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4-{[6-(4,4′-Bipyridin-1-ium-1-yl)-2-(4-carboxyanilino)-1,3,5-triazin-2-yl]-amino}benzoate monohydrate

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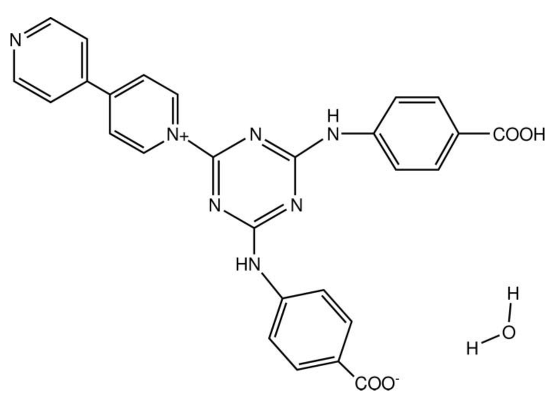
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.003 Å; R factor = 0.052; wR factor = 0.161; data-to-parameter ratio = 12.3.

Reaction of 2,4,6-tris(4-carboxyanilino)-1,3,5-triazine with 4,4′-bipyridine yields the zwitterionic title compound, $C_{27}H_{19}N_7O_4\cdot H_2O$. The zwitterionic form is confirmed by the the C—O distances of the carboxylate group. The crystal structure involves intermolecular N—H···O, O—H···O and O—H···N hydrogen bonds.

Related literature

For related literature, see: Sahouani (2006); Sahouani & Vogel (2002); Sahouani, Vogel & Schaberg (2002); Sahouani *et al.* (2001); Thurston *et al.* (1951); Allen (2002).



Experimental

Crystal data

$C_{27}H_{19}N_7O_4\cdot H_2O$
M_r = 523.51
Triclinic, $P\bar{1}$
a = 9.500 (5) Å
b = 9.523 (5) Å
c = 13.669 (7) Å
α = 97.527 (3)°
β = 98.781 (6)°
γ = 101.555 (6)°
V = 1181 (1) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.11 mm^{-1}
T = 293 (2) K
0.78 × 0.20 × 0.05 mm

Data collection

Rigaku Mercury CCD diffractometer
Absorption correction: multi-scan (*SPHERE* in *CrystalStructure*; Molecular Structure Corporation & Rigaku, 2000)
T_{min} = 0.975, T_{max} = 0.995
9219 measured reflections
5350 independent reflections
3866 reflections with $I > 2\sigma(I)$
R_{int} = 0.025

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.052
$wR(F^2)$ = 0.161
S = 1.00
5350 reflections
436 parameters
All H-atom parameters refined
$\Delta\rho_{max}$ = 0.24 e Å^{-3}
$\Delta\rho_{min}$ = −0.22 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N6—H6···O3^{i}	0.92 (3)	1.90 (3)	2.791 (2)	164 (2)
N7—H7···O5^{ii}	0.90 (2)	1.96 (2)	2.847 (3)	167 (2)
O2—H3···O4^{iii}	1.09 (4)	1.42 (4)	2.507 (2)	172 (3)
O5—H1···N5^{iv}	0.87 (3)	2.05 (3)	2.914 (3)	173 (3)
O5—H2···O3	0.84 (4)	1.94 (4)	2.769 (3)	173 (4)

Symmetry codes: (i) $x-1, y-1, z$; (ii) $-x+1, -y+2, -z+1$; (iii) $-x+1, -y+1, -z$; (iv) $x+1, y+1, z-1$.

Data collection: *CrystalClear* (Molecular Structure Corporation & Rigaku, 2000); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *CrystalStructure* (Molecular Structure Corporation & Rigaku, 2000); software used to prepare material for publication: *SHELXL97* (Sheldrick, 1997).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: IM2030).

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supplementary materials

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4-{[6-(4,4'-Bipyridin-1-ium-1-yl)-2-(4-carboxyanilino)-1,3,5-triazin-2-yl]amino}benzoate monohydrate

J. Chen and **Y. Ruan**

Comment

It is well known that chlorine atoms in cyanuric chloride are easily replaced by other organic groups (Thurston *et al.*, 1951). Using cyanuric chloride as reactant and controlling stoichiometry and reaction temperature, we have synthesized a new triazine derivative, 2-[(4-carboxylatephenyl)amino]-4-[(4-carboxyphenyl)amino]- 6-(4,4'-bipyridin-1-yl)-1,3,5-triazine (Fig. 3). The title organic compound exists as a zwitterion. Some highly related zwitterionic triazine derivatives have been published by some patents (Sahouani, 2006; Sahouani & Vogel, 2002; Sahouani, Vogel & Schaberg, 2002; Sahouani *et al.*, 2001). Nevertheless, to the best of our knowledge, no crystal data are known for zwitterionic triazines (Cambridge Structural Database, Version 5.28 of May 2007; Allen, 2002).

