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Single crystal X-ray structure of C.I. Disperse Yellow 3

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Abstract

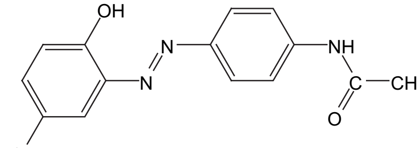
Crystals of C.I. Disperse Yellow 3, an aminoazobenzene derivative, were grown in an acetonitrile solution and its crystal structure was determined by single crystal X-ray diffraction analysis. It was found that the asymmetric unit consisted of two dye molecules (A and B) and one acetonitrile solvent. In each dye molecule, the aminoazobenzene framework was almost planar due to intramolecular H-bonds. The dye molecules are connected by weak intermolecular H-bonds to form a molecular pair in "head-to-tail" mode. The acetonitrile molecule is also bound to the dye molecule by H-bonding. In the packed structure, interlayer association occurs by further π–π stacking of the molecular pairs formed. Results from thermogravimetric analysis and X-ray powder diffraction studies of a crystalline sample of the title compound support the contribution of the solvent molecule to the formation of the crystal lattice.

Keywords: Disperse dye; C.I. Disperse Yellow 3; Crystal structure; H-bond; π–π stacking interaction

1. Introduction

Due to their central role in the dyeing of polyester fibres as well as various high-technology applications, disperse dyes have attracted the attention of researchers from various backgrounds [1]. In particular, the structural investigation of disperse dyes in the solid state has been of particular interest because the dye's absorption behaviour on polyester fibre depends not only on the conformation of the solid dye but also on the interactions occurring between the dye molecule and the substrate surface [2–15]. The technical performance of disperse dyes is strongly related to their particle size, morphology and conformation in the crystalline or solid state [16]. Furthermore, the demand for the development of new functional dyes with specific properties requires additional information on the structural conformation of the existing dyes at a molecular level.

As part of a research study concerning the structure/function relationships of dye molecules, we have reported the crystal structures of several types of disperse dyes such as monoazo [12,13], methine [14] and anthraquinone [15] classes. As a continuation of this research, we describe herein the crystal structure of C.I. Disperse Yellow 3, one of the most important aminoazobenzene disperse dyes. We also report the role of solvent molecules which stabilize the crystal lattice using thermogravimetric analysis and X-ray powder diffraction.



C.I. Disperse Yellow 3

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Table 1
Crystallographic data for C.I. Disperse Yellow 3

Empirical formula	$C_{32}H_{33}N_7O_4$
Formula weight	579.65
Temperature (K)	173(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	*P*-1 (no. 2)
a (Å)	8.3985(11)
b (Å)	11.7924(16)
c (Å)	15.938(2)
α (°)	106.913(3)
β (°)	103.418(3)
γ (°)	94.078(3)
Volume (Å^3)	1452.6(3)
Z	2
D_{calc} (g/cm^3)	1.325
μ (mm^{-1})	0.090
F(000)	612
Crystal dimensions (mm)	0.20 × 0.20 × 0.03
Color of crystal	Yellow
Shape of crystal	Plate
$2\theta_{max}$ (°)	56.66
No. of reflections measured	9258
No. of reflections observed [$I > 2\sigma(I)$]	6462
No. of variables	388
R	0.0699
R_w	0.1888
Largest diffraction peak and hole (e Å^{-3})	0.577 and −0.611
Maximum shift in final cycles	<0.001

Table 2
Atomic coordinates (×10^4) and equivalent isotropic displacement parameters (Å × 10^3) for C.I. Disperse Yellow 3

