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Spectrophotometric Determination and Linear Free Energy Relationship Analysis of Acidity Constants for 1,3-Diphenyltriazenes

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Acid dissociation equilibrium constants for substituted 1,3-diphenyltriazenes were determined by means of spectrophotometric titrations. Measured acidity constants correspond to macroscopic equilibrium constants, since target substrates display prototropic tautomerism. Interestingly, experimental acidity constants for both symmetrically and unsymmetrically substituted 1,3-diphenyltriazenes obey a linear Hammett equation, implying that the Hammett reaction constants corresponding to substitution at the azo and amino phenyl sites are experimentally indistinguishable.

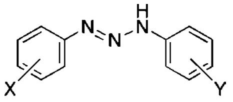
Introduction

Triazenes (compounds characterized by having a diazoamino group, —N═N—N<) are versatile materials known not only for their biological activity (e.g., as mutagenic/carcinogenic[1–3] and antiviral[4] agents) and utility in organic synthesis (e.g., as alkylating reagents and protecting groups/source of amines)[5] but also for their chelating properties. The ability of triazenes to coordinate to metal ions constitutes the basis of important analytical (spectrophotometric) methods for the detection of trace amounts of transition metal cations.[6] Furthermore, over the course of the past few years, the study of transition-metal complexes containing 1,3-diaryltriazenide ligands has attracted much attention, primarily as a result of the variety of bonding modes with distinct properties available in these systems.[7–10]

Because of the relevant role acid—base equilibria play in determining the biological and chelating, among other, capabilities of 1,3-diaryltriazenes, knowledge of their acid dissociation equilibrium constants becomes essential. The work reported herein focuses on the influence of substituents on acidity constants (determined via spectrophotometric titrations) of a set of symmetrically (**1**) and unsymmetrically (**2**) substituted 1,3-diphenyltriazenes dissolved in aqueous media. These substrates, as shown by X-ray diffraction measurements,[11,12] appear to always adopt the *trans* configuration in the ground state. Furthermore, 1,3-diphenyltriazenes are known to exhibit prototropic tautomerism;[13–15] hence, they exist indeed as a mixture of tautomeric isomers (for convenience of notation, however, unsymmetrically substituted triazenes are referred in this work by a single name). The role phenyl substituents play in influencing acidity constants of 1,3-diphenyltriazenes is analyzed quantitatively by means of Hammett linear free energy relationships. Interestingly, tautomerism does not seem to play a key role in determining acidity, as substituents at either phenyl ring have nearly the same effect.

Experimental Section

Materials and Solutions. The 1,3-diphenyltriazenes employed were existing samples from previous studies.[16–18] Stock buffer solutions were prepared using analytical grade reagents (EM Science), freshly distilled tetrahydrofuran (THF, ACS grade, EM Science), and water purified by passage through a Millipore apparatus. Solutions for spectral titrations were made by transferring microliter aliquots from stock triazene solutions in THF to 5 mL volumetric flasks filled with stock buffers; resulting aqueous buffer solutions contained 30 % (v/v) THF, ionic strength maintained at 0.2 M (NaCl), and substrate concentrations ranging in the order of (3 to 5)$\cdot 10^{-5}$ M.



1, X = Y **2**, X ≠ Y

Instrumentation. Electronic absorption spectra were recorded on a Varian Cary 1 Bio UV—visible spectrophotometer at 2 nm resolution. pH measurements were performed on an Orion Perphet model 350 digital pH meter using a combination glass electrode calibrated with standard aqueous buffers.

Procedures. Acid dissociation equilibrium constants (K_a) for the deprotonation of the amino moiety of target triazenes were determined via the classical spectrophotometric titration method,[19] by measuring the absorbance, at (or near to) the wavelength of maximum absorption (λ_{max}) corresponding to the neutral (HT) and anionic (T^-) triazene conjugate species, of sets of solutions having constant triazene concentration and varying pH. For such a series of solutions, the absorbance (A) at any given wavelength can be written as shown in eq 1,[19]

$$A = \frac{A_{HT_o}\cdot 10^{-pH} + A_{T_o^-}\cdot 10^{-pK_a}}{10^{-pH} + 10^{-pK_a}} \tag{1}$$

where A_{HT_o} and $A_{T_o^-}$ represent, respectively, the absorbance of solutions of neutral and anionic triazene conjugate forms at a concentration equal to the total triazene concentration employed in the study.

