J. Chem. Soc., Faraday Trans. 1, 1985, **81**, 311–319

^{35}Cl Nuclear Quadrupole Resonance Studies of Hydrogen Bonding in Solid Complexes of Chlorobenzoic Acids with Amines

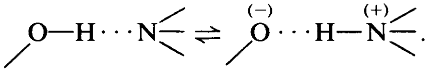
By Eugeniusz Grech,† Jerzy Kalenik and Lucjan Sobczyk*

Institute of Chemistry, University of Wrocław, 50-383 Wrocław, Poland

Received 9*th February*, 1984

^{35}Cl nuclear quadrupole resonance studies of hydrogen-bonded adducts containing *o*-, *m*- and *p*-chlorobenzoic acid and 2,6-dichlorobenzoic acid have been carried out. Average frequencies are correlated with ΔpK_a values in terms of the proton-transfer model. The results obtained for various proton donors are compared and discussed taking into account both intra- and inter-molecular effects.

Numerous spectroscopic studies of the complexes of chlorobenzoic acids with amines carried out in solution[1,2] have indicated the existence of a proton-transfer tautomeric equilibrium. Dipole-moment measurements[3] in non-polar solvents have shown that in these systems an inversion region for ΔpK_a [defined by $pK_a(BH^+) - pK_a(AH)$], corresponding to a stepwise increase in the hydrogen-bond polarity, $\Delta\mu$, occurs and can be interpreted in terms of a shift of the proton-transfer equilibrium



The proton-transfer equilibrium constant, K_{PT}, may be related, according to the Huyskens and Zeegers–Huyskens model,[4] to ΔpK_a *via* the equation

$$\log_{10} K_{PT} = \xi \Delta pK_a + C' \qquad (1)$$

where ξ and C' are constants. The constant ξ expresses the coupling of hydrogen-bonded (HB) and proton-transfer (PT) states, whereas the constant C' depends on the environment and is related to the value of ΔpK_a for which $K_{PT} = 1$ (the inversion point).

Infrared investigations of crystalline complexes of benzoic acids with pyridines[5] have revealed the presence of such an inversion region in the solid state also. The purpose of this work was to investigate the influence of changes in the charge-density distribution of hydrogen bonds for crystalline complexes of chlorobenzoic acids with nitrogen bases of various strengths using the ^{35}Cl n.q.r. technique. From earlier investigations on solid complexes with trichloroacetic acid,[6,7] pentachlorophenol[8] and 2,6-dichloro-4-nitrophenol[9] it follows that the complexation process is accompanied by a decrease in the average n.q.r. frequencies in relation to the average frequency of the pure proton donor. This means that the n.q.r. frequencies of nuclei in chlorine atoms which do not participate directly in hydrogen-bond formation can be applied successfully as a probe in order to examine the changes in charge-density distribution which take place in hydrogen bonds.

---

† Permanent address: Institute of Fundamental Chemistry, Technical University, 71-065 Szczecin, Poland.

Table 1. ^{35}Cl quadrupole resonance frequencies and pK_a values of bases for the 2,6-dichlorobenzoates

no.	amine	$\nu_{\text{n.q.r.}}$/MHz	no. of resonance lines	$\bar{\nu}$/MHz	pK_a[a] (amine)
a	2,6-dichlorobenzoic acid	35.622; 35.683; 36.018; 36.067	4	35.85	1.59[b]
b	potassium 2,6-dichlorobenzoate	34.632; 34.812	2	34.72	—
1	3-cyanopyridine	35.508; 35.682	2	35.60	1.35
2	4-cyanopyridine	35.542; 35.662; 35.730; 35.785	4	35.68	1.86
3	4-formylpyridine	35.345; 35.821	2	35.58	4.53
4	aniline	35.388; 35.774	2	35.58	4.61
5	quinoline	34.971; 35.788	2	35.38	4.93
6	isoquinoline	34.885; 35.093; 35.554; 36.058	4	35.40	5.40
7	4-methylquinoline	35.259; 35.768	2	35.51	5.59
8	2-methylpyridine	35.115; 35.331	2	35.22	5.94
9	4-methylpyridine	34.981; 35.245	2	35.11	6.03
10	3,4-dimethylpyridine	35.075	1	35.08	6.48
11	4-methylmorpholine	34.483; 35.401	2	34.94	7.38
12	morpholine	34.694; 35.266	2	34.98	8.49
13	triethylenediamine	34.888; 35.004	2	34.95	8.82
14	4-dimethylaminopyridine	34.862; 35.305	2	35.08	9.61
15	tributylamine	34.893	1	34.89	9.93
16	ethylpiperidine	34.828; 35.109	2	34.97	10.45
17	triethylamine	34.669; 34.947	2	34.81	10.75
18	piperidine	35.023	1	35.02	11.20
19	dibutylamine[c]	35.218; 35.274	2	35.25	11.25

