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Stable Simple Enols. 5. Solvent Dependence of the Conformation of the OH Group in 2,2-Dimesitylethenol and Several 1,2,2-Triarylethenols[1,2]

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Abstract: ^3J(HCOH) and δ(OH) values of 2,2-dimesitylethenol ($Mes_2C{=}CHOH$, **6**) and δ(OH) values of five stable triarylethenols were measured in 12–14 solvents and found to be strongly solvent dependent. ^3J(HCOH) values for **6** at 293 K decreased from 14.1 Hz in CCl_4, via 8.2 for CD_3COCD_3, to 4.6 in DMF-d_7, and δ(OH) increased from 4.30 in $C_6D_5CD_3$, via 7.65 in CD_3COCD_3, to 9.17 in DMF-d_7. The δ(OH) values of all enols are linearly related. A use of a Karplus-type equation argues strongly that in nonpolar solvents where ^3J(HCOH)'s are the highest known, the conformation of the OH group is syn-periplanar, **1a**; i.e., the hydroxylic hydrogen is directed toward the *cis*-β-mesityl group. Extensive correlations with the Kamlet–Taft solvatochromic parameters show that the ^3J and δ values are approximately linear with the hydrogen bond accepting ability parameter β. This and the ^3J(HCOH)'s were interpreted as due to a rapid equilibrium on the NMR time scale between **1a** and a solvent-associated anti-clinal conformer, which predominates in the hydrogen bond accepting solvents. The difference in δ(OH) values between the isotopomers **16-*E*** and **16-*Z*** [Mes*C(Mes)=C(OH)Mes (Mes* = 2,4,6-$(CD_3)_3C_6H_2$)] is 9.1 ± 1.5 ppb in nonpolar solvents, and 0 in three hydrogen bond accepting solvents, indicating that in the latter solvents the OH hydrogen is directed away from the *cis*-mesityl group. IR studies in CCl_4 show a weak ν_{OH} band at 3580–3628 cm^{-1} which is ascribed to a free OH and a main ν_{OH} band at 3490–3528 cm^{-1} which indicates an intramolecular OH–π(*cis*-β-mesityl) hydrogen bonding in **1a**. Two OH absorptions, ascribed to intramolecularly bound OH and to a solvent-bound OH, were observed in PhBr and $PhNO_2$, but only a wider OH band was observed at lower wavenumbers in MeCN and THF. Conformational syn-planar $\rightleftharpoons$ anti-clinal equilibrium constants were calculated from the NMR and the IR data and were in satisfactory agreement. Addition of low concentrations of Me_2SO-d_6 to CCl_4 reduces strongly ^3J(HCOH) and increases strongly δ(OH) of **6**, and analysis of the data in CCl_4–Me_2SO-d_6 mixtures strongly suggests that the anti-clinal conformer is associated with only one Me_2SO molecule. The conformational conclusions are compared with those for other enols.

Introduction

Simple enols (i.e., those substituted only by hydrogen, alkyl, or aryl groups) are usually considered as being of inherent low thermodynamic and kinetic stability compared with their keto isomers. However, this is not always the case[3] and syntheses of simple enols in the gas phase[4a] and in solution[5] were recently developed, enabling mechanistic and spectroscopic studies.[4–6]

Thermodynamically and kinetically stable 2,2-diaryl- and 1,2,2-triarylethenols, where most or all the aryl groups are sterically crowded, were prepared decades ago by Fuson and coworkers.[7–9] Surprisingly, except for isolated studies,[10–12] they seem to be forgotten, although structural, spectroscopic, and kinetic investigations of enols will certainly benefit by studying these stable species. We previously reported their gas-phase behavior, as related to both the functional group[13] and the crowded vinyl skeleton,[1] their dynamic NMR behavior, which is mainly related to their propeller structure,[14] and their equilibria with the keto isomers.[15] In the present paper we use them for determination of the conformation of the hydroxyl group in solution.

Of the infinite number of possible conformations of the hydroxyl group in enols or of the O–R group in enol ethers, the two extreme planar conformations syn (**1**, s-cis) and anti (**2**, s-trans) are the most frequently considered.[16] This is due both to the assumed stabilization of these conformers by a π(C=C)–p(O) conjugation and to experimental evidence for their presence.[16] Gauche conformers are also considered, but we will use the Klyne–Prelog descriptive nomenclature for the relationship between the substituents on adjacent carbon atoms[17] as applied to the adjacent vinylic carbon and oxygen atoms.

Consequently, six conformers will be considered: syn- (**3**) and anti- (**4**) periplanar, which include **1** and **2** and deviate from

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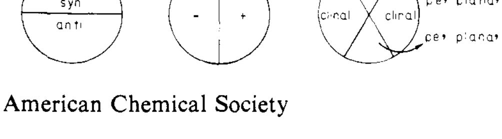
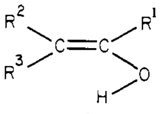
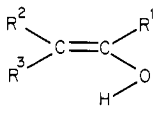


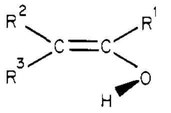
planarity up to 30° (sp, $\theta = 0 - \pm 30°$; ap, $\theta = 180 - \pm 30°$), and



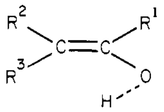
syn-planar
1



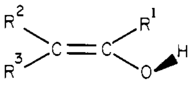
(±)-syn-periplanar
(±sp)-**3**



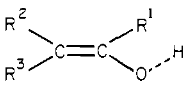
(+)-syn-clinal
(+sc)-**5**



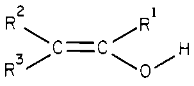
(−)-syn-clinal
(−sc)-**5**



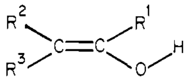
(+)-anti-clinal
(+ac)-**5**



(−)-anti-clinal
(−ac)-**5**



(±)-anti-periplanar
(±ap)-**4**



anti-planar
2

four "gauche"-type forms which belong to two pairs of cisoid and transoid nonplanar (clinal) conformers, i.e., (+sc)-**5**, (−sc)-**5**, (+ac)-**5**, and (−ac)-**5**. Enantiomeric conformers (e.g., (+ac)-**5** and (−ac)-**5**) should become diastereomers by the chiral propellar conformation of the polyarylvinyl skeleton. At room temperature the helical conformations of **7** and **9** are frozen on the NMR time scale,[14] and those of **6**, **8**, and **10** are mixtures of rapidly interconverting enantiomers.[14c] However, since only a single OH signal was observed, we will not consider this chiral element in the present discussion.

Data on the conformation of several enols are available from MO[18] and molecular mechanics (MM) calculations,[19] gas-phase microwave (MW) studies,[4a] NMR in solution,[20] and X-ray structure of the solids.[21] MO calculations[18a,c] suggest that conformer **1** of vinyl alcohol is ca. 2 kcal mol^{-1} more stable than **2**. Both structures are minima on the potential energy surface, but a minimum corresponding to a nonplanar gauche conformer was not found. These results were reproduced by MM calculations.[19a] Likewise, the MW[4a] and IR[4c] spectra of vinyl alcohol were interpreted in terms of the conformer **1**. Molecular mechanics calculations on (*Z*)-1,2-dimesityl-2-phenylethenol (**10**) gave two low-energy conformations of nearly identical stabilities: **1** (θ = 0.40°) and **4** (θ = 176.5°).[19b] The solid-state conformation of the OH of trimesitylvinyl alcohol (**7**) is **3** (θ = 16°) and of the ethenolate of 1-(9-anthryl)-2,2-dimesitylethenol (**9**) is **4** (θ = 163°).[21] An early IR study of mesityl-substituted vinyl alcohols concluded that these enols exist in a syn conformation.[10] Capon and co-workers[20] recently measured the following ^3J(HCOH) coupling constants for enols $R^3R^2C{=}CHOH$ in slightly wet acetone at −80 °C: 9.98 ($R^2 = R^3 = H$), 9.52 ($R^2 = H$, $R^3 = Me$, *E* isomer), 5.90 ($R^2 = H$, $R^3 = Me$, *Z* isomer), 5.50 ($R^2 = R^3 = Me$).[20b] They concluded that the two former compounds exist predominantly in s-cis conformation and the latter in the s-trans conformation, and ascribed it to destabilization of the syn form by steric interaction between the cis OH and methyl groups.[20a]

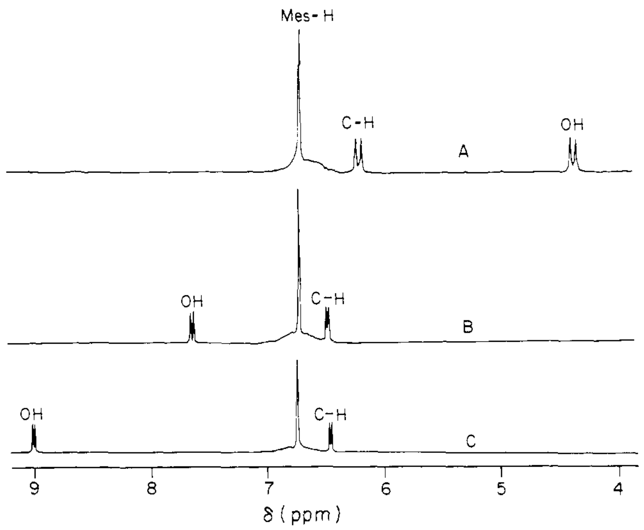
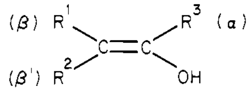


Figure 1. ^1H NMR 300-MHz spectra for the CH and OH groups of **6** at 293 K: (A) in CCl_4; (B) in CD_3COCD_3; (C) in CD_3SOCD_3. The aromatic signal broadening is due to a coalescence process.

Data are also available for the analogous enol ethers.[16,22-29] The major conformer of methyl vinyl ether is s-cis,[22a,23,26,27,29] but there is disagreement whether the minor conformer is trans[22b,23b,24] or gauche.[23b] Calculations show that the torsional potential function is very flat in the θ = 150–180° region.[18c] It was suggested that *Z*-enol ethers $ROCH{=}CHR^1$ exist mainly in the s-trans form,[28] and that $ROCR{=}CR^1R^2$ exist as a conformer mixtures.[27,28]

In the present work we studied the enol of aldehyde **6**, and several triarylethenols **7–10** which are enols of ketones. The main technique was NMR spectroscopy. Both ^3J(HCOH) and δ(OH) values were measured for **6**, but only δ(OH)'s are available for **7–10**. Additional IR measurements supplement Rodebush's data.[10b]



6, $R^1 = R^2 = Mes$; $R^3 = H$ ($Mes = 2,4,6\text{-}Me_3C_6H_2$)
7, $R^1 = R^2 = R^3 = Mes$
8, $R^1 = R^2 = Mes$; $R^3 = Ph$
9, $R^1 = R^2 = Mes$; R^3 = 9-anthryl
10, $R^2 = R^3 = Mes$; $R^1 = Ph$

Results and Discussion

^3J(HCOH) and δ(OH) Values in Various Solvents. The ^1H NMR 300-MHz spectra of **6** at 293 K were measured in 14 aprotic solvents differing in their polarities and their hydrogen bonding accepting abilities. The spectra of **7–10** were measured in 13 of these solvents (CD_2Cl_2 excluded).

The spectra of identical concentrations of **6** (20 mg/0.5 mL of solvent) showed an extensive broadening of the signals of the methyl groups and the aromatic protons,[30] whereas the vinylic and hydroxylic protons exhibited a well-resolved AX spectrum.

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Table I. δ(OH), δ(α-CH), and ^3J(HCOH) for **6** in Various Solvents at 293 K and the Relevant Solvatochromic Parameters

no.	solvent	π^{*a}	β^a	δ^a	δ(OH), ppm^b	δ(CH), ppm^b	^3J(HCOH), Hz
1	$DCON(CD_3)_2$	0.88	0.69	0.0	9.17	6.6	4.6
2	CD_3SOCD_3	1.00	0.76	0.0	9.01 (8.61)^c	6.5	5.9 (6.1)^c
3	CD_3COCD_3	0.72	0.48	0.0	7.65 (8.90)^d	6.5	8.2 (7.3)^d
4	THF-d_8	0.58	0.55	0.0	7.51	6.4	9.2
5	dioxane-d_8	(0.55)	0.37	0.0	6.84	6.4	10.6
6	CD_3CN	(0.85)	0.31	0.0	6.22 (6.55)^e	6.5	8.6 (7.8)^e
7	$C_6D_5NO_2$	1.01	[0.39]	1.0	5.79 (5.56)^c	6.6	11.4 (11.5)^c
8	CD_2Cl_2	[(0.80)]	0.00	0.5	4.72 (5.23)^f	6.4	12.9 (12.3)^f
9	C_6D_5Br	0.79	(0.06)	1.0	4.65	6.3	12.5
10	$CDCl_3$	[(0.76)]	0.00	0.5	4.66 (4.84)^g	6.4	13.5 (13.7)^g
11	C_6D_{12}	0.00	0.00	0.0	4.59	6.2	11.0
12	C_6D_6	0.59	(0.10)	1.0	4.49	6.3	12.9
13	CCl_4	0.29	0.00	0.5	4.47	6.3	14.1
14	$C_6D_5CD_3$	0.54	(0.11)	1.0	4.30	6.2	12.3

[a] Solvatochromic parameters for the nondeuterated solvent taken from ref 31. Value in square brackets denotes a tertiary value. The values in parentheses denote secondary values, and values with bracketed parentheses [(E)] denote a value which is almost certain to be changed.[31] [b] Using Me_4Si as an internal standard. [c] At 320 K. [d] At 191 K. [e] At 236 K. [f] At 220 K. [g] At 213 K.

