# LOW TEMPERATURE ENOL–ENOL ASSOCIATION OF STABLE 2,2-DIARYLETHENOLS*

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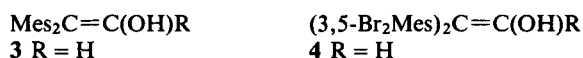*Department of Organic Chemistry, The Hebrew University of Jerusalem, Jerusalem 91904, Israel*

The low temperature ^{1}H NMR spectra of 2,2-bis(3,5-dibromomesityl)ethenol in CS_2–CD_2Cl_2 (3:7) display new signals which indicate the presence of four enol species whose OH is hydrogen bonded. Oligomerization to intermolecularly hydrogen-bonded enol dimers or tetramers is suggested.

Hydrogen-bond associations observed for stable 2,2-diarylethenols (for a review on hydrogen bonding of enols, see Ref. 2) include intramolecular $\pi(cis$-Ar)$\cdots$HO in a *syn* periplanar conformation (**1**) in non-hydrogen bond-accepting solvents,[3] intermolecular with hydrogen bond-accepting solvents (S) in the *anti*-clinal conformation (**2**)[3] or in a solid solvate[4a,b] and intermolecular enol–enol association in the solid when R = H.[4b,c,5] We report here observations which reflect the hitherto unobserved enol–enol association in solution.
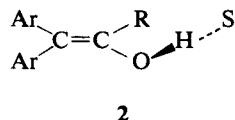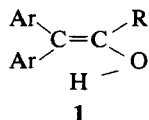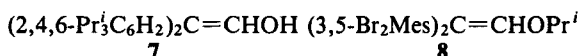

The room-temperature ^{1}H NMR spectra of 2,2-dimesityl-1-R- and 2,2-bis(3,5-dibromomesityl)-1-R-ethenols display two *p*-Me and one to four *o*-Me signals which are sometimes broad.[6] When R = H the =CHOH moiety appears as coupled =CH (δ *ca* 6 ppm) and OH doublets. δ(OH) shifts from *ca* 4·5 in **1** to 9·2 in **2**;[3a] $^3J_{HCOH}$ changes from 14·2 Hz in **1** to 4·6 Hz in **2**.[3a] At lower temperature, the diastereotopic *o*-Me signals decoalesce and a frozen propeller conformation is observed above 200 K. ^{2}H NMR gave rotational barriers for the correlated rotations of the aryl rings around the Ar—C=C bonds.[1,6] For example, for **4** the barriers are 12·1 and 13·0 kcal mol^{-1}

(1 kcal = 4·184 kJ) for the one- and two-ring flip, respectively.[1]

$$Mes_2C{=}C(OH)R \qquad (3,5\text{-}Br_2Mes)_2C{=}C(OH)R$$
3 R = H \qquad\qquad **4** R = H

5a R = Me; **b** R = Bu^t \qquad **6a** R = Me; **b** R = Bu^t

Mes = mesityl

$$(2,4,6\text{-}Pr^i_3C_6H_2)_2C{=}CHOH \quad (3,5\text{-}Br_2Mes)_2C{=}CHOPr^i$$
**7** \qquad\qquad\qquad **8**

We now found additional changes in the ^{1}H NMR on further cooling of solutions of enols **3** and **4** in a 3:7 CS_2–CD_2Cl_2 mixture. These are described here for the OH and CH regions of **4** (0·04 M at 400 MHz, Figure 1). Splitting of the OH, CH and *m*-H signals of **3** also takes place, but the decoalescence of signals is clearer for **4**. Changes in the Me region of **4** due to aryl group rotations are described elsewhere.[1]

