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$^nJ(^{13}C, O^1H)$ coupling constants of intramolecularly hydrogen-bonded compounds†

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ABSTRACT: $^nJ(^{13}C,O^1H)$ carbon–hydrogen couplings were measured for a broad series of intramolecularly hydrogen-bonded compounds, some of which display tautomerism. A plot of J^{obs}(C-3,OH) + J^{obs}(C-1,OH) *vs.* δOH showed reasonable correlation both for compounds displaying tautomerism and for those with localized hydrogen bonds. Ketones and aldehydes fall on one line and esters on another line corresponding to a lower sum. The $^4J^{obs}$(C-1,OH) coupling depends on orbital overlap between the hydrogen-bonded hydrogen and the carbonyl oxygen. This coupling can therefore also be useful for monitoring twisting of the carbonyl group out of the plane of the hydrogen bond. An interesting finding is that for aromatic compounds $^3J^{obs}(C\text{-}2,OH)_{cis}$ is larger than that for an olefin both having the same ^1H OH chemical shift. A plot of J^{obs}(C-3,OH) *vs.* J^{obs}(C-1,OH) is very useful for monitoring tautomerism, and J^{obs}(C-1′,OH) and J^{obs}(C-1″,OH) are both well suited for estimating the mole fractions of tautomeric systems. © 1998 John Wiley & Sons, Ltd.

KEYWORDS: NMR; ^{13}C-NMR; $^{13}C,^1H$ spin–spin coupling; intramolecular hydrogen bonding; structure dependence; two-bond coupling; coupling through oxygen; three-bond coupling

INTRODUCTION

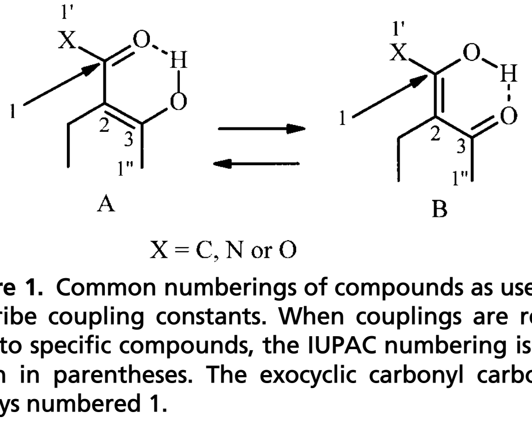
^3J(C,H) coupling constants have been used extensively to obtain structural information.[1–4] In addition, ^2J(C–X,H) may also be used.[5] ^nJ(C,OH) couplings can be measured in intramolecularly hydrogen-bonded systems[1–12] in which the OH proton is in slow intermolecular exchange or in simple alcohols in solvents such as DMSO. ^2J(C,OH) and ^3J(C,OH) couplings have been estimated in a number of cases.[1–12] For 2-hydroxybenzaldehyde (**17**), a very detailed analysis led to the couplings[3] shown in Scheme 1. Observation of long-range couplings may be of help in assignments,[6] especially in cases with several OH groups. ^nJ(C,OH) couplings have been used to monitor the dynamic equilibrium of hydrogen bonding for tautomeric systems.[11,12] Sopchick and Kingsbury[10] claimed that ^3J(C,OH) couplings are insensitive to structural variations.

The high-frequency position of the OH resonance allows the ready determination of ^nJ(C,OH) by using the SELJRES technique.[12,13]

In this work, ^nJ(C,OH) couplings were investigated as tools for the determination of hydrogen bond strength and to estimate the amount of each tautomer in tautomeric equilibria.[12] The results were compared with those obtained using deuterium isotope effects.[14–20]

The compounds investigated covered a wide range of OH environments and included *o*-hydroxyacyl aromatics,[17] one of which is known to be severely sterically hindered[18] (**5**), the enol form of β-diketones,[21] β-triketones,[14] β-ketoamides[19] and β-ketoesters,[21] including acyl Meldrum's acids,[14,22] and acyl *N*,*N*-dimethylbarbituric acids,[14,23] some of which have previously been investigated using deuterium isotope effects on chemical shifts.

In referring to coupling constants, the numberings in Fig. 1 are used. The corresponding IUPAC nomenclature is given in parentheses for specific compounds. The number of bonds between the OH proton and the carbon to which it is coupled is not specified for tautomeric compounds as it is ambiguous. The coupling to C-2 is an exception as it is a three-bond coupling in both tautomers.



X = C, N or O

Figure 1. Common numberings of compounds as used to describe coupling constants. When couplings are referring to specific compounds, the IUPAC numbering is also given in parentheses. The exocyclic carbonyl carbon is always numbered 1.

