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Dominant $\pi\cdots\pi$ interaction in the self assemblies of 4-benzylidene imidazolin-5-one analogues

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Abstract. Crystal structures of five imidazolin-5-ones are discussed. While molecules **1–3** show a donor–acceptor type of $\pi\cdots\pi$ lateral offset stacking, C–H$\cdots\pi$ interactions are found to play dominant roles in molecules **2** and **4**. In molecule **2**, C-H$\cdots\pi$ interactions further form lateral offset stack to form extended C–H$\cdots\pi\cdots\pi\cdots$H–C hydrogen bonds. Molecule **4**, however shows a layer structure with interlayer C–H$\cdots\pi\cdots$H–C hydrogen bonds and interlayer stacking of imidazolin-5-one heterocycles. These structures show how weak $\pi\cdots\pi$ interactions can be exploited for tailoring supramolecular assemblies.

Keywords. Self assemblies; imidazolin-5-one; donor–acceptor; $\pi\cdots\pi$ stacking; C–H$\cdots\pi$ interactions.

1. Introduction

Weak noncovalent intermolecular forces such as hydrogen bonds, $\pi\cdots\pi$ stacking play an important role in the formation of stable and structurally well-defined supramolecular structures.[1] Among the noncovalent intermolecular forces $\pi\cdots\pi$ stacking or aromatic–aromatic interactions in delocalized π-systems play a wide range of molecular recognition and self assembly phenomena.[2] Weak hydrogen bonds viz. C–H$\cdots$O[3] and C–H$\cdots$N[4] have been well exploited in the design and construction of organic supramolecules. The relatively weak C–H$\cdots\pi$[3g] interactions also play an important roles in several fields of chemistry such as organic conformations,[5] molecular recognitions,[6] host–guest encapsulations,[7] guanine-nucleotide binding proteins[8] and covalently modified carboxypeptidase A.[9] Recently, we observed self assemblages of imidazolin-5-ones governed by interplay of donor–acceptor type of $\pi\cdots\pi$ stacking, C–H$\cdots$O and C–H$\cdots\pi$ interactions where $\pi\cdots\pi$ interactions were found to play the dominant role.

p-Hydroxybenzylidene imidazolin-5-one is the luminophore in green fluorescent proteins (GFP).[10] The wide applicability of GFP and its mutants[11] inspired us to synthesize several analogues of GFP luminophore with an intention to evaluate their potential as synthetic extrinsic fluorophores. In this context we have studied solution and solid state fluorescence of a series of imidazolin-5-ones and their X-ray crystal structures. We report here crystal structures of five imidazolin-5-ones (figure 1): (4*Z*)-4-(4-*N*, *N*-dimethylaminobenzylidene)-1-methtyl-2-phenyl-1, 4-dihydro-5*H*-imidazolin-5-one (**1**); (4*Z*)-4-(4-*N*, *N*-dimethylaminobenzylidene)-1-(2, 6-dimethylphenyl)-2-phenyl-1, 4-dihydro-5*H*-imidazolin-5-one (**2**); (4*Z*)-4-(4-*N*,*N*-diphenylaminobenzylidene)-1-methyl-2-phenyl-1, 4-dihydro-5*H*-imidazolin-5-one (**3**); (4*E*)-4-(4-*N*,*N*-dimethylaminobenzylidene)-1-methyl-2-phenyl-1, 4-dihydro-5*H*-imidazolin-5-one (**4**); (4*Z*)-4-(4-*N*,*N*-diphenylaminobenzylidene)-1,2-diphenyl-1,4-dihydro-5*H*-imidazolin-5-one (**5**). Among these, molecule **4** is a geometrical isomer of molecule **1**.

2. Materials and methods

All chemicals were purchased from SDFine Chemicals and they were used as such unless otherwise indicated. Anhydrous $ZnCl_2$ was purchased from Aldrich and was used as received. All solvents were purchased from SDFine Chemicals and purified by following established procedures.[12] Melting points of the synthesized compounds were determined on a JSGW apparatus and are uncorrected. Proton NMR spectra were recorded in a JEOL JNM LA 400 and 500 MHz FT NMR in solutions of $CDCl_3$ using

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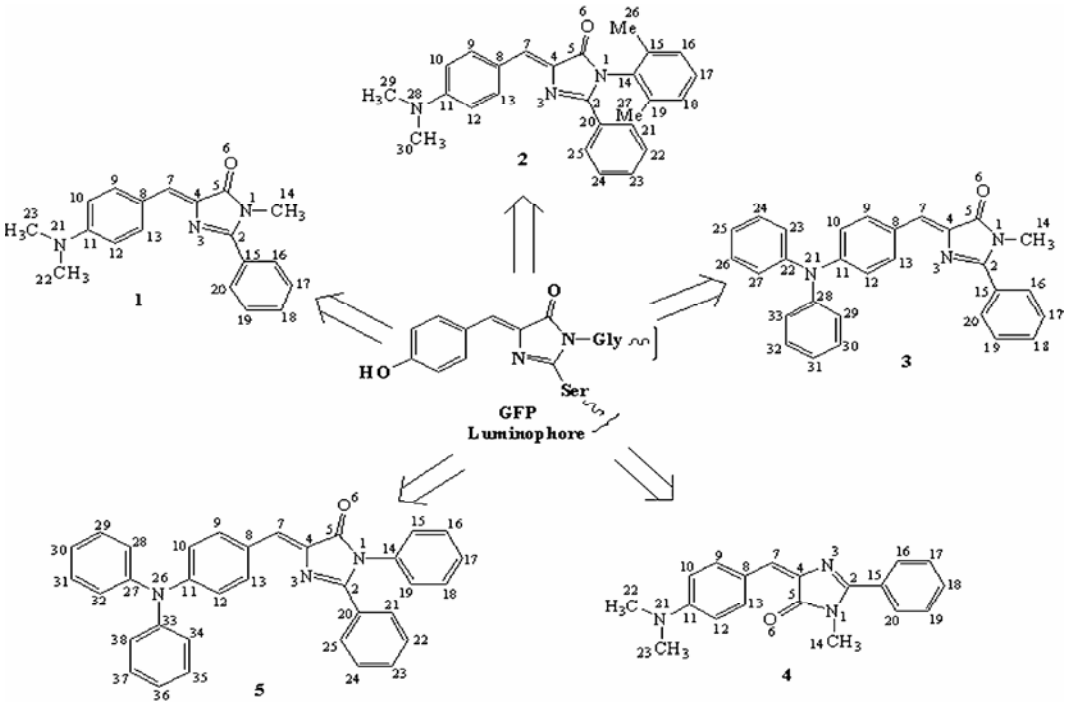

Figure 1. Synthesized 4-benzylidene imidazolin-5-one analogues. Molecule **4** is not an analogue of GFP luminophore because of its opposite geometrical isomerism.

tetramethyl silane as the internal standard. Infra red spectra were recorded in a Bruker Vector 22 FT–IR spectrometer. X-ray data were collected at the Bruker Nonius SMART APEX CCD detector at the Department of Chemistry, IIT Kanpur, India.