[a] Ref. (10). [b] Ref. (11). [c] This complex has not been used in further calculations.

EXPERIMENTAL

Solid complexes were prepared by crystallization from equimolar chlorobenzoic acid + amine solutions in acetonitrile. The complex compositions were determined from chlorine analysis. Measurements of the resonance frequencies were performed at liquid-nitrogen temperature (77 K) on an ISSh-1-13M pulse spectrometer. Since not all the complexes with a given chlorobenzoic acid exhibited the same number of resonance lines, the average resonance frequencies $\bar{\nu}_{\text{n.q.r.}}$, being arithmetic means of the all frequencies measured, were used in the correlations.

RESULTS AND DISCUSSION

The resonance frequencies of the 1 : 1 complexes with 2,6-dichlorobenzoic acid and with *o*-, *m*- and *p*-chlorobenzoic acid, together with the frequencies for the pure acids and their salts (mainly those of potassium) are summarized in tables 1–4. Also given are the average frequencies $\bar{\nu}_{\text{n.q.r.}}$ and the pK_a values for amines as components of the hydrogen-bonded adducts investigated.

Table 2. ^{35}Cl quadrupole resonance frequencies and pK_a values of bases for the *o*-chlorobenzoates

no.	amine	$\nu_{\text{n.q.r.}}$/MHz	no. of resonance lines	$\bar{\nu}$/MHz	pK_a[a] (amine)
a	*o*-chlorobenzoic acid	36.312	1	36.31	2.92[b]
b	ammonium *o*-chlorobenzoate[c]	35.05; 35.18; 35.27	3	35.17	—
1	3-cyanopyridine	35.983; 36.060	2	36.02	1.35
2	4-cyanopyridine	35.825	1	35.83	1.86
3	4-acetylpyridine	35.634; 36.114	2	35.87	3.51
4	quinoline	35.587; 36.312	2	35.95	4.93
5	isoquinoline	35.484	1	35.48	5.40
6	4-methylquinoline	35.639; 35.998	2	35.82	5.59
7	3-methylisoquinoline	35.876	1	35.88	5.64
8	4-methylpyridine	35.697	1	35.70	6.03
9	3,4-dimethylpyridine	35.675	1	35.68	6.48
10	2,6-dimethylpyridine	35.505; 35.996	2	35.75	6.64
11	2-amino-4-methylpyridine	35.453	1	35.45	7.38
12	triethylenediamine	34.891	1	34.89	8.82
13	4-aminopyridine	34.344	1	34.34	9.12
14	4-amino-2-methylquinoline[d]	35.797	1	35.80	9.42
15	4-dimethylaminopyridine	34.579	1	34.58	9.61
16	piperidine	34.599; 34.719	2	34.66	11.20
17	dibutylamine[e]	34.59	1	34.59	11.25

[a] Ref. (10). [b] Ref. (12). [c] Ref. (13). [d] This complex has not been used in further caclulations. [e] Since the resonance line was very broad the n.q.r. frequency was measured with an accuracy of ±10 kHz.

