Calculated pK_{Enol} Values for β,β-Diarylacetic Acids and β,β-Diarylacetaldehydes. Effect of Steric Bulk of Substituents on the Relative Stability of Enols of Carboxylic Acids and Aldehydes

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Abstract: The energies, pK_{Enol} values, structures, and conformations of vinyl alcohol (**3a**), acetaldehyde (**4a**), 1,1-ethenediol (**5a**), acetic acid (**6a**), and six derivatives of each (**3b**−**g, 4b**−**g, 5b**−**h**, and **6b**−**h**) substituted by two β-aryl groups of increasing bulk from Ph to Tip (2,4,6-tri-*i*-PrC_6H_2) were calculated by the B3LYP method in order to evaluate quantitatively the pK_{Enol} reducing effect of bulky aryl groups. Also calculated were the same parameters for the ArCHXCO_2H/ArC(X)═C(OH)$_2$ pairs for Ar = Ph, X = CN (**9a**/**9b**), OH (**10a**/**10b**), for which pK_{Enol} is known, and for Ar = Mes (mesityl), X = CN. All the substituents significantly decrease the pK_{Enol} values from 22.4 (**6a**/**5a**) and 9.1 (**4a**/**3a**). For example, pK_{Enol} = 0.2, −2.7, −2.0, and −2.7 for ArAr′CHCHO/ArAr′C═CHOH and 13.3, 11.5, 9.2, and 9.3 for ArAr′CHCO_2H/ArAr′C═C(OH)$_2$ when Ar,Ar′ = Ph,Ph, Ph,Mes, Mes,Mes, and Tip,Tip, respectively. For **9a**/**9b** and **10a**/**10b**, the calculated pK_{Enol} values resemble the observed ones. The enols and enediols (except **3b** and **5b**, when Ar$_2$C═ = fluorenylidene) have a propeller conformation. The Ar−C═C torsional angles increase with increasing bulk of the aryl group, but for Ph,bulkier Ar the Ar−C═C torsional angle strongly exceeds the Ph−C═C angle. The *syn*-C═C−O−H conformer is preferred over the *anti* conformer for all the enols **3**. For the 1,1-enediols, the *syn,syn* conformer is preferred for most Ar,Ar′ combinations, but the *syn,anti* conformer is preferred for **5a**, **5b**, **5h** (Ar = Ph, Ar′ = 2,4,6-(*t*-Bu)$_3C_6H_2$), and **10a**, and the *anti,anti* conformation is the least stable. The stabilization and conformational preferences were analyzed both qualitatively and with the aid of appropriate isodesmic reactions. Superposition of stabilizing Ar−C═C conjugation effects, stabilization of the carbonyl forms, and π(Ar)···O hydrogen bonding and destabilizing geminal Ar/Ar′ and vicinal *cis*-Ar/OH steric interactions account for the results. The low enol or enediol content is mainly due to the relative stabilization of the aldehyde or acid form, and the β-Ar groups stabilize the enols mainly by conformation-dependent Ar−C═C conjugation and π(Ar)···HO H-bonding.

$$\underset{\mathbf{2}}{R^1R^2CH\overset{O}{\overset{\|}{C}}X} \;\xrightleftharpoons{K_{\mathrm{Enol}}}\; \underset{\mathbf{1}}{R^1R^2C{=}C(OH)X} \qquad (1)$$

X = H, OH, OR, OCOR′, NR″R‴, Hal

Enols (**1**, X = H) of simple aldehydes are thermodynamically much less stable than their aldehyde tautomers (**2**, X = H).[1] For example, for acetaldehyde (**4a**)/vinyl alcohol (**3a**) and acetone/propen-2-ol, the pK_{Enol} (=−log K_{Enol}) values for eq 1 are 6.23 [2] and 8.33,[2,3] respectively. Nevertheless, these species were extensively investigated. Enols of simple carboxylic acids and their derivatives (**1**, X = OH, OR, OCOR′, NR″R‴, Hal) are also much less stable than their tautomeric acid counterparts (**2**, X = OH, OR, OCOR′, NR″R‴, Hal), but the energy differences between the tautomers are much higher than for the aldehyde/enol pairs.[4] Enols of carboxylic acids and their derivatives were suggested as intermediates in several reactions,[5] but *isolation* of the parent species $H_2C{=}C(OH)_2$ (**5a**), the tautomer of AcOH (**6a**), or its simple derivatives has not been achieved so far. Calculation of the relative stabilities of the parent species **1**/**2** ($R^1 = R^2 =$ H)[6,7] in terms of ΔG or pK_{Enol} values has shown that for X = OH, OR, NH_2, ΔG = 27−33 kcal/mol and pK_{Enol} = 19.5−24; i.e., the relative thermodynamic stabilities of **1**, X = OH, OR, OCOR′, NR″R‴, Hal, are very low. Despite this, several enols of carboxylic acids have been observed as short-lived intermediates. Wirz, Kresge, and coworkers[8] have obtained short-lived ketenes by flash photolysis, and hydration of these ketenes gave the short-lived enols of cyclopentadiene-5-carboxylic acid (**7**),[8a,b] indene-1-carboxylic acid (**8**),[8c] fluorene-9-carboxylic acid (**5b**),[8d] cyano(phenyl)acetic

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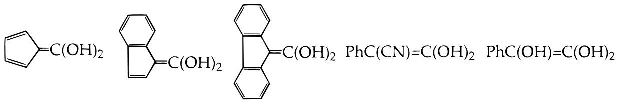
acid (**9a**),[8e] mandelic acid (**10a**),[8f,g] and benzothiophenecarboxylic acid.[8h] They were identified by the method of their formation and the acids formed from them by tautomerization but not directly, although their structures seem mostly unequivocal. Moreover, their pK_{Enol} values were determined. These values indicate that β-electron-withdrawal by a cyano or a cyclopentadienyl moiety significantly increases K_{Enol} values over those of the parent species.

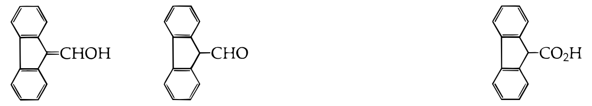


	7	**8**	**5b**	**9a**	**10a**
pK_{Enol}	8.4	9.3	9.7	7.2	16.2

The parent vinyl alcohol **3a** was isolated as a short-lived intermediate,[9] and other enols such as **3c** derived from diphenylacetaldehyde (**4c**) were observed by flash photolysis.[10] An approach made it possible to stabilize enols of aldehydes sufficiently as to make them observable is based on stabilizing them kinetically by bulky β-aryl substituents, as pioneered by Fuson.[11] This approach enabled observation of the fluorenylidene enol **3b**,[12] the mesityl-substituted enols **3d**−**f**,[13−15] and the ditipyl-substituted enol **3g**.[16] Enols **3b**,**d**−**g** are more stable than their aldehydes **4b**,**d**−**g**. Attempts to prepare isolable 2,2-diaryl-1,1-ethenediols on the basis of this approach led only to the *observation* of the enediols of dimesityl (**5e**),[17] ditipyl (**5g**),[18] mesityl tipyl (**5f**),[19] and bis(pentamethylphenyl) (**5i**)[17] acetic acids. The most stable of these, i.e., **5g**, which was observed and analyzed by NMR spectroscopy, can be retained for hours at −18 °C in THF.[18] However, in none of these cases is the pK_{Enol} value known. Although two mesityl or two tipyl substituents in acetaldehyde or acetone decrease pK_{Enol} by ca. 8 units,[16,20] this large effect is still insufficient to make enediols **5b**−**i** thermodynamically more stable than their isomeric acids **6b**−**i**.

The effect of resonatively β-electron-withdrawing groups (EWGs), such as CN or CO_2R, on decreasing pK_{Enol} values of carbonyl compounds is well known.[1] When such EWGs substitute a carboxylic acid derivative, its enediol can also become more stable than the “acid“ species due to the contribution of a dipolar hydrogen-bonded structure. This was observed, e.g., with the anilides of Meldrum acid (at C-5)[21] or of methyl cyanoacetate $(MeO_2C)CH(CN)CONHPh$[22] in the solid state. Compounds such as $RO_2CCH(Y)CONHPh$ (R = Me, Y = CO_2Me or R = Et, Y = NO_2) display signals in $CDCl_3$ for both the enolic and the acid species with K_{Enol} values of ca. 0.05.[21,22] Calculations indicated that several of these species are, indeed, more stable as the enediols or that the acid and the isomeric enediol species have comparable stability.[21,22]

3a	**4a**	**5a**	**6a**
$H_2C=CHOH$	$CH_3CH=O$	$H_2C=C(OH)_2$	CH_3COOH



3b **4b** **6b**

ArAr′C=CHOH	ArAr′CHCHO	ArAr′C=C(OH)$_2$	ArAr′CHCO$_2$H
3c: Ar=Ar′=Ph	**4c**: Ar=Ar′=Ph	**5c** : Ar=Ar′=Ph	**6c** : Ar=Ar′=Ph
3d: Ar=Ph; Ar′=Mes	**4d**: Ar=Ph; Ar′=Mes	**5d** : Ar=Ph; Ar′=Mes	**6d** : Ar=Ph; Ar′=Mes
3e: Ar=Ar′=Mes	**4e**: Ar=Ar′=Mes	**5e** : Ar=Ar′=Mes	**6e** : Ar=Ar′=Mes
3f: Ar=Mes; Ar′=Tip	**4f**: Ar=Mes; Ar′=Tip	**5f** : Ar=Mes; Ar′=Tip	**6f** : Ar=Mes;Ar′=Tip
3g: Ar=Ar′=Tip	**4g**: Ar=Ar′=Tip	**5g**: Ar=Ar′=Tip	**6g** : Ar=Ar′=Tip
		5h : Ar=Ph; Ar′=Sup	**6h**: Ar=Ph; Ar′=Sup
		5i : Ar=Ar′=C_6Me_5	**6i** : Ar=Ar′=C_6Me_5

Mes = mesityl = 2,4,6-$Me_3C_6H_2$; Tip = tipyl = 2,4,6-(*i* -Pr)$_3C_6H_2$;

Sup = supermesityl = 2,4,6-(*t*-Bu)$_3C_6H_2$

In the present work, calculations on several aldehydes and carboxylic acids and their isomeric enols or enediols were performed with several goals: (i) To evaluate the extent by which the B3LYP method reproduces the data on several of the systems for which pK_{Enol} values in water (for the acids) or in hexane (for the aldehydes) were experimentally determined. We hoped that this would enable us to predict within several units the pK_{Enol} values for systems for which experimental data are unknown, thus directing future synthetic work to systems where the enols and especially enediols could be isolated or at least easily detected. (ii) To calculate systematically the effect of two β-aryl substituents of increasing bulk on pK_{Enol} values of both the aldehydes and acids in order to assess the limits of the approach of increasing the thermodynamic stability of 1,1-enediols and ethenols by using β,β-di(bulky)aryl substituents. (iii) To compare the effect of the β-aryl substituents on pK_{Enol} values in the aldehyde and the acid series. (iv) To evaluate, at least in one case, the effect of a combination of one bulky aromatic substituent and one EWG on pK_{Enol} and to see if both approaches for stabilizing the enol species will enforce one another. (v) To dissect by various isodesmic reactions the effect of the substituents mentioned above to the separate contributions of species **1** and **2** to the change in pK_{Enol} values.