At 295 K the OH and CH doublets of **4** ($J = 12·5$ Hz) at 4·775 and 6·373 ppm, respectively, were assigned by deuteration of both the α-H and the OH. On cooling, the signals shift and broaden: at 240 K they are doublets ($J \approx 12$ Hz), at 5·215 and 6·295 ppm, at 230 K they are broad at 5·34 and 6·17 ppm and at *ca* 220 K a very broad signal at *ca* 5·93 ppm which persists and nearly merges with the background at 208 K is observed. At 167 K two groups of four doublets appear, =CH at 3·83, 4·23, 4·32 and 4·35 ppm and OH at 7·90, 8·19, 8·28 and 8·31 ppm. From the expanded spectrum at 170 K (Figure 2), all the doublets display $^3J_{HCOH}$ values of 4–5 Hz. The spectra of **4**-OD and of **4**-α-D corroborate the assignments of the doublet components. The spectrum of **4**-OD at 210–170 K displays a broad signal at *ca* 6·05 ppm
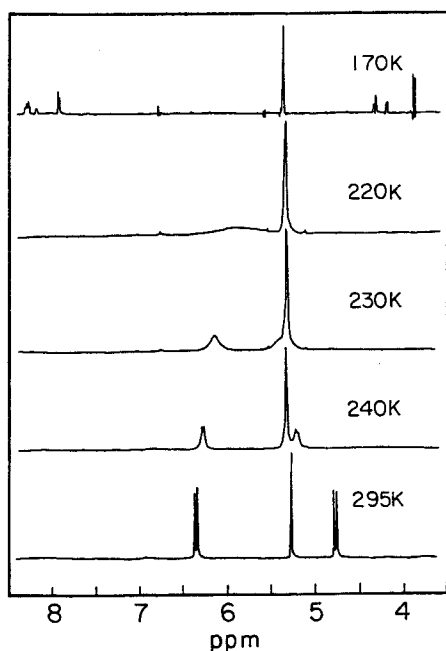
Figure 1. 400 MHz spectra of **4** from 295 to 170 K
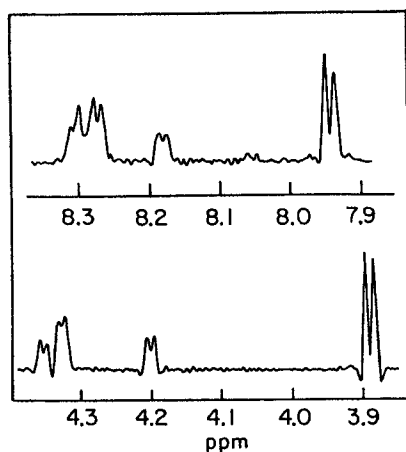
Figure 2. Expanded spectra of the OH (upper) and CH (lower) regions of **4** at 170 K

Figure 3. The CH signals of 4-OD at 180 K

which decreases in intensity on lowering the temperature. The intensities of the four signals at 3·83–4·35 ppm increase in parallel (Figure 3). The number of Me groups is >20 at 170 K. At 155 K all these signals broaden, suggesting that another dynamic process may take place, and two new signals appear at 5·06 and 5·22 ppm. However, since these changes
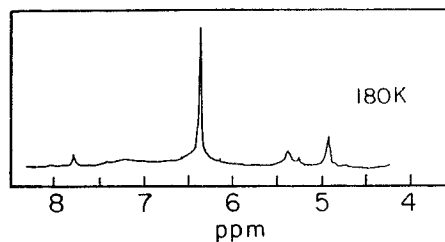
occur near the freezing point of the solvent, the broadening may be due to increased viscosity. A 0·0033 M solution of **4** at 170 K displayed a similar spectrum to that of a 0·04 M solution with an additional doublet at 6·40 ppm ($\delta = 13$ Hz) and a broad signal at 5·0 ppm, which can be ascribed to monomeric **4**. All these changes are reversible.

Coalescence processes which were observed for the 6·05 ppm signal with the 3·83–4·35 ppm signals in the spectrum of 4-OD, for the signals at 4·32 and 4·35 ppm with that at 3·83 ppm and for the signals at 4·32 and 4·35 ppm gave the same $\Delta G_c^{\neq}$ value of *ca* $9 \pm 0·5$ kcal mol^{-1}. Similar barriers were measured for the coalescence of the CH signals of 4-α-D.

