149. Intramolecular Hydrogen Bonds of the C=O···H–O Type as Studied by ^{17}O-NMR

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The ^{17}O-NMR spectra of 1,4-naphthoquinone and 5-hydroxy-1,4-naphthoquinone (juglone) have been recorded in $CDCl_3$ solution at 40°. In juglone the ^{17}O resonance of the carbonyl *peri* to the OH group was displaced by 70 ppm to low frequency relative to the resonance in the *para*-position. It is shown that this chemical shift arises mainly from intramolecular H-bonding, the substituent and steric effects being one order of magnitude smaller. Large carbonyl ^{17}O chemical shifts between −34 and −100 ppm were also observed in a series of aromatic aldehydes and ketones where intramolecular H-bonds of the C=O···H–O type are formed. The H-bond-induced carbonyl ^{17}O chemical shifts were linearly correlated with both the ^{17}O and ^{1}H chemical shifts of the OH groups. They represent a most sensitive measure of the strength of intramolecular H-bonds. The ^{17}O resonances of the OH groups were directed to high frequency on H-bonding. Analysis of the ^{17}O chemical shifts in 2,2′-dihydroxybenzophenone showed clearly that the two OH groups build H-bonds simultaneously to the single carbonyl group. The ^{17}O linewidths decreased strongly on H-bonding; the linewidth of the H-bonded carbonyl O-atom in juglone, for example, was reduced by 25% with respect to that of the free carbonyl O-atom. The carbonyl O-atom quadrupole coupling constants in juglone, evaluated from the combined use of ^{13}C and ^{17}O relaxation times, were 9.5 and 11.0 MHz, respectively. No correlation was observed between the H-bond-induced ^{17}O chemical shifts and the variations in ^{17}O quadrupole coupling constants.

Introduction. – H-Bonding is widely recognized as a fundamental feature of chemical and biological systems [1] [2]. Intramolecular H-bonding has been extensively studied by IR techniques [3] and by ^{1}H-NMR spectroscopy [2] [4]. With regard to ^{13}C-NMR studies of H-bonding, it was found that carbonyl resonances were shifted to high frequency by 3–7 ppm in, for example, *ortho*-hydroxybenzoates, acetophenones, and benzophenones [5]. In other work, ^{15}N-NMR [6] and ^{17}O-NMR [7] [8] have proved to be very informative with regard to charge densities at donor and acceptor sites. Only since *Reuben* [8] began to examine ^{17}O-NMR in a systematic manner, the long-standing question as to whether additional understanding can be gained by observing the effects of H-bonding on the NMR resonances of heteronuclear atoms has been addressed. ^{17}O-NMR Spectroscopy appears to be especially promising for use in H-bonding studies because of the large chemical-shift range of the O-nucleus [9] and the sensitivity of the carbonyl O-atoms chemical shifts [10]. The dominance of intramolecular H-bonding effects over substituent effects was clearly demonstrated in the ^{17}O-NMR spectra of acetophenones and benzaldehydes [10]. Intramolecular H-bonds between *ortho*-substituents on aromatic rings occur frequently also for carboxylic acids and amides [11]. *Fiat* and coworkers have investigated by ^{17}O-NMR the solvation and H-bonding of amides and peptides [12] [13]. *Schwartz et al.* have performed an ^{17}O-NMR study of the self association of nucleosides [14]. We have been involved in an extensive study of H-bonding interactions of the

C=O···H–N type as part of our conformational studies of amino acids and peptides [15] [16]. H-Bonding of the C=O···H–O type occurs, for example, in natural quinones. *peri*-Hydroxynaphthoquinone moieties have been frequently encountered in microbial quinone antibiotics [17]. ^{17}O-NMR studies of polycyclic quinones and hydroxyquinones, models for anthracycline intercalators, have been recently reported [18]. A considerable number of C=O···H–O bonds exist in oligosaccharides [19]. In peptides, C=O···H–O bond interactions are provided by polar side chains, for example, through the OH groups of serine, threonine, and tyrosine. ^{17}O-NMR could facilitate the otherwise difficult identification of side chain H-bonding of peptides in solution.

In the present work, we have extended ^{17}O-NMR studies of intramolecular H-bonds of the C=O···H–O type to a greater range of compounds including hydroxynaphthoquinones and have measured the chemical shifts and linewidths of both the CO and OH ^{17}O resonances. All molecules were suggestive of a H-bond configuration with short O···O distances and strong deviations from linearity (OH···O bond angle less than 150°). H-bond-induced ^{17}O chemical shifts have been compared with those from ^{1}H- and ^{13}C-NMR and correlations between the shifts have been attempted. We also started a search for correlations between the H-bond-induced ^{17}O chemical shifts and various structural parameters, such as H-bond distances as obtained from X-ray or neutron diffraction. At last, it will be demonstrated that the quadrupole constants of the carbonyl O-atoms as derived from the ^{17}O linewidths are strongly dependent on the H-bond geometry. Work is in progress to calculate H-bond distances and energies from *ab initio* studies [20].

Experimental. – *Materials.* The compounds used for natural-abundance ^{17}O-NMR studies were purchased from *Fluka* or *Aldrich*. 5-Hydroxy-2-methyl-1,4-naphthoquinone (plumbagin) was also isolated from natural sources (Dr. *A. Marston*, Ecole de pharmacie, Lausanne). 2,2'-Dihydroxybenzophenone was prepared according to the procedure described in [21]. Alkylation of 5-hydroxy-1,4-naphthoquinone (juglone) was performed by a standard procedure [22].

1,4-Naphthoquinone and juglone were enriched in ^{17}O by a method similar to that described in [10]. The quinone (0.3 mmol) was dissolved in 3 ml of 1,4-dioxane and 10 µl of acidified $H_2{}^{17}O$ (20 atom-% in ^{17}O; *Yeda*) was added. The temp. was raised to 60° and maintained during 20 h. The solvents were then evaporated and the obtained product dried (P_2O_5), and recrystallized in acetone. The degree of enrichment was determined by MS (*Finnigan 1020*) to be *ca.* 7 atom-%.

^{17}O-NMR Measurements. Spectra were obtained at 40 ± 1° on a *Bruker WH-360* instrument operating at 48.8 MHz, 90° Pulses (≈ 30 µs) were applied and the data acquired during $T_{acq} \geq 5\ T_2$. Spectral width = 50 kHz. Quadrature-phase detection. The FID (1K-words data size) was treated by exponential multiplication (a typical line broadening (LB) factor was 200 Hz, similar to the actual linewidth of the resonances) and zero-filled to 16 K resulting in a digital resolution of 6 Hz/point after FT.