Results

Systems Studied. The energies, pK_{Enol} values, structures, and conformations of 11 pairs of enediol/acid, **1**/**2** (X = OH),

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isomers were calculated. These include the parent 1,1-ethenediol/AcOH (**5a**/**6a**) which was previously calculated,[6,23] six noncyclic β,β-diarylacetic acids with a systematic increase in the formal bulk of the aryl groups, i.e., diphenyl (**5c**/**6c**), mesityl phenyl (**5d**/**6d**), dimesityl (**5e**/**6e**), mesityl tipyl (**5f**/**6f**), ditipyl (**5g**/**6g**), and phenyl supermesityl (**5h**/**6h**) acetic acids and the cyclic fluorenyl system (**5b**/**6b**), which differs from the diphenyl-substituted system by the planarity constraint. For both systems, as well as for the β-phenyl-β-cyano (**9a**/**9b**) and the β-phenyl-β-hydroxy (**10a**/**10b**) systems, the pK_{Enol} values in water were experimentally determined. Also calculated are the parameters for the β-cyano-β-mesityl system (**11a**/**11b**), which differs from system **9** in the bulk of the aryl group. These systems make it possible for us to investigate the main goals stated above.

$PhCH(X)CO_2H$	$MesC(CN){=}C(OH)_2$	$MesCH(CN)CO_2H$
9b: X = CN **10b**: X = OH	**11a**	**11b**

Calculation Methods. The acid, aldehyde, enol, and enediol were calculated for each system first by the ab initio HF/3-21G method, and all optimized structures including higher energy conformers were verified by means of their Hessian matrixes to be local minima on the potential energy surfaces. These structures were then reoptimized by the hybrid density functional B3LYP/6-31G** method.[24] Structures determined at the B3LYP level showed the same geometrical characteristics as those at the HF level. The B3LYP/6-31G** method was extensively used in recent calculations of enols of carboxylic acid derivatives **1**/**2** ($R^1 = R^2 = H$) with changing X and for the cyclopentadiene-5-carboxylic acid/enol **7** system.[6] At the B3LYP level of theory, the frequency calculations were too demanding for larger molecules and could be carried out only for systems **5a**, **6a**, **9a**, and **10a**. However, the calculated electronic energy (ΔE) and free energy (ΔG) differences between **1** and **2** at B3LYP/6-31G** agree within 0.5 kcal/mol for each of these systems, and therefore we will use below the electronic energy differences. The absolute energies of the various compounds, including those used to construct the isodesmic reactions (eqs 2−13), are given in Table S1 of the Supporting Information. The energy differences between the acids and their 1,1-enediol isomers are given in terms of ΔE (in kcal/mol) in Table 1 and between the aldehydes and the isomeric ethenols in Table 2. Optimized structures are illustrated in Figure 1 and in Figure S1 of the Supporting Information, and corresponding selected geometrical parameters are listed in Tables 3, 4, and S2.

Table 1. Calculated B3LYP/6-31G** Energy Differences (ΔE in kcal/mol) between the Acid and the Enediol, and pK_{Enol} Values for the Different Systems

R^1,R^2 in **1**/**2**	compds	torsional angles[a]	E_{conj} (enediol)[b]	ΔE = [E(enediol) − E(acid)]	pK_{Enol}
H,H	**5a**/**6a**			30.5	22.4
Flu[c]	**5b**/**6b**	6.6, 9.9	8.8	15.4	11.3
Ph,Ph	**5c**/**6c**	44.7, 44.7	4.5	18.2	13.3
Ph,Mes	**5d**/**6d**	37.0, 69.3	3.5	15.7	11.5
Mes,Mes	**5e**/**6e**	56.0, 56.0	3.0	12.6	9.2
Mes,Tip	**5f**/**6f**	53.2, 62.3	2.8	12.8	9.4
Tip,Tip	**5g**/**6g**	57.0, 57.0	2.7	12.7	9.3
Ph,Sup	**5h**/**6h**	7.0, 88.8	4.4	9.9	7.3
Ph,CN	**9a**/**9b**	42.6	2.4	10.9	8.0
Ph,OH	**10a**/**10b**	14.8	4.2	21.8	16.0
Mes,CN	**11a**/**11b**	71.6	0.5	10.0	7.3

[a] ArC═C and Ar′C═C torsional angles (in degrees) of enediols calculated at the B3LYP/6-31G** level. [b] The sum of the Ar—C═C conjugation energy (in kcal/mol) of the two Ar groups calculated according to $E(\theta) = [E_0(1 + \cos 2\theta)]/2$,[37] where $E_0 = 4.5$ kcal/mol for Ph[34] and 4.8 for Mes,[35] Tip, or Sup. [c] $R^1R^2C{=} = $ 9-fluorenylidene.

Table 2. Calculated B3LYP/6-31G** Energy Differences (ΔE in kcal/mol) between the Aldehyde and Its Enol, and pK_{Enol} Values for the Different Systems

R^1,R^2 in **1**/**2**	compd	torsional angle in **3**[a]	E_{conj} of **3**[b]	ΔE = [E(**3**) − E(**4**)]	pK_{Enol}
H,H	**3a**/**4a**			12.3	9.1
Flu[c]	**3b**/**4b**	4.2, 7.2	8.9	2.2	1.6
Ph,Ph	**3c**/**4c**	36.7, 48.2	4.9	0.2	0.2
Ph,Mes	**3d**/**4d**	29.3, 72.0	3.9	−3.7	−2.7
Mes,Mes	**3e**/**4e**	50.2, 58.9	3.2	−2.8	−2.0
Mes,Tip	**3f**/**4f**	57.0, 53.8	3.1	−3.7	−2.8
Tip,Tip	**3g**/**4g**	51.0, 61.4	3.0	−3.6	−2.7

[a] ArC═C and Ar′C═C torsional angles (in degree) of enols calculated at B3LYP/6-31G**. [b] The sum of the Ar—C═C conjugation energy (in kcal/mol) of the two Ar groups calculated according to $E(\theta) = [E_0(1 + \cos 2\theta)]/2$,[37] where $E_0 = 4.5$ kcal/mol for Ph[34] and 4.8 for Mes, Tip,[35] or Sup. [c] $R^1R^2C{=} = $ 9-fluorenylidene.

Geometrical Features of β,β-Disubstituted Acids and Their Enediol Tautomers. (a) Acid Form. The following geometrical features arise from the calculations. (a) Two conformations were found for AcOH. In the more stable one (by 0.4 kcal/mol), the C═O bonds and a Me C—H bond are eclipsed, and in the second the C—OH and C—H bonds are in the same plane. (b) In acid **6b**, the conformer with nearly eclipsed O—H and C—H bonds is 0.1 kcal/mol more stable than that with eclipsed C═O and C—H bonds. (c) For other β-ArRCHCO$_2$H, the stable conformation is that with eclipsed O—H and C—H bonds. The more stable conformer (by 2.0 kcal/mol) of acid **10b** has the O—H and the C—H bonds almost in the same plane, and in the other conformer the O—H and β-C—OH bonds eclipse and a β-OH···α-OH hydrogen bond is possible. (d) In symmetrically disubstituted acids, the Ar_1—C_β—$C_{ipso(Ar_2)}$ and $C_{ipso(Ar_1)}$—C_β—Ar_2 torsional angles, measuring the degree of twist from the Ar_1(C-*ipso*)—C_β—Ar_2(C-*ipso*) plane, are 2.0°/2.2°, 63.7°/88.5°, 44.8°/67.8°, and 42.6°/67.2° for 9-fluorenyl (**6b**, Figure S1-a), Ph,Ph (**6c**), Mes,Mes (**6e**), and Tip,Tip (**6g**), respectively. (e) The two Ar—C—C bond angles are nearly identical (within 2°) for **6b** and **6c** and differ by 7−8° for all other acids. The angle for the bulkier aryl is smaller and close to the tetrahedral value (Table S2). Both angles for **6h** differ by only 1.1° and deviate by 5−6° from the tetrahedral value. The C—OH bond is perpendicular to the β-C—H bond, whereas the two bonds are nearly parallel in other diaryl-substituted acids. The Ar—C—C bond angles are close to tetrahedral in **9b** and **10b**. (f) The $C_\alpha(sp^2)$—$C_\beta(sp^3)$ bond lengths are as expected for AcOH and slightly longer (1.524−1.531 Å) for the β-diaryl-substituted systems. (g) The C_β—Ar bond lengths are long for C(sp^3)—C(sp^2) bonds, being 1.546−1.557 Å for the bulkier aryls in **6f**,**g**, but shorter for **6b**,**c**. Several conformers were observed for the acids having sterically hindered aromatic group such as Tip or Sup. For example, for **6f** (cf. Figure S1-b) the two conformers differ by 10.4 kcal/mol. The most stable conformation of **6h** is shown in Figure S1-c.

