SHORT PAPER

J. Chem. Research (S),
2001, 534–535

The configuration of N-alkyl-anilino-s-triazine derivatives[†]

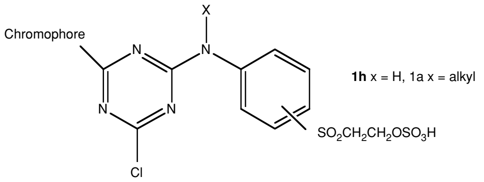
Zuwang Wu*, Haiyan Yang and Zhonghai Sun

State Key Laboratory of Fine Chemicals, Dalian University of Techmology, Dalian 116012, P.R.China

The alkyl group on the imino bridge of heterobifunctional reactive dyes plays a major role in improving the dyeing properties. The configurations of a pair of model compounds 2,4-dimethoxy-6-anilino-s-triazine and 2,4-dimethoxy-6-(N-metyl-anilino)-s-triazine have been determined by X-ray diffraction analysis of single crystals. The planar angle between the triazinyl and phenyl rings of the above models are 8.35° and 72.22° respectively. It indicates that the steric effect of the ethyl group produces a non-planar configuration and leads to the improvement of the dyeing properties.

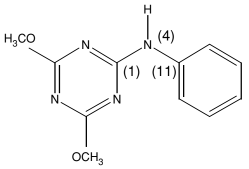
Keywords: N-alkyl-anilino-s-triazines

The introduction of an alkyl group at the imino bridge of a MCT/VS bifunctional reactive dye (**1a**) is a structure modification which improves dyeing properties.[1] It was reported that reactive dyes (**1a**) would confer higher solubility, lower substantivity and a better wash off property for the hydrolysed dye from the dyed fiber than that of the corresponding dyes (**1h**).[2,3] Kinetic studies show that the dye with N-alkyl imino bridge (**1a**) possessed higher reactivity than the corresponding dye with a bare imino bridge under the same dyeing condition. Fisichella[4] and Aspland[5,6] suggested that the imino group of dye (**1h**) was dissociated to give a nitrogen anion at the fixation condition (pH near 11), thus reducing the reactivity of the attached triazine ring. Wu and Li[2,3] had noted that, the steric effect of the alkyl group in the dye (**1a**) could not be neglected. An alkyl group located on the nitrogen atom causes the benzene ring to twist from the triazine plane to give a non-coplanar configuration. The electron density at the reactive centre decreases and the reactivity of the dye (**1a**) increased. However, no exact configuration of these compounds has been reported so far.

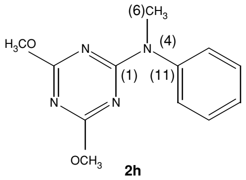


1h x = H, 1a x = alkyl

A pair of model, compounds, (**2h**) and (**2a**), have been synthesised.[7,8] Their single crystals were prepared and the structures were determined by X-ray diffraction.[9,10]



2a



2h

[1]The bond lengths, bond angles of the imino bridge and the planar angles between cyanuric and phenyl ring of compound (**2h**) and (**2a**) determined by X-ray diffractometry are listed in Tables 1 and 2, the molecular configurations are shown in Figs 1 and 2.

Table 1 Bond lengths, Bond angles of the imino bridge and planar angle between triazinyl and phenyl plane of compound (**2h**)

Length of C1-N4 bond	1.343Å
Length of C11-N4 bond	1.409Å
Bond angle of –C1-N4-C11	131.57°
Angle between triazinyl and phenyl plane	8.35°

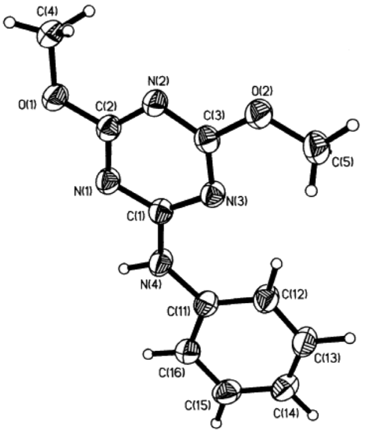


Fig. 1 The configuration of compound (**2h**).

Table 2 Bond lengths, bond angles of the imino bridge and planar angle between triazinyl and phenyl plane of compound (**2a**)

Length of C1-N4 bond	1.351Å
Length of C11-N4 bond	1.428Å
Length of N4-C6 bond	1.462Å
Bond angle of ∠ C11-N4-C6	100.8°
Bond angle of ∠ C1-N4-C11	118.8°
Bond angle of ∠ C1-N4-C6	120.2°
Angle between triazinyl and phenyl plane	72.22°

Table 1, shows the planar angle between triazinyl of 2,4-dimethoxy-6-anilino-triazine and phenyl ring is 8.35°, and the configuration is a co-planar structure.

Due to the steric effect of the ethyl group, the corresponding planar angle for compound (**2a**) is 72.2°, the phenyl ring is twisted from triazinyl plane, and the exact configuration is shown in Fig. 2. Computer calculations were 10.6° and 72.5°

---

* To receive any correspondence. E-mail: zuwangwu@dlut.edu.cn

[†] This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*

respectively,[7] which were very close to the experimental results. The bond length of C1-N4, the linkage bonds between triazine and aniline, are 1.343 Å (2h) and 1.351 Å (2a), indicating that these bonds are of a double bond nature, the bond had somewhat elongated by the N-ethyl group, and the double bond character diminished. This explains the lower substantivity and higher reactivity of those bifunctional reactive dyes containing N-alkyl imino bridge.

