

3-Hydroxyanilinium bromide

Dominik Cinčić* and Branko Kaitner

Department of Chemistry, Laboratory of General and Inorganic Chemistry, Faculty of Science, University of Zagreb, Horvatovac 102a, HR-10000 Zagreb, Croatia
Correspondence e-mail: dominik@chem.pmf.hr

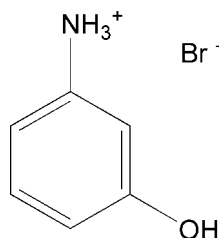
Received 17 July 2007; accepted 27 July 2007

Key indicators: single-crystal X-ray study; $T = 295$ K; mean $\sigma(\text{C}-\text{C}) = 0.004$ Å; R factor = 0.030; wR factor = 0.082; data-to-parameter ratio = 18.8.

The asymmetric unit of the title compound, $\text{C}_6\text{H}_8\text{NO}^+\cdot\text{Br}^-$, consists of a 3-hydroxyanilinium cation and a bromide anion. The ions are connected into a three-dimensional hydrogen-bonded network via $\text{O}-\text{H}\cdots\text{Br}$, $\text{N}-\text{H}\cdots\text{Br}$ and $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds, with four characteristic graph-set motifs: $C_2^1(8)$, $C_3^2(6)$, $R_4^2(8)$ and $R_6^4(12)$.

Related literature

For related literature, see: Lemmerer & Billing (2006); Bernstein *et al.* (1995). For bond length data, see: Allen *et al.* (1987).



Experimental

Crystal data

$\text{C}_6\text{H}_8\text{NO}^+\cdot\text{Br}^-$
 $M_r = 190.03$
Monoclinic, $P2_1/n$
 $a = 7.6661$ (14) Å
 $b = 6.1482$ (9) Å
 $c = 15.792$ (2) Å
 $\beta = 96.437$ (13)°

$V = 739.6$ (2) Å³
 $Z = 4$
Mo $K\alpha$ radiation
 $\mu = 5.48$ mm⁻¹
 $T = 295$ K
 $0.45 \times 0.11 \times 0.11$ mm

Data collection

Oxford Diffraction Xcalibur CCD diffractometer

Absorption correction: analytical (Alcock, 1970)
 $T_{\min} = 0.182$, $T_{\max} = 0.605$

7503 measured reflections
1786 independent reflections

1554 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.037$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.030$
 $wR(F^2) = 0.082$
 $S = 0.95$
1786 reflections
95 parameters

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\max} = 0.53$ e Å⁻³
 $\Delta\rho_{\min} = -0.56$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{O1}-\text{H1}\cdots\text{Br1}$	0.82	2.52	3.222 (2)	145
$\text{N31}-\text{H31A}\cdots\text{Br1}^{\text{i}}$	0.88 (4)	2.42 (4)	3.279 (3)	168 (3)
$\text{N31}-\text{H31B}\cdots\text{Br1}^{\text{ii}}$	0.84 (4)	2.57 (5)	3.355 (3)	156 (4)
$\text{N31}-\text{H31C}\cdots\text{O1}^{\text{iii}}$	0.87 (4)	2.01 (5)	2.833 (4)	158 (4)

Symmetry codes: (i) $x - \frac{1}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$; (ii) $-x + \frac{3}{2}, y + \frac{1}{2}, -z + \frac{3}{2}$; (iii) $-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{3}{2}$.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2003); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2003); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999), *PARST97* (Nardelli, 1995) and *Mercury* (Version 1.4; Macrae *et al.*, 2006).

Financial support by the Ministry of Science, Education and Sport of the Republic of Croatia is gratefully acknowledged (grant No. 119-1193079-3069).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: RK2028).

References

- Alcock, N. W. (1970). *Crystallographic Computing*, edited by F. R. Ahmed, S. R. Hall & C. P. Huber, p. 271. Copenhagen: Munksgaard.
- Allen, F. H., Kennard, O., Watson, D. G., Brammer, L. & Orpen, A. G. (1987). *J. Chem. Soc. Perkin Trans 2*, pp. S1–19.
- Bernstein, J., Davis, R. E., Shimon, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
- Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
- Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
- Lemmerer, A. & Billing, D. G. (2006). *Acta Cryst. E* **62**, o1562–o1564.
- Macrae, C. F., Edgington, P. R., McCabe, P., Pidcock, E., Shields, G. P., Taylor, R., Towler, M. & van de Streek, J. (2006). *J. Appl. Cryst.* **39**, 453–457.
- Nardelli, M. (1995). *J. Appl. Cryst.* **28**, 659.
- Oxford Diffraction (2003). *CrysAlis CCD* and *CrysAlis RED*. Version 1.170. Oxford Diffraction Ltd, Wroclaw, Poland.
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.

supplementary materials

Acta Cryst. (2007). E63, o3873 [doi:10.1107/S1600536807036884]

3-Hydroxyanilinium bromide

D. Cincic and B. Kaitner

Comment

This work is part of our research on intermolecular interactions in hydrogen-bonded ionic crystals, acid salts. The title compound (I), $C_6H_8NO^+ Br^-$, was originally prepared as part of salt screening of the hydroxy- and carboxyanilines.