The dependence of $\bar{\nu}_{\text{n.q.r.}}$ on ΔpK_a for 2,6-dichlorobenzoates (fig. 1) and for *o*-chlorobenzoates (fig. 2) may be interpreted in terms of a formal proton-transfer model (as previously[8, 9]) such that

$$\bar{\nu}_{\text{n.q.r.}} = x_{\text{HB}}\,\bar{\nu}_{\text{HB}} + x_{\text{PT}}\,\bar{\nu}_{\text{PT}} \qquad (2)$$

where x_{HB} and x_{PT} are the mole fractions of the complexes with no proton transfer and with full proton transfer, while $\bar{\nu}_{\text{HB}}$ and $\bar{\nu}_{\text{PT}}$ are average resonance frequencies of two boundary forms of the hydrogen bonding. (This means that the observed average resonance frequency $\bar{\nu}_{\text{n.q.r.}}$ is a linear function of the proton-transfer fraction.)

From the $\bar{\nu}_{\text{n.q.r.}}$ and pK_a values gathered in table 1 (for the 2,6-dichlorobenzoates) and in table 2 (for the *o*-chlorobenzoates), the parameters in eqn (1) and (2) have been estimated using the generalized least-squares method. Thus the values obtained for ξ, C', $\bar{\nu}_{\text{HB}}$ and $\bar{\nu}_{\text{PT}}$ are 0.92, −3.86, 35.62 MHz and 34.95 MHz for the 2,6-dichlorobenzoates and 0.82, −4.00, 35.83 MHz and 34.95 MHz for the *o*-chlorobenzoates.

The experimental points and the plots of $\bar{\nu}_{\text{n.q.r.}}$ against ΔpK_a calculated for the estimated values of ξ, C', $\bar{\nu}_{\text{HB}}$ and $\bar{\nu}_{\text{PT}}$ are presented in fig. 1 (2,6-dichlorobenzoates) and 2 (*o*-chlorobenzoates). The average frequencies of the pure acids and their salts are also shown. The scattering of experimental points visible in fig. 1 and 2 is presumably

Table 3. ^{35}Cl quadrupole resonance frequencies and pK_a values of bases for the *m*-chlorobenzoates

no.	amine	$\nu_{\text{n.q.r.}}$/MHz	no. of resonance lines	$\bar{\nu}$/MHz	pK_a[a] (amine)
a	*m*-chlorobenzoic acid	35.232	1	35.23	3.83[b]
b	potassium *m*-chlorobenzoate[c]	34.74	1	34.74	—
1	4-cyanopyridine	34.710	1	34.71	1.86
2	quinoline	34.242	1	34.24	4.93
3	isoquinoline	34.607	1	34.61	5.40
4	4-methylpyridine	34.767	1	34.77	6.03
5	3,4-dimethylpyridine	34.985	1	34.99	6.48
6	2-aminopyridine	34.589	1	34.59	6.71
7	2-amino-4-methylpyridine	35.116	1	35.12	7.38
8	morpholine	34.617	1	34.62	8.49
9	piperidine	34.513; 34.823	2	34.67	11.20

[a] Ref. (10). [b] Ref. (12). [c] Ref. (13).

Table 4. ^{35}Cl quadrupole resonance frequencies and pK_a values of bases for the *p*-chlorobenzoates

no.	amine	$\nu_{\text{n.q.r.}}$/MHz	no. of resonance lines	$\bar{\nu}$/MHz	pK_a[a] (amine)
a	*p*-chlorobenzoic acid	34.673	1	34.67	3.98[b]
b	potassium *p*-chlorobenzoate[c]	35.48	1	35.48	—
1	2-amino-4-methylpyridine	34.758	1	34.76	7.38
2	4-amino-2-methylquinoline	34.302	1	34.30	9.42
3	piperidine	34.571	1	34.57	11.20

[a] Ref. (10). [b] Ref. (12). [c] Ref. (13).

due to contributions from lattice effects to the effective electric-field gradient on the quadrupole nuclei, which are not the same for all compounds. These contributions are dependent on the arrangement of molecules in the unit cell, which unfortunately is not known. The procedure of averaging the resonance frequencies allows us to eliminate some of the lattice effects.