Table II. Solvent Dependence of δ(OH) for Several Enols at 293 K

solvent	**7**	**8**	**9**	**10**	$\Delta\delta_1^a$	$\Delta\delta_2^b$	$\Delta\delta_3^c$
$DCON(CD_3)_2$	8.27	8.72	9.05	8.32	−0.05	0.40	0.45
CD_3SOCD_3	8.34	8.51	9.19	8.29	0.05	0.22	0.17
CD_3COCD_3	6.83	7.25	7.70	6.77	0.06	0.48	0.42
THF-d_8	7.09	7.30	8.11	7.01	0.08	0.29	0.21
dioxane-d_8	6.64	6.89	7.59	6.53	0.11	0.36	0.25
CD_3CN	5.84	6.12	6.55	5.66	0.18	0.46	0.28
$C_6D_5NO_2$	5.46	5.67	5.92	5.35	0.11	0.32	0.21
C_6D_5Br	5.08	5.17	5.59	4.77	0.31	0.40	0.09
$CDCl_3$	5.20	5.17	5.70	4.72	0.48	0.45	−0.03
C_6D_{12}	5.11	5.01	5.58	4.59	0.52	0.42	−0.10
C_6D_6	4.94	5.02	5.19	4.61	0.33	0.41	0.08
CCl_4	5.10	5.01	5.59	4.57	0.53	0.44	−0.09
$C_6D_5CD_3$	4.90	4.98	5.13	4.56	0.34	0.42	0.08

[a] $\Delta\delta_1 = \delta(\mathbf{7}) - \delta(\mathbf{10})$. [b] $\Delta\delta_2 = \delta(\mathbf{8}) - \delta(\mathbf{10})$. [c] $\Delta\delta_3 = \delta(\mathbf{8}) - \delta(\mathbf{7})$.

The δ(OH) and the ^3J(HCOH) values of the two doublets were unaffected by reducing the sample concentration in $CDCl_3$ by 10-fold. Irradiation of either the OH or the α-CH signal indicated that the splitting is due to a ^3J(HCOH) coupling. The δ(α-CH) changed by a maximum of 0.4 ppm on changing the solvent. In contrast, both δ(OH) and the ^3J(HCOH) showed large variation in opposite directions on changing the solvents: the larger the δ(OH), the smaller the ^3J(HCOH) (Table I). Examples are shown in Figure 1. A plot of ^3J(HCOH) vs. δ(OH) for **6** (Figure 2) is roughly linear with a significant scatter of the points:

$$^3J(\text{HCOH}) = 19.86 - 1.85\delta(\text{OH}) \quad (r = 0.938,\ \sigma = 1.00,\ n = 14) \tag{1}$$

Decreasing the temperature in five solvents invariably decreased ^3J(HCOH) and increased δ(OH). The changes are moderate and solvent dependent (Table I). E.g., lowering the temperature by 102° decreased ^3J(HCOH) by 0.9 Hz in CD_3COCD_3, but a 57° temperature reduction in CD_3CN lowered ^3J(HCOH) by 0.8 Hz.

The δ(OH) values of **7**–**10** (Table II) are sharp singlets, which are also strongly solvent dependent. The changes from $C_6D_5CD_3$ in which the OH signal is invariably at the highest field (δ = 4.56–5.13) to Me_2SO-d_6 or DMF-d_7 where the OH signal is at the lowest field (δ = 8.32–9.19) are substrate dependent. However, the effects of the solvents are proportional as shown by the linear plots of δ(OH) for **6** and **8**–**10** vs. δ(OH) of **7** (eq 2–5 and Figure 3).

$$\delta(\mathbf{6}) = -2.39 + 1.40\delta(\mathbf{7}) \quad (r = 0.986,\ \sigma = 0.29) \tag{2}$$

$$\delta(\mathbf{8}) = -0.44 + 1.10\delta(\mathbf{7}) \quad (r = 0.996,\ \sigma = 0.12) \tag{3}$$

$$\delta(\mathbf{9}) = -0.39 + 1.17\delta(\mathbf{7}) \quad (r = 0.994,\ \sigma = 0.15) \tag{4}$$

$$\delta(\mathbf{10}) = -1.02 + 1.13\delta(\mathbf{7}) \quad (r = 0.997,\ \sigma = 0.11) \tag{5}$$

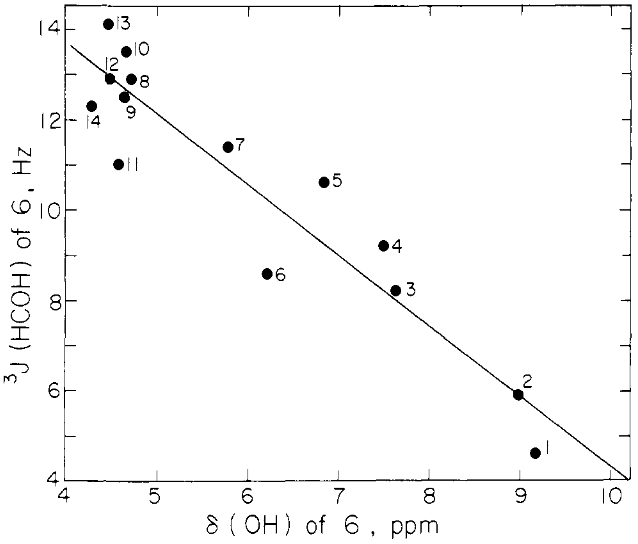


Figure 2. Plot of ^3J(HCOH) vs. δ(OH) for **6** in 14 solvents. The numbers of the solvents are those in Table I.

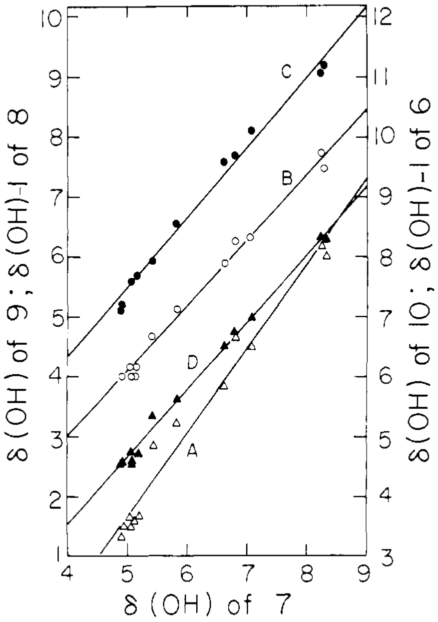


Figure 3. Plots of δ(OH) of **6** (A, △) and δ(OH) of **10**(D, ▲) (right scale) and of δ(OH) of **9** (C, ●) and δ(OH) of **8** (B, ○) (left scale) vs. δ(OH) of **7** in 13 solvents.

The response of the solvent as measured by the slopes is significantly higher for **6** than for the triarylethenols **8**–**10** which have similar slopes. Table II also gives the δ(OH) differences between three pairs of enols, $\Delta\delta_1 = \delta(\mathbf{7}) - \delta(\mathbf{10})$, $\Delta\delta_2 = \delta(\mathbf{8}) - \delta(\mathbf{10})$, and $\Delta\delta_3 = \delta(\mathbf{8}) - \delta(\mathbf{7})$. The $\Delta\delta_1$ values measure the change caused by replacing a β-mesityl by a β-phenyl group. They are low (0.05–0.11) in all the hydrogen bond accepting solvents[31] (CD_3CN excluded), but higher (0.31–0.53) in the non-hydrogen-bonded and chlorinated aliphatic solvents. The opposite is observed for a change from an α-phenyl to an α-mesityl group. The $\Delta\delta_3$ values are low (0.03–0.10) in the nonpolar solvents and higher in the hydrogen bond accepting solvents (0.17–0.45). The $\Delta\delta_2$ values which reflect the combined change from an α-phenyl to an α-mesityl and from a β-mesityl to a β-phenyl group are all relatively high.

The temperature effect on δ(OH) is solvent dependent. In $CDCl_3$ the effect is small. δ(OH) for **7** is 5.20 (293 K) and 5.27 (223 K); for **8**, 5.17 (293 K) and 5.28 (213 K); and for **10**, 4.72 (293 K) and 4.84 (213 K). In contrast, in CD_3COCD_3, when the temperature was reduced from 293 to 181 K, δ(OH) increased from 7.25 to 8.20 for **8**, from 7.70 to 8.58 for **9**, and from 6.77 to 7.79 for **10**. For **7** δ(OH) is 6.83 at 293 K and 7.35 at 220 K.

The relative change in ^3J(HCOH) values with the solvent is the largest known to us. Coupled with the IR data which show the presence of two species even in a single solvent,[10b] it suggests that the change reflects a conformational change. Moreover, in line with the IR data, the concurrent downfield shift in δ(OH) in the hydrogen bond accepting solvents tentatively suggests that one of the conformers is hydrogen bonded. The strongest tool for obtaining geometrical information on the conformers is the use of a Karplus-type equation,[32] provided that the change in ^3J(HCOH) is not due to a simple solvent effect on a single conformer. Indeed, in most cases[33–37] the solvent effect on J values, which is not due to conformational change, is negligible.[33–37] However, since few solvent-dependent values were found, caution should be exercised when using the values as a measure of a conformational change.[36]

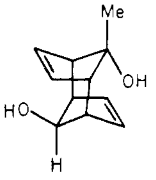
The use of ^3J(HCOH) as a conformational probe was suggested by Rader[38] and by Uebel and Goodwin,[39] and in many cases a smaller change in the ^3J(HCOH) values than in our case was used for conformational analysis.[40–43] E.g., the change in ^3J(HCOH) of nucleosides follow a solvent order similar to that of Table I, and was interpreted as due to the increase of population of the syn conformer.[42]

The existence of a Karplus-type relationship[32] between ^3J(HCOH) values and the H–C–O–H dihedral angle was suggested by several workers.[40,41,44,45] The equation mostly used is eq 6 of

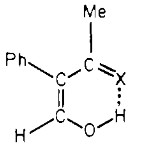
$$^3J(\mathrm{HCOH}) = 10.4 \cos^2 \theta - 1.5 \cos \theta + 0.2 \text{ (in Hz)} \quad (6)$$

Fraser and co-workers,[41] and its validity was recently "verified" by MO calculations.[45] A very slightly different equation was suggested by Stolow and Gallo.[40] It should be emphasized that the calibration of the parameters used molecules where an anti HCOH arrangement[46] (θ = 160–180°; ^3J = 10.5–12.5 Hz) was forced on the molecule by hydrogen bonding, MeOH (^3J = 5.7 Hz) for which a free rotation was assumed, and one compound with θ = 80° (^3J = 0.1 Hz),[41] and the geometries were mostly based on molecular models.

Equation 6 predicts a maximal ^3J(HCOH) value of 12.1 Hz for the planar syn enol conformer **1**. A literature search revealed many ^3J(HCOH) values of ca. 11–12.5 Hz in CCl_4 or $CDCl_3$ which are in line with an anti H-C-O-H arrangement.[46] Almost all of them involve hydrogen bonds of the hydroxylic proton to a π system,[47–50] an epoxide group,[51] an oxygen,[40,52–54] or an halogen.[55] Higher ^3J(HCOH)'s values were found for compounds **11** (13 Hz in $CDCl_3$),[47] **12** and **13** (13.3 Hz in $CDCl_3$),[56] and **14** (13.5 Hz in CCl_4).[57] This is not surprising since Fraser warned



11



12, R = OMe; X = O
13, R = OEt; X = O
14, R = SMe; X = S

that, "No accounts of changes of hybridization and electronegativity due to substituent effects have been made. . . the equation can probably predict ^3J(HCOH) to no better than 1 or 2 Hz."[41]

Although the average ^3J(HCCH) value decreases on increasing the electronegativity of a substituent attached to this fragment,[58] certain orientations of electronegative substituents relative to the coupled protons result in increase in ^3J(HCCH).[59–61] Moreover, ^3J(HCOH) for RCH_2OH increases on increasing the electronegativity of R.[43] Consequently, ^3J(HCOH) can be >12 Hz for the electron-withdrawing $=CR_2$ substituent in the enol conformer **1**. However, comparison of the Karplus plots for ^3J(HCCH=C) and ^3J(HCCH)[62a] suggests that a ^3J(HCOH) > 13 Hz could be used as very strong evidence for an almost planar anti arrangement of the H-C-O-H group, i.e., for conformer **1**.

