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Solvent and α- and β-Substituent Effects on the Association with Hydrogen Bond Accepting Solvents and the OH Conformation of Stable Simple Enols[1,2]

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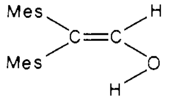
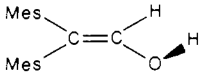
Abstract: The association of stable simple enols with hydrogen bond accepting solvents was investigated by ^{1}H NMR. δ(OH) values for β,β-dimesityl-α-arylethenols **2** (Ar = Mes, *p*-An, *p*-Tol, Ph, *p*-$CF_3C_6H_4$, 3,5-$Br_2C_6H_3$), α,β-dimesityl-β-R-ethenols **3** (R = Ph, Me, Et, *i*-Pr), and β,β-dimesityl-α-(trimethylsilyl)ethenol (**4c**) in CCl_4–DMSO-d_6 mixtures were measured. The OH signal is sharp and enol–enol association is absent. The large changes in δ(OH) are ascribed to the formation of a 1:1 enol·DMSO hydrogen-bonded association complex, and association constants K_{assn} were calculated from the δ(OH) values. For compounds **2**, K_{assn} = 1.6–5.2 and it increases with the polar electron withdrawal of the α-Ar, and ρ = 0.35. In DMSO-d_6, ≥98% of the enol is associated. The calculated δ(OH) values for the associated form are linear with Hammett's σ values. Steric effects of the α-mesityl group on K_{assn} or δ(OH) are minor. The δ(OH) for compounds **3** are linear with the δ(OH) of the β,β-dimesityl-α-R analogues **4**, but K_{assn} values of **3** (1.7–2.8) are 1.3–2.3-fold higher. K_{assn} values for **4c** (0.52) and for **4**, R = *t*-Bu, are close. The changes in δ(OH) and ^3J(HCOH) for β,β-dimesitylethenol (**1**) were determined in binary CCl_4–solvent mixtures in eight solvents and found to be parallel in most cases. $K_{assn}(\delta)$ and $K_{assn}(J)$ values were determined. For each solvent they are reasonably similar in most cases and are solvent dependent. $K_{assn}(J)$ values range from 0.05 (C_6D_6) to 9.7 (DMSO-d_6). The log K_{assn} values are approximately linear with the hydrogen bond accepting ability parameter β of the solvent. The dihedral C=C—O—H angle increases with β, e.g., the conformation is anti-periplanar in C_6D_6 or dioxane-d_8 but anti-clinal in DMSO-d_6 and DMF-d_7. In CCl_4 the conformation is syn-planar with an intramolecular π(Ar)···HO hydrogen bonding. δ(OH) and ^3J(HCOH) values were also measured in several solvent–DMSO-d_6 mixtures. The K_{assn} values with acetone for β,β-dimesityl-α-methyl (0.25) (and α-*tert*-butyl, 0.09) ethenols in CCl_4–acetone mixtures are lower than those for association with DMSO.

Recently we investigated the association of β,β-dimesitylethenol (**1**) with various solvents and the solvent-dependent conformation of its OH group by a combination of ^{1}H NMR and IR techniques.[3] From the correlation between the H—C—O—H dihedral angle and the ^3J(HCOH) coupling constants,[4] the C=C—OH conformation around the C–O bond is syn-planar (**1a**) in non-hydrogen bond accepting solvents, (e.g., CCl_4) and anti-clinal (**1b**) in strong hydrogen bond accepting solvents, (e.g., DMSO). In moderate hydrogen bond accepting solvents (e.g., acetone), the two conformers are present in appreciable population and are in a rapid equilibrium. The solvent-dependent conformation is due mainly to hydrogen bonding: intermolecular with the solvent S (C-O—H···S) in hydrogen bond accepting solvents and intramolecular [π(Ar)···HO] between the OH and the *cis*-mesityl group.


1a


1b

Mes = mesityl = 2,4,6-$Me_3C_6H_2$

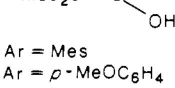
The association constant K_{assn} for the 1:1 solvate (of **1b**) with DMSO was obtained from the changes of δ(OH) and ^3J(HCOH) for **1** with the composition of the CCl_4–DMSO-d_6 mixtures. The reported K_{assn} values based on ^3J(HCOH) and δ(OH) were 9.35 and 7.9, respectively.[3] The analogous δ(OH) and K_{assn} values for α-alkyl-β,β-dimesitylethenols were recently determined.[1] The decrease of the K_{assn} values with the increased bulk of the α-alkyl group was ascribed to a combination of predominant electronic effects and steric effects.[1]

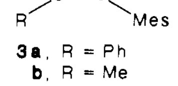
These studies raised several questions: These include (a) the contribution of polar effects to K_{assn} in the absence of steric effects, (b) the dependence of K_{assn} on the structure of isomeric dimesitylethenols, (c) the correlation of K_{assn} values with solvent parameters, (d) the dependence of the OH conformation on the solvent, and (e) the comparison of the effect of an α-Si substituent and related α-alkyl substituents on K_{assn}.

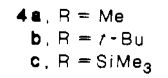
Some of the answers are given in the present paper which describes the effect of α-aryl and α-trimethylsilyl and of β-phenyl and β-alkyl substituents in the enols on K_{assn} in DMSO and the solvent effect on the K_{assn} values of **1** and derivatives.

Results

The change in the hydroxyl chemical shift δ(OH) for β,β-dimesityl-α-aryl (**2a–f**) and α-trimethylsilyl and of (*Z*)-α,β-dimesityl-β-alkyl and β-phenyl (**3a–d**) ethenols in binary CCl_4–DMSO-d_6 mixtures and for α-methyl- and α-*tert*-butyl-β,β-dimesitylethenols (**4a** and **4b**) in CCl_4–acetone mixtures was studied. Both δ(OH) and the ^3J(HCOH) coupling constants for β,β-di-


2a, Ar = Mes
b, Ar = *p*-$MeOC_6H_4$ (*p*-An)
c, Ar = *p*-MeC_6H_4 (*p*-Tol)
d, Ar = Ph
e, Ar = *p*-$CF_3C_6H_4$
f, Ar = 3,5-$Br_2C_6H_3$


3a, R = Ph
b, R = Me
c, R = Et
d, R = *i*-Pr


4a, R = Me
b, R = *t*-Bu
c, R = $SiMe_3$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[1] Part 21: Stable Simple Enols. Part 20: Rappoport, Z.; Nugiel, D. A.; Biali, S. E. *J. Org. Chem.* **1988**, *53*, 4814.

[2] Presented in part in (a) Rappoport, Z. Kyushu "Zen" Symposium on Physical Organic Chemistry, Kyushu University, Fukuoka, Japan, September 1986; Abstract pp 53–62. (b) Nadler, E. B.; Rappoport, Z., The 53rd Meeting of the Israel Chemical Society, Beer-Sheva, Israel, February 9–10, 1988.

[3] Biali, S. E.; Rappoport, Z. *J. Am. Chem. Soc.* **1984**, *106*, 5641.

[4] (a) Fraser, R. R.; Kaufman, M.; Morand, P.; Govil, G. *Can. J. Chem.* **1969**, *47*, 403. (b) Watanabe, S. *J. Mol. Struct.* **1980**, *64*, 285.

0002-7863/89/1511-0213$01.50/0

mesitylethenol (**1**) were determined in several binary solvent mixtures and for (*Z*)-β-tolyl-β-mesitylethenol (**5**) in CCl_4 and in DMSO-d_6. First we will describe the method of calculation of the association constant from the NMR parameters; then the results for each series will be presented separately.

Absence of Intermolecular Hydrogen Exchange. The absence of an intermolecular enol–enol association is deduced from the absence of exchange of the OH groups of different enol molecules on the NMR time scale, as demonstrated by the following observations: (a) sharp OH signals; (b) a 10-fold increase in the concentration of **1** in CCl_4 resulted in a negligible change in δ(OH) and ^3J(HCOH) (cf. Table IX); (c) a mixture of **1** and **2d** (5 mg each) in CCl_4 (0.5 mL) at 292 K displays an OH doublet at δ 4.45, ^3J(HCOH) = 14.5 Hz, and an OH singlet at δ 5.01 which are at the positions of the individual OH signals of **1** and **2d**, respectively. When 0.1 mL of DMSO-d_6 was added to this mixture, the separate signals shifted to δ 8.58 (^3J = 6.3 Hz) and δ 7.88, which are the approximate δ(OH) values of **1** and **2d** in 80:20 CCl_4–DMSO-d_6 (v/v) mixtures.

Calculation of the Association Constant $K_{\rm assn}$. When a nonsolvated (I) and a 1:1 solvated (II) enolic (ROH) species exist in equilibrium in a solvent S (eq 1), the equilibrium constant $K_{\rm assn}$

$$\mathrm{I} + \mathrm{S} \overset{K_{\rm assn}}{\rightleftharpoons} \mathrm{II} \qquad (1)$$

is defined by eq 2, where $[\mathrm{S}]_{\rm f}$ is the nonassociated solvent and

$$K_{\rm assn} = [\mathrm{II}]/[\mathrm{I}][\mathrm{S}]_{\rm f} = F_{\rm II}/F_{\rm I}[\mathrm{S}]_{\rm f} \qquad (2)$$

F's are the corresponding mole fractions. Equations 3 and 4 represent the mass balance where the subscript 0 designates the initial concentration of the species before complexation.

$$[\mathrm{ROH}]_0 = [\mathrm{I}] + [\mathrm{II}] \qquad (3)$$

$$[\mathrm{S}]_0 = [\mathrm{S}]_{\rm f} + [\mathrm{II}] \qquad (4)$$

The following analysis applies for a case when I and II are in a rapid equilibrium on the NMR time scale and the solvent effect on the NMR parameters δ(OH) or ^3J(HCOH), which is not related to solvation, is small. Although the equations are written for the parameter δ, the same analysis applies for ^3J(HCOH).

Each observed value ($\delta_{\rm obs}$) corresponding to a different CCl_4–solvent mixture is a weighted average of the δ values of I and II ($\delta_{\rm I}$, $\delta_{\rm II}$) (eq 5). Inserting eq 3 into 5 gives eq 6 and 7.

$$\delta_{\rm obs} = \delta_{\rm I}(1 - F_{\rm II}) + \delta_{\rm II}F_{\rm II} \qquad (5)$$

$$\delta_{\rm obs} = \delta_{\rm I}([\mathrm{ROH}]_0 - [\mathrm{II}])/[\mathrm{ROH}]_0 + \delta_{\rm II}[\mathrm{II}]/[\mathrm{ROH}]_0 \qquad (6)$$

$$[\mathrm{II}] = [\mathrm{ROH}]_0(\delta_{\rm obs} - \delta_{\rm I})/(\delta_{\rm II} - \delta_{\rm I}) \qquad (7)$$

A priori, neither $\delta_{\rm I}$ nor $\delta_{\rm II}$ are known. IR studies indicate that in CCl_4 the enols are $\geq$98% intramolecularly associated[3,5] and hence the error introduced by assuming that $\delta_{\rm I} = \delta_{CCl_4}$ is small. This is consistent with the absence of intermolecular association with CCl_4, a solvent with a hydrogen bond accepting parameter of 0 in the Kamlet–Taft solvatochromic equation,[6] and with the extensive use of CCl_4 as a solvent for association studies of alcohols and phenols.[7a] Both $K_{\rm assn}$ and $\delta_{\rm II}$ are unknown and cannot be assumed. By combination of eq 2, 4, and 7, eq 8 is obtained. A

$$[\mathrm{S}]_0/(\delta_{\rm obs} - \delta_{\rm I}) = ([\mathrm{ROH}]_0 + [\mathrm{S}]_0 - [\mathrm{II}])/(\delta_{\rm II} - \delta_{\rm I}) + 1/K_{\rm assn}(\delta_{\rm II} - \delta_{\rm I}) \qquad (8)$$

plot of the experimentally known $[\mathrm{S}]_0/(\delta_{\rm obs} - \delta_{\rm I})$ values vs the $[\mathrm{ROH}]_0 + [\mathrm{S}]_0 - [\mathrm{II}]$ term should give both $K_{\rm assn}$ and $\delta_{\rm II}$. The unknown [II] term is estimated by an iteration procedure: $[\mathrm{S}]_0/(\delta_{\rm obs} - \delta_{\rm I})$ is plotted first against ($[\mathrm{ROH}]_0 + [\mathrm{S}]_0$) values, and the obtained slope is used to calculate [II] from eq 7. This value is then inserted into eq 8, and the derived linear plot gives a slope of $1/(\delta_{\rm II} - \delta_{\rm I})$ and an intercept of $1/K_{\rm assn}(\delta_{\rm II} - \delta_{\rm I})$. Since for all our experimental points $[\mathrm{II}] \ll [\mathrm{S}]_0 + [\mathrm{ROH}]_0$, a convergent value is obtained after one or two iterations.

