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X-ray crystal structure of C.I. Disperse Blue 79

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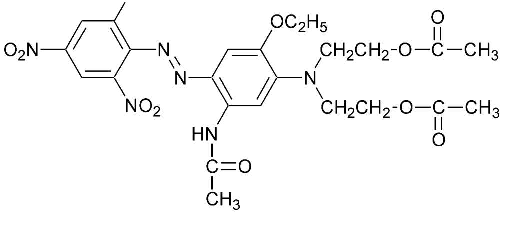
Abstract

Crystals of C.I. Disperse Blue 79, a commercial aminoazobenzene dye, were grown from an ethyl acetate solution and the crystal structure was determined by single crystal X-ray diffraction analysis. The dye molecule crystallizes in the triclinic space group P-1 with the unit cell dimensions: $a = 11.467(2)$ Å, $b = 11.952(2)$ Å, $c = 12.372(2)$ Å, $\alpha = 101.047(4)^\circ$, $\beta = 113.221(4)^\circ$, $\gamma = 108.204(4)^\circ$. Results showed that the 4-nitro-4′-aminoazobenzene skeleton of the dye is quasi planar, with a dihedral angle of 9.4(3)° between two aromatic rings. The intra- and intermolecular hydrogen bonds, together with the interlayer aromatic π–π stacking interactions, stabilize the molecular conformation and packing in the crystal structure. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: C.I. Disperse Blue 79; X-ray crystal structure; Hydrogen bond; π–π Stacking

1. Introduction

The X-ray single crystal structures of disperse dyes [1–3] have been important, not only because it serves details of the molecular conformation including the intra- and intermolecular interactions in solid state but also since this information assists towards understanding the technical performance of the products [4]. C.I. Disperse Blue 79 is one of the representative commercial products of aminoazobenzene dyes in polyester colouration [1]. In the view of the practical significance of the C.I. Disperse Blue 79, it is somewhat surprising that no single crystal structure determinations have been previously reported, although our search for the X-ray crystal structures of the compounds based on 4-nitro-4′-aminoazobenzene in the Cambridge Crystallographic Data Base [5] gave 18 hits [4,6–11]. The absence of the single crystal structural data may be due in part to the difficulty in growing single crystals acceptable for X-ray diffraction analysis. Additionally, disordered systems make difficult to crystallize, and



C.I. Disperse Blue 79 **(1)**

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this often prevents an X-ray determination of such structures [4].

Recently our attempts to grow single crystals which have suitable quality including the thickness of this dye molecule were successful. Herein, we present the results of the X-ray analysis of the C.I. Disperse Blue 79 during the course of our investigation [12] concerning the structures and properties of disperse dyes.

2. Experimental

The C.I. Disperse Blue 79 (Clariant Co.) was extracted with dichloromethane to separate the colorant from diluents. The single crystals suitable for the X-ray analysis were obtained by evaporating an ethyl acetate solution of the dye. X-ray crystallographic analysis was performed with a Siemens SMART diffractometer equipped with a graphite monochromated MoK_α ($\lambda = 0.71073$ Å) radiation source and a CCD detector. A total of 45 frames of two-dimensional diffraction images

Table 1
Crystallographic data and intensity collection for C.I. Disperse Blue 79

Empirical formula	$C_{24}H_{27}BrN_6O_{10}$
Formula weight	639.43
Temperature (K)	298(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	*P*-1 (No. 2)
a (Å)	11.467(2)
b (Å)	11.952(2)
c (Å)	12.372(2)
α (°)	101.047(4)
β (°)	113.221(4)
γ (°)	108.204(4)
Volume (Å^3)	1380.7(4)
Z	2
D_{calc} (g/cm^3)	1.538
μ (mm^{-1})	1.555
F(000)	656
Crystal dimensions (mm)	0.30 × 0.12 × 0.05
Color of crystal	Greenish blue
Shape of crystal	Plate
$2\theta_{max}$ (°)	56.60
No. of reflections measured	9179
No. of reflections observed [$I > 2\sigma(I)$]	6421
No. of variables	371
Goodness-of-fit on F^2	0.969
R	0.0572
R_w	0.1134
Largest diff. peak and hole (e Å^{-3})	0.440 and −0.534
Maximum shift in final cycles	< 0.01