2.1 *Synthesis of molecules* (**1–3** *and* **5**)

The molecules **1–3** and **5** were synthesized using oxazol-5-ones as the starting materials following reported procedures.[13] Oxazol-5-ones were synthesized following established procedure.[14,15] Molecule **4** was obtained while trying to crystallize molecule **1** from cyclohexane under heating condition.

Molecule **1** was synthesized by fusing a mixture of (4*Z*)-4-(4-*N,N*-dimethylaminobenzylidene)-2-phenyl-5(4*H*)-oxazolone (0·10 g, 0·34 mmol), methylamine in 40% aqueous solution (0·04 mL, 0·41 mmol) and anhydrous zinc chloride (0·02 g, 0·14 mmol) at 170°C for 1·5 h. The brown reaction mixture was quenched with water and extracted with ethyl acetate (20 ml × 3). The crude product was purified by column chromatography using silica gel (100–200 mesh) and ethyl acetate-petroleum ether (b.p. range 60–80°C) as the eluent. A concentrated solution of the column purified product in methanol on slow evaporation in air produced orange and rod shaped crystals. Isolated yield 65%, m.p. 162–163°C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3·06 (*s*, 6H, NMe_2), 3·36 (*s*, 3H, NMe), 6·71 (*d*, J = 9·2 Hz, 2H, Ar), 7·24 (*s*, 1H, =CH–), 7·52 (*m*, 3H, Ar), 7·84 (*m*, 2H, Ar), 8·17 (*d*, J = 9·0 Hz, 2H, Ar). IR (KBr) ν_{max}/cm^{-1}: 1695 *vs* (C=O stretch), 1634 *m* (C=C stretch), 1587 *s* (C=C stretch of Ph), 1523 *s* (C=C stretch of Ph), 1433*w* (C–H asymmetrical bending of Me), 1367 *s* (C–H symmetrical bending of Me), 1197 *w* (C–N stretch of aliphatic amine), 1190 (Ph–H in plane bending), 817 (=C–H out of plane bending), 728 (Ph–H out of plane bending).

Molecule **2** was synthesized by fusing a mixture of (4*Z*)-4-(4-*N,N*-dimethylaminobenzylidene)-2-phenyl-5(4*H*)-oxazolone (0·10 g, 0·34 mmol) with 2,6-dimethylaniline (0·04 mL, 0·34 mmol) and anhydrous zinc chloride (0·01 g, 0·07 mmol) at 180°C for 2 h. Similar work-up and purification process was followed as applied for molecule **1** to yield orange product. Crystallization from 1 : 3 mixture of dichloromethane and petroleum ether by slow evaporation in air produced orange crystals. Isolated yield 50%, m.p. 168–170°C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2·09 (*s*, 6H, CH_3 –C), 3·07 (*s*, 6H, NMe_2), 6·74 (*d*, J = 8·6 Hz, 2H, Ar), 7·12 (*d*, J = 7·4 Hz, 2H, Ar), 7·21–7·29 (*m*, 3H, Ar), 7·24 (*s*, 1H, =CH–), 7·35 (*t*, 1H, Ar), 7·54 (*d*, J = 8·0 Hz, 2H, Ar), 8·23 (*d*, J =

8·3 Hz, 2H, Ar). IR (KBr) ν_{max}/cm^{-1}: 1706 *s* (C=O stretch), 1631 *w* (C=C stretch), 1589 *s* (C=C stretch of Ph), 1524 *s* (C=C stretch of Ph), 1440 *w* (C–H asymmetrical bending of Me), 1364 *s* (C–H symmetrical bending of Me), 1323 *w* (C–N stretch of aromatic amine), 1248 (C–N stretch of aliphatic amine).

Molecule **3** was synthesized by fusing a mixture of (4*Z*)-4-(4-*N,N*-diphenylaminobenzylidene)-2-phenyl-5(4*H*)-oxazolone (0·10 g, 0·25 mmol), methylamine in 40% aqueous solution (0·01 mL, 0·35 mmol) and anhydrous zinc chloride (0·013 g, 0·10 mmol) at 170°C for 2 h. Similar work-up and purification process was followed as applied for molecule **1** and **2** to yield deeply orange product. Crystallization from methanol and slow evaporation in air yielded deeply orange and rod shaped crystals. Isolated yield 53%, m.p. 161–162°C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3·35 (*s*, 3H, NMe), 7·00 (*d*, J = 8.8 Hz, 2H, Ar), 7·06–7·16 (*m*, 6H, Ar), 7·19 (*s*, 1H, =CH–), 7·27 (*t*, J = 8·0 Hz, 4H, Ar), 7·47–7·51 (*m*, 3H, Ar), 7·81 (*d*, J = 7·8 Hz, 2H, Ar), 8·08 (*d*, J = 8·5 Hz, 2H, Ar). IR (KBr) ν_{max}/cm^{-1}: 1708 *s* (C=O stretch), 1634 *m* (C=C stretch), 1584 *s* (C=C stretch of Ph), 1491 (C=C stretch of Ph), 1447 (C–H asymmetrical bending of Me), 1382 (C–H symmetrical bending of Me), 1286 *s* (C–N stretch of aromatic amine), 1151 (C–N stretch of aliphatic amine).