Many spectra were recorded with an extended spin-echo sequence for suppression of the acoustic ringing [23],

$$90_x\text{-}\Delta\text{-}180_x\text{-}\Delta\text{-FID}(-)\text{-}T_d\text{-}$$
$$\text{-}90_{-x}\text{-}\Delta\text{-}180_{-x}\text{-}\Delta\text{-FID}(+)\text{-}T_d\text{-}$$
$$\text{-}180\text{-}\tau\text{-}90_x\text{-}\Delta\text{-}180_x\text{-}\Delta\text{-FID}(+)\text{-}T_d\text{-}$$
$$\text{-}180\text{-}\tau\text{-}90_{-x}\text{-}\Delta\text{-}180_{-x}\text{-}\Delta\text{-FID}(-)\text{-}T_d\text{-}$$

with T_d = 10 ms, τ = 1 µs and Δ = 20 µs. This resulted in a significant reduction in the uncertainty in the linewidths measurements. Because of the limited power for 180° magnetization-inversion over the entire spectral range, it was necessary to adjust the carrier frequency near to the observed frequency. As a consequence, the ^{17}O-NMR spectrum of a compound containing both C=O and OH groups had to be recorded in two steps [23].

Transverse relaxation times (T_2) were obtained from the linewidths (L) at half heights after correction for the LB factor [24] according to the relationship $T_2 = {}^1/\pi L$. A representative number of resonances were fitted by

Lorentzian line shapes. No influence of ^{1}H decoupling was detected on the linewidth of the OH resonances. The magnetic field inhomogeneity broadening during an overnight accumulation without lock was < 5 Hz.

Solns. of 2 ml were prepared in 10-mm NMR tubes at 0.3M concentrations for natural-abundance studies and at variable concentrations > 0.005M using the ^{17}O-enriched compounds. Deuterated solvents were used, if not otherwise mentioned, not for lock purposes but in order to obtain identical soln. conditions as in the comparative ^{1}H- and ^{13}C-NMR measurements. The ^{17}O chemical shifts were measured in ppm relative to external 1,4-dioxane (−0.2 ppm relative to the H_2O resonance at 40° [25]).

^{1}H- and ^{13}C-NMR Measurements. Spectra were recorded at 40 ± 1° using a *Bruker WP-80 CW* (80 MHz, ^{1}H-NMR) and a *Bruker WH-360* (90.5 MHz, ^{13}C-NMR), respectively. Chemical shifts (ppm) were determined relative to internal TMS. $T_1(^{13}C)$ measurements were performed by the inversion-recovery technique with samples degassed by three freeze-pump-thaw cycles and sealed under vacuum. 12 variable delays between the pulses were chosen. The relaxation delay was 30 s. The T_1 values were calculated by a three-parameter least-squares fit procedure [26].

Viscosity Measurements. These were performed at 40° with a *Schott AVS 300* capillary viscometer. Average values of 6 measurements were taken.

Results and Discussion. – 1. *H-Bond-Induced ^{17}O Chemical Shifts of the Carbonyl Groups.* ^{17}O-NMR spectra were recorded of 1,4-naphthoquinone (**1a**), juglone (5-hydroxy-1,4-naphthoquinone; **1b**), 2-methyl-1,4-naphthoquinone (**2a**), and plumbagin (5-hydroxy-2-methyl-1,4-naphthoquinone; **2b**), as well as of a series of aromatic aldehydes and ketones (**3**–**7**) of which compounds **b** and **c** bear one or two OH groups in *ortho*-position (see *Table 1*). *Fig. 1* shows as a typical example the ^{17}O-NMR spectrum of the carbonyl region of **1a** and **1b** in $CDCl_3$. We observed that one of the carbonyl ^{17}O resonances of **1b** is shifted to low frequency relative to the other, 498.3 *vs.* 570.4 ppm, and also relative to the resonance position of the O-atoms in **1a** (568.7 ppm). Obviously, this chemical shift must be attributed to H-bonding between the carbonyl O-atom and the OH group in the *peri*-position of **1b**. The presence of a strong intramolecular C=O···H–O bond forming a six-membered ring has been proved earlier by ^{1}H-NMR [27] and IR [2] spectroscopy.

Table 1. *Carbonyl Chemical Shifts in the C=O···H–O-Bond-Forming Compounds* **1b**–**7b**, **c** *Compared with the Parent Compounds* **1a**–**7a**[a])

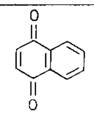
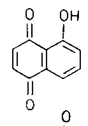
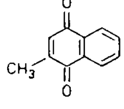
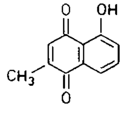
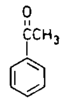
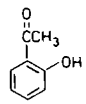
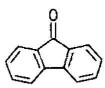
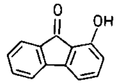
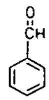
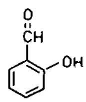
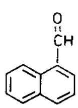
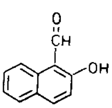
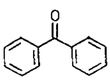
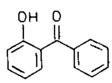
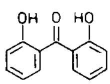
Compound		^{17}O Chemical shifts [ppm]				^{13}C Chemical shifts [ppm]			
			δ(C=O)[b])	$\Delta\delta$[d])	Ref.[c])		δ(C=O)[c])	$\Delta\delta$[d])	Ref.[e])
1a			568.7				184.9		[29a, b, c]
1b		O–C(1)	570.4	−72.1		C(1)	184.1	6.0	[29a, b]
		O–C(4)	498.3			C(4)	190.1		
2a			558.2[f])			C(1)	184.7		[29a]
						C(4)	185.3		
2b		O–C(1)	560.3	−71.8		C(1)	184.7	5.5	
		O–C(4)	488.5			C(4)	190.2		

Table 1 (cont.)

Compound		^{17}O Chemical shifts [ppm]			^{13}C Chemical shifts [ppm]		
		δ(C=O)[b])	Δδ[d])	Ref.[e])	δ(C=O)[c])	Δδ[d])	Ref.[e])
3a		544.2		[10]	195.7		[30]
			−55.9			8.7	
3b		489.3		[10]	204.4		[31]
4a		510.1			193.7		[32]
			−33.7			2.6	
4b		476.4			196.3		
5a		557.4		[10]	192.9		[31]
			−53.1			4.1	
5b		504.3		[10]	197.0		[31]
6a		571.8			192.9		[30]
			−99.8			0.2	
6b		472.0			193.1		
7a		543.0			196.3		[33]
			−58.0			5.2	
7b		485.0			201.5		
			−102.7[g])				
			−44.7			0.9	
7c		440.3			202.4		[31]

a) Natural-abundance measurements of 0.3M solns. in $CDCl_3$; $T = 40°$.
b) Relative to external dioxane (−0.2 ppm from H_2O) [25]. Estimated error ±1 ppm.
c) Relative to internal TMS. Estimated error ±0.1 ppm.
d) H-Bond-induced shifts, negative sign denotes a low frequency shift.
e) The chemical-shift values found in the literature are comparable to ours, notice that solvent, concentration, and temp. are in general different.
f) Composite resonance.
g) Difference **7c**–**7a**.