All measurements were carried out at room temperature, (21 ± 1) °C. Values of pK_a and Hammett reaction constants were obtained by curve fittings using the general curve-fitting procedure of KaleidaGraph (version 3.6.4) from Synergy Software.

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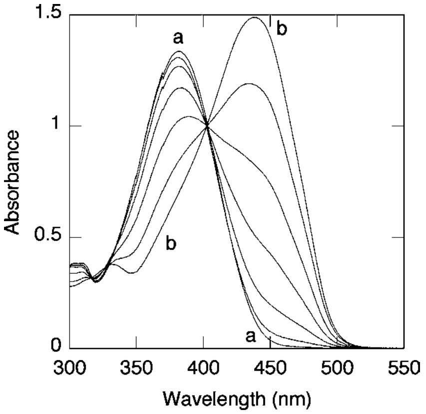


Figure 1. Absorption spectra of 1,3-bis(4-acetylenylphenyl)triazene (**1c**) in 30 % THF aqueous solution (pH = 10.22, 11.34, 12.20, 12.58, 12.88, 13.24, and 13.75, from a to b).

Table 1. Absorption Wavelength λ and pK_a Values for Symmetrically Substituted 1,3-Diphenyltriazenes Dissolved in Aqueous Solution[a]

1	X = Y	λ_{HT} nm	λ_{T^-} nm	pK_a	**1**	X = Y	λ_{HT} nm	λ_{T^-} nm	pK_a
a	4-H	355		> 13.8[b]	g	3-NO_2	338	391	10.81 ± 0.03
b	4-Cl	364	412	13.2 ± 0.1[c]	h	3,5-$(Cl)_2$	357	416	10.59 ± 0.04
c	4-CCH	381	439	13.03 ± 0.03	i	4-CN	374	448	10.52 ± 0.02[c]
d	3-CF_3	352	405	12.09 ± 0.05	j	3,4,5-$(Cl)_3$	364	426	9.77 ± 0.05
e	4-CF_3	357	415	11.71 ± 0.05[c]	k	4-NO_2	405	534	9.46 ± 0.04[c]
f	3-CN	357	414	11.49 ± 0.02					

[a] Solvent contains 30 % (v/v) THF; T = 21 °C. [b] No inflection point detected up to pH = 13.84 (highest pH of series employed). [c] Value taken from ref 16.

Table 2. Absorption Wavelength λ and pK_a Values for Unsymmetrically Substituted 1,3-Diphenyltriazenes Dissolved in Aqueous Solution[a]

2	X	Y	λ_{HT}/nm	λ_{T^-}/nm	pK_a
a	4-OCH_3	4-CN	367	426	13.06 ± 0.02
b	4-Cl	4-CN	360	427	11.81 ± 0.06
c	3-CF_3	4-CN	361	429	11.31 ± 0.04
d	3,5-$(Cl)_2$	4-CN	362	430	10.69 ± 0.03
e	3,4,5-$(Cl)_3$	4-CN	365	430	10.22 ± 0.03
f	4-OCH_3	4-H	365		> 13.8[b]
g	4-OCH_3	4-CF_3	364	413	13.48 ± 0.05
h	4-H	4-CF_3	355	409	13.05 ± 0.04
i	4-Cl	4-CF_3	356	413	12.38 ± 0.05

[a] Solvent contains 30 % (v/v) THF; T = 21 °C. [b] No inflection point detected up to pH = 13.84 (highest pH of series employed).

