The Dissociation Constants of the *E*- and *Z*-αβ-Diarylacrylic Acids

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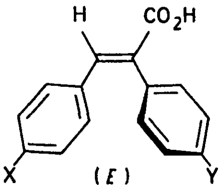
The p*K* values of 36 αβ-diarylacrylic acids, in both *E*- and *Z*-configurations, have been measured in 80% aqueous 2-methoxyethanol at 25 °C. The *Z*-isomers are stronger acids than the *E*-isomers because of the deconjugation of the carboxy-group which is out of the plane of the aromatic rings. In agreement with these conformational factors, the transmission of electrical effects (Hammett ρ-values) is more effective in *E*- than in *Z*-isomers. The heterocycle-containing acrylic acids (2-furyl, 2-thienyl, selenophen-2-yl) are weaker than the corresponding benzene derivatives. This has been ascribed to a combination of polar and steric effects, as shown by correlation with a two-parameter equation. The experimental p*K* values, corrected for the contribution due to the different size of β-aryl ring systems, follow the order of polar effects.

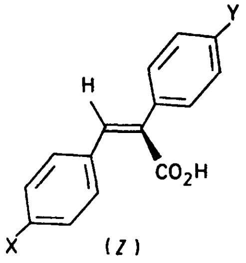
THE dissociation constants of carboxylic acids (RCO_2H) are a fundamental property which may provide an insight into the structural effects of the R groups.[1] In particular, five-membered heterocycles are considered electron-withdrawing groups since they show an acid-strengthening effect compared with the benzene ring. Positive Hammett constants relative to benzoic acid (σ_{BA}) are associated with the heteroatoms in furan, thiophen, and selenophen.[2] Electron-withdrawing effects are also indicated by Taft's polarity constants (σ^*) derived from rates of ester hydrolysis.[3,4]

Although five-membered heterocycles show a strong mesomeric effect in electrophilic substitutions,[5] the results just mentioned indicate that these rings do not facilitate π-electron delocalization towards the carboxy-group in the ground state.

In addition, spectral red-shifts with respect to cinnamic acid are observed in β-2-furyl-,[6] β-2-thienyl-,[7] and β-selenophen-2-yl-acrylic acid;[8] however, this through-resonance is not reflected by their dissociation constants, which are strictly similar.[9] Moreover, in the α-phenyl-β-*para*-X-substituted-phenylacrylic acids the transmission of the electrical effects (ρ_X) is different for *E* (1) and *Z* (2) isomers owing to steric effects.[10] A combination of polar and steric effects could affect the p*K* values of the *E*- and *Z*-αβ-diarylacrylic acids (1)—(4), as a result of differences in stereochemistry.[11,12]



(1)

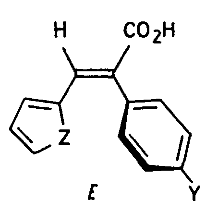


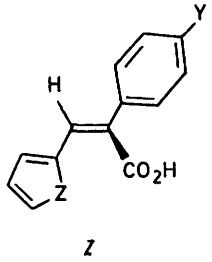
(2)

X = OMe_3, Me_3, H, Cl, NO_2; Y = H
X = H; Y = OMe, Me, Cl, NO_2

We are interested in the acid-catalysed isomerizations of *E*-αβ-diarylacrylonitriles;[13,14] any information on electrical and conformational effects in the parent diaryl-acrylic acids obtained from p*K* measurements could be useful for a wider understanding of the isomerization process.

We now report the p*K* values of 36 acids of the types (1)—(4) determined for solutions in 80% aqueous 2-methoxyethanol at 25 °C. These dissociation constants are not thermodynamic quantities, but they can be analysed analogously by linear free-energy relationships.[15]





(3)

(4)

Z = O, S, Se; Y = Me, H, Cl, NO_2

RESULTS AND DISCUSSION

The p*K* values of the acrylic acids in Table 1 were measured with the usual potentiometric apparatus, using a procedure requiring correction for the hydrogen-ion concentration.[16]

TABLE 1

p*K* values of *E*- and *Z*-αβ-diarylacrylic acids in 80% aqueous 2-methoxyethanol at 25 °C [a]

