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Received December 13, 1999

Although azo dyes containing benzotriazole are of interest as substrates for surface enhanced resonance Raman scattering, SERRS, little is known of their molecular structure due to their poor crystal growth properties. We recently synthesised a highly crystalline dihydroquinoline *via* an unusual condensation reaction and we report herein that the azo-benzotriazole dye subsequently formed was sufficiently crystalline to allow structural elucidation using synchrotron radiation. It was found that this benzotriazole dye exists as the unexpected 6-isomer and the structure of the dihydroquinoline moiety changes markedly on coupling due to increased delocalisation.

J. Heterocyclic Chem., **37**, 1555 (2000).

Benzotriazole compounds are currently finding use as substrates for surface enhanced Raman scattering, SERS, studies. [1, 2] Suitable surfaces for SERS are roughened metal surfaces such as colloidal silver particles. [3] These colloidal particles are easy to work with and generally consist of a silver colloid prepared by either citrate [4] or borohydride [5] reduction. In order to produce reliable SERS the analyte must complex irreversibly to the metal surface. Benzotriazole fulfils this criteria and can also be functionalised to provide a suitable chromophore for resonance enhancement to produce surface enhanced resonance Raman scattering, SERRS. [1] We have managed for the first time to crystallise a benzotriazole azo dye and to analyse the bonding within the molecule by crystallographic and spectroscopic methods. This confirmed that the benzotriazole moiety is unchanged once functionalised therefore leaving the metal complexing properties unaffected. In doing so we were also able to determine that the dye existed in an unexpected isomeric form.

Previously four different benzotriazole dyes have been used for extensive SERRS studies. [1, 2] In common with other azo dyes they have very poor crystal growth properties and as such structural elucidation was by NMR alone. To obtain a crystalline benzotriazole dye it was decided that the part of the dye that the diazotised benzotriazole coupled to should be a highly crystalline compound that could impart a large degree of crystallinity. The compound chosen was 7-methoxy-2,2,4-trimethyl-1,2-dihydroquinoline, **1**. This compound is highly crystalline, its structure has recently been elucidated [6] and it is highly activated towards electrophilic diazonium substitution. The ring must be activated towards electrophilic substitution, as the diazotised benzotriazole is a weak electrophile. The 7-methoxy-2,2,4-trimethyl-1,2-dihydroquinoline was produced whilst attempting the synthesis of alkylated anisidine using bromohexanol in a mixture of refluxing petroleum ether and acetone. The dihydroquinoline was the major product formed by the cyclic condensation of two molecules of acetone that

utilised the alkyl bromide as the activator for the first time as opposed to the more commonly employed iodine. 6-(6'-Azobenzotriazolyl)-7-methoxy-2,2,4-trimethyl-1,2-dihydroquinoline **2** was easily synthesised by diazotisation of aminobenzotriazole and subsequent electrophilic attack of compound **1** by the diazonium (Figure 1). After purification by wet flash chromatography, crystals suitable for study using synchrotron radiation were grown from methanol.

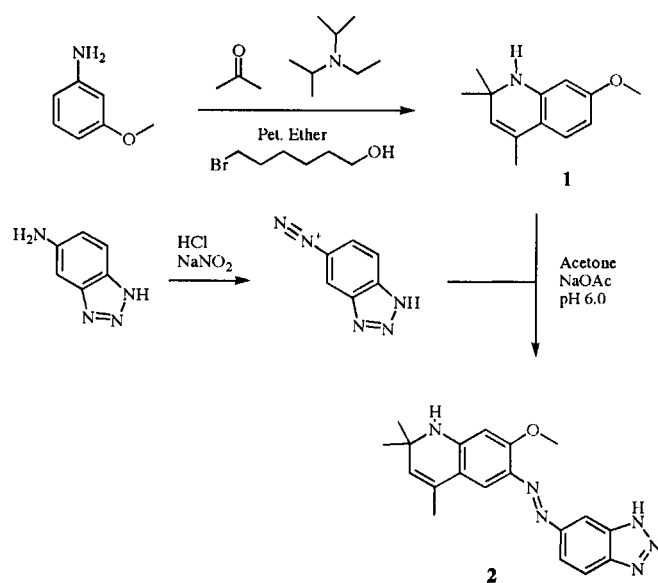


Figure 1. Synthesis of 6-(6'-azobenzotriazolyl)-7-methoxy-2,2,4-trimethyl-1,2-dihydroquinoline.