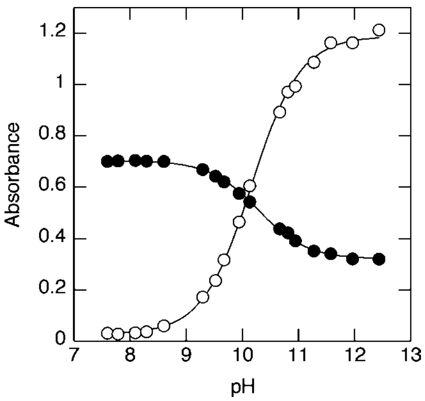
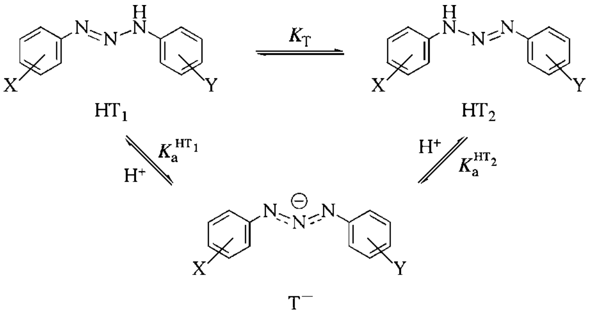


Figure 2. Titration curves for 3-(4-cyanophenyl)-1-(3,4,5-trichlorophenyl)-triazene (**2e**) in 30 % THF aqueous solution (obtained by recording absorbance values at λ_{max} of corresponding neutral (●) and anionic (○) triazene conjugate forms).

Scheme 1. Acid−Base Equilibria for 1,3-Diphenyltriazenes



Results and Discussion

Deprotonation of target triazenes leads in all cases to a bathochromic (red) shift of the longest wavelength absorption band (associated with the $\pi-\pi^*$ transition of the triazeno moiety[20]), as illustrated in Figure 1. The position of the visible absorption bands corresponding to the neutral and anionic conjugate forms of target symmetrically (**1**) and unsymmetrically (**2**) substituted 1,3-diphenyltriazenes are given in Tables 1 and 2, respectively.

Acidity constants of target substrates were determined, according to eq 1, from nonlinear curve fittings of absorbance values recorded as a function of pH (Figure 2 is representative); resulting pK_a values are summarized in Tables 1 and 2. Comparison of these pK_a values shows, as expected, an increase in acidity with increasingly stronger electron-withdrawing substituents. It is important to point out here that these pK_a values correspond indeed to macroscopic acidity equilibrium constants since target substrates, as mentioned in the Introduction Section, exist in solution as pairs of tautomeric isomers.[13–15] As illustrated in Scheme 1, however, deprotonation of the NH group of tautomerizing triazenes HT_1 and HT_2 yields the same anion (T^-).

The macroscopic acid dissociation equilibrium constant K_a corresponding to the 1,3-diphenyltriazene system depicted in Scheme 1 is defined as shown in eq 2, in which A stands for activity, whereas the relationship between K_a and the two microscopic equilibrium constants $K_a^{HT_1}$ and $K_a^{HT_2}$ is given in eq 3.

$$K_a = \frac{A_{T^-} \cdot A_{H_3O^+}}{A_{HT_1} + A_{HT_2}} \tag{2}$$

$$K_a = \frac{K_a^{HT_1} \cdot K_a^{HT_2}}{K_a^{HT_1} + K_a^{HT_2}} \tag{3}$$

In the case of symmetrically substituted substrates, the two microscopic equilibrium constants are identical, that is, $K_a^{HT_1} = K_a^{HT_2} = K_a^{S}$; hence the macroscopic (measured) pK_a value can be expressed as shown in eq 4.