	x	*y*	*z*	*U* (eq)
O(1)	2064(3)	5533(2)	95(2)	36(1)
O(2)	3394(3)	10340(2)	5452(1)	36(1)
O(3)	8432(3)	8304(2)	8996(1)	35(1)
O(4)	4177(3)	5839(2)	2826(1)	35(1)
N(1)	502(3)	7038(2)	103(2)	25(1)
N(2)	1687(3)	9758(2)	3784(2)	24(1)
N(3)	729(3)	10530(2)	3957(2)	24(1)
N(4)	6550(3)	9101(2)	8138(2)	23(1)
N(5)	5686(3)	6275(2)	4511(2)	24(1)
N(6)	6547(3)	5434(2)	4344(2)	25(1)
N(7)	5628(4)	8840(3)	1396(2)	38(1)
C(1)	289(4)	5512(3)	−1327(2)	33(1)
C(2)	1050(4)	6016(3)	−311(2)	26(1)
C(3)	860(4)	7683(2)	1039(2)	22(1)
C(4)	−121(4)	8571(3)	1279(2)	27(1)
C(5)	108(4)	9262(3)	2169(2)	26(1)
C(6)	1355(4)	9076(2)	2849(2)	23(1)
C(7)	2335(4)	8209(3)	2617(2)	24(1)
C(8)	2097(4)	7494(3)	1719(2)	25(1)
C(9)	1047(4)	11228(3)	4878(2)	24(1)
C(10)	5(4)	12091(3)	5061(2)	26(1)
C(11)	185(4)	12863(3)	5925(2)	26(1)
C(12)	1439(4)	12738(3)	6630(2)	29(1)
C(13)	2492(4)	11898(3)	6470(2)	31(1)
C(14)	2327(4)	11135(3)	5595(2)	25(1)
C(15)	−900(4)	13823(3)	6112(2)	35(1)
C(16)	7396(4)	10034(3)	9767(2)	31(1)
C(17)	7520(4)	9065(3)	8935(2)	24(1)
C(18)	6393(3)	8348(2)	7245(2)	20(1)
C(19)	7292(4)	7393(3)	7042(2)	26(1)
C(20)	7081(4)	6702(3)	6150(2)	26(1)
C(21)	5980(4)	6945(3)	5442(2)	22(1)
C(22)	5084(3)	7893(3)	5648(2)	23(1)
C(23)	5291(4)	8594(3)	6539(2)	24(1)
C(24)	6248(4)	4758(3)	3419(2)	24(1)
C(25)	7167(4)	3812(3)	3240(2)	26(1)
C(26)	6983(4)	3044(3)	2371(2)	27(1)
C(27)	5840(4)	3257(3)	1657(2)	31(1)
C(28)	4911(4)	4186(3)	1811(2)	30(1)
C(29)	5104(4)	4947(3)	2690(2)	26(1)
C(30)	7939(4)	2003(3)	2195(2)	37(1)
C(31)	6026(5)	6611(3)	859(2)	42(1)
C(32)	5823(4)	7867(3)	1157(2)	30(1)

2. Experimental

C.I. Disperse Yellow 3 (C.I. no. 11855, 30% dye content, Aldrich) was extracted with dichloromethane to remove the dye from diluents. The single crystals suitable for X-ray analysis were obtained by the slow evaporation of acetonitrile solution of the purified dye. The suitable crystal was mounted on a Bruker SMART diffractometer equipped with a graphite monochromated Mo Kα ($\lambda = 0.71073$ Å) radiation source and a CCD detector and 45 frames of two-dimensional diffraction images were collected and processed to deduce the cell parameters and orientation matrix. A total of 1271 frames of two-dimensional diffraction images were collected, each of which was measured for 10 s. The frame data were processed to give structural factors using the program SAINT [17]; the intensity data were corrected for Lorentz and polarization effects. The structures were analysed using a combination of direct and difference Fourier methods provided by the SHELXTL [18] computer program and were refined as a full matrix least square against F^2 for all data; all non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in calculated positions with isotropic thermal parameters, 1.2 times those of the attached atoms. Crystallographic data are summarized in Table 1, the CCDC reference number is 616427.

Thermogravimetric analysis was conducted using a Scinco TGA1000 model under a nitrogen flow; X-ray powder patterns were obtained by a Bruker Gaddz D8 diffractometer.

3. Results and discussion

The absence of the single crystal structural data for the title compound may be due, in part, to the difficulty in growth of the crystals that are acceptable for X-ray diffraction analysis. Our attempts to grow single crystals from organic solvents such as methanol, ethanol, dichloromethane, ethyl acetate and *n*-hexane always afforded thin or needle-shaped crystals, none of which diffracted well enough to obtain information about the crystal structure. Bright-yellow crystals suitable for X-ray analysis were secured by the slow evaporation of the acetonitrile solution of the purified dye after two weeks of storage in a refrigerator. The crystal used exists in the triclinic space group *P*-1. The atomic coordinates, bond lengths and angles are reported in Tables 2 and 3; the crystal structure with atomic numbering is given in Fig. 1.