The structure shows the exclusive existence of the unexpected isomer of the dye relative to the benzotriazole (Figure 2). (It should be noted that the crystal numbering differs from the IUPAC nomenclature.) As the starting material was the 5-isomer it was expected that the 5-isomer would exist in the dye structure. However in this case the 6-isomer

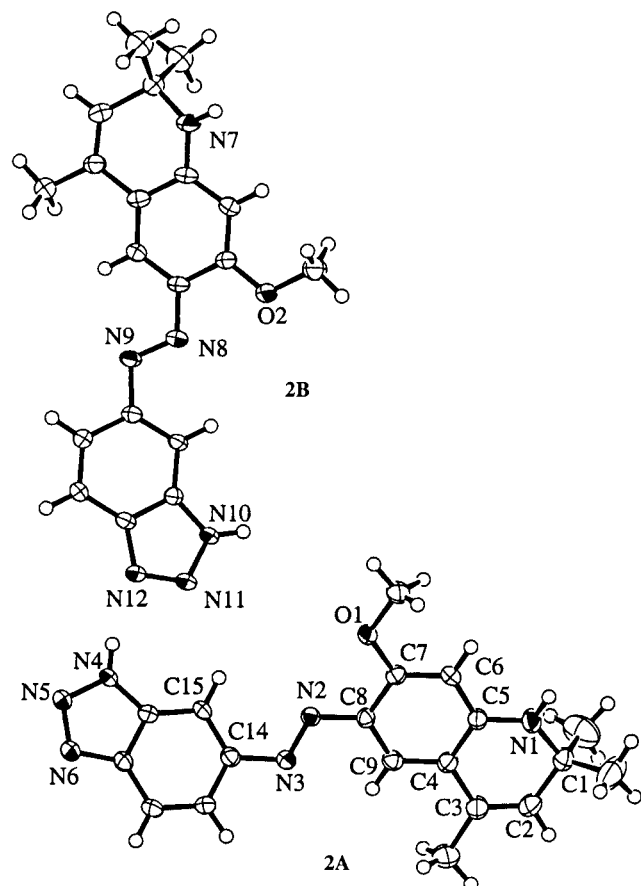


Figure 2. The molecular conformations of **2** with essential atom labels. Selected distances and angles (Å and °): N(4)-N(5) 1.341(3) N(5)-N(6) 1.308(4) N(1)-C(1) 1.443(4) C(1)-C(2) 1.484(5) C(3)-C(4) 1.470(4) C(4)-C(5) 1.419(4) N(3)-N(2)-C(8) 115.1(2) N(2)-N(3)-C(14) 112.8(2) C(1)-C(2)-C(3) 125.3(3) N(3)-N(2)-C(8)-C(7) -167.7(3) N(2)-N(3)-C(14)-C(15) 26.4(4).

is exclusively favoured. This suggests the 6-isomer is lower in energy than the 5-isomer once functionalised into an azo.

The bond distances and angles of the two crystallographically independent molecules do not present significant differences (bond distances are equivalent and the maximum difference in bond angles is 1°). As one molecule contains a disordered CMe₂ group, **2B**, only the geometric parameters of the other molecule, **2A**, will be discussed. **2A** clearly exists predominately as the azo rather than the hydrazo tautomer. However the slight lengthening of the N=N bond [1.267(3) Å] and especially the shortening of the N(2)-C(8) bond [1.397(4) Å cf. 1.424(4) Å for N(3)-C(14)] confirm that there is a degree of conjugation with the dihydroquinoline fragment consistent with some hydrazo character. This observation is also consistent with the vibrational frequency, measured by Raman spectroscopy, for the azo bond (Figure 3). The measured value of 1392 cm⁻¹ lies between the values normally expected for azo (~1440 cm⁻¹) and hydrazo (~1370 cm⁻¹) stretches. (For a typical recent example of azo bonding see Crispini *et al.* [7] which gives 1.250(3) and 1.425(3) Å.) The geometry of the dihydroquinoline fragment also supports an increase in conjugation compared to unsubstituted **1** as the heterocyclic ring is more planar [C(5)-N(1)-C(1)-C(2) -16.7(5)° N(1)-C(1)-C(2)-C(3) 10.8(5)° cf. 36.7(3) and -23.6(3)° in **1**], the C(1)-N(1)-C(5) angle is wider [124.9(3) cf. 122.6(2)° in **1**] and the bond lengths have altered [see especially N(1)-C(5) 1.353(4) cf. 1.381(2) Å and C(2)-C(3) 1.328(5) cf. 1.338(3) Å]. Each benzotriazole unit forms two hydrogen bonds (Table 1) giving parallel chains of benzotriazole moieties with their aromatic planes perpendicular to the *b* direction (Figure 4). The dihydroquinoline groups lie out of the benzotriazole plane, N(2)-N(3)-C(14)-C(15) 26.4 (4)° and N(3)-N(2)-C(8)-C(9) 8.0(4)°, with only much weaker interactions between them