(b) Enediol Form. The three possible conformers as a function of the C═C—O—H dihedral angles are the symmetrical *syn,syn* and *anti,anti*, where the O−H bonds are *syn* (dihedral angles close to 0°) or *anti* (dihedral angles close to 180°),

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(23) (a) In several of the works referred to in ref 7, pK_{Enol} values of AcOH were calculated. (b) For a recent calculation on the **6a** → **5a** tautomerization, see: Sung, K. *J. Mol. Struct. (THEOCHEM)* **1999**, *468*, 105.

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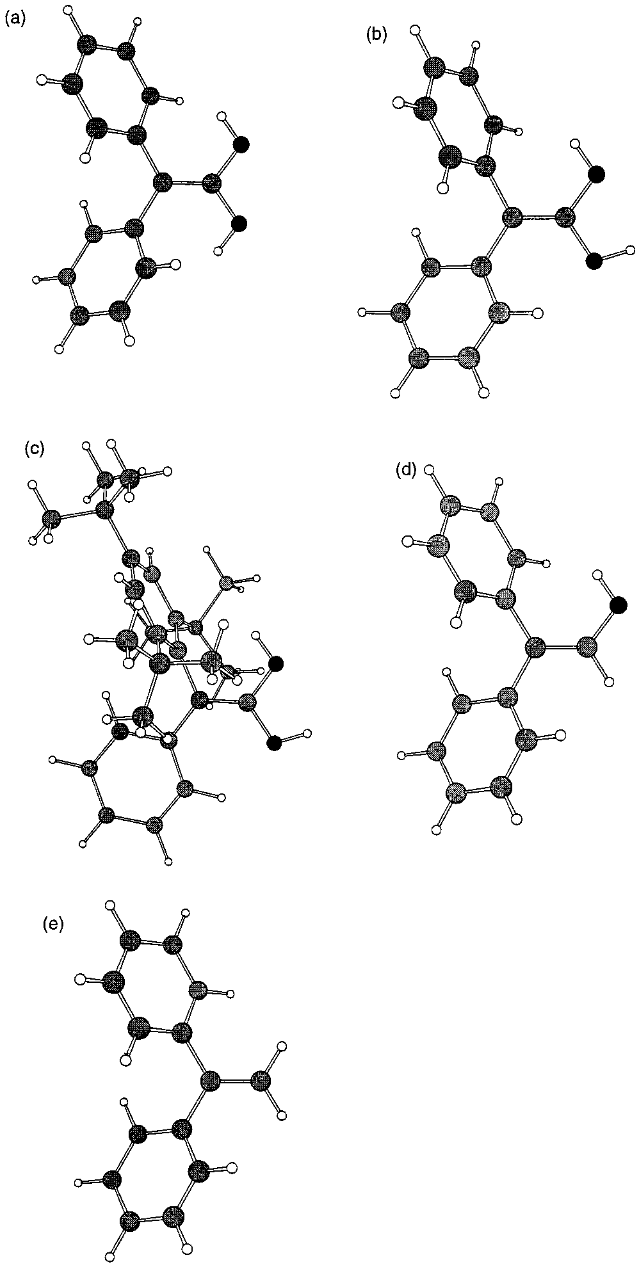
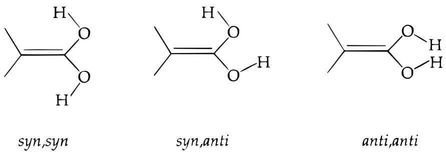


Figure 1. Optimized structures of representative ethene, enols, and 1,1-enediols: (a) *syn,syn-β,β*-diphenylethenediol **5c**, (b) *syn,anti-β,β*-diphenylethenediol **5c**, (c) *anti,syn-β,β*-phenyl(supermesityl)ethenediol **5h**, (d) *syn-β,β*-diphenylethenol **3c**, and (e) *β,β*-diphenylethene.

respectively, to the C═C bond and the asymmetrical *syn,anti* conformer. All three conformers were optimized as local minima



for **5a**−**c**, and the *syn,syn* and *syn,anti* conformers were determined for **5d**−**h**, **9a**, **10a**, and **11a**. No conformation with dihedral angles deviating significantly from 0° and 180° was observed. The energies of the conformers relative to the *syn,syn* conformer are given in Table 3.

Eight parameters are of interest. (a) The most stable conformer of 1,1-ethenediol **5a** is *syn,anti*, which is 1.2 and 2.8 kcal/mol more stable than the *syn,syn* and the *anti,anti* conformers, respectively. The preference for this conformer was previously revealed by MO calculations.[23b,25] In all other cases, except for **5b**,**h** and **10a**, the two $C{=}C_\alpha{-}OH$ dihedral angles are *syn* in the most stable conformation. For example, the *syn,syn* conformer for **5c** is more stable than the *syn,anti* and the *anti,anti* conformers by 1.0 and 6.7 kcal/mol, respectively (Figure 1a,b). With identical β-Ar groups, the molecule has a C_2 axis, and the geometries at the two β-substituents and the C═C−O−H dihedral angles are equivalent. However, when the β-aryl groups are different, the bond angle of the bulkier Ar group becomes smaller than that of the other aryl group, as seen for **5h** (Figure 1c).

The *syn,anti* conformer of **5b** is more stable than the *syn,syn* and *anti,anti* conformers by 1.6 and 3.6 kcal/mol, respectively. Similarly, for **10a** and **5h** $Ph(X)C{=}(OH)_2$ (X = OH, Sup), the torsional angles of the Ph ring are small, the OH *cis* to the Ph is in a less crowded environment in the *anti* conformation, and hence the *syn,anti* conformers become more stable than the *syn,syn* counterparts by 1.2 and 0.7 kcal/mol, respectively.

(b) Enediols **5c**−**h** have propeller conformations with the two aryl groups twisted in the same sense.[26] Several torsional angle relationships were observed (Table 1). The fluorenylidene system is nearly planar, with both angles <10°. For the symmetrical enediols **5c**,**e,g** both torsional angles are significant. For **5e**,**g** the torsional angles differ only slightly between the *syn,syn* and the *syn,anti* conformers, reflecting steric constraint on the angle in these bulky systems, but the difference is ca. 10° in the more flexible **5c**. For the Ph,bulkier Ar systems the Ph torsional angle is significantly smaller than that of the other aryl. A similar phenomenon was previously calculated for the β-Mes, β-Ph systems of a vinyl cation,[27a] a vinyl radical,[27b] and a ketene.[27a]

(c) The bond angles show subgroups similar to those of the torsional angles. The fluorenyl bond angles are the largest, which makes the internal angle in the five-membered ring 107°. For the symmetrical systems **5c**,**e**,**g** and the Mes,Tip system **5f**, the two angles are identical or similar in their most stable *syn,syn* form. For **5h** one angle is 125° and the other is ca. 9° smaller. (d) The $C_\alpha{-}C_\beta$ bond is longer in all diaryl systems than in the parent **5a**, but the values differ only by 0.011 Å between the extremes. (e) The C−O bond lengths are nearly constant at 1.347 Å for the *syn,syn* systems **5c**−**f**, but one bond is ca. 0.012 Å longer than the others in the *syn,anti* fluorenyl system **5b** and in **5g**,**h**. Most values are shorter than those in **5a**. (f) The two $C_\beta{-}Ar$ bond lengths are nearly identical in the symmetrical systems and differ by 0.03 Å in **5d**,**h**. (g) Several conformers were found to be minima for bulky-aryl-substituted enediols. The conformations of the tipyl-substituted systems **5f**,**g** resemble those of their acid isomers. However, for **5h**, a Me group of one *ortho t*-Bu substituent is directed toward the β-carbon rather than away from it (Figure 1c). (h) Another conformer in which the methyls of both *ortho-t*-Bu groups are directed away from the β-carbon is 0.8 kcal/mol less stable at the HF level.

Geometrical Features of the Aldehydes and the Ethenols. (a) Aldehydes. The $C_\alpha{-}C_\beta$ and C−OH bond lengths are normal and nearly constant. The R−C bond lengths increase from 1.521, 1.521 Å for **4b** to 1.543, 1.553 Å for **4g**. The $R^1{-}C{-}C$ and $R^2{-}C{-}C$ bond angles are nearly tetrahedral for **4a**,**b**, but they

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[26] For a discussion of the stereochemical behavior of polyarylvinyl propellers, see: Rappoport, Z.; Biali, S. E. *Acc. Chem. Res.* **1997**, *30*, 307.

[27] (a) Yamataka, H.; Alexiuk, O.; Biali, S. E.; Rappoport, Z. *J. Am. Chem. Soc.* **1996**, *118*, 12580. (b) Chen, X.; Yamataka, H.; Galli, C.; Rappoport, Z. *J. Chem. Soc., Perkin Trans. 2* **1999**, 1369.

Table 3. Relative Stabilities of and Selected Geometrical Parameters in Enediols **5**^{a}

