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Deuterium Isotope Effects on ^{13}C Chemical Shifts of Enaminones

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Deuterium isotope effects on ^{13}C chemical shifts have been studied in a series of substituted *N*-alkyl and *N*-phenyl keto-enamines. The intramolecularly hydrogen bonded *Z*-forms show the largest two-bond isotope effects, $^{2}\Delta$C-1(ND). Methyl-substitution at C-1 leads to a larger two-bond isotope effect in the *N*-phenyl-substituted derivatives. This effect is ascribed to steric compression. Space-filling substituents at the *ortho*-position of the *N*-phenyl ring lead to a decrease of the two-bond isotope effect. A correlation is found between $^{2}\Delta$C-1(ND) and $^{3}\Delta$C-2′(ND). The latter becomes negative in the sterically hindered cases. $^{3}\Delta$C-2′(ND) may therefore be used as a gauge of the twist of the phenyl ring.

o-Hydroxy substitution of the CO-phenyl rings enables intramolecular hydrogen bonding to the carbonyl group. This kind of hydrogen bond with two donors to one acceptor leads to smaller $^{2}\Delta$C-2(ND) and $^{2}\Delta$C-2″(OD) isotope effects equivalent to weaker hydrogen bonds for the *Z*-isomer. This is ascribed to competition for the acceptor. For the *E*-isomer $^{2}\Delta$C(OD) is enhanced. The same feature is seen for *N*,*N*-dimethylamino enamines. This increase is ascribed to delocalization of the nitrogen lone-pair onto the carbonyl oxygen, thereby strengthening the hydrogen bond and thus leading to larger two-bond, $^{2}\Delta$C(OD), isotope effects.

Keto-enamines are a class of compounds with unusual features concerning the *E*:*Z* ratio.[1] The ratio is clearly dependent on the solvent and is possibly be related to hydrogen bonding. This feature is not yet fully clarified. The *Z*-form shows intramolecular hydrogen bonding. This feature can be studied to advantage by means of deuterium isotope effects on ^{13}C chemical shifts.[2–17] These isotope effects in intramolecularly hydrogen bonded olefins show interesting relationships between $^{2}\Delta$C(ND), δN*H* and δC-1 or δC-2.[4] Of interest is also the increase in $^{2}\Delta$C(ND) with *N*-phenyl substitution.[3,11–13]

Steric effects may be studied by means of deuterium isotope effects on carbon chemical shifts. Steric compression has been shown to have a large increasing effect on the two-bond isotope effects of 1,3-indanediones.[4] Steric hindrance of acyl groups of *o*-hydroxy acyl aromatics can also be detected by means of isotope effects.[10] Steric interactions may also influence the conformation of the phenyl ring (the dihedral angle between the lone-pair and the phenyl ring). This is of interest and has been monitored in *N*,*N*-dialkylamines by means of ^{13}C chemical shifts of the *p*-carbons[18] or by photoelectron[19] or UV[20] spectroscopy. The twist angle can also be calculated by semiempirical calculations.[21] Substitution at C-1 or at the *ortho*-positions of the *N*-phenyl ring (A of Fig. 1) of the present compounds leads to a gradual increase in the steric interaction and the series of compounds is thus a very suitable indicator of how the various steric effects may be detected simultaneously. It is also shown that an estimation of the phenyl group twist can be based on three-bond deuterium isotope effects on C-2′ carbons.

For the compounds investigated, the intramolecular hydrogen-bonding is of resonance assisted (RAHB) type. An important feature of this is the charged forms

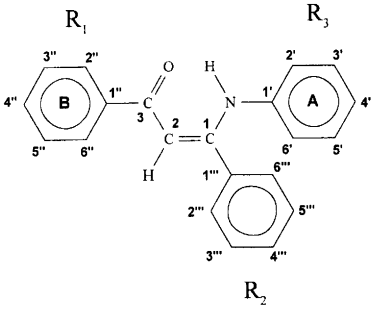

Fig. 1. Numbering of the enaminones.

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(Fig. 2). However, the importance of charge generated by features outside the RAHB system is unknown, a feature that can be studied in the present compounds via substitution of the phenyl rings at the nitrogen [ring A (Fig. 1)] or at the phenyl rings at the carbonyl group (ring B) as well as substitution at C-1.

Intramolecular hydrogen bonding with two hydrogen bond donors to one acceptor is of much interest. This has been studied in OH···C=O···HO cases by means of both $''\Delta C(D)$ and $^1\Delta C(^{18}O)$ isotope effects.[10,16] OH groups in the *ortho*-position of the B phenyl rings enables formation of this kind of dual donor to the carbonyl groups, with the two different donors, OH and NH.