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ASSIGNMENTS

The very close-lying ^{13}C chemical shifts of the C-1, C-3 and C-7 carbons of the cyclic ketones (**13**–**15**) and C-1, C-3 and C-11 of **16** and **16Ac** made the assignment of C-3 and C-7 (C-3 and C-11 for **16** and **16Ac**) difficult. In **16Ac** the assignment was achieved by measurement of long-range carbon–hydrogen couplings from H-4. C-3 is therefore assigned to the high-frequency position, which differs from the assignment in Ref. 17.

RESULTS

$J^{obs}(C,OH)$ coupling constants were measured using the SELJRES[13] technique and are presented in Scheme 1. For some of the compounds measurements were made at low temperature to sharpen the OH resonances, presumably by slowing the intermolecular OH exchange. The best sensitivity was generally obtained at 250 K. The simple alcohols were measured in DMSO-d_6 at 300 K (Table 1). Couplings smaller than 0.3 Hz were generally not measurable. Couplings were measured at four different temperatures (300, 280, 250 and 200 K) for **8** as they show a temperature dependence (Scheme 1). For **16** only couplings to OH-3 were measured, as couplings to CH_3-12 and C-2 could not be observed because of poor signal-to-noise ratio. For **16Ac**, couplings to both OH-3 and OH-7 were measured (Scheme 1). Compound **20** was measured at different temperatures in order to resolve the three-bond coupling to C-1″(C-4).

The two-, three- and four-bond couplings are structurally the most interesting, although longer range couplings were occasionally detected, e.g. to the CH_3 groups of **3b**. It is interesting to relate the coupling constants to the two NMR parameters used for qualitatively grading hydrogen bonds, $^2\Delta C(OD)$[14–20] and δOH.[3]

A plot of δOH *vs.* $^2J(C\text{-}3,OH)$ revealed a weak correlation for compounds having a localized hydrogen bond, whereas a plot of δOH *vs.* $^2\Delta C(OD)$ for compounds with localized hydrogen bonds gave a correlation coefficient of 0.96, when omitting **5**, which is sterically hindered[18] (Fig. 2) (see Discussion).

A plot of $^4J^{obs}(C\text{-}1,OH)$ *vs.* δOH gave for aromatic compounds a fair correlation for ketones (Fig. 3), and the data point for sterically hindered **5** is under the correlation line. It is interesting that such couplings are small on ester carbonyl carbons.

Figure 4 shows a plot of the sum of $J^{obs}(C\text{-}3,OH)$ and $J^{obs}(C\text{-}1,OH)$ *vs.* δOH. The signs of $J^{obs}(C\text{-}3,OH)$ and $J^{obs}(C\text{-}1,OH)$ were not determined. From the analysis of salicylaldehyde[3] (**17**), both can be assumed to be negative. In the plots only absolute values for the coupling constants are given. It is seen that the data for aldehydes, ketones and to some extent amides fall on one line, whereas those of the esters fall on a correlation line corresponding to a smaller sum. It is likewise evident that the triketones, with the exception of usnic acid (**16**), fall on or above the line for aldehydes and ketones. Other exceptions are clearly **4** and **5**.