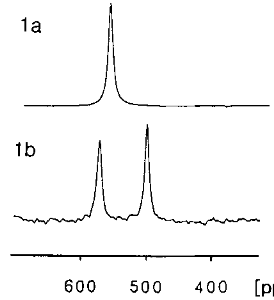


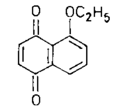
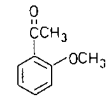
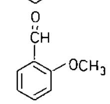
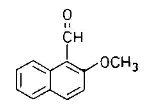
Fig. 1. *48.8-MHz ^{17}O-NMR Spectrum (carbonyl region) of 1,4-naphthoquinone* (**1a**) *and 5-hydroxy-1,4-naphthoquinone* (**1b**) *in $CDCl_3$ at 40°*

The ^{17}O chemical shift (−70 ppm) observed for the H-bonded carbonyl group in **1b** *(Table 1)* cannot be explained by a substituent or steric effect due to the OH group for the following reasons: *a)* the free carbonyl ^{17}O resonance in **1b** was displaced by less than 2 ppm relative to the position in **1a** *(Table 1)*; *b)* alkylation of the OH group restored the resonance position of the *peri*-carbonyl group to −10 ppm (see *Table 2*); *c)* in MeOH, where the internal H-bond is no longer stable [28], the carbonyl groups of both **1a** and **1b** appeared as single resonances at 566.0 ppm.

Similarly, the molecules **3b**–**7b**, *ortho*-substituted by an OH group and capable of H-bonding, were found to shift the carbonyl ^{17}O resonance to low frequency relative to the parent molecules, **3a**–**7a**, without OH groups *(Table 1)*. Several studies of substituent effects on the ^{17}O-NMR shifts of functional groups directly attached to aromatic rings have been reported [10] [34]. *Fiat* and coworkers [10] found that shifts in *para*-substituted acetophenones are spread over 60 ppm, while those in the *meta*-series are restricted to a 10 ppm range. Similar trends were noted in benzaldehydes [10]. Of course, the different ranges of the *meta*- and *para*-shifts reflect the dominance of resonance effects in the *para*- compared with the *meta*-series. The situation was more difficult in the *ortho*-substituted acetophenones and benzaldehydes. In general, the carbonyl ^{17}O chemical shifts were displaced to high frequency, determined by steric and/or electronic effects [10] [34d]. However, in the case of molecules, where the possibility for formation of an intramolecular H-bond exists, as in **3b** and **5b** for example, the carbonyl resonances were significantly shielded with respect to similar molecules that cannot form the intramolecular H-bonded chelate structure. The ^{17}O chemical-shift difference between *ortho*-hydroxyacetophenone (**3b**) and *ortho*-methoxyacetophenone (**3d**) was observed [10] to be −73 ppm (−64 ppm according to our measurements, *cf. Tables 1* and *2*), but only −22 and −5 ppm between the corresponding *para*- and *meta*-substituted compounds, respectively. This observation, as well as the study of mono- and polyhydroxy-substituted acetophenones led to the conclusion that the chemical shifts induced by intramolecular H-bonding clearly dominate over substituent effects.

We attribute the origin of the large carbonyl ^{17}O chemical shifts in **1b**–**7b, c** to intramolecular H-bonding. *Table 2* shows that on alkylation of **1b**, **3b**, **5b**, and **6b** a considerable reduction of these low frequency shifts was obtained. In the case of *ortho*-methoxyacetophenone (**3d**), the chemical shift was even to high frequency relative to **3a**. Thus the substituent effects of the *ortho*-OH groups in **1b**–**7b, c** are of variable sign and can be estimated to be < 10 ppm, inferior to the intramolecular H-bonding effects.

Table 2. *Carbonyl ^{17}O Chemical Shifts in the MeO- or EtO-Substituted Compounds* **1d**, **3d**, **5d**, *and* **6d**

Compound		^{17}O Chemical shifts [ppm]	
		$\delta(C{=}O)$[a])	$\Delta\delta$[b])
1d		560.2[c])[d])	−8.5
3d		553.4[e])	9.2 (11)[f])
5d		551.2[e])	−6.2 (−7)[f])
6d		565.3[e])	−6.5

[a]) Relative to external dioxane (−0.2 ppm from H_2O) [25]. Estimated error ±1 ppm.
[b]) Substituent shifts by MeO or EtO groups.
[c]) For reasons of solubility, an enriched compound (~ 7 atom-% ^{17}O) was used, 0.05M in dioxane; T = 40°.
[d]) Composite resonance from O–C(1) and O–C(4).
[e]) Natural-abundance measurements of 0.3M solns. in $CDCl_3$; T = 40°.
[f]) Values from [10].

To confirm that the H-bonding in **1b–7b** was exclusively intramolecular in $CDCl_3$, several concentration-dependence studies were performed. The carbonyl ^{17}O chemical shifts of **1b** were independent of concentration down to 0.005M (measured with an ^{17}O-enriched compound). Furthermore, the OH ^1H chemical shifts did not change between 0.1 and 0.0001M for the whole series of derivatives **1b–7b**.

Table 1 summarizes the carbonyl ^{17}O chemical shifts as well as the H-bond-induced chemical shifts ($\Delta\delta$) of compounds **1b–7b, c**. $\Delta\delta$ was measured relative to the ^{17}O chemical shifts of the free carbonyl group in **1b** and **2b**, or relative to those in the parent compounds **3a–7a**. Throughout, it was assumed that the substituent effects of the OH groups was negligible. We observed a variation of $\Delta\delta$ between −34 ppm in 1-hydroxy-9-fluorenone (**4b**) and −99 ppm in 2-hydroxynaphtalene-1-carboxaldehyde (**6b**). The carbonyl ^{13}C chemical shifts of the same compounds were measured for comparative purposes (*Table 1*). As expected [5], the H-bond-induced ^{13}C chemical shifts are directed to high frequency, for example, by 6.0 ppm in juglone (**1b**); however, the magnitude of the shifts was inferior to the ^{17}O chemical shifts by at least one order of magnitude. This difference should certainly explain the increased relative sensitivity of the ^{13}C chemical shifts to contributions other than H-bonding (see below).