Our ^3J(HCOH) value of 14.1 Hz in CCl_4 is the highest known, and the values in six solvents are ≥12.3 Hz. The previously observed highest values of 13.3–13.5 Hz are for compounds **12–14** which include the hydrogen-bonded, presumably planar, ArCX=CHOH fragment. The higher value for **6** in CCl_4 may be therefore due to the presence of two β-aryl groups. We conclude that the predominant conformer (98% according to the IR[10b]) in CCl_4 is a planar (or almost planar) conformer **1a**.[63]

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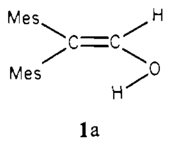
(63) The conformational analysis below, together with the IR results, may suggest that ^3J(HCOH) for pure **1a** is 14.3 Hz.



1a

Since only one OH signal is observed at room temperature, we assume that the decrease of ^3J(HCOH) in the other, especially hydrogen-bond accepting, solvents is due to a rapid equilibration on the NMR time scale of **1a** with a second conformer which has a much lower intrinsic ^3J(HCOH) value. The geometry of this conformer is much less clear than that of **1a**. It is reasonable that its ^3J(HCOH) is the lowest found, i.e., 4.6 Hz as in DMF. A simple analysis (see below) based on the assumption that the ^3J(HCOH) value for this conformer is solvent independent will give a 14:86 ratio of **1a** to this conformer in Me_2SO where ^3J(HCOH) = 5.9 Hz. However, this is inconsistent with the fact that ^3J(HCOH) in CCl_4-Me_2SO is solvent independent above 50% (v/v) Me_2SO (see below). We therefore conclude that the exact dihedral angle of this conformer may be solvent dependent.

The question as to whether this conformer is **2**, **4**, or **5** depends on the shape of the Karplus–Fraser plot. Equation 6 leads to four solutions for gauche-type conformers [(±sc)-**5**, (±ac)-**5**], and the resulting ambiguity "makes a discussion of the stereochemistry of the OH bond rather speculative".[64] Nevertheless, we exclude the (±sc) conformers for several reasons. They are sterically unfavorable to the hydrogen-bonding interaction which characterized this conformer as described below. They are inconsistent with the MM calculations on **10**,[19b] with the solid X-ray data of **9**·EtOH,[21] and with the previous analysis of the conformations of enols[20] and enol ethers discussed above. Only conformers **2**, **4**, and (±ac)-**5** are therefore considered.

The ^3J(HCOH) value of the planar anti form **2** should be 9.1 Hz according to eq 6. Although the electronegative Mes_2C= substituent may reduce this value, as found for X substituents which are trans coplanar to hydrogen in H–C–C–H fragments,[58] it is hardly expected to be reduced to 4.6, or even to 5.9 Hz, in view of the increase in the experimental ^3J(HCOH) for **6** for a 180° dihedral angle over the value calculated by eq 6. It is therefore more realistic to assume that the Fraser plot for our enols is shifted up compared with that for aliphatic alcohols. Its shape may remain the same and then the constant of eq 6 becomes 2.2, or the shape of the plot for ^3J(HCCH=C) is retained[62] and shifted up by 2.6 Hz since ^3J(HCCH=C) for θ = 180° is 11.5 Hz. Since the ^3J(HCOH) values for **2** will be 11.1 and 9.1 Hz, respectively, this structure for the second conformer is excluded by either treatment.

In analysis of aliphatic alcohols, ^3J(HCOH) values of 1.8–2.6 were observed or calculated for the gauche form.[42b,44b,55,65,66] The assumption that the Karplus-type plot for vinyl alcohol is shifted upward compared with Fraser's plot leads to ^3J(HCOH) values of 4.1 and 6.4 Hz for θ = 60°, respectively. Consequently, the most likely structure of the other conformer is an anti-clinal structure, (±)-**5**.

Stabilizing Interactions of 1a and 5. Role of the Solvent. Rodebush's IR data suggest that **1a** is stabilized by internal OH-π-mesityl hydrogen bonding.[10b] The discussion above of the ^3J(HCOH) values shows qualitatively that **5** is favored in hydrogen bond accepting solvents. These interactions were better understood by using three probes: Kamlet–Taft solvatochromic relationships, comparison of δ(OH) for **6**–**10** and related substrates, and IR studies.

Kamlet–Taft Solvatochromic Relationships. The general "solvatochromic equation" is eq 7,[31] whre XYZ is the property

$$XYZ = XYZ_0 + s(\pi^* + d\delta) + a\alpha + b\beta \qquad (7)$$

correlated (δ(OH) or ^3J(CHOH) in our case), XYZ_0 is a constant, and π^*, α, and β are measures of the solvent "dipolarity-polarizability", its hydrogen bond donating ability, and its hydrogen bond accepting ability, respectively. The polarizability correction term δ, is added in order to bring nonchlorinated aliphatic (δ = 0.0), polychlorinated aliphatic (δ = 0.5), and aromatic solvents (δ = 1.0) to the same scale. The *s*, *a*, *b*, and *sd* values are the responses of *XYZ* to these parameters. The π^* and β values are given in Table I.

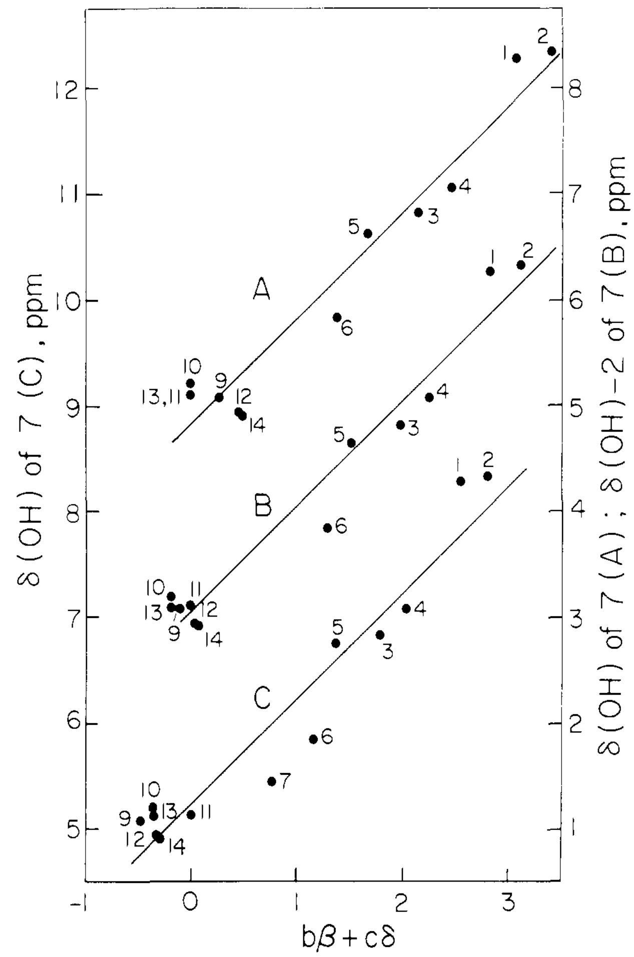


Figure 4. Plots of δ(OH) of **7** vs. combinations of solvatochromic parameters: (A) vs. β ($C_6D_5NO_2$ excluded, right scale); (B) vs. β and δ ($C_6D_5NO_2$ excluded, right scale); (C) vs. β and δ (all points, left scale). The numbers of the points are those of Table I and the best *b* and *c* values of the lines are given in Table III.

In a search for the best correlation of our extensive list of ^3J(HCOH) and δ(OH) values, we first correlated ^3J(HCOH) or δ(OH) with all the four parameters of eq 8 using the 14 solvents for **6** and the 13 solvents for **7**–**10**. The α term turned out to be usually insignificant,[67] and we tried five other correlations for each parameter: with π^*, β, δ; with π^*, β, α; with π^*, β; with β, δ; and with β alone. We judged the quality of the correlations by their correlation coefficients (*r*) and their standard deviations (σ) together with the number of variables used. If *r* and σ were improved only insignificantly when a parameter was dropped from the equation, the correlation applying a lower number of variables was considered to give a better fit. Plots of δ(OH) and ^3J(HCOH) vs. the β, π^*, and δ combinations showed that in most cases $C_6D_5NO_2$ deviates negatively and DMF deviates positively from the best line. This is demonstrated in Figure 4 for the enol **7** which shows that in spite of the good *r*'s there is scatter in the plots. The most significant deviation is of $C_6D_5NO_2$, and all the δ(OH) correlations for **6**–**10** were improved when this point was excluded (cf. Figure 4). This is also shown in Table III which gives a

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[67] When the δ parameter is dropped from the correlation, the response parameter to α, i.e., *a*, becomes significant (Table III). We attribute no mechanistic importance to this.

Table III. Selected Kamlet-Taft Correlations of NMR Parameters of Enols

compd	solvatochromic equation	n^a	r^b	σ^c	n^d	r^d	σ^d
6	$^3J(\text{HCOH}) = 12.49 + 5.09\alpha - 5.30\beta - 2.83\pi^* + 2.61\delta$	13	0.944	1.21	14	0.939	1.19
	$^3J(\text{HCOH}) = 12.88 - 2.19\alpha - 10.63\beta + 0.85\pi^*$	13	0.930	1.27	14	0.919	1.30
	$^3J(\text{HCOH}) = 12.97 - 10.04\beta + 0.25\pi^*$	13	0.928	1.22	14	0.911	1.30
	$^3J(\text{HCOH}) = 12.56 - 8.09\beta - 0.72\pi^* + 1.51\delta$	13	0.940	1.18	14	0.935	1.16
	$^3J(\text{HCOH}) = 12.32 - 8.66\beta + 1.29\delta$	13	0.938	1.13	14	0.934	1.12
	$^3J(\text{HCOH}) = 13.10 - 9.92\beta$	13	0.928	1.17	14	0.907	1.27
	$\delta(\text{OH}) = 4.56 - 0.40\alpha + 4.97\beta + 0.79\pi^* - 0.97\delta$	13	0.991	0.30	14	0.988	0.32
	$\delta(\text{OH}) = 4.42 + 2.30\alpha + 6.96\beta - 0.58\pi^*$	13	0.986	0.35	14	0.981	0.39
	$\delta(\text{OH}) = 4.31 + 6.34\beta + 0.05\pi^*$	13	0.980	0.35	14	0.969	0.47
	$\delta(\text{OH}) = 4.56 + 5.20\beta + 0.62\pi^* - 0.88\delta$	13	0.991	0.28	14	0.988	0.30
	$\delta(\text{OH}) = 4.76 + 5.69\beta - 0.69\delta$	13	0.988	0.30	14	0.986	0.31
	$\delta(\text{OH}) = 4.34 + 6.36\beta$	13	0.980	0.37	14	0.968	0.46
7	$\delta(\text{OH}) = 5.04 + 0.33\alpha + 4.23\beta - 0.08\pi^* - 0.32\delta$	12	0.979	0.33	13	0.967	0.39
	$\delta(\text{OH}) = 4.95 + 4.62\beta - 0.26\pi^*$	12	0.974	0.32	13	0.952	0.42
	$\delta(\text{OH}) = 5.06 + 4.10\beta - 0.37\delta$	12	0.979	0.29	13	0.967	0.35
	$\delta(\text{OH}) = 4.83 + 4.47\beta$	12	0.974	0.31	13	0.942	0.44
8	$\delta(\text{OH}) = 4.99 + 0.01\alpha + 4.41\beta + 0.24\pi - 0.43\delta$	12	0.985	0.31	13	0.975	0.38
	$\delta(\text{OH}) = 5.05 + 4.63\beta - 0.34\delta$	12	0.985	0.28	13	0.974	0.34
	$\delta(\text{OH}) = 5.11 + 4.29\beta - 0.38\delta$	11	0.988	0.22			
	$\delta(\text{OH}) = 4.84 + 4.98\beta$	12	0.981	0.29	13	0.956	0.42
9	$\delta(\text{OH}) = 5.65 - 0.05\alpha + 4.29\beta + 0.21\pi^* - 0.77\delta$	12	0.981	0.36	13	0.973	0.42
	$\delta(\text{OH}) = 5.69 + 4.50\beta - 0.69\delta$	12	0.981	0.32	13	0.973	0.37
	$\delta(\text{OH}) = 5.26 + 5.20\beta$	12	0.968	0.39	13	0.933	0.55
10	$\delta(\text{OH}) = 4.55 - 0.04\alpha + 4.67\beta + 0.17\pi^* - 0.37\delta$	12	0.986	0.31	13	0.977	0.37
	$\delta(\text{OH}) = 4.50 + 0.93\alpha + 5.45\beta - 0.38\pi^*$	12	0.985	0.30	13	0.973	0.38
	$\delta(\text{OH}) = 4.54 + 1.02\alpha + 5.22\beta - 0.41\pi^*$	11	0.985	0.27			
	$\delta(\text{OH}) = 4.55 + 4.69\beta + 0.15\pi^* - 0.36\delta$	12	0.986	0.29	13	0.977	0.35
	$\delta(\text{OH}) = 4.47 + 5.23\beta - 0.15\pi^*$	12	0.983	0.30	13	0.967	0.40
	$\delta(\text{OH}) = 4.59 + 4.83\beta - 0.31\delta$	12	0.986	0.27			
	$\delta(\text{OH}) = 4.40 + 5.14\beta$	12	0.983	0.28	13	0.961	0.41