This treatment,[7b,8a] which gave excellent plots with correlation coefficients of usually >0.99, still has several drawbacks. First, the simultaneous calculation of $K_{\rm assn}$ and $\delta_{\rm II}$ from the slope and intercept of the same plot leads to mutually dependent errors in both terms. The errors due to this and to the small intercept will not be discussed here since they were treated extensively both for hydrogen bond association[8b–i] and in relation to the Benesi–Hildebrand equation.[9] Second, when small changes in the solvent compositions result in large changes in $\delta_{\rm obs}$ all the first experimental points are grouped together near the intercept in these plots. This treatment accords equal weight to every point. Since there are more points for lower concentrations of base, these points are ultimately more influential in determining $K_{\rm assn}$. Third, it does not include iterative search for the best $\delta_{\rm I}$ value. Consequently, following a related treatment by Taft and co-workers,[10] we used eq 2 and 6 to derive eq 9 which gives $\delta_{\rm obs}$ as a function of $\delta_{\rm I}$, $\delta_{\rm II}$,

$$\delta_{\rm obs} = [(\delta_{\rm II} - \delta_{\rm I})/2[\mathrm{ROH}]_0] \times [[\mathrm{ROH}]_0 + [\mathrm{S}]_0 + 1/K_{\rm assn} - ([\mathrm{S}]_0^2 - 2[\mathrm{S}]_0[\mathrm{ROH}]_0 + 2[\mathrm{S}]_0/K_{\rm assn} + 2[\mathrm{ROH}]_0/K_{\rm assn} + 1/K_{\rm assn}^2)^{1/2}] + \delta_{\rm I} \qquad (9)$$

and $K_{\rm assn}$. By using $\delta_{\rm I} = \delta_{CCl_4}$ and $K_{\rm assn}$ and $\delta_{\rm II}$ values derived from eq 8, a calculated value for $\delta_{\rm obs}$ is obtained. A least-squares procedure, which minimizes $\sum(\Delta\delta_{{\rm obs}_i})$,^{2} is then applied where $\Delta\delta_{{\rm obs}_i}$ is the difference between the measured and the calculated $\delta_{\rm obs}$ (with the parameters derived from eq 8) where *i* runs over the data points for the $[\mathrm{S}]_{0,i}$ values. The RNLIN subroutine from the IMSL package, which fits a nonlinear model using least squares, was employed. RNLIN is based on HINPACK routines LMDIF and LMDER[11b] and uses a modified Levenberg–Marquardt[11a] method to generate a sequence of approximations to a minimum point. The following statistical quantities are derived directly: DFE, degree of freedom for errors; SSE, sums of squares for errors; Rank of matrix **R**, where **R** is the upper triangular matrix containing the QR decomposition of the Jacobian; R_δ, the multiple correlation coefficient; and SD, the standard deviation of δ.[11c] Examples are given in the Experimental Section. The $K_{\rm assn}$ and δ values derived from eq 8 and 9 are given in the tables.

$K_{\rm assn}{}^{\rm app}$ values obtained on assuming a complete association in any pure solvent (i.e., $\delta_{\rm II} = \delta_{\rm s}$) are sometimes given for comparison.

***α*-Aryl-Substituted Systems.** The δ(OH) values of the triarylethenols **2**[12] in CCl_4 are 4.96–5.10 ppm. Addition of a small amount of DMSO-d_6 to a solution of **2** in CCl_4 results in a relatively large downfield shift of the sharp OH signal. E.g., addition of 0.2% (v/v) DMSO-d_6 brings about downfield shift of ca. 0.2 ppm in systems with electron-donating α-aryl groups (**2a–c**), and 0.4–0.6 ppm in **2e** and **2f** with the α-electron-withdrawing aryls. In 99% CCl_4–1% DMSO-d_6 (v/v), δ(OH) values are already 5.72–5.86 for **2a–2d** and 6.36–6.74 for **2e** and **2f**. Since δ(OH)

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[5] Buswell, A. M.; Rodebush, W. H.; Whitney, R. McL. *J. Am. Chem. Soc.* **1947**, *69*, 770.

[6] (a) Kamlet, M. J.; Abboud, J.-L. M.; Taft, R. W. *Prog. Phys. Org. Chem.* **1981**, *13*, 485. (b) For a list of recent β values, see: Kamlet, M. J.; Doherty, R. M.; Abraham, M. M.; Carr, P. W.; Doherty, R. F.; Taft, R. W. *J. Phys. Chem.* **1987**, *91*, 1996. Kamlet, M. J.; Taft, R. W. *Acta Chem. Scand.* **1986**, *B40*, 619.

[7] (a) Joesten, M. D.; Schaad, L. J. *Hydrogen Bonding*; Marcel Dekker: New York, 1974; pp 293–363; (b) pp 173–175.

[8] (a) Nakano, M.; Nakano, N. I.; Higuchi, J. *J. Phys. Chem.* **1967**, *71*, 3954. (b) Berkeley, P. J., Jr.; Hanna, M. W. *J. Phys. Chem.* **1963**, *67*, 846. (c) Hanna, M. W.; Ashbaugh, A. L. *J. Phys. Chem.* **1964**, *68*, 811. (d) Mathur, R.; Becker, E. D.; Bradley, R. B.; Li, N. C. *J. Phys. Chem.* **1963**, *67*, 2190. (e) Foster, R.; Fyfe, C. A. *Trans. Faraday Soc.* **1965**, *61*, 1626. (f) Goldstein, M.; Mullins, C. B.; Willis, H. A. *J. Chem. Soc. B* **1970**, 321. (g) Siung, J. H.; Goldberg, E.; Miller, S. I. *Org. Magn. Reson.* **1972**, *4*, 683. (h) Slejko, F. L.; Drago, R. S. *Inorg. Chem.* **1973**, *12*, 176. (i) Rosseinsky, D. R.; Kellawi, H. *J. Chem. Soc. A* **1969**, 1207.

[9] (a) Benesi, H. A.; Hildebrand, J. H. *J. Am. Chem. Soc.* **1949**, *71*, 2703. (b) Mulliken, R. S.; Person, W. B. *Molecular Complexes*; Wiley: New York, 1969; Chapter 7, pp 81–90. (c) Person, W. B. *J. Am. Chem. Soc.* **1965**, *87*, 167. (d) Hammond, P. R. *J. Chem. Soc.* **1964**, 479.

[10] (a) Taft, R. W.; Klingensmith, G. B.; Ehrenson, S. *J. Am. Chem. Soc.* **1965**, *87*, 3620. (b) Gurka, D.; Taft, R. W. *Ibid.* **1969**, *91*, 4794.

[11] (a) Dennis, J. E., Jr.; Schnabel, R. B. *Numerical Methods for Unconstrained Optimization and Nonlinear Equations*; Prentice-Hall: Englewood Cliffs, NJ, 1983. Levenberg, K. *Q. Appl. Math.* **1944**, *2*, 164. Marquardt, D. W. *SIAM J. Appl. Math.* **1963**, *11*, 431. (b) More, J. J.; Garbow, B. S.; Hillstrom, K. E. *User Guide for MINPACK-1*; Argonne National Labs Report ANL-80-74, Argonne, IL, 1980. (c) Daniel, C.; Wood, F. S. *Fitting Equations to Data*; Wiley: New York, 1971.

[12] Nadler, E. B.; Rappoport, Z. *J. Am. Chem. Soc.* **1987**, *109*, 2112.

Table I. δ(OH) Values for α-Aryl-β,β-dimesitylethenols **2** in Binary CCl_4–DMSO-d_6 Mixtures

% DMSO-d_6 in CCl_4–DMSO-d_6 (v/v)	[DMSO-d_6], M	**2a**[a]	**2b**[b]	**2c**[a]	**2d**[c]	**2e**[d]	**2f**[e]	% DMSO-d_6 in CCl_4–DMSO-d_6 (v/v)	[DMSO-d_6], M	**2a**[a]	**2b**[b]	**2c**[a]	**2d**[c]	**2e**[d]	**2f**[e]
0	0	5.10	4.96	4.97	5.00	5.08	5.03	7	0.99						7.92
0.2	0.028	5.31	5.15	5.16	5.23	5.52	5.67	10	1.41	7.44	7.31	7.41	7.54	7.91	8.13
0.4	0.057	5.44	5.29	5.31	5.42	5.77	6.06	20	2.83	7.76	7.72	7.76	7.91	8.22	8.38
0.6	0.085	5.55	5.44	5.51	5.57	5.96	6.22	40	5.66	8.02	8.02	8.05	8.14	8.43	8.58
0.8	0.11	5.73	5.54	5.57	5.69	6.16		50	7.07		8.08	8.17			
1	0.14	5.84	5.72	5.76	5.86	6.36	6.75	60	8.48	8.10	8.19	8.22	8.25	8.60	8.71
2	0.28	6.16	6.07	6.23	6.22	6.74	7.27	80	11.31	8.27	8.29	8.33	8.43	8.65	8.79
4	0.57						7.76	100	14.14	8.36	8.38	8.43	8.53	8.78	8.91
5	0.71	7.00	6.84	6.93	7.08	7.49									

[a] [**2**] = 0.027 M; measured at 289 K. [b] [**2**] = 0.026 M; measured at 292 K. [c] [**2**] = 0.028 M; measured at 290 K. [d] [**2**] = 0.024 M; measured at 293 K. [e] [**2**] = 0.019 M; measured at 289 K.

Table II. Parameters of the Linear Correlations $\delta(OH)[Mes_2C{=}C(OH)Ar] = A\delta(OH)[\mathbf{1}] + B$ in Binary CCl_4–DMSO-d_6 Mixtures[a,b]

Ar	A	B	R	σ	A'[c]	B'[c]	R[c]	σ[c]	A''[d]	B''[d]	R[d]	σ[d]
Mes	0.77	1.17	0.9677	0.32	0.36	3.47	0.9933	0.04	1.25	−2.91	0.9991	0.01
p-An	0.81	0.80	0.9664	0.34	0.38	3.20	0.9920	0.05	1.48	−4.92	0.9957	0.03
p-Tol	0.82	0.81	0.9721	0.31	0.43	2.99	0.9858	0.07	1.41	−4.24	0.9987	0.02
Ph	0.83	0.82	0.9718	0.32	0.42	3.11	0.9966	0.03	1.34	−3.50	0.9984	0.02
p-$CF_3C_6H_4$	0.83	1.09	0.9874	0.21	0.56	2.61	0.9991	0.02	1.16	−1.69	0.9962	0.03
m,*m*-$Br_2C_6H_3$	0.83	1.29	0.9976	0.09	0.76	1.69	0.9976	0.06	1.05	−0.57	0.9982	0.02

[a] Data for enols **2** from Table I and for **1** from ref 3. [b] For 12 δ(OH) values, except for *m*,*m*-$Br_2C_6H_3$ where 13 points were used. [c] Parameters of the correlation for the first six points only. [d] Parameters of the correlation for the last six points only.

