Correlation of Excited-state Acidity Constants of 2,4-Dinitrophenylhydrazones of Substituted Acetylfluorenes and Acetylbiphenyls

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The excited-state acidity constants, pK^*, of several 2,4-dinitrophenylhydrazones of 7-substituted 2-acetylfluorenes and 4'-substituted 4-acetylbiphenyls have been determined in dioxane–water (50% v/v) at 30 °C employing the Förster cycle. The pK^* values are correlated with the Hammett σ_p constants. Exalted σ constants are required for $-K$ substituents in fluorene system for a better correlation. The interplanar angle between the planes of the phenyl rings in biphenyl system has been evaluated from the pK^* values and found to be 36°.

One of the most important and useful concepts in chemistry is that of the acid–base properties of molecules. There is an intimate relationship between acid–base properties and charge distribution. Since charge densities are often modified by electronic excitation, it is expected that the acid–base properties of a molecule in an excited state will also vary from its properties in the ground state. Direct measurements of acid–base properties of molecules in excited states remains an active area of research.[1] The pioneering work of Förster,[2] Weller,[3] and Jackson and Porter[4] has paved the way to the measurement of chemical equilibria between molecules in their excited states. The measurement of the pK^* values of the lowest triplet state has been achieved by the method of Porter. It involves excitation of the substrate in buffered solution into the triplet state by flash photolysis, followed by triplet–triplet absorption measurements. An alternative method of obtaining the pK^* values of excited singlet state is due to Förster and is based on a thermodynamic cycle (Figure 1). In this cycle, which is applicable to either absorption or fluorescence spectra, ΔE_{A^-} and ΔE_{HA} are the energy differences between ground and excited states for conjugate base (A^-) and acid (HA), respectively, and ΔH and ΔH^* are the enthalpies of ionization in the ground and excited states. Proceeding from ground state HA, the excited state A^{-*} can be reached by two different routes (Figure 1) and this leads to equation (1).

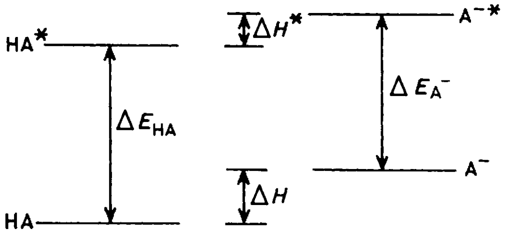


Figure 1. Förster cycle

$$\Delta E_{HA} + \Delta H^* = \Delta E_{A^-} + \Delta H$$

$$\Delta H - \Delta H^* = \Delta E_{HA} - \Delta E_{A^-} \quad (1)$$

If $\bar{\nu}_{HA}$ and $\bar{\nu}_{A^-}$ are the electronic transition frequencies of the acid and conjugate base respectively, equation (1) becomes (2).

$$\Delta H - \Delta H^* = Nhc\bar{\nu}_{HA} - Nhc\bar{\nu}_{A^-} \quad (2)$$

From the fundamental laws of thermodynamics, the enthalpies of ionization can be related to free energy changes for the corresponding processes [equations (3) and (4)]. Since $\Delta G = -RT \ln K$ and $\Delta G^* = -RT \ln K^*$, where K and K^* are

$$\Delta H = \Delta G + T\Delta S \quad (3)$$

$$\Delta H^* = \Delta G^* + T\Delta S^* \quad (4)$$

protolytic equilibrium constants in the ground and excited states respectively, and, if $\Delta S \approx \Delta S^*$, we have equation (5).

$$\Delta H - \Delta H^* = -RT(\ln K - \ln K^*) \quad (5)$$

From equations (2) and (5), (6) and (7) follow.

$$-RT(\ln K - \ln K^*) = (Nhc\bar{\nu}_{HA} - Nhc\bar{\nu}_{A^-}) \quad (6)$$

$$\mathrm{p}K - \mathrm{p}K^* = \frac{Nhc(\bar{\nu}_{HA} - \bar{\nu}_{A}u^{-}g}{2.303\,RT} \quad (7)$$

Thus the excited-state acidity constant, pK^*, can be evaluated from the ground-state acidity constant, pK, and from the absorption maxima of the acid and its conjugate base. Such values may not reflect any physically attainable equilibrium because of the short life-time of the excited states involved, but nevertheless have the same thermodynamic significance as the ground-state pK values.