$$pK_a = pK_a^{S} + \log(2) \tag{4}$$

The dependence of pK_a on phenyl substitution would be determined by the influence of phenyl substituents on the two microscopic acid dissociation equilibrium constants. Both $K_a^{HT_1}$ and $K_a^{HT_2}$ are assumed to obey the multiparametric Hammett equation[21] given by eqs 5 and 6,

$$\mathrm{p}K_{\mathrm{a}}^{\mathrm{HT_1}} = \mathrm{p}K_{\mathrm{a}}^{\mathrm{o}} - \rho_{\mathrm{N1}}\cdot\sigma_{\mathrm{X}} - \rho_{\mathrm{N3}}\cdot\sigma_{\mathrm{Y}} \qquad (5)$$

$$\mathrm{p}K_{\mathrm{a}}^{\mathrm{HT_2}} = \mathrm{p}K_{\mathrm{a}}^{\mathrm{o}} - \rho_{\mathrm{N1}}\cdot\sigma_{\mathrm{Y}} - \rho_{\mathrm{N3}}\cdot\sigma_{\mathrm{X}} \qquad (6)$$

in which $\mathrm{p}K_{\mathrm{a}}^{\mathrm{o}}$ represents the microscopic $\mathrm{p}K_{\mathrm{a}}^{\mathrm{S}}$ value for 1,3-diphenyltriazene (i.e., X = Y = H), ρ_{N1} and ρ_{N3} denote the sensitivity of the acid−base equilibrium to substitution at the azo and amino phenyl sites, respectively, and σ_{X} and σ_{Y} are the σ constants of substituents at each of the phenyl rings (in the case of multiple substitution at a ring, σ_{i} represents indeed the sum of the corresponding σ_{meta} and σ_{para} substituent constants). Replacing the parameters $K_{\mathrm{a}}^{\mathrm{HT_1}}$ and $K_{\mathrm{a}}^{\mathrm{HT_2}}$ in eq 3 by the terms obtained from eqs 5 and 6, respectively, leads to eq 7, which shows the relation between pK_{a} and Hammett substituent constants. In the case of symmetrically substituted triazenes, where $\sigma_{\mathrm{X}} = \sigma_{\mathrm{Y}}$, eq 7 reduces to eq 8.

$$\mathrm{p}K_{\mathrm{a}} = \mathrm{p}K_{\mathrm{a}}^{\mathrm{o}} - \log\left(\frac{10^{(\rho_{\mathrm{N1}}+\rho_{\mathrm{N3}})\cdot(\sigma_{\mathrm{x}}+\sigma_{\mathrm{y}})}}{10^{(\rho_{\mathrm{N1}}\cdot\sigma_{\mathrm{x}}+\rho_{\mathrm{N3}}\cdot\sigma_{\mathrm{y}})} + 10^{(\rho_{\mathrm{N3}}\cdot\sigma_{\mathrm{x}}+\rho_{\mathrm{N1}}\cdot\sigma_{\mathrm{y}})}}\right) \qquad (7)$$

$$\mathrm{p}K_{\mathrm{a}} = \mathrm{p}K_{\mathrm{a}}^{\mathrm{o}} + \log(2) - (\rho_{\mathrm{N1}} + \rho_{\mathrm{N3}})\cdot\sigma \qquad (8)$$

Figure 3 illustrates a plot of experimental pK_{a} values for symmetrically substituted triazenes versus σ values[22] (open symbols). This plot clearly shows that pK_{a} decreases with increasingly stronger electron-withdrawing substituents; moreover, it displays an excellent linear correlation between pK_{a} and σ values, with the exception of two points (i.e., 4-CN and 4-NO_2 substituents, open triangles). Fitting of data in Figure 3 (excluding 4-CN and 4-NO_2 data points) according to eq 8 leads to values of 13.84 ± 0.09 and 4.6 ± 0.1 for $\mathrm{p}K_{\mathrm{a}}^{\circ}$ and $(\rho_{\mathrm{N1}} + \rho_{\mathrm{N3}})$, respectively.