2. *Shielding Theory of the ^{17}O Nucleus.* To explain the H-bond-induced shifts of the carbonyl O-atoms in **1b–7b, c**, it is necessary to understand the various electronic parameters which influence the ^{17}O chemical shifts. It has been shown by *Webb* and coworkers [35] that the dominant contribution to the total ^{17}O screening constant is the paramagnetic term, which for a nucleus A bonded to other nuclei B may be written [36]

$$\sigma_p^A = -\,\text{const.}\,\Delta E^{-1}\,\langle r^{-3}\rangle\,\{Q_{AA} + \sum_{B \neq A} Q_{AB}\}\,, \qquad (1)$$

where ΔE is the average excitation energy usually taken as the magnitude of the lowest-energy electronic transition, $\langle r^{-3}\rangle$ is the so-called orbital-expansion term, and Q_{AA} and Q_{AB} are defined in terms of the appropriate matrix elements used to calculate atomic-charge densities and interatomic bond orders, respectively.

The intramolecular H-bond structures of **1b**–**7b** can be considered as charge-transfer structures where the OH group acts as a proton donor and the carbonyl group as a proton acceptor [1–3]. In this case, the resonance structure $> C^+{-}O^-$ is stabilized, with the effect of altering the different terms in *Eqn. 1* which contribute to the ^{17}O chemical shift. Of course, all the terms in *Eqn. 1* are interdependent; a change in the electron density at the O-atom, for example, expresses itself in both the $\langle r^{-3}\rangle$ and Q_{AA} terms. However, it has proved useful to discuss the terms separately in order to estimate the importance of the various contributions of inductive, steric, electric field, mesomeric, or other effects to chemical-shift changes.

The average distance between an O-nucleus and its 2p electrons increases through H-bonding. This results in a decrease in $\langle r^{-3}\rangle$, and reduces the paramagnetic contribution to the screening (because of the negative sign in *Eqn. 1*, a decreased magnitude of σ_p^A increases the total shielding). However, since the nonbonding O-orbitals in the ground state will be stabilized by H-bonding (the excited state supposedly shows little or no H-bonding), the energy of the n-π^* transition will increase, *i.e.* ΔE^{-1} is expected to decrease also. Thus, variation of both the parameters $\langle r^{-3}\rangle$ and ΔE^{-1} can explain the shielding of the carbonyl O-atoms on H-bonding. However, although not always taken into consideration, the term which characterizes the π-bond order of the C=O group should also decrease on H-bonding, and this can again explain the low frequency shifts of the carbonyl O-atoms. A particularly demonstrative example of π-bond order perturbation on the ^{17}O chemical shifts has been given recently by *Olah et al.* [37] with respect to the protonation of ketones, *e.g.* a shift of –250 ppm was observed when acetone was fully protonated. The sign and magnitude of the ^{17}O chemical shift were explained by consideration of the canonical forms of the protonated molecule.

The magnitude of the H-bond-induced shifts of the carbonyl O-atoms varied appreciably in **1b**–**7b** *(Table 1)*. Certainly, this should reflect the different H-bonding energies of the structures. We shall attempt to establish correlations of the carbonyl ^{17}O chemical shifts with other NMR-spectroscopic parameters. The large size of the ^{17}O chemical shifts and their independence, to a good approximation, of substituent, steric, or ring current effects should make them ideally suited for quantitative considerations.

3. *H-Bond-Induced ^{17}O-Chemical Shifts of the OH Groups.* The ^{17}O chemical shifts of the OH resonances of **1b**–**7b** were observed between 72 and 96 ppm *(Table 3)*, displaced to high frequency relative to the range of –40 to 70 ppm established for simple alcohols [38]. The OH resonance from neat phenol occurs at 69.3 ppm [38], however, its position varies strongly on dilution. *Sugawara et al.* [39] reported a value of 79 ppm for 33 vol-% phenol in benzene at 76°. We measured 73.2 and 68.8 ppm for 0.5M solutions of phenol and α-naphthol, respectively, in $CDCl_3$ at 40°. Obviously, it is difficult to estimate the anisotropic and electron-withdrawing effects of the carbonyl groups of the quinone moiety on the OH group in **1b**. In the absence of better reasons, we can assume that the influence of H-bonding in **1b**–**7b** expresses itself in deviations of the OH chemical shifts

from the mean value of the free aromatic OH groups (~ 69 ppm). The magnitudes of these shifts, between 3 and 27 ppm, are, however, considerably smaller than those for the carbonyl O-atoms (see above). Also, the sign of the shifts is the opposite, the OH ^{17}O resonances being displaced to high frequency, as are those of the OH protons, on H-bonding [2]. This direction agrees with that observed by *Reuben* [8] in H_2O-dilution studies: formation of H-bonds involving the O-atom of a OH group led to a high frequency shift of the ^{17}O resonance. The effect of proton donation on the H_2O O-atom was estimated as a shift of 12 ppm [8].

Table 3. *OH Chemical Shifts in the C=O··· H–O-Bond-Forming Compounds* **1b–7b**, **c**[a])

Compound	$\delta(^{17}OH)$[b])	$\delta(O^1H)$[c])
1b	84.1	11.86
2b	84.4	11.84
3b	86.0	12.05
4b	72.1	8.20
5b	80.3	10.98
6b	96.4 (95)[d])	13.15
7b	84.4	12.02
7c	79.5	10.54

[a]) Natural-abundance measurements of 0.3M solns. in $CDCl_3$; $T = 40°$.
[b]) Relative to external dioxane (–0.2 ppm from H_2O) [25]. Estimated error ±1 ppm.
[c]) Relative to internal TMS. Estimated error ±0.2 ppm.
[d]) Value reported by *Lapachev et al.* [40].

The ^1H chemical shifts of the OH groups in **1b–7b** were measured for comparative purposes under the same solution conditions *(Table 3)*. The absorption region between 8.2 and 13.1 ppm was indicative of H-bonds of variable strength. The OH ^1H chemical shift of phenol was 4.7 ppm, comparable to the value measured by *Takasuka* and *Matsui* [41] at infinite dilution. We do not, however, propose this value as a reference for evaluating the H-bond-induced OH ^1H shifts in **1b–7b**, since it is strongly dependent on substituent effects [41]. The phenolic OH H-atoms of naphthoquinones that are not intramolecularly H-bonded, were reported to occur between 6.5 and 7.5 ppm [27]. Furthermore, the chemical shifts of naphthols were dependent on the position of the OH group: α-naphthol, 5.2 ppm; β-naphthol, 4.1 ppm [42]. The chemical shifts of the OH H-atoms, contrary to those of the OH O-atoms, seem to be very sensitive to changes of anisotropy and ring currents. For these reasons, in the forthcoming chemical-shift correlations, we preferred to discuss the ^1H and ^{17}O chemical shifts of the OH groups with reference to their normal standards.