Table 2
Atomic coordinates (×10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) for C.I. Disperse Blue 79

	x	*y*	*z*	*U*(eq)
Br(1)	7737(1)	6482(1)	3671(1)	58(1)
O(1)	11051(4)	10453(3)	−1334(3)	76(1)
O(2)	11095(3)	8696(3)	−2289(2)	59(1)
O(3)	8303(3)	3744(3)	−5069(3)	63(1)
O(4)	8486(4)	2000(3)	−4818(3)	92(1)
O(5)	10822(3)	7416(3)	538(2)	57(1)
O(6)	5778(4)	2475(4)	−4304(3)	101(1)
O(7)	3485(4)	2326(4)	−1420(3)	90(1)
O(8)	4920(4)	1617(3)	−433(3)	89(1)
O(9)	1985(4)	1956(4)	2130(4)	95(1)
O(10)	3403(4)	3474(4)	3911(3)	83(1)
N(1)	9959(3)	6250(3)	−2013(3)	48(1)
N(2)	5729(3)	3138(3)	−2491(3)	50(1)
N(3)	6471(3)	4290(3)	−79(3)	45(1)
N(4)	6876(3)	4826(3)	1100(3)	47(1)
N(5)	4332(4)	2302(4)	−472(3)	60(1)
N(6)	3081(4)	2896(4)	2845(4)	61(1)
C(1)	10217(6)	9776(5)	−3547(4)	83(2)
C(2)	10825(4)	9710(4)	−2273(4)	55(1)
C(3)	11641(5)	8529(4)	−1095(4)	63(1)
C(4)	11431(4)	7184(4)	−1340(4)	53(1)
C(5)	9340(4)	5707(4)	−3388(3)	51(1)
C(6)	9463(5)	4494(4)	−3803(4)	60(1)
C(7)	7880(5)	2497(5)	−5440(4)	61(1)
C(8)	6570(5)	1823(5)	−6676(4)	76(1)
C(9)	9173(4)	5792(4)	−1467(3)	42(1)
C(10)	9571(4)	6365(4)	−157(3)	43(1)
C(11)	8696(4)	5881(4)	290(3)	45(1)
C(12)	7403(4)	4814(4)	−471(3)	42(1)
C(13)	7008(4)	4221(4)	−1751(3)	42(1)
C(14)	7869(4)	4731(4)	−2213(4)	46(1)
C(15)	11260(5)	8086(4)	1814(4)	63(1)
C(16)	12610(6)	9241(5)	2289(4)	88(2)
C(17)	5198(5)	2327(4)	−3681(4)	60(1)
C(18)	3829(5)	1220(5)	−4166(4)	78(2)
C(19)	5872(4)	4262(4)	1446(3)	43(1)
C(20)	6127(4)	4936(4)	2651(3)	43(1)
C(21)	5224(4)	4486(4)	3105(3)	49(1)
C(22)	4040(4)	3377(4)	2358(4)	47(1)
C(23)	3724(4)	2678(4)	1170(4)	50(1)
C(24)	4665(4)	3138(4)	758(3)	45(1)

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

were collected and processed to obtain the cell parameters and orientation matrix. Data were collected over a hemisphere of reciprocal space, by a combination for three sets of exposures. A total 1271 frames of two-dimensional diffraction images were collected, each of which was measured for 30 s. The frame data were processed to give structure factors by the program SAINT [13]. The crystal showed no significant decay and no correction was applied for absorption or decay. Crystal structure was solved by the direct method, using the program package SHELXTL [14], and refined with full-matrix least-squares against F^2 for all data, resulting in final R and R_w indices of 0.0572 and 0.1134, respectively. All the non-H atoms were refined anisotropically. All hydrogen atoms were

Table 3
Selected bond lengths (Å), bond angles, and torsion angles (°) for C.I. Disperse Blue 79