R^1,R^2 in $R^1R^2C{=}C(OH)_2$	conformation/ relative stability^b	$R^1{-}C{=}C$/ $R^2{-}C{=}C$ bond angle	$R^1{-}C{=}C$/ $R^2{-}C{=}C$ torsional angle	$C(Ar_{ipso}){\cdots}HO$(*syn*) distance^c	$C{=}C{-}O{-}H$ dihedral angle	$R^1{-}C_\beta$/ $R^2{-}C_\beta$ length	$C_\alpha{-}C_\beta$ length	$C_\alpha{-}OH$/ $C_\alpha{-}OH$ length
H,H	*syn*^{d},*syn*^{e}/1.17	121.2/121.2			0.0/0.0	1.083/1.083	1.342	1.353/1.353
	syn,*anti*/0.00	121.0/120.0			0.0/180.0	1.082/1.080	1.337	1.366/1.352
	anti,*anti*/2.78	120.0/120.0			137.0/137.0	1.081/1.081	1.331	1.369/1.369
Ph,Ph	*syn*,*syn*/0.00	120.4/120.4	44.7/44.7	2.426/2.426	7.0/7.0	1.487/1.487	1.366	1.346/1.346
	syn,*anti*/0.99	118.2/122.7	52.0/34.5	2.375	3.0/−178.4	1.492/1.485	1.358	1.360/1.350
	anti,*anti*/6.70	121.0/121.0	44.0/44.0		135.5/135.5	1.492/1.492	1.351	1.369/1.369
Flu^f	*syn*,*syn*/1.56	126.6/126.6	3.1/3.1	2.643/2.643	19.3/19.3	1.469/1.469	1.365	1.342/1.342
	syn,*anti*/0.00	126.0/126.8	9.9/6.6	2.606	18.2/−169.7	1.469/1.470	1.358	1.343/1.355
	anti,*anti*/3.56	126.7/126.7	0.0/0.0		138.0/138.0	1.475/1.475	1.349	1.363/1.363
Mes,Mes	*syn*,*syn*/0.00	118.8/118.8	56.0/56.0	2.386/2.386	7.9/7.9	1.500/1.500	1.363	1.348/1.348
	syn,*anti*/1.35	117.7/120.5	57.4/55.5	2.362	7.5/−168.0	1.503/1.500	1.356	1.362/1.350
Tip,Tip	*syn*,*syn*/0.00	117.5/117.5	57.0/57.0	2.363/2.363	6.2/6.2	1.513/1.513	1.361	1.348/1.348
	syn,*anti*/1.16	116.3/120.0	59.7/55.4	2.337	6.7/−165.3	1.516/1.511	1.355	1.363/1.350
Ph,Mes	*syn*,*syn*/0.00	121.9/118.3	37.0/69.3	2.497/2.319	9.3/6.3	1.481/1.500	1.363	1.347/1.349
	anti,*syn*/0.28	125.8/114.9	0.0/89.9	2.216	180.0/0.3	1.479/1.507	1.357	1.350/1.362
Mes,Tip	*syn*,*syn*/0.00	118.5/117.8	53.2/60.3	2.400/2.355	7.4/7.0	1.502/1.511	1.363	1.348/1.348
	anti,*syn*/1.24	120.2/116.7	52.6/62.0	2.334	−167.5/6.9	1.500/1.513	1.355	1.350/1.362
Ph,OH	*syn*,*syn*/1.17	127.5/113.6	31.9	2.629	12.9/−0.9	1.462/1.411	1.358	1.347/1.343
	anti,*syn*/0.00	129.5/112.3	14.8		−169.7/2.9	1.461/1.412	1.354	1.349/1.355
Ph,CN	*syn*,*syn*/0.00	123.6/115.7	42.6	2.324	5.8/1.3	1.484/1.421	1.377	1.332/1.332
	anti,*syn*/0.05	127.9/112.6	9.8		−179.0/0.3	1.482/1.426	1.371	1.336/1.345
Ph,Sup	*syn*,*syn*/0.70	123.4/117.7	20.4/86.9	2.600/2.300	13.5/3.4	1.481/1.510	1.360	1.349/1.351
	anti,*syn*/0.00	125.0/115.6	7.0/88.8	2.241	0.8/−175.4	1.482/1.511	1.354	1.351/1.363
Mes,CN	*syn*,*syn*/0.00	121.5/116.7	71.6	2.374	3.8/0.6	1.498/1.419	1.371	1.335/1.333
	anti,*syn*/1.38	124.3/114.9	68.8		180.0/0.3	1.496/1.423	1.364	1.337/1.346

^{a} Angles are in degrees and distances in Å. ^{b} Relative stability in kcal/mol. ^{c} Ar = R^1. ^{d} Conformation of OH *cis* to R^1. ^{e} Conformation of OH *cis* to R^2. ^{f} $R^1R^2C{=}$ = 9-fluorenylidene.

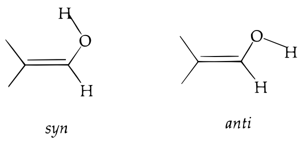
Table 4. Relative Stabilities and Selected Geometrical Parameters of Enols **3**^{a}

R^1,R^2 in $R^1R^2C{=}CHOH$	conformation/ relative stability^b	$R^1{-}C{=}C$/ $R^2{-}C{=}C$ bond angle	$R^1{-}C{=}C$/ $R^2{-}C{=}C$ torsional angle	$C(Ar_{ipso}){\cdots}HO$(*syn*) distance^c	$C{=}C{-}O{-}H$ dihedral angle	$R^1{-}C_\beta/R^2{-}C_\beta$ length	$C_\alpha{-}C_\beta$ length	$C_\alpha{-}OH$ length
H,H	*syn*/0.00	122.4/120.2			0.3	1.087/1.083	1.334	1.362
	anti/0.26	121.4/120.0			180.0	1.084/1.082	1.331	1.369
Ph,Ph	*syn*/0.00	121.0/119.4	48.2/36.7	2.482	4.5	1.490/1.485	1.353	1.357
	anti/3.52	123.6/117.0	35.5/43.9		179.6	1.487/1.491	1.350	1.367
Flu^d	*syn*/0.00	129.3/124.3	7.2/−4.2	2.700	10.0	1.475/1.476	1.351	1.351
	anti/0.13	128.7/124.9	0.0/0.0		180.0	1.472/1.476	1.347	1.361
Ph,Mes	*syn*/0.00	120.9/119.2	29.3/72.0	2.376	4.2	1.483/1.502	1.349	1.359
	anti/4.24	119.4/121.2	32.6/70.0		174.8	1.483/1.500	1.346	1.368
Mes,Mes	*syn*/0.00	119.0/118.7	58.9/50.2	2.411	5.4	1.500/1.503	1.351	1.359
	anti/3.95	121.4/117.2	57.2/52.7		175.8	1.500/1.505	1.347	1.368
Mes,Tip	*syn*/0.00	118.9/118.0	57.0/53.8	2.417	5.5	1.505/1.508	1.351	1.360
	anti/3.83	121.0/116.7	55.7/55.7		174.6	1.503/1.511	1.347	1.369
Tip,Tip	*syn*/0.00	117.9/117.9	61.4/51.0	2.380	4.3	1.511/1.515	1.350	1.360
	anti/3.73	121.0/116.4	59.4/53.9		171.0	1.513/1.514	1.346	1.368

^{a} Angles are in degrees and distances in Å. ^{b} In kcal/mol. ^{c} Ar = R^1. ^{d} $R^1R^2C{=}$ = 9-fluorenylidene

differ from tetrahedral for other compounds (except for **4e**) by 2.3−10°. **4g** adopts a conformation in which the four *o*-*i*-Pr methine H's are nearly on the top of the aromatic plane directed toward the *β*-carbon (Figure S1-d). Another conformer (Figure S1-e) is 10.8 kcal/mol less stable.

(b) Ethenols. Four features are of interest. (i) Ethenols can take two conformations of the C═C−O−H moiety, i.e., with *syn* and *anti* OH bonds with respect to the double bond. The calculated minimum energy conformers are *syn*- and *anti*-planar, with the C═C−O−H dihedral angles of 0.3−5.5° for the *syn* (10° for enol **3b**) and 174.6−180° for the *anti* conformer. The *syn* conformers of **3a** and other enols were previously calculated to be the most stable.[28,29] The data in Table 4 indicate that for **3a** and for the six *β*,*β*-diarylethenols investigated, the *syn* conformer is preferred. This preference is low for **3a** and negligible (0.1 kcal/mol) for **3b**, but it is 3.5−4.2 kcal/mol for the other enols. These results are attributed to a significant contribution of a π(Ar)$\cdots$OH hydrogen bond interaction, which is absent in **3a**,**b**. The OH$\cdots$C(Ar_{ipso}) distances of 2.38−2.48 Å are consistent with this deduction.



(ii) The torsional angles of the *β*-Ar groups differ, and the angle is larger for the group located *cis* to the α-OH group. Except for **3b**, these angles are mainly due to the Ar/Ar′ interaction in the ArAr′C═ moiety, as shown by the calculated angles for $Ar_2C{=}CH_2$ system given below (Figure 1d,e).

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Table 5. Energies (ΔE, kcal/mol) for the Isodesmic Reactions 2−13 and the Enolization of Aldehydes (Eq 1, X = H) at B3LYP/6-31G**

R^1,R^2	eq 2	eq 3	eq 4	eq 5	eq 6	eq 7	eq 8	eq 9	eq 10	eq 11	eq 12	eq 13	eq 1, X = H
H, H	0.0	2.8	0.0	0.0	0.0	0.0	0.0	21.0	0.0	0.0	0.0	18.2	12.3
Ph, Ph	−0.2	2.9	−0.2	11.3	11.5	−1.0	−12.3	20.9	−12.5	−12.1	−12.3	18.0	0.2
Flu[a]	−1.0	6.4	1.6	13.1	11.5	−2.0	−11.2	19.6	−13.5	−10.2	−15.2	13.2	2.2
Mes, Mes	1.5	2.6	2.8	19.7	16.9	1.8	−13.6	18.0	−15.1	−15.1	−17.9	15.4	−2.8
Tip,Tip	0.6	2.3	0.6	21.0	20.5	3.2	−15.4	18.6	−17.3	−16.0	−17.8	16.4	−3.6
Ph,Mes	1.8	0.6	1.4	15.3	13.9	0.4	−14.2	19.9	−13.5	−16.0	−14.9	19.4	−3.7
Mes,Tip	1.2	2.1	1.8	20.1	18.3	2.3	−14.9	18.7	−16.0	−16.1	−17.8	16.5	−3.7
Ph,OH	−1.4	2.6	−3.0	9.1	12.1	0.4	−9.7	20.4	−11.8	−18.3	−8.7	17.8	4.0
Ph,CN	2.9	1.8	4.8	14.2	9.4	−5.4	−12.4	15.7	−14.9	−15.4	−19.7	13.9	−3.0
Mes,CN	4.2	1.6	7.3	17.3	10.0	−3.3	−12.4	15.9	−13.3	−16.6	−20.6	14.3	−4.3

[a] $R^1R^2C{=}$ = fluorenylidene in species **3** and **5** and R^1R^2C = fluorenyl in species **4** and **6**.

(iii) All the β,β-diaryl ethenediols, except for **3b**, have a propeller conformation, in which the two aryl groups are twisted in the same direction.[26]

(iv) The Ar−C_β bond and torsional angles increase slightly with the increase in the bulk of the aryl group.