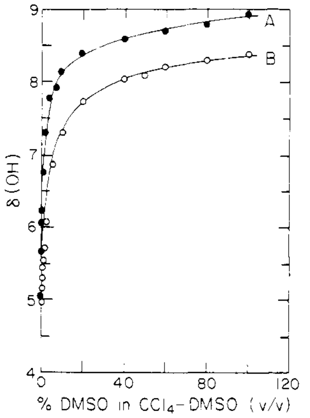

Figure 1. Plot of δ(OH) values of $Mes_2C{=}C(OH)Ar$ vs percent DMSO-d_6 (v/v) in CCl_4–DMSO-d_6. A (●) Ar = 3,5-$Br_2C_6H_3$ (**2c**); B (○) Ar = *p*-$MeOC_6H_4$ (**2f**).

in pure DMSO-d_6 is 8.36–8.91, a large percentage of the shift is already achieved on addition of the first 1% of DMSO-d_6; ≥85% of the change takes place at up to 60% CCl_4–40% DMSO-d_6. This is demonstrated for **2b** and **2f** in Figure 1. The δ(OH) values for **2a–f** in 14–15 binary CCl_4–DMSO-d_6 mixtures [5–6 at 0–1% ([0.14 M] v/v) DMSO-d_6, 5 at 1–10% DMSO-d_6, and the rest at higher [DMSO-d_6]] are given in Table I.

Plots of δ(OH) for **2** vs δ(OH) of **1** in the binary mixtures are linear according to their reasonable correlation coefficients (eq 10 and Table II). However, visual inspection (cf. Figure 2) shows

$$\delta(OH)(\mathbf{2}) = A\delta(OH)(\mathbf{1}) + B \qquad (10)$$

that the plots are actually concave (e.g., Figure 2A for the α-*p*-tolyl derivative **2c**), and near linearity (A = 0.83, R = 0.9976) was observed only for the most electron-withdrawing *m*,*m*-$Br_2C_6H_3$-substituted system **2f** (Figure 2B). A division into two linear plots, one up to δ(OH)[**1**] values of ca. 7.5 and one at the higher δ(OH) values, gives better correlation coefficients for each part of the plot as shown in Table II, where the A', B' and the A'', B'' values relate to the first and the second part of the plot, respectively.

Plots according to eq 8 are linear (Figure 3), and the slope and intercept remain unchanged after one or two iterations. The derived K_{assn} and δ(OH) values for conformer II together with the δ_{CCl_4} and δ_{DMSO} values and the fraction of species II in DMSO are given in Table III. Also given are $K_{assn}{}^{app}$ values calculated

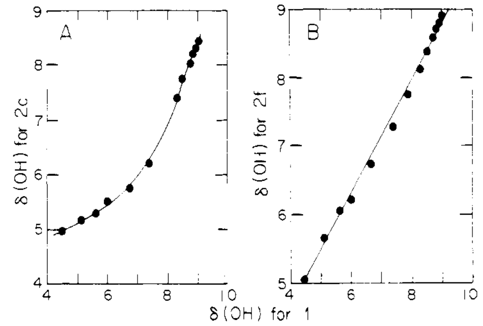

Figure 2. Plots of δ(OH) for $Mes_2C{=}C(OH)Ar$ vs δ(OH) for $Mes_2C{=}CHOH$ in CCl_4–DMSO-d_6 mixtures. A, Ar = *p*-MeC_6H_4 (**2c**); B, Ar = 3,5-$Br_2C_6H_3$ (**2f**).

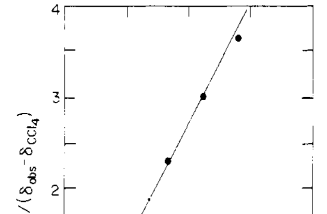

Figure 3. Plot of $[DMSO]_0/(\delta_{obs} - \delta_{CCl_4})$ vs $[ROH]_0 + [DMSO]_0 - [II]$ for $Mes_2C{=}C(OH)C_6H_3Br_2$-3,5 in CCl_4–DMSO-d_6 mixtures.

for the region of 0–10% DMSO-d_6 in CCl_4. K_{assn} values calculated according to eq 9 varied by 0–5% for **2a–2e** compared to K_{assn} values according to eq 8. However, K_{assn} for **2f** was much larger, i.e., 5.16. The $\delta_{II\text{-}DMSO}$ value was 8.73, 0.18 ppm lower than the observed value in the pure solvent, whereas $\delta_{I\text{-}CCl_4}$ was 5.19, 0.16 ppm higher than the observed value. The calculated $\delta_{I\text{-}CCl_4}$ values were also higher by 0.05–0.17 ppm than the observed δ_{CCl_4} values. Since a justification of the $\delta_{II\text{-}DMSO}$ values according to eq 9 is not obvious and the only significant difference in K_{assn} is for **2f**, and

Table III. δ(OH) (in ppm) and K_{assn} Values for $Mes_2C{=}C(OH)Ar$ in CCl_4–DMSO-d_6 Mixtures

Ar	Mes	*p*-An	*p*-Tol	Ph	*p*-$CF_3C_6H_4$	*m,m*-$Br_2C_6H_3$
n^a	14	15	15	14	14	14
δ_{CCl_4}	5.10	4.96	4.97	5.00	5.08	5.03
δ_{DMSO}	8.36	8.38	8.43	8.53	8.78	8.91
$K_{\text{assn}}^{\text{app } b}$	1.84	1.58	1.73	1.84	2.33	2.84
$\delta_{\text{II·DMSO}}$ (eq 8)	8.42	8.45	8.49	8.58	8.79	8.89
K_{assn} (eq 8)	1.82	1.69	1.79	1.94	3.00	3.87
% II·DMSO in DMSO-d_6 (eq 8)	98.2	98.0	98.3	98.6	99.7	100
$\delta_{\text{I·CCl}_4}$ (eq 9)	5.15	5.03	5.03	5.08	5.25	5.19
$\delta_{\text{II·DMSO}}$ (eq 9)	8.36	8.41	8.43	8.51	8.69	8.73
K_{assn} (eq 9)	1.82	1.61	1.84	1.93	2.99	5.16

[a] Number of experimental points. [b] Calculated by using the first nine points in the range of 0–10% DMSO.

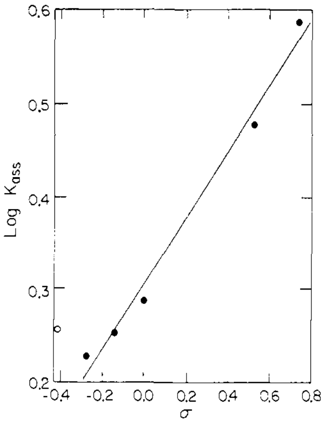

Figure 4. Log K_{assn} with DMSO for **2a–f** (from eq 8) vs σ plot (●). The open circle is for Mes with $\sigma = -0.42$.

since previous reported values were derived from eq 8, we used values from eq 8 for the correlations below.

Correlations Involving log K_{assn} and δ(OH). Log K_{assn} values were plotted against Hammett's σ values. The σ values recommended by Exner[13] were used except for *p*-MeO, where a recommended value is not given, and hence we used the value based on the pK_a of *p*-$MeOC_6H_4COOH$ in water (−0.28).[13] The linear plot (eq 11 and Figure 4) shows a low response to the substituents

$$\log K_{\text{assn}} = 0.35\sigma + 0.31 \qquad (R = 0.9926;\ \text{SD} = 0.017) \quad (11)$$

($\rho = 0.35$).[14a] Addition of the point for mesityl by arbitrarily using $\sigma = -0.42$ ($3\sigma_{p\text{-Me}}$) results in deterioration of the plot ($\rho = 0.31$; $R = 0.9636$; SD = 0.036). A σ_{Mes} value of −0.1 will put the point on the line.

The δ(OH) values for compounds **2** in DMSO ($\delta_{\text{II·DMSO}}$) increase with the increased electron withdrawal by the α-aryl substituent (Table III). A plot of $\delta_{\text{II·DMSO}}$ vs σ values[13] shows excellent linearity (eq 12),[14b] and the point for the mesityl deviates

$$\delta_{\text{II·DMSO}} = 0.43\sigma + 8.57 \qquad (R = 0.9983;\ \text{SD} = 0.01) \quad (12)$$

only slightly (slope = 0.42; $R = 0.9966$; SD = 0.015). Consequently, a plot of log K_{assn} vs $\delta_{\text{II·DMSO}}$ is also linear, and the point for mesityl deviates (eq 13, Figure 5).

$$\log K_{\text{assn}} = 0.82\delta_{\text{II·DMSO}} - 6.68 \qquad (R = 0.9916;\ \text{SD} = 0.018) \quad (13)$$

(*Z*)-β-Alkyl- and β-Phenyl-α,β-dimesitylethenols. All the signals of these enols are sharp singlets. The δ(OH) values for (*Z*)-β-phenyl- (**3a**), β-methyl- (**3b**), β-ethyl- (**3c**), and β-isopropyl- (**3d**) α,β-dimesitylethenols were determined in 13–17 binary CCl_4–DMSO-d_6 mixtures (Table IV), which enabled comparison with δ(OH) values of the α-alkyl-[1] and α-phenyl-β,β-dimesityl[3] isomers. The derived K_{assn}, $\delta_{\text{I·CCl}_4}$, and $\delta_{\text{II·DMSO}}$ values, which were calculated by eq 9, are given in Table V. The K_{assn} values for the β derivatives decrease in the order Me > Et > *i*-Pr as was found for the isomeric α-substituted series, but they are generally higher.

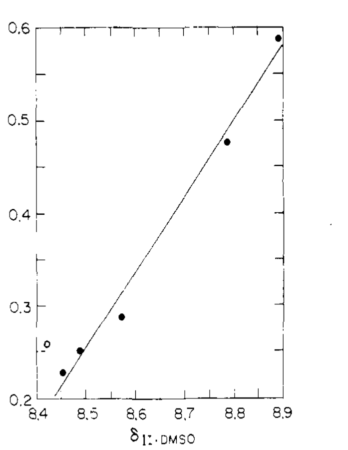

Figure 5. Plot of log K_{assn} for **2a–f** in DMSO vs $\delta_{\text{II·DMSO}}$ from eq 8 (●). The open circle is for Ar = Mes.

Plots of the δ(OH) values for the β-alkyl or phenyl derivatives **3** vs the δ(OH) values for the isomeric α-alkyl or α-phenyl derivative **4a**, **4** (R = Et, *i*-Pr),[1] and **2d** are linear with slopes of unity (Table VI). The values for the β-alkyl-substituted systems are shifted by 0.7 ppm to higher field. These enols are much less stable than the α derivatives and they decompose slowly on standing.[15] Consequently, the measurements were conducted immediately after dissolution, in order to avoid a concentration change that affects δ_{obs}.

Association of 1 in Binary Solvent Mixtures. The previous study of the association of **1** with DMSO-d_6 in binary CCl_4–DMSO-d_6 mixtures enabled comparison of the δ(OH) and the ^3J(HCOH)[3] and gave information on the conformation of the C=C—OH moiety. The present work examines δ(OH) and ^3J(HCOH) values for **1** in seven new CCl_4–solvent mixtures and in mixtures of $(CD_3)_2CO$, CD_3CN, and C_6D_6 with DMSO-d_6 (Tables VII and VIII).

If a 1:1 association complex of **1** with the solvent exists under all conditions, this should be reflected in unaltered values of δ(OH) and ^3J(HCOH) on changing the concentration of **1**. A 10-fold increase in [**1**] from 0.036 M to 0.36 M in 0.4% DMSO-d_6 [0.057 M]–99.6% CCl_4 shifted δ(OH) downfield by 0.55 ppm and decreased ^3J(HCOH) by 1 Hz, as expected from eq 6 (Table IX). With the increase in concentration, the OH signal became broader and the error in ^3J became significant. Finally, a broad singlet was obtained. The broadening appears at lower [**1**] values in 99:1 CCl_4–DMSO-d_6. We attribute this behavior to increased viscosity at the higher concentration.