Br(1)–C(20)	1.885(4)	O(1)–C(2)	1.195(5)
O(2)–C(2)	1.340(5)	O(2)–C(3)	1.441(5)
O(3)–C(7)	1.334(5)	O(3)–C(6)	1.450(5)
O(4)–C(7)	1.200(5)	O(5)–C(10)	1.365(4)
O(5)–C(15)	1.424(4)	O(6)–C(17)	1.204(5)
O(7)–N(5)	1.204(5)	O(8)–N(5)	1.209(5)
O(9)–N(6)	1.218(5)	O(10)–N(6)	1.209(4)
N(1)–C(9)	1.371(5)	N(1)–C(4)	1.466(5)
N(1)–C(5)	1.469(4)	N(2)–C(17)	1.362(5)
N(2)–C(13)	1.402(5)	N(3)–N(4)	1.295(4)
N(3)–C(12)	1.370(5)	N(4)–C(19)	1.407(5)
N(5)–C(24)	1.477(5)	N(6)–C(22)	1.472(5)
C(1)–C(2)	1.481(6)	C(3)–C(4)	1.500(6)
C(5)–C(6)	1.511(6)	C(7)–C(8)	1.485(6)
C(15)–C(16)	1.512(6)	C(17)–C(18)	1.493(6)
C(2)-O(2)–C(3)	115.4(3)	C(7)-O(3)–C(6)	117.1(3)
C(10)-O(5)–C(15)	119.4(3)	C(9)–N(1)–C(4)	125.9(3)
C(9)–N(1)–C(5)	118.8(3)	C(4)–N(1)–C(5)	115.1(3)
C(17)–N(2)–C(13)	129.0(3)	N(4)–N(3)–C(12)	115.2(3)
N(3)–N(4)–C(19)	112.8(3)	O(7)–N(5)-O(8)	125.4(4)
O(7)–N(5)–C(24)	118.6(4)	O(8)–N(5)–C(24)	116.0(4)
O(10)–N(6)-O(9)	123.9(4)	O(10)–N(6)–C(22)	118.3(4)
O(9)–N(6)–C(22)	117.7(4)	O(1)–C(2)-O(2)	123.1(4)
O(1)–C(2)–C(1)	125.3(5)	O(2)–C(2)–C(1)	111.6(4)
O(2)–C(3)–C(4)	108.3(3)	N(1)–C(4)–C(3)	114.7(4)
N(1)–C(5)–C(6)	112.1(3)	O(3)–C(6)–C(5)	107.2(3)
O(4)–C(7)-O(3)	122.9(4)	O(4)–C(7)–C(8)	125.2(5)
O(3)–C(7)–C(8)	111.9(4)	N(1)–C(9)–C(14)	119.3(3)
N(1)–C(9)–C(10)	124.1(3)	C(14)–C(9)–C(10)	116.5(3)
C(11)–C(10)-O(5)	124.4(3)	C(11)–C(10)–C(9)	120.1(4)
O(5)–C(10)–C(9)	115.4(3)	N(3)–C(12)–C(11)	125.1(3)
N(3)–C(12)–C(13)	116.5(3)	C(14)–C(13)–N(2)	122.9(3)
N(2)–C(13)–C(12)	117.8(3)	O(5)–C(15)–C(16)	106.7(4)
O(6)–C(17)–N(2)	123.3(4)	O(6)–C(17)–C(18)	121.8(4)
N(2)–C(17)–C(18)	114.9(4)	C(24)–C(19)–N(4)	128.3(3)
N(4)–C(19)–C(20)	115.7(3)	C(21)–C(20)-Br(1)	118.8(3)
C(19)–C(20)-Br(1)	119.7(3)	C(21)–C(22)–N(6)	118.9(3)
C(23)–C(22)–N(6)	118.6(4)	C(23)–C(24)–N(5)	114.7(3)
C(19)–C(24)–N(5)	121.3(3)		
N(1)–C(4)–C(3)-O(2)	52.5(4)	N(1)–C(5)–C(6)-O(3)	152.3(3)

included in calculated positions with isotropic thermal parameters 1.2 times those of attached atoms. The crystal and experimental data are given in Table 1.