Isodesmic Reactions. Analysis of the substituent effects of the β,β-disubstituted systems is aided by calculation of the isodesmic reactions 2−13 at the B3LYP/6-31G** level for 10 sets of β-substituents. This required the calculations of the structures and energies of the corresponding $Ar_2C{=}CH_2$ systems. Symmetrical 1,1-diarylethenes have a C_2 symmetry axis, and we calculated torsional angles of 0.0°, 38.7°, 53.5°, and 54.7° for 9-methylenefluorene and for $Ar_2C{=}CH_2$, Ar = Ph, Mes, and Tip, respectively. For unsymmetrically substituted Ar(Mes)$C{=}CH_2$ the torsional angle is larger for the bulkier Ar group: 27.0°,77.2° for Ar = Ph and 50.8°,57.4° for Ar = Tip. It is noteworthy that in Sup$CH{=}CH_2$ the Sup group is perfectly perpendicular to the plane of the double bond at the HF level. The results of the isodesmic reactions are given in Table 5.

$$R^1R^2C{=}CHOH + H_2C{=}CH_2 \rightleftharpoons R^1R^2C{=}CH_2 + H_2C{=}CHOH \quad (2)$$

$$R^1R^2C{=}C(OH)_2 + R^1R^2C{=}CH_2 \rightleftharpoons 2R^1R^2C{=}CHOH \quad (3)$$

$$R^1R^2C{=}C(OH)_2 + H_2C{=}CH_2 \rightleftharpoons R^1R^2C{=}CH_2 + H_2C{=}C(OH)_2 \quad (4)$$

$$R^1R^2C{=}C(OH)_2 + CH_3CH_3 \rightleftharpoons R^1R^2CHCH_3 + H_2C{=}C(OH)_2 \quad (5)$$

$$R^1R^2C{=}CH_2 + CH_3CH_3 \rightleftharpoons R^1R^2CHCH_3 + H_2C{=}CH_2 \quad (6)$$

$$R^1R^2CHCOOH + CH_3CH_3 \rightleftharpoons R^1R^2CHCH_3 + CH_3COOH \quad (7)$$

$$R^1R^2CHCHO + H_2C{=}CH_2 \rightleftharpoons R^1R^2C{=}CH_2 + CH_3CHO \quad (8)$$

$$R^1R^2CHCOOH + R^1R^2C{=}CH_2 \rightleftharpoons R^1R^2C{=}CHOH + R^1R^2CHCHO \quad (9)$$

$$R^1R^2CHCOOH + H_2C{=}CH_2 \rightleftharpoons R^1R^2C{=}CH_2 + CH_3COOH \quad (10)$$

$$R^1R^2CHCHO + H_2C{=}CHOH \rightleftharpoons R^1R^2C{=}CHOH + CH_3CHO \quad (11)$$

$$R^1R^2CHCOOH + H_2C{=}C(OH)_2 \rightleftharpoons R^1R^2C{=}C(OH)_2 + CH_3COOH \quad (12)$$

$$R^1R^2CHCOOH + R^1R^2C{=}CHOH \rightleftharpoons R^1R^2CHCHO + R^1R^2C{=}C(OH)_2 \quad (13)$$

Equations 2 and 8 evaluate the bis-β-substituent effect for the ethenols and their tautomeric aldehydes by transfer of the substituents into the sp^2-hybridized ethylene. Their sum is eq 11, which gives the substituent effect on the aldehyde/enol equilibrium compared with that for the parent **3a**/**4a** pair. The effect is much smaller and variable (−1.0 to +1.8 kcal/mol) for the enols (eq 2) than for the aldehydes (eq 8), where it is always negative (−11.2 to −15.4 kcal/mol). Consequently, the ΔE for the equilibria of eq 11 are all highly negative. Table 5 also includes data for the nonisodesmic aldehyde ⇌ enol equilibria (eq 1, X = H). Equations 4 and 10 are their analogues for evaluating the substituent effect on the 1,1-ethenediol/acetic acid equilibrium. Their sum is eq 12, for the acid/ethenediol equilibria compared with the **5a**/**6a** pair. Here again, the effect on the ethenediol (eq 4, $\Delta E = -0.2$ to -2.8 kcal/mol) is much smaller than that on the acids (eq 10, −12.5 to −17.3 kcal/mol), which are the main contributors to eq 12. Equations 3 and 9 compare the ethenols or aldehydes with the corresponding ethenediols and acids. Their sum (eq 13) gives the relative substituent effects in both series. The ΔE values of eq 3 are all positive, but mostly they are an order of magnitude (except for the fluorenylidene system) lower than the values of eq 9. Equations 5 and 7 are similar to eqs 4 and 10, but the substituent is transmitted here to the sp^3-hybridized ethane. Their sum gives again eq 12. Equation 6 measures the conjugation effect in the absence of hydroxy groups, i.e., the extent of preference of the aryl substituents to be attached to an sp^2 vs an sp^3 carbon.

Discussion

Ar−C=C Torsional and Bond Angles in the Ethenols and the Ethenediols. The Ar−C=C torsional angles in the ethenols (Tables 2 and 4) and the ethenediols (Tables 1 and 3) are significant. Except for **5b** and **3b**, they are mainly due to inherent Ar/Ar′ interaction in the ArAr′C= moiety, as shown by the small difference between the angles in ethenes, enediols, and enols $Ar_2C{=}CXX'$, X = X′ = H, OH and X = H, X′ = OH. Experimental X-ray data are available for three ethenols, for which the calculated angles are given in Table 4. For **3e** the observed torsional angles (average of four crystallographically different molecules) are 56.7° and 50.2° and the bond angles are 118.1° and 120.8°,[30] compared with calculated values of 58.9°, 50.2°, 119.0°, and 118.7°, respectively. For **3g**, the corresponding observed values are 54.4°, 58.9°, 116.6°, and 122.8°,[16] while the calculated values are 61.4°, 51.0°, 117.9°, and 117.9°, respectively. For **3d**, the values are 28.4°, 74.8°, 123.1°, and 116.2°,[31] and the calculated values are 29.3°, 72.0°, 120.9°, and 119.2°. The calculated angles in **3** for the aryl *cis* to the α-hydrogen are within ±4° of the range calculated for $Ar_2C{=}CH_2$. The torsional angle of the aryl *cis* to the OH increases by a moderate 5.4−9.5° over the value in $Ar_2C{=}CH_2$, but it decreases by 0.4−5.2° in the unsymmetrical systems. The calculated torsional angles of the enediols (X = OH) exceed those for the ethenes (X = H) by 6.0° (Ph,Ph), 2.5° (Mes,Mes), 2.3° (Tip,Tip), 10.0° and −7.9° (Ph,Mes), and 2.4° and 2.9° (Mes,Tip). Hence, the influence of one or two added α-OH groups on the geometry of the system is not large (see further discussion below). The maximum conjugation will be achieved if both Ar−C=C moieties will be planar. However, for steric reasons the two aryl groups cannot be mutually in the plane of the C=C bond and *ipso* carbons. The angle observed is due to a compromise between the opposing effects of Ar−C=C conjugation and steric effects. The symmetrical systems adopt nearly identical torsional angles, and the unsymmetrical ones respond differently to the Ar/Ar′ interaction. The conjugative stabilization of the bulkier and more electron-donating aryl group (Mes, Tip, Sup) at full planarity exceeds by only a fraction of a kilocalorie per mole the value for Ar=Ph, but when the bulky aryl is in the C=C plane, one of its *ortho*-substituents interacts sterically strongly with the geminal aryl group, even when its torsional angle is significant. In contrast, when the torsional angle of the smaller aryl ring is smaller and that of the bulkier aryl is larger, the Ar/Ar′ steric interaction is reduced. Consequently, this conformation is adopted, with differences in the calculated torsional angles of the *syn,syn* conformation of 32.3° (Ph,Mes), 66.5° (Ph,Sup), and 7.1° (Mes,Tip).

NMR and IR studies indicate π(Ar)···HO hydrogen bonding in β-Ar-substituted ethenols in nonpolar solvents,[32] and it should also exist in the gas phase. The interaction will be stronger the closer and more orthogonal are the π(Ar) system and the O−H bond. In the planar fluorenylidene system such a H bond is impossible, and in unsymmetrical systems it will be significant only with the closer aryl with the higher torsional angle. Indeed, due to the Ar−C=C bond angle being smaller when Ar is smaller than Ar′, the Ar′ ring in $ArAr'C{=}C(OH)_2$ is closer to the vicinal OH than the Ar ring. In a *syn* (to Ar′),*anti* (to Ar) conformation, the two torsional angles differ by 89.9° (Mes,Ph), 81.8° (Sup,Ph), and 9.4° (Mes,Tip) and the corresponding bond angles differ by 10.9°, 9.4°, and 3.5°, respectively. Caution should be exercised in deducing the presence of a H bond from such bond angle differences since to a large part such differences exists even in Ph(Mes)C=C=O (7.3°) or $Ph(Mes)C{=}C^+{-}Mes$ (3.2°).[27a] Nevertheless, the differences in the angles in the ethenediols suggest the presence of a stabilizing π(Ar)···HO hydrogen bond. The use of the π(Ar)···HO distance to confirm this conclusion is problematic, since this term is not easily defined, especially since the calculated rings show some deformation. In Tables 3 and 4, we arbitrarily used the Ar_{ipso-C}···HO distance as a parameter which we presume is parallel to other distances.

Calculated vs Observed pK_{Enol} Values. (a) 1,1-Ethenediols. The B3LYP/6-31G** pK_{Enol} values for the gas-phase equilibria of the three compounds investigated by Kresge[8d−g] are 1.6−0.2 pK_{Enol} units higher than the experimental values in water: 11.3, 8.0, and 16.0 for the enediols **5b**, **9a**, and **10a**, compared with the experimental 9.7, 7.2, and 16.2 values. A difference of <0.1 pK_{Enol} unit was calculated previously[6] for system **7**,[8a,b] but there is some question concerning the experimental value.[6] The calculated solvent effect on the parent system is small, being 0.8−1.6 kcal/mol at various levels of theory.[6,7b]

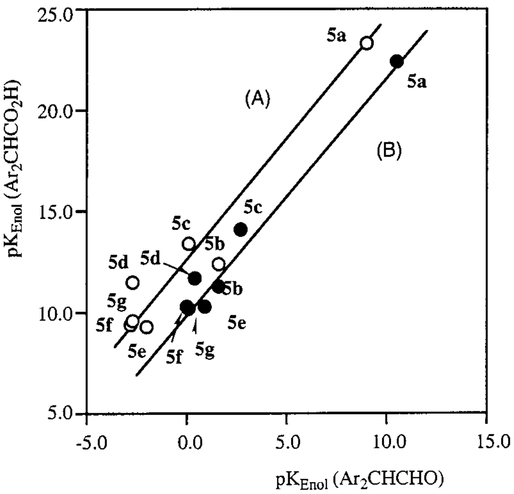

Figure 2. Correlations between pK_{Enol} values of acids Ar_2CHCO_2H and aldehydes Ar_2CHCHO for (A) *syn* conformation of ethenols and *syn,syn* conformations of 1,1-enediols (○, slope = 1.19, r^2 = 0.94) and (B) *anti* conformation of ethenols and *syn,anti* conformation of 1,1-enediols (●, slope = 1.19, r^2 = 0.97). Numbers in plots represent the enediols.