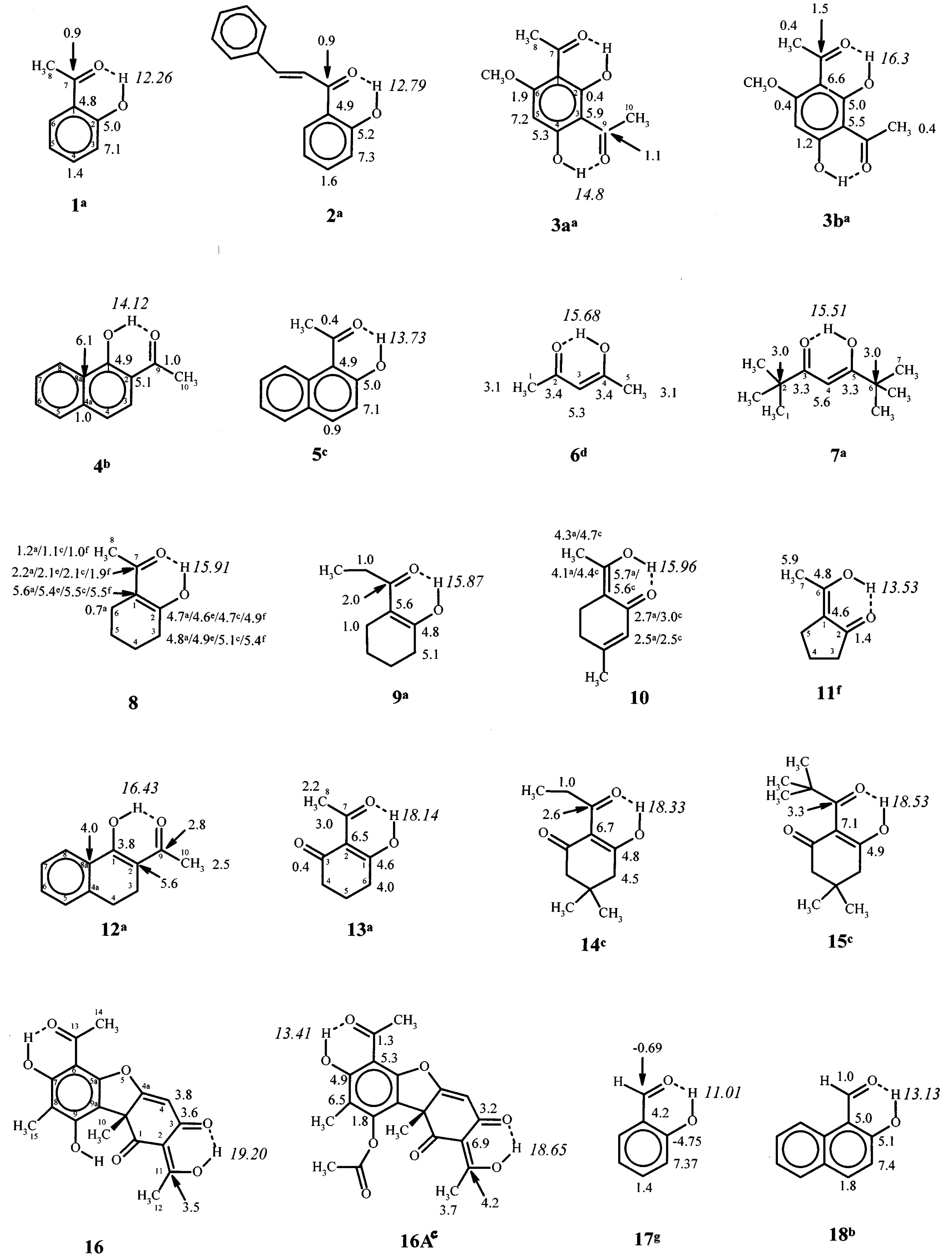
A plot of $^3J(C\text{-}2,OH)_{cis}$ *vs.* δOH (Fig. 5) revealed that the data for benzene derivatives and olefinic compounds fall on different correlation lines, possibly with that of 1,2-disubstituted naphthalenes (**4**, **5**, **18**, **23**, **25**) in between. The data point of 2,3-disubstituted naphthalene (**24**) falls on the benzene derivative line. A correlation coefficient of 0.98 for the olefinic and of 0.998 for the *o*-hydroxyacylbenzenes was found. Having the plots mentioned above, published values can be better understood. Approximate values of $^nJ(C,OH)$ couplings have used for assignment purposes. In other cases they have been related to structure. The values measured for salicylaldehyde[3] and acylphloroglucinols[4] fall nicely within the range found in this paper, whereas the values measured for naringenin[9] and methyl salicylate[10] are on the lower side. The values of $^2J(C,OH)$ determined for simple alcohols are similar to those reported,[3] whereas those values found for $^3J(C,OH)$ differ considerably from those reported previously (Table 1).

For the tautomeric compounds (**6**–**16**, **19**–**21** and **28**), $J^{obs}(C\text{-}3,OH)$, $J^{obs}(C\text{-}1',OH)$, $J^{obs}(C\text{-}1'',OH)$ and $J^{obs}(C\text{-}1,OH)$ are seen to increase with increase in $^n\Delta C(OD)$ (Table 2). This table can be read by comparing the columns in pairs. The first two columns show the coupling and isotope effect observed on C-1; both parameters are seen to decrease from top to bottom.