Some influence on the scattering of the experimental points may also be caused by differences in the conformations of the complexed chlorobenzoic acid molecules, these being characterized by a dihedral angle α between the planes of the carboxylic group and aromatic ring. The magnitude of the dihedral angle α is affected by two factors: (i) the interaction between the carboxylic group and substituents in *ortho* positions and (ii) the interaction between the neighbouring molecules (especially *via* hydrogen

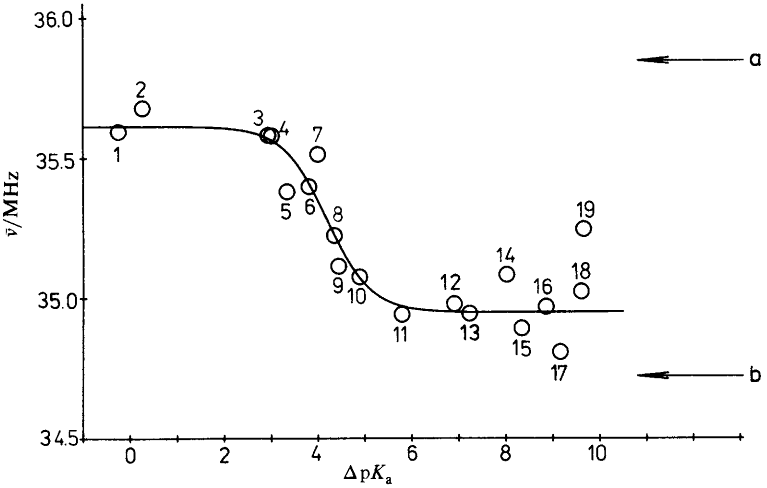


Fig. 1. Plot of $\bar{\nu}_{\text{n.q.r.}}$ against ΔpK_a for the 2,6-dichlorobenzoates; for notation see table 1.

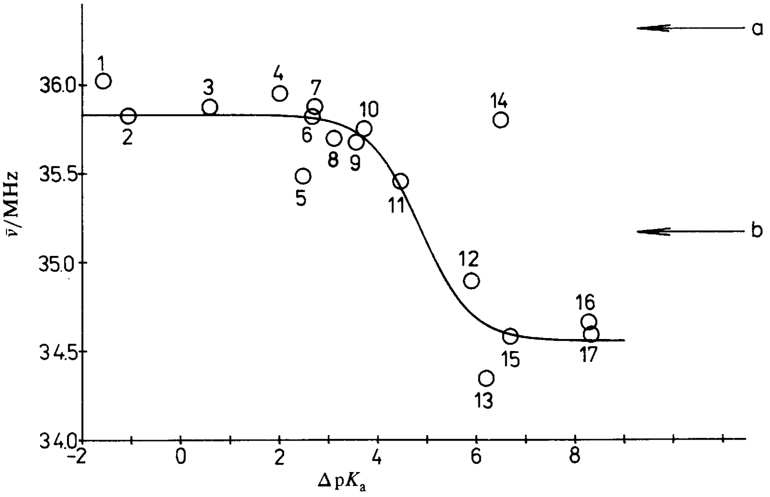


Fig. 2. Plot of $\bar{\nu}_{\text{n.q.r.}}$ against ΔpK_a for the *o*-chlorobenzoates; for notation see table 2.

bonds). The first of these factors determines the minimal value of α in the case when no specific interaction with the groups in *ortho* positions takes place. It can be easily calculated using the van der Waals radii.[14] In the case of *o*-chlorobenzoic and 2,6-dichlorobenzoic acids the calculated values of α are 10 and 45°, respectively.[15] The second factor, connected with the arrangement of molecules in the crystalline lattice, leads to an additional enhancement of this angle. Thus in pure *o*-chlorobenzoic acid α is equal to 13.7°,[16] while *e.g.* in 2-chloro-5-nitrobenzoic acid it reaches 23.0°.[17] Moreover, note that when there is only one substituent *ortho* to the carboxylic group the C(O)—OH group is arranged *trans* to that substituent.[16, 17]

The phenomenon of a differentiation in the values of the dihedral angle α is particularly well illustrated for 2,6-dichlorobenzoates, where in some complexes both chlorine atoms are equivalent (one resonance line is observed), which means that the carboxylic group is perpendicular to the plane of the aromatic ring. However, in other 2,6-dichlorobenzoic acid complexes both chlorine atoms are not equivalent and two or four resonance lines are visible. This clearly suggests that the carboxylic group is not perpendicular to the plane of the aromatic ring.