The title compound was synthesized by treating 2,4,6-tri((4-carboxyphenyl) amino)-1,3,5-triazine and 4,4'-bipy in DMF solution. In the title organic compound, as shown in figure 1, the 6-position of triazine ring is occupied by the cationic 4,4'-bipyridin-1-yl group and whereas the anionic (4-carboxylatephenyl)amino substituent is observed in the 2-position, making the title compound a zwitterion. The zwitteric character is also confirmed by the C—O distances of the carboxylate and carboxy group. The double bond C=O (C4—O1: 1.201 (2) Å) in the carboxy moiety is clearly shorter than the single bond C—O (C4—O2: 1.299 (2) Å) and the nearly equivalent distances of C5—O3(1.251 (2) Å) and C5—O4 (1.262 (2) Å) vertify the anionic nature of the carboxylate function in the 2-position of triazine ring. The torsional angles [C14—C13—C21—C25] and [C12—C13—C21—C22] are 19.5 (3)° and 17.3 (3)°, respectively, confirming that the two pyridine subunits of the 4,4-bipy are not coplanar. The H atoms of water molecule, N—H group and carboxy build up an intricated H-bond network with O and N atoms (figure 2).

Experimental

2,4,6-tri((4-carboxyphenyl)amino)-1,3,5-triazine: 4.6 g (0.025 mol) cyanuric chloride reacted with 21.3 g (0.155 mol) *p*-aminobenzoic acid in 250 ml acetone at 45° for 12 h creating a substantive white deposit. After cooling, the white product was filtered from the reaction mixture, washed free of hydrochloric acid salt of *p*-aminobenzoic acid with water and oven-dried at 60° (76% yield).

2-((4-carboxylatephenyl)amino)-4-((4-carboxyphenyl)amino) −6-(4,4'-bipyridin-1-yl)-1,3,5-triazine: 9.7 g (0.02 mol) 2,4,6-tri ((4-carboxyphenyl)amino)-1,3,5-triazine reacted with 3.1 g (0.02 mol) 4,4-bipy in 150 ml DMF at 100° for 8 h creating an orange–yellow deposit. After cooling, the orange–yellow product was filtered from the reaction mixture, washed free of impurity with DMF and acetone and oven-dried at 60° (95% yield). A solution of 0.15 g product and 25 ml H_2O was heated in an autoclave at 160° for 1 days and then cooled to room temperature for 3 days, creating the red crystal of the title compound.

Refinement

Anisotropic thermal parameters were applied to all non-hydrogen atoms. All hydrogen atoms were located in a difference map and refined isotropically. All calculations were performed with *SHELXL97* program package (Sheldrick, 1997).

Figures

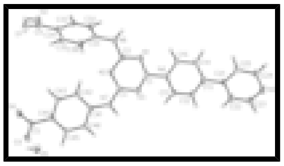


Fig. 1. *ORTEP* drawing of the title compound with thermal ellipsoids at the 30% probability level.

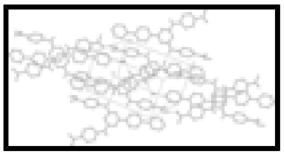


Fig. 2. Crystal structure of the title compound with hydrogen bonds indicated as dashed lines. Hydrogen atoms not taking part in hydrogen bonds are omitted for the sake of clarity.


Fig. 3. The formation of the title compound.

4-{[6-(4,4'-Bipyridin-1-ium-1-yl)-2-(4-carboxyanilino)-1,3,5-triazin- 2-yl]amino}benzoate monohydrate

Crystal data

$C_{27}H_{19}N_7O_4 \cdot H_2O$	$Z = 2$
$M_r = 523.51$	$F_{000} = 544$
Triclinic, $P\overline{1}$	$D_x = 1.473$ Mg m^{-3}
Hall symbol: -P 1	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
$a = 9.500$ (5) Å	Cell parameters from 2378 reflections
$b = 9.523$ (5) Å	$\theta = 3.1$–27.5°
$c = 13.669$ (7) Å	$\mu = 0.11$ mm^{-1}
$\alpha = 97.527$ (3)°	$T = 293$ (2) K
$\beta = 98.781$ (6)°	Prism, red
$\gamma = 101.555$ (6)°	0.78 × 0.20 × 0.05 mm
$V = 1181$ (1) Å^3	

Data collection

Rigaku Mercury CCD diffractometer	5350 independent reflections
Radiation source: rotating-anode generator	3866 reflections with $I > 2\sigma(I)$
Monochromator: Graphite Monochromator	$R_{int} = 0.025$
$T = 130.1500$ K	$\theta_{max} = 27.5$°