4. *^{17}O Chemical Shift Correlations.* The ^1H chemical shifts of phenolic OH groups involved in intramolecular H-bonds have been correlated earlier with the frequency changes $\Delta\nu$ of their IR stretching vibrations [41] [43]. ^{13}C-NMR studies of H-bonding in phenols have, however, shown discrepancies with respect to a correlation with the OH vibrational frequencies [31]. The ^{13}C chemical shift of the H-bonded carbonyl group in **1b** is 6 ppm to high frequency from the non-bonded carbonyl group *(Table 1)*. However, H-bonding is little in evidence in **6b** (the ^{13}C chemical shift of the carbonyl group is practically unchanged with respect to **6a**). This could lead to the assumption that the strength of the H-bond structure of **1b** with rigid geometry overwhelms that of the

structure of **6b** with non-rigid geometry. In fact, IR data suggest that the H-bond is stronger for **6b** despite steric hindrance to coplanarity [44]: for example, $\Delta\nu$ of the carbonyl stretching frequency is larger for **6b** (~ 360 cm^{-1}) than for **1b** (~ 300 cm^{-1}). The ^{1}H and ^{17}O chemical shifts of the OH groups point in the same direction *(Table 3)*. However, the most distinct discrimination was obtained from the H-bond-induced ^{17}O chemical shifts of the carbonyl groups: $\Delta\delta = -100$ and -70 ppm for **6b** and **1b**, respectively. The great sensitivity of the carbonyl ^{17}O chemical shift to H-bonding has been demonstrated in a number of other examples [7] [8] [10] [15] [16] [18]. We shall show in a forthcoming article [20] that the magnitude of the H-bond-induced ^{17}O chemical shifts in **1b–7b** correlates with the OH vibrational frequencies, *i.e.* with the strenghts of the H-bonds.

The ^{17}O and ^{1}H chemical shifts of the OH groups of **1b–7b** show a moderately good linear correlation with the H-bond-induced ^{17}O chemical shifts of the carbonyl groups (*Figs. 2* and *3*). In these correlations, obviously several systematic deviations of the chemical shifts are contained which are not related to H-bonding; *e.g.* the ^{1}H and ^{17}O chemical shifts of the OH group of **3b** are strongly increased with respect to those of **5b**. These deviations should originate from the substituent effects discussed above. Because of the linear correlations of *Figs. 2* and *3*, the ^{1}H and ^{17}O chemical shifts of the OH groups are also linearly correlated with each other ($r = 0.938$). However, the ^{13}C chemical shifts of the carbonyl groups in **1b–7b** *(Table 1)* do not show any functional relationship with the ^{1}H- and ^{17}O-NMR parameters. Obviously, the substituent effects are no longer inferior to the H-bonding effects in the ^{13}C-NMR of carbonyl groups conjugated to aromatic systems.

It is of great interest to compare the observed H-bond-induced ^{17}O chemical shifts with the amount of variation of the different electronic terms in *Eqn. 1* in order to confirm which is the main cause of these shifts. However, this demands the calculation of average excitation energies, π-bond orders, and charge densities at the O-atoms. Work on theoretical calculations is in progress [20]. Unfortunately, the ^{17}O chemical shifts of **1–7** cannot be examined for their correlation with ΔE^{-1}, since the n-π^* transitions are strongly overlapped by the intense π,π^* bands of these aromatic compounds.

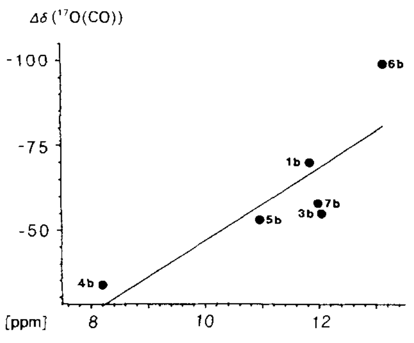


Fig. 2. *Linear correlation of the H-bond-induced carbonyl ^{17}O chemical shifts and the OH ^{1}H chemical shifts* (6 points, correlation coefficient $r = 0.941$)

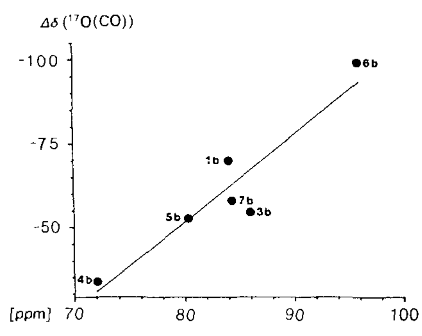


Fig. 3. *Linear correlation of the H-bond-induced carbonyl ^{17}O chemical shifts and the OH ^{17}O chemical shifts* (6 points, correlation coefficient $r = 0.938$)

5. *^{17}O Chemical Shifts and H-Bond Lengths.* Of the investigated H-bond structures **1b–7b**, X-ray structures exist only of juglone (**1b**) [45] and 1-hydroxy-9-fluorenone (**4b**) [46]. However, the position of the OH H-atom was precisely located only in **4b** [46]. The H-atom position in **1b** was, therefore, calculated from the heavy atom coordinates by attaching the proton with the assumption of standard geometries for an aromatic OH group (in plane, O–H bond length 0.97 Å, C–O–H angle 106°) [47]. Evaluation of the distance between the OH H-atom and the carbonyl O-atom gave d = 1.94 Å in the case of **1b** and d = 2.35 Å in the case of **4b**. If we consider that a smaller distance implies a stronger H-bond, these results agree qualitatively with the size of the H-bond-induced carbonyl ^{17}O chemical shifts $\Delta\delta$. A knowledge of the functional dependence $\Delta\delta = f(d)$ appears to be of great interest for an understanding of the physical origin of the ^{17}O chemical shifts (see above). A similar relationship was discussed earlier for the ^{1}H chemical shifts of OH and amide H-atoms on H-bonding [48]. A d^{-3} dependence was expected, *e.g.* from the polarization of the electron cloud near the H-atom by the proximity of the O-atom [49], and it was recently confirmed experimentally from data in proteins [50]. From the ^{17}O chemical shifts in **1b** and **4b**, we evaluated a ratio $\Delta\delta$(**1b**)/$\Delta\delta$(**4b**) = 2.08 which is not too far from the ratio d^{-3}(**1b**)/d^{-3}(**4b**) = 1.78 which corresponds to a d^{-3} dependence also for the carbonyl ^{17}O chemical shifts. Because of the lack of further X-ray data, we are presently performing *ab initio* SCF calculations to locate the OH groups in the H-bond structures **1b–7b** and to evaluate the H-bond distances [20].

6. *The Case of 2,2'-Dihydroxybenzophenone* (**7c**). It is well-known [31] that the benzophenones **7a**, **7b**, and **7c** cannot be planar for steric reasons, *e.g.* in the X-ray structure of **7a** the angle between the two benzene rings is 56° [51]. The question arises, therefore, whether an intramolecular H-bond is formed in **7b** and **7c** despite the twisting of the benzene rings, and more interesting, whether H-bonding from the two OH groups to the single carbonyl acceptor exists simultaneously in **7c**. Neither the ^{13}C chemical shift of the carbonyl group of **7c** (~ 6 ppm to high frequency from **7a**) [31] nor the IR spectrum of the OH groups [52] could distinguish between a situation where each OH group of **7c** is fully H-bonded, or where there exist two alternating single C=O···H–O interactions, in which the other OH is free to occupy a variety of conformations [31]. The large ^{3}J(C(6)–OH) value seemed, however, indicative of an *anti*-geometry of the OH groups [31].