The particularly large deviations visible for point (19) in fig. 1 and for point (14) in fig. 2 are probably due to either steric effects (4-amino-2-methylquinoline–*o*-chlorobenzoate) or the formation of additional hydrogen bonds (dibutylamine–2,6-dichlorobenzoate). Note that the calculated values of the parameters ξ and C' are similar for both acids (this has also been observed for phenols).[9] The position of the inversion point determined from eqn (1) (where the degree of proton transfer is 50%) in the ΔpK_a scale is 4.2 for the 2,6-dichlorobenzoates, while for the *o*-chlorobenzoates it is 4.9. The above values are close to the value of 3.75 estimated from the i.r. investigations of crystalline complexes of benzoic acids with pyridines.[5]

The values of the parameters $\bar{\nu}_{HB}$ and $\bar{\nu}_{PT}$ calculated for the 2,6-dichlorobenzoates and the *o*-chlorobenzoates differ from those corresponding to average resonance frequencies of the pure acids and their salts.

The differences between $\bar{\nu}_{HB}$ and the average resonance frequencies of the pure acids are probably caused by the fact that molecules of the pure acids in an associated form (most frequently dimers[18]) participate in O—H···O hydrogen bonding, differing greatly from the formation of O—H···N bonds in complexes without proton transfer.

On the other hand, the discrepancies between $\bar{\nu}_{PT}$ and the average resonance frequencies of the salts mainly result from the fact that, unlike the hydrogen-bonded proton-transfer complexes $O^-\cdots H—N^+$, in salts one must deal with electric fields arising from ions which are a source of additional resonance-frequency shifts.[19] The magnitudes and directions of these shifts depend on the arrangement of ions in the unit cell. Therefore the method of determining the degree of proton transfer in crystalline hydrogen-bonded complexes suggested by Chihara and Nakamura[20] and based on the assumption that $\bar{\nu}_{HB}$ is equal to the average resonance frequency of the pure acid and $\bar{\nu}_{PT}$ is equal to the average resonance frequency of its salt, could lead to incorrect results.

In the case where the Cl atoms are sufficiently far from the hydrogen bond the shifts in the average resonance frequencies caused by changes in the hydrogen-bond polarity are small in comparison with the shifts caused by the lattice effects, and no correlation between $\bar{\nu}_{n.q.r.}$ and ΔpK_a is observed. This is clearly visible in the *m*-chlorobenzoates, the results for which are shown in fig. 3. The scatter of the experimental points in fig. 3, more distinct than those in fig. 1 and 2, may be caused additionally by two possible conformations of the carboxylic group in relation to the chlorine atom in the *meta* position. Similarly no correlation can be expected for *p*-chlorobenzoic acid as a proton donor (see table 4). The resonance frequency of pure *p*-chlorobenzoic acid is even lower than that of its potassium salt, which can be explained by the presence of electric fields arising from the ions[19] which, when the difference between $\bar{\nu}_{HB}$ and $\bar{\nu}_{PT}$ is not high, can increase the resonance frequency of the salt to a value above that of the pure acid. Lynch *et al.*[13] have tried to explain this anomaly in terms of the mesomeric effect in *p*-chlorobenzoic acid. If this were the case, the average resonance frequencies of complexes containing the ionic form of the hydrogen bond, where the carboxylic group is almost entirely ionized, should be closer to the resonance frequency of potassium *p*-chlorobenzoate than to that of the pure acid. It thus seems that the role of the mesomeric effect in *p*-chlorobenzoic acid has been overestimated by Lynch *et al.*[13]

Let us now try to compare the results of n.q.r. investigations for five series of the