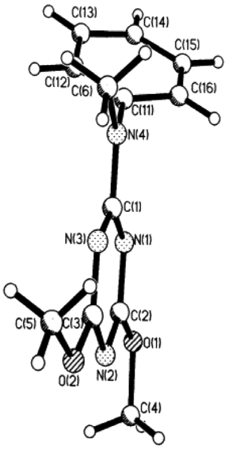


Fig. 2 Configuration of compound (**2a**).

Preparation of 2,4-dimethoxy-6-anilinos-triazine (compound **2h***) single crystal:* Cyanuric chloride 0.02mol and crushed ice 10g were stirred in a 250ml beaker for 15min, 0.02 mol aniline in 10ml acetone was dropwise added at 0–5°C This temperature was maintained and the pH of the medium to 6–7 with sodium carbonate solution. The precipitate was filtered off and dried. 2,4-dichloro-6-anilino-s-triazinel was reacted with 14ml methanol and 5g sodium hydroxide in a three-necked flask. The mixture was kept at 35°C for 1h and then refluxed for 7h. It was filtered and re-crystallised acetone, a colorless crystal 2,4-dimethoxy-6-anilino-triazine was obtained, m.p. 130–1°C. Analysis data: M.S. (API-ES positive model) MW 233.3(M+H); ^{1}HNMR: 3.98(s. 6H) 7.11, (m. 1H), 7.33(m. 2H), 7.60(m. 2H), 8.08(s. 1H). ^{13}CNMR: 54.71(O-CH_3), 120.84(C12, C1'), 123.84(C 14) 128.70(C13, C15), 137.78(C11), 166.35,172.31(C1, 2,3). 0.5g purified 2,4-dimethoxy-6-anilino-s-triazine (0.5g) was dissolved in 15ml acetone, the solution was allowed to evaporate slowly. The solvent was removed and the crystal washed by *n*-heptane, a single crystal was obtained.

Preparation of 2,4-dimethoxy-6- (N-methylanilino)-s-triazine (compound **2a***) single crystal*: 2,4-dimethoxy-6-(N-methylanilino)-triazine was synthesised by a similar way using N-methylaniline instead of aniline. The crude product was recrystallised from ligroin. The m.p, of the colourless product is 52–53°C. Analysis data: M.S.(API-ES source, positive model), MW 247.3 (M+H); ^{1}HNMR: 3.53(s. 3H) 3.89 (s. 6H), 7.24(m. 1H), 7.28(m. 2H), 7.40(m. 2H); ^{13}CNMR: 38.35(N-CH3), 54.54(O-CH3), 126.51(C12, C16, C14), 128.93(C13, C15), 144.00(C11), 167.5,172.2 (C1, 2, 3). Purified 2,4-dimethoxy-6- (N-methyl)-anilino-s-triazine (0.5g) was dissolved in 25ml ligroin (b.p. 30–60°C), the solution was allowed to evaporate slowly, a single crystal was obtained.

Crystal data for compound **2h***:* $C_{11}H_{12}N_4O_2$, MW=232.25; monoclinic system, P21/c space group, *a*=10.947(2)Å, *b*=6.2890(10)Å, *c*=16.235(3)Å; α=90.00(0)°, β=90.59(3)°, γ=90.00(0)°, V=1117.7Å^3, Dx=1.380Mg/m^3, Z=4. A total of 1986 independent reflections was collected at room temperature, of which 1914 reflections were to be observed;ω/2θscan mode: θ_{max}=25°, Cell parameters were determined from 25 reflections with θ range 8.15–12.05° measured on an ENRAF-NONIUS CAD-4 diffractometer with MoKα radiation (λ=0.071073nm), graphite monochromate. The structure was solved by direct method and refined to R=0.0898 for 1914 independent reflections.

Crystal data for compound **2a**: $C_{12}H_{14}N4O_2$, MW=246.27; monoclinic system, P21/c space group, *a*=5.5970(10)Å, *b*=7.870(2)Å, *c*=28.640(6)Å; α=90.00(0)°, β=90.77(3)°, γ=90.00(0)°, V=1261.4Å^3, Dx=1.297Mg/m^3, Z=4. A total of 2165 independent reflections were collected at 293(2) Å;, of which 2120 reflections were to be observed;ω/2θscan mode: θ_{max}=25°, Cell parameters were determined from 25 reflections with θ range 7.76–12.30° measured on an ENRAF-NONIUS CAD-4 diffractometer with MoKα radiation (λ=0.071073nm), graphite monochromate. The structure was solved by direct method and refined to R=0.0481 for 2120 independent reflections.

Data manipulation: The H atoms were placed in calculated positions, the H atoms attached to the N atoms and the O atoms were not found in the ΔF map. The H atoms attached to the C atoms were added theoretically and were refined with riding model and fixed isotropic thermal parameters. The data collection and the cell refinement were performed by using a CAD4 program; the solution and the refinement were performed by using the SHELXTL-PC program; molecular graphics by using a SDP-PLUS program

Received 29 March 2001; accepted 10 June 2001
Paper 01/804

References

1 Z. Wu, G. Wu and L. Lin *Dyestuff Indust (Chi)*, 1999, **36**, 1.
2 Z. Wu, P. Li and S. Wang, *Dyes Pigment*, 1998, **38**, 1.
3 Z. Wu, D. Wang, H.Yang and L. Lin, *Adv. Col. Sci. Technol.*, 2000, **3**, 41.
4 J. R. Aspland and A. Johnson *J. Soc. Dyer Col.*, 1965, **81**, 425.
5 J. R. Aspland and A. Johnson *J. Soc. Dyer Col.*, 1965, **81**, 477.
6 S. Fishichella, S. Occhipinti, G. Alberghina and M. E. Amato, *Text. Res. J*, 1981, **51**, 683.
7 S. Wang, P. Li and Z. Wu, *Dyestuff Indus (Chin)* 1997, 34, 1.