Therefore, the K_{assn} values obtained from each experiment by using eq 2–5 are not concentration-independent. However, the substantial broadening of the signals, the nonconformational solvent effects on the signals which are demonstrated by the change of δ(CH) in CCl_4 with the concentration, and the small $[\text{DMSO-}d_6]_f$ term at high [**1**] lead to large errors in the calculated K_{assn} values. Nevertheless, at the low concentrations of **1** they are reasonably constant.

Two sets of K_{assn} values were calculated from the data of Table VII. $K_{\text{assn}}(\delta)$ values were calculated by using eq 9 and $K_{\text{assn}}(J)$ values from an equation analogous to eq 9. $J_{\text{II·s}}$ was obtained by an iterative procedure from eq 14. The plots were all linear with

$$[S]_0/(J_I - J_{\text{obs}}) = ([ROH]_0 + [S]_0 - [II])/(J_I - J_{\text{II·s}}) + 1/K_{\text{assn}}(J_I - J_{\text{II·s}}) \quad (14)$$

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(13) Exner, O. In *Correlation Analysis in Chemistry*; Chapman, N. B., Shorter, J., Eds.; Plenum Press: New York, 1978; Chapter 10, p 438.

(14) (a) By using the log K_{assn} calculated by eq 9 the correlation deteriorates: $\rho = 0.45$, $R = 0.9666$, SD = 0.048. (b) Use of the $\delta_{\text{II·DMSO}}$ values calculated by eq 9 gives $\rho = 0.33$ ($R = 0.9911$, SD = 0.018).

(15) (a) Fuson, R. C.; Byers, D. J.; Rabjohn, N. *J. Am. Chem. Soc.* **1941**, *63*, 2369. (b) Nadler, E. B. Unpublished results.

Table IV. δ(OH) Values for (Z)-MesC(R)=C(OH)Mes (**3a–d**) and for $Mes_2C{=}C(OH)SiMe_3$ (**4c**) in CCl_4–DMSO-d_6 Mixtures

% DMSO-d_6 in CCl_4–DMSO-d_6 (v/v)	[DMSO-d_6], M	δ(OH) for **3a**^{a,b}	**3b**^{c,d}	**3c**^{a,c}	**3d**^{c,d}	**4c**^{b,d}
0	0	4.58	4.12	4.13	4.06	4.66
0.2	0.028	4.85	4.32	4.33	4.21	4.74^f
0.4	0.057	5.04	4.54	4.52	4.35	4.79
0.6	0.085	5.26	4.69	4.66	4.46	4.84
0.8	0.113	5.45				4.91
1	0.141	5.65	5.03	4.99	4.70	4.93
2	0.283	6.23	5.57	5.56	5.15	5.15
4	0.566		6.15	6.04		
5	0.707	7.02	6.28	6.23	5.87	5.55
6.7	0.947		6.55	6.46	6.17	
8	1.13		6.61	6.56	6.24	
10	1.41	7.47	6.76			5.95
12.6	1.78		6.87	6.79^e	6.58	
20	2.83	7.81	7.04	7.01	6.73	6.36
40	5.66	8.03	7.27	7.26	7.08	6.84
60	8.48	8.18	7.39	7.40	7.23	7.02
80	11.31	8.26	7.46	7.51	7.32	7.22
100	14.1	8.28	7.52	7.54	7.37	7.32

[a] At 292 K. [b] [**3a**] or [**4c**] = 0.028 M. [c] [**3**] = 0.034 M. [d] At 289 K. [e] The OH signal is not observed and it is apparently hidden below an aromatic singlet as deduced by integration (aryl region, CH_3CH_2 = 3.1:5). [f] Relatively broad signal with various batches of DMSO.

Table V. K_{assn} and δ(OH) Values for (Z)-MesC(R)=C(OH)Mes **3** in CCl_4–DMSO-d_6 Mixtures at 289–292 K

parameter	R = Ph (**3a**)	Me (**3b**)	Et (**3c**)	i-Pr (**3d**)
n^a	14	17	16	14
δ_{CCl_4}	4.58	4.12	4.13	4.06
$\delta_{I\cdot CCl_4}{}^b$	4.60	4.12	4.16	4.07
δ_{DMSO}	8.28	7.52	7.54	7.37
$\delta_{II\cdot DMSO}{}^b$	8.31	7.53	7.56	7.45
$K_{assn}{}^b$	2.75	2.58	2.27	1.65
% **II**·DMSO in DMSO-$d_6{}^b$	99.2	99.7	99.4	97.6

[a] Number of points used for the iterative calculations. [b] From eq 9.

Table VI. Parameters of the Linear Correlation of δ(OH)(**3**) vs δ(OH)(**4**) for Different R Groups

R	n^a	slope	intercept	R^b	SD^b
Ph	14	1.07	–0.64	0.9972	0.10
Me	6	1.00	–0.51	0.9937	0.12
Et	6	1.07	–0.72	0.9854	0.18
i-Pr	7	1.10	–0.66	0.9630	0.26

[a] Number of points in the correlation. [b] R, correlation coefficient; SD, standard deviation.

$R \approx 0.99$, except for benzene and nitrobenzene. The values together with $\delta_{II\cdot s}$, $\delta_{I\cdot CCl_4}$, $F_{II\cdot s}$, and $K_{assn}{}^{app}$ values are given in Table X. $K_{assn}(J)$ and $K_{assn}(\delta)$ show reasonable agreement in most of the solvents, except in dioxane where $K_{assn}(\delta) = 2.4K_{assn}(J)$. The relatively small changes in δ(OH) and ^3J for nitrobenzene and benzene resulted in an appreciable scatter in the plots according to eq 8 and corresponding errors and differences between the two K_{assn} values. δ(OH) in benzene changed in the opposite direction so that only $K_{assn}(J)$ was calculated.

Both δ(OH) and ^3J(HCOH) are temperature dependent. On lowering the temperature, δ(OH) shifts downfield and ^3J(HCOH) decreases (Table XI). The two changes are approximately parallel, and they become more pronounced with the increase in the hydrogen bond accepting ability of the solvent.

^3J(HCOH) vs δ(OH) Correlation. The changes in the ^3J(HCOH) and the δ(OH) values in the binary CCl_4–solvent mixtures are parallel. Plots of $\Delta J = J_{CCl_4} - J_{obs}$ vs $\Delta\delta = \delta_{obs} - \delta_{CCl_4}$ are linear ($R > 0.995$; eq 15) in all the binary mixtures (Table XII and Figure 6), as found previously for CCl_4–DMSO mixtures,[3] except for the CCl_4–dioxane plot, which is curved.

$$^3J(\mathrm{HCOH}) = C\delta(\mathrm{OH}) + D \qquad (15)$$

Enol 1 in Solvent-DMSO-d_6 Mixtures. The changes in δ(OH) and ^3J(HCOH) values for **1** in C_6D_6–DMSO-d_6, CD_3CN–DMSO-d_6, and CD_3COCD_3–DMSO-d_6 mixtures were also studied (Table VIII). As expected, the addition of small percentage of DMSO-d_6 to the solvent resulted in a larger change for C_6D_6–DMSO-d_6 and a small change for CD_3COCD_3–DMSO-d_6. Δ^3J(HCOH) vs $\Delta\delta$(OH) plots for CCl_4–CD_3CN, CD_3CN–DMSO-d_6, and CCl_4–DMSO-d_6 mixtures were linear.

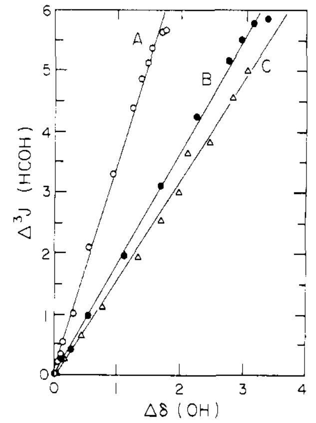


Figure 6. Plot of Δ^3J(HCOH) vs $\Delta\delta$(OH) for binary CCl_4–solvent mixtures. A (○) CCl_4–CD_3CN; B (●) CCl_4–CD_3COCD_3; C (△) CCl_4–THF-d_8.

In these binary mixtures the equilibria involve three species, I (with δ_I), the solvent-associated species II·S (with $\delta_{II\cdot s}$), and the DMSO-d_6-associated species II·DMSO (with $\delta_{II\cdot DMSO}$). Equations 16 and 17 give the observed δ(OH) value and the mass balance.

$$\delta_{obs} = \delta_I F_I + \delta_{II\cdot s} F_{II\cdot s} + \delta_{II\cdot DMSO} F_{II\cdot DMSO} \qquad (16)$$

$$F_I + F_{II\cdot s} + F_{II\cdot DMSO} = 1 \qquad (17)$$

The δ_I, $\delta_{II\cdot s}$, and $\delta_{II\cdot DMSO}$ values are known from Tables VII and X. Defining $K_{assn}{}^3$ by eq 18 and 19, approximating $[S]_f$ by $[S]_0$

$$\mathrm{II\cdot S + DMSO} \overset{K_{assn}^3}{\rightleftharpoons} \mathrm{II\cdot DMSO + S} \qquad (18)$$

$$K_{assn}{}^3 = [\mathrm{II\cdot DMSO}][S]_f/[\mathrm{II\cdot S}][\mathrm{DMSO}]_f \qquad (19)$$

and $[DMSO]_f$ by $[DMSO]_0$ and rearranging the equation, gives eq 20 where $K_{assn}{}^1$ and $K_{assn}{}^2$ are the association constants for **1** with the solvent and DMSO respectively.

$$K_{assn}{}^3 = K_{assn}{}^2/K_{assn}{}^1 \qquad (20)$$

A large error in $K_{assn}{}^3$ calculated from $K_{assn}{}^1$ and $K_{assn}{}^2$ values from Table X is due to the combined errors in these values and to the small changes in δ_{obs} and J_{obs} values for $(CD_3)_2CO$–DMSO-d_6. Hence, the conclusion is only qualitative: even a small percentage of added DMSO-d_6 associates effectively with the free **1** in the mixture.

δ(OH) and K_{assn} for the α-Trimethylsilyl Enol 4c. The δ(OH) values for the α-silylenol **4c** in 12 binary CCl_4–DMSO-d_6 mixtures are given in Table IV. The values in pure CCl_4 (4.66) and pure DMSO (7.32) differ slightly from those for **4b** (4.77 and 7.30, respectively). A plot of δ(OH) vs δ(OH) for **1** is nonlinear, resembling Figure 2A.

The linear plot according to eq 8 gives a K_{assn} = 0.71 and $\delta_{II\cdot DMSO}$ = 7.52, and $F_{II\cdot DMSO}$ is 0.93. However, although $R >$ 0.99 for the plot, the first two experimental points are below the regression line. Application of eq 9 gives K_{assn} = 0.52, $\delta_{II\cdot DMSO}$ = 7.60, and $\delta_{I\cdot CCl_4}$ = 4.72.