[a] Number of points used for the correlation. For **6**: $n = 14$, all solvents of Table **I**; $n = 13$, all solvents excluding $C_6D_5NO_2$; $n = 12$, all solvents excluding $C_6D_5NO_2$ and DMF. For **7**-**10**: $n = 13$, all solvents of Table II; $n = 12$, all solvents excluding $C_6D_5NO_2$; $n = 11$, all solvents excluding $C_6D_5NO_2$ and DMF. [b] Correlation coefficient. [c] Standard deviation. [d] Parameters for correlations (not shown) with a larger number of points than for the equation shown. See footnote *a*.

selected list of the correlations, by comparison of the r and σ values for correlations with and without nitrobenzene. Correlations excluding C_6D_5Br or DMF or their combination with $C_6D_5NO_2$ were not improved significantly, except for a slight improvement for some correlations for **8** on excluding DMF, for **9** on excluding C_6D_5Br, or for **8** and **10** when both DMF and $C_6D_5NO_2$ were excluded.

Several conclusions emerge from Table III.

(a) Almost all the correlations with $\delta(\text{OH})$ are satisfactory according to the arbitrary criterion that $r > 0.95$ is satisfactory in a multiparameter equation.[68]

(b) Correlations with $^3J(\text{HCOH})$ of **6** are much poorer, as shown by the severe scatter of the four-parameter correlation in Figure 5. This may reflect the fact that almost half of the $^3J(\text{HCOH})$ values are close to the value in CCl_4, whereas their π^* values (but not the β values) change significantly.

(c) The most dominant factor in all the correlations is the hydrogen bond accepting ability of the solvent β; i.e., the b term is usually the largest response parameter. Correlations with β alone are improved by addition of the π^* or δ variables, and the best two-parameter correlations are always with β and δ, whereas correlations with β and π^* have lower r's and higher σ's. However, the improvement over the correlation with β alone is not dramatic as shown in Figure 4 for **7**, which is similar to the corresponding figures for all the other substrates. Consequently the best solvatochromic equations are

$$\delta(\text{OH}) = b\beta + c\delta + e \qquad (8)$$

$$^3J(\text{HCOH}) = b\beta + c\delta + e \qquad (9)$$

but eq 10 and, to a lower extent, eq 11 should also be considered.

$$\delta(\text{OH}) = b\beta + e \qquad (10)$$

$$^3J(\text{HCOH}) = b\beta + e \qquad (11)$$

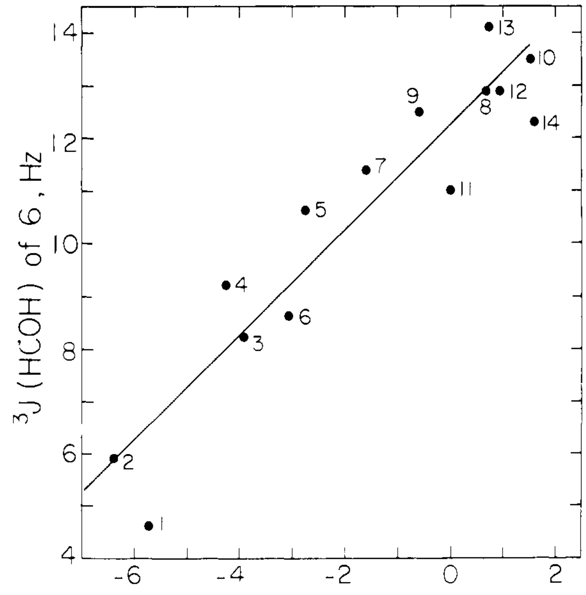

Figure 5. Plot of $^3J(\text{HCOH})$ of **6** vs. the complete solvatochromic equation (eq 7): $^3J(\text{HCOH}) = -4.85\beta + 5.05\alpha + 3.04\delta - 2.71\pi^* + 12.21$.

(d) In eq 8 and 10 all the b values are positive and all the c values are negative, but in eq 9 and 11 the b value is negative and the c value is positive. The structural dependence of the b, c, and e values is shown in Table IV for correlations according to eq 8-11 with and without $C_6D_5NO_2$.

(e) The dependence on δ (the correction to the π^* term) is unusual since it is difficult to visualize both a dependence on δ and an independence on π^*, and this was never observed previously.[31,69] The data of Tables III and IV and Figure 4 demon-

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(68) Kamlet, M. J.; Dickinson, C.; Taft, R. W. *J. Chem. Soc., Perkin Trans. 2* **1981**, 353.

strate how the correlation is changed when the dependence on δ disappears, and how the response parameter c (i.e., sd in eq 7) changes when nitrobenzene is excluded from the correlations. When the apparently significant c values of −0.3 to −0.4 for **7**, **8**, and **10** are neglected, the r's change very little, and we conclude that the dependence on δ may be either an artifact resulting from the fact that half of our solvents are polychlorinated aliphatic or aromatic solvents, or that it points to some specific interaction with some of the solvents. The only case of a positive sign of c is for the lowest energy band of $PhCH{=}C(CN)_2$. A specific interaction such as formation of multicomplexes with the aromatic solvents may be suggested in this and in our case.[70] The deviation of $C_6D_5NO_2$ may be relevant to this question since it may serve as an acceptor in interactions with both the aromatic and the OH groups.

(f) The large b values indicate that **5** is stabilized by a hydrogen-bonding interaction with the solvent. Hence the b values are expected to be larger for the more hydrogen-bonded systems. Table III shows that the order of the b values in the δ(OH) correlations is **6** > **9** > **10** > **8** > **7** (eq 10) or **6** > **10** > **8** > **9** > **7** (eq 8) which is the order expected for combination of steric and, to a lower extent, electronic effects. It is therefore not surprising that the b value for the α-unsubstituted enol **6** surpasses all the other b values.

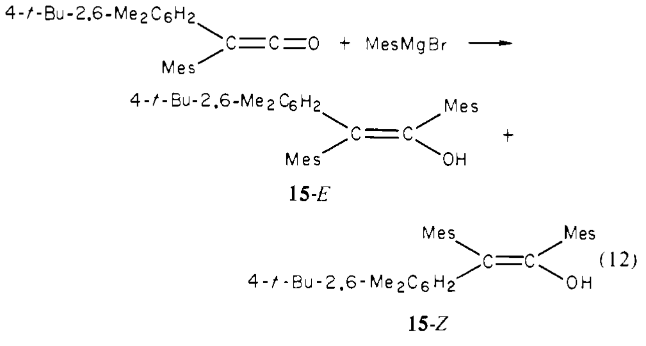
(g) Our b value for **6** is the largest, and the other b values are among the larger known to us in ^{1}H NMR correlations by LSER.[31,71] In the relevant linear solvatochromic relationships from the literature [$\delta(t\text{-BuOH}) = 1.17 + 0.74\pi^* + 3.14\beta$;[72] $\delta(\text{PhOH}) = 5.36 + 1.72\pi^* + 3.28\beta$[73]], the response to π^* and β is in the same direction with significant contribution from both parameters. The lack of dependence on the π^* term may be due to insulation of the non-hydrogen-bonding solvent molecules from the O–H bond as reflected by the s terms for PhOH and t-BuOH (see above),[71] and as observed in solvatochromic equations for UV and IR spectra.[31,74]

(h) Only a few solvatochromic correlations for J's are known.[71] $J(^{13}C^1H)$ for $CHCl_3$[75] and $J(^{119}Sn,C,^1H)$ and $J(^{119}Sn,C,^{19}F)$ values of Me_3SnCl and Me_3SnCF_3 and of other tin derivatives[76] were correlated successfully with β and π^* or with β, π^*, and δ. Both π^* and β affect the J's in the same direction and contribute significantly. However, a more significant chemical change occurs for these compounds, since the bonding of Sn to the solvent changes its valency.[76c] In our correlations the signs of b and c of eq 9 are opposite: J increases with the solvent polarity and decreases with its hydrogen bond accepting ability. We attribute this behavior to the role of the solvent in destroying the intramolecular OH–π bond at the expense of formation of new OH··· solvent bond. Since the OH–π bond is apparently weak, a good solvent is capable of an extreme conformational change, with an associated large change in J. Several precedents for a parallel large change in J are known.[37,42–44,54a,77] These should give a negative b in a solvatochromic correlation.

$\Delta\delta$(OH) Values of Isomeric Triarylethenols as Probes for the Geometry of the Two Conformers. The structures of the two conformers were deduced from the ^3J(HCOH) values and are therefore applicable only to the enol **6**. The rough correlation between ^3J(HCOH) and δ(OH) for **6** (Figure 2), the similarity of the Kamlet–Taft correlations for **6** with those for **7–10**, and the linear relationship between all the δ(OH) values (Figure 3) argue that similar conformations are also present for **7–10**. Nevertheless, it seems advisable to use the δ(OH) values for **7–10** for corroborating this conclusion and to distinguish at least between the (sc)- and the (ac)-type conformers.

The low $\Delta\delta_3$ values (Table II) in solvents with $\beta \sim 0$ and the higher values in hydrogen bond accepting solvents indicate that the molecular environment of the OH group is similar in the former solvents but different in the latter. This is consistent with a syn-type conformation when $\beta \sim 0$, since the closer neighbor of the OH proton is the *cis*-β-mesityl group, and mainly with an anti-type conformer in the strongly hydrogen bond accepting solvents where the OH group is closer to the α-aryl group which differs in **7** and in **8**. This argument is too simplified: for enols **7** and **10** which have α- and *cis*-β-mesityl groups the apparent molecular environment is similar in both conformers. The $\Delta\delta_1$ values in hydrogen bond accepting solvents are low, as expected, but the values are appreciable in solvents with $\beta \sim 0$. The remote aryl group therefore affects the $\Delta\delta$ values. We attribute it not to a different ring current effect, but to a change in the geometry of the *cis*-β-aryl group caused by the remote *trans*-β-aryl group, and this is corroborated by the different twist angles of the β-aryl groups in **7** and in **10**.[21] The complexity of the situation is reflected in the differences of δ(OH) of **9** and **7**. They are larger in the hydrogen bond accepting solvents, as expected since the α-aryl groups are both different and have different torsional angles,[21] but even in solvents where $\beta \sim 0$ the δ(OH)'s differ. This long-range effect of the α-aryl group may reflect different ring currents due to different torsional angles or an indirect effect on the geometry of the two β-aryl rings in the two substrates. This is also shown by the larger variation in δ(OH) of **9** in the six nonpolar solvents at the bottom of Table II. For **7**, **8**, **10**, and **9** the δ(OH) values are 5.07 ± 0.08, 5.06 ± 0.07, 4.64 ± 0.07, and 5.46 ± 0.20 ppm, respectively.

Because of this complexity, it seems advisable to compare pairs of substrates structurally as similar as possible. The pair of E,Z isomers 2-(4-*tert*-butyl-2,6-dimethylphenyl)-1,2-dimesitylethenols (**15**-E and **15**-Z) differ from **7** only by having a remote p-*tert*-butyl instead of a p-methyl group at the para position of one of the β rings. A mixture of the two isomers which was prepared according to eq 12 was therefore analyzed by NMR.[78] Indeed, the average position of δ(OH) for both isomers which display different OH signals is very close to δ(OH) of **7** (Table V). Both isomers give Kamlet–Taft correlations (eq 13–16)



15-E

(12)

15-Z

$$\delta(\text{OH},\mathbf{15}\text{-}E) = 3.77\beta - 0.40\delta + 5.13 \quad (13)$$

$$\delta(\text{OH},\mathbf{15}\text{-}E) = 4.21\beta + 4.87 \quad (14)$$

$$\delta(\text{OH},\mathbf{15}\text{-}Z) = 3.81\beta - 0.45\delta + 5.46 \quad (15)$$

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[70] We are indebted to Dr. M. J. Kamlet for this suggestion.