ω scans	$\theta_{min} = 3.1°$
Absorption correction: multi-scan (SPHERE in CrystalStructure; Molecular Structure Corporation & Rigaku, 2000)	$h = -12 \rightarrow 10$
$T_{min} = 0.975$, $T_{max} = 0.995$	$k = -12 \rightarrow 12$
9219 measured reflections	$l = -17 \rightarrow 17$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.052$	All H-atom parameters refined
$wR(F^2) = 0.161$	$w = 1/[\sigma^2(F_o^2) + (0.0989P)^2 + 0.007P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.00$	$(\Delta/\sigma)_{max} < 0.001$
5350 reflections	$\Delta\rho_{max} = 0.24$ e Å^{-3}
436 parameters	$\Delta\rho_{min} = -0.22$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: none

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit S are based on F^2, conventional *R*-factors *R* are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on F, and R– factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.03809 (18)	0.35605 (19)	0.58550 (13)	0.0311 (4)
C2	0.08201 (19)	0.2646 (2)	0.43911 (13)	0.0327 (4)
C3	0.20747 (18)	0.48675 (19)	0.51904 (12)	0.0299 (4)
C4	0.2237 (2)	0.1994 (2)	−0.01844 (14)	0.0393 (4)
C5	0.73347 (19)	0.8236 (2)	0.29767 (13)	0.0348 (4)
C11	−0.0278 (2)	0.4560 (2)	0.74022 (16)	0.0432 (5)
H11	0.041 (3)	0.541 (3)	0.7332 (18)	0.060 (7)*
C12	−0.0998 (2)	0.4443 (2)	0.81892 (16)	0.0461 (5)
H12	−0.081 (2)	0.528 (3)	0.8678 (18)	0.054 (6)*
C13	−0.1926 (2)	0.3146 (2)	0.82586 (14)	0.0366 (4)
C14	−0.2132 (2)	0.2012 (2)	0.74647 (16)	0.0442 (5)
H14	−0.281 (2)	0.111 (3)	0.7402 (16)	0.048 (6)*