4a and 4b in Binary CCl_4–CD_3COCD_3 Mixtures. The δ(OH) values for the α-methyl- (**4a**) (at 292 K) and α-*tert*-butyl- (**4b**) β,β-dimesitylethenols (at 290 K) in binary CCl_4–acetone-d_6

Table VII. δ(OH) (in ppm) and ^3J(HCOH) (in Hz) Values for **1** in Binary CCl_4–Solvent (S)[a] Mixtures

% S in CCl_4–S (v/v)	C_6D_6[b]			$C_6D_5NO_2$[d]			dioxane-d_8[e]			THF-d_8[f]			CD_3CN[g]			$(CD_3)_2CO$[h]			$(CD_3)_2SO$[i]			$(CD_3)_2NCDO$[j]		
	M	δ-(OH)[c]	^3J	M	δ-(OH)	^3J	M	δ-(OH)	^3J	M	δ-(OH)	^3J	M	δ-(OH)	^3J	M	δ-(OH)	^3J	M	δ-(OH)	^3J	M	δ-(OH)	^3J
0	0	4.45	14.0	0	4.46	14.0	0	4.50	14.0	0	4.46	14.0	0	4.45	14.0	0	4.45	14.0	0	4.47	14.1	0	4.45	14.0
0.1																						0.01	4.78	13.5
0.2																			0.03	5.11	12.3	0.03	5.11	12.9
0.3										0.04	4.61	13.8	0.06	4.50	13.8									
0.4																			0.06	5.63	11.5	0.05	5.35	12.6
0.5							0.06	4.63	13.8	0.06	4.69	13.6				0.07	4.60	13.7	0.07	5.96	11.0			
0.6													0.11	4.55	13.7				0.09	6.00	10.8	0.08	5.64	12.1
0.8																						0.10	5.94	11.4
1	0.11	4.44	14.1	0.10	4.49	13.9	0.12	4.77	13.7	0.12	4.90	13.4	0.19	4.60	13.5	0.14	4.74	13.5	0.14	6.69	9.6	0.13	6.22	11.6
2				0.20	4.52	13.8	0.24	5.00	13.4	0.25	5.23	12.9	0.38	4.75	13.0	0.27	4.99	13.0	0.28	7.37	8.2	0.26	7.04	9.9
4																			0.57	7.89	7.2			
5	0.56	4.43	14.0	0.49	4.59	13.7	0.59	5.51	12.9	0.61	5.79	12.1	0.95	5.04	11.9	0.68	5.56	12.0				0.64	7.87	8.6
8										0.98	6.17	11.5												
10	1.13	4.43	13.9	0.98	4.73	13.4	1.18	5.88	12.4				1.91	5.40	10.7	1.36	6.15	10.9	1.41	8.28	6.5	1.29	8.28	7.7
12										1.47	6.46	11.0												
20	2.26	4.41	13.8	1.96	4.96	12.9	2.35	6.16	12.0	2.45	6.60	10.4	3.81	5.72	9.6	2.72	6.72	9.7	2.83	8.52	6.2	2.57	8.60	7.1
30				2.93	5.08	12.6							5.72	5.85	9.1									
40				3.91	5.23	12.3	4.70	6.54	11.2	4.89	6.95	10.2	7.62	5.95	8.9	5.44	7.24	8.8	5.66	8.73	6.0	5.14	8.85	7.1
50	5.65	4.35	13.5										9.53	6.03	8.6									
60				5.87	5.49	11.8	7.05	6.69	10.9	7.34	7.30	9.5				8.16	7.46	8.5	8.48	8.82	6.0	7.71	8.99	7.0
70	7.90	4.30	13.3																					
80				7.82	5.66	11.5	9.40	6.80	10.6	9.78	7.54	9.0	15.5	6.19	8.4	10.88	7.64	8.2	11.3	8.93	5.9	10.28	9.18	6.9
100	11.29	4.28	13.1	9.78	5.94	11.3	11.75	6.86	10.5	12.23	7.56	9.0	19.1	6.23	8.4	13.60	7.86	8.1	14.1	9.01	5.9	12.85	9.22	6.8

[a] All solvents are ≥99% deuteriated except for dioxane-d_8 which is 98.5% deuteriated. [b] Spectra of 1–10% and of 50% C_6D_6 (v/v) were measured at 296 K, that of pure C_6D_6 at 297 K, and the rest at 294 K. [c] The change in δ(OH) from 0 to 20% is within the experimental error. [d] Spectra of 1–5% and 40–80% $C_6D_5NO_2$ were measured at 294 K, of 10% of 20% and 100% solutions at 290 K, and of 30% $C_6D_5NO_2$ at 296 K. [e] Spectra were measured at 293–294 K. [f] Spectra at 293 K except for 2, 8, and 12% (293 K) and pure CCl_4 (290 K). [g] Spectra measured at 290 K. [h] Spectra measured at 294 K. [i] Data from ref 3. [j] Spectra measured at 292–294 K.

Table VIII. δ(OH) (in ppm) and ^3J(HCOH) (in Hz) Values for **1**[a] in Solvent (S)–DMSO-d_6[b] Mixtures

% DMSO-d_6 in S-DMSO-d_6 (v/v)[b]	DMSO-d_6,[b] [M]	$(CD_3)_2CO$[c]		CD_3CN[d]		C_6D_6[c]	
		δ(OH)	^3J(HCOH)	δ(OH)	^3J(HCOH)	δ(OH)	^3J(HCOH)
0	0	7.76	8.10	6.22	8.36	4.27	13.15
0.1	0.014					5.38	11.62
0.15	0.021					5.96	10.98
0.2	0.028					6.17	10.16
0.25	0.035					6.25	10.14
0.3	0.042			6.58	8.04	6.82	9.48
0.45	0.064					6.92	9.12
0.6	0.085			6.86	7.88	7.53	8.59
1.0	0.14	8.12	7.51	7.06	7.68	7.95	8.04
2.0	0.28	8.30	7.12	7.49	7.29	8.48	7.29
5.0	0.71	8.54	6.78	8.01	6.81	8.91	6.74
10.0	1.41	8.75	6.43	8.42	6.46	9.19	6.31
20.0	2.83	8.92	6.17	8.71	6.21	9.26	6.15
40.0	5.66	9.00	6.01	8.86	6.04	9.27	6.01
60.0	8.48	9.04	5.92	8.95	6.00	9.22	5.94
80.0	11.31	9.05	5.96	8.98	5.96	9.14	5.90
100.0	14.14	9.06	5.86	9.01	5.90	9.06	5.86

[a] [**1**] = 0.036 M. [b] DMSO-d_6 and the solvent (S) are all perdeuteriated with ≥99.9% D. [c] Measurements at 290 K, when δ(OH) = 4.46 and ^3J(HCOH) = 14.01 Hz in CCl_4. [d] Measurement at 293 K, when δ(OH) = 4.45 and ^3J(HCOH) = 13.96 Hz in CCl_4.

Table IX. Effect of Concentration of **1** on δ, J, K, and K_{assn} Values

[**1**], M	solvent	T, K	δ(OH), ppm	δ(CH), ppm	^3J(HCOH), Hz	K_{assn} $(\delta)^d$	K_{assn} $(J)^d$
0.036	CCl_4[a]	292	4.45	6.30	13.2		
0.072	CCl_4[a]	292	4.48	6.29	13.5		
0.108	CCl_4[a]	292	4.50	6.28	11.6[b]		
0.144	CCl_4[a]	292	4.51	6.28			
0.360	CCl_4[a]	290	4.56	6.13	13.4[c]		
0.036	99.6:0.4 CCl_4–DMSO-d_6[a]	289	6.03	6.32	10.8	11.1	15.0
0.072	99.6:0.4 CCl_4–DMSO-d_6[a]	289	5.94	6.30	10.9	12.8	20
0.144	99.6:0.4 CCl_4–DMSO-d_6[a]	289	5.78	6.27	11.6	20.9	30
0.360	99.6:0.4 CCl_4–DMSO-d_6[a]	289	5.48	6.18	9.8[c]		
0.720	99.6:0.4 CCl_4–DMSO-d_6[a]	289	5.41	6.04	[c]		
0.036	99:1 CCl_4–DMSO-d_6 (v/v)[b]	292	7.01	6.35	8.8	10.0	15.0
0.072	99:1 CCl_4–DMSO-d_6 (v/v)[b]	292	6.85	6.33	8.8	10.8	18.5
0.108	99:1 CCl_4–DMSO-d_6 (v/v)[b]	292	*d,e*	6.34	*d,e*		
0.144	99:1 CCl_4–DMSO-d_6 (v/v)[b]	292	*d,e*	6.33	*d,e*		

[a] [DMSO-d_6] = 0.057 M. [b] [DMSO-d_6] = 0.143 M. [c] Broad singlet at reduced resolution with a considerable error. [d] δ(OH) and ^3J(HCOH) values used for the calculations are from Table X. [e] Poor resolution and the OH signal coincides with the aromatic signal.

Table X. K_{assn}, δ(OH), and ^3J(HCOH) Values in Various Solvents from Data in CCl_4–Solvent Mixtures at 20 °C[a]

	solvent =							
parameter	C_6D_6	$C_6D_5NO_2$	CD_3CN	CD_3COCD_3	dioxane-d_8	THF-d_8	DMF-d_7	DMSO-d_6
K_{assn} (δ)		0.08	0.47	0.61	1.1	1.1	4.6	7.4 (5.2)[b]
$\delta_{11\cdot S}$		7.68	6.41	8.15	6.99	7.68	9.11	8.86
K_{assn} (J)	0.053	0.12	0.58	0.67	0.46	0.87	5.0	9.7
$J_{11\cdot S}$	11.58	9.0	7.7	7.4	9.9	8.7	6.7	5.9
$\delta_{1\cdot CCl_4}$		4.47	4.45	4.46	4.49	4.52	4.57	4.51
$J_{1\cdot CCl_4}$	14.04	13.86	14.06	14.00	13.87	13.89	13.85	13.96
$F_{11\cdot S}$ from δ		0.46	0.91	0.92	0.95	0.96	1.00	1.00
$F_{11\cdot S}$ from J	0.46	0.53	0.89	0.90	0.85	0.95	0.99	1.00
$K_{assn}^{app}(\delta)$		0.07	0.14	0.44	0.39	0.55	3.30	3.79
$K_{assn}^{app}(J)$	0.011	0.07	0.36	0.47	0.20	0.41	5.36	9.21
δ_{solv}	4.28	5.94	6.23	7.86	6.86	7.56	9.22	9.01
J_{solv}	13.1	11.3	8.4	8.1	10.5	9.0	6.8	5.9

[a] Data from eq 9. [b] From ref 1. Calculated by eq 8.

Table XI. Temperature Dependence of δ(OH) and ^3J(HCOH) for **1**[a] in CCl_4–Solvent Mixtures

solvent (S)	% S in CCl_4–S (v/v)	T, K	δ(OH), ppm	^3J(HCOH), Hz	T, K	δ(OH), ppm	^3J(HCOH), Hz
$(CD_3)_2CO$	10	274	6.44	10.7	307	5.93	11.2
CD_3CN	10	276	5.53	11.4	308	5.24	11.0
dioxane-d_8	10	293	5.88	12.4	306	5.76	12.6
$C_6D_5NO_2$	30	276	5.21	12.5	308	5.02	12.7
C_6D_6	50	276	4.34	13.5	308	4.33	13.5

[a] [**1**] = 0.036 M.

Table XII. Correlation of ^3J(HCOH) vs δ(OH) for **1** (eq 15) in CCl_4–Solvent Mixtures

solvent	n^a	C^b	D^b	R^b	SD[b]
DMSO-d_6[c]	14	1.79	0.47	0.9962	0.24
DMF-d_7	15	1.55	0.01	0.9978	0.18
CD_3COCD_3	11	1.80	−0.002	0.9988	0.11
THF-d_8	13	1.61	−0.07	0.9977	0.12
dioxane-d_8	11	1.43	−0.21	0.9894	0.19
CD_3CN	13	3.31	0.09	0.9984	0.13
$C_6D_5NO_2$	11	1.93	0.09	0.9949	0.10

[a] Number of experimental points. [b] C, slope; D, intercept; R, correlation coefficient; SD, standard deviation of the linear regression (eq 15). [c] Data from ref 3.

mixtures (Table XIII) complement similar data for **1** in Table VII. Half of the change in δ(OH) occurs at 20% and 40% CD_3COCD_3 for **4a** and **4b**, respectively whereas the corresponding change in δ(OH) for **1** is at 10% CD_3COCD_3. The K_{assn} and $\delta_{11\cdot acetone}$ values were calculated by both eq 8 and 9 and are given together with the F_{11} values in Table XIV.