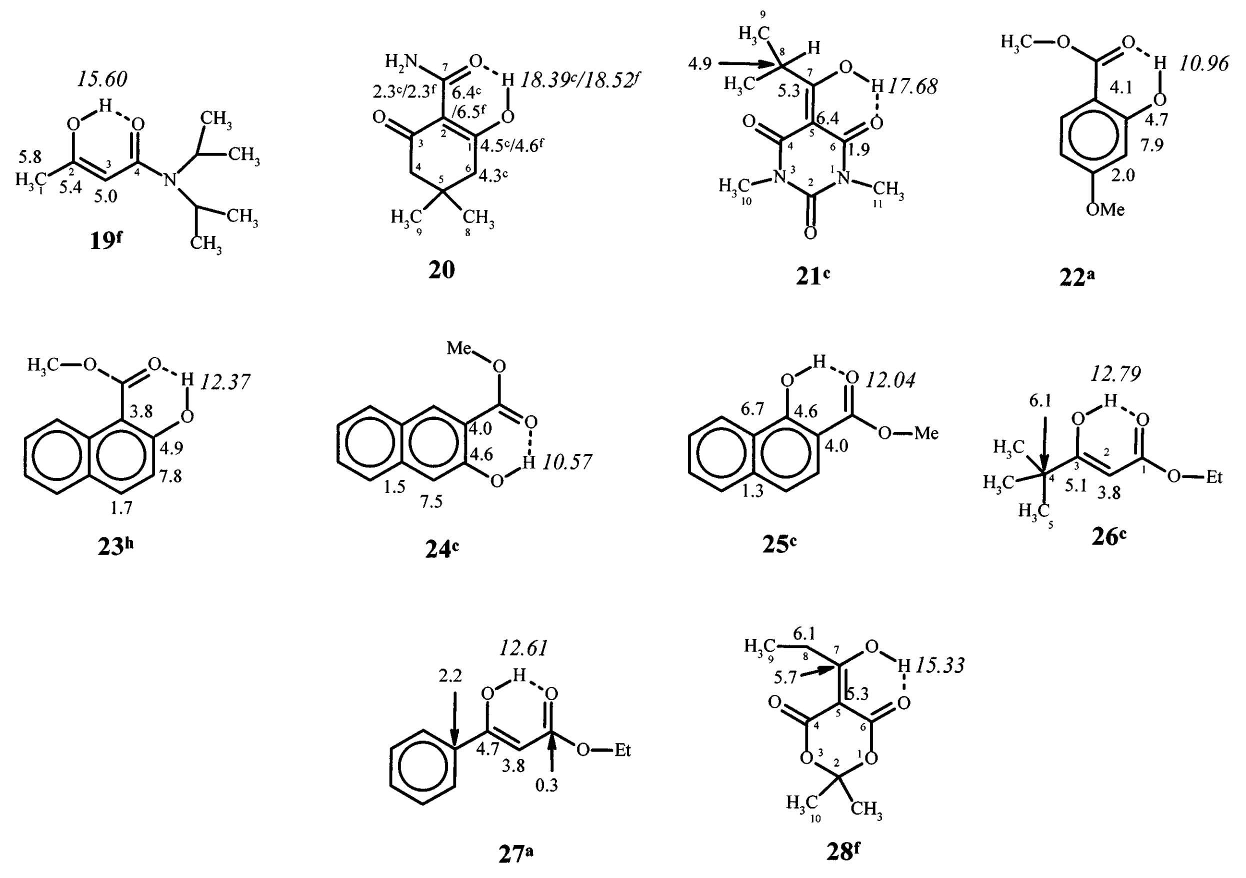
The mole fractions, *x*, of **6**–**12** were determined in previous work.[14] Good correlations are seen for enolic β-diketones when plotting $J^{obs}(C\text{-}3,OH)$, $J^{obs}(C\text{-}1',OH)$, $J^{obs}(C\text{-}1'',OH)$ and $J^{obs}(C\text{-}1,OH)$ *vs.* the mole fractions [Fig. 6(a)–(d)]. Compound **10** is seen to fall off this correlation. The mole fraction of **10** varies from 0.33 to 0.62 depending on the method used for the determination.[21] In an AM1 study, the mole fraction was determined to be 0.50.[24] From *ab initio* calculations, a value of 0.50 was determined. From the graphs in Fig. 6(a)–(d) a mole fraction of 0.36–0.39 is suggested. From Fig. 6, the couplings corresponding to a mole fraction of 1 can

Table 1. $J(C,OH)$ (Hz) measured in DMSO-d_6 at 300 K

Compound	$^2J(C\text{-}1,OH)$	$^3J(C\text{-}2,OH)$	δOH (ppm)
Methanol	3.0	—	4.09
Ethanol	3.0	3.2	4.36
Propan-2-ol	2.5	3.3	4.35
2-Methylpropan-2-ol	2.3	2.9	4.18



Scheme 1. Observed carbon–hydrogen coupling constants, ${}^{n}J(C,OH)$ (Hz). [a] 300 K. [b] 265 K. [c] 250 K. [d] 220 K. [e] 280 K. [f] 200 K. [g] From Ref. 3. [h] 290 K.



