoline	3·42	36·336	36·34	1 000	0·31
3-Methylisoquinoline	3·47	36·743	36·74	720	0·33
2-Methylpyridine	3·77	36·160; 36·460	36·31	1 220	0·50
3,5-Dimethylpyridine	3·97	36·502	36·50	970	0·61
5,6,7,8-Tetrahydroquinoline	4·48	36·186	36·19		0·84

TABLE I
(*Continued*)

Amine	ΔpK_a	ν_{NQR} MHz	ν_{NQR} MHz	ν_{cg} cm^{-1}	x_{PT}
2-Amino-3-methylpyridine	5·07	36·603	36·60	1 920	0·95
N-Methylmorpholine	5·21			1 550	0·96
Morpholine	6·32	35·855	35·86	2 380	1·00
Triethylenediamine	6·65	35·609; 36·185[b] 36·481	36·12		1·00
4-Aminopyridine	6·95	36·546	36·55	2 360	1·00
Pentylamine	8·46	35·714	35·71	2 800	1·00
Dipropylamine	8·83	35·620	35·62	2 730	1·00
Dibutylamine	9·08	35·870; 36·134	36·00	2 760	1·00
Pyrrolidine	9·14	35·405	35·41	2 780	1·00

2,6-Dichloro-3-nitrobenzoates

3-Cyanopyridine	0·40	35·999; 38·487	37·24	1 820	0·00
4-Cyanopyridine	0·91	36·328; 38·141	37·23	1 950	0·00
6-Nitroquinoline	1·77			1 320	0·01
3-Bromopyridine	1·90			1 160	0·01
Quinoline	3·98	35·755; 38·246	37·00	710	0·62
6-Methylquinoline	4·20	35·716; 38·177	36·95	690	0·73
7-Methylquinoline	4·34			1 290	0·79
2,6-Dimethylquinoline	4·51	35·683; 37·920	36·80	1 380	0·85
3-Methylisoquinoline	4·69	35·440; 38·088	36·76	1 450	0·89
5,6,7,8-Tetrahydroquinoline	5·70	35·773; 37·475	36·62	1 600	0·99
2,4-Dimethylpyridine	5·82			1 640	0·99
1-Methylimidazole	6·25	35·801; 38·215	37·01		1·00
2-Amino-3-methylpyridine	6·29	35·954; 37·709	36·83	2 020	1·00
Morpholine	7·54	36·032; 37·937	36·98	2 430	1·00
4-Aminopyridine	8·17			2 200	1·00
4-Amino-2-methylquinoline	8·47	35·843; 37·492	36·67	2 320	1·00
Dipropylamine	10·05			2 770	1·00
Pyrrolidine	10·36	35·774; 37·352	36·56	2 820	1·00

2-Chloro-3,5-dinitrobenzoates

2-Cyanopyridine	−1·79			1 920	0·00
3-Cyanopyridine	−0·18	38·652	38·65	1 740	0·00
4-Cyanopyridine	0·33	39·023	39·02	1 590	0·00
6-Nitroquinoline	1·19	39·266	39·27	1 660	0·00
2-Methoxypyridine	1·53	39·094	39·09	1 710	0·01
Quinoline	3·40	37·967	37·97	970	0·30
2,4-Dimethylquinoline	3·59			1 470	0·40
2,6-Dimethylquinoline	3·93	37·971	37·97	980	0·59

TABLE I
(Continued)

Amine	ΔpK_a	ν_{NQR} MHz	ν_{NQR} MHz	ν_{cg} cm^{-1}	x_{PT}
4-Methylquinoline	4·06	38·261	38·26	650	0·66
3-Methylisoquinoline	4·11	38·449	38·45		0·69
2-Methylpyridine	4·41	38·746	38·75	1 430	0·81
5,6,7,8-Tetrahydroquinoline	5·12	38·22^a; 38·30^a	38·26		0·96
2,4-Dimethylpyridine	5·24			1 310	0·97
2-Amino-3-methylpyridine	5·71			1 570	0·99
Morpholine	6·96	37·917	37·92	2 480	1·00
4-Aminopyridine	7·59	38·704; 38·806	38·76	2 490	1·00
4-Amino-2-methylquinoline	7·89	38·043	38·04	2 460	1·00
Dipropylamine	9·47			2 740	1·00
Dibutylamine	9·72			2 750	1·00