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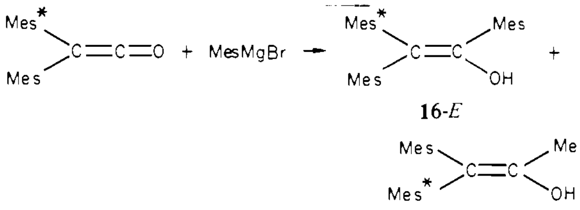
[78] The structure of the conformers was deduced by comparison of the NMR spectra with the corresponding acetates. The structure of one of the acetates is known from X-ray data (Biali, S. E.; Rappoport, Z., unpublished results).

$$\delta(\mathrm{OH},\mathbf{15}\text{-}Z) = 4.30\beta + 4.87 \qquad (16)$$

similar to those of **7**. Not surprisingly, the average $\Delta\delta_4 = \delta(\mathbf{15}\text{-}E)\text{-}\delta(\mathbf{15}\text{-}Z)$ values are smaller than the three $\Delta\delta$ values of Table II. Since the geometries of the two isomers are presumably identical, we expected that the main effect will be the different electron-donating ability of *t*-Bu compared with Me. This should be more predominant in a syn-type conformation, where the OH is close to the *cis*-β-aryl group, than in anti-type conformations where the OH group is remote from this ring. This expectation was fulfilled only partially. Although the $\Delta\delta_4$ values are on the average higher in solvents of high β's than in solvents of low β's, there are strong deviations (CD_3CN and $CDCl_3$). More importantly, the aromatic solvents show strong negative $\Delta\delta_4$ values, except for PhBr. The higher values are in those solvents where the differences were expected to be smaller. We conclude that either the long-range effect of the *trans*-β-aryl group is larger than the short-range effect of the *cis*-β-aryl group, or that the perturbations introduced by changing a Me to a *t*-Bu group are too large for a useful application of our model. The most likely effect is that the bulky *p*-*t*-Bu group affects the interaction of the aryl group to which it is attached with the solvent. This is reflected by the $\Delta\delta_4$ values of the aromatic solvents and emphasizes the fact that solvation of the aryl groups and their interaction with the solvent may be more important than assumed by dealing only with the OH···solvent interaction.

We therefore studied another pair of isomers where the perturbation is indeed minimal. Reaction of mesityl magnesium bromide with dimesitylketene, where one ring is labeled by deuterium at the three methyl groups (Mes* = 2,4,6-$(CD_3)_3C_6H_2$), gave a nearly 1:1 mixture of the isotopomers **16**-*E* and **16**-*Z* (eq 17).[79] In two different syntheses samples containing 86 and 98.4% methyl deuteration were obtained. Each sample showed two OH signals, and those of the more deuterated compound were sharper.[80] The separation of the two OH peaks ($\Delta\delta_5$) was larger for the more deuterated sample, but the $\Delta\delta_5$ values of both samples were roughly proportional. The data are given in Table V.



16-*E*

(17)

16-*Z*

As expected, the $\Delta\delta_5$ values are much lower than the $\Delta\delta_4$ values, being 0–10.4 ppb.[81] Their relative error is larger than for other $\Delta\delta$ values, and we did not attempt to correlate them with solvatochromic parameters. However, the two signals merge in the hydrogen bond accepting solvents CD_3SOCD_3, CD_3COCD_3, and CD_3CN to a singlet, i.e., $\Delta\delta_5 = 0$. In contrast, in the six solvents with $\beta \sim 0$, the two signals are well separated with $\Delta\delta_5 = 9.1 \pm 1.5$ ppb.

These results are consistent with the predominance of a syn-type conformer in the nonpolar solvents and with a significant contribution of an anti-type conformer in the hydrogen bond accepting solvents. The differential effect of the β' ring (Mes and Mes*) on the OH signal is expected to be small and to fall steeply with the distance between the *cis*-aryl group and the OH proton. That $\Delta\delta_5 \neq 0$ in nonpolar solvents suggests that the OH proton is very close to the *cis*-β-mesityl ring, i.e., in a syn conformation. This requirement for a close contact between the groups is more consistent with the planar conformer **1** than with other conformers. Regardless of the origin of the effect, which may be electronic, due to a better electron-donating ability of the labeled ring, or steric, since the smaller bulk of CD_3 compared with CH_3 will be reflected in a minor geometrical change,[82] the effect on a remote group should be minimal. Hence, the other conformer may be either (±ac)-**5** or (±ap)-**5**. We believe that the solvent effect on $\Delta\delta_5$ values is the strongest evidence for the geometry of the two conformers of triarylethenols.

Table IV. Parameters of the Solvatochromic Equations $XYZ = b\beta + c\delta + e$ and $XYZ = b\beta + e$

		13 points			12 points		
compd	*XYZ*	*b*	*c*	*e*	*b*	*c*	*e*
6[a]	^3J(HCOH)	−8.13	1.74	12.09	−8.66	1.29	12.32
		−9.65		13.18	−9.92		13.10
	δ(OH)	5.46	−0.88	4.86	5.69	−0.69	4.76
		6.24		4.30	6.36		4.34
7	δ(OH)	3.71	−0.69	5.24	4.10	−0.37	5.06
		4.35		4.78	4.47		4.83
8	δ(OH)	4.24	−0.67	5.23	4.63	−0.34	5.05
		4.86		4.79	4.98		4.84
9	δ(OH)	4.11	−1.02	5.87	4.50	−0.69	5.69
		5.05		5.20	5.20		5.26
10	δ(OH)	4.45	−0.62	4.76	4.83	−0.31	4.59
		5.03		4.35	5.14		4.40

[a] 14-point correlations.

Intramolecular Stabilization of the Syn Conformers 1 by OH···π(Ar) Bonding. IR Studies. An early IR study of **6**, **7**, and **10** in CCl_4 revealed two OH peaks: a strong one at 3510 cm^{-1} and a weaker one around 3620 cm^{-1}.[10b] It was suggested that these are due to two conformers. The conformer with the higher wavenumber has a free OH group and should have an anti-type structure which is favored on steric grounds. The other conformer has an OH group directed as in **1** and it absorbs at a lower wavenumber. The latter is in a large excess, as judged by the relative intensity of the two bands, and its lower energy "can only be explained by postulating a considerable attraction between the hydrogen atom and some adjacent position in the molecule".[10b] This interaction can be identified with an OH···π(Ar) interaction to which many precedents are available.[83-85] Ōki and Iwamura[84] observed two ν_{OH} bands in many systems and ascribed the band with lower ν_{OH} value to internally OH···π(Ar) and OH···π(C=C) bound forms. The existence of intramolecular OH···π(C=C) bonding was confirmed recently by crystallography,[86] photoelectron spectroscopy,[50,87,88] and MO calculations.[89] The distribution of free and bound OH conformers was analyzed.[84h,90]

The advantage of a syn-type conformation is not necessarily due to OH···π(C=C) or OH···π(Ar) bonding. Repulsion between the oxygen lone-pair orbitals and the aromatic π cloud are avoided in this conformation.[91] It was recently suggested that this effect is dominant and that it is not necessary to invoke intramolecular hydrogen bonding when the NMR data are not supported by IR data.[92]

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(79) The slight deviation from a 1:1 ratio is ascribed to a steric isotope effect and will be discussed elsewhere.

(80) Incomplete deuteration amounts to the formation of d_8 and d_7 species together with the d_9 species. The pure species with lower extent of deuteration (e.g., the d_8 compound) would show smaller $\Delta\delta_5$ values, thus increasing the width of the peak of the major d_9 species.

(81) ppb: part per billion. 1000 ppb = 1 ppm.

(82) A more detailed discussion of the possible sources of this effect will be given in a future publication.

(83) For a recent reference dealing with conformational analysis of intramolecular hydrogen-bonded compounds by IR spectrsocopy, see: Aaron, H. S. In *Top. Stereochem.* **1979**, *11*, 1.

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Table V. Solvent Effect on δ(OH) and on $\Delta\delta$(OH) of Isomeric Triarylethenols

solvent	δ(OH), ppm **15**-*E*	δ(OH), ppm **15**-*Z*	$\Delta\delta_4$,[a] ppb	δ(OH), ppm[b] **16**-*E* + **16**-*Z*	$\Delta\delta_5$, ppb[c] 98.4% d_9-**16**	$\Delta\delta_5$, ppb[c] 86% d_9-**16**
CD_3SOCD_3	8.38	8.30	77	8.34	0	0
CD_3COCD_3	6.87	6.83	34	6.83	0	0
THF-d_8	7.15	7.10	48			
dioxane-d_8	6.71	6.65	60			
CD_3CN	5.85	5.845	4	5.84	0	0
$C_6D_5NO_2$	5.40	5.48	−81	5.47	5.9	5.2
C_6D_5Br	5.08	5.08	0	5.08	9.1	7.8
$CDCl_3$	5.27	5.20	74	5.20	7.2	6.7
C_6D_{12}	5.13	5.13	0	5.11	8.0	4.9
C_6D_6	4.92	4.95	−29	4.94	11.6	10.4
CCl_4	5.12	5.10	18	5.10	7.2	5.9
$C_6D_5CD_3$	4.87	4.92	−48	4.90	10.4	9.8

[a] $\Delta\delta_4 = \delta$(**15**-*E*) − δ(**15**-*Z*). [b] Average δ(OH) value for **16**-*E* and **16**-*Z*. [c] $\Delta\delta_5 = \delta$(major isomer of **16**) − δ(minor isomer of **16**).

Table VI. IR Absorptions (in cm^{-1}) of Enols in the OH Region in Several Solvents[a]

enol	solvent CCl_4	$PhCH_3$	PhBr	$PhNO_2$[b]	MeCN	THF
6	3528 (s), 3628 (w)	3500 (s)	3500 (s), 3560 (w)	3500 (s), 3570 (sh, m)	3390 (s)	3270 (s)
7	3508 (s), 3585 (w)	3480 (s), 3520 (sh, w)	3480 (s), 3540 (w)	3480 (s), 3570 (m)	3410 (s)	3270 (s)
8	3508 (s), 3610 (w)	3500 (s)	3500 (s)	3500 (s), 3570 (m)	3400 (s)	3280 (s)
9	3490 (s), 3580 (w)	3470 (s), 3500 (w)	3480 (s), 3540 (w)	3480 (s), 3575 (m)	3380 (s)	3230 (s)
10	3490 (s), 3580 (w)	3480 (s), 3505 (sh, w)	3470 (s), 3540 (w)	3480 (s), 3560 (sh, m)	3400 (s)	3250 (s)
1:1 **16**-*E*/**16**-*Z*	3508 (s), 3585 (w)					

[a] Substrate concentration: 0.02 M. [b] An absorption at 3660 cm^{-1} was also observed (see text).

Table VII. F_{ac} and K Values for Enols in Several Solvents at 293 K[a]

	6				7		**8**		9		**10**	
solvent	F_{ac}[b]	K[b]	F_{ac}	K	F_{ac}	K	F_{ac}	K	F_{ac}	K	F_{ac}	K
CD_3SOCD_3	1.00		1.00		1.00		1.00		1.00		1.00	
CD_3COCD_3	0.72	2.57	0.71	2.46	0.56	1.27	0.64	1.80	0.63	1.70	0.59	1.45
THF-d_8	0.60	1.48	0.68	2.1	0.64	1.78	0.66	1.91	0.73	2.76	0.66	1.91
dioxane-d_8	0.43	0.74	0.54	1.17	0.51	1.04	0.54	1.18	0.61	1.54	0.53	1.12
CD_3CN	0.67	2.04	0.41	0.69	0.27	0.38	0.32	0.48	0.35	0.54	0.29	0.42
$C_6D_5NO_2$	0.33	0.44	0.32	0.46	0.16	0.19	0.20	0.24	0.19	0.24	0.21	0.27
C_6D_5Br	0.20	0.24	0.07	0.08	0.05	0.055	0.05	0.057	0.11	0.11	0.06	0.06
$CDCl_3$	0.07	0.079	0.08	0.08	0.09	0.096	0.05	0.057	0.14	0.16	0.04	0.045
C_6D_{12}	0.38	0.44	0.06	0.066	0.06	0.065	0.01	0	0.11	0.11	0.01	0.008
C_6D_6	0.15	0.17	0.04	0.042	0.01	0.010	0.01	0	0.01	0.015	0.01	0.014
CCl_4	0		0.04	0.037	0.06	0.064	0.01	0	0.11	0.11	0	0
$C_6D_5CD_3$	0.22	0.28	0	0	0	0	0	0	0	0	0	0

[a] Based on δ(OH). Calculated from eq 21 and 23. [b] Based on ^3J(HCOH). Calculated from eq 20 and 22.