Results

Deuteriation was normally done by treatment of the compounds with a mixture of CH_3OD and CH_3OH followed by evaporation and dissolution of the deuteriated compound in the NMR solvent or by dissolving the compounds in $CDCl_3$ and stirring the solution with a mixture of H_2O–D_2O followed by drying. For compounds dissolved in DMSO-d_6, deuteriation was done by addition of a mixture of H_2O–D_2O. The degree of deuteriation can be varied in all three methods. Variation of the H : D ratio was used to confirm the signs of the isotope effects. As all the compounds are unsubstituted at C-2, deuteriation may also take place at this position in addition to the NH group or at the OH position for compounds **5**, **9** and **30–32**. As the rates for exchange at C-2 and at NH are different, isotope effects due to deuteriation at the two sites can be differentiated, especially using mixtures of H_2O–D_2O for deuteriation. The three types of deuterium isotope effect on ^{13}C chemical shifts are denoted $''\Delta C(ND)$, $''\Delta C(OD)$ and $''\Delta C(D)$ and are the result of deuteriation at NH, OH or C-2 positions, respectively. The isotope effects are defined as $''\Delta C(D) = \delta C(H) - \delta C(D)$, n being the number of bonds from the site of deuteriation to the nucleus in question. The more specific notations, $''\Delta C(XD)$ is used to identify unambiguously the site of deuteriation.

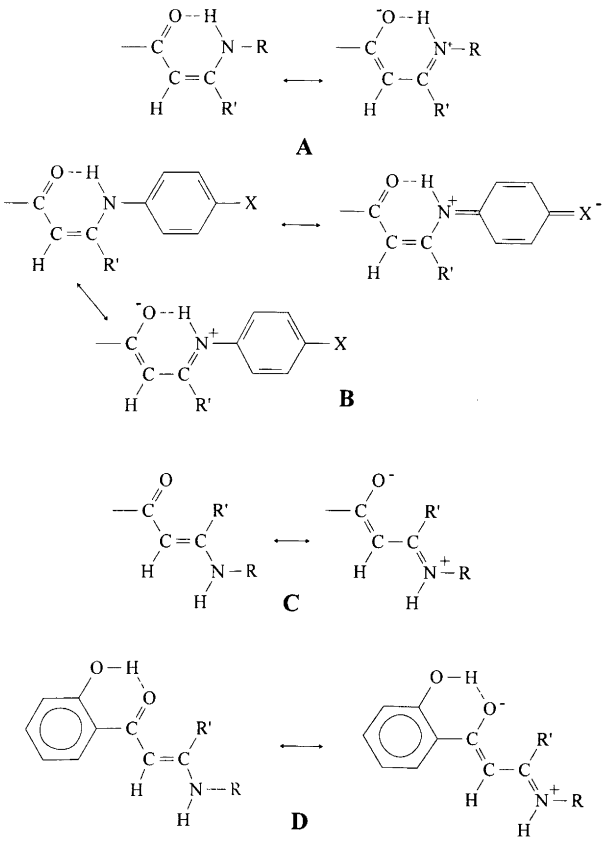


Fig. 2. Resonance forms of enaminones.

The compounds exist exclusively as the *Z*-form in $CDCl_3$, whereas in DMSO-d_6 the compounds (**1–9**, **17**, **18**, **28**) appear in both forms. This feature has previously been studied.[1,22]