The two points off the σ-line in Figure 3 are not unexpected, since in corresponding substrates there is a direct resonance interaction between the charge (being developed) at the triazeno moiety and the *para* phenyl-substituents. Such a strong conjugative interaction manifests itself spectrophotometrically as well. While the red shift observed upon deprotonation of symmetrically substituted triazenes is typically in the (50 to 60) nm range (Table 1), it increases to 74 nm in the case of 1,3-bis(4-cyanophenyl)triazene (**1i**) and to 129 nm in the case of 1,3-bis(4-nitrophenyl)triazene (**1k**). In fact, ab initio calculations have shown that amines with unsaturated bonds adjacent to the N atom can undergo valence tautomerization on deprotonation, such that a substantial portion of the negative charge of the anion resides at the (more electronegative) substituent.[23]

Although the σ^- scale is generally used to analyze data in systems in which a negative charge can be stabilized by delocalization via resonance with the substituent(s),[21] when compared to data for the other symmetrically substituted triazenes shown in Figure 3, pK_{a} values for **1i** and **1k** do not correlate well with σ^- values[22] (closed triangles) either. This observation is not unprecedented. Indeed, a similar behavior has been reported for the ionization of symmetrically disubstituted 1,3-diphenyltriazenes in 20 % ethanol aqueous solutions at 20 °C.[24] Deviation from the σ-line of points corresponding to substrates containing mesomerically withdrawing substituents was interpreted in terms of the Yukawa−Tsuno modification of the Hammett equation as given in eq 9,[24] in which r denotes the enhance resonance effect parameter (in relation to benzoic acids dissociation, for which $r = 0$).[21]

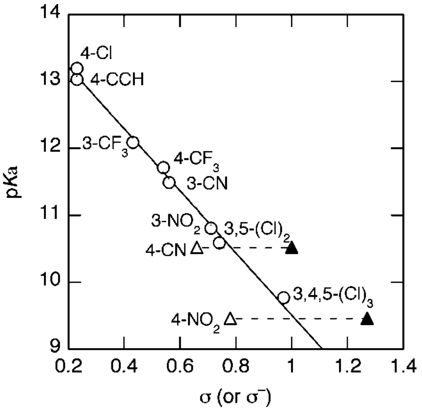


Figure 3. Plot of pK_{a} values for symmetrically substituted triazenes vs Hammett substituent constants (open symbols, σ; closed symbols, σ^-).

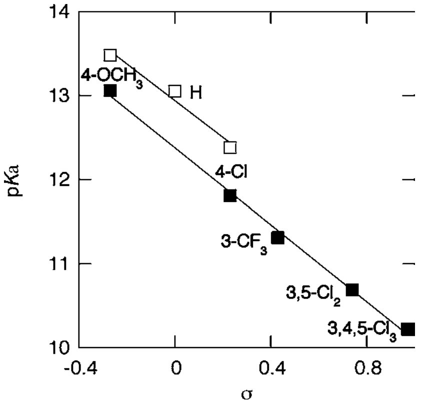


Figure 4. Plot of pK_{a} values for unsymmetrically substituted triazenes containing a 4-CN (■) or 4-CF_3 (□) group vs the Hammett substituent constant for variable substituent(s).

$$\mathrm{p}K_{\mathrm{a}} = \mathrm{p}K_{\mathrm{a}}^{\mathrm{H}} - \rho\cdot[\sigma + \mathrm{r}(\sigma^- - \sigma)] \qquad (9)$$

By replacing the factor σ in eq 8 with the terms $[\sigma + r(\sigma^- - \sigma)]$, eq 10 results. Fitting of data in Figure 3 according to eq 10 leads to values of 13.8 ± 0.1 and 4.6 ± 0.2 for $\mathrm{p}K_{\mathrm{a}}^{\circ}$ and $(\rho_{\mathrm{N1}} + \rho_{\mathrm{N3}})$, respectively (i.e., identical to the values first obtained by omitting the 4-CN and 4-NO_2 data points), and 0.43 ± 0.05 for r. This r-value should certainly be taken cautiously since it results from only two points off the σ-line. Nevertheless, the resulting $[\sigma + \mathrm{r}\ (\sigma^- - \sigma)]$ values for 4-CN and 4-NO_2 substituents are 0.81 ± 0.05 and 0.99 ± 0.05, respectively.