^{a} Broad line; ^{b} doublet.

where $R_{ZZZ} = \delta V_{ZZ}/\delta E_Z$ is the parameter dependent on the character of the chemical bond in which the Cl atom is participating[25], e — the elementary charge, Q — the quadrupole moment of the ^{35}Cl nucleus, h — the Planck constant and E_Z — the Z component (in the principal axes system of the EFG tensor) of the electric field strength vector created by the dipole moment $\Delta\mu$ of a hydrogen bond[26]:

$$\mathbf{E} = \frac{1}{4\pi\varepsilon_0\varepsilon}\left(\frac{\Delta\mu}{r^3} - \frac{3(\Delta\mu r)\,r}{r^5}\right),\qquad(2)$$

where ε_0 is the electric permittivity of vacuum, ε — permittivity of a medium and r — the vector linking the nucleus of the Cl atom with the centre of the dipole $\Delta\mu$. As one can gain the information about $\delta v/\delta E_Z = (eQ/2h)\,R_{ZZZ}$, from the measurements of NQR frequencies in the external electric field, it is convenient to express the Eq. (1) in the form:

$$\Delta v = \left(\frac{\delta v}{\delta E_Z}\right)E_Z.\qquad(3)$$

The value of $\delta v/\delta E_Z$ depends, similarly to R_{ZZZ}, on the chemical nature of the bond in which the Cl atom is participating. In our case we assumed $\delta v/\delta E_Z = 38·5 \cdot 10^{-11}$ MHz m V^{-1}(ref.[25]).

The Eqs (2) and (3) allow us to estimate the Δv values caused by the increase of the

hydrogen bond polarity induced by the proton transfer. For the estimation of E_Z and, hence Δv value the dihedral angle between the planes of the phenyl ring and the carboxylic group was accepted to be equal to 10° in 2-chlorobenzoates and 45° in 2,6-dichlorobenzoates[27]. In monochlorobenzoates the hydrogen bonding occupies the *trans*-position with respect to the chlorine atom. In the calculations of E_Z we assumed that the $O\cdots H \cdots N$ bridges are located in the plane of carboxylic group and the bond lengths C_{ar}—C_{ar}, C_{ar}—Cl, C_{ar}—C, C—$O^{(-)}$ and $O\cdots N$ are equal to 0·1395, 0·173, 0·152, 0·126 and 0·28 nm, respectively, while the angles C_{ar}—C_{ar}—C_{ar}, C_{ar}—C_{ar}—Cl, C_{ar}—C_{ar}—C, C_{ar}—C—$O^{(-)}$ and C—$O\cdots N$ are 120°, 120°, 120°, 117° and 120°, respectively. In addition, it was assumed that the Z axis of the EFG tensor in the place of Cl atoms is consistent with the C—Cl bond and directed from the C atom towards Cl (ref.[28]), while the $\Delta\mu$ moment is located in the centre of the $O\cdots N$ bridge and directed from N towards O (ref.[18]). Let us assume, then, that the full proton transfer leads to a change of dipole moment $\Delta\mu \simeq 22 . 10^{-30}$ C m (ref.[29]) and, finally, as a first approximation, that $\varepsilon \simeq 1$.