The molecular structure of (I) is shown in Fig. 1. The asymmetric unit consists of 3-hydroxyanilinium cation with protonated amino-group and bromine anion. All bond lengths and bond angles correspond to the geometry parameters expected for atom types and the type of hybridization (Allen *et al.*, 1987). The ions are connected in three-dimensional hydrogen-bonded network *via* O–H \cdots Br, N–H \cdots Br, and N–H \cdots O hydrogen bonds. All ammonium group H atoms are involved in the hydrogen bonding with two Br atoms and O-atom of hydroxyl group of neighbouring cation, with three-centred geometry motif observed. Four characteristic graph-set motifs can be recognized: $C_2^1(8)$, $C_3^2(6)$, $R_4^2(8)$ and $R_6^4(12)$ in the notation of Bernstein *et al.*, (1995). Two infinite one-dimensional chains are detected with the donor participations of H31A in $C_2^1(8)$ motif and H31B and H31C in $C_3^2(6)$ graph-set motif. An eight-membered ring moiety [$R_4^2(8)$] is formed of two hydroxyanilinium cations and two bridging bromine anions through the N31–H31A \cdots Br1 \cdots H31B–N31 hydrogen bonds. The centre of 8-membered ring is situated on a crystallographic centre of symmetry. A twelve-membered ring moiety [$R_6^4(12)$] is formed of four hydroxyanilinium cations and two bridging bromine anions by means of O1–H1 \cdots Br1 \cdots H31A–N31–H31C \cdots O1 hydrogen bonding. The aggregation of two ring moieties results in infinite one-dimensional chains spreading along the *c* axis, with intercalated array of bromine ions, Fig. 2. The bromine anions act as acceptor atoms for two different H atoms, one of the ammonium group, and one of the hydroxyl group. Fig. 3 neatly shows two-dimensional packing of ions in *ac* plane where layers of 3-hydroxyanilinium cations are embedded between ionic layers of bromide anions, forming of alternating hydrocarbon-ionic structure.

Experimental

Single crystals of (I) were obtained by slow evaporation method. A solution of 100 mg 3-aminophenol dissolved in 2 ml of 1-butanol was heated at 343 K. The clear solution was obtained, added to the 1 ml of hydrobromic acid (2 M) and then left at room temperature. The crystals of (I) were collected by vacuum filtration, washed out with cold acetone and dried in air.

Refinement

All N- and O-bound H atoms were located in difference Fourier map. The positions and isotropic parameters of N-bound H atoms were refined, but O-bound H atom was treated as riding atom. Aromatic H atoms were placed in calculated positions and treated as riding on their parent C atoms, with C–H = 0.93 Å and $U_{iso}(H) = 1.2U_{eq}(C)$ for Csp^2 .

Figures

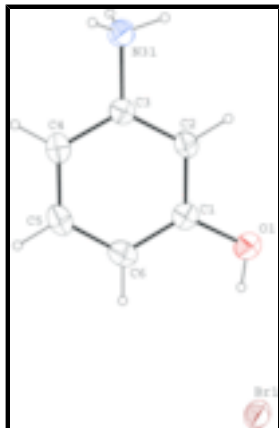


Fig. 1. The asymmetric unit of (I), showing the crystallographic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radius.

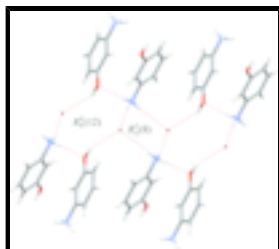


Fig. 2. A view of the one-dimensional H-bonded chain along *a* axis showing the aggregation of two different H-bonding motifs, $R_4^2(8)$ and $R_6^4(12)$. Hydrogen bonds are drawn as red dotted lines.

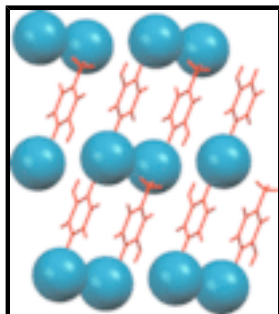


Fig. 3. Packing diagram of (I) viewed along *b* axis. The 3-hydroxyanilinium cations are shown in red colour and bromide anions are shown as blue spheres.