The asymmetric unit consists of two dye molecules and one acetonitrile as trapped solvent. Two dye molecules (A and B), which show no significant geometrical difference, exist in the same plane and are arranged in anti-parallel fashion (Fig. 1a). The aminoazobenzene framework of each dye is essentially

Table 3
Selected bond lengths (Å), bond angles, and torsion angles (°) for C.I. Disperse Yellow 3

O(1)−C(2)	1.224(3)	C(9)−C(10)	1.400(4)
O(2)−C(14)	1.351(3)	C(9)−C(14)	1.411(4)
O(3)−C(17)	1.230(3)	C(10)−C(11)	1.378(4)
O(4)−C(29)	1.350(3)	C(11)−C(12)	1.401(4)
N(1)−C(2)	1.362(4)	C(11)−C(15)	1.509(4)
N(1)−C(3)	1.412(3)	C(12)−C(13)	1.383(4)
N(2)−N(3)	1.270(3)	C(13)−C(14)	1.392(4)
N(2)−C(6)	1.423(3)	C(16)−C(17)	1.509(4)
N(3)−C(9)	1.410(3)	C(18)−C(23)	1.398(4)
N(4)−C(17)	1.354(3)	C(18)−C(19)	1.401(4)
N(4)−C(18)	1.412(3)	C(19)−C(20)	1.380(4)
N(5)−N(6)	1.272(3)	C(20)−C(21)	1.396(4)
N(5)−C(21)	1.417(4)	C(21)−C(22)	1.394(4)
N(6)−C(24)	1.409(4)	C(22)−C(23)	1.383(4)
N(7)−C(32)	1.135(4)	C(24)−C(25)	1.400(4)
C(1)−C(2)	1.513(4)	C(24)−C(29)	1.409(4)
C(3)−C(8)	1.398(4)	C(25)−C(26)	1.384(4)
C(3)−C(4)	1.400(4)	C(26)−C(27)	1.404(4)
C(4)−C(5)	1.375(4)	C(26)−C(30)	1.508(4)
C(5)−C(6)	1.401(4)	C(27)−C(28)	1.387(4)
C(6)−C(7)	1.379(4)	C(28)−C(29)	1.391(4)
C(7)−C(8)	1.394(4)	C(31)−C(32)	1.454(4)
C(2)−N(1)−C(3)	128.9(3)	O(2)−C(14)−C(9)	121.9(3)
N(3)−N(2)−C(6)	114.4(2)	C(13)−C(14)−C(9)	118.5(3)
N(2)−N(3)−C(9)	115.5(2)	O(3)−C(17)−N(4)	123.8(3)
C(17)−N(4)−C(18)	129.2(2)	O(3)−C(17)−C(16)	121.3(3)
N(6)−N(5)−C(21)	115.2(2)	N(4)−C(17)−C(16)	114.8(2)
N(5)−N(6)−C(24)	115.4(2)	C(23)−C(18)−C(19)	119.5(3)
O(1)−C(2)−N(1)	123.5(3)	C(23)−C(18)−N(4)	117.1(2)
O(1)−C(2)−C(1)	122.1(3)	C(19)−C(18)−N(4)	123.3(2)
N(1)−C(2)−C(1)	114.4(3)	C(20)−C(19)−C(18)	120.0(3)
C(8)−C(3)−C(4)	119.3(3)	C(19)−C(20)−C(21)	120.7(3)
C(8)−C(3)−N(1)	124.9(2)	C(22)−C(21)−C(20)	119.1(3)
C(4)−C(3)−N(1)	115.8(2)	C(22)−C(21)−N(5)	116.7(2)
C(5)−C(4)−C(3)	121.4(3)	C(20)−C(21)−N(5)	124.2(3)
C(4)−C(5)−C(6)	119.3(3)	C(23)−C(22)−C(21)	120.7(3)
C(7)−C(6)−C(5)	119.7(3)	C(22)−C(23)−C(18)	120.0(3)
C(7)−C(6)−N(2)	117.3(2)	C(25)−C(24)−N(6)	115.2(3)
C(5)−C(6)−N(2)	123.0(2)	C(25)−C(24)−C(29)	119.1(3)
C(6)−C(7)−C(8)	121.4(3)	N(6)−C(24)−C(29)	125.6(3)
C(7)−C(8)−C(3)	119.0(3)	C(26)−C(25)−C(24)	122.4(3)
C(10)−C(9)−N(3)	115.2(2)	C(25)−C(26)−C(27)	117.2(3)
C(10)−C(9)−C(14)	119.5(3)	C(25)−C(26)−C(30)	121.6(3)
N(3)−C(9)−C(14)	125.3(3)	C(27)−C(26)−C(30)	121.1(3)
C(11)−C(10)−C(9)	122.1(3)	C(28)−C(27)−C(26)	121.8(3)
C(10)−C(11)−C(12)	117.5(3)	C(27)−C(28)−C(29)	120.2(3)
C(10)−C(11)−C(15)	121.9(3)	O(4)−C(29)−C(28)	119.3(3)
C(12)−C(11)−C(15)	120.7(3)	O(4)−C(29)−C(24)	121.5(3)
C(13)−C(12)−C(11)	121.7(3)	C(28)−C(29)−C(24)	119.2(3)
C(12)−C(13)−C(14)	120.6(3)	N(7)−C(32)−C(31)	178.2(4)
O(2)−C(14)−C(13)	119.5(3)		
C(1)−C(2)−N(1)−C(3)	174.9(3)	C(16)−C(17)−N(4)−C(18)	178.9(3)
O(1)−C(2)−N(1)−C(3)	−4.8(5)	O(3)−C(17)−N(4)−C(18)	−1.7(5)
C(6)−N(2)−N(3)−C(9)	−179.2(3)	C(21)−N(5)−N(6)−C(24)	179.4(3)
C(9)−C(10)−C(11)−C(15)	177.6(3)	C(24)−C(25)−C(26)−C(30)	−177.8(3)
N(3)−C(9)−C(14)−O(2)	0.10(5)	N(6)−C(24)−C(29)−O(4)	0.8(5)