Molecule **4**: m.p. 169–170°C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3·06 (*s*, 6H, NMe_2), 3·36 (*s*, 3H, NMe), 6·71 (*d*, J = 9·2 Hz, 2H, Ar), 7·24 (*s*, 1H, =CH–), 7·52 (*m*, 3H, Ar), 7·84 (*m*, 2H, Ar), 8·17 (*d*, J = 9·0 Hz, 2H, Ar). IR (KBr) ν_{max}/cm^{-1}: 1677 *m* (C=O stretch), 1650 *m* (C=C stretch), 1585 (C=C stretch of Ph), 1513 (C=C stretch of Ph), 1437 (C-H asymmetrical bending of Me), 1376 (C-H symmetrical bending of Me), 1197 (C-N stretch of aliphatic amine).

Molecule **5** was synthesized by fusing a mixture of (4*Z*)-4-(4-*N,N*-diphenylaminobenzylidene)-2-phenyl-5(4*H*)-oxazolone (0·10 *g*, 0·25 mmol), aniline (0·023 mL, 0·26 mmol) and anhydrous zinc chloride (0·007 g, 0·05 mmol) at 210°C for 2 h. Similar work-up and purification process was followed as applied for molecules **1** and **2** to yield deeply orange product. A concentrated solution of the column purified compound in methanol on slow evaporation in air produced deeply orange and rod shaped crystals. Isolated yield 52%, m.p. 216–218°C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8·15 (*d*, J = 9 Hz, 2H, ArH), δ 7·05 (*d*, J = 8·5 Hz, 2H, ArH), δ 7·10–7·13 (*t*, J = 7·5 Hz, 2H, ArH), 7·16–7·18 (*m*, 5H, ArH), δ 7·20 (*s*, 1H, =CH–), δ 7·27–7·31 (*m*, 7H, ArH), 7·35–7·42 (*m*, 4H, ArH), δ 7·52 (*d*, J = 8·5 Hz, 2H, ArH). IR (KBr) ν_{max}/cm^{-1}: 1712 *s* (C=O stretch), 1634 *m* (C=C stretch), 1585 (C=C stretch of Ph), 1491 (C=C stretch of Ph), 1285 (C–N stretch of aromatic amine).

2.2 *X-ray crystallography*

The intensity data were collected at 298 K on a siemens P4 single crystal diffractometer equipped with a molybdenum sealed tube (λ = 0·71073 Å) and highly oriented graphite monochromator. The data were collected in 2θ–θ scan mode with a variable scan speed ranging from 2·0° to a maximum of 28·4°. The data integration and reduction were processed with SAINT+.[16] The structures were solved using WinGX version 1.70.01 package. Direct methods using SHELX 97,[17] Sir92, Sir97 and Sir2002 were also used for solving the structures. The structures were further refined using full matrix least square on F^2 (SHELX 97).[17] All the non-hydrogen atoms were refined anisotropically. The hydrogen atoms were refined isotropically and treated as riding atoms by using SHELXL default parameters. The crystal structure of molecule **4** showed one disordered water molecule. However, it was difficult to model the water molecule and it was eliminated by use of the SQUEEZE function of PLATON.[18] After solving the structures, DIAMOND (version 3.0) and Mercury (version 1.4.1) were used to view the structures.

3. Results and discussion

The X-ray crystal structure data obtained for the molecules **1–5** are shown in table 1. The details of hydrogen bonding interactions that play a major part in the crystal structures are shown in table 2 and the parameters of aromatic stacking are tabulated in table 3.

3.1 *Crystallographic descriptions of the molecules* **1–5**

The crystal structure of molecule **1** shows lateral offset stacking (figure 2a) of the electron rich 4-dimethylamino benzene donor with the electron deficient imidazolin-5-one heteroaromatic ring (see table 3 for stacking parameters). Both the electron donor and the acceptor of a molecule form offset

Table 1. Crystallographic data for molecules **1–5**.

Molecule	**1**	**2**	**3**	**4**	**5**
Formula	$C_{19}H_{19}N_3O$	$C_{26}H_{25}N_3O$	$C_{29}H_{23}N_3O$	$C_{19}H_{19}N_3O$	$C_{34}H_{25}N_3O$
Formula weight	305·37	395·51	429·52	305·37	491·57
Temperature/K	298(2)	298(2)	298(2)	298(2)	298(2)
Crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	*P*-1	$P2_1/c$	$P2_1/c$	$C2/c$	$C2/c$
a/Å	6·3150(0)	10·256(5)	9·966(5)	16·172(5)	37·721(9)
b/Å	11·7970(0)	13·319(5)	11·959(5)	16·221(5)	5·4739(13)
c/Å	12·1440(0)	31·784(5)	19·798(5)	13·792(5)	30·928(8)
α/°	62·950 (0)	90·000(5)	90·000(5)	90·000(5)	90·000(0)
β/°	80·090(0)	93·315(5)	103·611(5)	117·980(5)	124·146(10)
γ/°	86·560(0)	90·000(5)	90·000(5)	90·000(5)	90·000(0)
V/Å^3	793·60(0)	4335(3)	2293·3(16)	3195·10(18)	5285(2)
Z	2	8	4	8	8
D_c/g cm^{-3}	1·28	1·212	1·244	1·27	1·236
μ/mm^{-1}	0·081	0·075	0·077	0·081	0·075
F (000)	324	1680	904	1296	2064
Crystal size/mm	0·23 × 0·17 × 0·12	0·23 × 0·17 × 0·12	0·23 × 0·17 × 0·12	0·23 × 0·17 × 0·12	0·23 × 0·17 × 0·12
θ range/°	1·91–27·00	2·00–26·00	2·00–25·00	2·5 1–27·0	2·2–27·0
Reflections collected	4830	24104	11655	9595	15229
Independent reflections	3369	8506	4012	3491	5708
Data/restraints/parameters	3369/0/208	8506/0/541	4012/0/298	3491/0/208	5708/0/343
Goodness-of-fit on F^2	1·056	1·015	0·945	1·083	0·848
Final *R* indices	*RI* = 0·0591,	*RI* = 0·0671,	*RI* = 0·0614,	*RI* = 0·0640,	*RI* = 0·0544
[$I > 2\sigma(I)$]	*wR*2 = 0·1843	*wR*2 = 0·1930	*wR*2 = 0·1869	*wR*2 = 0·1989	*wR*2 = 0·1506

Table 2. Significant intermolecular interactions (interatomic distances in Å and bond angles in °) observed in the crystal structures of molecules **1–5**.