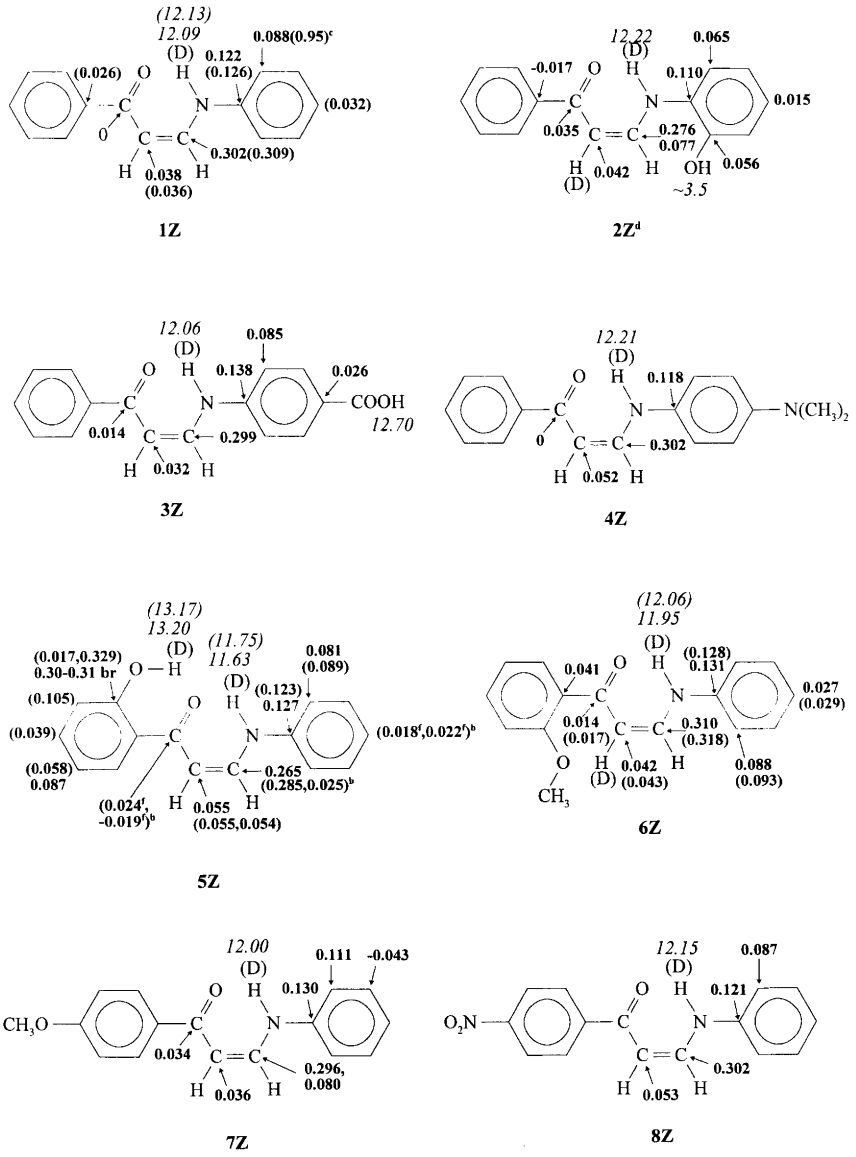
The ^{13}C chemical shifts are given in Table 1 (available from the authors upon request). The assignments are based on substituent effects, carbon–fluorine coupling constants and on HETCOR and COLOC experiments in cases of doubt.

Some of the ^1H and ^{13}C chemical shifts have previously been published.[1,23,24] The deuterium isotope effects and XH chemical shifts for the *Z*-forms are given in Scheme 1. Values (ppm) for the *E*-forms are given in the following order: compound, XH chemical shift, deuterium isotope effects on ^{13}C chemical shifts, $''\Delta C(D)$: **1***E*, $\delta(NH) = 10.15$; **3***E*, $\delta(NH) = 10.39$ $^2\Delta C\text{-}1(ND) = 0.169$, $^3\Delta C\text{-}2(ND) = 0.057$, $^2\Delta C\text{-}1'(ND) = 0.123$, $^3\Delta C\text{-}2'(ND) = 0.057$; **5***E*, $\Delta(NH) = 10.50$ and $\delta(OH) = 13.89$, $^2\Delta C\text{-}1''(OD) = 0.434$; **6***E*, $\delta(NH) = 10.00$, $^2\Delta C\text{-}1(ND) = 0.186$, $^1\Delta C\text{-}2(ND) = 0.048$; $^2\Delta C\text{-}1'(ND) = 0.122$, $^3\Delta C\text{-}2'(ND) = 0.085$; **7***E*, $\delta(NH) = 10.02$, $^2\Delta C\text{-}1(ND) = 0.174$, $^4\Delta C\text{-}3(ND) = 0.023$, $^2\Delta C\text{-}1'(ND) = 0.123$, $^3\Delta C\text{-}2'(ND) = 0.087$; **8***E*, $\delta(NH) = 10.36$ $^2\Delta C\text{-}1(ND) = 0.172$; **9***E*, $\delta(NH) = 9.84$, $\delta(OH\text{-}2'') = 14.11$, $\delta(OH\text{-}2') = 8.38$, $^2\Delta C\text{-}2''(OD) = 0.439$. As can be seen isotope effects are not observed for all *E*-forms. In **4** and **5** the ^{13}C resonances of the deuteriatied species are broad and for **2** and **9** the *E*-isomer is not very abundant. Despite the indication of rather strong hydrogen bonds [large $^2\Delta C\text{-}2''(OD)$] the OH resonances of **5***E* and **9***E* and **31** are broad at room temperature and only the very large $^2\Delta C\text{-}2''(OD)$ isotope effects are observed. The broadness of the ^{13}C resonances is probably related to OH and NH exhange as it disappears for **31** at lower temperature.