Consequently, taken together with the calculated vs observed pK_{Enol} values of the ethenols (see below), the B3LYP pK_{Enol} values of Table 1 can be regarded as reliable measures within ca. 2 pK_{Enol} units of the values in solution. From the 7.3−16.0 values for the **5b−h**/**6b−h** systems, we draw three relevant conclusions. (i) It will be difficult to obtain thermodynamically stable enediols by substituting AcOH by two β-bulky aromatic groups. (ii) Since **10a** was observed by flash photolysis as a short-lived intermediate[8f,g] and **5g** was observable by NMR,[18] if we assume a rough thermodynamic/kinetic stability correlation, all compounds of Table 1, excluding **5a**, could be observable by the techniques used to observe **5g**, **9a**, and **10a**. (iii) The effect of the bulky aromatic substituents on the 1,1-ethenediol is somewhat larger than those for the analogous ethenols. The 17.9 kcal/mol (ΔpK_{Enol} = 13.2) difference between the enediols of AcOH and dimesitylacetic acid exceed by 2.8 kcal/mol (ΔpK_{Enol} = 2.1) the 15.1 kcal/mol difference between ethanal and dimesitylethanal. Indeed, both plots of pK_{Enol}-($ArAr'C{=}C(OH)_2$) vs pK_{Enol}($ArAr'C{=}CHOH$) for the *syn,syn* and the *syn,anti* conformers (Figure 2) have slopes of 1.19.

Effect of the β-Aryl Groups. Upon substitution of the β-hydrogens of AcOH by β-aryl groups, the K_{Enol} (pK_{Enol}) values increase (decrease) with the increasing bulk of these groups. A large effect (12.3 kcal/mol; 9.1 pK_{Enol} units) is observed for the change β-H_2 → β-Ph_2. Retaining one phenyl group and increasing the bulk (and the electron-donating ability) of the other group from Ph to Mes and Sup further decreases regularly pK_{Enol}. In $Ar(Ph)CHCO_2H$, the values for Ar are Ph (13.3) > Mes (11.5) > Sup (7.3). The change β-Ph_2 → β(bulkier Ar)$_2$ leads to a higher effect than the change of a single aryl group, but the effect of replacing the second mesityl group by a tipyl is small. Thus, for $ArAr'CHCO_2H$, the pK_{Enol} values for Ar,Ar′ are Mes,Mes (9.2) > Mes,Tip (9.4) > Tip,Tip (9.3). Finally,

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by linking the two aryl groups when Ar = Ar′ = Ph to give the planar fluorenylidene moiety, pK_{Enol} is reduced by 2.0 pK_{Enol} units.

Qualitative analysis of the effect of β-aryl groups on the pK_{Enol} values of aldehydes and ketones was reported previously,[11,16,33] and similar considerations apply for the acids/enediols. In the sp^3-hybridized carbon of acids **6b**−**i**, the aryl and the carboxyl groups are not conjugated. In contrast, the sp^2-hybridized ethenediols **5b**−**i** have two conjugated styrene type Ar−C=C moieties. The conjugation energy of a single phenyl group in the fully planar system was estimated as ca. 4.5 kcal/mol,[34,35] and the electronic effect of the three methyl groups in the mesityl ring was estimated to add 0.3 kcal/mol to this value.[35] Since the electronic effects of alkyl groups do not differ much, if at all,[36] we use the value of 4.8 kcal/mol also for Tip and Sup.

The maximal 9.0−9.6 kcal/mol conjugative stabilization of the fully planar ethenediols is reduced by the severe deviation of the 1,1-diarylvinyl system from planarity. The torsional angles given in Table 1 increase, and hence the conjugation energy decreases when the bulk of the aryls increases. We estimated the conjugation energies given in Table 1 from the relationship $E(\theta) = E_0[1 + \cos 2\theta]/2$, where E_0 is the conjugation energy at full planarity and θ is the Ar−C=C torsional energy.[37] For example, a conjugative stabilization of 4.5 kcal/mol is estimated for 2,2-diphenyl-1,1-ethenediol **5c**, where the Ph-C=C torsional angles are ca. 45°. Since this value accounts for 36% of the decrease in pK_{Enol} compared with the value for **5a**, steric and polar effects should also contribute significantly to the reduced pK_{Enol} values. The steric effect is clearly manifested for all the other diaryl-substituted systems since, despite the higher θ values and the reduced conjugation (Table 1), the pK_{Enol} values of the symmetrical systems **5c**,**e** decrease rather than increase. This is ascribed to thermodynamic destabilization of the acid form. The steric interaction between bulky aryls in the ArCAr′ unit is more pronounced when they are on the acid's sp^3-hybridized carbon than on an sp^2-hybridized carbon in the enediols. With bulkier aryls the destabilization of the acid increases, shifting the equilibrium in the direction of the ethenediol form. This is analyzed more quantitatively below.

As discussed above with asymmetric systems (Ar ≠ Ar′), the steric effect dictates the conformation and the Ar′−C=C torsional angles differ, the group with smaller *ortho*-substituents displaying the smaller torsional angle. The overall conjugation effect is not necessarily reduced, since the lower bulkier-Ar−C=C conjugation is compensated by the higher planarity and conjugation of the smaller aryl (cf. Table 1).

Comparison of the fluorenylidene (**5b**) with the β,β-diphenylvinyl (**5c**) ethenediols shows that more than one effect is operative. The planar **5b** should display maximal $\pi(\mathrm{Ar})-\pi(\mathrm{C=C})$ conjugation, thus reducing pK_{Enol} compared with that of **5c**. The 4.3 kcal/mol difference between the E_{conj} values of **5b** and **5c** is semiquantitatively consistent with this effect. However, the conjugative effect in **5b** should be even larger since **5b** is a potentially push−pull system with the $C_\alpha(OH)_2$ moiety at the positive end and the "aromatic" fluorenyl moiety at the negative end of the dipole. This effect should stabilize **5b**, as was found for other push−pull enediol systems.[21,22] The consequent reduction of pK_{Enol} should be much lower for **5c**−**h**, whose aryl groups are less capable of negative charge dispersion. That ΔpK_{Enol} between **5b** and **5c** is only 2 units suggests that other effects, such as steric interaction of vicinal substituents or stabilization of acid **6b**, may be operating. A reduced steric destabilization in **6b** compared to that in **6c** due to the rigid fluorenyl ring may contribute to this difference, but it is difficult to dissect the steric and conjugative effects for the fluorenyl systems, which should be treated separately from the other β-diaryl-substituted systems due to their unique ring structure and the higher electron-withdrawing conjugative ability.

Dissection of β-Aryl Substituent Effects. Isodesmic reactions 3−5, 7, 9−13 enable a quantitative dissection of substituent effects on several of the equilibria discussed qualitatively above. The equations allow us to evaluate the interactions between the two aryl substituents attached to the $C=C(OH)_2$ and CHCOOH moieties by calculating the equilibria between species in which both functionalities interact across the $C_\alpha-C_\beta$ bond and species in which the two functionalities are on different molecules. The data are given in Table 5, where positive values mean that the reactant in these equations is more stable. The dissection of the equilibria of eq 12 to the effects of the acids and the enols (eqs 4 and 10, and 5 and 7) is revealing. The values in Table 5 indicate that for all β,β-diaryl groups, the 2,2-diaryl-1,1-enediols **5b**−**h** are strongly stabilized (by 12.3−17.9 kcal/mol) compared with the parent **5a**/**6a** pair. Comparison with eq 11, which gives the substituent effect on the analogous aldehyde/enol equilibria for the same substituents compared with the parent pair **3a**/**4a**, shows a difference of 0.2−2.8 kcal/mol stabilization between the two series, except for a 5.0 kcal/mol difference for the fluorenylidene derivative.

Equation 7 compares the interaction of the β-ArAr′ moiety in nonconjugated systems with a CO_2H vs a CH_3 group. The comparison includes the steric interactions of the two aryl groups in the two species with the sp^3-hybridized carbon. The effect is not large. 2,2-Diphenyl and 9-fluorenyl acetic acids are destabilized by 1.0−2.0 kcal/mol, and the other acids are stabilized by 0.4−3.2 kcal/mol.

Equation 4 compares the conjugation of the β-ArAr′ moiety with that of the α-$(OH)_2$ moiety in an ethylenic system vs the separate stabilizations of the double bond by two geminal OH groups and by two aryl groups. Again, all β-aryl (except for β-Ph_2) groups stabilize the doubly conjugated ethenediol compared with non-cross-conjugated systems. Comparison of the stabilization energies with their analogous terms from eq 2 for the corresponding ethenols shows that the effect of the second OH group on the equilibria is not large. The differences in the values of eqs 2 and 4 are −0.4−1.3 kcal/mol, except for the fluorenylidene system (2.6 kcal/mol). We attribute these similarities to the close Ar−C=C torsional angles of both the cross-conjugated and the non-cross-conjugated systems and to a small contribution of cross-conjugation due to the low negative charge dispersal ability of the β-aryl groups, except for fluorenyl, in the push−pull zwitterionic hybrid. The 1.8 kcal/mol higher value for **5b** than for the β-Ph_2 moiety is not high, considering the aromaticity of the fluorenyl moiety in the planar zwitterionic hybrid.