Molecule	D–H···A	D–H (Å)	H···A (Å)	D···A (Å)	<D–H···A (°)	Symmetry codes
1	C(7)–H(7)···O(6)	0·93(23)	2·58(14)	3·408(24)	148(14)	1 – *x*, 2 – *y*, 1 – *z*
	C(9)–H(9)···O(6)	0·93(25)	2·59(20)	3·397(33)	145(15)	1 – *x*, 2 – *y*, 1 – *z*
	C(23)–H(23C)···O(6)	0·96(41)	2·62(22)	3·558(47)	165(20)	2 – *x*, 2 – *y*, 1 – *z*
	C(13)–H(13)···N(3)	0·93(17)	2·49(21)	3·127(28)	126(14)	*x*, *y*, *z*
2*	C(24)–H(24)···O(6)	0·93(34)	2·48(22)	3·202(39)	134(20)	–1 + *x*, 1 + *y*, *z*
	C(7)–H(7)···O(6)	0·93(31)	2·60(20)	3·142(35)	117(18)	3 – *x*, – *y*, –*z*
	C(46)–H(46)···N(3)	0·93(30)	2·69(23)	3·614(38)	169(18)	2 – *x*, 1/2 + *y*, 1/2 – *z*
	C(56)–H(56A)···C20	0·96(30)	2·81(29)	3·649(41)	146(18)	1 – *x*, –*y*, – *z*
	C(42)–H(42)···C10	0·93(30)	2·84(29)	3·421(39)	121(17)	3 – *x*, –2 – *y*, – *z*
	C(60)–H(60C)···π	0·96(28)	2·81(5)	3·737(28)	163(17)	1 – *x*, – *y*, –*z*
	C(56)–H(56A)···π	0·96(30)	2·95(5)	3·541(29)	121(17)	2 – *x*, –1 – *y*, –*z*
3	C(29)–H(29)···O(6)	0·93(30)	2·31(22)	3·197(38)	158(18)	2 – *x*, 2 – *y*, –*z*
	C(20)–H(20)···C(32)	0·93(33)	2·77(39)	3·537(53)	140(22)	*x*, 2·5 – *y*, – 1/2 + *z*
	C(7)–H(7)···C(25)	0·93(25)	2·86(31)	3·758(39)	162(17)	1 – *x*, 2 – *y*, – *z*
4	C(16)–H(16)···O(6)	0·93(25)	2·61(17)	3·498(29)	161(15)	–*x*, –*y*, 1 – *z*
	C(14)–H(14B)···C(5)	0·96(27)	2·72(26)	3·499(39)	138(15)	–*x*, –*y*, 1 – *z*
	C(22)–H(22B)···π	0·96(29)	2·72(10)	3·64(32)	161(15)	1 – *x*, *y*, 1·5 – *z*
	C(22)–H(22C)···π	0·96(30)	2·66(10)	3·42(33)	136(15)	1 – *x*, –*y*, 1 – *z*
	C(22)–H(23A)···C(18)	0·96(27)	2·88(22)	3·79(33)	158(17)	–1 + *x*, –*y*, –0·5 + *z*
5	C(18)–H(18)···O(6)	0·93(30)	2·71(25)	3·36(44)	128(18)	1 – *x*, –*y*, 2 – *z*
	C(19)–H(19)···O(6)	0·93(24)	2·59(20)	3·50(33)	167(1)	*x*, –1 + *y*, *z*
	C(12)–H(12)···C(22)	0·93(28)	2·78(23)	3·60(34)	147(16)	1 – *x*, *y*, 1·5 – *z*
	C(29)–H(29)···C(8)	0·93(50)	2·78(27)	3·71(55)	172(27)	1·5 – *x*, 0·5 – *y*, 2 – *z*
	C(15)–H(15)···C(21)	0·93(29)	2·86(26)	3·78(39)	172(17)	*x*, – 1 + *y*, *z*

