J. Chem. Research (S),
1999, 178–179
J. Chem. Research (M),
1999, 0834–0853

Tautomerisation in 1-(4-Methylphenylazo)naphthalen-2-ol and 2-(4-Methylphenylazo)-4-methylphenol: A Crystallographic and $^{13}C\{^1H\}$NMR Study

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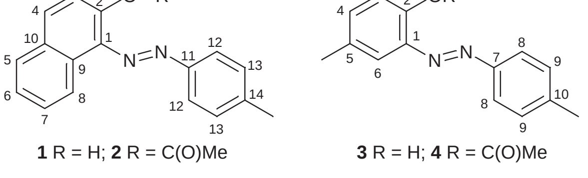
The acetic acid esters of 1-(4-methylphenylazo)naphthalen-2-ol **1** and 2-(4-methylphenylazo)-4-methylphenol **3** are prepared and characterised by single crystal X-ray diffraction studies and $^{13}C\{^1H\}$NMR spectroscopy; the position of the $C(2)^{13}C$ resonance for the ester is used to predict the position of resonant frequency of the equivalent carbon in the parent alcohols and hence, calculate the position of the azo-hydrazone equilibrium in these compounds.

A wide range of techniques have been used to study the tautomeric behaviour of 1-(phenylazo)-naphthalen-2-ol dyes including infra red spectroscopy,[3] UV–VIS spectroscopy, [4] X-ray crystallography,[5–8] and NMR spectroscopy, where investigation of a variety of nuclei, ^{13}C, ^{14}N, ^{15}N, in solution and solid state have been carried out.[8–15] We recently became interested in this equilibrium as a result of preparing the azo containing phosphines 1-(4-R-phenylazo)-6-(diphenyl)-phosphino-naphthalen-2-ol (R = Me, Et).[15] We found, like many others have in the past, that the 1-(4R-phenylazo)naphthalen-2-ols exist as an azo hydrazone tautomeric mixture; however, we prevented the tautomeric process by synthesizing the acetic acid [1-(4-R-phenylazo)-6-(diphenyl)phosphino-naphthalen-2-ol] esters (R = Me, Et), two phosphines containing an azo moiety that cannot equilibrate with the hydrazone tautomer.[16] The $^{13}C\{^1H\}$NMR for these compounds show a C(2) resonance (Fig. 1) at 151.9 ppm implying that, based on accepted substituent effects, the C(2) resonance for the parent hydroxy-azo tautomer should be in the region of 156 ppm. This is at variance with the previously predicted value of 147 ppm and has implications for the position of the equilibrium calculated using this value.[8]

To see if the shift to higher frequency of the C(2) resonance was an artefact of the diphenylphosphino moiety the parent 1-(4-methylphenylazo)-naphthalen-2-ol **1** was prepared and esterified to give acetic acid [1-(4-methylphenylazo)-naphthalen-2-ol] ester **2**, which was fully characterised spectroscopically and by a single crystal X-ray diffraction study (Fig. 2, see full text). The $^{13}C\{^1H\}$NMR resonance for C(2) in **2** was observed at 151.49 ppm suggesting the 6-diphenylphosphino moiety did not affect the position of the C(2) resonance; further, based upon accepted substituent effects, the parent hydroxy-azo tautomer should have a C(2) resonance nearer to 156 ppm rather than the previously suggested value of 147 ppm. This means that the equilibrium constants calculated by Olivieri *et al.*[8] using the equation: $K = [180 - \delta C(2)]/[\delta C(2) - 147]$ [where 180 is the predicted ^{13}C resonance for C(2) in the hydrazone tautomer and 147 is the predicted value for the azo tautomer] for 1-phenylazonaphthalen-2-ol is incorrect. The equation in light of these data should be modified to: $K = [180 - \delta C(2)]/[\delta C(2) - 156.5]$, which has the effect of modifying the value of the equilibrium constant K_{298} from 0.62 to 0.39. Since Bekarek *et al.*[9] reported that 2-hydroxy-5-*tert*-butylazobenzene exists as 2.2% of the hydrazone tautomer at room temperature, based upon the value of $J_{^{15}N}$ coupling constants, we prepared 2-(4-methylphenylazo)phenol **3** and acetic acid-[2-(4-methylphenylazo)phenol] ester **4**, fully characterised them spectroscopically and by single crystal X-ray diffraction studies (Figs. 3 and 4, see full text). The shift difference for the C(2) carbon resonances for **3** and **4** in the $^{13}C\{^1H\}$NMR spectra is 5.36 ppm. This difference is larger than the expected value of 4.5 ppm implying the presence of some hydrazone tautomer; using the equation: $K = [180 - \delta C(2)]/[\delta C(2) - 147.85]$ [where 147.85 is the predicted value for the C(2) resonance based on accepted substituent effects] gives a value for K_{298} of 36.4 meaning that 2.7% of **3** exists as the hydrazone tautomer. This observation is supported by the crystal structure determination for **3** which displays a short C(2)–O(1) bond length of 1.344(4) Å, compared to 1.395(5) Å in **4**. Further, slight deviations in the bond lengths around the azo moiety, although not as noticeable as in the 1-phenylazo- naphthalen-2-ols, is significant in suggesting the presence of some of the hydrazone tautomer. Based on these observations extinction coefficients for each of the tautomers were calculated from UV data.



1 R = H; **2** R = C(O)Me   **3** R = H; **4** R = C(O)Me

Fig. 1. Numbering scheme used in assignment of ^{13}CNMR data

W. I. Cross thanks the EPSRC for the award of a studentship.

References: 23

Schemes: 2

Figs, 2, 3 and 4: ORTEP diagrams of **2**, **3** and **4** showing atom numbering schemes

Table 1: ^1HNMR data (δ) ppm for **1**–**4**

Table 2: $^{13}C\{^1H\}$NMR data (δ) for compounds **1**–**4**

Tables 3–15: Crystal data for **2**, **3**, **4**

Received, 26th November 1998; Accepted, 30th November 1998
Paper E/8/09257E

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Table 3 Summary of crystal data

Compound	**2**	**3**	**4**
Formula	$C_{19}H_{16}N_2O_2$	$C_{14}H_{14}N_2O$	$C_{16}H_{16}N_2O_2$
M_w	304.34	226.27	268.31
Space group	*Pbca*	*C*2/*c*	*P*2(1)2(1)2(1)
Unit cell	*a* 22.171(3) Å	*a* 17.9480(10) Å	*a* 4.682(17) Å
	b 18.599(5) Å	*b* 17.6850(10) Å	*b* 9.1593(16) Å
	c 7.573(9) Å	*c* 17.1556(10) Å	*c* 27.977(6) Å
		β 92.070(10)°	
$V/Å^3$	3123(4)	2364.7(4)	1401.2(6)
Z	8	8	4
T/k	203(2)	203(2)	203(2)
λ/Å	0.71069	0.71073	0.71073
F(000)	1280	960	568
ϑ range	1.84 to 24.97°	2.27 to 24.99°	1.46 to 24.97°
Reflections/unique	5233/2738	4165/2089	1476/1476
Refinement	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Residuals	$R = 0.0592$	$R = 0.0542$	$R = 0.0491$
	$R_w = 0.0909$	$R_w = 0.0944$	$R_w = 0.0987$

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