In eq 5, **5b**−**h** are stabilized by 11.3−20.8 kcal/mol compared with AcOH, but the β-Ar_2 conjugative stabilizations in the absence of α-$(OH)_2$ groups are 11.5−18.3 kcal/mol (eq 6). The ΔE differences for the same substituents in eqs 5 and 6 are only −0.2 to 2.8 kcal/mol; i.e., cross-conjugation is, indeed, not a major stabilizing factor. The observable trend of higher stabilization for two bulkier aryls in **5e**−**f** (19.7−20.8 kcal/mol

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in eq 5 and 16.9−20.5 kcal/mol in eq 6) should mainly reflect geminal interactions between the aryl rings.

The major contribution to the decrease of pK_{Enol} of **5b**−**h**, i.e., the high negative ΔE values of eq 12, comes from the effect on the acids, rather than on the ethenediols, as shown in eq 10. Acids **6b**−**h** are destabilized by 12.5−17.3 kcal/mol compared with $Ar_2C{=}CH_2$. The destabilization follows the order of increased bulk of the aryl groups: Tip,Tip > Mes,Tip > Mes,Mes > Mes,Ph > Ph,Ph. Since the Ar−C═C torsional angles decrease in this order and the conjugation should therefore increase rather than decrease, this differential effect should be due to Ar/Ar′ repulsion interactions, which are larger in the sp^3-hybridized than in the sp^2-hybridized systems.

That enediols of acids are much less known than enols of aldehydes does not mean that the former are less stable. Equation 3 compares the stability of the enediols vs that of the enols, and eq 13 compares them using the carboxylic acids/aldehydes as references. All the values in eq 3 are positive; i.e., the 1,1-enediols are more stable than the corresponding enols, as was found previously for the parents **3a** and **5a**.[23b] The higher stabilization of the enediols is mainly due to the conjugative stabilization of the additional OH group, superimposed on an anomeric effect and OH/OH repulsion. This is reflected by the similarity of the values for four of the six β-ArAr′ systems with that for the parent β-H_2 system and by the fact that the highest effect is displayed by the more conjugated planar fluorenylidene system. The apparent higher stabilization of the enols than of the enediols (eq 13) mostly reflects the higher destabilization of the acids than of the aldehydes.

(b) Ethenols. Isodesmic reactions for the enols are eqs 2, 8, 9, 11, and 13. From eq 2, the interaction between the α-OH and the β-Ar groups is slightly stabilizing by 0.6−1.8 kcal/mol for the bulkier aryls and very slightly destabilizing (by 0.2 and 1.0 kcal/mol) for the β-Ph_2 and the fluorenylidene moieties, respectively. As found for the enediols, the cross-conjugation with a push−pull stabilization is small. The smaller than expected effect of the fluorenylidene moiety is ascribed to a steric interaction between the *syn* α-OH and the in-plane *o*-hydrogens and to the lack of OH···π(Ar) hydrogen bonding, which becomes more important with the increased Ar−C═C torsional angle.

Equation 8 compares the effects of two aryl groups in the aldehyde and in ethylene. The geminal aryl groups are strongly stabilizing (by 11.2−15.4 kcal/mol) for $Ar_2C{=}CH_2$ compared with Ar_2CHCHO, and the more crowded aryls increase this effect. Hence, eq 11, derived from eqs 2 and 8, shows a large stabilization of 12.1−16.1 kcal/mol for **3b**−**g** compared with **3a**. These values give lower pK_{Enol} values of 0.2 to −2.8 for **3b**−**g**, compared with 9.1 for **3a**, as shown in Table 2.

Several pK_{Enol} values for aldehydes are available. For **3d**,**e**,**g** in hexane, ≥95% enol was observed at equilibrium.[16,20,31] The pK_{Enol} values are −2.0 for **3e** and −2 to −3 (larger error when the aldehyde is <5% of the mixture) for **3d**,**g**. For **3c** the observed values are 0.98 in water,[38] −1.12 in $(CD_3)_2CO$, and −0.70 in DMSO-d_6;[39] for **3b** it is −1.3 in water;[40] and for **3a** the gas-phase value is 6.6.[41] Consequently, when the known[28] small solvent effects on the values are considered, the agreement between the calculated and the observed values is very good, excluding **3b**, whose calculated pK_{Enol} value is 2.9 units higher than the observed value in water. We have no explanation for this discrepancy.

Equations 9 and 13 compare the carboxylic acid/aldehyde with the enol/alkene or enediol/enol, respectively. For both equations the carboxylic acid side of the equation is of much higher stability. The stabilizing energies of eq 13 are 13.2−19.4 kcal/mol, values that reflect the relative stability of the acids **6** vs the aldehydes **4** plus the relative stabilities of the enols vs the enediols. The high values are consistent with the pK_{Enol} values of carboxylic acids being much higher than those of aldehydes and show again the deviation of the fluorenyl system from the other β,β-diaryl-substituted systems.

The C═C−O−H Conformations of the 1,1-Enediols and the Enols. (a) 1,1-Enediols. The order of stability of the three possible conformers of the two C═C−O−H moieties depends on the enediol. We have examples of the higher stability of either the *syn*,*syn* or the *syn*,*anti* conformer, which are always at local minima, but the *anti*,*anti* conformer is always the least stable. The energy differences are small in most cases. The *syn*-planar,*syn*-planar conformer (the C═C−O−H dihedral angles are 6.2−9.3°) is the most stable for 7 out of the 11 systems studied, which include 5 β,β'-diaryl-substituted systems. In 4 cases the *anti*,*syn* conformer is more stable. One is **5b**, in which the *syn*,*anti* conformer is significantly more stable than the *syn*,*syn* and *anti*,*anti* conformers. The *syn* moieties in these conformers are less planar (angles of 18.2−19.3°) than all other *syn*-C═C−O−H arrangements. The *anti*,*syn* arrangement is also more stable in 2-phenyl,2-supermesityl-1,1-enediol **5h** and the parent **5a**, in line with previous calculations for **5a**.[25] These preferences reflect the extent of steric hindrance and hydrogen bonding that the enolic OH experiences in the *syn* conformation. It is minimal in **5a** with the small β-H, which lacks π(Ar)···HO hydrogen bonding, but it is maximal in **5b**, where the two aryl groups are in the double bond plane. The fluorenylidene 1- and 8-hydrogens and the *syn* enolic OH cannot be accommodated in the same plane despite the Ar−C═C bond angles being higher (ca. 126.5°) than those for all other 2,2-diaryl-1,1-enediols, and hence the *syn*-C═C−O−H angle increase. A π(Ar)···HO hydrogen bond is impossible in this geometry.

System **5h** also demonstrates the interplay of steric and hydrogen-bonding effects. The Sup group is nearly perpendicular to the C═C plane (Sup−C═C torsional angles of 87−89°), and the Ph is nearly in the molecular plane, more so in the *anti*,*syn* than in the *syn*,*syn* conformation (Ph−C═C torsional angles of 7.0° and 20.4°, respectively). The Ph−C═C bond angle was opened, and the Sup−C═C angle was reduced. Consequently, π(Ar)···HO bonding to the Ph ring is unfavored, whereas the OH−Sup distance (2.241 Å) is most favorable for such H-bonding. This will favor a *syn* conformer of the OH group *cis* to Sup, whereas the HO/Ph steric repulsion will destabilize the *syn* conformer for the OH *cis* to the Ph, leading to a higher stability of the *anti*,*syn* conformer. The other *syn*,*anti* conformation, with the bulkier Sup “enforced” into the C═C plane and a perpendicular Ph, would be extremely unstable since a similar enforced *syn*,*anti* conformation in the less bulky **5g** was calculated to be 21.6 kcal/mol less stable than the *syn*,*syn* conformer.

The *anti*,*syn* conformer of mandelic acid enol **10a** is also 1.17 kcal/mol more stable than the *syn*,*syn* conformer. The situation resembles that for **5h**. The Ph−C═C torsional angle is lower than that for the β,β-diaryl derivatives, and the Ph−C═C bond angle increases significantly. This change increases the conjugation energy by 1.0 kcal/mol, which is close to the

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energy difference between the two conformers. Formation of a nearly planar (the C═C─O─H dihedral angles are 0.9−2.9°) five-membered hydrogen bond between the two vicinal ═C(OH) groups is possible in both conformers of **10a**. The strengths of these bonds are moderate, judging by the O···H and O···O distances of 2.614 and 2.652 Å and 2.026 and 2.069 Å, respectively. The bond in the *anti*,*syn* conformer reduces the HO─C═C bond angle to 112.3° and makes it possible sterically to achieve a lower Ph─C═C bond angle, with a consequent increase in conjugation energy, and this conformer becomes more stable.

The dissection of the total effect on the relative stabilization of various conformers to steric destabilization, π(Ar)···HO and OH···HO hydrogen-bonding stabilization, and Ph-C═C conjugation is difficult since the effects are mostly not large and the observed geometry represents compensation of the various effects. Nevertheless, some comparisons are worthwhile and meaningful, especially those of two closely related systems.

The 2-aryl-2-cyano-1,1-ethenediols **9a** and **11a** (Ar = Ph, Mes) could be compared. The linear cyano substituent has a relatively low steric demand, and the CN−HO distance is too long to form an intramolecular hydrogen bond. Indeed, in enol $(MeO_2C)C(CN)═C(OH)NHPh$ the CN···HO bond is intermolecular.[22] The Mes─C═C torsional angle in **11a** is higher than the Ph─C═C angle in **9a**, and hence **11a** is less affected by the conformation of the α-substituents. For Ar = Ph, the *syn*,*syn* and *anti*,*syn* conformations have almost the same energies, which reflects a combination of 2.4 kcal/mol of a Ph─C═C conjugation energy (cf. Table 1) and a Ph···HO H bond. When this H bond is lost by converting the *syn* to *anti* conformation, the Ph─C═C torsional angle is reduced to 9.8° with a gain of ca. 1.9 kcal/mol conjugation energy. This is the order of magnitude of the loss of the stabilizing H bond. In **11a**, the π(Mes)···HO bonding is slightly stronger, with nearly the same OH−C(Ar_{C-ipso}) distances for Ar = Mes or Ph due to a better electron-donating ability of Mes than of Ph. Changing the C═C─O─H conformation from *syn* to *anti* reduces the Mes─C═C torsional angle by 2.8°, with a gain of only 0.1 kcal/mol. Hence, the π(Mes)···HO bonding is the dominant effect, and the *syn*,*syn* conformation predominates by ca. 1.4 kcal/mol over the *anti*,*syn* conformation.