Table 4
Intra- and intermolecular hydrogen-bonding geometry (Å, °) for C.I. Disperse Blue 79

D–H···A	D-H	H···A	D···A	D-H···A
N2–H2A. . .N3	0.96	2.29	2.686(4)	108.2
N2–H2A. . .O7	0.96	2.45	3.309(5)	173.1
C3–H3B. . .O5	0.96	2.39	2,911(5)	113.4
C5–H5A. . .O2	0.96	2.59	3.186(5)	119.6
C11–H11A. . .N4	0.96	2.46	2.728(5)	96.8
C14–H14. . .O6	0.96	2.24	2.847(5)	124.3
C21–H21A. . .O10	0.96	2.42	2.710(5)	97.8
C23–H23A. . .O9	0.96	2.43	2.706(5)	97.0
C18–H18B. . .Br1^{i}	0.96	2.93	3.800(6)	152.1
C21–H21A. . .O10^{ii}	0.96	2.51	3.409(5)	163.0
C23–H23A. . .O1^{iii}	0.96	2.37	3.213(5)	150.9

Symmetry transformations used to generate equivalent atoms: (i) 1−*x*, 1−*y*, 1−*z*; (ii) 1−*x*, 1−*y*, 1−*z*; (iii) *x*−1, *y*−1, *z*.

3. Results and discussion

Attempts to grow crystals of the C.I. Disperse Blue 79 from organic solvents such as methanol, ethanol, dichloromethane, acetonitrile and *n*-hexane always gave thin plates having a thickness less than 0.03 mm, none of which diffracted well enough for solving the crystal structure. Acceptable crystals were produced by slow evaporation of the solution of the dye in ethyl acetate.

The crystal used exists in the triclinic space group *P*-1. The atomic coordinates, bond lengths and angles, and torsion angles are reported in Tables 2 and 3. The molecular structure and the atomic numbering are given in Fig. 1.

The 4-nitro-4′-aminoazobenzene skeleton of the dye is essentially planar as expected [4,6–11] and the dihedral angle between the two aromatic rings is 9.4(3)°. Two ester chains tend to be separated as far apart as possible with one ester chain being above the aminoazobenzene plane and another

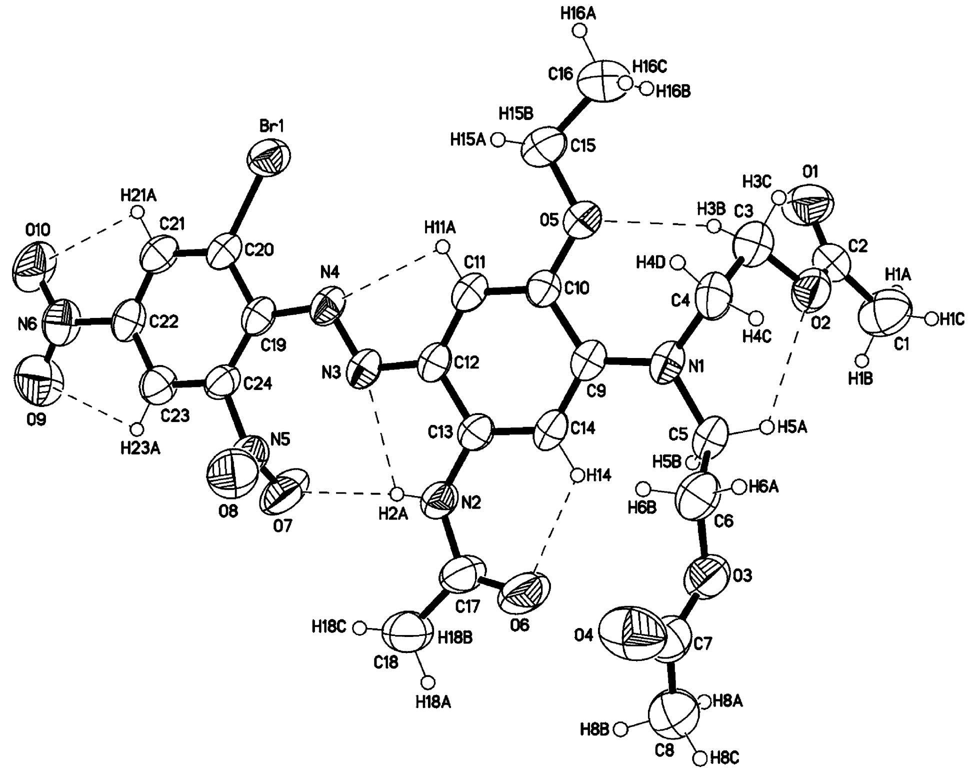

Fig. 1. ORTEP view of molecular structure of C.I. Disperse Blue 79 with possible intramolecular hydrogen bonds (dashed lines).