*Atom number higher than 30 corresponds to two molecules in the asymmetric unit

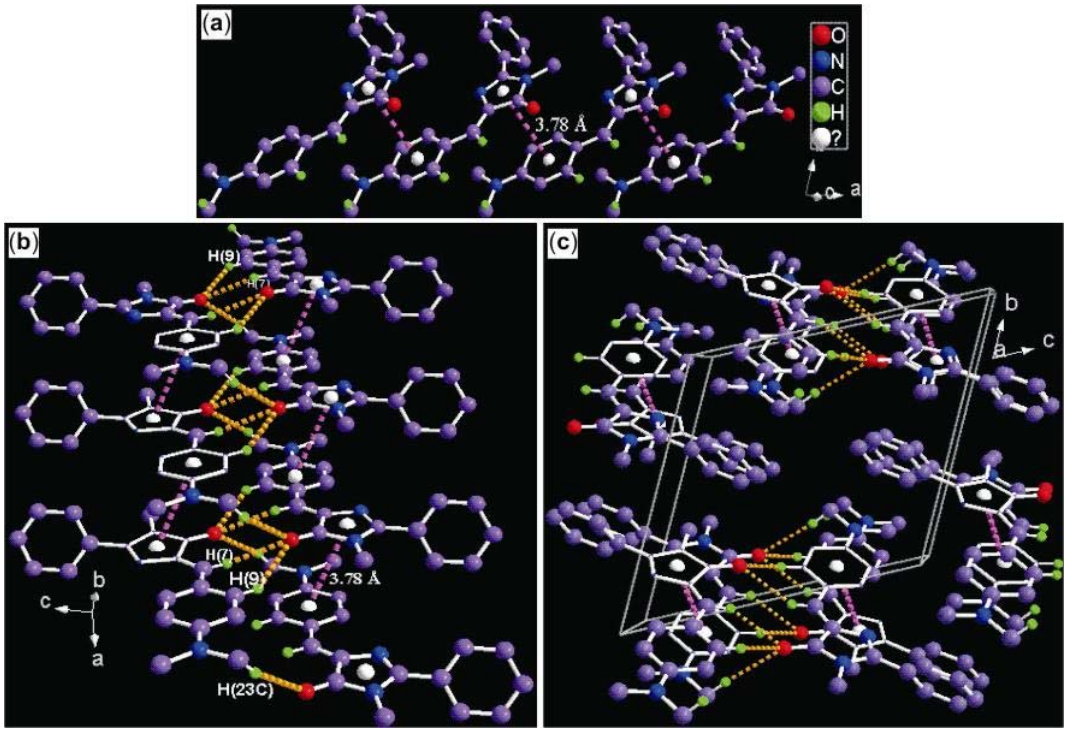

Figure 2. $\pi\cdots\pi$ Offset stacked and hydrogen bonded layer structure of molecule **1**. (**a**) Donor–acceptor type of $\pi\cdots\pi$ offset stacked interaction. Dotted pink lines represent $\pi\cdots\pi$ offset stack, (**b**) hydrogen bonded sheets and layers formed by C(5)–O(6)···H(7) (2·58 Å), C(5)–O(6)···H(9) (2·59 Å) and C(5)–O(6)···H(23C) (2·62 Å) hydrogen bonds (represented by dotted orange lines) between the offset stacked arrays, (**c**) packing of the hydrogen bonded and offset stacked layers. The adjacent layers are bound by van der Waals force. Hydrogen atoms not involved in short contact are removed for clarity. Atom colour code is same in all subsequent figures.

Table 3. Stacking parameters of the offset stacking observed in molecules **1–5**.

Molecule	h[a]/Å	r[b]/Å	d[c]/Å	θ [d]/°
1[i]	3·42	1·61	3·78	21
2[ii]	3·45	1·27	3·67	22
3[iii]	3·48	1·62	3·85	21
4[iv]	3·58	0·02	3·59	0·7
5[v]	3·57	1·67	3·94	20

[a]Perpendicular distance from the centre of one ring plane to the other ring plane; [b]lateral displacement; [c]centroid to centroid distance; [d]displacement angle. Symmetry operators are: (i) x, y, z; (ii) $2-x$, $-1-y$, $-z$; (iii) –x, $2-y$; $-z$; (iv) $1-x$, y, $0{\cdot}5-z$; (v) $1-x$, $-y$, $1-z$

stack from opposite faces at (x, y, z) above and below the average molecular plane with dihedral angle between the stacked rings of 3·7(73)°. The centroid to centroid distance is 3·78 Å and the perpendicular distance between the offset stacked rings is 3·42 Å with displacement angle[19] 21° and lateral displacement 1·61 Å. The offset stacked molecules form a zig–zag pattern through the $\pi\cdots\pi$ offset stacks (3·78 Å) and stacked molecules. A similar array of offset stacked molecules form C(5)–O(6)···H(7), C(5)–O(6)···H(9) and C(5)–O(6)···H(23C) hydrogen bonds centrosymmetrically and form an extended layer structure (figure 2b). The hydrogen bonded molecules through C(5)–O(6)···H(7) and C(5)–O(6)···H(9) hydrogen bonds at ($1-x$, $2-y$, $1-z$) form sheet like structures with the 4-dimethylamino benzene rings and imidazolin-5-one rings lying in parallel planes with interplanar distance of 0·94 Å. The packing of the offset stacked and hydrogen bonded layer structure is shown in figure 2c. The layers pack across the (110) plane and there is no short contact between the adjacent layers and these are bound by van der Waal force.

The asymmetric unit of molecule **2** contains two molecules (figure 3a) with intermolecular interactions C(46)–H(46)···N(3) (d(H···A) = 2·69 Å), C(56)–H(56A)···C(20) (d(H···A) = 2·81 Å) and C(56)–H(56B)···π(d(H···π) = 2·95 Å). Two asymmetric units form $\pi\cdots\pi$ offset stack with the electron rich 4-

dimethylamino benzene ring ($d(\pi\cdots\pi)$ = 3·67 Å at (2 – z, –1 – y, –z)) interacting with the electron deficient 2-substituent benzene ring (figure 3b). The centroid to cenroid distance is 3·67 Å, interplanar distance 3·45 Å, with displacement angle 22° and lateral displacement 1·27 Å. The dihedral angle between the interacting phenyl rings is 9°. Unlike molecule **1** stacking here is between 4-dimethylamino benzene ring and the 2-substituted benzene ring. The imidazolin-5-one ring cannot form stack because of the steric grounds of the N1-substituted o-dimethyl benzene ring. The dihedral angle between the imidazolin-5-one ring and the 1-substituted *o*-dimethyl benzene ring is 86°. The offset stacked 4-dimethylamino benzene ring forms C(60)–H(60C)···π···(d(H···π) = 2·81 Å) and C(42)–H(42)···C(10) (d(H···C) = 2·84 Å) hydrogen bonds. The offset stack together with the C–H···π interactions appear like an extended C–H···π···π···H–C hydrogen bond. This supramolecular organizational feature involving both the offset stack and C–H···π interactions is reminiscent of the aryl–pyrazole[19a] embrace and pyrazole–pyrazole embrace.[20] The C–H···π interactions observed here are weak and comparable to that observed in aryl–pyrazole embrace[19a], the supramolecular organization observed here, therefore can be regarded as an aryl–aryl embrace. The two offset stacked asymmetric units are further tethered by another molecule through C(7)–H(7)···O(6) and C(24)–H(24)···O(6) hydrogen bonds in antiparallel fashion maintaining centre of symmetry in the crystal.