$$\mathrm{p}K_{\mathrm{a}} = \mathrm{p}K_{\mathrm{a}}^{\mathrm{o}} + \log(2) - (\rho_{\mathrm{N1}} + \rho_{\mathrm{N3}})\cdot[\sigma + r(\sigma^- - \sigma)] \qquad (10)$$

Figure 4 (filled squares) displays a plot of the experimental acid dissociation equilibrium constants of unsymmetrically substituted triazenes containing a 4-CN group (Table 2, **2a**−**e**) versus Hammett substituent constants for variable substituent(s). As expected, similar to the case of symmetrically substituted triazenes, acidity increases with increasingly stronger electron-withdrawing substituents. Since an excellent linear relationship between pK_{a} and σ is obtained, this would imply that in eq 7 the value of ρ_{N1} is (experimentally) indistinguishable from that of ρ_{N3}, that is, $\rho_{\mathrm{N1}} \approx \rho_{\mathrm{N3}} = \rho$. Thus, eq 7 simplifies to eq 11.

$$\mathrm{p}K_\mathrm{a} = \mathrm{p}K_\mathrm{a}^{\circ} + \log(2) - \rho\cdot(\sigma_\mathrm{X} + \sigma_\mathrm{Y}) \qquad (11)$$

A linear fitting of data in Figure 4 for substrates having a 4-CN group leads to values of 12.08 ± 0.05 and 2.29 ± 0.08 for ($\mathrm{p}K_\mathrm{a}^{\circ} - \rho\cdot\sigma_{4\text{-CN}}$) and ρ, respectively. It should be noted that this ρ value is half the slope value obtained from symmetrically substituted triazenes (i.e., Figure 3, slope = 4.6 ± 0.2), a parameter that corresponds indeed to the sum of the reaction constants ρ_N1 and ρ_N3 (eq 8). On the other hand, from the ($\mathrm{p}K_\mathrm{a}^{\circ} - \rho\cdot\sigma_{4\text{-CN}}$) and slope ($\rho$) values obtained from data in Figure 4, the factor $\sigma_{4\text{-CN}}$ can be calculated using the $\mathrm{p}K_\mathrm{a}^{\circ}$ value obtained from data in Figure 3 (i.e., 13.8 ± 0.1). Thus, $\sigma_{4\text{-CN}}$ is determined to be 0.75 ± 0.07. This value, which would represent the "effective" electronic character of a 4-CN group in the 1,3-diphenyltriazene system, is consistent with the value of 0.81 ± 0.05 calculated, from data in Figure 3 according to eq 10, for the parameter $[\sigma + r(\sigma^{-} - \sigma)]$ corresponding to 4-CN.

Although the number of experimental points is indeed limited (Figure 4, open squares), it is important to point out that a similar fitting using acid dissociation equilibrium constants of unsymmetrically substituted triazenes having a 4-CF_3 group (Table 2, **2g−i**) yields a slope (ρ) value of 2.2 ± 0.4 (i.e., essentially half the slope value obtained for symmetrically substituted substrates) and an intercept (i.e., ($\mathrm{p}K_\mathrm{a}^{\circ} + \log(2) - \rho\cdot\sigma_{4\text{-CF3}}$)) value of 12.94 ± 0.08 that is fully consistent with the $\mathrm{p}K_\mathrm{a}^{\circ}$ value of 13.8 ± 0.1 obtained from data in Figure 3 and the literature value of 0.54 for $\sigma_{4\text{-CF3}}$.[22]

By using the "effective" $\sigma_{4\text{-CN}}$ value calculated from data in Figure 4, a plot of experimental acid dissociation equilibrium constants of target symmetrically and unsymmetrically substituted substrates versus ($\sigma_\mathrm{X} + \sigma_\mathrm{Y}$) yields, as illustrated in Figure 5, an excellent straight line. A linear fitting according to eq 11 leads to values of 13.88 ± 0.05 and 2.33 ± 0.04 for $\mathrm{p}K_\mathrm{a}^{\circ}$ and ρ, respectively, consistent with fitted parameters obtained from data in Figures 3 and 4. It should be noted that these $\mathrm{p}K_\mathrm{a}^{\circ}$ and ρ values ultimately yield estimated $\mathrm{p}K_\mathrm{a}$ values of 14.2 and 14.8 for 1,3-diphenyltriazene (**1a**) and 1-(4-methoxyphenyl)-3-phenyltriazene (**2f**), respectively, in excellent agreement with experimental observations.