C15	−0.1397 (2)	0.2162 (2)	0.66821 (16)	0.0417 (4)
H15	−0.145 (3)	0.142 (3)	0.6113 (18)	0.058 (7)*
C21	−0.2584 (2)	0.2992 (2)	0.91672 (14)	0.0396 (4)
C22	−0.2628 (3)	0.4192 (3)	0.9843 (2)	0.0690 (8)
H22	−0.242 (4)	0.514 (4)	0.967 (3)	0.107 (11)*
C23	−0.3071 (3)	0.4008 (3)	1.0745 (2)	0.0700 (8)
H23	−0.312 (3)	0.481 (4)	1.127 (2)	0.090 (9)*
C24	−0.3487 (2)	0.1571 (3)	1.03494 (16)	0.0474 (5)
H24	−0.378 (3)	0.060 (3)	1.053 (2)	0.079 (8)*
C25	−0.3074 (2)	0.1647 (2)	0.94255 (15)	0.0424 (5)
H25	−0.314 (2)	0.073 (3)	0.8954 (17)	0.052 (6)*
C31	0.0955 (2)	0.17036 (18)	0.26628 (13)	0.0334 (4)
C32	−0.0094 (2)	0.1463 (2)	0.18007 (14)	0.0405 (4)
H32	−0.114 (3)	0.123 (2)	0.1836 (17)	0.053 (6)*
C33	0.0321 (2)	0.1576 (2)	0.08816 (15)	0.0410 (4)
H33	−0.042 (2)	0.138 (2)	0.0292 (16)	0.043 (5)*
C34	0.1787 (2)	0.19018 (19)	0.08102 (13)	0.0341 (4)
C35	0.2832 (2)	0.2111 (2)	0.16743 (15)	0.0385 (4)
H35	0.385 (3)	0.232 (2)	0.1634 (17)	0.052 (6)*
C36	0.2429 (2)	0.2014 (2)	0.25980 (14)	0.0381 (4)
H36	0.319 (2)	0.219 (2)	0.3164 (16)	0.042 (5)*
C41	0.40884 (18)	0.65630 (18)	0.46672 (13)	0.0304 (4)
C42	0.4296 (2)	0.5703 (2)	0.38177 (14)	0.0379 (4)
H42	0.372 (2)	0.476 (2)	0.3605 (16)	0.045 (6)*
C43	0.5345 (2)	0.6248 (2)	0.32829 (14)	0.0375 (4)
H43	0.547 (3)	0.561 (3)	0.2705 (19)	0.058 (7)*
C44	0.61918 (18)	0.76485 (19)	0.35593 (13)	0.0322 (4)
C45	0.5971 (2)	0.8504 (2)	0.44022 (14)	0.0378 (4)
H45	0.659 (2)	0.954 (3)	0.4624 (17)	0.050 (6)*
C46	0.4942 (2)	0.7971 (2)	0.49517 (14)	0.0366 (4)
H46	0.479 (2)	0.855 (2)	0.5542 (16)	0.043 (6)*
N1	0.00548 (16)	0.24207 (17)	0.51393 (11)	0.0352 (3)
N2	0.18480 (16)	0.38337 (16)	0.43910 (11)	0.0330 (3)
N3	0.13091 (16)	0.48030 (16)	0.59582 (11)	0.0338 (3)
N4	−0.04689 (16)	0.34248 (16)	0.66637 (11)	0.0328 (3)
N5	−0.3460 (2)	0.2723 (2)	1.10135 (13)	0.0534 (5)
N6	0.04740 (19)	0.15736 (18)	0.35875 (12)	0.0401 (4)
H6	−0.039 (3)	0.092 (3)	0.3552 (19)	0.065 (8)*
N7	0.30777 (16)	0.61188 (17)	0.52825 (12)	0.0338 (3)
H7	0.314 (2)	0.673 (2)	0.5862 (17)	0.042 (6)*
O1	0.34478 (19)	0.1932 (3)	−0.03132 (13)	0.0833 (7)
O2	0.12177 (15)	0.21458 (18)	−0.08863 (11)	0.0496 (4)
H3	0.160 (4)	0.229 (4)	−0.159 (3)	0.108 (11)*
O3	0.77794 (16)	0.95853 (16)	0.30828 (12)	0.0505 (4)
O4	0.77886 (16)	0.73177 (16)	0.24276 (10)	0.0455 (4)
O5	0.6274 (2)	1.1778 (2)	0.29330 (13)	0.0610 (5)
H1	0.640 (3)	1.213 (3)	0.239 (2)	0.072 (8)*
H2	0.677 (4)	1.116 (4)	0.302 (3)	0.106 (13)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0306 (9)	0.0380 (9)	0.0294 (8)	0.0086 (7)	0.0126 (7)	0.0133 (7)
C2	0.0323 (9)	0.0368 (9)	0.0299 (8)	0.0055 (7)	0.0091 (7)	0.0084 (7)
C3	0.0294 (8)	0.0334 (9)	0.0303 (8)	0.0077 (7)	0.0101 (7)	0.0108 (7)
C4	0.0406 (10)	0.0429 (11)	0.0379 (10)	0.0118 (8)	0.0144 (8)	0.0070 (8)
C5	0.0307 (9)	0.0410 (10)	0.0336 (9)	0.0034 (7)	0.0087 (7)	0.0138 (8)
C11	0.0543 (12)	0.0339 (10)	0.0435 (11)	0.0040 (9)	0.0225 (9)	0.0073 (9)
C12	0.0621 (13)	0.0354 (10)	0.0427 (11)	0.0048 (9)	0.0259 (10)	0.0044 (9)
C13	0.0410 (10)	0.0377 (10)	0.0367 (9)	0.0118 (8)	0.0159 (8)	0.0119 (8)
C14	0.0506 (12)	0.0396 (10)	0.0428 (11)	0.0001 (9)	0.0215 (9)	0.0084 (9)
C15	0.0478 (11)	0.0379 (10)	0.0388 (10)	0.0003 (8)	0.0190 (9)	0.0055 (8)
C21	0.0441 (11)	0.0419 (10)	0.0373 (10)	0.0096 (8)	0.0186 (8)	0.0098 (8)
C22	0.110 (2)	0.0455 (13)	0.0607 (15)	0.0097 (13)	0.0539 (15)	0.0101 (12)
C23	0.097 (2)	0.0574 (15)	0.0566 (15)	0.0019 (14)	0.0446 (15)	−0.0007 (12)
C24	0.0440 (11)	0.0574 (13)	0.0426 (11)	0.0045 (10)	0.0142 (9)	0.0187 (10)
C25	0.0437 (11)	0.0433 (11)	0.0410 (10)	0.0053 (9)	0.0141 (9)	0.0099 (9)
C31	0.0401 (10)	0.0292 (9)	0.0299 (8)	0.0009 (7)	0.0132 (7)	0.0044 (7)
C32	0.0338 (10)	0.0497 (11)	0.0360 (10)	0.0009 (8)	0.0112 (8)	0.0071 (9)
C33	0.0374 (10)	0.0520 (12)	0.0333 (9)	0.0067 (9)	0.0089 (8)	0.0085 (8)
C34	0.0394 (10)	0.0315 (9)	0.0335 (9)	0.0084 (7)	0.0126 (8)	0.0054 (7)
C35	0.0343 (10)	0.0427 (10)	0.0399 (10)	0.0073 (8)	0.0134 (8)	0.0059 (8)
C36	0.0369 (10)	0.0440 (10)	0.0321 (9)	0.0070 (8)	0.0071 (8)	0.0032 (8)
C41	0.0305 (8)	0.0311 (8)	0.0326 (8)	0.0065 (7)	0.0108 (7)	0.0103 (7)
C42	0.0417 (10)	0.0317 (9)	0.0386 (10)	−0.0003 (8)	0.0167 (8)	0.0028 (8)
C43	0.0421 (10)	0.0356 (10)	0.0349 (9)	0.0027 (8)	0.0171 (8)	0.0036 (8)
C44	0.0308 (9)	0.0348 (9)	0.0324 (9)	0.0042 (7)	0.0094 (7)	0.0111 (7)
C45	0.0420 (10)	0.0319 (9)	0.0368 (9)	−0.0003 (8)	0.0127 (8)	0.0040 (8)
C46	0.0437 (10)	0.0351 (9)	0.0309 (9)	0.0050 (8)	0.0145 (8)	0.0021 (7)
N1	0.0356 (8)	0.0398 (8)	0.0315 (7)	0.0038 (6)	0.0127 (6)	0.0098 (7)
N2	0.0338 (8)	0.0358 (8)	0.0295 (7)	0.0029 (6)	0.0108 (6)	0.0071 (6)
N3	0.0363 (8)	0.0359 (8)	0.0319 (7)	0.0068 (6)	0.0136 (6)	0.0089 (6)
N4	0.0352 (8)	0.0374 (8)	0.0292 (7)	0.0079 (6)	0.0128 (6)	0.0102 (6)
N5	0.0499 (10)	0.0721 (13)	0.0376 (9)	0.0039 (9)	0.0175 (8)	0.0113 (9)
N6	0.0431 (9)	0.0397 (9)	0.0327 (8)	−0.0052 (7)	0.0138 (7)	0.0026 (7)
N7	0.0394 (8)	0.0331 (8)	0.0304 (7)	0.0044 (6)	0.0157 (6)	0.0055 (6)
O1	0.0547 (10)	0.165 (2)	0.0506 (10)	0.0497 (12)	0.0267 (8)	0.0323 (12)
O2	0.0458 (8)	0.0701 (10)	0.0386 (8)	0.0144 (7)	0.0163 (6)	0.0179 (7)
O3	0.0485 (8)	0.0426 (8)	0.0592 (9)	−0.0049 (6)	0.0213 (7)	0.0139 (7)
O4	0.0533 (8)	0.0507 (8)	0.0432 (7)	0.0160 (7)	0.0264 (7)	0.0190 (7)
O5	0.0852 (13)	0.0693 (11)	0.0385 (9)	0.0276 (10)	0.0260 (8)	0.0119 (8)