Intramolecular hydrogen bonding has a profound effect on $^2\Delta C\text{-}1(ND)$ as seen from a comparison of the data for *E*- and *Z*-compounds. The isotope effects for the *E*-compounds do not vary very much as also found previously.[3]

Data for the compounds investigated dissolved in the two solvents, $CDCl_3$ and DMSO-d_6, are generally similar, a situation that is found to hold for most intramolecular hydrogen bonds of the RAHB type.[14,15]

For the *Z*-compounds *N*-phenyl substitution leads to an increase in $^2\Delta C\text{-}1(ND)$ and in δNH as seen by



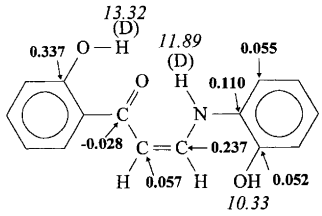
Scheme 1. Deuterium isotope effects on ^{13}C chemical shifts.[a]

[a]Compounds are dissolved in DMSO-d_6. Values are given in ppm. [b]The N*H* and O*H* chemical shifts are given in italics. The deuterium isotope effects are given in the order $^{n}\Delta C(ND)$, $^{n}\Delta C(D)$. For **5** and **9** the order is $^{n}\Delta C(ND)$, $^{n}\Delta C(OD)$. [c]Numbers in brackets are obtained from $CDCl_3$. [d]The *E*-form is not observed in DMSO-d_6. [e]Isotope effects are not observed. br means broad. [f]May be interchanged. [g]Only large isotope effects are observed. [h]This isomer is not very abundant. [i]At 250 K. [j]At 230 K. [k]$^{3}J(H,H)$ in Hz.

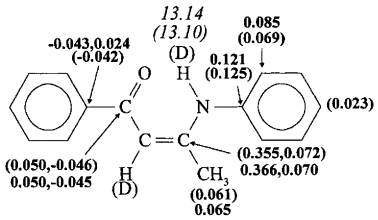
comparison of compounds **1***Z* and compounds **2**–**11** and **14**–**29** in general (Scheme 1) with those of **12** and **13** (see also Fig. 3). This feature has also been observed in a few keto- and nitro-enamines.[3] The origin of this effect might possibly be clarified by the study of derivatives with substituents in the phenyl ring. As seen in Fig. 3 substitution at the *para*-position of the A-ring with an electron-attracting substituent leads to an increase of $^{2}\Delta C$-1(ND), whereas electron-donating substituents have the opposite effect. The effect at δNH is small and no regular pattern is seen.

Methyl substitution at C-1 led to a small increase of $^{2}\Delta C$-1(ND) of an enaminone with an NH[CH$(CH_3)_2$] group.[3] In the compounds with phenyl substitution at nitrogen the increase in $^{2}\Delta C$-1(ND) is clearly much larger (**10**, **11**, **15**, **24**–**29**) (Fig. 3). It is also interesting to note that a phenyl group at C-1 (**14**) has only a small effect. A difference in the chemical shifts of, e.g., C-2, C-4′ or C-6′ between compounds with and without a methyl substituent at C-1 is also found. The increase in $^{2}\Delta C$-1(ND) can be related roughly to the ^{13}C chemical shift of the C-1 carbon as seen by a comparison of this with the two-bond isotope effects for **1***Z*, **10***Z*, **15** and **29**.

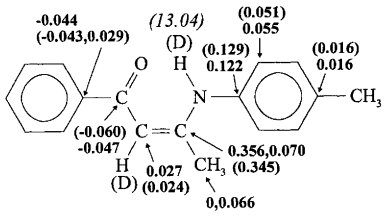
Strong steric hindrance is introduced in compounds such as **26** and **27**, in which the phenyl group has