Finally, the tautomeric equilibrium constant K_T depicted in Scheme 1 can be written as a function of the two microscopic acidity constants $K_\mathrm{a}^{\mathrm{HT}_1}$ and $K_\mathrm{a}^{\mathrm{HT}_2}$, as shown in eq 12. In the case of symmetrically substituted 1,3-diphenyltriazenes, tautomeric isomers HT_1 and HT_2 are indistinguishable; hence the two microscopic equilibrium constants, as already stated, are identical and $K_\mathrm{T} = 1$. The fact that Hammett reaction constants ρ_N1 and ρ_N3 cannot be distinguished experimentally, at least under the conditions of this study, implies that tautomeric equilibrium constants for unsymmetrically substituted 1,3-diphenyltriazenes dissolved in aqueous solution are close to unity. This observation is consistent with results for a series of monosubstituted 1,3-diphenyltriazenes (i.e., in Scheme 1, X = H; Y = *meta* or *para* CH_3, Cl, NO_2) singly labeled with ^{15}N; K_T values (determined by means of infrared spectroscopy) are found to range (in CCl_4 solution) between 1.3 and 1.9 (except for Y = 4-NO_2, for which $K_\mathrm{T} = 0.47$).[14]

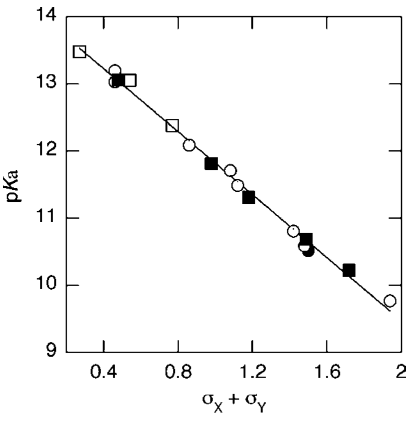


Figure 5. Plot of $\mathrm{p}K_\mathrm{a}$ vs the sum of Hammett substituent constants for symmetrically substituted triazenes with no 4-CN groups (○), symmetrically substituted triazene containing 4-CN groups (●), unsymmetrically substituted triazenes with no 4-CN group (□), and unsymmetrically substituted triazenes containing a 4-CN group (■).

$$\mathrm{p}K_\mathrm{T} = \mathrm{p}K_\mathrm{a}^{\mathrm{HT}_1} - \mathrm{p}K_\mathrm{a}^{\mathrm{HT}_2} \qquad (12)$$

Conclusions

Acidity constant ($\mathrm{p}K_\mathrm{a}$) values for symmetrically and unsymmetrically substituted 1,3-diphenyltriazenes were determined in 30 % THF aqueous solutions via spectrophotometric titrations. Phenyl substitution strongly influences the equilibrium distribution of neutral and anionic conjugate forms of target triazenes, particularly in the presence of strong mesomerically electron-withdrawing substituents at the *para* position. Quantitative analysis of substituent effects by means of Hammett linear free energy relationships renders values of about 4.6 and 13.8 for the sum of reaction constants for substitution at the azo and amino phenyl sites (i.e., $\rho_\mathrm{N1} + \rho_\mathrm{N3}$) and the microscopic acidity constant of 1,3-diphenyltriazene ($\mathrm{p}K_\mathrm{a}^{\circ}$), respectively. Moreover, correlation of data for both symmetrically and unsymmetrically substituted substrates indicates that, under the conditions of this study, ρ_N1 and ρ_N3 cannot be distinguished. Fitted parameters reported herein should prove useful in predicting macroscopic acidity constants of tautomerizing *meta*/*para* substituted 1,3-diphenyltriazenes of utility in various fields.

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