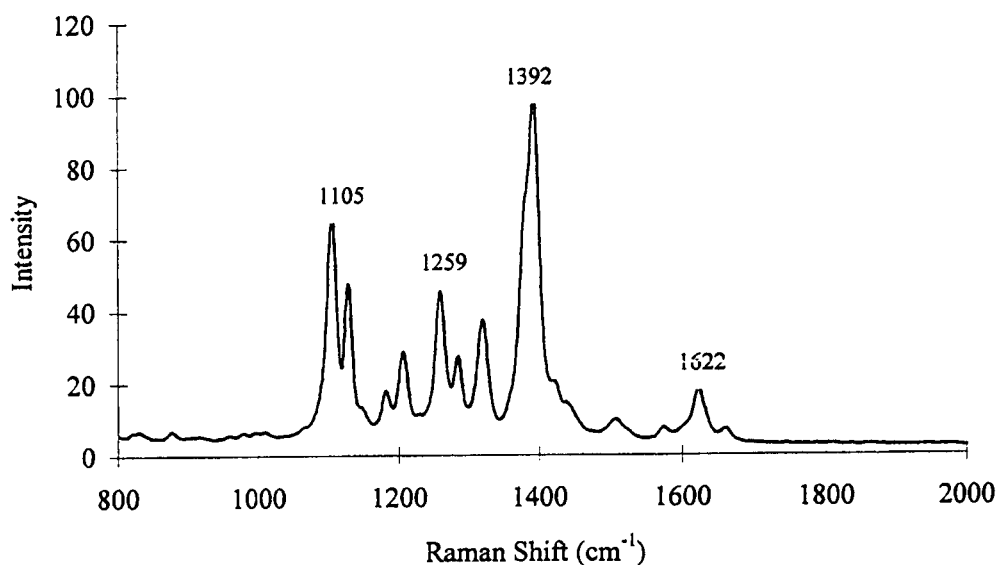


Figure 3. Expanded FT-Raman spectra of the azo dye demonstrating the presence of a partially bonded azo species.

(Table 1) giving the layered structure seen in Figure 4. Such a highly anisotropic crystal structure may be related to the anisotropic growth habit and consequently to the poor crystal growth properties of these compounds.

EXPERIMENTAL

^1H and ^{13}C spectra were recorded on a Bruker DPX 400MHz spectrometer and FT Raman was recorded on a Perkin Elmer 2000

Table 1
Selected Intermolecular Hydrogen Interactions

D-H...A	D-H (Å)	H...A (Å)	D...A (Å)	D-H...A ($^\circ$)	Symmetry (*) Operation
N(4)-H(4)---N(12)	0.88	1.96	2.831(4)	169	—
N(10)-H(10)---N(6)*	0.88	1.98	2.849(4)	168	$x + 1, y, z$
N(1)-H(1)---O(2)*	0.88	2.50	3.307(4)	152	$x, -y + 3/2, z + 1/2$
N(7)-H(7)---N(2)*	0.88	2.55	3.336(4)	149	$x + 1, -y + 3/2, z - 1/2$
N(7)-H(7)---O(1)*	0.88	2.56	3.329(4)	146	$x + 1, -y + 3/2, z - 1/2$
C(15)-H(15)---N(11)	0.95	2.62	3.363(3)	135	—
C(34)-H(34)---N(5)*	0.95	2.64	3.383(4)	135	$x + 1, y, z$