X	Y	*E* (1)	*Z* (2)
Me	H	7.28 (7.23)	5.73 (5.71)
Me	H	7.31 (6.99)	5.75 (5.73)
H	H	7.03 (7.00)	5.60 (5.59)
Cl	H	6.95 (6.66)	5.39 (5.36)
NO_2	H	6.32 (6.33)	5.05 (5.08)
H	Me	7.31	5.82
H	Me	7.40	5.86
H	Cl	6.83	5.50
H	NO_2	6.20	5.00
Z	Y	*E* (3)	*Z* (4)
O	Me	7.40	6.25
O	H	7.36	6.15
O	Cl	7.17	5.95
O	NO_2	6.44	5.42
S	Me	7.50	6.36
S	H	7.35	6.24
S	Cl	7.17	6.00
S	NO_2	6.51	5.29
Se	H	7.30	6.40

[a] Literature p*K* values are in parentheses.[10]

Table 2

Application of the Hammett equation to the pK values of E- and Z-$\alpha\beta$-*para*-substituted-diphenyl and α-*para*-substituted-phenyl-β-arylacrylic acids

		E (1)	Z (2)
Y = H	ρ_X	−0.942	−0.692
	pK_0	7.09	5.58
	r [a]	0.986	0.992
	s [b]	0.094	0.051
X = H	ρ_Y	−1.13	−0.816
	pK_0	7.08	5.65
	r [a]	0.986	0.988
	s [b]	0.11	0.075
		E (3)	Z (4)
Z = O	ρ_Y	−1.06	−0.892
	pK_0	7.32	6.13
	r [a]	0.980	0.997
	s [b]	0.15	0.047
Z = S	ρ_Y	−1.05	−1.15
	pK_0	7.35	6.21
	r [a]	0.996	0.995
	s [b]	0.07	0.08

[a] Linear correlation coefficient. [b] Standard deviation of estimated ρ value.

The Z-isomers are stronger acids than the E-isomers, the differences being 1.6—1.2 pK units for substituted diphenylacrylic acids and 1.2—0.9 pK units for the heterocyclic derivatives. This is due to specific conformational factors of the β-aromatic ring. In the Z-acids both aromatic rings are coplanar with the ethylenic fragment, while the carboxy-group is deconjugated, being non-coplanar.[11,12] In the E-acids the β-aromatic ring is almost coplanar with the carboxy-group, and conjugative effects weakening acidity become possible.

The i.r. stretching frequencies of the carbonyl group are a measure of conjugative interactions between the aromatic rings and the carboxy-group, a lower frequency being associated with such interactions.[17] This behaviour has been observed in α-phenyl-β-arylacrylic acids,[12,18] where the ν_{CO} ranges are 1 660—1 680 and 1 685—1 710 cm^{-1} for E- and Z-isomers, respectively.

The pK values vary linearly with the Hammett σ-values for the substituents, electron-withdrawing groups facilitating the acid dissociation. Hammett ρ-values for the series of acrylic acids examined are in Table 2. The transmission of electrical effects of the X-substituents is more effective in E- than in Z-isomers for the stereochemical reasons already indicated. In the Y-substituted acids ρ_Y-values do not show significant variations, in agreement with their structural analogies. Moreover, in the Z-isomers ρ_Y-values are higher than ρ_X (absolute values) because of the proximity of the α-phenyl ring to the carboxy-group.

The heterocycle-substituted acrylic acids, for both the E- and the Z-configurations, are weaker than the corresponding benzene derivatives. The obvious explanation of a greater electron-donating effect of the heterocyclic nucleus to the carboxy-group is really only applicable to the E-isomers, where functional conjugation is possible; this explanation is unreliable for the Z-isomers, where the carboxy-group is twisted out of the plane.

Electron-withdrawing effects in the ground state cannot themselves explain the observed trends in the pK values, since a strengthening of the acidity would be expected compared with the phenyl derivatives.

It is reasonable that a combination of polar and steric effects may contribute to the observed pK values. There are two alternative methods for examining this problem: the Hammett treatment and the separation of polar and steric effects.