Acid–base equilibria have been one of the original and most fruitful areas for the application of linear free energy relationships and the question arises naturally whether such relations will be equally applicable to electronically excited states also. The pK^* values of substituted phenols[5] show a reasonably good correlation with substitutent constants. Jaffé and Jones[6] have reported a treatment of pK^* by means of the Hammett equation and showed that pK^* values can be correlated by the Hammett equation with moderate precision employing $\sigma^{\pm}$ constants. Favaro *et al.*[7] reported a better correlation with σ^+ than with σ for the pK^* values of 4'-substituted 3-styrylpyridines. Baldry[8] analysed the published data on pK^* and derived a new set of substituent constants, σ_{ex}, which gives better correlation than σ. These results show that the Hammett equation can also be applied to the excited state. Although much attention has been paid to correlate pK^* of benzene derivatives, relatively little attention has been paid to such studies in polynuclear aromatic system. In the present study, we report our investigations on the pK^* of 2,4-dinitrophenylhydrazones (DNP) of several substituted acetylbiphenyls and acetylfluorenes.

Experimental

All the substituted acetylfluorenes and acetylbiphenyls were prepared by the literature method.[9,10] The dinitrophenyl-

Table 1. Analytical data for DNPs of acetylfluorenes and acetylbiphenyls

No.	Sub-stituent	Molecular formula	M.p. (°C)	Found (%) (Required) C	H
		DNPs of 7-substituted 2-acetylfluorenes			
1	NH_2	$C_{21}H_{17}N_5O_4$	208—209 (decomp.)	62.7 (62.5)	4.05 (4.25)
2	OCH_3	$C_{22}H_{18}N_4O_5$	220—221	63.3 (63.15)	4.4 (4.3)
3	C_2H_5	$C_{23}H_{20}N_4O_4$	249—250	66.3 (66.3)	4.7 (4.8)
4	H	$C_{21}H_{16}N_4O_4$	261—262	64.8 (64.9)	4.25 (4.15)
5	F	$C_{21}H_{15}FN_4O_4$	273—274	62.2 (62.1)	3.9 (3.7)
6	Cl	$C_{21}H_{15}ClN_4O_4$	267—268	59.5 (59.65)	3.4 (3.6)
7	Br	$C_{21}H_{15}BrN_4O_4$	267—268	54.3 (54.0)	3.0 (3.2)
8	I	$C_{21}H_{15}IN_4O_4$	282—283	49.25 (49.0)	2.8 (2.9)
9	CN	$C_{22}H_{15}N_5O_4$	256—257	63.7 (63.9)	3.8 (3.7)
10	NO_2	$C_{21}H_{15}N_5O_6$	284—285	58.4 (58.2)	3.35 (3.5)
		DNPs of 4′-substituted 4-acetylbiphenyls			
11	OCH_3	$C_{21}H_{18}N_4O_5$	276—277	62.2 (62.1)	4.3 (4.5)
12	CH_3	$C_{21}H_{18}N_4O_4$	223—224	64.9 (64.6)	4.8 (4.65)
13	H	$C_{20}H_{16}N_4O_4$	232—233	64.1 (63.8)	4.5 (4.3)
14	F	$C_{20}H_{15}FN_4O_4$	200—201	61.2 (60.9)	3.8 (3.8)
15	Cl	$C_{20}H_{15}ClN_4O_4$	222—223	58.9 (58.5)	3.5 (3.7)
16	Br	$C_{20}H_{15}BrN_4O_4$	216—217	52.4 (52.8)	3.1 (3.3)
17	NO_2	$C_{20}H_{15}N_5O_6$	273—274	57.3 (57.0)	3.4 (3.6)

hydrazones (DNPs) prepared by the usual method were crystallized and their purities checked (t.l.c.). The DNPs were characterized by their m.p.s and elemental analysis (Table 1). All the spectral measurements were made on a Perkin-Elmer-Hitachi-200 u.v.–visible spectrophotometer provided with a variable-temperature accessory. The ground state-acidity constants, p*K*, were determined by the method previously reported.[11] The excited-state acidity constants, p*K**, were calculated from the Förster cycle [equation (7)]. All the spectral measurements were carried out at 30 °C in 50% (v/v) dioxane–water at a constant ionic strength of 0.4M (NaCl).