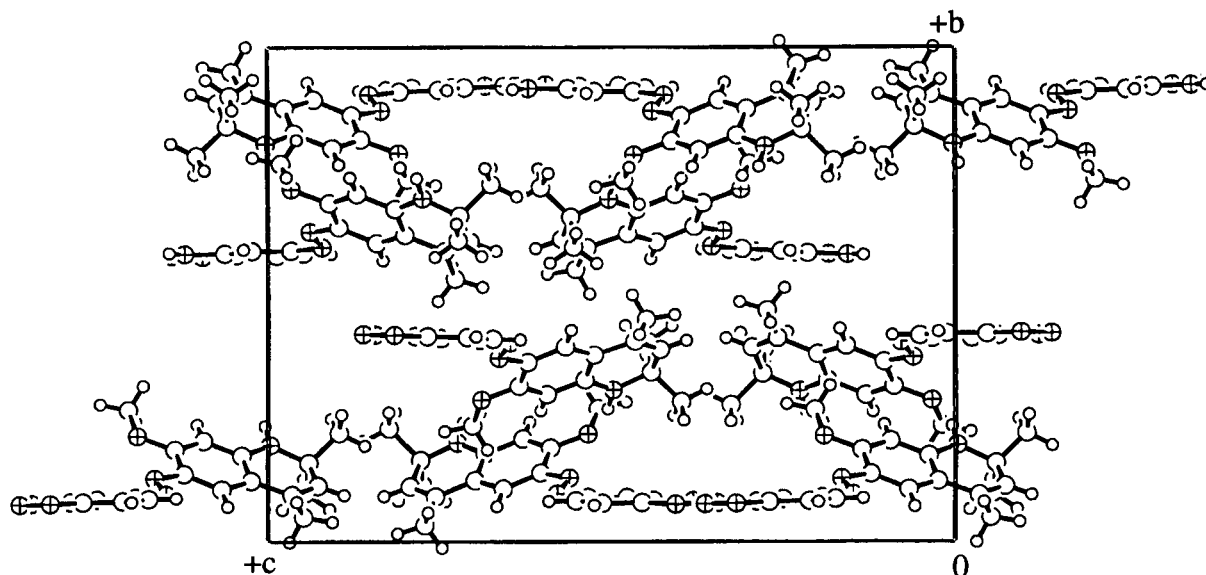


Figure 4. Crystal packing diagram of **2** viewed down the a axis.

The elucidation of this structure allows a greater understanding into the nature of the bonding within benzotriazole azo dyes by determining their bonding patterns and the unexpected isomerisation. In conclusion it can be said that the azo bond delocalises into the dihydroquinoline fragment and not the benzotriazole thus diminishing the azo character. This leaves the benzotriazole largely unaffected and free to complex to the metal surface as normal. The information obtained in this study can be applied to other benzotriazole azo dyes that do not crystallise but are commonly used in SERS studies. This structural information is currently being used to accurately calculate and assign vibrational frequencies commonly observed for this class of compound.

series FTIR with a NIR Raman attachment exciting with 1064 nm radiation. Reagent grade solvents were used throughout, preparative chromatography was performed by wet flash column chromatography using silica gel (Merck silica gel 60, mesh 240-400 nm), thin layer chromatography was performed on aluminium sheets, silica gel 60 F₂₅₄, 0.2 mm (Merck) and the products visualised by UV absorption at 254 nm.

7-Methoxy-2,2,4-trimethyl-1,2-dihydroquinoline (1).

m-Anisidine (3 eq., 2.09 g, 13.66 mmol) was dissolved in a mixture of petroleum ether (60-80) (20 ml) and acetone (20 ml) with diisopropylethylamine (5 eq., 2.94 g, 3.97 ml, 22.78 mmol) before 6-bromohexanol (1 eq., 0.82 g, 0.59 ml, 4.55 mmol) was added and the mixture left to reflux for 18 hours. The solvent was then removed and the residue dissolved in ethyl acetate (150 ml), washed (sat. KCl 3 x 100 ml), dried and the product isolated by

wet flash column chromatography eluting with dichloromethane. White crystals were obtained from water/ethanol (9/1) in 56% yield mp 73–75 °C; R_f dichloromethane/methanol (9/1) 0.56; δ ^1H NMR (CDCl_3) 1.28 (6 H, s, 2 x CH_3) 1.98 (3 H, d, $J = 1.4$, CH_3) 3.77 (3 H, s, OCH_3) 5.21 (H, d, $J = 1.2$, H8) 6.05 (H, d, $J = 2.5$, H2) 6.22 (H, dd, $J = 2.5 + 8.4$, H4) 6.99 (H, d, $J = 8.4$, H5); δ ^{13}C NMR (CDCl_3) 18.81 (CH_3) 31.19 (CH_3) 52.13 (C) 55.26 (CH_3) 98.82 (CH) 102.52 (CH) 115.56 (C) 124.81 (CH) 126.13 (CH) 128.38 (C) 144.69 (C) 160.32 (C).