Application of the Hammett equation to equilibria or reactivity data for five-membered heterocyclic compounds could provide information on the structural effects of heteroatoms.[2,19] In fact, if we consider the heterocyclic nucleus as a substituted benzene, σ_{het} constants for the replacement of a CH=CH group of the benzene ring by the heteroatom can be calculated by using the appropriate ρ_X and pK_0 values in the Hammett equation (1). The calculated σ_{het} values indicate a

$$\sigma_{het} = (\mathrm{p}K - \mathrm{p}K_0)/\rho_X \qquad (1)$$

greater electron-donating effect of the heteroatoms in the Z-isomers.† This is misleading since it is in contrast with the stereochemical data.[11,12,18]

The different size of β-aromatic ring systems does not allow a unified treatment for derivation of reliable σ_{het} constants; in fact, differences in steric effects, within the series examined, usually cause deviations from linear free-energy relationships.[20]

Then Thije and Janssen [3] have pointed out that failure of the Hammett equation might be expected for 2-substituted five-membered heterocyclic compounds, and suggested correlation of the data by use of Taft's σ^* constants. The pK values of arylcarboxylic acids are correlated well by these constants.[3,4] However, in α-phenyl-β-arylacrylic acids the occurrence of steric as well as polar effects complicates the application of correlation analysis. The Taft–Pavelich equation (2),[21] which takes into account both polar (σ^*) and steric

$$\log k/k_0 = \rho^*\sigma^* + \delta E_s \qquad (2)$$

effects (E_s), appears to be a better model for relating pK values to substrate structure. Nevertheless, the E_s values for aromatic and unsaturated groups cannot be considered to be totally reliable measures of steric effects including conjugative contributions.[21] The practical utility of this equation for five-membered heterocyclic compounds is then greatly reduced.

To elucidate quantitatively the role of steric as well as polar effects, we have tested the application of equation (3), which has already been used in a kinetic study of the acidic isomerization of E-$\alpha\beta$-diarylacrylonitriles.[14]

$$\mathrm{p}K = \rho\sigma + \psi\theta + \text{constant} \qquad (3)$$

The electronic effects of the heteroatoms in the ground state are represented well by σ_{BA}-values,‡ while the dif-

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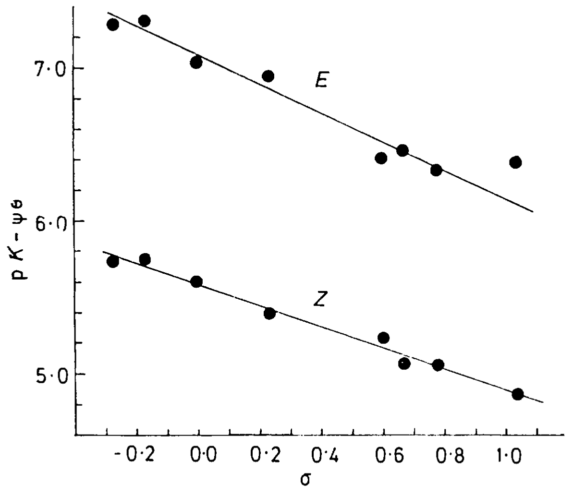
† $\sigma_{het}(E,Z)$: 2-furyl (−0.29, −0.79); 2-thienyl (−0.28, −0.92); selenophen-2-yl (−0.22, −1.16).

‡ σ_{BA}-Values: 2-furyl, 1.04; 2-thienyl, 0.67; selenophen-2-yl, 0.60.[2]

ference between the internal angles in the heterocycles [∠Z-C(2)-C(3)] [*] and the phenyl ring (120°) was chosen as a measure of steric effects (θ). The ρ and ψ parameters are the susceptibilities of the equilibrium to polar and steric effects. In this way the value of the constant term affords the calculated pK_0 for the unsubstituted phenyl derivative, whose σ and θ values are zero.

We have used a computer to analyse the relationship between the p*K* values for α-phenyl-β-*para*-X-substituted phenylacrylic acid (X = OMe, Me, H, Cl, NO_2) and β-2-furyl, β-2-thienyl, and β-selenophen-2-yl compounds and the appropriate σ and θ values. Regression analysis provided the empirical equations (4) and (5).