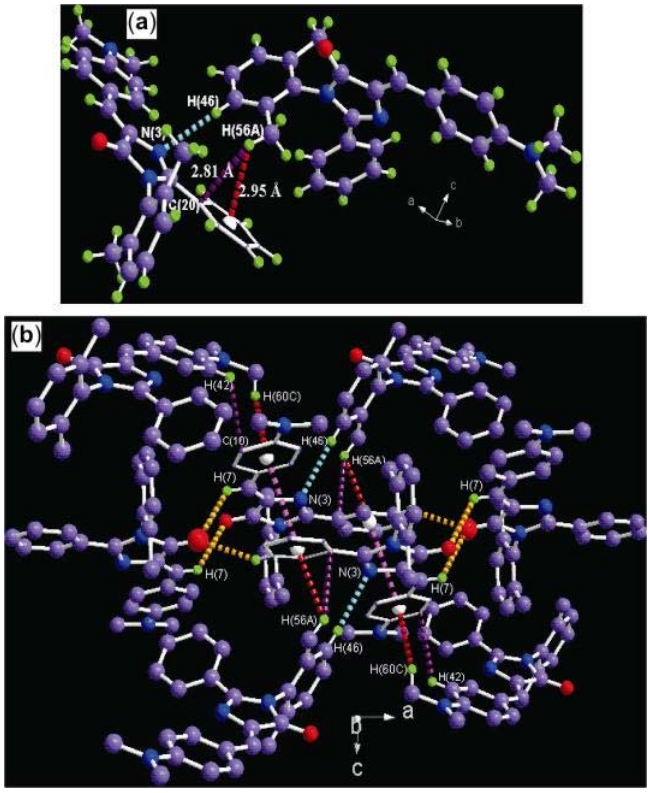

Figure 3. (**a**) Asymmetric unit of molecule **2** containing C(46)–H(46)···N(3), C(56)–H(56A)···π and C(56)–H(56A)···C(20) hydrogen bonds. (**b**) Lateral offset stacking of two asymmetric units. The C(56)–H(56A)···π···π···H(60C)–C(60) hydrogen bonds form an aryl–aryl embrace. The molecules with bigger size oxygen atoms tether the offset stacks through C(7)–H(7)···O(6) (2·60 Å) and C(24)–H(24)···O(6) (2·48 Å) hydrogen bonds. Hydrogen atoms not involved in hydrogen bond formation are removed for clarity. The dotted coloured lines represent short contacts. Colour code: pink ($\pi\cdots\pi$), orange (C–H···O), violet (C–H···C), red (C–H···π), aqua (C–H···N).

Molecule **3** forms lateral offset stack ($d(\pi\cdots\pi)$ = 3·85 Å at (–x, 2 – y, –z)) in an antiparallel orientation involving the electron-rich 4-diphenylamino benzene donor and the electron deficient imidazolin-5-one acceptor (figure 4a). The centroid to centroid distance is 3·85 Å, interplanar distance of the offset stacked molecules is 3·48 Å with displacement angle 22° and lateral displacement 1·62 Å. The dihedral angle between the offset stacked rings is 9° and the offset stacked molecules are antiparallel. A strong hydrogen bond C(29)–H(29)···O(6) (d(H···A) = 2·31 Å at (2 – x, 2 – y, –z)) binds the two offset stacked molecules and stabilizes the supramolecular organization. The offset stacked bimolecular motifs form C(7)–H(7)···C(25) hydrogen bonds (d(H···A) = 2·86 Å at (1 – x, 2 – y, –z)) and form a two-dimensional array of the offset stacked molecules along the crystallographic (0 0 1) axis (figure 4b).

Molecule **4** is a geometrical isomer of molecule **1** (E configuration about C4–C7 bond). A consequence of this geometric constraint is that the highly electron-rich 4-dimethylamino benzene ring cannot form an aromatic stack. The so-called 'donor–acceptor aromatic interaction' is not observed here. Instead, the imidazolin-5-one heteroaromatic rings form face to face stack (figure 5a) ($d(\pi\cdots\pi)$ = 3·59 Å). The stacking organization is similar to the staggered conformation of ferrocene (figure 5b). The stacked imidazolin-5-one rings have a torsion angle 29°. The supramolecular feature of the molecules is layer structure (figure 5c). The highly electron-rich 4-dimethylamino benzene ring in the absence of aromatic interaction forms C(22)–H(22B)···π (d(H···A) = 2·72 Å, D(D–H···A) = 3·64 Å, θ(D–H···A) = 161°) and C(22)–H(22C)···π (d(H···A) = 2·66 Å, D(D–

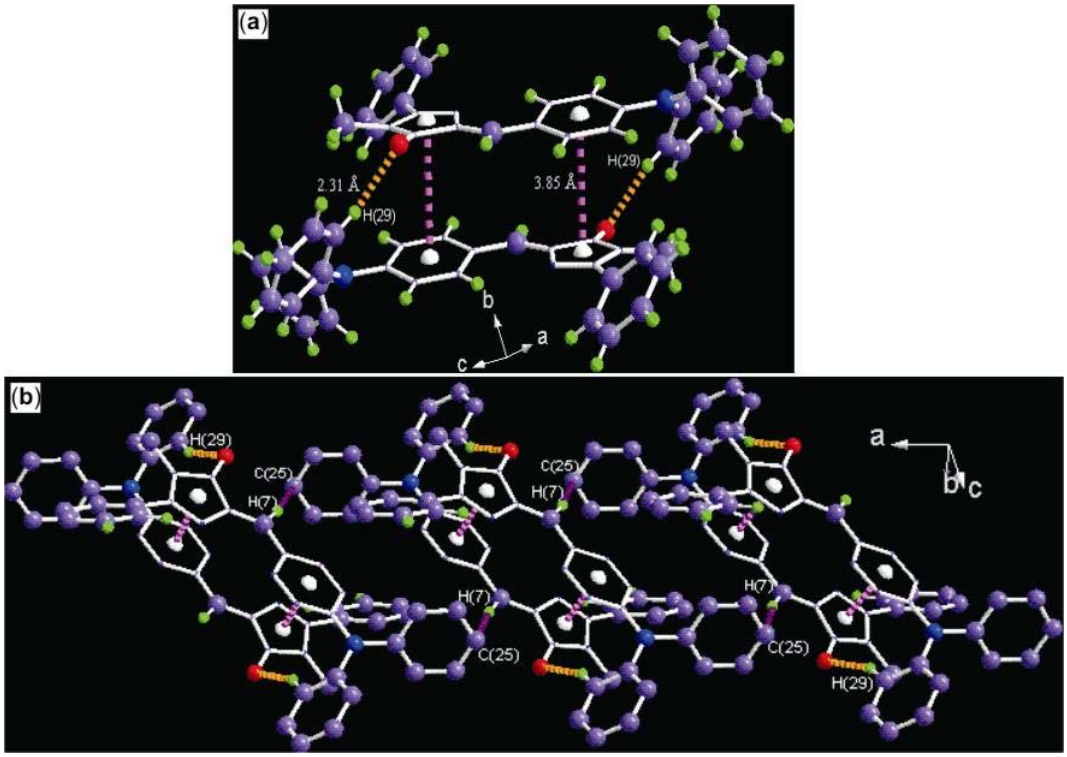

Figure 4. Molecular organization in molecule **3**. (**a**) Lateral offset stack in antiparallel orientation. (**b**) The offset stacks form a two-dimensional array through C(7)–H(7)···(25) hydrogen bonds. Colour code: pink ($\pi\cdots\pi$), orange (C–H···O), violet (C–H···C), hydrogen bonds. Hydrogen atoms not involved in hydrogen bond formation are removed for clarity.