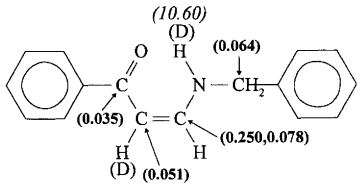
9Z



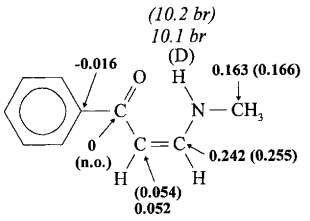
10Z



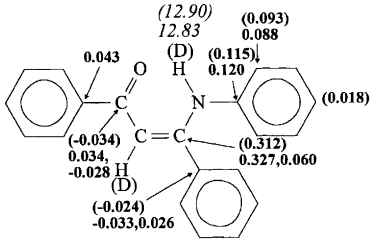
11Z



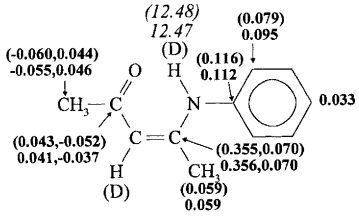
12Z



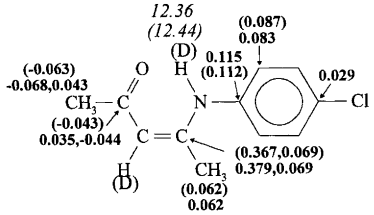
13Z



14Z[d]



15Z[d]



16Z

Scheme 1. (*Continued.*)

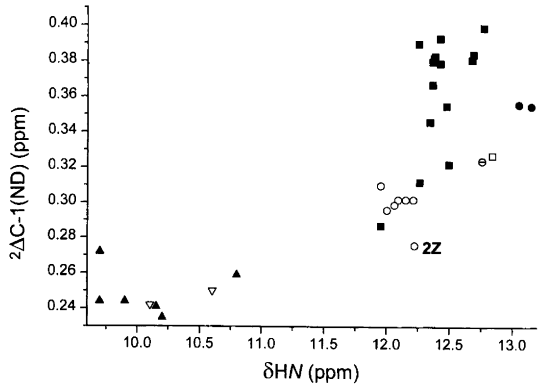
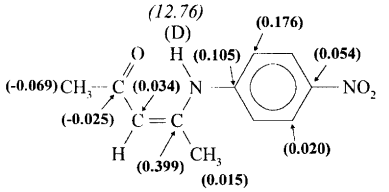


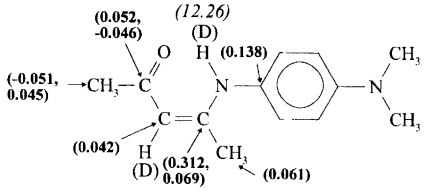
Fig. 3. Plot of $^2\Delta$C-1(ND) vs. δNH: R_1, R_2 and R_3 (see Fig. 1). ■, CH_3, CH_3, Ph; □, Ph, Ph, Ph; ●, Ph, CH_3, Ph; ○, Ph, H, Ph; ▲, alkyl, CH_3, alkyl (data taken from Ref. 3); ⊖, alkyl, H, Ph (data taken from Ref. 3); ▽, Ph, H, alkyl.

to twist, which leads to a concomitant reduction of $^2\Delta$C-1(ND). Negative three-bond isotope effects at C-2′ and C-6′ and a negative five-bond effect at C-4′ are observed. Smaller than usual effects are also observed in **21**–**23**, but not in **25**. A plot of $^3\Delta$C-2′(ND) vs. $^2\Delta$C-1(ND) shows a correlation (Fig. 4). A plot of $^3\Delta$C-2′(ND) vs. δN*H* gave a poorer correlation (not shown) possibly due to anisotropy effects on the N*H* chemical shift.

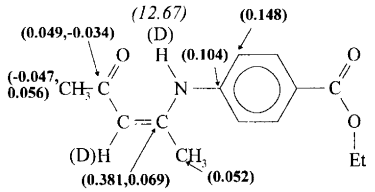
Compounds with OH groups in the *ortho*-position of ring A or B are a special case as they form intramolecular hydrogen bonds to either the carbonyl group or the N*H* group. An OH substituent in the *ortho*-position of the A-ring as found in **2** causes a decrease in $^2\Delta$C-1(ND). The C-2′(OH) proton is clearly exchanged quickly as no isotope effects due to OD′-2 are seen. This excludes a strong hydrogen bond to the N*H* nitrogen. However, a weak effect cannot be excluded. The value for **2***Z* falls under the line in Fig. 3, supporting the above.