In order to evaluate the hydrogen-bond interactions of both conformers, we studied briefly the IR spectra of **6–10** in several solvents. The data are in Table VI. We used CCl_4, PhBr, and $PhCH_3$ as solvents where hydrogen bonding to the solvent is expected to be minimal, and $PhNO_2$, MeCN, and THF as solvents where both solvent-associated and solvent-free conformers are apparently present, as judged by the NMR. The two ν_{OH} frequencies in CCl_4 are approximately in the positions and with the intensities reported previously,[10b] and for **6–10** the percentage of the isomer at the lowest ν_{OH} was 97–98%. The weaker absorption appeared at 3580–3628 cm^{-1} and the stronger absorption at 3490–3528 cm^{-1}, and both absorptions were the highest for **6**. Based on ^3J(HCOH) values these absorptions were attributed to the syn-planar and to the anti-clinal conformers, respectively. Since β of CCl_4 is 0,[31] the ν_{OH} at ca. 3600 cm^{-1}, which appears in the region associated with a free OH for PhOH,[62b] is that of the free (i.e., solvent unbound) anti-clinal conformer. The 80–100-cm^{-1} lower ν_{OH} for the other conformer can be therefore attributed to an OH group which is intramolecularly associated with the β'-mesityl group.

The spectra in $PhCH_3$, PhBr, and $PhNO_2$ also display a strong absorption at 3470–3500 cm^{-1} consistently lower than that in CCl_4 and a weaker absorption at 3505–3520 cm^{-1} in $PhCH_3$, at 3540–3560 cm^{-1} in PhBr, and at 3560–3575 cm^{-1} in $PhNO_2$. The latter absorption was weak in $PhCH_3$ and PhBr and in few cases it could not be observed, whereas the absorption in $PhNO_2$ was of medium intensity. Again, the stronger band is ascribed to internally hydrogen-bonded OH to the β'-mesityl ring, and the weaker band to the solvent-bound OH. The latter band is shifted to higher wavenumbers when the basicity of the aromatic solvent is reduced in the order $PhCH_3$ > PhBr > $PhNO_2$. This is due to a reduction in the hydrogen bond accepting ability and the slightly lower wavenumber for the intramolecular associated OH to the mesityl group, as compared with the intramolecularly bonded OH to $PhCH_3$, is consistent with this behavior. The average value of ν_{OH} for the intermolecularly bound OH to ArX (X = Me, Br, NO_2) follows the Hammett relationship: $\nu_{OH} = 3511 + 0.83\sigma_m$ (in cm^{-1}).

In $PhCH_3$ the two peaks were too close to enable a valuable comparison of their areas, but in PhBr and $PhNO_2$ the fraction of the anti-clinal conformer F_{ac} (see below and Table VII) could be evaluated from the relative areas, although the error in F_{ac} is rather large owing to overlap of the peaks. In PhBr, the average F_{ac} for **6**, **7**, **9**, and **10** is 0.06 ± 0.01 compared with $F_{ac} = 0.07 \pm 0.01$ from the δ(OH) values (Table VII). In $PhNO_2$ $F_{ac} = 0.22$ (**6**), 0.16 (**7**), 0.10 (**8**), 0.26 (**9**), and 0.15 (**10**), as compared with the values of 0.32 (**6**), 0.16 (**7**), 0.20 (**8**), 0.19 (**9**), and 0.21 (**10**) from the NMR (Table VII). We consider the agreement as

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(92) Abraham, R. J.; Bakke, J. M. Third European Symposium on Organic Chemistry (ESOC III), University of Kent, 5–9 Sept 1983; Abstr, p OA 3.

satisfactory in view of the error in the F_{ac} values obtained by the IR method.

Only a single wide band was observed in MeCN at 3390–3410 cm^{-1} (average half-width 140 cm^{-1}) and in THF at 3230–3270 cm^{-1} (average half-width 140 cm^{-1}). The extents of shifts are again consistent with the hydrogen bond accepting abilities of the solvents since β(THF) is the highest β of all the solvents studied. According to Table VII we expected to see an appreciable band for the intramolecular hydrogen-bonded conformer at ca. 3480 cm^{-1}, but this region is hidden under the very wide band of the intermolecularly bonded OH.

We conclude that the IR gives unequivocal evidence for the intramolecular OH–π(*cis*-β-mesityl) hydrogen-bonding interaction and to the intermolecular OH–solvent hydrogen bonding. The F_{ac} values obtained from the IR corroborate the conclusions concerning the conformer distributions from the NMR. The IR evidence for the OH–π(*cis*-β-aryl) bonding is important in view of the criticism directed to conclusions based on NMR alone,[92] and since in the solid state there is no indication for a very short bond between the OH and the *cis*-β-aryl group.[21]

Conformational Equilibria in Various Solvents. From the NMR data we calculated the conformational equilibria between the syn-planar and the anti-clinal conformers (eq 18). Three assumptions were used. First, the interconversion of the two conformers is fast on the NMR time scale since only one OH signal for all the compounds in all the solvents at room temperature was observed. Second, the observed ^3J(HCOH) and δ(OH) values are weighted averages of the values for the pure conformers (J_{ac} and J_{sp}) each multiplied by its population (i.e., eq 19, where F_{ac} is the fraction of the anti-clinal conformer). Third, the highest and lowest observed ^3J(HCOH) or δ(OH) values are equal to J_{sp} (or δ_{ac}) and J_{ac} (or δ_{sp}).

$$\text{syn-planar (sp)} \overset{K}{\rightleftharpoons} \text{anti-clinal (ac)} \qquad K = [\text{ac}]/[\text{sp}] \qquad (18)$$

$$^3J \text{ (or } \delta) = J_{sp}(1 - F_{ac}) + J_{ac}F_{ac} \qquad (19)$$

According to the second assumption, solvent effects other than those on the conformational equilibria are negligible. We noted that geometrical variations far away from the reaction center, such as twist of a remote aryl group or complexation of the aryl groups with aromatic solvents (reflected in the ASIS phenomenon[14b]), may change δ(OH) significantly. Nevertheless, since the observed changes in δ(OH) are large (Table II), we believe that approximate equilibrium constants could be obtained.

The third assumption is troublesome for two reasons. First, even in CCl$_4$ where ^3J(HCOH) is very high, the IR indicates the presence of 2% of the other conformer. Consequently, J_{sp} may be slightly higher than ^3J(HCOH, CCl$_4$), but this minor effect[63] was neglected. Second, ^3J(DMF) is significantly lower than ^3J(Me$_2$SO), although the evidence below from data in CCl$_4$–Me$_2$SO mixtures for conformational purity in Me$_2$SO is strong. This may reflect a slightly different C=C—O—H angle of the hydrogen-bonded ac conformer in the various solvents. The calculated gas-phase-energy differences for vinyl alcohol between the anti-planar (**2**) and the anti-clinal conformers, where $\theta = 150°$ or even 120°, are <0.5 and ca. 1.2 kcal mol^{-1}, respectively.[18c] These values are much lower than the energies of the hydrogen bonds to the good hydrogen-bond acceptors, and slight geometrical changes of these conformers in the various solvents are therefore possible. This will be reflected in the ^3J(HCOH) values which are much more sensitive to the dihedral angles than are the conformer energies. A similar problem is the substrate dependence of the relative order of δ[DMF-d_7] and δ[Me$_2$SO-d_6] (Table II). Moreover, in contrast to the behavior of the ^3J values, the lowest field δ(OH) value is in C$_6$D$_5$CD$_3$ rather than in CCl$_4$. These deviations may reflect the above-mentioned different C=C—O—H conformer angles, as well as the operation of the ASIS phenomenon in aromatic solvents.[14b]

In spite of these deficiencies, we calculated the fractions of the ac conformer and the equilibrium constants of eq 18 from the δ(OH) data for compounds **6–10** and from ^3J(HCOH) for **6** from eq 20–23, where J and δ are the ^3J(HCOH) and δ(OH) in the solvent of interest.

$$F_{ac} = [J - J(\text{CCl}_4)]/[J(\text{Me}_2\text{SO}) - J(\text{CCl}_4)] \qquad (20)$$

$$F_{ac} = [\delta - \delta(\text{C}_6\text{D}_5\text{CD}_3)]/[\delta(\text{Me}_2\text{SO}) - \delta(\text{C}_6\text{D}_5\text{CD}_3)] \qquad (21)$$

$$K = [J - J(\text{CCl}_4)]/[J(\text{Me}_2\text{SO}) - J] \qquad (22)$$

$$K = [\delta - \delta(\text{C}_6\text{D}_5\text{CD}_3)]/[\delta(\text{Me}_2\text{SO}) - \delta] \qquad (23)$$

The data are given in Table VII and lead to several conclusions. (a) The fraction of the ac conformer in solvents such as CD$_3$COCD$_3$, dioxane-d_8, THF-d_8, CD$_3$CN, and even C$_6$D$_5$NO$_2$ is appreciable. (b) The F_{ac} values for **6** which are based on ^3J(HCOH) and δ(OH) values do not differ much in most of the hydrogen bond accepting solvents (CD$_3$CN excluded). The values in the other solvents where F_{ac} is small contain a very large error and are unsuitable for comparison. The similarity of the values is very encouraging since it indicates that the limitations mentioned above are not very severe. Most important, it suggests that the F_{ac} values that are based on δ(OH) for **7–10** are reliable, in spite of the fact that the δ(OH) values do not give direct geometrical information. (c) Although the F_{ac} values are substrate dependent, they do not differ much in the solvents where they are more reliable. The values for **6** may be slightly higher than the others, but a change of the α substituent from H to Ph, to mesityl, or to 9-anthryl changes usually the percentage of the ac conformer within 15%. Consequently, the different geometries do not affect enormously the conformer distributions, suggesting that the dominant effects are the identical common interactions, i.e., the hydrogen bonding to the solvents and to the *cis*-β-mesityl ring.

The change in ^3J(HCOH) and the δ(OH) values with the temperature is associated, at least partially, with a change in F_{ac} and K. However, a quantitative analysis is possible only if the effect of the temperature on these parameters for the pure conformers is known. From literature data the effect seems to be small.[93,94]

For all our systems lowering the temperature reduced ^3J(HCOH) (Table I) and shifted the OH proton to a lower field. However, the significant result is that the effect is of a different magnitude in solvents where F_{ac} is small and large. In CDCl$_3$ where F_{ac} is small (ca. 0.08), a 70–80° temperature lowering changed ^3J(HCOH) of **6** by only 0.2 Hz and δ(OH) for **6–8** and **10** by only 0.12 ± 0.03 ppm. In contrast, the effect is much larger when F_{ac} is appreciable. ^3J(HCOH) for **6** changes by 0.8–0.9 Hz on 57–102° lowering in CD$_3$COCD$_3$ and CD$_3$CN, and δ(OH) for **6–10** in CD$_3$COCD$_3$ shifts by 1.02 ± 0.09 ppm. The temperature interval studied for Me$_2$SO-d_6 is much smaller, but qualitatively the effect is similar to that in acetone-d_6. We believe that this behavior is a further validation for the suggested hydrogen-bond interactions of the two conformers. The external hydrogen bonds to the solvent in the anti-clinal conformer are stronger (i.e., have higher $\Delta H°$ value) than the intramolecular OH⋯π(Ar) bond in the syn conformer. Consequently, the equilibria are shifted in the direction of the more stable conformer on reducing the temperature. The extent of the shift depends on the $\Delta\Delta H° = \Delta H°(\text{OH}\cdots\text{solvent}) - \Delta H°(OH\cdots\pi(\text{Ar}))$ values, and in CDCl$_3$, where $\beta = 0$ (i.e., negligible $\Delta H°$(OH⋯solvent), it is negligible and the main observed changes of ^3J(HCOH) and δ(OH) with the temperature are not due to a change in the conformational equilibria.

Equilibrium constants at the other temperatures could be calculated, but the calculations required assumptions concerning the similarity of the "intrinsic" effects in all the solvents and on the temperature dependence of these effects. Instead, we calculated approximate K's in CD$_3$COCD$_3$ at both 293 K and the other

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Table VIII. NMR Parameters and Derived Equilibrium Constants for **6** in Binary CCl_4–Me_2SO-d_6 Mixtures at 293 K[a]

Me_2SO-d_6, %[b]	[Me_2SO-d_6], M	^3J(HCOH), Hz	$F_{ac}(J)$[c]	$K(J)$[d]	$K_{ass}(J)$[e]	δ(OH), ppm	$F_{ac}(\delta)$[c]	$K(\delta)$[d]	$K_{ass}(\delta)$[f]
0	0	14.1	0	0	0	4.47	0	0	0
0.2	0.028	12.3	0.22	0.28	13.9	5.11	0.14	0.16	7.9
0.4	0.056	11.5	0.32	0.46	10.3	5.63	0.26	0.34	7.6
0.5	0.070	11.0	0.38	0.61	10.8	5.96	0.33	0.49	8.7
0.6	0.084	10.8	0.40	0.67	9.6	6.00	0.34	0.51	7.3
1	0.14	9.6	0.55	1.22	10.1	6.69	0.49	0.96	8.0
2	0.28	8.2	0.72	2.57	10.1	7.37	0.64	1.77	7.0
4	0.56	7.2	0.84	5.29	10.0	7.89	0.75	3.05	5.8
10	1.4	6.5	0.93	13.28	9.3	8.28	0.84	5.22	3.8
20	2.8	6.2	0.96	26.02	9.4	8.52	0.89	8.27	3.0
40	5.6	6.0	0.99	82.33		8.73	0.94	15.21	2.7
60	8.4	6.0	0.99	82.33		8.82	0.96	22.89	
80	11.2	5.9	1.00	∞		8.93	0.98	55.75	
100	14.0	5.9	1.00	∞		9.01	1.00	∞	

[a] [**6**] = 0.0357 M. [b] Me_2SO-d_6, mL, completed to a volume of 100 mL by CCl_4. [c] Calculated from eq 26 or a similar equation in δ. [d] Calculated from eq 27 or a similar equation in δ. [e] Calculated from eq 28. [f] Calculated from eq 29.