Enol 5. Enol **5** was investigated only in two solvents at 293 K. In CCl_4 δ(OH) = 4.03 and ^3J(HCOH) = 13.85 and in DMSO-d_6 δ(OH) = 8.81 and ^3J(HCOH) = 5.92.

Discussion

The present data extend our knowledge on the association of stable enols with hydrogen bond accepting solvents in several directions. The polar contribution of α substituents is shown to be relatively small from the effect of α-aryl substituents on K_{assn}.

Table XIII. δ(OH) Values for $Mes_2C{=}C(OH)R$ **4**[a] in CCl_4–CD_3COCD_3 Mixtures

% CD_3COCD_3 (v/v)	[CD_3COCD_3], M	δ(OH) for R = Me (**4a**)[b]	δ(OH) for R = t-Bu (**4b**)[c]
0	0.0	4.74	4.77
0.5	0.07	4.80	4.80
1	0.14	4.81	4.83
2	0.27	4.88	4.86
5	0.68	5.16	5.00
10	1.36	5.40	5.18
20	2.72	5.86	5.45
40	5.44	6.22	5.62
60	8.16	6.42	6.00
80	10.9	6.58	6.11
100	13.6	6.87	6.44

[a] [**4**] = 0.034 M. [b] At 292 K. [c] At 290 K.

Table XIV. δ(OH) (in ppm) and K_{assn} Values for **4a** and **4b** in CCl_4–acetone-d_6

	4a[a]	**4b**[b]		**4a**[a]	**4b**[b]
n^c	11	11	$F_{11\cdot acetone}$ in acetone (eq 8)	0.80	0.77
δ_{CCl_4}	4.74	4.77			
δ_{DMSO}	6.87	6.44	$\delta_{1\cdot CCl_4}$ (eq 9)	4.74	4.81
$\delta_{11\cdot acetone}$ (eq 8)	7.39	6.93	$\delta_{11\cdot acetone}$ (eq 9)	7.34	7.60
K_{assn} (eq 8)	0.24	0.17	K_{assn} (eq 9)	0.25	0.09
			$F_{11\cdot acetone}$ in acetone (eq 9)	0.82	0.58

[a] At 292 K. [b] At 290 K. [c] Number of points in the correlations.

A moderate sensitivity to the arrangement of substituents is deduced by comparing K_{assn} values of isomeric enols. The data for **1** point to the importance of hydrogen bond accepting ability of the solvent in determining K_{assn} and give a qualitative relationship between K_{assn} and the conformation of the C=C—O—H moiety in different environments. The similarity of the association behavior of α-alkyl and α-aryl-β,β-substituted enols is extended to CD_3COCD_3. Finally, the effects of an α-Me_3Si and of α-alkyl substituents are compared.

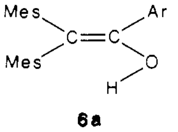
α-Aryl-Substituted Systems. The steep change in δ(OH) for compounds **2** on addition of only a small percentage of DMSO-d_6 (Figure 1) indicates clearly that the phenomenon probed is chemical association rather than a polar effect of the solvent on the δ(OH) value. This is supported by the regularity of the K_{assn} values.

Several important conclusions emerge from the data of Tables I and III. First, the sharp OH signals even at low temperature indicate that equilibration of the I and II conformers is rapid on the time scale of the measurement. Second, the effect of meta- and para-substituted α-aryl substituents on the association is rather small: K_{assn} (from eq 8) increases only 2.3-fold from the α-anisyl to α-3,5-dibromophenyl. The linear Hammett plot suggests that polar effects are responsible for the change in K_{assn}. The positive ρ is consistent with expectations since electron withdrawal increases the acidity and the hydrogen bond donating ability of an OH group. The low ρ value of 0.35 reflects the fact that the substituents are remote from the association center. The OH group is attached to a vinylic carbon which itself enhances the hydrogen bond donating ability, but we did not find a Hammett ρ value for the association of $XC_6H_4CH_2OH$ with solvents which would enable an estimation of these two factors. We note that a similar plot for α-alkyl-β,β-dimesitylethenols (**4**) vs σ* gives a slope of 1.30.[1]

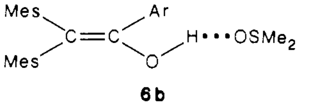
Third, the steric effect on the association is negligible. The K_{assn} values for **2a** (α-Mes) and **2c** (α-p-Tol) are almost identical, suggesting that the steric effects of the two o-methyl groups increase the extent of association with DMSO by the same amount that their electronic effects decrease it. From Table III this is 1.17-fold, i.e., only 0.1 kcal mol^{-1}.

Finally, the fraction of species II in DMSO (≥0.98) is very close to unity. This is reminiscent of the behavior of **1** in DMSO, but differs from that of α-alkyl-[1] and α-(trimethylsilyl)-β,β-dimesitylethenols where $F_{II\text{-}DMSO}$ in DMSO in ≤0.95. The nonlinearity of most of the plots of δ(OH)(**2**) vs δ(OH)(**1**) reflects the fact that most of the changes in δ(OH) for **1** occur at a smaller percentage of DMSO-d_6 than required for corresponding changes for **2**, resulting in the shallow first part of the curves in Figure 2A. When **1** is almost completely associated, δ(OH)(**1**) reaches a plateau, but δ(OH) for **2** continues to increase due to increased percentage of the associated species, and Figure 2A displays the steep part of the curve.

The Nature of Species II of Enols 2. There is little doubt that the large chemical shift of the OH is due to hydrogen bonding association of the hydrogen bond donor enol with the hydrogen bond acceptor DMSO. This is corroborated by the linear correlation of δ(OH) for **1**, **2a**, **3a**, or α-anthryl-β,β-dimesitylethenol with Kamlet-Taft hydrogen bond accepting parameter of the solvent β in a large number of solvents.[3]



6a



6b

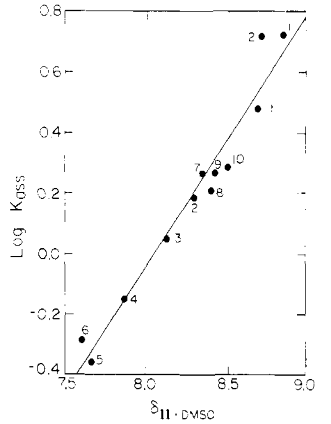


Figure 7. Plot of log K_{assn} vs δ_{11} (both calculated by eq 9) for $Mes_2C{=}C(OH)R$. R: 1, H; 2, Me; 3, Et; 4, i-Pr; 5, t-Bu; 6, Me_3Si; 7, Mes; 8, p-An; 9, p-Tol; 10, Ph; 11, p-$CF_3C_6H_4$; 12, 3,5-$Br_2C_6H_3$. Point 6 was not used for drawing the slope.

The chemical shifts cannot give information on the conformation of the C=C—OH moiety of either species II, or of I in CCl_4. However, the stretching absorption of the OH in the IR spectra of **2b–f** at ν = 3518–3524 cm^{-1}[12] is ascribed to an intramolecular hydrogen bonding to the π system of the mesityl group cis to the OH, which is possible only for a syn arrangement (**6a**) of the C=C—O—H moiety. The ^3J coupling constant for **1** in solution[1] (see below) and data on trimesitylethenol in the solid state[16] and on isotopomeric (E)- and (Z)-2,4,6-$(CD_3)_3C_6H_2C(Mes){=}C(OH)Mes$[17] strongly indicate that the conformation in CCl_4 is **6a** for Ar = Mes. By analogy, and in line with the IR data, we suggest that this is true also for compounds **2**.

Calculations on very simple enols suggest that the two most stable conformers of the C=C—O—H are syn and anti.[18] Hence, it is reasonable that the second conformer will be similar to **6b**, since a linear hydrogen bond to the solvent in the plane of the O–H bond in **6a** is sterically impossible. However, the energy gain by hydrogen bond formation exceeds the calculated energy difference between unsolvated syn and anti conformers in simple systems, and other conformations, even one with a C=C—O—H dihedral angle of 90° cannot be excluded. Analogy with **1** suggests that II is a periplanar or clinal anti-type conformer, but direct evidence is lacking.

Log K_{assn}–δ(OH) Correlations. Table III and Figure 5 show a linear correlation of log K_{assn} values in DMSO with the $\delta_{II\text{-}DMSO}$ values for the same substrates for **2a–f**. The slope (0.82) and intercept (−6.68) of eq 13, resemble those (0.77 and −6.3, respectively) of a similar linear plot for compounds **4** (R = Me, Et, i-Pr, t-Bu) and **1** in CCl_4–DMSO.[1] Indeed, Figure 7 shows that a plot (data from eq 9) for the six aromatic (**2a–f**), the five aliphatic (**4a–c**, **4**, R = Et, i-Pr), and the 1 H (**1**) derivatives of $Mes_2C{=}C(OH)R$ is reasonably linear (eq 21), although inspection

$$\log K_{assn} = 0.83\delta_{II\text{-}DMSO} - 6.6 \qquad (R = 0.9782;\ SD = 0.07) \tag{21}$$

shows separation to α-aryl and α-alkyl derivatives and deviation of **4c** from the line.

Log K_{assn} shows large sensitivity to $\delta_{II\text{-}DMSO}$ values: δ(OH) changes by ca. 1.2 ppm for a change of 1 order of magnitude in K_{assn}. The linearity may indicate that the same (presumably polar) effect operates for all these substituents, and it will be interesting to delineate the reason for the deviations from the line by a study of additional substituents.

(Z)-MesC(R)=C(OH)Mes Systems. The exchange of positions of an α-alkyl or an α-aryl substituent in **4** or **2** with the β-mesityl group cis to it leads to two main changes. First, δ(OH) in CCl_4 decreases by 0.42 ppm for α-phenyl and by 0.61–0.62 ppm for the α-alkyl substituents, and δ_{II} in DMSO decreases by 0.21 ppm for α-Ph and by 0.40–0.63 ppm for α-alkyl groups. Second, the K_{assn} values, which follow the order β-Ph > β-Me > β-Et > β-i-Pr for R, are 1.3-, 1.7-, 2.0-, and 2.3-fold higher than for the α-R derivatives.[1,3]

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[16] Kaftory, M.; Biali, S. E.; Rappoport, Z. *J. Am. Chem. Soc.* **1985**, *107*, 1701.

[17] Biali, S. E.; Rappoport, Z.; Hull, W. J. *J. Am. Chem. Soc.* **1985**, *107*, 5450.

[18] (a) Samdal, S.; Seip, H. M. *J. Mol. Struct.* **1975**, *28*, 193. (b) Bouma, W. J.; Radom, L. *Ibid.* **1978**, *43*, 267. (c) Nobes, R. H.; Radom, L.; Allinger, N. L. *Ibid.* **1981**, *85*, 185. (d) Schleyer, P. v. R. *Pure Appl. Chem.* **1987**, *59*, 1647. (e) Arad, D.; Apeloig, Y.; Rappoport, Z. Unpublished results.

The increase of K_{assn} values of **3** relative to those for **4** is ascribed to electron withdrawal by the aryl compared with alkyl groups. This effect should roughly bring K_{assn} for all the β-R derivatives to that (1.82) of trimesitylethenol (**2a**) in the absence of other effects. However, despite the larger distance from the association center, K_{assn} for β-R's is not constant and follows the order β-*i*-Pr < β-Et < β-Me. This can be explained by the geometry of **4**. If the β-Mes—C=C dihedral angle increases with the size of the β-alkyl group, the intramolecular π(β-Mes)···HO association is strengthened, leading to an accompanying decrease in K_{assn}.