Anal. Calcd. for $\text{C}_{13}\text{H}_{17}\text{N}$: C, 76.85; H, 8.37; N, 6.90. Found: C, 76.72; H, 8.73; N, 6.87.

6-(6'-Azobenzotriazolyl)-7-methoxy-2,2,4-trimethyl-1,2-dihydroquinoline **2**.

5-Aminobenzotriazole (0.50 g, 1.1 eq., 3.73 mmol) was dissolved in HCl (5 ml, 50% v/v) and diazotised by dropwise addition of sodium nitrite (0.28 g, 1.2 eq., 4.10 mmol in 5 ml H_2O) at 0 °C. The diazotised aminobenzotriazole was added dropwise over 30 minutes to a stirred solution of 7-methoxy-2,2,4-trimethyl-1,2-dihydroquinoline (0.69 g, 1 eq., 3.39 mmol) dissolved in sodium acetate buffer (1.0 M, 20 ml, pH = 6.0) and acetone (25 ml). After one hour the solvent was removed *in vacuo* and the residue dissolved in ethyl acetate (100 ml), washed (sat. KCl 3 x 100 ml) and dried (Na_2SO_4) prior to purification by wet flash column chromatography eluting with methanol in dichloromethane (0–3%). The pure product was obtained as a red powder after trituration from chloroform using pet. ether (40–60) in 76% (0.949 g, 2.58 mmol); R_f [$\text{CH}_3\text{COOCH}_2\text{CH}_3/\text{CH}_3\text{OH}/\text{NH}_3$ (5/1/1)] 0.62, δ ^1H NMR ($\text{DMSO}-d_6$): δ 1.28 (6H, s, 2 x CH_3) 1.94 (3H, s, CH_3) 3.91 (3H, s, OCH_3) 5.35 (1H, s, H3) 6.22 (1H, s, H8) 7.14 (1H, s, H5) 7.52 (1H, s, H7') 7.87 (1H, d, $J = 8.8$, H4') 7.95 (1H, d, $J = 8.8$, H5') 8.09 (1H, s, NH); λ_{max} (MeOH) 506.4 nm.

Anal. Calcd. for $\text{C}_{19}\text{H}_{20}\text{N}_6\text{O}$ C, 65.52; H, 5.75; N, 24.14. Found: C, 64.30; H, 5.85; N, 23.23.

Crystal data for **2**.

$\text{C}_{19}\text{H}_{20}\text{N}_6\text{O}$, $M = 348.41$, orange needle of dimensions 200 x 40 x 25 μm , monoclinic, space group $\text{P}2_1/c$, $a = 9.0595(5)$, $b =$

$17.0532(9)$, $c = 23.3239(13)$ Å, $\beta = 90.196(2)^\circ$, $V = 3603.4(3)$ Å³, $Z = 8$, $\lambda = 0.6875$ Å, $\mu = 0.085$ mm⁻¹, $T = 160$ K. Refinement on F^2 gave [8] $R = 0.0780$ and $R_w = 0.1721$ for 4996 "observed" reflections, $R_w = 0.1978$ for all 7931 unique reflections and 478 parameters, $\text{GoF} = 1.028$. Data were collected at station 9.8 of Daresbury SRS using methods and programs as published [9] to a maximum 2θ angle of 55°. All hydrogen atoms were observed in difference syntheses but were included in the final refinement in idealised positions and in riding modes. Supplementary data has been deposited with the Cambridge Crystallographic Data Centre (CCDC) as entry number CCDC143733.

Acknowledgements.

The authors would like to thank the BBSRC for the award of a David Phillips fellowship to DG and Geoff Dent of Avecia (formerly known as Zeneca Specialities) for performing the FT-Raman experiments.

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