H···A) = 3·42 Å, θ(D–H···A) = 136°) hydrogen bonds. There are also interlayer C(16)–H(16)···O(6) and C(14)–H(14B)···O(6) hydrogen bonds which contribute to the stability of the layer structure. Adjacent molecules in a layer are interacting through C(23)–H(23A)···C(18) (d(H···A) = 2·88 Å) hydrogen bonds with torsion angle of the C=O dipoles 174° and for the alternate molecules the C=O dipoles are aligned by 180° torsion angle.

In molecule **5** both the donor 4-diphenylamino benzene and the acceptor imidazolin-5-one are sterically hindered. As a consequence of steric hindrance near the donor and the acceptor, none of these can form aromatic stack. Instead the N1-substituted benzene rings form offset stack (figure 6a) in (–1 3 1) plane. The centroid to centroid distance is 3·94 Å, perpendicular distance of ring planes is 3·57 Å with displacement angle 20° and lateral displacement 1·67 Å. The 4-diphenylaminobenzylidene part of the offset stacked molecules form C(29)–H(29)···C(8) and C(12)–H(12)···C(22) hydrogen bonds (figure 6b). These hydrogen bonds together with the aromatic offset stacks form a two-dimensional lattice. The offset stacked molecules form C(19)–H(19)···O(6) and C(15)–H(15)···C(21) hydrogen bonds with another aromatic offset stack and extends the lattice in the third dimension. The aromatic offset stack and the C(19)–H(19)···O(6), C(15)–H(15)···C(21) hydrogen bonds seem to be cooperative and so this supramolecular organizational feature may be termed as an aryl–aryl embrace.[19a]

In all the molecules the main skeleton benzylidene imidazolin-5-one assumes planar configuration or nearly so depending on the substituents attached to the donor benzene ring and acceptor imidazolin-5-one ring. In the Z-configuration of the benzylidene imidazolin-5-one (molecules **1–3** and **5**) the dihedral angle between the donor plane and the acceptor planes is minimum (2°) and in the *E*-configuration (molecule **4**) it is highest (12·2°). An intramolecular C(13)–H(13)···N(3) hydrogen bond is formed in molecules with the *Z*-configuration, whereas in molecule **4** with *E*-configuration an intramolecular C(13)–H(13)···O(6) hydrogen bond is formed. In molecule **1**, the C(22) and C(23) methyl groups lie in the same plane as the benzylidene imidazolin-5-one plane and so there is contribution to the highest occupied molecular orbital of the mole-