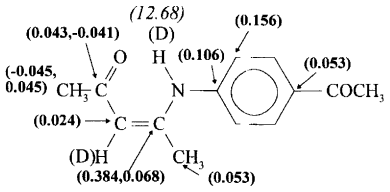
17Z



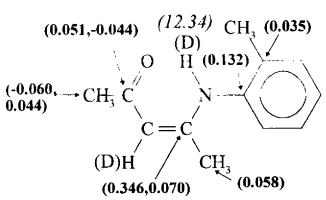
18Z



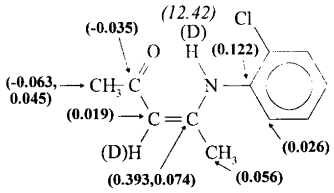
19Z



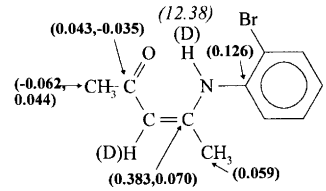
20Z



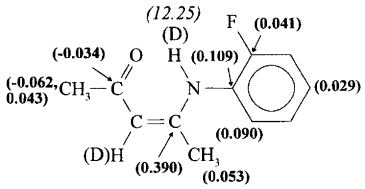
21Z



22Z



23Z



24Z[a]

Scheme 1. (*Continued.*)

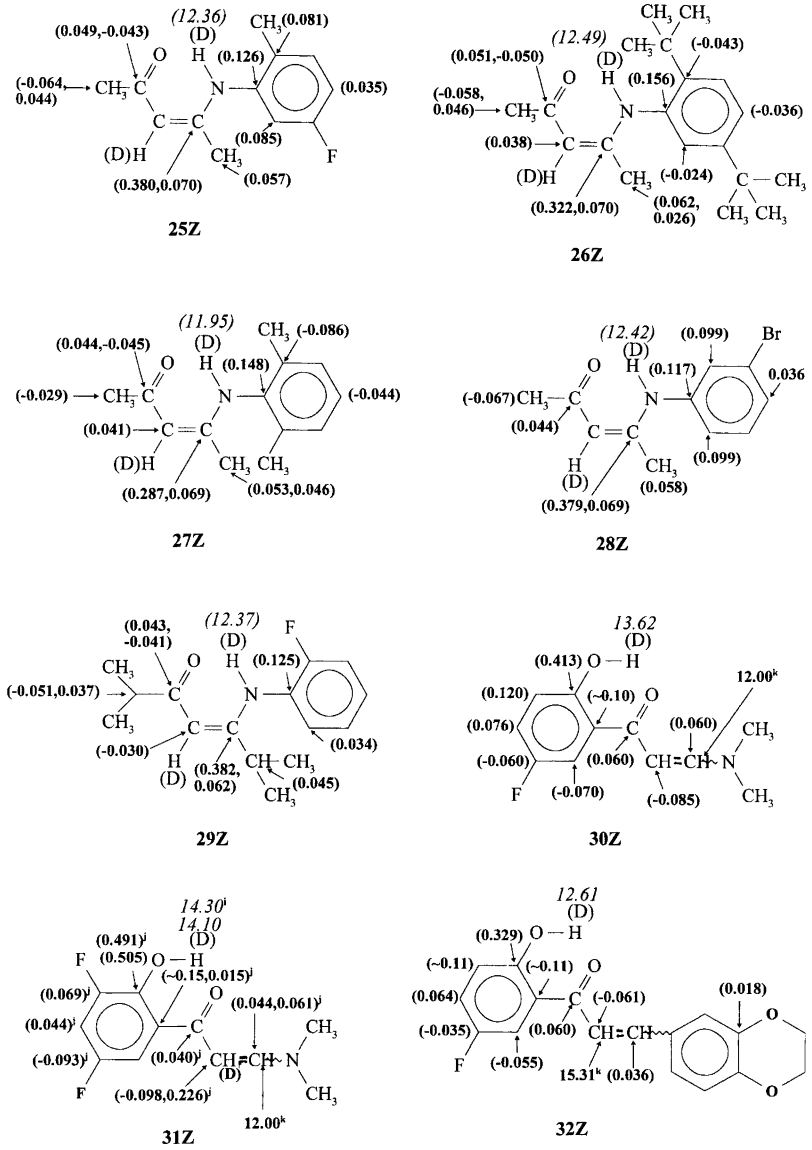
The isotope effects, $^{n}\Delta C(OD)$, observed in **30–32** correspond roughly to the isotope effects found for *o*-hydroxy acyl aromatics,[8] and the isotope effects for C-3 of **30** and **31** do not fall on the δOH vs. $^{4}\Delta C(OD)$ plot.[14]

Discussion

$^{2}\Delta C(OD)$. Compounds **5*E***, **9*E***, **30** and **31** show an interesting increase in $^{2}\Delta C(OD)$ as compared to, e.g., 2-hydroxychalcone[14] and **32**. This can be ascribed to the amino substitutent. This effect of the amino substituent is related to the negative charge at the carbonyl oxygen caused by delocalization of the enamine–nitrogen lone-pair (Fig. 2B) and thus illustrating the importance of charge in the strength of the hydrogen bond.