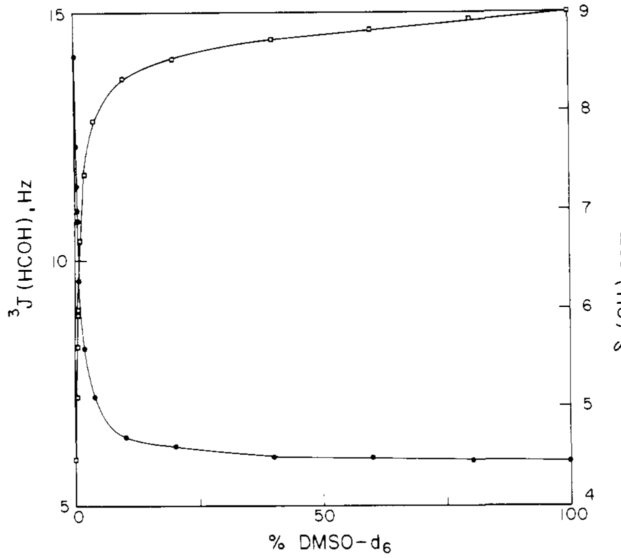


Figure 6. Plot of ^3J(HCOH) (left scale, ●) and δ(OH) (right scale, □) of **6** vs. % Me_2SO-d_6 in CCl_4–Me_2SO mixtures.

temperature by using the expression $K = [\delta - \delta(CDCl_3)]/[\delta(Me_2SO\text{-}d_6) - \delta]$.[95] The approximate $\Delta\Delta H°$ values calculated from these values are 1.2, 0.6, 0.9, 1.1, and 0.8 kcal mol^{-1} for **6–10**, respectively. The only qualitative conclusion is that the external hydrogen bond to acetone is ca. 1 kcal mol^{-1} stronger than the OH–π(Ar) bond.

^3J(HCOH) and δ(OH) Values in CCl_4–Me_2SO Mixtures. The use of a variety of pure solvents in our studies raised two questions. First, the number of solvent molecules involved in the hydrogen-bond interaction cannot be determined. Second, the geometry of the anti-clinal conformer may differ in the various solvents owing to the presence of the hydrogen-bonded solvent molecule. Consequently, the response of the ^3J(HCOH) and δ(OH) parameters to the conformer distributions may be different, and the derived F_{ac} and K values may not be the same. In order to evaluate these problems, we measured the ^3J(HCOH) and the δ(OH) values of **6** in binary CCl_4–Me_2SO mixtures. In this case only the conformers present in pure CCl_4 and pure Me_2SO will be present in equilibrium, and the problem of a possible variation in the geometry of the anti-clinal conformer does not arise.

The data are given in Table VIII, and their most characteristic feature is that a large change in both ^3J(HCOH) and δ(OH) results from addition of a relatively small molar concentration of Me_2SO to the CCl_4. Plots of ^3J(HCOH) and δ(OH) vs. [Me_2SO] (Figure 6) are very steep at low Me_2SO concentrations and approach a plateau at [Me_2SO] ~ 2 M. Even a 1% volume of Me_2SO in CCl_4 changes ^3J(HCOH) from 14.1 to 9.6 Hz, which amounts to 55% of the overall change between CCl_4 and Me_2SO. The corresponding change in δ(OH) is from 4.47 to 6.69 ppm, i.e., 49% of the overall change. Since the polarity change caused by 1% Me_2SO is minor, the observed effect substantiates the conclusion that the polarity effect (i.e., the π* dependence) is negligible. The interaction involved should be much more specific. It is important that the changes in the coupling constants are linearly related to the changes in the chemical shifts. This is shown in Figure 7 where $\Delta^3J(HCOH) = {}^3J(CCl_4) - {}^3J(CCl_4\text{–}Me_2SO)$ is plotted vs. $\Delta\delta = \delta(CCl_4\text{–}Me_2SO) - \delta(CCl_4)$.

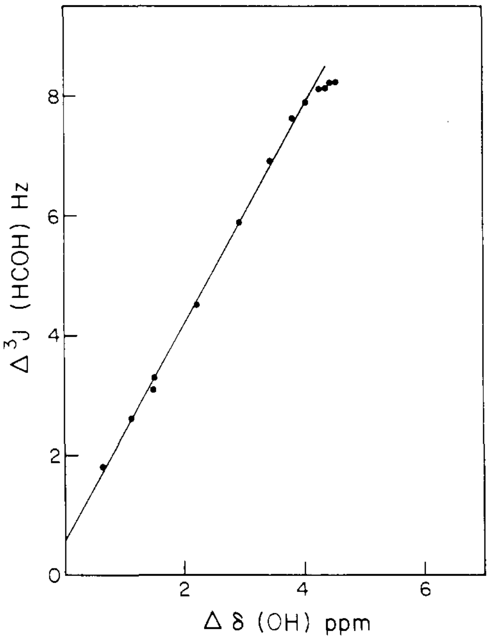
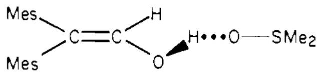


Figure 7. Plot of Δ^3J(HCOH) vs. Δδ(OH) of **6** in CCl_4–Me_2SO-d_6 mixtures.

The discussion above clearly demonstrates that the interaction involved is hydrogen bonding to the Me_2SO in the anti-clinal conformer. The simplest assumption is that only a single Me_2SO molecule is involved in this interaction; i.e., the anti-clinal conformer is the 1:1 hydrogen-bonded complex **17**.



$Mes_2C{=}CH{-}O{-}H\cdots O{-}SMe_2$

17

Since only a single OH absorption was observed in all the mixtures, we calculated the equilibrium constants between **1a** and

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[95] This is equivalent to the assumption that $F_{ac}(CDCl_3) = 0$ rather than 0.04–0.14 (Table VII). This assumption is sufficient if only approximate $\Delta\Delta H°$ values are required.

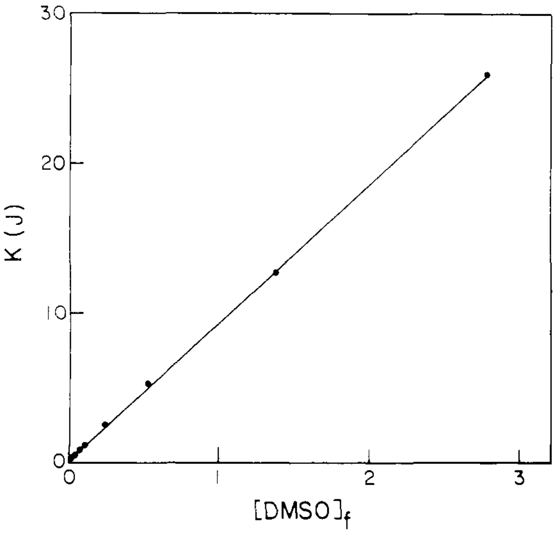


Figure 8. Plot of $K(J)$ vs. the molarity of nonassociated Me_2SO for **6** in CCl_4-Me_2SO-d_6 mixtures.

17 (K = [**17**]/[**1a**]; cf. eq 18) from eq 19. The association constant K_{ass} for the formation of **17**

$$\mathbf{6} + Me_2SO \xrightleftharpoons{K_{ass}} \mathbf{17} \qquad (24)$$

is given by

$$K_{ass} = [\mathbf{17}]/([\mathbf{1a}][Me_2SO]_f) = K/[Me_2SO]_f \qquad (25)$$

where $[Me_2SO]_f$ is the concentration of the nonassociated Me_2SO; i.e., $[Me_2SO]_f = [Me_2SO]_0 - [\mathbf{17}]$. The F_{ac} and the K values which are based on ^3J(HCOH), i.e., $F_{ac}(J)$ and $K(J)$ were calculated from eq 26 and 27, and the corresponding values, which

$$F_{ac}(J) = [J(CCl_4) - J(CCl_4\text{-}Me_2SO)]/[J(CCl_4) - J(Me_2SO)] \qquad (26)$$

$$K(J) = [J(CCl_4) - J(CCl_4\text{-}Me_2SO)]/[J(CCl_4\text{-}Me_2SO) - J(Me_2SO)] \qquad (27)$$

are based on δ(OH), i.e., $F_{ac}(\delta)$ and $K(\delta)$, were calculated from similar equations. By using the above equations and the relationship [**6**] = [**1a**] + [**17**], we obtained eq 28 and 29 for K_{ass}

$$K_{ass}(J) = K(J)/([Me_2SO]_0 - (K(J)/(K(J) + 1))[\mathbf{6}]) \qquad (28)$$

$$K_{ass}(\delta) = K(\delta)/([Me_2SO]_0 - (K(\delta)/(K(\delta)+ 1))[\mathbf{6}]) \qquad (29)$$

which is calculated from ^3J(HCOH) and δ(OH), respectively. The $F_{ac}(J)$, $F_{ac}(\delta)$, K(J), $K(\delta)$, $K_{ass}(J)$, and $K_{ass}(\delta)$ are given in Table VIII.

According to eq 25 a plot of $K(J)$ or $K(\delta)$ vs. $[Me_2SO]_f$ should be linear with a slope of K_{ass}. When the $K(J)$ values were plotted against $[Me_2SO]_f$ for the nine mixtures, where the errors in $K(J)$ are relatively small (when $[Me_2SO]_0 < 2.8$ M), an excellent linear relationship with a slope of 9.35 and an intercept of 0 ($r = 0.9993$) was obtained (Figure 8). This is strong evidence for our basic assumption, i.e., that only one Me_2SO molecule is involved in the hydrogen-bond interaction. However, the plot of $K(\delta)$ vs. $[Me_2SO]_f$ is not linear (Figure 9). This is not surprising since comparison of the $F_{ac}(J)$ and $K(J)$ values with $F_{ac}(\delta)$ and $K(\delta)$ values show differences between the parameters calculated by the two probes. Consistently the $F_{ac}(J)$ and $K(J)$ values are larger, and hence $K_{ass}(\delta) < K_{ass}(J)$. The difference is reflected in the constancy of $K_{ass}(J)$ values, whereas the $K_{ass}(\delta)$ values decrease strongly below 1 M Me_2SO. The $K_{ass}(\delta)$ value for 0.2-1 M Me_2SO is 7.9 ± 0.4, ca. 15% smaller than $K_{ass}(J)$. Hence, the better linearity in Figure 6 compared with Figure 1 is not completely reflected in the K values which are based on the two probes (Tables VII and VIII). Our feeling is that the ^3J(HCOH) values, at least in CCl_4-Me_2SO mixtures, are better probes than the δ(OH) values, since the latter involve long-range conformational effects as well as the assumption that the Me_4Si position is solvent independent. Although the differences in CCl_4-Me_2SO are not large, they emphasize the fact that, even when some of the difficulties mentioned above for various solvents are excluded by using binary mixtures, the two probes do not give identical results in analysis of conformational equilibria.[96]

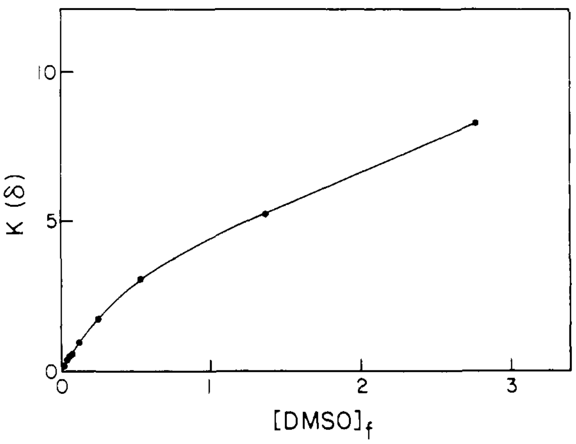
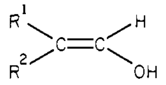


Figure 9. Plot of $K(\delta)$ vs. the molarity of nonassociated Me_2SO for **6** in CCl_4-Me_2SO-d_6 mixtures.