Scheme 1 *Continued*

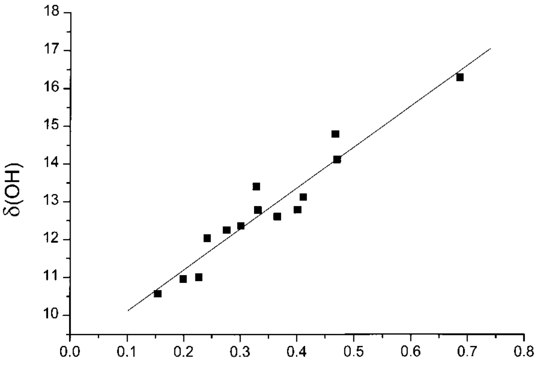


Figure 2. Plot of δ*OH* *vs.* $^2\Delta$C-3(OD). Correlation coefficient = 0.96.

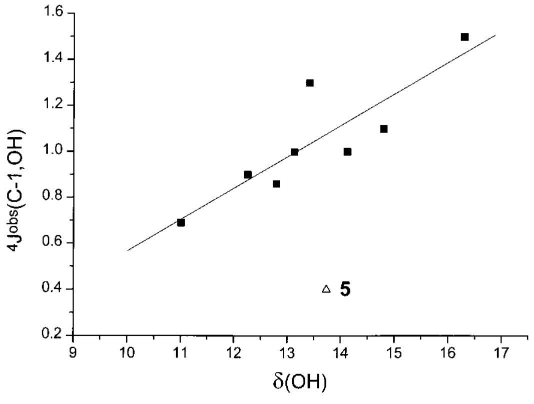


Figure 3. Plot of $^4J^{obs}$(C-1,OH) *vs.* δ*OH* for *o*-hydroxyacyl aromatics. △ is compound **5** (sterically hindered) in Scheme 1.

be estimated as ^2J(C-3,OH) = 5.8 Hz and ^3J(C-1″,OH)$_{trans}$ = 6.1 Hz. For a mole fraction of zero the couplings are estimated as ^2J(C-1,OH) = 5.7 Hz and ^3J(C-1′,OH)$_{trans}$ = 7.1 Hz.

DISCUSSION

$^3J^{obs}$(C-2,OH)$_{cis}$ *vs.* δ*OH*

In the plot of $^3J^{obs}$(C-2,OH)$_{cis}$ *vs.* δ*OH*, a difference is found between benzene derivatives and olefinic com-

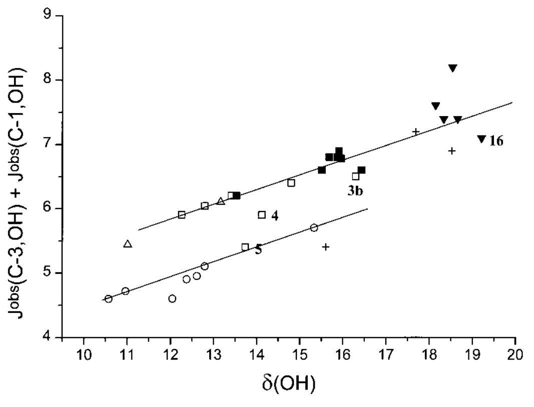


Figure 4. Plot of J^{obs}(C-3,OH) + J^{obs}(C-1,OH) *vs.* δ*OH*. □, Ketones; ○, esters; ■, diketones; ▼, triketones; △, aldehydes; +, amides. The numbers refer to the compounds in Scheme 1. The lines are guidelines to the eye.

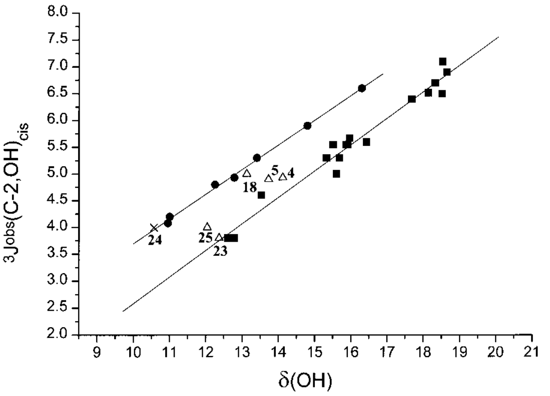


Figure 5. Plot of $^{3}J^{\mathrm{obs}}(\mathrm{C\text{-}2,OH})_{cis}$ *vs.* δOH. ■, Olefinic; ●, *o*-hydroxyacylbenzenes; △, 1,2-disubstituted naphthalenes; ×, 2,3-disubstituted naphthalenes. The numbers refer to the compounds in Scheme 1.