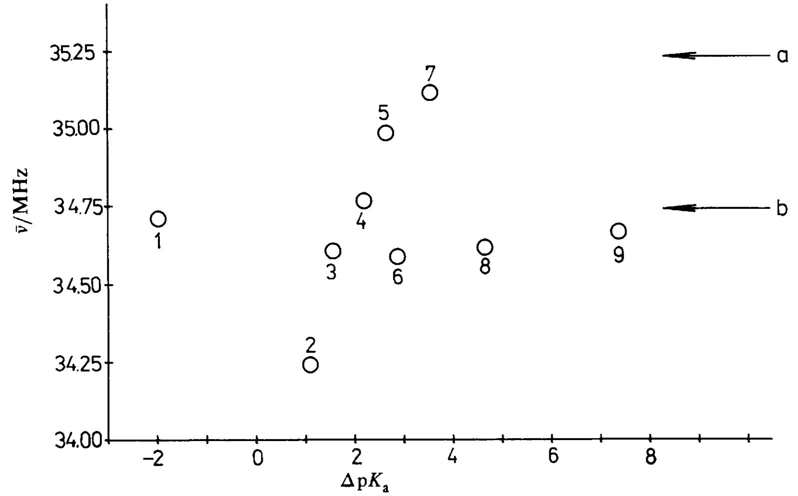


Fig. 3. Plot of $\bar{\nu}_{n.q.r.}$ against ΔpK_a for the *m*-chlorobenzoates; for notation see table 3.

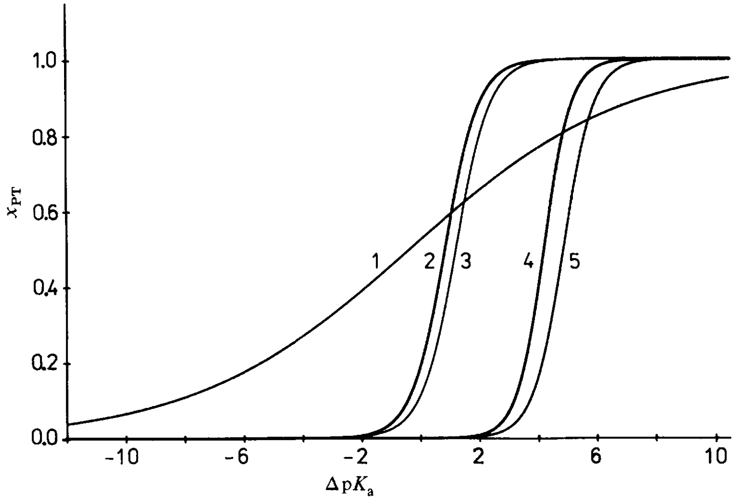


Fig. 4. Calculated x_{PT} values for various series of hydrogen-bonded adducts plotted against ΔpK_a; for notation see table 5.

complexes containing trichloroacetic acid,[7] pentachlorophenol,[8] 2,6-dichloro-4-nitrophenol,[9] 2,6-dichlorobenzoic acid (this work) and *o*-chlorobenzoic acid (this work). We describe the behaviour of all the complexes using a generalized scheme of the proton-transfer equilibrium model, although we have already stressed[7] that a quantitative description of the resonance-frequency changes can also be expressed in terms of the Mulliken theory by using *a* and *b* coefficients, which are in turn connected to the contribution of non-polar and dative states.[21]

In fig. 4 are presented plots expressing the dependence of x_{PT} on ΔpK_a for the series of complexes under consideration. The parameters of eqn (1) describing these curves

Table 5. Values of ξ and C' in eqn (1) and ΔpK_a values for which $K_{PT} = 1$ for a series of complexes with various proton donors

no.	proton donor	ξ	C'	ΔpK_a ($K_{PT} = 1$)
1	trichloroacetic acid[a]	0.12	0.04	−0.4
2	2,6-dichloro-4-nitrophenol[b]	0.75	−0.62	0.8
3	pentachlorophenol[c]	0.76	−0.91	1.2
4	2,6-dichlorobenzoic acid[d]	0.92	−3.86	4.2
5	*o*-chlorobenzoic acid[d]	0.82	−4.00	4.9

[a] Values of the parameters calculated from data taken from ref. (7). [b] Ref. (9). [c] Ref. (8). [d] This work.

are listed in table 5. The ΔpK_a values at which 50% proton transfer takes place are also included. We note an unusual broadening (a small value of ξ) of the curve for the complexes of trichloroacetic acid. A similar broadening has been found when describing the dipole-moment dependences for complexes of carboxylic acids with triethylamine.[3] Undoubtedly only the chemical properties of aliphatic carboxylic acids are of importance here since complexes of aromatic acids behave normally, a fact confirmed by the results obtained in this work. Attempts to explain this anomaly may seem premature since we have no information about the configuration of the complexes formed in the crystalline state.