Comparison with Conformations of Other Enols. It is interesting to compare our structural conclusions with those of Capon and co-workers.[20] From the ^3J(HCOH) values given in the Introduction, it was concluded that in >99.5% acetone the enols **18a,b** exist predominantly in the syn (**1**) arrangement, while **18c,d** exist predominantly in the anti conformation. The Fraser equation[41] was not used, but the results were supported by ^4J(HCCOH) values. If the Fraser equation is used, it can be estimated that the syn isomer consists of, at most, 80% of the mixture of conformers for both **18a** and **18b**.



18

18a, $R^1 = R^2 = H$
b, $R^1 = Me$; $R^2 = H$
c, $R^1 = H$; $R^2 = Me$
d, $R^1 = R^2 = Me$

Consequently, there are two major differences between the results of the simple aliphatic enols **18** and the aryl-substituted enols **6**–**10**. We considered an equilibrium between syn-planar and anti-clinal conformations and an anti-periplanar structure was excluded. For the aliphatic enols both syn and anti conformations were assumed, although the ^3J(HCOH) values for **18c** and **18d** are more consistent, in our opinion, with a contribution of an anti-clinal structure. A more important difference is that the results for **18** were ascribed to a reduced contribution of the syn form for **18c** and **18d** due to steric interaction with the β-alkyl groups. However, the β-mesityl substituents of system **6** are bulkier than methyl groups, but nevertheless the syn conformer predominates in several solvents. Part of this may be a solvent effect since the ^3J(HCOH) value of 8.2 Hz for **6** in acetone should further decrease in aqueous acetone as judged by the J's in CCl_4-Me_2SO. Nevertheless, the value in acetone is still appreciably higher than those for **18c** and **18d**, indicating that the OH–π(Ar) stabilization and the O(lone pair)–π(Ar) destabilization more than compensate for the steric destabilization by bulky β substituents.

Another similarity with the behavior of enols **18** is that at higher temperatures the equilibrium is shifted in the direction of the less

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[96] (a) We note that in contrast with our results, the ^3J(HCOH) values for the enols of α-formyl cyclic ketones in CCl_4 give a linear relationship with the conformational equilibrium constants which are calculated from the chemical shifts.[54b] (b) ^3J(HCOH) for *syn*-2-hydroxyindan 3a,7a-oxide in *t*-BuOH–Me_2SO-d_6 mixtures shows both a first-order and a second-order dependence on the *t*-BuOH concentration.[77]

stable conformer.[20b] This effect is observable only when one conformer is not in a very large excess, and the decrease of ^3J(HCOH) values for **18a** and **18b** indicates that the syn conformer is in equilibrium with an appreciable amount of a second conformer. In contrast, the relative temperature insensitivity of ^3J(HCOH) of **6** in $CDCl_3$ is reminiscent of the similar insensitivity of ^3J(HCOH) for the hydrogen-bonded syn conformation of the enol **14** between −85 and 100°.[57]

Conclusions

The study of ^3J(HCOH) and δ(OH) values in several solvents for di- and triarylethenols, including isotopomeric pairs, the Kamlet–Taft correlations, an IR study, and a study of the NMR parameters in CCl_4–Me_2SO-d_6 mixtures led to the following conclusion. In nonpolar non-hydrogen-bond accepting solvents the conformation of the hydroxylic group is syn-planar, and it derives stabilization from a OH–π(Ar) interaction. In hydrogen bond accepting solvents, a second, anti-clinal conformer, hydrogen bonded to one solvent molecule, also exists. Both conformers are in a rapid equilibrium on the NMR time scale, and the anti-clinal conformer strongly predominates in solvents with high hydrogen bond accepting ability.

Experimental Section

^{1}H NMR spectra were recorded on a Bruker WH-300 pulsed FT spectrometer operating at 300.133 MHz. The free induction decay signals were digitized and accumulated on an Aspect 2000 computer (32K). IR spectra were recorded with a Nicolet MX-1 FT and a Perkin-Elmer 137G grating spectrometers. Mass spectra were measured on a MAT 311 instrument. Melting points are uncorrected.

Solvents and Materials. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl under nitrogen immediately before use. Acetonitrile and nitrobenzene were dried over P_2O_5 and distilled; the middle fractions were used. CCl_4 was dried over 4A molecular sieves. The deuterated NMR solvents were the best commercial samples and were used without further purification. **Mesitylene-*methyl-d*$_9$.** Mesitylene was deuterated in the three methyl groups by exchanging it two and three consecutive times, respectively, with 99.5% Me_2SO according to the literature procedure.[97] The two samples used for the further synthesis were 86 and 98.4% deuterated in the methyl groups (according to the 300-MHz ^{1}H NMR). Literature procedures were used for the preparation of the enols 7,[14b] **8**,[8b] 9,[14b] and **10**.[9b]

2,2-Dimesitylethenol (6). The enol was prepared by a slight modification of Fuson's work[9] which reduced dimesitylketene with *tert*-butylmagnesium bromide. Dimesitylketene (0.38 g, 1.36 mM), prepared by the modification described in ref 14b, was dissolved in dry THF (10 mL), and $LiAlH_4$ (75 mg) was slowly added. After the mixture was stirred for 1 h, 3 drops of water were carefully added in order to destroy the unreacted $LiAlH_4$. Anhydrous $MgSO_4$ (50 mg) was then added, the inorganic salts were filtered, and the filtrate was evaporated, giving **6** (160 mg). Addition of 3% HCl (10 mL) to the filtrate and extraction five times with ether (4-mL portions) yielded, after evaporation, an additional 100 mg of **6**. Recrystallization of the combined fractions from ethanol afforded 240 mg (62%) of pure **6**, mp 126 °C (lit.[9] 128–129 °C).

***(E,Z)*-2-(4-*tert*-Butyl-2,6-dimethylphenyl)-1,2-dimesitylethenols (15-*E* and 15-*Z*). (a) (4-*tert*-Butyl-2,6-dimethylphenyl)mesitylacetic Acid.** Mesitylglycolic acid[98] (2 g, 10.3 mM) was added to 1-*tert*-butyl-3,5-dimethylbenzene[99] (20 g, 123 mM), and the mixture was warmed to 70 °C with stirring. $SnCl_4$ (3.15 mL, 26.9 mM) was added dropwise during 15 min and the resulting red solution was kept at 60–70 °C for 16 h with stirring. The mixture was then poured on an ice–water mixture (20 mL) and extracted with ether (2 × 20 mL); the organic phase was extracted with an aqueous K_2CO_3 solution. On addition of hydrochloric acid, the substituted acetic acid (3.1 g, 89%), mp 188–193 °C, was separated. Two crystallizations from ethanol gave 2.8 g (80%) of pure acid, mp 200 °C: IR ν_{max}(Nujol) 1700 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$), δ 1.27 (9 H, s, *t*-Bu), 2.10 (6 H, s, *o*-Me), 2.15 (6 H, s, *o*-Me), 2.24 (3 H, s, *p*-Me), 5.34 (1 H, s, CH), 6.80 (2 H, s, Mes-H), 6.96 (2 H, s, Mes-H); mass spectrum *m/z* 338 (M, 28%), 293 (M − COOH, B).

Anal. Calcd for $C_{23}H_{30}O_2$: C, 81.61; H, 8.93. Found: C, 81.44; H, 8.76.

(b) 4-*tert*-Butyl-2,6-dimethylphenyl)mesitylketene. This ketene was prepared by adaptation of Fuson's method[9a] for the preparation of dimesitylketene. To a solution of (4-*tert*-butyl-2,6-dimethylphenyl)mesitylacetic acid (2.9 g, 5.92 mmol) in dry benzene (10 mL), thionyl chloride (0.5 mL, 6.95 mmol) was added and the solution was cooled to 5 °C. Pyridine (0.1 mL, 1.3 mmol) was added, and the solution was warmed (gas was evolved) and refluxed for 8 h. The liquid was decanted from the solid pyridinium hydrochloride and the solvent was evaporated, giving a yellow oil with strong absorption at 2100 cm^{-1}. The oil was used immediately for the next step.

(c) 15-*E*:15-*Z* Mixture. To a Grignard reagent which was prepared from bromomesitylene (2.55 g, 12.8 mmol) and magnesium (0.31 g, 12.8 mM) in dry THF (50 mL), the ketene of the previous step (ca. 2.7 g) in dry THF (40 mL) was added dropwise during 20 min. The dark red solution was refluxed for 3.5 h and then poured into a 5% aqueous solution of NH_4Cl in water (100 mL). The THF was evaporated, the remainder was extracted with ether (2 × 50 mL), and the organic phase was dried and evaporated. The green oil obtained was crystallized by dissolution in the minimal amount of warm ethanol and addition of petroleum ether to turbidity. The oily solid obtained (1.5 g) was recrystallized from ethanol giving 1.1 g (33%) of a 60:40 mixture of the 1:1 ethanol adduct of **15-*E*** and **15-*Z***, mp 105–111 °C. The composition of the mixture was determined from the relative intensities of the two *t*-Bu singlets in the ^{1}H NMR spectrum in $CDCl_3$. IR: ν_{max}(CCl_4) 3490 cm^{-1} (OH); ^{1}H NMR ($CDCl_3$) **15-*Z*** δ 1.30 (9 H, s, *t*-Bu), 1.81, 1.86, 1.88, 1.89, 2.14, 2.22, 2.44, 2.64 (8 × 3 H, 8 s, Me), 5.27 (1 H, s, OH), 6.60, 6.68 (2 × 1 H, s, Mes-H), 6.63 (2 H, s, Mes-H), 6.98, 7.18 (2 × 1 H, d, J = 1.9 Hz, Mes-H); **15-*E*** δ 1.19 (9 H, s, *t*-Bu), 1.84, 1.84, 1.85, 1.87, 2.22, 2.27, 2.44, 2.60 (8 × 3 H, 8 s, Me), 5.20 (1 H, s, OH), 6.60–6.63 (1 H, s, Mes-H covered by a **15-*Z*** signal), 6.73, 6.78 (2 × 1 H, d, J = 1.9 Hz, Mes-H), 6.81, 6.88, 7.03 (3 × 1 H, s, Mes-H); mass spectrum *m/z* 440 (B, M), 425 (9%, M − Me), 307 (3%, M − $MesCH_2$), 265 (11%, M − $CH_2C_6H_2Me_2Bu$-*t*).

Anal. Calcd for $C_{34}H_{46}O_2$ (**15**·EtOH): C, 83.90; H, 9.53. Found: C, 83.76; H, 9.35.

***(E,Z)*-2-(2,4,6-Trideuteriomethylphenyl)-1,2-dimesitylethenols (16-*E* and 16-*Z*). (a) 2,4,6-Trideuteriomethylphenyl(mesityl)acetic Acid.** The compound was prepared according to the literature procedure for the nonlabeled compound.[100] To a solution of mesitylglycolic acid (2 g, 10.3 mM) in acetic acid (15 mL), mesitylene-*methyl-d*$_9$ (1.5 mL, 15.2 mM) was added. After the mixture was cool in an ice bath, concentrated H_2SO_4 (10 mL) was added dropwise. The mixture was stirred for 1 week at 25 °C and poured on ice (100 g); the solid obtained was recrystallized from ethanol, giving 2.7 g (86%) of the acid, mp 193–194 °C (lit.[8b] for the unlabeled compound, 197–198 °C).

(b) 16-*E* + 16-*Z*. A ca. 1:1 mixture of **16-*E*** and **16-*Z*** was obtained by addition of mesitylmagnesium bromide in THF to the labeled ketene according to ref 14b.

Evaluation of the Coupling Constants. The coupling constants were read directly from the computer output. In the case that the values calculated for the OH proton and for the CH moiety differed (at most by 0.2 Hz), their average value was used.

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Registry No. 6, 54288-04-9; **6** (ketene), 87871-33-8; 7, 26905-20-4; **8**, 77787-80-5; 9, 80062-28-8; **10**, 77787-79-2; **15-*E***, 88180-86-3; **15-*Z***, 91110-62-2; **16-*E***, 88180-83-0; **16-*Z***, 88180-82-9; 4-*t*-Bu-2,6-Me_2-(Mes)C=C=O, 91110-64-4; MesBr, 576-83-0; Mes*(Mes)C=C=O, 91110-63-3; Mes*H, 15690-50-3; MesCH(OH)CO_2H, 20797-56-2; 1-*t*-Bu-3,5-$Me_2C_6H_3$, 98-19-1; 4-*t*-Bu-2,6-Me_2(Mes)$CHCO_2H$, 91110-65-5; Mes*(Mes)$CHCO_2H$, 91110-66-6.

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