one below it. The torsion angle of N(1)–C(5)–C(6)–O(3), which has the value 152.3(3)° is nearly in *trans* arrangement. Otherwise, that of N(1)–C(4)–C(3)–O(2) has *gauche* arrangements with torsion angles of 52.5(4)°, due to the intramolecular C(5)-H···O(2) hydrogen bond. For the idealized position of the hydrogen atom, the H···O(2) distance is 2.59 Å, the O(2)′ C(5) distance is 3.186(5) Å, and the C(5)–H···O(2) angle is 119.6°.

Indeed, the hydrogen bonding arrangements found in the structure are noteworthy. As illustrated in Fig. 1, the molecular conformation is stabilized by formation of several intramolecular hydrogen bonds such as C-H···O, C-H···N and N-H···N types [15,16], which have bond length of

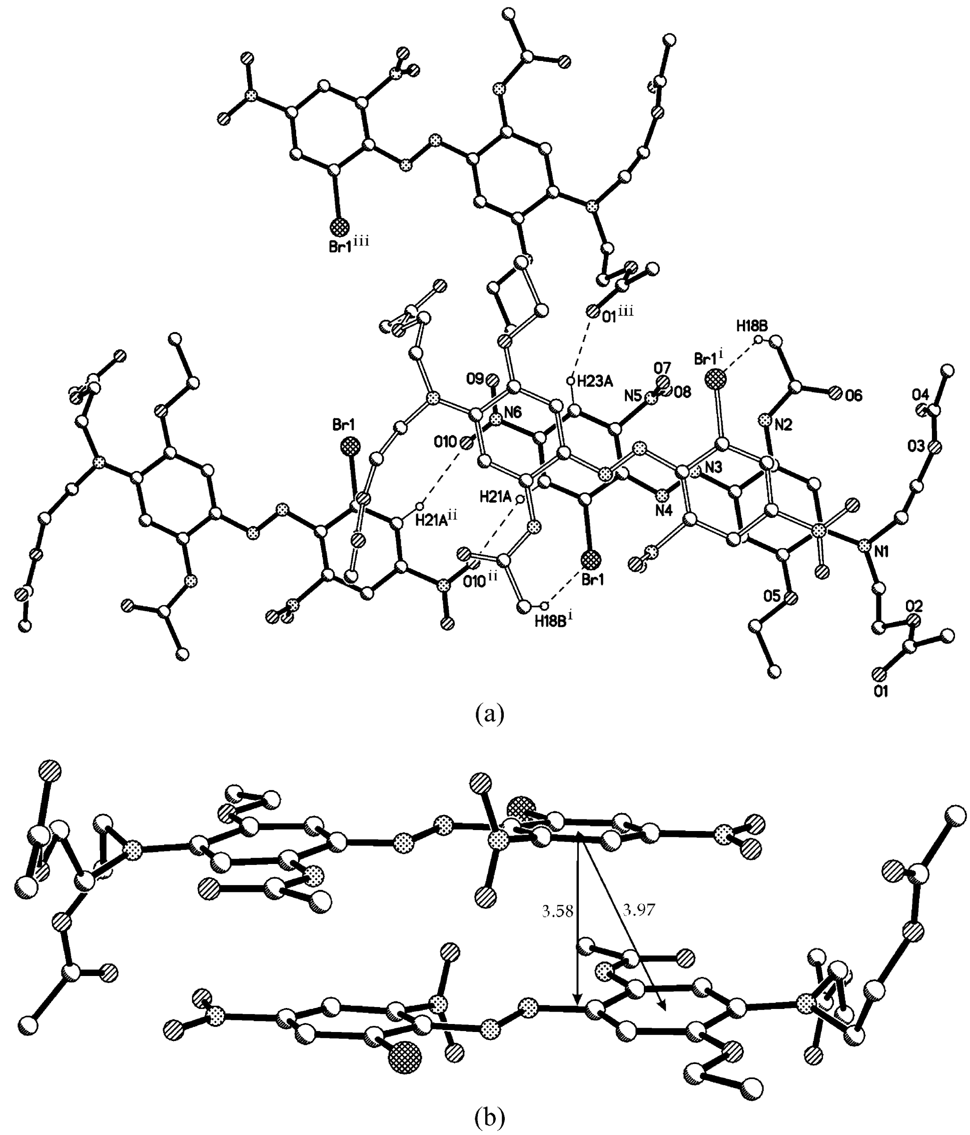

Fig. 2. Representation of (a) intermolecular hydrogen bonds [symmetry codes: (i) $1-x$, $1-y$, z; (ii) $1-x$, $1-y$, $1-z$; (iii) $x-1$, $y-1$, z] and (b) interlayer stacking (Å).

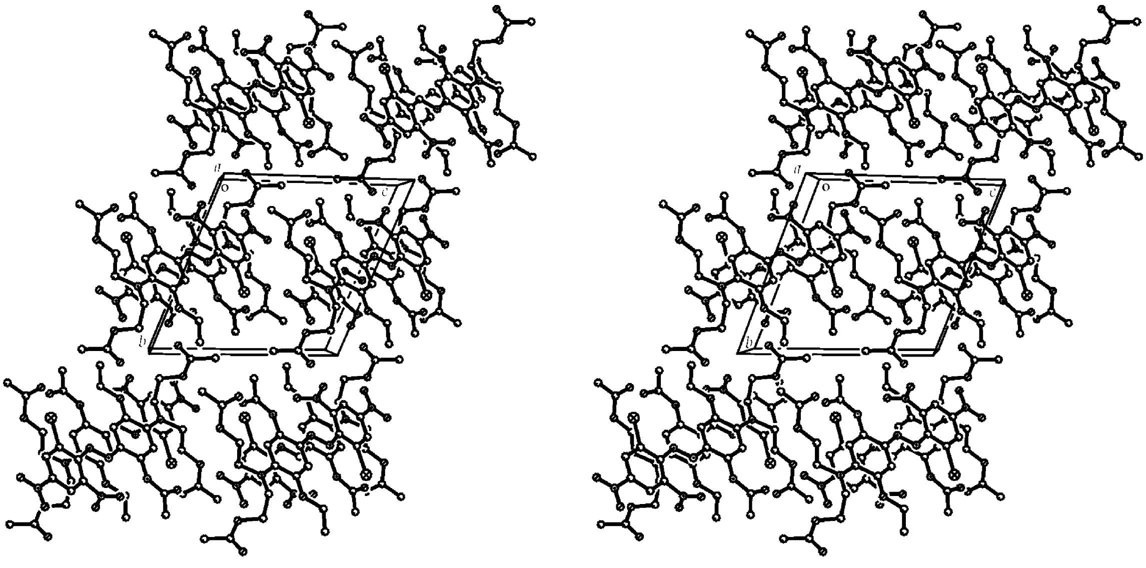

Fig. 3. Stereoview of crystal packing structure in the unit-cell.

ca. 2.2–2.6 Å. The structural parameters for the hydrogen bonds are summarized in Table 4. The 4-nitro group is almost coplanar with the aromatic ring as indicated by the dihedral angle of 5.16(4)°, which is due to the formation of hydrogen bonds of two nitro O atoms with nearby aromatic CH atoms [O(9)··· H–C(23); 2.426 Å, O(10)···H–C(21); 2.422 Å]. Because of one point hydrogen bond between O(7) and H–N(2) (2.450 Å), however, the plane of 2-nitro group is nearly perpendicular to the aromatic ring with the dihedral angle of 82.2(2)°.

Furthermore, the molecules are connected by hydrogen bonds in such a way that they form side-by-side in the same layer and inter-layer associations (Fig. 2a). Molecular pairing occurs in the reversible direction between the interlayer structures by means of intermolecular hydrogen bonds and the aromatic π–π stacking interaction [17] between the molecules (centroid-to-centroid distance; 3.97 Å) (Fig. 2b). The corresponding mean layered distance is found to be ca. 3.58 Å. Fig. 3 shows the packing arrangement of the unit-cell. Consequently, the stabilization of the crystal structure is due to close packing of molecules by multiple intra- and intermolecular hydrogen bonds together with the arene-arene stacking interactions.

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