Compounds **5*Z*** and **9*Z*** are very useful in the investigation of simultaneous intramolecular hydrogen bonding to one acceptor. **5*Z*** is soluble enough in $CDCl_3$ to allow recording of ^{13}C spectra. The compound is almost entirely on the *Z*-form in this solvent. The good solubility also indicates that the OH group is engaged in intramolecular hydrogen bonding. $^{2}\Delta C\text{-}2''(OD) = 0.329$ and $^{2}\Delta C\text{-}1(ND) = 0.285$ ppm in $CDCl_3$ and very similar values are found in DMSO-d_6 (Scheme 1). A comparison with **6*Z*** shows a larger $^{2}\Delta C\text{-}1(ND)$ in the latter. The **5*E***- and **9*E*** isomers show a much larger $^{2}\Delta C\text{-}2''(OD)$ than do the **5*Z***- and **9*Z*** isomers. Both findings show that the two donors simultaneously form hydrogen bonds to one acceptor leading to weaker hydrogen bonds for both donors.

$^{2}\Delta C(ND)$. The finding that values of $^{2}\Delta C\text{-}1(ND)$ of *E*-derivatives are smaller than for the *Z*-isomer and do not vary very much, shows that the charged resonance



Scheme 1. (*Continued.*)

form (Fig. 2C) is effective only in conjunction with the hydrogen bonds as found in the *Z*-compounds (see below) or, alternatively, in the hydrogen bond between the C=O group and an *o*-OH group as found in **5***E*, **9***E*, **30** and **31** (Fig. 2D).

The effect of *p*-substitution at the A-ring is due to lone-pair delocalization of the nitrogen lone-pair into the A-ring leading to increased double bond character of the N–C-1′ bond and a more positively charged nitrogen (Fig. 2B). This also leads to positive long-range isotope effects at C-4′, $^{5}\Delta$C-4′(ND), as clearly observed in **15**–**17**, **20**, but not in **18** in which the substituent, X, is electron-donating. A similar trend is seen for the *ortho*-substituted derivatives **24** and **25**. The five-bond isotope effects on C-4′ for **17** and **24** are smaller than for **15**. For the strongly sterically hindered compounds **26** and **27**, the effects are negative as explained below.

Steric interference. The methyl group at C-1 causes an increase of $^{2}\Delta$C-1(ND) of the order of 0.05 ppm for most compounds, but no so for the strongly sterically hindered compounds **26** and **27**. A small increase in $^{2}\Delta$C-1(ND) upon methyl substitution at C-1 of *N*-alkyl enamines is observed.[3] For enamino esters no significant effect on the two-bond isotope effect was found.[4] The increase in $^{2}\Delta$C-1(ND) can be seen as the result of two counteracting effects. The methyl group at C-1 leads both to a steric compression of bonds and to a twist of the phenyl ring. The compression increases the hydrogen-bond strength as indicated by the increase in $^{2}\Delta$C-1(ND). Twisting of the phenyl ring decreases the hydrogen bond strength as seen in the decrease in $^{1}\Delta$C-1(ND). For compounds with no or only one *ortho*-substituent the compression effect is dominant.

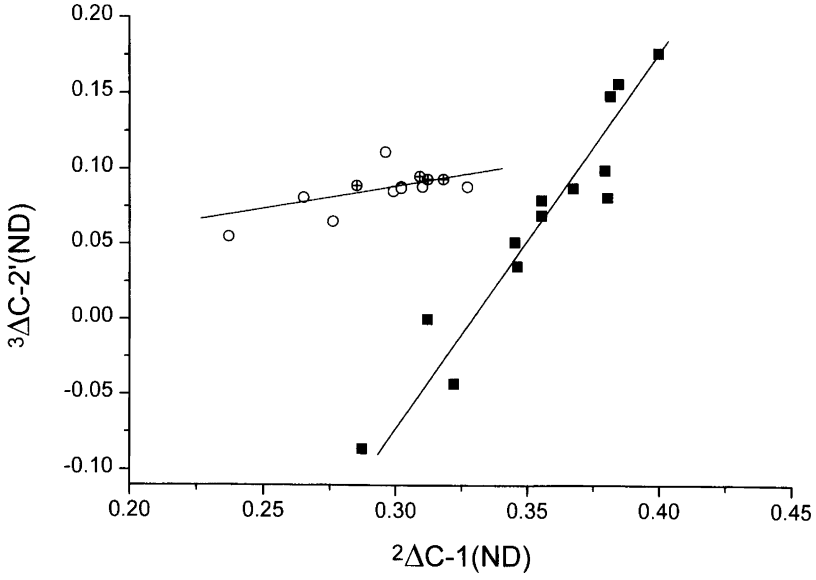


Fig. 4. Plot of $^2\Delta$C-1(ND) vs. $^3\Delta$C-2′(ND): ○, H or Ph at C-1, solvent DMSO-d_6; ⊕, H or Ph at C-1, solvent, $CDCl_3$; ■, CH_3 at C-1, solvent, $CDCl_3$. Data for compunds **22–24** and **29**, compounds with halogens in *ortho*-positions are not included.