Correlation of (p*K* − ψθ) with σ values for the ionization of *E*- and *Z*-α-phenyl-β-arylacrylic acids

E isomers:

$$pK = -0.843\sigma - 0.105\theta + 7.07 \qquad (4)$$

$$(r = 0.950;\ s_\rho = 0.095;\ s_\psi = 0.010;\ s_{pK_0} = 0.05)$$

Z isomers:

$$pK = -0.699\sigma - 0.139\theta + 5.58 \qquad (5)$$

$$(r = 0.996;\ s_\rho = 0.036;\ s_\psi = 0.021;\ s_{pK_0} = 0.02).$$

The negative signs of both ρ and ψ constants are consistent with the expected effects, since the increase in σ and θ values tends to decrease the p*K* values. The more effective transmission of polar effects in *E* isomers $|\rho_E > \rho_Z|$ is confirmed by this extended treatment including heterocyclic compounds. Also, the greater ψ value for the *Z* isomers $|\psi_Z > \psi_E|$ is in agreement with the foregoing stereochemical arguments.

The chemical meaning of these equations is that the observed p*K* values, corrected for contributions due to steric effects (p*K* − ψθ), follow the order of the σ-values (Figure). It is noteworthy that the oxygen, sulphur, and selenium atoms in 2-furyl, 2-thienyl, and selenophen-2-yl rings, which seem to behave as electron-donating substituents using the Hammett treatment, appear to be electron-withdrawing as suggested by their σ_{BA} values.

EXPERIMENTAL

Materials.—The *E*- and *Z*-αβ-diarylacrylic acids (1)—(4) were synthesized by Perkin condensation of the appropriate arenecarboaldehyde and phenylacetic acid in acetic anhydride with triethylamine or pyridine as catalyst, following a procedure already described.[12,23] The previously reported acids had m.p.s in agreement with the literature.[10-12,23,24]

E-α-*phenyl*-β-*selenophen-2-ylacrylic acid* had m.p. 189 °C (from benzene–light petroleum); ν_{CO} 1 660 cm^{-1} (KBr disc) (Found: C, 56.2; H, 3.7. $C_{13}H_{10}O_2Se$ requires C, 56.3; H, 3.6%); *Z*-α-*phenyl*-β-*selenophen-2-ylacrylic acid* had m.p. 130 °C (from benzene–light petroleum); ν_{CO} 1 685 cm^{-1} (KBr disc) (Found: C, 56.45; H, 3.5%); Z-α-p-*tolyl*-β-*phenylacrylic acid* had m.p. 128 °C (from benzene–light petroleum) (Found: C, 80.5; H, 6.0. $C_{16}H_{14}O_2$ requires C, 80.65; H, 5.9%); *Z*-α-p-*chlorophenyl*-β-*phenylacrylic acid* had m.p. 126 °C (from benzene–light petroleum) (Found: C, 69.5; H, 4.4. $C_{15}H_{11}ClO_2$ requires C, 69.6; H, 4.3%). The stereochemical purity of the crystallized acids was checked by ^{1}H n.m.r. spectroscopy in each case.[10,12]

2-Methoxyethanol (commercial sample) and doubly distilled water (' carbon dioxide free ') were used to prepare 80% (w/w) aqueous 2-methoxyethanol.

Acidity Constants.—p*K* Measurements were made in duplicate or triplicate runs by potentiometric titration of the acid by a digital pH-meter (Amel 333) equipped with an automatic burette using a combined glass–calomel electrode. The acrylic acid concentrations were about 2 × 10^{-3}M. The solutions (100 ml) were titrated in a thermostatted cell (25 ± 0.1 °C) under nitrogen with 0.1M sodium hydroxide. The electrode was standardized with buffer solutions before and after each titration. The p*K* values were calculated by equation (6) [16] where the hydrogen ion concentration was

$$pK = pH + \log(C_{HA} - C_{H^+}) - \log(C_{A^-} + C_{H^+}) \qquad (6)$$

taken to be antilog pH, and can be neglected above pH 6. The maximum error was ±0.03 p*K* units for all compounds.

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[*] Internal angles [22] and θ-values are 110.68° and −9.32 for the furan, 111.47° and −8.53 for the thiophen, and 111.56° and −8.44 for the selenophen.

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