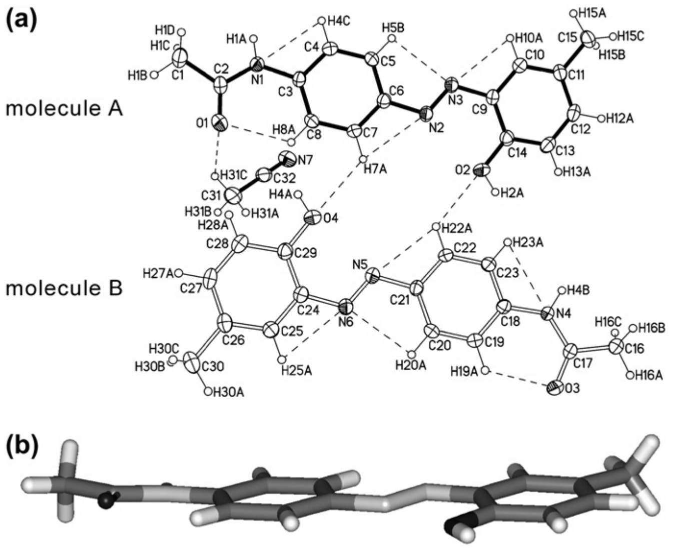

Fig. 1. X-ray crystal structure of C.I. Disperse Yellow 3; (a) top view with H-bonds (dashed lines) and (b) side view of the molecule A showing the planarity.

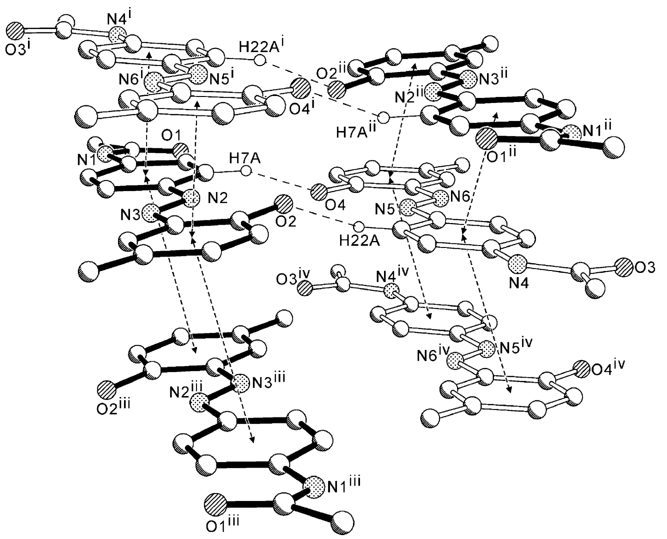

Fig. 2. Representation of molecular pairing by H-bonds (dashed lines) and π–π stacking between layers (dashed arrows). The acetonitrile molecules and non-H-bonded hydrogen atoms are omitted for clarity. [Symmetry codes: (i) $-x+1, -y+2, -z+1$; (ii) $-x+1, -y+2, -z+1$; (iii) $-x, -y+2, -z+1$; (iv) $-x+1, -y+1, -z+1$].