The ^{17}O chemical shift of the carbonyl group of **7c** was displaced by −103 ppm relative to that of **7a** *(Table 1)*. The high sensitivity of the ^{17}O chemical shifts allows us to resolve the above problem independently of the results from 2-hydroxybenzophenone (**7b**). The OH groups of **7c** are chemically equivalent, since in both the ^{1}H- and ^{17}O-NMR spectra a single peak was observed. Entering the ^{1}H and ^{17}O chemical shifts of the OH groups of **7c** into the linear correlations established from compounds **1b–7b** (*Figs. 2* and *3*), an apparent $\Delta\delta$(C=O) of ~ 51 ppm was obtained in both cases. This value agrees well with half the $\Delta\delta$(C=O) = 103 ppm value observed in **7c**. Half the value must be used, since the carbonyl group of **7c** is under the influence of two OH groups, whereas the OH chemical shifts can only account for one H-bond. We conclude, therefore, that the two OH groups bind simultaneously to the single carbonyl acceptor.

The H-bond-induced carbonyl chemical shift in **7b** (−58.0 ppm) confirmed the above conclusions. The superiority of this shift over the chemical-shift difference between **7b** and **7c** (−44.7 ppm) indicates that the energy of the first H-bond is slightly larger than that of the second. This phenomenon is also apparent in the ^{1}H and ^{17}O chemical shifts of the OH groups of **7b** which were reduced from 12.02 to 10.54 ppm, and from 84.4 to 79.5 ppm, respectively (*Table 3*). In conclusion, ^{17}O-NMR seems to be a very useful technique for the quantitative measurement of the effects of multiple H-bonds on carbonyl groups.

7. *The ^{17}O Linewidths of the Carbonyl Groups on H-Bonding.* The relaxation of the O-nucleus is usually dominated by the quadrupole mechanism [9]. Under the extreme narrowing conditions of our experiments, the ^{17}O linewidths are given by

$$\pi L = 1/T_2 = 1/T_1 = \frac{12\pi^2}{125}\cdot(1 + \varepsilon^2/3)\left(\frac{e^2 q_{zz} Q}{\hbar}\right)^2 \cdot \tau_c\,, \quad (2)$$

where Q is the electric quadrupole moment of the ^{17}O nucleus ($-2.63 \cdot 10^{-26}$ cm^2), q is the electric field gradient tensor at the nucleus, with q_{zz} as its largest component, ε is the asymmetry parameter for q. The expression $\chi = e^2 q_{zz} Q/\hbar$ is called the oxygen quadrupole coupling constant (QCC). τ_c is the correlation time for isotropic molecular tumbling. For roughly spherical molecules the *Stokes-Einstein* model [53] predicts that

$$\tau_c = V_m \cdot \frac{\eta f_r}{kT}\,, \quad (3)$$

where V_m is the molecular volume, η is the medium viscosity, and f_r is a microviscosity factor < 1 depending on the relative sizes of solute and solvent [54]. V_m may be approximated [53a] by

$$V_m = 0.74\,\frac{M_w}{\rho N}\,, \quad (4)$$

where M_w is the molecular weight, ρ is the density of the solute, and N is *Avogadro*'s number, *Eqns. 3* and *4* predict that τ_c should be directly proportional to mol. wt., if the other parameters do not change significantly within the series of **1**–**7** studied. Under our solution conditions, the viscosities increased relative to that of neat $CHCl_3$ ($\eta = 0.500$ cP at 40°), however, no differences in viscosities were observed within the pairs of compounds **a**, **b** (*e.g.* we measured $\eta = 0.550$ and 0.551 cP for solutions of **6a** and **6b**, respectively). Thus, intramolecular H-bonding did not express itself in viscosity changes. A small increase in the viscosities was observed with increasing molecular weight of the compounds; as a maximum spread we measured $\eta = 0.531$ and 0.567 cP for the solutions of **5a** and **7a**, respectively. Evaluation of the microviscosity factors from the *van der Waals* volumes using the atomic increments of *Edwards* [55] resulted in a variation between $f_r = 0.18$ and 0.21 for the above solutions. Neglecting a possible variation of the solute density, the τ_c *vs.* mol. wt. plot would be expected to be slightly concave, with a maximum deviation from linearity of *ca.* 25%.

Table 4 presents the ^{17}O linewidths of the carbonyl resonances of **1a**–**7a**, as well as those of the C=O···H–O-bond-forming compounds **1b**–**7b**, **c**. *Fig. 4* shows that the linewidths of the carbonyl groups which do not undergo H-bonding increase linearly with molecular weight. On the basis of the data in the least-squares fit, the linear dependence is described by

$$L = (3.94 \pm 0.54) M_w - (316 \pm 87) \quad (5)$$

No systematic deviation from linearity was observed. As a consequence, the expression $(1 + \varepsilon^2/3)\cdot\chi^2$ in *Eqn. 2*, as a good approximation, must be constant. Since the variation of

Table 4. *Carbonyl* ^{17}O *Linewidths in the* $C{=}O\cdots H{-}O$*-Bond-Forming Compounds* **1b–7b**, **c** *Compared with the Parent Compounds* **1a–7a**[a])

Compound	Mol. weight		L[b]) [Hz]	L'[c]) [Hz]	$\Delta L'$[d]) [%]	$\Delta\chi$[e]) [%]
1a*	158		288			
1b*	174	O–C(1)	315		–24.8	–13.3
		O–C(4)	237			
2a	172	O–C(1), O–C(4)	371			
2b	188	O–C(1)	423		–19.6	–10.3
		O–C(4)	340			
3a	120		188			
3b	136		160	141	–25.0	–13.4
4a*	180		396			
4b*	196		351	322	–18.7	–9.8
5a	106		103			
5b	122		102	89	–13.6	–7.1
6a	156		248			
6b	172		163	148	–40.3	–22.7
7a	182		480			
7b	198		447	411	–14.4	–7.5
7c*	214		440	374	–22.1	–4.6

a) 0.3M Solns. in $CDCl_3$; $T = 40°$. Natural-abundance measurements except for compounds marked by an asterisk which were enriched to ~ 7 atom-% ^{17}O.
b) Observed linewidths at half-height, estimated errors < ±5%.
c) Linewidths corrected according to *Eqn. 6* for the increase in molecular weight on going from compounds **a** to **b**, **c**.
d) Relative changes of the linewidths on H-bonding.
e) Relative changes of the oxygen QCC's calculated according to *Eqn. 10*.