After such assumptions, we find out that for monochlorobenzoates $\Delta v = -0.65$ and for dichlorobenzoates $\Delta v = -0.66$ MHz i.e. there is a negligible difference in spite of the substantial difference in the configuration. For dichlorobenzoates the calculated value of Δv is close to that found experimentally (-0.57 MHz). The inaccuracy of the calculated Δv values results from the fact that the $\delta v/\delta E_Z$ evaluated from the internal Stark effect do not take into account the parameter of the internal field reaction[30] which is always bigger than 1. On the other hand, the electric permittivity ε in the expression (3) is certainly bigger than 1, too. Both factors contribute in opposite directions, but the latter one seems to be of greater importance. If we assume that $\varepsilon = n^2 = 2$, one gets twice lower Δv values, but even in such a case the discrepancy between the calculated and experimental results are not so remarkable in the light of approximations which had to be accepted. This relates above all to the localization of point dipole moment $\Delta\mu$ (mid-point of the $O\cdots N$ bridge).

However, a veritable difference between the calculated and experimental value of Δv_{NQR} has to be noticed for monochlorobenzoates. This difference can be understood in terms of a possible mesomeric effect. The mesomeric contribution to the mechanism of the influence of the hydrogen bond polarity on the quadrupole nucleus in 2,6-dichloro- and 2-chlorobenzoates should be entirely different. In the case of monochlorobenzoates the angle between the phenyl and carboxylate planes is only 10° so that there are no obstacles for the π-electron conjugation involving the bridge atoms. In 2,6-dichlorobenzoate the conjugation is completely extinguished.

For the estimation of the formal degree of the proton transfer, x_{PT}, in each series of complexes (about 20 adducts for each of them) the experimental v_{NQR} values were fitted to the Eq. (4) (ref.[31])

$$v_{NQR} = x_{PT}v_{PT} + (1 - x_{PT}) v_{HB} \qquad (4)$$

and the mole fraction of the PT form was related to the ΔpK_a value of interacting components according to Eq. (5) (ref.[32]):

$$\log \frac{x_{PT}}{1 - x_{PT}} = \Delta pK_a + \text{const.} \qquad (5)$$

Thus, it was possible to include all the results in one common plot shown in Fig. 2. During the fitting procedure all points (full circles) were omitted for which the deviation from the correlation curve was greater than 40%. The considerable scattering of experimental points is undoubtedly due to a different packing of molecules in the crystal lattice and, consequently, different orientation of polar groups in neighbouring molecules with respect to quadrupole nuclei. In addition, one cannot disregard some fluctuations of the angle between the planes of phenyl and carboxylate ones.

Notwithstanding, such a scattering, which can be generally defined as lattice noises, one can discern two regions on the ΔpK_a scale corresponding to HB ($\Delta pK_a <$ < 2) and PT ($\Delta pK_a > 4$) complexes. The inversion (critical) point at which K_{PT} is formally equal to 1 corresponds to $\Delta pK_a \simeq 3.77$.

As follows from the IR studies performed previously for complexes of penta-chlorophenol with amines[33] this inversion range is distinguished by an extreme shift of the gravity centre of protonic bands to lower frequencies. The data collected
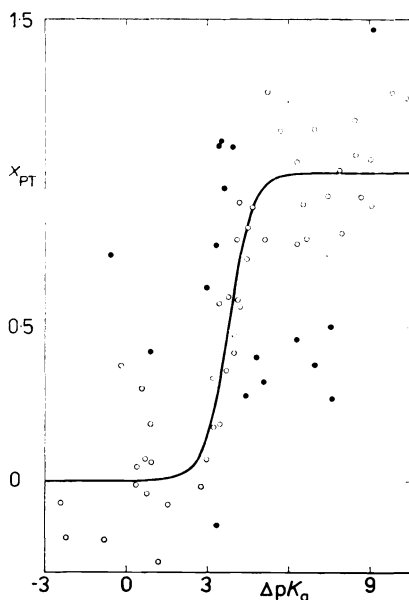
FIG. 2

Mole fraction of proton transfer state x_{PT} plotted versus ΔpK_a for benzoic acids complexes

in this paper for four series of carboxylic acid complexes are correlated in Fig. 3. The number of complexes was 81. There is clearly seen general regularity valid for all those complexes. Namely, in all cases there is manifested a deep minimum of v_{cg} close to $\Delta pK_a \simeq 3.7$. This inversion point is amazingly consistent with the one found from the NQR data analysis.