The decrease of δ(OH) in CCl_4 and DMSO-d_6 can be related to the geometry of the system. We assume a (*Z*) structure for all compounds **3** although complete X-ray structure is available only for **3a**,[16] and a qualitative X-ray information indicates a (*Z*) structure for **3c** as well.[15b]

In CCl_4, the higher the β-Mes—C=C torsional angle the stronger is the intramolecular π-β-Mes···HO interaction which is responsible for the trend in δ(OH). For **3a**, this dihedral angle is larger than for all the β,β-dimesityl-α-R derivatives.[16,19] If this behavior is general, then a larger β-Mes—C=C angle in **3** is responsible for a decrease in δ(OH) relative to **4** in CCl_4.

In DMSO, the decrease of δ(OH) in the order Me > Et > *i*-Pr probably reflects a major contribution of the ring current by the α-mesityl ring on the δ(OH). This is dependent on the α-Mes—C=C angle, which probably increases with the bulk of the β-alkyl group. This effect is manifested by the $\Delta\delta$(OH) of 0.42 ppm between **1** and **5**, although the change in the β-aryl ring is at a remote position from the OH.

Trimethylsilyl Enol 4c. The study of **4c** complements the previous study on α-alkyl derivatives.[1] A linear correlation between log K_{assn} for compounds **4** and **1** (calculated by eq 8) and σ^* was previously found.[1] Silicon is more electropositive than carbon, and whereas $\sigma^*(Me_3Si)$ is not available, comparison of σ^* values[20] of Me_3SiCH_2 (−0.26), *t*-$BuCH_2$ (−0.165), and *t*-Bu (−0.30) suggests that $\sigma^*(Me_3Si) = -0.47$. Since the K_{assn} of 0.71 (by eq 8) for **4c** is similar to that for **4**, R = *i*-Pr and σ^*(*i*-Pr) = −0.19, the point for **4c** shows a high positive deviation from the plot. A correlation of log K_{assn} with the σ_I values[13] is linear with a slope of 14.6,[1] and $\sigma_I(Me_3Si) = -0.06$ is required to put **4c** on the regression line. Six different $\sigma_I(Me_3Si)$ values ranging from 0.02 to −0.13 were determined[21] and their average is −0.08, but this has little mechanistic significance since the spread in σ_I values is much higher than the difference $\sigma_I(Me_3Si) - \sigma_I$(*i*-Pr).

The effect of Me_3Si on K_{assn} may be alternatively evaluated by comparing the acidities of R_3SiCH_2OH and R_3CCH_2OH. Unfortunately, quantitative data for R_3SiCH_2OH are not available.[22a] Other data are contradictory. Ph_3SiOH is 0.22 pK_a unit more acidic than Ph_3COH[22b] in DMSO, and $Ph_3SiCOOH$ is 0.47[22c] or 0.68[22d] pK_a unit more acidic than Ph_3CCOOH in aqueous EtOH, but p$K_a(Me_3SiCOOH)$ − p$K_a(Me_3CCOOH)$ = 0.19 in 45% EtOH and 0.22 in 76% EtOH.[22d] Obviously, a clear conclusion from these values is difficult, except that the somewhat higher K_{assn} value for **4c** than that for the carbon analogue **4b** is not inconsistent with expectation based on the electron-donating ability of carbon and silicon substituents. The longer C_α–Si bond has little influence, in agreement with the small contribution of steric effects on K_{assn} discussed previously[1] and above.

Association and Conformation of 1 in Several Solvents. Enol **1** was investigated previously very extensively due to the availability of both the δ(OH) and ^3J(HCOH) probes.[3] Correlation of both parameters with the Kamlet–Taft solvatochromic equation[6] shows that the hydrogen bond accepting ability of the solvent is mainly responsible for the chemical shift. From the ^3J probe it was deduced that the conformation is **1a** in CCl_4, **1b** in DMSO, and their mixture in most other solvents and that the association of **1** with the pure solvents (except for DMSO and DMF) is not complete.[3]

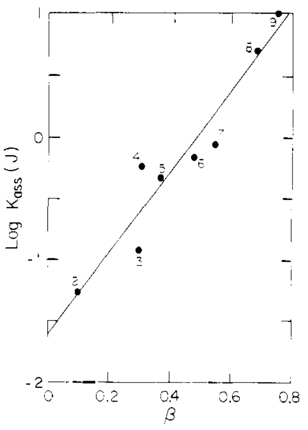

Figure 8. Plot of log $K_{assn}(J)$ vs Kamlet–Taft's β. Numbering of solvents: 2, C_6D_6; 3, $C_6D_5NO_2$; 4, CD_3CN; 5, dioxane-d_8; 6, $(CD_3)_2CO$; 7, THF-d_8; 8, DMF-d_7; 9, DMSO-d_6.

In binary CCl_4–solvent mixtures three conformers should be considered: one with "free" OH which constitutes ≤2% for **1** in CCl_4,[3,5] an intramolecularly hydrogen bonded conformer which is the main one present in CCl_4, and a conformer that is hydrogen bonded to the other solvent component of the mixture. The rapid equilibration of the two latter conformers under our conditions enables us to obtain K_{assn} and ^3J(HCOH) for the latter, solvent-bound conformer, and hence the conformations of **1** in the various solvents.

We have seen that the change of δ(OH) and ^3J(HCOH) values in CCl_4–solvent mixtures qualitatively parallels the reported behavior in CCl_4–DMSO-d_6 mixtures.[3] However, whereas in CCl_4–DMSO-d_6 and CCl_4–DMF-d_7 mixtures addition of <1% of the cosolvent raises δ(OH) and lowers ^3J(HCOH) appreciably, the changes are more moderate in solvents that are less efficient hydrogen bond acceptors.

Several important features emerge from Table X: (a) K_{assn} values change appreciably with the solvent. (b) Although Δ^3J(HCOH) and $\Delta\delta$(OH) values are linear (Figure 6), $K_{assn}(\delta)$ and $K_{assn}(J)$ are not identical. $K_{assn}(J)$ is 1.1–1.45-fold higher than $K_{assn}(\delta)$, except in THF and dioxane (which is the only solvent where the Δ^3J(HCOH) vs $\Delta\delta$(OH) plot is not linear) and where $K_{assn}(\delta) = 2.4K_{assn}(J)$. (c) In most cases, the "improvement" in calculating K_{assn} by eq 9 rather than by eq 8 changes K_{assn} by ≤10%, which is the magnitude of the error due to the intercept of eq 8. The improvement is more significant for $C_6D_5NO_2$ and for C_6D_6, where the overall changes in δ and J are relatively small, and for $K_{assn}(J)$ in DMSO-d_6, where the corresponding changes on addition of a small amount of the solvent are large. (d) The fraction of the anti-type conformer obtained by both probes is very similar. It is ≥0.9, except in benzene and nitrobenzene (and the value calculated from ^3J in dioxane). (e) δ_{II} and J_{II} for the anti conformers differ from δ_{DMSO} and J_{DMSO}, but not to the same extent. (f) ^3J values for the anti conformer are solvent dependent and are roughly proportional to log K_{assn}.

A plot of log $K_{assn}(J)$ vs Kamlet–Taft's β is monotonous and approximately linear (eq 22 and Figure 8). A plot of log $K_{assn}(\delta)$ vs β shows a larger scatter (slope 3.1; R = 0.868; SD = 0.30),

$$\log K_{assn}(J) = 3.26\beta - 1.62 \qquad (n = 8;\ R = 0.9520;\ SD = 0.21) \quad (22)$$

but if the points for dioxane and acetonitrile are excluded a linear correlation (eq 23) is obtained for the other five solvents. The slope of eq 24 resembles the slope of a similar correlation for the

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[19] Kaftory, M.; Biali, S. E.; Nugiel, D. A.; Rappoport, Z. Unpublished results.

[20] Taft, R. W. In *Steric Effects in Organic Chemistry*; Newman, M. S., Ed.; Wiley: New York, 1956; Chapter 13.

[21] For a tabulation and discussion of various σ values of silicon substituents, see: Bassindale, A. R.; Taylor, P. G. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; in press.

[22] (a) For a discussion of acidity of organic silicon compounds, see: Bassindale, A. R.; Taylor, P. G. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; in press. (b) Steward, O. W.; Fussaro, D. R. *J. Organomet. Chem.* **1977**, *129*, C28. (c) Steward, O. W.; Erwin, H. W.; Gartska, R. A.; Frohlinger, J. *J. Chem. Soc. A* **1968**, 3119. (d) Steward, O. W.; Dziedzic, J.; Johnson, J. S.; Frohlinger, J. O. *J. Org. Chem.* **1971**, *36*, 3480.

$$\log K_{\text{assn}}(\delta) = 4.3\beta - 2.34 \qquad (n = 5;\ R = 0.9979;\ \text{SD} = 0.59) \quad (23)$$

$$\log K_{\text{assn}}(\delta) = 3.43\beta - 0.83\pi^* - 1.05 \qquad (n = 7;\ R = 0.9203;\ \text{SD} = 0.31) \quad (24)$$

association of 4-fluorophenol with hydrogen bond accepting solvents but not for CF_3CH_2OH.[23] A dual-parameter equation involving also the solvent polarity $(\pi^*)^6$ is poorer than eq 22 ($R = 0.523$), whereas a slight improvement over eq 23 (cf. eq 24) was achieved. Consequently, the main parameter affecting the association with the solvent is its hydrogen bond accepting ability.

The linear correlation between Δ^3J(HCOH) and $\Delta\delta$(OH) values (Figure 6) for almost all the solvents suggests that the hydrogen bond formation is accompanied by a conformational change that also involves a change in the orientation of the OH in relation to the β-mesityl ring. Since the observed J and δ values are weighted averages of the values for the two conformers, we conclude that there is no unusual change either in the conformation or in the hydrogen bond association with a gradual change in the solvent compositions. We have no explanation for the curved plot for dioxane, although it may be connected with the presence of two association sites.

Due to the linearity of the two parameters it is reasonable to expect that $K_{\text{assn}}(\delta) \approx K_{\text{assn}}(J)$, but this is not always the case because $\Delta^3J(\text{HCOH})/(J_{CCl_4} - J_{\text{II-s}})$ and $\Delta\delta(\text{OH})/(\delta_{\text{II-s}} - \delta_{CCl_4})$ are not parallel. In spite of the improvement that eq 9 gives over eq 8 the error in K_{assn}, which is determined simultaneously with $\delta_{\text{II-s}}$, can be appreciable, and on the basis of previous treatments[8] we suggest that an error of ±10%, i.e., a difference of up to 20% between $K_{\text{assn}}(\delta)$ and $K_{\text{assn}}(J)$, could be attributed to this reason. With this arbitrary criterion the agreement between the $K_{\text{assn}}(J)$ and $K_{\text{assn}}(\delta)$ values is reasonable for four out of the seven solvents for which data are available. The large discrepancy between the values for dioxane may result from the nonlinearity of the Δ^3J(HCOH) vs $\Delta\delta$(OH) plot. The small deviation of $K_{\text{assn}}(J)$ from the plot of Figure 8 as compared with the large deviation of the $K_{\text{assn}}(\delta)$ vs β plot suggests that for dioxane $K_{\text{assn}}(J)$ is a better representation of K_{assn}.