pounds (Fig. 5). For a given δOH, the $^{3}J^{\mathrm{obs}}(\mathrm{C\text{-}2,OH})_{cis}$ is larger for the benzene derivative than for the olefinic compound. This is unusual as the coupling normally is larger for compounds with the higher double-bond order.[25] The corresponding plot of δOH *vs.* $^{2}\Delta\mathrm{C\text{-}2(OD)}$ gave a very good correlation (Fig. 2), indicating that the variation most likely is not a variation in, e.g., anisotropy or ring current effects on the ^{1}H chemical shifts. For the 1,2-substituted naphthalenes, in which the double-bond order of the intervening bond is between those of benzenes and double bonds, the values fall in between for **4** and **5**, but not for **18**. The values for the naphthoic esters **23**–**25** fall on the line with other esters.

The plot of $^{4}J^{\mathrm{obs}}(\mathrm{C\text{-}1,OH})$ *vs.* δOH revealed a reasonable correlation for *o*-hydroxyacyl aromatics (Fig. 3). The systems investigated here are of the resonance-assisted hydrogen bond (RAHB) type.[26] A distinct overlap between the C=O oxygen and the O—H orbitals is likely. For compounds such as **3**, theoretical calculations on the non-methoxy derivative, 1,3-diacetyl-2,4-dihydroxybenzene, show that the O—H bond length is considerably increased compared with 2-hydroxyacetophenone and the C=O···H—O distance decreased.[27] The large coupling observed for **3b** can therefore be ascribed partly to orbital overlap. The very small value observed for **5** can be related to twisting of the carbonyl group, thereby reducing the overlap between the C=O group and the OH group and simultaneously decreasing the conjugation. The values for amides have not been studied systematically as most of the aromatic amides are rather insoluble.

$J^{\mathrm{obs}}(\mathrm{C\text{-}3,OH}) + J^{\mathrm{obs}}(\mathrm{C\text{-}1,OH})$ *vs.* δOH

The finding that values for ketones, aldehydes and amides fall on one line and those of esters predominantly on another (Fig. 4) can be understood as the latter show only small $J^{\mathrm{obs}}(\mathrm{C\text{-}1,OH})$ (Scheme 1). The data point for **5** falls between these lines as $J^{\mathrm{obs}}(\mathrm{C\text{-}1,OH})$ is unusually small, as discussed previously. Other compounds showing a value between these lines are **16** and **4**. It can be speculated that this is related to twisting of the OH group out of the C=O···O plane, because of the very short O···O distance (2.40 Å[28] for **16**). For **3b**, the data point is also between the two lines. However, in this case $J^{\mathrm{obs}}(\mathrm{C\text{-}1,OH})$ falls on the correlation line in the plot of $J^{\mathrm{obs}}(\mathrm{C\text{-}1,OH})$ *vs.* δOH.

Tautomeric equilibria

The observed coupling constants for tautomeric compounds are an average of the coupling constants of the two enolic forms. The observed coupling constant can be expressed as

$$J^{\mathrm{obs}}(\mathrm{C\text{-}}i,\mathrm{OH}) = x\ {}^{n}J(\mathrm{C\text{-}}i,\mathrm{OH}) + (1-x)\ {}^{m}J(\mathrm{C\text{-}}i,\mathrm{OH}) \quad (1)$$

where $J^{\mathrm{obs}}(\mathrm{C\text{-}}i,\mathrm{OH})$ is the experimentally measured coupling constant, x is the mole fraction of the tauto-

Table 2. Coupling constants (Hz) and deuterium isotope effects on ^{13}C chemical shifts (ppm)[a]

Compound	J^{obs}C-1	ΔC-1	J^{obs}C-1′	ΔC-1′	J^{obs}C-1″	ΔC-1″	J^{obs}C-3	ΔC-3
21	5.3	1.027	4.9	0.250	—	—	1.9	0.387
11	4.8	0.949	5.9	0.158	—	−0.125	1.4	−0.080
7	3.3	0.745	2.96	0.013	2.96	0.013	3.33	0.745
6	3.4	0.639	3.1	0.050	3.1	0.050	3.4	0.639
16	3.5	0.610	—	−0.070	3.82	—	3.6	0.540
28	5.7	0.589	6.1	0.141	—	—	—	0.426
20	2.3	0.349	—	—	4.3	0.212	4.6	0.953
13	3.0	0.310	2.19	−0.254	4.0	0.185	4.58	1.109
15	3.3	0.304	—	−0.269	—	0.207	4.9	1.182
19	—	0.267	—	—	5.8	0.190	5.4	1.029
14	2.6	0.349	1.0	−0.267	4.5	0.237	4.8	1.237
12	2.8	0.237	2.5	−0.199	4.0	0.033	3.8	0.981
10	4.07	0.106	4.31	−0.150	2.46	0.187	2.71	1.233
8	2.22	−0.331	1.23	−0.329	4.81	0.267	4.68	1.663
9	1.97	−0.331	0.99	−0.277	5.05	0.269	4.81	1.681

[a] The deuterium isotope effects on ^{13}C chemical shifts are from Refs 14, 15 and 21.