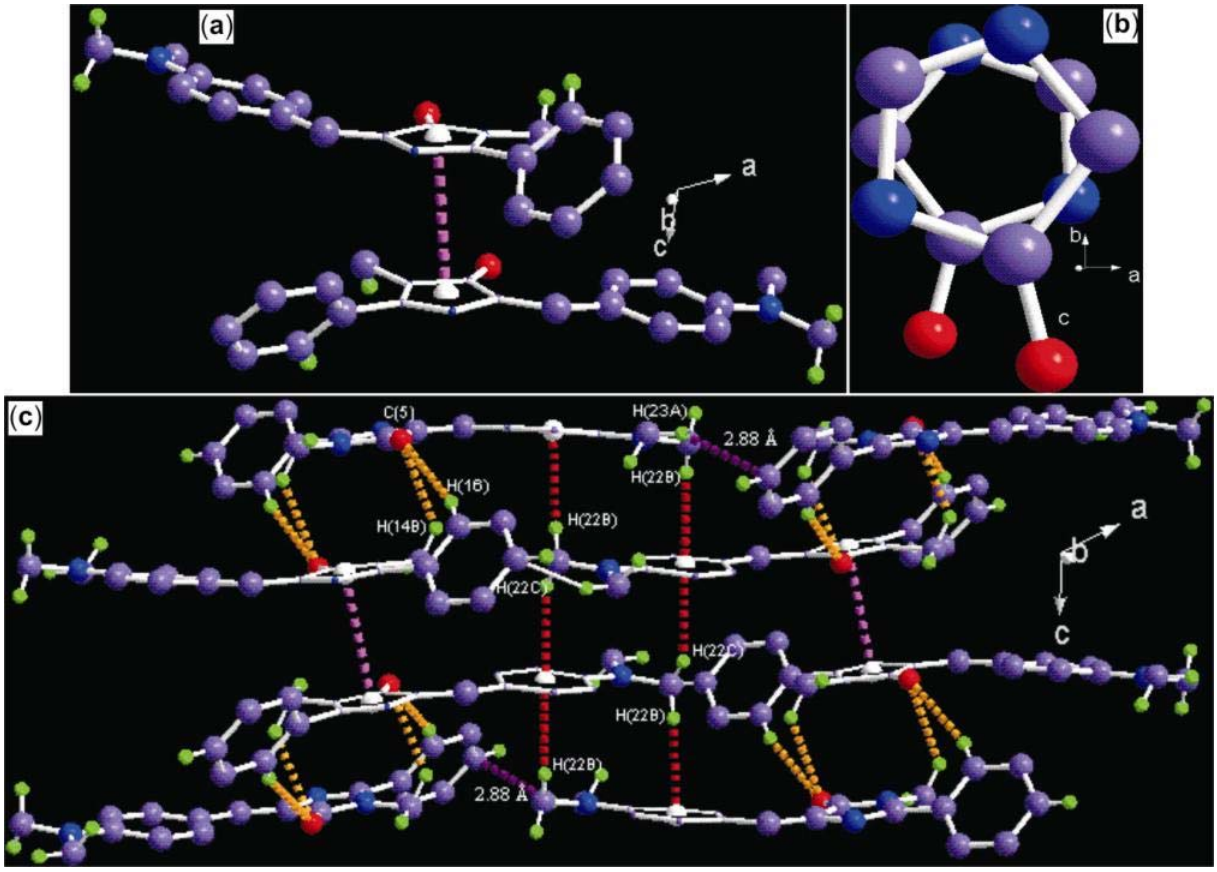

Figure 5. Hydrogen bonding and aromatic interactions in molecule **4**. (**a**) Stacking of the imidazolin-5-one heterocycles ($d(\pi\cdots\pi)$ = 3·59 Å at $(1-x, -y, 1-z)$), (**b**) the imidazolin-5-one rings stack similar to the conformation of staggered ferrocene, (**c**) layer structure formed by interlayer stacking of imidazolin-5-one heterocycles, and interlayer C(22)–H(22B)$\cdots\pi$, C(22)–H(22C)$\cdots\pi$, C(16)–H(16)···O(6), C(14)–H(14B)···O(6) hydrogen bonds. Dotted lines represent short contact. Colour code: pink ($\pi\cdots\pi$), red (C–H$\cdots\pi$), orange (C–H···O), violet (C–H···C). Hydrogen atoms not involved in hydrogen bonding are removed for clarity.

cule from these two methyl groups. The torsion angles C5–N1–C14–C19 and C35–N31–C44–C49 in molecule **2** are 89° and 95° respectively, so N1-substituted 2,6-dimethylamino benzene rings are almost perpendicular to the imidazolin-5-one ring. The dihedral angle of the C2-substituted benzene ring and the imidazolin-5-one rings is lowest in molecule **2** (12°) and highest in molecule **1** (58°).

4. Conclusion

The most common structural feature in these molecules is aromatic offset stacking. In absence of any undue steric crowding (molecule **5**) or geometric constraint (molecule **4**) the tendency to form a stable crystal structure is interaction of the electron-rich benzylidene ring with the electron-deficient imidazolin-5-one ring. This has been observed in several of the previously reported 4-benzylidene imidazolin-5-one analogues[21] and triptycene derivatives.[22] Substituents in the vicinity of the donor and the acceptor play a dominant role in staking and dipolar alignment of the molecules. Majority of the interactions observed in the crystal structures are weak . The distance between the aromatic centroids in the offset stacks is around 3·7 Å and this indicates a remarkably strong interaction. The variations in the hydrogen bonding patterns in the crystal structures is therefore suggested to be the consequence of only aromatic offset stacking and substituent effects on it. The strong donor–acceptor aromatic interactions observed in these crystal structures suggest that by appropriate design of the molecules one can attempt to synthesize imidazolin-5-one based organic dyes[23] and organic solar cell materials.[24]

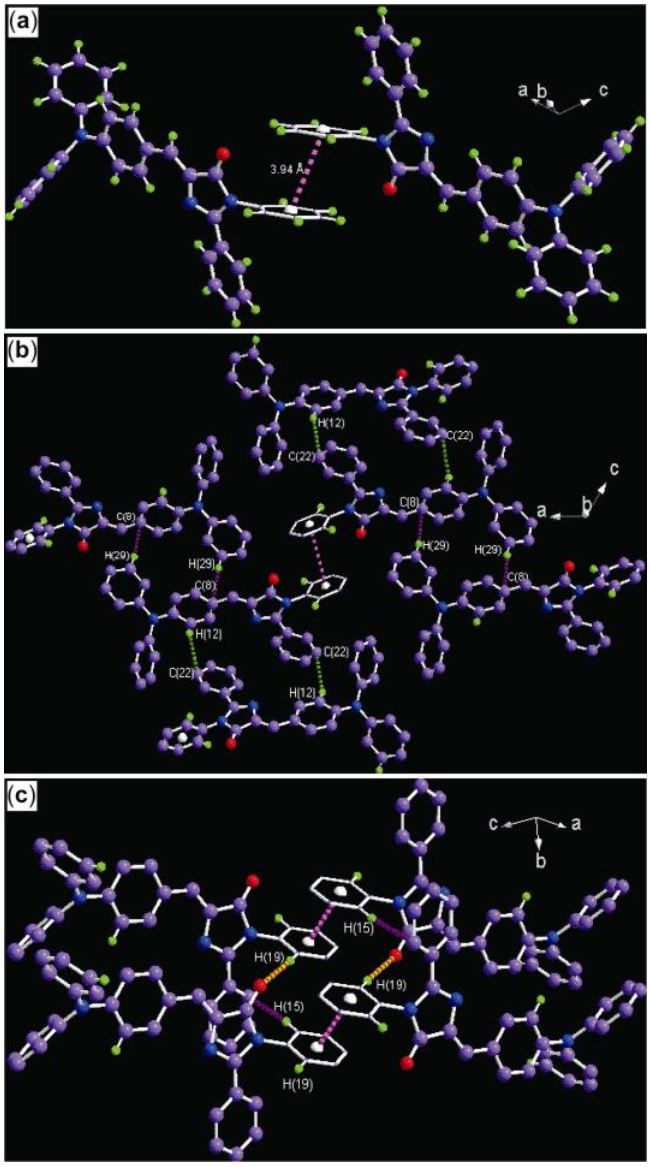

Figure 6. Hydrogen bonded and aromatic offset stacked lattice of molecule **5**. (**a**) Offset stacking of the N1-substituterd benzene rings (3·94 Å), (**b**) a two-dimensional lattice formed by $\pi\cdots\pi$ offset stack, C(29)–H(29)···C(8) and C(12)–H(12)···C(22) hydrogen bonds, (**c**) the C(19)–H(19)···O(6) and C(15)–H(15)···C(21) hydrogen bonds between adjacent offset stacked molecules extend the lattice in the third dimension. The $\pi\cdots\pi$ offset stack together with the C(19)–H(19···O(6) and C(15)–H(15···C(21) hydrogen bonds form an aryl–aryl embrace. Colour code: pink ($\pi\cdots\pi$), green (C(12)–H(12)···C(22)), violet (C(29)–H(29)···C(8)), (C(15)–H(15)···C(21)), orange (C(19)–H(19)···O(6)). Hydrogen atoms not involved in hydrogen bond formation are removed for clarity.

5. Supplementary material

Crystallographic data for the molecules **1–5** in CIF format have been deposited with Cambridge Crystallographic Data Center, CCDC No. 698656–698660.

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