$^2\Delta$C-1(ND) vs. $^3\Delta$C-2′(ND). The twist is much larger in **26** and **27** in which the two-bond isotope effects, $^2\Delta$C-1(ND), decrease, meaning that in this case the twist effect predominates. As seen from Fig. 4 a correlation is found between $^3\Delta$C-2′(ND) and $^2\Delta$C-1(ND) for compounds with a methyl group at C-1. For those compounds with no methyl substituent at C-1, the slope is much less steep. **14** is also seen to fall on this line. The negative or small effects at C-2′, and C-6′ are clearly related to the steric interference with the methyl group at C-1. Deuteriation at the NH position leads to a shorter NH bond on average, but also to a lengthening af the O···N distance.[25] The latter effect is apparently the dominant one. The negative effect can therefore be understood in terms of the chemical shift differences observed between C-2′ of, e.g., **1** and **10** or **15**. On deuteriation more of the twisted form is produced, which means that the chemical shift moves to low field. A similar trend for $^5\Delta$C-4′(ND) can be similarly explained and lends support to the suggestion.

Experimental

Compounds. Compounds **1–7**, **9**, **12** and **13** were prepared by the procedure of Claisen,[26] Rateb[27] and de Kimpe[28] in which an aqueous or ethanolic solution of equimolar amounts of the sodium salts of benzoylacetaldehyde and the hydrochloride of the appropriate amine are stirred at room temperature for 30 min to 1 h. Compounds **8**, **10**, **11**, **15** and **16** were synthesized according to Brown and Nonhebel.[29] An alcoholic solution of equimolar amounts of the corresponding β-dicarbonyl compound and the appropriate amine was gently boiled in a water bath for 2 h. **14** was obtained according to Roberts and Turner[30] and Grimshaw[31] by refluxing a mixture of equimolar amounts of dibenzoylmethane and freshly distilled aniline in the absence of a solvent until violent bumping occurred. Compounds **17–28** were synthesized according to Martin *et al.*[22] using acetylacetone and the appropriate amine and 2,6-dimethyl-3,5-heptanedione and *o*-fluoroaniline for **33**. The compounds were distilled and recrystallized before use. The yields were about 50% after distillation and recrystallisation. The melting points (in °C) and colours were: **1**, 139 (pale yellow); **2**, 207 (yellow); **3**, 265–266 (pale yellow); **4**, 171 (scarlet); **5**, 144 (yellow); **6**, 103 (yellow); **7**, 157 (yellow); **8**, 173 (yellow); **9**, 184–185 (yellow); **10**, 109–110 (pale yellow); **11**, 91–92 (yellow); **12**, 77–81 (cream); **13**, 136 (cream); **14**, 95.5 (yellow); **15**, 46 (white, colourless); **16**, 64–65 (light brown); **17**, 140.5–141.1 (yellow); **18** (red oil); **19**, 78.5–79.8 (cream); **20**, 77.9–79.1 (yellow); **21** (yellow oil); **22**, 59.5–60.5 (cream); **23** (red oil); **24**, 49.4–49.7; **25** (red oil); **26** (red oil); **27**, 45.2–45.6. In those cases in which an oil was obtained too little compound was available for boiling point determination except for **29**, b.p. 268 °C. **30–32** were bought from Maybridge Chemical Company, Tintagel, UK and were used without further purification. 2,6-Dimethyl-3,5-heptanedione was synthesized according to Adams and Hauser.[32,33] Acetylacetone was purchased from Aldrich, Weinheim, Germany and the fluoroanilines from Fluorochem, Glossop, UK.

NMR. The ^{13}C NMR spectra of deuteriated species were recorded at 300 K in $CDCl_3$ or at 310 K in DMSO-d_6 on a Bruker AC 250 NMR spectrometer at 62.896 MHz with a digital resolution of 0.55 Hz per point. Chemical shifts are measured relative to internal $SiMe_4$. Spectra of both deuteriated and non-deuteriated species, and of

mixtures of the two species were recorded for all compounds.

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