On the other hand, it seems easier to explain the large difference in the position of the inversion point (at which $x_{PT} \approx 1/2$) for the phenol derivatives and benzoic acids. The essential factor here is the additional contribution of the mesomeric effect in phenol complexes, which does not play a prominent role in benzoic acid complexes.

In conclusion, measurements of the n.q.r. frequencies of hydrogen-bonded complexes can serve as an useful indicator of the inversion region of donor–acceptor properties, where a stepwise charge rearrangement and proton-transfer equilibrium can be anticipated. Knowledge of this region seems to be important since hydrogen-bonded complexes from this region are characterized by an unusual potential for proton motion.

We thank a referee for helpful remarks.

[1] G. M. Barrow, *J. Am. Chem. Soc.*, 1956, **78**, 5802.
[2] J. Nasielski and E. Vander Donckt, *Spectrochim. Acta*, 1963, **19**, 1989.
[3] L. Sobczyk and Z. Pawełka, *J. Chem. Soc., Faraday Trans. 1*, 1974, **70**, 832.
[4] P. Huyskens and Th. Zeegers-Huyskens, *J. Chim. Phys.*, 1964, **61**, 81.
[5] S. L. Johnson and K. A. Rumon, *J. Phys. Chem.*, 1965, **69**, 74.
[6] O. Kh. Poleshchuk, Yu. K. Maksyutin, O. F. Sychev, K. K. Koshelev and I. G. Orlov, *Izvest. Akad. Nauk SSSR, Ser. Khim.*, 1975, **6**, 1431.
[7] J. Pietrzak, B. Nogaj, Z. Dega-Szafran and M. Szafran, *Acta Phys. Polon. A*, 1977, **52**, 779.
[8] E. Grech, J. Kalenik and L. Sobczyk, *J. Chem. Soc., Faraday Trans. 1*, 1979, **75**, 1587.
[9] E. Grech, J. Kalenik, Z. Malarski and L. Sobczyk, *J. Chem. Soc., Faraday Trans. 1*, 1983, **79**, 2005.
[10] D. D. Perrin, *Dissociation Constants of Organic Bases in Aqueous Solution* (Butterworths, London, 1965; supplement, 1972).
[11] J. F. Dippy, S. R. C. Hughes and L. G. Bray, *J. Chem. Soc.*, 1959, 1717.
[12] G. Kortüm, W. Vogel and K. Andrussow, *Dissociation Constants of Organic Acids in Aqueous Solution* (Butterworths, London, 1961).

[13] R. J. Lynch, T. C. Waddington, T. A. O'Shea and J. A. S. Smith, *J. Chem. Soc., Faraday Trans. 2*, 1976, **72**, 1980.
[14] H. A. Staab, *Einführung in die theoretische organische Chemie* (Verlag Chemie, Weinheim, 1959).
[15] M. K. Chantooni Jr and I. M. Kolthoff, *J. Phys. Chem.*, 1974, **78**, 839.
[16] G. Ferguson and G. A. Sim, *Acta Crystallogr.*, 1961, **14**, 1262.
[17] G. Ferguson and G. A. Sim, *J. Chem. Soc.*, 1962, 1767.
[18] L. Leiserowitz, *Acta Crystallogr., Sect. B*, 1976, **32**, 775.
[19] C. H. Townes and B. P. Dailey, *J. Chem. Phys.*, 1952, **20**, 35.
[20] H. Chihara and N. Nakamura, *Bull. Chem. Soc. Jpn*, 1971, **44**, 1980.
[21] R. S. Mulliken, *J. Am. Chem. Soc.*, 1952, **74**, 811.

(PAPER 4/235)