Geometric parameters (Å, °)

C1—N3	1.303 (2)	C24—N5	1.323 (3)
C1—N1	1.314 (2)	C24—C25	1.385 (3)
C1—N4	1.469 (2)	C24—H24	0.99 (3)

C2—N2	1.338 (2)	C25—H25	1.00 (2)
C2—N6	1.349 (2)	C31—C32	1.384 (3)
C2—N1	1.357 (2)	C31—C36	1.390 (3)
C3—N2	1.331 (2)	C31—N6	1.420 (2)
C3—N7	1.346 (2)	C32—C33	1.384 (3)
C3—N3	1.366 (2)	C32—H32	0.99 (2)
C4—O1	1.201 (2)	C33—C34	1.386 (3)
C4—O2	1.299 (2)	C33—H33	0.96 (2)
C4—C34	1.494 (3)	C34—C35	1.386 (3)
C5—O3	1.251 (2)	C35—C36	1.383 (3)
C5—O4	1.262 (2)	C35—H35	0.96 (2)
C5—C44	1.505 (2)	C36—H36	0.95 (2)
C11—N4	1.342 (3)	C41—C46	1.392 (3)
C11—C12	1.365 (3)	C41—C42	1.394 (3)
C11—H11	0.96 (3)	C41—N7	1.409 (2)
C12—C13	1.390 (3)	C42—C43	1.383 (3)
C12—H12	0.94 (2)	C42—H42	0.93 (2)
C13—C14	1.388 (3)	C43—C44	1.383 (3)
C13—C21	1.484 (3)	C43—H43	0.96 (2)
C14—C15	1.371 (3)	C44—C45	1.390 (3)
C14—H14	0.95 (2)	C45—C46	1.379 (3)
C15—N4	1.347 (2)	C45—H45	1.02 (2)
C15—H15	0.97 (2)	C46—H46	0.96 (2)
C21—C25	1.382 (3)	N6—H6	0.92 (3)
C21—C22	1.384 (3)	N7—H7	0.90 (2)
C22—C23	1.383 (3)	O2—H3	1.09 (4)
C22—H22	0.96 (4)	O5—H1	0.87 (3)
C23—N5	1.321 (3)	O5—H2	0.84 (4)
C23—H23	0.99 (3)		