The plot v_{cg} versus ΔpK_a consists of two branches on left and right sides of the critical ΔpK_a value corresponding to HB and PT complexes. In the inversion range a particularly big shift of the protonic bands takes place along with the vanishing of absorption above $1\,700\,cm^{-1}$, where usually the $v(OH)$ or $v(NH^+)$ bands are located. Simultaneously, we notice a particular behaviour of the $v(CO_2)$ band, i.e. intermediate between the $v(C{=}O)$ vibrations in $-COOH$ group and asymmetric $v(COO^-)$ vibrations. In addition, a pronounced broadening of the carbonyl band is observed in the inversion range.

The scattering of experimental points shown in Fig. 3 is also remarkable, but not as large as in the case of v_{NQR} frequencies correlated with ΔpK_a. This is probably due to the fact that in both cases the packing effects upon the shape of the potential for the proton motion play the same role but for the NQR frequency the fluctuations of the resulting EFG in the lattice seem to be more impoitant.

Let us notice that the branches of the plot on both sides of the inversion point are not mutual mirror images. The curve after proton transfer becomes steeper than before it, which was already reported for complexes of 2-chloro-4-nitrobenzoic
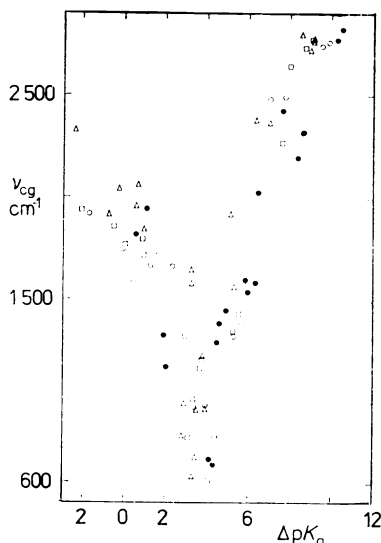

FIG. 3

Position of the gravity centre, v_{cg}, of protonic broad bands plotted versus ΔpK_a for hydrogen bonded adducts composed of 2,6-dichloro-3-nitrobenzoic acid (●), 2-chloro-3,5-dinitrobenzoic acid (○), 2-chloro-5-nitrobenzoic acid (△) and 2-chloro-4-nitrobenzoic acid (□)

acid[34]. Now we can state that this is a general behaviour of hydrogen bonded benzoic acid derivatives. The disturbance of the NH bond under an influence of carboxylate anion is diminished, by moving away from the inversion point, faster than the one taking place for the OH group affected by the nitrogen base.

The consistence of the inversion points revealed by NQR and IR spectra seems to possess significant implications. It means that the IR spectroscopic behaviour of hydrogen bonds is strictly related to the charge distribution. The inversion state revealed from NQR spectra as corresponding to 50% proton transfer should be characterized by a peculiar shape of the potential for the proton motion. It seems that there is a single minimum flat potential. Such conclusion is in agreement with the latest X-ray diffraction studies[35,36]. They showed that: (i) the $O \cdots H \cdots N$ bridges in the inversion region are the shortest ones; (ii) the proton is markedly shifted towards the centre of the bridge, though a central position of the proton has never been detected so far; (iii) the bond lengths in neighbouring groups are almost exactly intermediate between those in boundary HB and PT states. The most significant, from this point of view, is the situation in complexes of 3,5-dinitrobenzoic acid with 3,5-dimethylpyridine[37] which IR spectra show a behaviour typical of the inversion range. The hydrogen bond lengths equal to 0·253 nm, the O—H and H—N distances amount to 0·111 and 0·142 nm, respectively, while the C—O bond lengths in the carboxylic group are 0·128 and 0·121 nm i.e. correspond exactly to the situation in biscarboxylate salts where symmetric $O \cdots H \cdots O$ bridges are present[38].

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