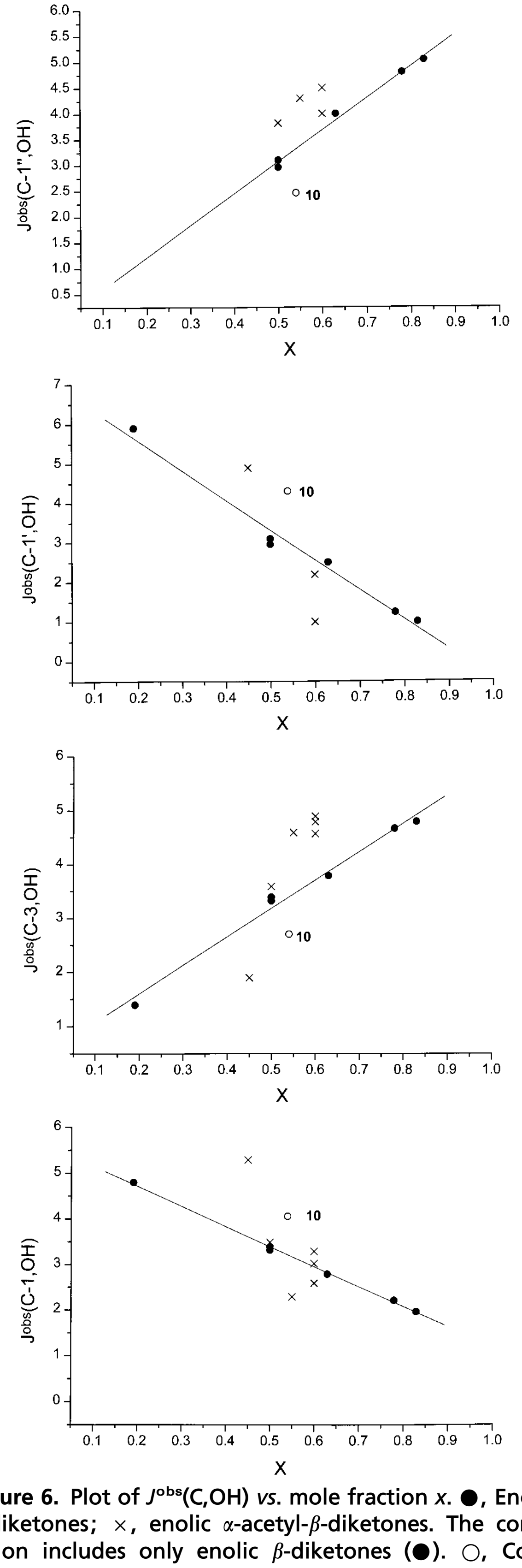


Figure 6. Plot of J^{obs}(C,OH) *vs.* mole fraction x. ●, Enolic β-diketones; ×, enolic α-acetyl-β-diketones. The correlation includes only enolic β-diketones (●). ○, Compound **10**. Correlation coefficients of the order of 0.991–0.999 are obtained.

mer A (Fig. 1) and ^nJ(C-i,OH) and ^mJ(C-i,OH) are the coupling constants for the respective tautomeric forms.

Figure 7 demonstrates clearly that **6**–**16** and **21** are tautomeric, as the J^{obs}(C-3,OH) coupling is small compared with the non-tautomeric aromatic compounds. This smaller coupling constant is due to the averaging of the coupling constant as expressed in Eqn (1). Conversely, **19** and **28** do not appear tautomeric based on this criterion. Likewise, none of the esters appear to be tautomeric. However, it should be noted that the detection of small amounts of one tautomer is difficult with these methods.

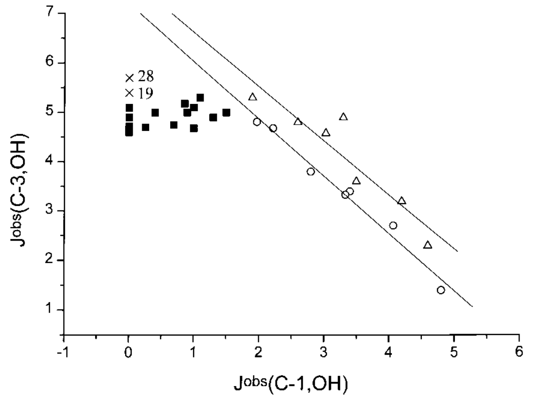


Figure 7. Plot of J^{obs}(C-3,OH) *vs.* J^{obs}(C-1,OH). ■, Compounds having a localized hydrogen bond; ○, enolic β-diketones, correlation coefficient = 0.99; △, enolic α-acetyl-β-diketones, correlation coefficient = 0.93; ×, compounds **19** and **28**.