Results and Discussion

It has been shown that the amino hydrogen of DNP is acidic[12] and the absorption maxima of DNPs of carbonyl compounds exhibit a bathochromic shift[13,14] when the solvent system is changed from neutral to basic. For the DNPs of benzaldehydes and acetophenones,[15] the difference between absorption frequencies of free acid (DNP) and the conjugate base (DNP^-), $\Delta\bar{\nu}$, was correlated with the Hammett substituent constants. According to the Förster cycle, this $\Delta\bar{\nu}$ is proportional to the difference, $\Delta pK = pK^* - pK$, between the p*K* of the ground state and the p*K** of the excited state. Since the ground-state p*K*s correlate with the Hammett σ constants it follows that the same is true for p*K**.

Table 2. Absorption maxima, and ground- and excited-state acidity constants for DNPs of 7-substituted 2-acetylfluorenes and 4′-substituted 4-acetylbiphenyls

No.	Substituent	$\lambda^{HA}_{max.}$/nm	$\lambda^{A^-}_{max.}$/nm	$-\Delta\bar{\nu}$/cm^{-1}	p*K*	p*K**
1	NH_2	408	471	3 278	11.73	4.96
2	OCH_3	406	482	3 884	11.62	3.60
3	C_2H_5	402	482	4 129	11.55	3.03
4	H	399	481	4 273	11.53	2.71
5	F	395	479	4 440	11.49	2.32
6	Cl	392	479	4 633	11.46	1.89
7	Br	390	477	4 677	11.45	1.79
8	I	389	477	4 743	11.42	1.63
9	CN	387	499	5 800	11.33	−0.64
10	NO_2	386	516	6 527	11.28	−2.20
	DNPs of 4′-substituted 4-acetylbiphenyls					
11	OCH_3	391	471	4 344	11.55	2.58
12	CH_3	396	480	4 419	11.52	2.40
13	H	391	478	4 654	11.51	1.90
14	F	392	481	4 720	11.48	1.74
15	Cl	393	485	4 850	11.47	1.46
16	Br	391	483	4 872	11.46	1.38
17	NO_2	397	508	5 504	11.37	0.01

Table 3. Statistical correlation of $-\Delta\bar{\nu}$ and p*K** of DNPs of acetylbiphenyls and acetylfluorenes

System	Quantity correlated	Constant	ρ	*i*	*r*	*s*
Biphenyl	$-\Delta\bar{\nu}$	σ_p	1 106 ±21	4 630 cm^{-1} ±21	0.998	26
Fluorene	$-\Delta\bar{\nu}$	σ_p	2 094 ±131	4 389 cm^{-1} ±56	0.967	251
Fluorene	$\Delta\bar{\nu}$	$\sigma_p - \sigma_p$	1 623 ±18	4 316 cm^{-1} ±32	0.997	81
Biphenyl	p*K**	σ_p	−2.45 ±0.04	1.94 ±0.01	0.998	0.051
Fluorene	p*K**	σ_p	−4.67 ±0.27	2.45 ±0.12	0.971	0.516
Fluorene	p*K**	$\sigma_p^- - \sigma_p$	−3.57 ±0.07	2.62 ±0.04	0.997	0.165

The absorption maxima of DNPs of acetylfluorenes and acetylbiphenyls and their conjugate bases are summarized in Table 2 together with p*K* and p*K**. The difference in absorption of DNP and DNP^- ($-\Delta\bar{\nu} = \bar{\nu}_{HA} - \bar{\nu}_{A^-}$) varies systematically with the substituents. Electron-releasing substituents decrease the $-\Delta\bar{\nu}$ value while electron-attracting substituents increase it. The p*K** values also show a regular variation with substituents. The $-\Delta\bar{\nu}$ and p*K** values were correlated with the Hammett σ_p constants and the results of statistical correlations are presented in Table 3. In the biphenyl system, both $-\Delta\bar{\nu}$ and p*K** correlate very well with σ_p. In the fluorene system the correlations with σ_p are fair. The p*K** values of the 7-cyano and 7-nitro substituents deviate from the corresponding Hammett plot (Figure 2). Improved correlations are obtained if σ_p^- constants are used for these substituents (Table 3). The need for σ_p^- constants for the 7-nitro and 7-cyano substituents suggests that the canonical structure (II) is important in the excited state of the DNP^- of acetylfluorenes.[16] The high ρ values for the p*K**–σ correlation (Table 3) imply a strong interaction between substituents and acidic centre in the excited state.[17,18]

The $-\Delta\bar{\nu}$ and p*K** values for the DNP of 2-acetylfluorene are 4 273 cm^{-1} and 2.71 respectively whereas for the DNP of 4-acetylbiphenyl the corresponding values are 4 654 cm^{-1} and 1.90. The low acidity and bathochromic shift for the DNP of 2-acetylfluorene compared with that of the DNP of acetyl-