$(1 + \varepsilon^2/3)$ is usually negligible [56], the oxygen QCC's should be similar in the series of compounds **1a–7a** (the standard deviation of the slope of *Fig. 4*, corresponding to that of the square of the QCC's, is ±14%; thus the scatter of the QCC's themselves is ±7%). A partial confirmation for the small range of variation of the QCC values is given by the work of *Cheng* and *Brown* [57] who determined $\chi = 10.41$ MHz in **4a** and $\chi = 10.88$ MHz

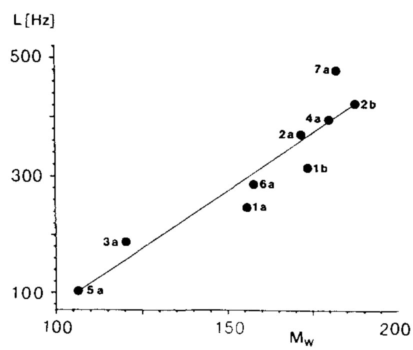


Fig. 4. *Plot of the* ^{17}O *linewidths of the carbonyl groups of* **1a–7a**, *as well as those of the free carbonyl groups of* **1b** *and* **2b**, vs. *the molecular weights*. The straight line obtained from a least-squares fit is given by *Eqn. 5* (9 points, $r = 0.941$).

in **7a**. The QCC of **7a** was recently measured also by high-field solid state NMR to be $\chi = 10.81 \pm 0.02$ MHz [58].

Table 4 shows that the linewidths of the H-bonding carbonyl groups of **1b** and **2b** were strongly reduced with respect to the free carbonyl groups: *e.g.* in **1b**, we measured $L = 237$ Hz for O–C(4) and 315 Hz for O–C(1) corresponding to a decrease of 25%. In **3b–7b, c** the linewidths of the H-bonding carbonyl groups had to be compared with those of the parent compounds **3a–7a**. Again, a general decrease of the linewidths was observed on H-bonding. For a fair comparison, effective linewidths (L') were calculated for the **b, c** compounds to correct for the increase in their molecular weights (and thus rotational correlation times) relative to the **a** compounds,

$$L'(\mathbf{b,c}) = L(\mathbf{b,c}) \cdot \frac{M_w(\mathbf{a})}{M_w(\mathbf{b,c})}. \tag{6}$$

As a result *(Table 4)*, the L' of salicylaldehyde (**5b**) became reduced by 14% relative to that of benzaldehyde (**5a**). This agrees with the earlier finding [10] that the linewidth in **5b** is narrower than in the corresponding *meta-* and *para*-OH substituted molecules.

The linear relationship between the carbonyl O-atom linewidths and the molecular weights no longer exists in the H-bond-forming compounds **1b–7b, c** *(Fig. 4)*. Obviously, the oxygen QCC's are dependent on the individual H-bond geometries, as was observed earlier by NQR for the deuterium [46] and oxygen [59] QCC's in nonlinear H-bonds. Unfortunately, in our series of compounds, 9-fluorenone (**4a**) and 1-hydroxy-9-fluorenone (**4b**) is the only couple where oxygen QCC data are available from NQR measurements: $\chi = 10.41$ MHz; $\varepsilon = 0.39$ for **4a**, and $\chi = 9.89$ MHz; $\varepsilon = 0.28$ for **4b** [59]. According to *Eqn. 2* the ratio of the ^{17}O linewidths of the two compounds must follow the relation

$$\frac{L(\mathbf{4a})}{L(\mathbf{4b})} = \frac{\{(1 + \varepsilon^2/3)\chi^2\}(\mathbf{4a}) \cdot \tau_c(\mathbf{4a})}{\{(1 + \varepsilon^2/3)\chi^2\}(\mathbf{4b}) \cdot \tau_c(\mathbf{4b})} \tag{7}$$

If that part of the variation in the L values which arises from changes in τ_c is taken into account by introducing the effective linewidth $L'(\mathbf{4b})$ *(Eqn. 6)*,

$$\frac{L(\mathbf{4a})}{L'(\mathbf{4b})} = \frac{\{(1 + \varepsilon^2/3)\chi^2\}(\mathbf{4a})}{\{(1 + \varepsilon^2/3)\chi^2\}(\mathbf{4b})}, \tag{8}$$

then χ and ε are the only parameters which may be different for **4a** and **4b**. From the ^{17}O linewidths in solution, we evaluated a ratio of 1.23. This is in good agreement with the ratio of 1.13 obtained from the NQR parameters in the solid state. Since secondary changes imposed by the effects of solid state and nearest neighbours seem not to be strongly reflected, the difference in linewidth of the two compounds is entirely explained by a change in the electric-field gradient at the O-nucleus due to H-bonding.

The largest reduction in the carbonyl O-atom linewidths on H-bonding was observed for **6b** relative to **6a**, indicating a very important change in the QCC, *i.e.* an increase in the symmetry around the O-nucleus with low values of q_{zz} and ε. Neglecting the influence of the asymmetry parameter and assuming that $\chi(\mathbf{6a}) = \chi(\mathbf{4a}) = 10.41$ MHz, from the ^{17}O linewidth ratio (1.68) a QCC value of 8.02 MHz was calculated for the H-bonded structure of **6b**.

The oxygen QCC's may be evaluated also from the ^{17}O linewidths measured in solution *(Table 4)*, if the re-orientational correlation times of the compounds are known

[56] [60]. One may obtain τ_c from the ^{13}C relaxation times (T_1) of the H-bearing C-atoms using the dipole-dipole relaxation equation [60]

$$1/T_1 = \hbar^2 \gamma_H^2 \gamma_C^2 r_{CH}^{-6} \tau_c = 2.14 \cdot 10^{10} \cdot \tau_c, \quad (9)$$

assuming the vibrationally-averaged C–H bond distance to be $r_{CH} = 1.09$ Å. *Table 5* collects the results of the ^{13}C-T_1 measurements of **1a** and **1b**. Isotropic motion of these molecules was indicated since the T_1's of all protonated C-atoms were identical within experimental error. Intermolecular interactions of either **1a** or **1b** could be excluded, since the ^1H and ^{17}O chemical shifts and linewidths were independent of concentration (see above). Since internal motion in naphthoquinones is absent, the τ_c from the ^{13}C data should represent also the re-orientational motions which modulate the ^{17}O quadrupolar interaction. Introducing τ_c in *Eqn. 2,* the oxygen QCC values can be calculated from the *L* values (assuming zero-asymmetry parameter). *Table 6* presents the results obtained for **1a** and **1b** by such an analysis. The QCC of 11.0 MHz evaluated for the O-atoms in **1a** compares well with the only value existing from NQR measurements of quinones ($\chi = 11.09$ MHz; $\varepsilon = 0.436$ for 2,3-dichloro-1,4-naphthoquinone at 77 K) [61]. In **1b**, the QCC of the free O–C(1) was the same as in **1a**, however, the QCC of O–C(4) was 9.5 MHz, strongly reduced by H-bonding.