For $C_6D_5NO_2$, $K_{\text{assn}}(J) = 1.5K_{\text{assn}}(\delta)$, and it seems that the use of a relatively large number of experimental points that do not differ much from one another leads to high error in both values. The situation is exactly opposite for DMSO, for which $K_{\text{assn}}(J) = 1.3K_{\text{assn}}(\delta)$ (by eq 9) since δ and J change appreciably on addition of a very low percentage of DMSO-d_6. However, eq 9 gives the same weight to values at both high and low [DMSO] regions. The resulting appreciable error is reflected in the increase of $K_{\text{assn}}(\delta)$ by 40% by using eq 9 at the expense of a change of only 0.15 ppm in $\delta_{\text{II-DMSO}}$. That $\delta_{\text{II-DMSO}}$ calculated by eq 9 is slightly *lower* than the observed value (Table X) is inconsistent with the assumption that the solvent effect on K_{assn} is negligible. In this highly associating solvent, where the 1:1 association is almost complete at low solvent concentrations, higher associates, e.g., 1:2 enol to solvent, with different δ's may be formed. Such association, which is not incorporated in the equations used for calculating K_{assn}, can lead to the discrepancy in the two values. $K_{\text{assn}}(J)$ is much less sensitive than $K_{\text{assn}}(\delta)$ to the calculation method, and for DMSO it is taken as a more reliable measure of K_{assn}.[24]

The fraction of the associated conformer in all the solvents, except for CCl_4 and the aromatic solvents, is high (>0.9). The lower values in the aromatic solvents reflect competition with intramolecular association to the neighboring β-mesityl. The $F_{\text{II-s}}$ values are higher than those previously calculated for **1** in the same solvents by using the incorrect assumption that $\delta_{\text{II-s}} = \delta_{\text{DMSO}}$ and $J_{\text{II-s}} = J_{\text{DMSO}}$ in all solvents. We see now that $\delta_{\text{II-s}}$ and $J_{\text{II-s}}$ values change appreciably with the solvent, from δ 6.41 (MeCN) to 9.11 (DMF) and from J = 11.6 (C_6H_6) to 5.9 in DMSO (Table X).

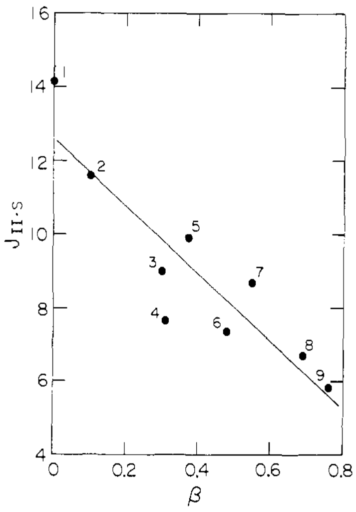

Figure 9. Plot of $J_{\text{II-s}}$ vs Kamlet–Taft's β. Numbering as in Figure 8 and solvent 1 is CCl_4.

Whereas there is no correlation between $K_{\text{assn}}(\delta)$ and $\delta_{\text{II-s}}$ ($R = 0.636$), there is a rough correlation between $K_{\text{assn}}(J)$ and $J_{\text{II-s}}$ values (eq 25). The most associated solvents (DMSO, DMF)

$$\log K_{\text{assn}}(J) = -0.37J + 0.29 \qquad (n = 8;\ R = 0.9005;\ \text{SD} = 0.31) \quad (25)$$

have the lowest ^3J(HCOH) values, and the least associated solvents ($PhNO_2$, C_6H_6) have the highest J's. The relation between ^3J(HCOH) values and the HCOH dihedral angle is through the Fraser equation[4] (eq 26), and its application suggests that the

$$^3J(\text{HCOH}) = 10.4 \cos^2\theta - 1.5 \cos\theta + 0.2 \qquad (\text{in Hz}) \quad (26)$$

conformation of **1** in CCl_4 is syn-planar, since ^3J is even higher than the expected value according to eq 26. The plot of eq 26 is close to a parabola, which means that in solvents with higher K_{assn} the HCOH dihedral angle is higher than in solvents with lower K_{assn}. If we accept the reasonable assumption[3] that II is an anti-type conformation, then (by eq 26) in C_6H_6, $C_6H_5NO_2$, dioxane, MeCN, and THF the conformation is anti-periplanar, whereas in DMF, DMSO, and probably in acetone it is anti-clinal. Since for good conjugation there is a preference of the anti-planar- over perpendicular- or anti-clinal-type conformations in the absence of solvent, as shown by calculations,[18c] we conclude that association with the solvent reduces the conjugation of the OH with the double bond.

However, the calculated potential energy change with the HCOH dihedral angle for vinyl alcohol is a relatively shallow function. The energy difference between the anti-planar and an anti-clinal conformation with HCOH angle of 40–50° (the calculated dihedral angle of **1** in DMSO and DMF) in the parent enol is ca. 1 kcal mol^{-1}.[18c]

The association with a perpendicular OH (dihedral HCOH angle 90°) is sterically the least hindered process. Although we deduced earlier that steric effects in the enol are not the dominant factor on the association,[1] some contribution from them is still expected. Apparently, the energy loss associated with the deconjugation of the planar arrangement is more than compensated by the stronger hydrogen bond formed with the solvent in an anti-clinal conformation.

Correlations Involving $\delta_{\text{II-s}}$ and $J_{\text{II-s}}$. In view of the approximate correlation between the experimental J or δ and β reported earlier for **1**,[3] it was of interest to discern whether the use of $J_{\text{II-s}}$ or $\delta_{\text{II-s}}$ would improve the approximate correlations between J_{obs} and δ_{obs} and β. Figures 9 and 10 and eq 27 and 28 show that the corre-

$$J_{\text{II-s}} = -9.1\beta + 12.6 \qquad (n = 9;\ R = 0.9009;\ \text{SD} = 1.05) \quad (27)$$

$$\delta_{\text{II-s}} = 5.7\beta + 4.9 \qquad (n = 8;\ R = 0.9340;\ \text{SD} = 0.50) \quad (28)$$

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[23] For these and other correlations with β, see: Taft, R. W.; Gramstad, T.; Kamlet, M. J. *J. Org. Chem.* **1982**, *47*, 4557. Abboud, J. L. M.; Sraidi, K.; Guiheneuf, G.; Negro, A.; Kamlet, M. J.; Taft, R. W. *Ibid.* **1985**, *50*, 2870.

[24] In correlations involving K_{assn} or δ values for both **1** and other substrates the $K_{\text{assn}}(\delta)$ value for **1** is used for consistency with values for other substrates.

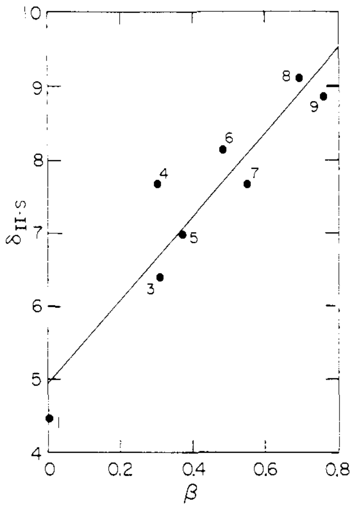

Figure 10. Plot of $\delta_{11\text{-}s}$ vs Kamlet–Taft's β. Numbering as in Figure 8 and solvent 1 is CCl_4.

lations are still approximate (R = 0.90–0.93). Both $J_{11\text{-}s}$ and $\delta_{11\text{-}s}$ are influenced by other effects in addition to the hydrogen bond accepting ability of the solvent. With dual-parameter equations including the solvent polarity parameter π^*, the correlation of $J_{11\text{-}s}$ improves and that of $\delta_{11\text{-}s}$ deteriorates (eq 27a and 28a). Better

$$J_{11\text{-}s} = -6.5\beta - 4.2\pi^* \qquad (n = 9;\ R = 0.9488;\ SD = 0.93) \qquad (27a)$$

$$\delta_{11\text{-}s} = 13.5\beta + 0.21\pi^* - 1.3 \qquad (n = 8;\ R = 0.8187;\ SD = 2.4) \qquad (28a)$$

correlations of NMR parameters with β, or β and π^* for *t*-BuOH and PhOH than those shown in eq 27, 27a, 28, and 28a were previously reported.[25]

K_{assn} Values for 4a and 4b in CCl_4–Me_2CO. The study of **4a** and **4b** in CCl_4–acetone-d_6 mixtures was undertaken in order to see if the differences of K_{assn} values for **1** with DMSO and acetone are parallel for α-alkyl derivatives of **1**. The previously determined K_{assn} values with DMSO (eq 8) were 1.38 for **4a** and 0.47 for **4b**, which are higher than the respective K_{assn} values of 0.24 and 0.17 (eq 8) with acetone (Table XIV) by 5.8- and 2.8-fold or by 6.19- and 4.9-fold from the values determined for both systems by eq 9. Since this ratio is 12.1 for **1** (Table X), the ratio between the K_{assn} values in DMSO and in acetone decreases with the increased bulk of the α substituent. The less associated enol is the less discriminating between solvents with which it associates.

The combination of electron-donating α-alkyl substituent on the enol and a moderate hydrogen bond acceptor solvent results in an appreciable fraction of the nonassociated conformer in pure acetone: F_1 = 0.18 for **4a** and 0.42 for **4b** in acetone, whereas it is ≤0.12 in DMSO.

The above mentioned differences have implications to solvent dependence of the values of the keto ⇌ enol equilibrium constants (K_{eq}). The carbonyl derivative is expected to be less associated than the enol with hydrogen bond accepting solvents. If the hydrogen bond donating ability of the solvent is less important, K_{eq} should be higher in a solvent with higher K_{assn} value and the differences in K_{eq} in various solvents should decrease with the increased bulk of the α substituent. The results of the single work that gives the solvent dependence on K_{eq} for a simple enol[26] are in agreement with the above prediction, but more K_{eq} values are required for evaluating the generality of this behavior.

Experimental Section

Materials and Solvents. The α-aryl-β,β-dimesitylethenols, **12a–f**,[12] the α-methyl- (**4a**),[27a] α-*tert*-butyl- (**4b**),[27b] α-(trimethylsilyl)- (**4c**),[27c] and α-H- (**1**) β,β-dimesitylethenols,[3] and (*Z*)-β-phenyl-α,β-dimesitylethenol (**13a**)[3] were prepared by us previously. β-Methyl- and β-ethyl-α,β-dimesitylethenols (**3b**, **3c**) and β-mesityl-β-tolylethenols (**5**) were prepared according to Fuson[28] and co-workers.[15a] Preliminary X-ray data suggest that **5** is the (*Z*) isomer. Preparation of (*Z*)-β-isopropyl-α,β-dimesitylethenol (**3d**) will be reported elsewhere. The deuteriated solvents, which were the best quality commercial grade (Aldrich), were dried before use over 4A molecular sieves.

Statistical Parameters Derived from Eq 9. Statistical parameters according to eq 9 are as follows. The Rank value (number of parameters to be optimized) is 3. The DFE's are the differences between the number of points and the Rank. The SSE values are 0.057 (**2d**), 0.1292 (**2e**), 0.2242 (**2f**), and 0.0272 (**4c**) in CCl_4-DMSO-d_6, 0.0303 (**4a**) and 0.0434 (**4b**) in CCl_4–CD_3COCD_3, and 0.018 (C_6D_6, *J*), 0.040 and 0.0464 (CD_3CN, δ and *J*), 0.0239 (CD_3COCD_3, δ), 0.0246 and 0.0695 (dioxane-d_8, δ and *J*), 0.3474 (THF-d_8, δ) and 0.1454 (CD_3SOCD_3) for **1** in CCl_4–solvent mixtures.

Spectra. NMR spectra were recorded with a Bruker W.P200 SY pulsed FT spectrometer operating at 200.133 MHz. The OH signals were either sharp singlets (enols **2–4**) or well-separated doublets (enols **1** and **5**).

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(25) Taft, R. W.; Kamlet, M. J. *Org. Magn. Reson.* **1980**, *14*, 485.

(26) Miller, A. R. *J. Org. Chem.* **1976**, *41*, 3599.

(27) (a) Nugiel, D. A.; Rappoport, Z. *J. Am. Chem. Soc.* **1985**, *107*, 3669. (b) Nadler, E. B.; Rappoport, Z.; Arad, D.; Apeloig, Y. *Ibid.* **1987**, *109*, 7873.

(28) Fuson, R. C.; Maynert, E. W.; Tan, T. L.; Trumbull, E. R. *J. Am. Chem. Soc.* **1957**, *79*, 1938.