N3—C1—N1	130.88 (16)	C31—C32—C33	120.11 (18)
N3—C1—N4	114.54 (15)	C31—C32—H32	120.5 (13)
N1—C1—N4	114.56 (15)	C33—C32—H32	119.4 (13)
N2—C2—N6	119.02 (16)	C32—C33—C34	120.60 (18)
N2—C2—N1	125.34 (16)	C32—C33—H33	118.9 (13)
N6—C2—N1	115.63 (16)	C34—C33—H33	120.4 (13)
N2—C3—N7	121.14 (15)	C33—C34—C35	118.96 (17)
N2—C3—N3	124.74 (16)	C33—C34—C4	120.67 (17)
N7—C3—N3	114.07 (15)	C35—C34—C4	120.36 (16)
O1—C4—O2	123.42 (19)	C36—C35—C34	120.89 (18)
O1—C4—C34	122.06 (18)	C36—C35—H35	119.3 (14)
O2—C4—C34	114.52 (16)	C34—C35—H35	119.8 (14)
O3—C5—O4	125.01 (17)	C35—C36—C31	119.67 (17)
O3—C5—C44	118.09 (17)	C35—C36—H36	117.2 (13)
O4—C5—C44	116.89 (17)	C31—C36—H36	123.1 (13)
N4—C11—C12	120.54 (19)	C46—C41—C42	118.70 (16)
N4—C11—H11	114.6 (15)	C46—C41—N7	116.19 (15)
C12—C11—H11	124.9 (15)	C42—C41—N7	125.12 (16)
C11—C12—C13	121.24 (19)	C43—C42—C41	119.96 (17)
C11—C12—H12	115.6 (15)	C43—C42—H42	119.8 (13)

C13—C12—H12	123.2 (15)	C41—C42—H42	120.2 (13)
C14—C13—C12	116.49 (18)	C42—C43—C44	121.60 (17)
C14—C13—C21	122.90 (18)	C42—C43—H43	117.4 (15)
C12—C13—C21	120.54 (18)	C44—C43—H43	121.0 (15)
C15—C14—C13	120.92 (19)	C43—C44—C45	118.13 (16)
C15—C14—H14	115.3 (14)	C43—C44—C5	121.43 (16)
C13—C14—H14	123.7 (14)	C45—C44—C5	120.44 (17)
N4—C15—C14	120.50 (18)	C46—C45—C44	121.02 (18)
N4—C15—H15	113.3 (15)	C46—C45—H45	119.5 (13)
C14—C15—H15	126.2 (15)	C44—C45—H45	119.5 (13)
C25—C21—C22	116.44 (19)	C45—C46—C41	120.59 (17)
C25—C21—C13	121.78 (18)	C45—C46—H46	121.7 (13)
C22—C21—C13	121.57 (19)	C41—C46—H46	117.7 (13)
C23—C22—C21	119.9 (2)	C1—N1—C2	111.57 (15)
C23—C22—H22	120 (2)	C3—N2—C2	115.17 (15)
C21—C22—H22	120 (2)	C1—N3—C3	112.10 (15)
N5—C23—C22	123.4 (2)	C11—N4—C15	120.22 (16)
N5—C23—H23	112.3 (19)	C11—N4—C1	119.24 (16)
C22—C23—H23	124.4 (19)	C15—N4—C1	120.50 (15)
N5—C24—C25	123.8 (2)	C23—N5—C24	116.8 (2)
N5—C24—H24	118.4 (16)	C2—N6—C31	124.14 (16)
C25—C24—H24	117.7 (17)	C2—N6—H6	114.7 (16)
C21—C25—C24	119.4 (2)	C31—N6—H6	116.0 (16)
C21—C25—H25	121.0 (13)	C3—N7—C41	130.48 (15)
C24—C25—H25	119.6 (13)	C3—N7—H7	112.8 (14)
C32—C31—C36	119.75 (17)	C41—N7—H7	116.5 (14)
C32—C31—N6	117.98 (16)	C4—O2—H3	113.1 (17)
C36—C31—N6	122.24 (16)	H1—O5—H2	111 (3)

N4—C11—C12—C13	1.1 (3)	O3—C5—C44—C45	−19.6 (3)
C11—C12—C13—C14	−3.2 (3)	O4—C5—C44—C45	159.23 (17)
C11—C12—C13—C21	173.84 (19)	C43—C44—C45—C46	0.4 (3)
C12—C13—C14—C15	3.0 (3)	C5—C44—C45—C46	−179.00 (17)
C21—C13—C14—C15	−173.97 (19)	C44—C45—C46—C41	−0.7 (3)
C13—C14—C15—N4	−0.7 (3)	C42—C41—C46—C45	0.1 (3)
C14—C13—C21—C25	19.5 (3)	N7—C41—C46—C45	179.55 (16)
C12—C13—C21—C25	−157.3 (2)	N3—C1—N1—C2	−1.7 (3)
C14—C13—C21—C22	−165.9 (2)	N4—C1—N1—C2	176.68 (13)
C12—C13—C21—C22	17.3 (3)	N2—C2—N1—C1	3.8 (3)
C25—C21—C22—C23	3.4 (4)	N6—C2—N1—C1	−175.18 (16)
C13—C21—C22—C23	−171.5 (2)	N7—C3—N2—C2	−179.89 (16)
C21—C22—C23—N5	0.4 (5)	N3—C3—N2—C2	−2.4 (2)
C22—C21—C25—C24	−3.9 (3)	N6—C2—N2—C3	176.99 (16)
C13—C21—C25—C24	170.90 (18)	N1—C2—N2—C3	−2.0 (3)
N5—C24—C25—C21	0.9 (3)	N1—C1—N3—C3	−2.0 (3)
C36—C31—C32—C33	−2.0 (3)	N4—C1—N3—C3	179.63 (13)
N6—C31—C32—C33	−179.95 (17)	N2—C3—N3—C1	4.2 (2)
C31—C32—C33—C34	1.3 (3)	N7—C3—N3—C1	−178.17 (15)
C32—C33—C34—C35	0.1 (3)	C12—C11—N4—C15	1.2 (3)
C32—C33—C34—C4	178.73 (18)	C12—C11—N4—C1	−176.76 (18)