The procedure of QCC determination described above has as its main advantage its relative ease of application. However, the QCC's can be measured only with severe

Table 5. *^{13}C Spin-Lattice Relaxation Times of 1,4-Naphthoquinone* (**1a**) *and 5-Hydroxy-1,4-naphthoquinone* (**1b**)[a])

Compound	Assignment[b])	Chemical shift[c]) [ppm]	T_1[d]) [s]
1a	C(2), C(3)	138.6	6.0
	C(6), C(7)	133.8	5.6
	C(5), C(8)	126.4	6.0
1b	C(2)	139.4	5.5
	C(3)	138.4	5.6
	C(6)	136.4	5.4
	C(7)	124.3	5.2
	C(8)	119.0	5.4

[a]) Solutions were 0.2M in $CDCl_3$; $T = 40°$.
[b]) From [29c] (**1a**) and [29b] (**1b**). Only data for the protonated C-atoms are given.
[c]) The chemical shifts are in agreement with those reported earlier [29].
[d]) Estimated error $< \pm 3\%$.

Table 6. *Determination of the ^{17}O Quadrupole Coupling Constants in* **1a** *and* **1b** *by the Double Nuclear Spin Probe Method*

Compound	$T_1(^{13}C)$[a]) [s]	$\tau_c(^{13}C)$[b]) [ps]		$T_2(^{17}O)$[c]) [ms]	$\chi(^{17}O)$[d]) [MHz]	
1a	5.9	7.9	O–C(1), O–C(4)	1.11	11.00[e])	10.67[f])
1b	5.4	8.7	O–C(1)	1.01	10.99[e])	
			O–C(4)	1.34	9.53[e])	

[a]) Values are averages over the protonated C-atoms *(Table 5)*. The spread is about ±2%.
[b]) Calculated using *Eqn. 8*. Estimated error ±5% taking into account an error of ±0.005 Å in r(C–H).
[c]) Calculated according to $T_2 = {}^1/\pi L$. Estimated error ±5%.
[d]) Calculated from *Eqn. 2* using the $\tau_c(^{13}C)$ values. Estimated error ±5%.
[e]) With the assumption $\varepsilon = 0$.
[f]) With $\varepsilon = 0.436$ obtained from NQR of 2,3-dichloro-1,4-naphthoquinone [61].

limitations of accuracy [56]. Under the conditions of our experiments, the QCC's of **1a** and **1b** were measured with an accuracy of roughly ±5% (see *Table 6* for error estimation). However, an additional error exists since the assumption of $\varepsilon = 0$ which is necessary to solve *Eqn. 2,* appears not to be justified for carbonyl functions [57]. For 2,3-dichloro-1,4-naphthoquinone, a value of $\varepsilon = 0.436$ was determined [61] which would correspond to a decrease of the QCC of **1a** by 3% *(Table 6)*.

By contrast, the relative QCC's in the pairs of compounds **a, b** can be considered to be more reliable, since they do not depend on the quality of the τ_c determination. After introducing L' (making use of the τ_c prop. M_w relation, *cf. Eqn. 6*), the relative change of the QCC's on H-bonding can be expressed as

$$\Delta\chi = \frac{\chi(\mathbf{b}) - \chi(\mathbf{a})}{\chi(\mathbf{a})} = \frac{\sqrt{L'(\mathbf{b})} - \sqrt{L(\mathbf{a})}}{\sqrt{L(\mathbf{a})}}. \qquad (10)$$

The values calculated in this manner are included in *Table 4*.

8. *The ^{17}O Quadrupole Coupling Constants of the Carbonyl Groups and their Correlation with the ^{17}O Chemical Shifts.* The oxygen QCC's, owing to their dependence on the electric-field gradient at the O-nucleus, are of independent interest as a probe for the local electric environment [9]. The linear correlation between the ^{17}O linewidths and the molecular weights in *Fig. 4* shows, however, that the oxygen QCC's of **1a–7a** in solution are relatively insensitive to the degree of conjugation of the carbonyl groups with the aromatic rings; at least, the changes in the QCC's seem to be too small to be observable within the precision of the ^{17}O linewidth determination (all points in *Fig. 4* lie within 95% confidence intervals). Indeed, the QCC value of 10.5 MHz obtained by *Delseth* and *Kintzinger* [60] for cyclic aliphatic ketones is also equal to that of 1,4-naphthoquinone (**1a** ($\chi = 11.0$ MHz) if the scatter of ±7% is taken into account. In contrast, the ^{17}O chemical shifts of **1a–7a** varied within a range of 60 ppm *(Table 1)* and seem, therefore, to be a more sensitive – if not easily explicable – indicator of changes in the electronic environment of the carbonyl O-atom (see *Chapt. 2*).

A large reduction of the oxygen QCC's was observed for the H-bonded carbonyl groups of **1b–7b, c** with respect to the carbonyl groups which do not undergo H-bonding. The relative changes in the QCC's were calculated according to *Eqn. 10* and are given in *Table 4*. According to *Townes* and *Dailey* [62] the electric-field gradient at the O-nucleus originates from the imbalance of the electron population in the 2p orbitals. For a carbonyl group, it has been shown both theoretically [57] [63] and experimentally [58] that the direction of the largest electric-field component (which defines the QCC) is perpendicular to the C=O direction. Therefore, changes in the QCC resulting from H-bonding perturbation of the 2p electronic distributions around the O-nucleus are to be expected. H-bonding decreases the QCC of the carbonyl O-atom by elongation of the 2p orbital which is approximately in the plane of the H-bond structure [59].

We examined, whether the H-bond induced $\Delta\chi$ is a parameter which characterizes the H-bond strengths of the various structures. However, no linear correlation was found between the $\Delta\chi$ values and the ^{1}H chemical shifts of the OH groups which are known to be related to H-bond strength [41] [43]. Although $\Delta\chi$ (23%), as well as the H-bond-induced chemical shift, were the largest for 2-hydroxynaphtalene-1-carboxaldehyde, $\Delta\chi$ of the other H-bonding structures was observed to vary only in a small range between 7 and 13% *(Table 4)*. We conclude, therefore, that the relationship of H-bond strength with $\Delta\chi$

is not characterized in the same way as with the ^1H and ^{17}O chemical shifts. The H-bond-induced chemical shifts seem to depend principally on H-bond distances *(cf. Chapt. 4)*; however, the H-bond-induced oxygen QCC changes in nonlinear H-bonds seem also to depend on H-bond angles. This was observed earlier for the deuterium QCC's in similar H-bonding systems [46].

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