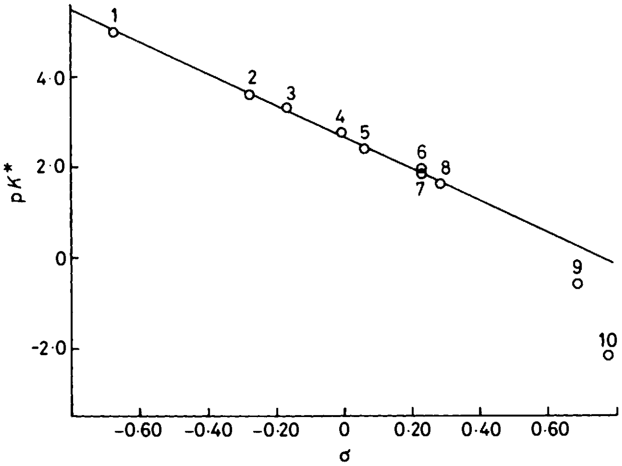
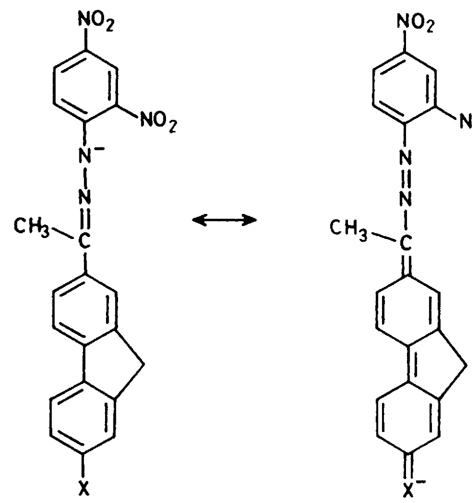


Figure 2. Hammet plot for excited-state acidity constants of DNPs of substituted 2-acetylfluorenes (numbering as in Table 2)



(I) (II)

X = NO_2 or CN

biphenyl may be due to the electron-releasing hyperconjugative effect of the methylene bridge in the former.[19]

Fluorene and biphenyl show considerable similarities in their reactions. The relative transmission of the electronic effects of the substituents in these two systems has been studied by employing a number of chemical reactions. In biphenyl the two aryl rings are not coplanar and molecular chlorination[20] studies indicate that the reactivity of biphenyl derivatives is determined by the angle between the planes of the aryl rings in the transition state. The solvolytic reactions[21] of (biphenyl) benzyl chlorides are less sensitive to substituent effects (ρ −1.2) than the corresponding reaction of the fluorene compounds (ρ −1.7). The fluorene system seems to transmit more electronic effects across the two phenyl rings than do the biphenyl fragments. On the other hand, the effects of substituents upon the rate of photodetritiation of either 7-X-2-tritiofluorene or 4′-X-4-tritiobiphenyl are the same in the two systems[22] and it has been suggested that the non-coplanarity of the aryl rings in the ground state does not have any influence on the transmission of electronic effects of the substituents as the aryl rings may become nearly coplanar in the transition state. The ρ value of −2.45 obtained in the present study for the pK^*–σ correlation for biphenyl system is less than the ρ value (−3.57) for the fluorene system. If the biphenyl system acts similarly to the fluorene system in transmitting the electronic effects of substituents, the ρ value will be as high as that for the fluorene system. But the experimentally obtained lower ρ value for the biphenyl system compared with that of the fluorene system shows that the biphenyl system transmits a lesser amount of electronic effects of the substituents than the fluorene system.

The interplanar angle, θ, and the extent of mesomeric relay are linked[20,21] by equation (8). If, in the fluorene system, the

$$E = E_0\cos^2\theta \qquad (8)$$

result of a substituent effect ($\Delta pK^* = p_xK^* - p_HK$) is dependent upon some function θ then the corresponding result in the biphenyl system ($\Delta pK'^*$) depends similarly on θ', the interplanar angle in biphenyl. As fluorene is planar θ is zero. A plot of pK^* of the DNPs of biphenyls against pK^* of the DNPs of fluorenes for five substituents (OMe, H, F, Cl, and Br) gives a good straight line of slope 1.53 (r 0.996). Since the slope of this line is equal to $1/\cos^2\theta'$, θ' can be evaluated and was found to be 36°. This value is in close agreement with the values observed from chemical reactivities.[20,21]

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