Estimation of mole fractions

In tautomeric compounds the $^3J(C,OH)_{trans}$ couplings will be observed at both C-1′ and at C-1″. For enolic β-diketones these two three-bond couplings, $J^{obs}(C\text{-}1',OH)_{trans}$ and $J^{obs}(C\text{-}1'',OH)_{trans}$, were shown to be very useful for estimating the equilibrium constants or mole fractions. The same method can probably also be used for enolic triketones, but more data are needed, as seen from Fig. 6. The mole fractions calculated for **8** and **9** using these couplings are very similar to those obtained using ^{13}C or ^{17}O chemical shifts,[21] as seen in Table 3. For **11** the correspondence is less good but the value obtained from coupling constants is only approximate as no coupling was measured at C-1″(C-3). For **13** a mole fraction of 0.65 is obtained, whereas a much larger value occurs for **14**. For **10** the coupling constants clearly demonstrate that the B tautomer is the most abundant. This is not confirmed from theoretical calculations; both AM1 and *ab initio* methods gave x close to 0.5.[29] From the use of ^{17}O chemical shifts, although cited incorrectly in Ref. 21, a value for x of 0.31 could be estimated for **10**. For the acetyl derivative of usnic acid (**16Ac**), $^3J[C\text{-}1'(CH_3)]$ showed an increase compared with **16**. This increase in conjunction with increase in the coupling at C-1(C-11) and the decrease in the coupling at C-3(C-3) demonstrates that tautomer B (Fig. 1) is increased for **16Ac**. A similar result was obtained from deuterium isotope effects using the reassignment made in this paper.

Table 3. Mole fractions of tautomer A (Fig. 1)

Compound	$^3J(\text{C,OH})_{trans}$	δ^{13}C	δ^{17}O	Theoretical	Temperature (K)
8	0.80	0.74[21]	0.78[21]	0.55[24]	280
8	0.84	0.84	—	—	200
9	0.84	0.75[21]	0.83[21]	0.86[24]	300
10	0.37	0.23[a]	0.31[a]	0.47[24]	300
11	—	0.17[21]	0.19[21]	~0[24]	300
12	0.62	0.58[21]	0.63[21]	0.15[24]	300
13	0.65	—	0.74[14]	—	300
14	0.82	—	0.77[14]	—	300

[a] In Ref. 21, is x estimated to 0.33 from δ^{13}C and to 0.54 from δ^{17}O due to an inverted assignment of C-1 and C-3. This also inverts the deuterium isotope effects on C-1 and C-3 given in Ref. 21.

For enolic β-diketones, plots of J^{obs}(C-3,OH) or J^{obs}(C-1,OH) *vs.* the mole fraction show good correlations, if it is assumed that the value for **10** must be reassigned. For the triketones, the mole fractions are less well determined, but it appears that reasonable plots of J(C,OH) *vs.* x could be obtained. The increase in the sum of J^{obs}(C-3,OH) + J^{obs}(C-1,OH) for the triketones can be ascribed to an increase in J^{obs}(C-3,OH).

EXPERIMENTAL

All NMR spectra were recorded at 50.3 or 62.9 MHz on a Bruker AC200 or AC250 spectrometer at temperatures between 180 and 300 K. The SELJRES pulse sequence[13] from the Bruker sequence library was used with minor modifications. The 90° pulse width for the C-13 observe channel was 4.5 µs, and the 180° soft pulse for the ^{1}H decoupling channel was 20 ms, which selectively excites H-1 resonances within a 50 Hz range. Two-dimensional data were collected (16 or 32 blocks times 8192 t_2 points) with 0.0625 or 0.03125 s increments in the evolution dimension, which gave a spectral width of 8.0 or 16.0 Hz, respectively, in the F_1 dimension. The spectral width in the F_2 dimension was between 16 and 18 kHz. At low temperatures (<270 K), 8 or 64 transients were recorded for each block, depending on the sample concentration. At ambient temperature (300 K), up to 640 transients were recorded for each block owing to the low ^{13}C signal intensity. In all the SELJRES experiments, a 5–10 s preparation period was used.

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