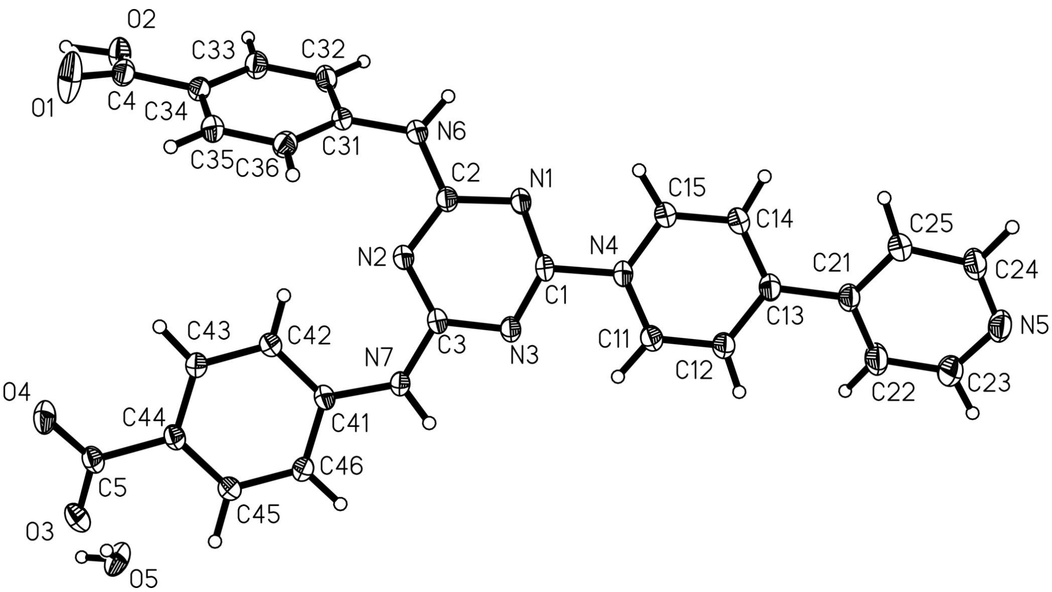
O1—C4—C34—C33	−162.1 (2)	C14—C15—N4—C11	−1.4 (3)
O2—C4—C34—C33	17.9 (3)	C14—C15—N4—C1	176.54 (17)
O1—C4—C34—C35	16.4 (3)	N3—C1—N4—C11	2.3 (2)
O2—C4—C34—C35	−163.47 (18)	N1—C1—N4—C11	−176.29 (16)
C33—C34—C35—C36	−0.7 (3)	N3—C1—N4—C15	−175.66 (17)
C4—C34—C35—C36	−179.34 (17)	N1—C1—N4—C15	5.7 (2)
C34—C35—C36—C31	0.0 (3)	C22—C23—N5—C24	−3.5 (4)
C32—C31—C36—C35	1.4 (3)	C25—C24—N5—C23	2.9 (3)
N6—C31—C36—C35	179.24 (17)	N2—C2—N6—C31	−10.6 (3)
C46—C41—C42—C43	0.7 (3)	N1—C2—N6—C31	168.53 (16)
N7—C41—C42—C43	−178.65 (17)	C32—C31—N6—C2	−122.3 (2)
C41—C42—C43—C44	−1.0 (3)	C36—C31—N6—C2	59.8 (3)
C42—C43—C44—C45	0.5 (3)	N2—C3—N7—C41	−4.3 (3)
C42—C43—C44—C5	179.85 (17)	N3—C3—N7—C41	177.97 (16)
O3—C5—C44—C43	161.03 (18)	C46—C41—N7—C3	177.20 (17)
O4—C5—C44—C43	−20.1 (3)	C42—C41—N7—C3	−3.4 (3)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N6—H6···O3^{i}	0.92 (3)	1.90 (3)	2.791 (2)	164 (2)
N7—H7···O5^{ii}	0.90 (2)	1.96 (2)	2.847 (3)	167 (2)
O2—H3···O4^{iii}	1.09 (4)	1.42 (4)	2.507 (2)	172 (3)
O5—H1···N5^{iv}	0.87 (3)	2.05 (3)	2.914 (3)	173 (3)
O5—H2···O3	0.84 (4)	1.94 (4)	2.769 (3)	173 (4)

Symmetry codes: (i) *x*−1, *y*−1, *z*; (ii) −*x*+1, −*y*+2, −*z*+1; (iii) −*x*+1, −*y*+1, −*z*; (iv) *x*+1, *y*+1, *z*−1.