The change from β-Sup in **5h** to β-Mes in **5d** when the other β-Ar group is Ph increases the [*anti*,*syn*] − [*syn*,*syn*] energy difference by 1.0 kcal/mol and makes the *syn*,*syn* conformer more stable. The sum of the Ar─C═C conjugation energies decreases by 1.0 kcal/mol for **5d** and by 0.4 kcal/mol for **5h**. The energy difference accompanying the *syn*,*syn* to *anti*,*syn* conformation change is nearly accounted for by the Ar─C═C conjugation changes for **5d**. A less efficient π(Ph)···HO H-bonding due to a long Ph─HO distance of 2.6 Å, close to those in the fluorenylidene system, and a low Ph─C═C torsional angle in the *syn*,*syn* conformer of **5h** can account for the low stability of *syn*,*syn*-**5h**.

There is ca. 2.5 kcal/mol difference between the fluorenylidene **5b** and the β,β-di-Ph (**5c**) systems, based on the [*syn*,*syn*] − [*anti*,*syn*] energy differences of 1.56 and −0.99 kcal/mol. The Ph─C═C conjugation energy shows a negligible gain of 0.3 kcal/mol for **5c** and a loss of 0.2 kcal/mol for **5b** for the *syn*,*syn* to *anti*,*syn* change. The loss of 1.0 kcal/mol for **5c** can be mainly due to the loss of one π(Ph)···HO hydrogen bond. The larger steric effect in the *syn*,*syn* conformer of **5b** (lacking an H bond) accounts for the main difference between the conformations. However, since the torsional angles are almost identical for *syn*,*syn*- and *anti*,*anti*-**5c**, if the H bond energies of both bonds are approximately additive in **5c** the *anti*,*anti* conformer is expected to be ca. 2 kcal/mol less stable than the *syn*,*syn* conformer. The much higher calculated value of 6.7 kcal/mol indicates that there is another source of instability, such as an OH/OH repulsion in the *anti*,*anti* conformer. Any explanation should consider the smaller preference of 1.6−2.0 kcal/mol for the *syn*,*syn* over the *anti*,*anti* conformers for systems **5a**,**b**. These results may suggest a weaker C═C─O─H conjugation in the *anti*,*anti* than in the *syn*,*syn* conformation as exemplified by shorter C_α─C_β bonds and longer C_α─OH bonds in the former conformers.

All the calculated *anti*,*anti* conformers are *anti*-clinal with angles of 135.5−138° rather than *anti*-planar arrangements. This has a steric origin since in the fully planar *anti*(180°),*anti*(180°) arrangement the H,H distance is 1.8 Å.

Finally, all the symmetrical and close to symmetrical 2,2-diaryl-substituted systems **5c**,**e**,**f**,**g** behave similarly. The *syn*,*syn* conformer is ca. 1 kcal/mol more stable than the *anti*,*syn* conformer, and the Ar─C═C torsional and bond angles do not differ much.

Experimental data are available only for **5g** in solution. The ^{1}H NMR chemical shift and the OD-induced shift of ^{13}C NMR signals had shown a “symmetrical” arrangement of the OH groups on the NMR time scale.[18] This is consistent with a *syn*,*syn*, or *anti*,*anti* conformer or with a rapid interconversion of conformers.

(b) Ethenols. The calculated conformers of the C═C─O─H moiety (Table 4) are *syn*- and *anti*-planar, with angles of 0.3−5.5° for the *syn* conformer (10° for **3b**) and 174.6−180° for the *anti* conformer, and are both at local minima. For all systems calculated, the *syn* conformer is significantly more stable than the *anti* conformer, as revealed by previous calculations,[27,42] except for **3b** (see below). We attribute this preference, at least partially, to stabilizing π(Ar)···HO hydrogen bonding in the *syn* isomer. In the nearly planar **3b** the 1-H interacts sterically with the O─H hydrogen with a consequent increase in the dihedral C═C─O─H angle to 10°, but hydrogen bonding is geometrically impossible. Since the energy of the *syn* isomer still slightly exceeds that for the *anti* isomer and *syn*-**3a** is more stable than *anti*-**3a**,[28,42] we conclude that the *anti* conformers are inherently destabilized compared with the *syn* conformers. The slight difference between the Ar─C═C torsional angles for the *syn* and *anti* conformers does not lead to a significant difference between the derived Ar─C═C conjugation energies. The preference for the *syn* isomer extends also to the solution and the solid phases. From ^{1}H NMR and IR studies in several solvents, especially on **3e**, we concluded[32] that in low dielectric non-hydrogen-bonding solvents such as CCl_4 and $CDCl_3$, the C═C─O─H conformation is *syn*. In the crystal structure of several β-arylethenols, including **3e**,**g**, the conformation is *syn*.[30]

Comparison of the 1,1-Enediols and the Ethenols. Comparison of the pK_{Enol} values, the C═C─O─H conformation, and the Ar─C═C torsional and bond angles can help in understanding the effect of the second vinylic OH on the behavior of the enols.

The pK_{Enol} values of the diarylacetic acids vs those of the corresponding aldehydes are plotted in Figure 2A for the *syn*,*syn*-enediols vs the *syn*-enols, and in Figure 2B for the *anti*,*syn*-enediols vs the *anti*-enols. The two lines obtained are reasonably linear, with deviations in Figure 2A for systems

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[42] (a) For summary of earlier calculations, see: Apeloig, Y. In *The Chemistry of Enols*; Rappoport, Z., Ed.; Wiley: Chichester, 1990; Chapter 1, p 1. (b) For a recent reference including calculations on **3e**, see: Frey, J.; Eventova, I.; Rappoport, Z.; Muller, T.; Takai, Y.; Sawada, M. *J. Chem. Soc., Perkin Trans. 2* **1995**, 621.

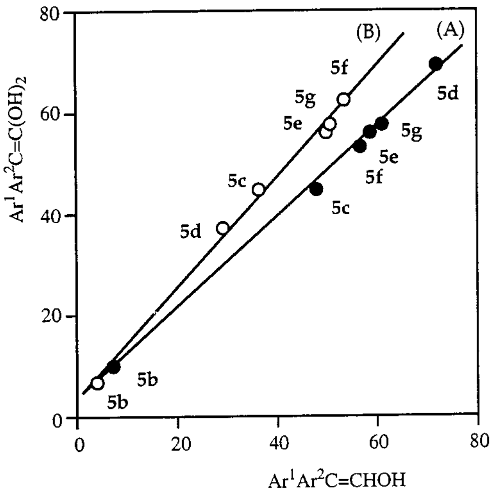


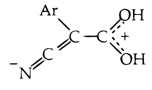
Figure 3. Plot of the Ar—C=C torsional angles (in degrees) for the 1,1-enediols vs those of the ethenols. Numbers represent the enediols, and each compound has two points (one for Ar^1 and one for Ar^2). (A) Ar^1 *cis* to the *syn* OH in the enols (●, slope = 0.90, $r^2 = 0.99$). (B) Ar^2 *cis* to the H in the enols (○, slope = 1.08, $r^2 = 0.99$).

having at least one in-plane Ar group, so that steric effects are more important than in other systems. Figure 2B, where steric interaction between the α- and β-substituents are reduced in the *anti* moieties, displays a better linearity. Since the main contribution to pK_{Enol} is the stabilization of the acid derivative or the aldehyde, the nearly linear correlation indicates that this effect is reflected mainly in the intercepts of the two correlations.

The effects of the β-substituents on the structures of the two series are parallel. The rigid bond angles do not show a significant substituent-dependent variation in both series, but plots of the more variable torsional angles for the enediols vs those of the enols (Figure 3) display two good ($r^2 = 0.99$) linear correlations which coincide at an angle of ca. 0° for the enols. The slightly steeper line is for the aryl ring *cis* to the H, and the other line is for the Ar *trans* to the H in the enols. The relatively small effect of the α-OH group in the enediols on the torsional angles is ascribed to the inherent crowding of the ArAr′C= moiety, so the substitution by one or two not too bulky α-OH groups serves mainly as a perturbation.

Effect of *β*-Cyano and *β*-Hydroxy Groups on the Acid/Ethenediol Equilibria. Compounds **9a** and **10a** show agreement between the calculated and observed pK_{Enol} values. The value for the β-mesityl analogue **11a** of **9a** was calculated in a search for an interaction between the steric effect of the aryl group and the electron withdrawal by the cyano group. The calculated ΔE value is reduced by 0.9 kcal/mol (0.7 pK_{Enol} value) by the β-Ph → β-Mes change. The 29.0° higher Ar—C=C torsional angle of **11a** (71.6°) than of **9a** (42.6°) results in a 1.9 kcal/mol lower conjugation energy for **11a**, which should make pK_{Enol} for **9a** lower.

ΔE is reduced by replacing a β-Ph or a β-Mes by a β-CN. The added stabilization of the ethenediol form by the dipolar push−pull form **12** is demonstrated by the positive values in eq 4 for **9a** and especially for **11a**. This effect is superimposed on a lower destabilizing effect in acids **9b** and **11b** due to repulsion between the CN and the CO_2H dipoles but also a stabilization due to decreased steric congestion. This conclusion is based on experiments/calculations with systems carrying β-EWGs.[21,22] One EWG is insufficient to form an observable enol of an acid or an amide, and the calculated pK_{Enol} value is higher than those calculated for the dicyano-substituted species $(NC)_2CHCONHR$ (R = H, Ph)[22] or that observed for the enol $MeO_2CC(CN)=C(OH)NHPh$.[22] From the calculated ΔE values of AcOH (30.5)[6], H_3CCONH_2 (27.4),[6] Ph_2CHCO_2H (18.2), $PhCH(CN)CO_2H$ (10.9), and $(NC)_2CHCONHPh$ (1.1),[22] we conclude that the cross-conjugation effect of EWGs on the stabilization of the enols much exceeds that of aryl groups.



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Supporting Information Available: Table S1 and S2, listing the calculated energies of the species studied and the geometries of aldehydes and acids, and Figure S1, showing the calculated geometries of several species (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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