planar with dihedral angles of 2.3(2)° for A and 2.3(2)° for B between two phenyl rings (Fig. 1b). The planar conformations are stabilized by intramolecular H-bonds such as C–H···O and C–H···N types, which have bond lengths of ca. 2.4–2.8 Å. The structural parameters for the H-bonds are summarized in Table 4. As mentioned, the acetonitrile interacts with the molecule A through weak C–H···O(C) type H-bonding, which may induce a slight conformational difference between the two dye molecules.

In packing, the molecular pairs that formed as a result of weak intermolecular H-bonds are stacked one on top of each other (Fig. 2) in such a way that they form a stacked array of interlayer associations by means of aromatic π–π stacking interaction, of 3.6–3.9 Å.

To examine the effect of the interior solvent in the crystal lattice on its thermal character and crystallinity, the crystalline sample of the title compound was characterized using thermogravimetric analysis (TGA) and X-ray powder diffraction (XRPD). TGA showed a first sharp mass loss of 6.95% from 85 to 120 °C which corresponds to the complete loss of one acetonitrile molecule (expected mass loss 7.08%), residing between the dye molecules which are loosely connected by H-bonds (Fig. 3).

The XRPD patterns for the crystalline sample of C.I. Disperse Yellow 3 and the desolvated sample after heating at 150 °C for 1 h were obtained (Fig. 4). The XRPD pattern of the desolvated sample differs with that of the original one; removal of the acetonitrile solvent molecule from the crystal maintains the bulk crystallinity but its framework structure is changed. The TGA and XRPD data indicate that the interior solvent molecule interacts efficiently with the dye molecules. We confirmed that the structural conformation of C.I. Disperse Yellow 3 in the crystal lattice is stabilized by interactions such

Table 4
Intra- and intermolecular H-bonds geometry (Å, °) for C.I. Disperse Yellow 3

D–H···A	D–H	H···A	D···A	D–H···A
C4–H4C···N1	0.95	2.52	2.382(4)	70.8
C5–H5B···N3	0.95	2.44	2.711(4)	95.9
C7–H7A···N2	0.95	2.53	2.394(4)	70.6
C7–H7A···O4	0.95	2.79	3.351(4)	118.8
C8–H8A···O1	0.95	2.34	2.919(4)	119
C10–H10A···N3	0.95	2.5	2.372(4)	71.3
C22–H22A···O2	0.95	2.79	3.367(3)	119.7
C19–H19A···O3	0.95	2.26	2.879(4)	121.9
C20–H20A···N6	0.95	2.48	2.744(4)	95.9
C22–H22A···N5	0.95	2.54	2.393(4)	70.3
C23–H23A···N4	0.95	2.55	2.398(4)	69.8
C25–H25A···N6	0.95	2.5	2.373(4)	71.4
C31–H31C···O1	0.95	2.53	3.284(4)	135.8

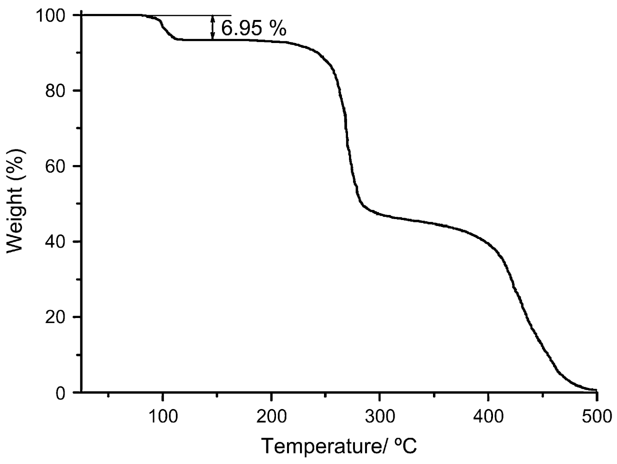

Fig. 3. TG curve of C.I. Disperse Yellow 3 in a nitrogen atmosphere with a heating rate of 10 °C/min.