Fig. 1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C32
O1
C4
C34
N6
C31
C35
C36
C2
N1
C15
C14
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N2
N4
C21
C24
C1
C13
C43
C42
C3
N5
N7
C11
N3
C12
C23
C22
O4
C41
C44
C46
C5
C45
O3
O5

Fig. 2

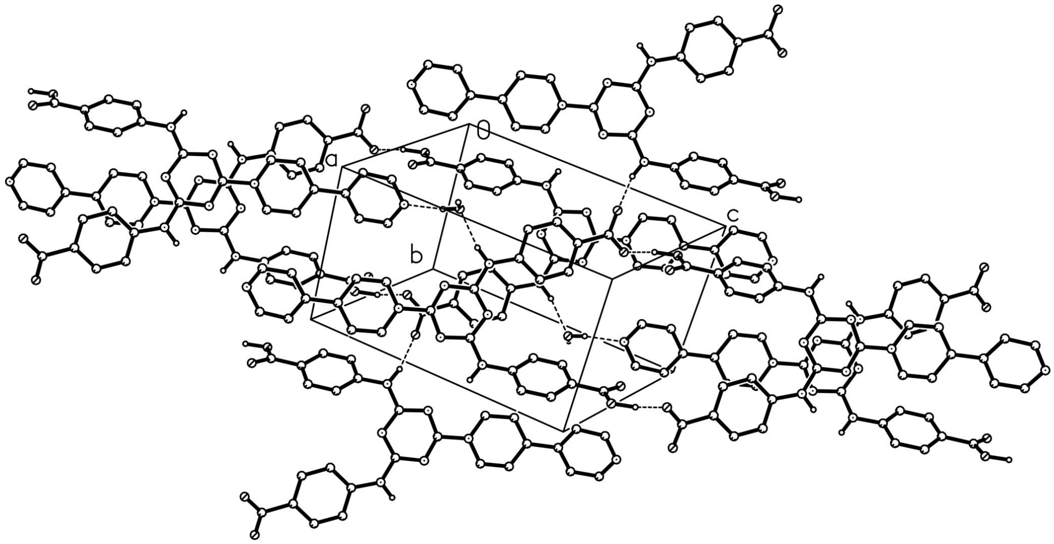
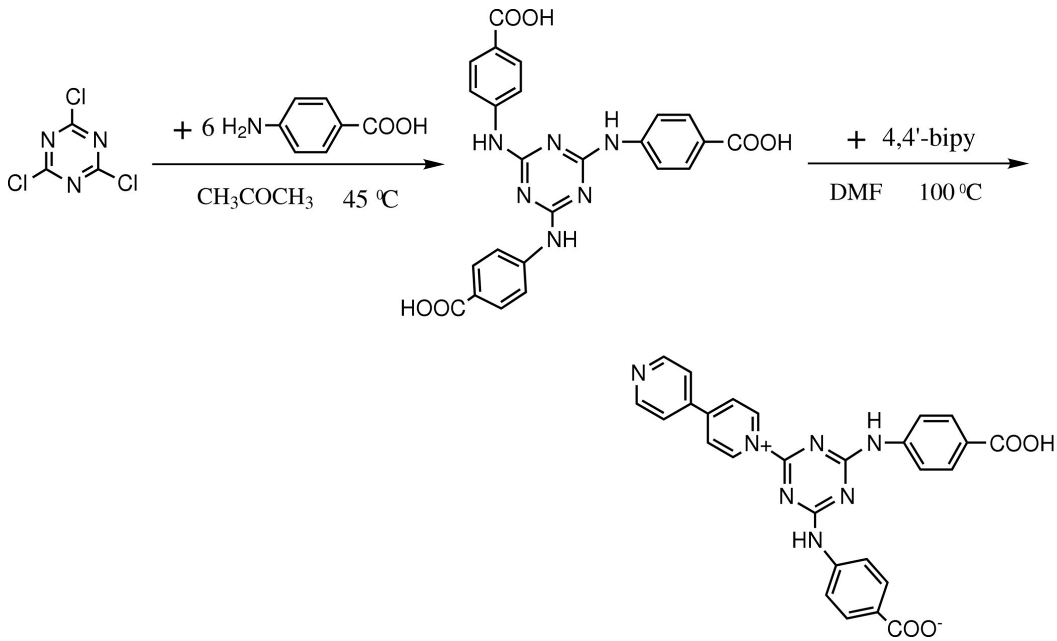


Fig. 3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COOH
CH3COCH3 45 °C
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+ 4,4'-bipy
DMF 100 °C
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COOH
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N
HN
COO-