Similar signals broadening, disappearance and appearance occur in CS_2–$CDCl_2F$ (3 : 7)[7] except that δ(CH) and δ(OH) are still broad at 155 K. In CD_2Cl_2–$(CD_3)_2CO$ (1 : 1) the OH and CH are still doublets at 9·69 and 6·76 ppm at 176 K, but small new signals start to appear. Enols **5–7** and the ether **8** in CS_2–CD_2Cl_2 (3 : 7) did not show similar spectral changes to those of **3** and **4**.

The following facts are relevant to interpretation. The observed four pairs of OH, CH doublets and the large number of Me signals at 170 K suggest the presence of four 'different' enol species. The low-field δ(OH) at low temperature indicates that a new type of hydrogen bonding replaces the intramolecular π(Ar)—HO present at 295 K. The $^3J_{HCOH}$ values indicate a C=C—O—H dihedral angle of 40–50° in an *anti*-clinal conformation.[3,8] The $\Delta G^{\neq}$ (coalescence) of the =CH signals among themselves and with that at δ 6·05 is *ca* 9 kcal mol^{-1}. The lack of similar spectral changes for **5–8** suggests that a relatively sterically unhindered OH group is essential for observing these phenomena. The shifts of δ(CH) to high field and of δ(OH) to low field on lowering the temperature suggest their fast exchange with the OH and CH signals of the species observed at 170 K, whose population increases at lower temperatures. The reappearance at 170 K at low concentrations of **4** of signals corresponding to δ(OH) and δ(CH) of **4** at room temperature, and their disappearance at high concentrations of **4**, indicate a monomer–oligomer equilibrium. The absence of similar changes in CD_2Cl_2–$(CD_3)_2CO$ (1 : 1) indicates

that the new phenomenon cannot compete effectively with the hydrogen bonding present in **2**, Ar = Mes, S = Me₂CO.

All these facts are consistent with a low-temperature intermolecular 'oligomerization' of **4** via weak enol–enol hydrogen bonding. The two different helicities of monomeric **4** (R and S) coupled with the OH position above or below the C=C plane (U and D) in an *anti* conformation lead to six diastereomeric cyclic dimers (RU–RU; RU–RD; RD–RD; RD–SU; RU–SU; RU–SD) which *a priori* differ in their NMR spectra. These can display less than four OH or CH signals provided that an 'up'-OH ⇌ 'down'-OH interconversion is slow on the measurement time scale. However, accidental isochrony or a low population of certain diastereomers may reduce the number of signals to four. Formation of four diastereomeric tetramers where 'up'-OH ⇌ 'down'-OH interconversion is fast, (RRRR, RRRS, RRSS, RSRS) also accounts for the observations. Although cyclic dimers of alcohols are known, steric effects and linearity of hydrogen bonds favour the tetramers.[9] Indeed, solid **3**,[4b] **7**[4c] and MesC(Ph)=CHOH[5a] are tetrameric. Unfortunately, only the structure of solid **4** · Et₂O where the OH is associated with the ether oxygen was determined.[1] As expected (see above), the monomer signals appear in dilute solution under conditions where only the oligomer is observed in more concentrated solution. Unfortunately, the relatively low solubility at low temperature prevented a quantitative concentration-dependent study which may distinguish a dimer from a tetramer. The coalescence processes probably reflect a monomer–oligomer equilibrium, but since its interpretation requires knowledge of the structure of the oligomer, at present we prefer not to analyse it.

The significant upfield shift of δ(CH) and the low $^3J_{HCOH}$ fit a conformation in with the OH groups are relatively remote from the bulky groups and the =C—H group of one enol is in the shielding region of an aromatic ring of another enol in the oligomer [the OH signals at low temperature are at sufficiently low δ values to exclude an alternative process of intramolecular *syn*-enol (**1**) ⇌ *anti*(unsolvated)-enol interconversion for the observed process] .

Intermolecular enol–enol association only when R = H is consistent with the higher K_{ass} values for the formation of **2** when R = H.[10] Association even with a single solvent molecule is strongly hindered by α-alkyl groups, and these stringent steric demands should be magnified in the association of two bulky enols. The additional signals observed at low temperature hint at even more complicated processes which may involve several oligomers. Further studies are in progress.

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