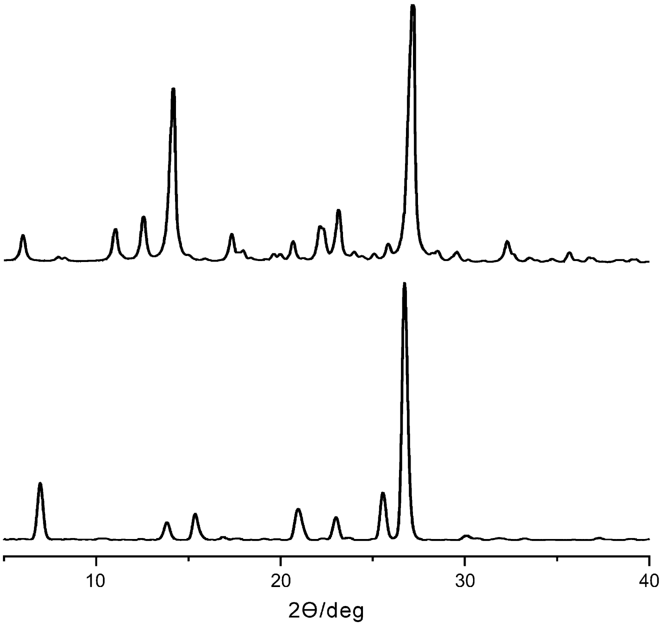

Fig. 4. XRPD patterns for Disperse Yellow 3; (a) original and (b) desolvated by drying at 150 °C for 1 h.

as H-bonds and π–π stacking between the dye molecules as well as H-bonds between the solvent and dye molecules.

4. Conclusions

The asymmetric unit of C.I. Disperse Yellow 3 comprises two dye molecules (A and B) and one acetonitrile solvent; in each dye molecule, the aminoazobenzene framework was almost planar due to intramolecular H-bonds. The dye molecules are connected by weak intermolecular H-bonds and the acetonitrile molecule is also bound to the dye molecule by H-bonding. In the packed structure, interlayer association occurs by further π–π stacking of the molecular pairs formed. TGA and XRPD studies support the contribution of the solvent molecule to the formation of the crystal lattice.

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References

[1] Dawson JF. J Soc Dyers Colour 1983;99:183.
[2] Annen O, Egli R, Hasler R, Henzo B, Jakob H, Matzinger P. Rev Prog Color 1987;17:72.
[3] Leadbetter PW, Leaver AT. Rev Prog Color 1989;19:33.
[4] McIntosh SA, Freeman HS. Text Res J 1989;59:389.
[5] McIntosh SA, Freeman HS, Singh P. Dyes Pigments 1992;20:147.
[6] Freeman HS, Posey Jr JC. Dyes Pigments 1992;20:147.
[7] Freeman HS, Posey Jr JC, Singh P. Dyes Pigments 1992;20:279.
[8] Freeman HS, McIntosh SA, Singh P. Dyes Pigments 1997;35:11.
[9] Freeman HS, McIntosh SA, Singh P. Dyes Pigments 1997;35:149.
[10] You X-L, Lu C-R, Huang Z-L, Zhang D-C. Dyes Pigments 2004;63:217.
[11] Singh K, Mahajan A, Robinson WT. Dyes Pigments 2007;74:95–102.
[12] Park K-M, Yoon I, Lee SS, Choi G, Lee JS. Dyes Pigments 2002;54:155.
[13] Seo J, Jo WJ, Choi G, Park K-M, Lee SS, Lee JS. Dyes Pigments 2007;72:327.
[14] Yoon I, Park K-M, Lee SS, Choi G, Lee JS. Anal Sci 2001;17:1355.
[15] Park K-M, Yoon I, Lee SS, Choi G, Lee JS. Anal Sci 2003;19:1219.
[16] McGeorge G, Harris RK, Batsanov AS, Churakov AV, Chippendale AM, Bullock JF, et al. J Phys Chem A 1998;102:3505.
[17] Bruker. Area detector control and integration software. Version 6.22, SAMRT and SAINT. Madison, Wisconsin (USA): Bruker Analytical X-ray Instruments Inc.; 2001.
[18] Bruker. Structure determination programs. Version 6.10, SHELXTL. Madison, Wisconsin (USA): Bruker Analytical X-ray Instruments Inc.; 2000.