3-Hydroxyanilinium bromide

Crystal data

$C_6H_8NO^+ \cdot Br^-$

$M_r = 190.03$

Monoclinic, $P2_1/n$

Hall symbol: $-P\ 2_1n$

$a = 7.6661(14)\ \text{\AA}$

$b = 6.1482(9)\ \text{\AA}$

$c = 15.792(2)\ \text{\AA}$

$\beta = 96.437(13)^\circ$

$V = 739.6(2)\ \text{\AA}^3$

$Z = 4$

$F_{000} = 376$

$D_x = 1.707\ \text{Mg m}^{-3}$

Mo $K\alpha$ radiation

$\lambda = 0.71073\ \text{\AA}$

$\mu = 5.48\ \text{mm}^{-1}$

$T = 295\ \text{K}$

Prism, colourless

$0.45 \times 0.11 \times 0.11\ \text{mm}$

Data collection

Oxford Diffraction Xcalibur CCD diffractometer	1786 independent reflections
Radiation source: fine-focus sealed tube	1554 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{\text{int}} = 0.037$
$T = 295$ K	$\theta_{\text{max}} = 28.1^\circ$
ω scans	$\theta_{\text{min}} = 4.2^\circ$
Absorption correction: analytical (Alcock, 1970)	$h = -10 \rightarrow 10$
$T_{\text{min}} = 0.182$, $T_{\text{max}} = 0.605$	$k = -8 \rightarrow 8$
7503 measured reflections	$l = -20 \rightarrow 20$

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.030$	$w = 1/[\sigma^2(F_o^2) + (0.0427P)^2 + 0.1564P]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.082$	$(\Delta/\sigma)_{\text{max}} = 0.004$
$S = 0.95$	$\Delta\rho_{\text{max}} = 0.53 \text{ e } \text{\AA}^{-3}$
1786 reflections	$\Delta\rho_{\text{min}} = -0.56 \text{ e } \text{\AA}^{-3}$
95 parameters	Extinction correction: SHELXL97, $F_c^* = kFc[1 + 0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Primary atom site location: structure-invariant direct methods	Extinction coefficient: 0.017 (2)
Secondary atom site location: difference Fourier map	

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 (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Br1	0.80396 (3)	0.27270 (4)	1.015679 (15)	0.04682 (14)
O1	0.4811 (2)	0.3603 (3)	0.87080 (11)	0.0526 (5)

supplementary materials

H1	0.5343	0.3778	0.9183	0.079*
N31	0.3571 (4)	0.7140 (4)	0.59956 (15)	0.0446 (5)
C1	0.5036 (3)	0.5387 (4)	0.82171 (15)	0.0398 (5)
C2	0.4210 (3)	0.5363 (4)	0.73883 (14)	0.0383 (5)
H2	0.3531	0.4181	0.7184	0.046*
C3	0.4423 (3)	0.7140 (4)	0.68767 (15)	0.0366 (5)
C4	0.5425 (3)	0.8913 (4)	0.71549 (16)	0.0457 (6)
H4	0.5557	1.0086	0.6796	0.055*
C5	0.6225 (3)	0.8901 (4)	0.79794 (17)	0.0505 (6)
H5	0.6907	1.0084	0.8179	0.061*
C6	0.6033 (4)	0.7159 (4)	0.85170 (19)	0.0473 (6)
H6	0.6571	0.7180	0.9075	0.057*
H31A	0.331 (4)	0.581 (6)	0.5828 (18)	0.058 (8)*
H31B	0.424 (5)	0.766 (5)	0.567 (3)	0.071 (12)*
H31C	0.260 (6)	0.787 (6)	0.599 (2)	0.073 (12)*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.0570 (2)	0.04004 (18)	0.04346 (18)	0.00182 (10)	0.00558 (11)	0.00423 (9)
O1	0.0576 (11)	0.0510 (11)	0.0477 (10)	-0.0046 (9)	-0.0012 (8)	0.0104 (8)
N31	0.0545 (13)	0.0391 (12)	0.0397 (11)	0.0020 (11)	0.0031 (10)	-0.0012 (9)
C1	0.0372 (11)	0.0413 (13)	0.0419 (12)	0.0029 (9)	0.0084 (9)	0.0001 (10)
C2	0.0359 (11)	0.0339 (12)	0.0451 (12)	-0.0015 (9)	0.0050 (9)	-0.0044 (9)
C3	0.0349 (10)	0.0369 (12)	0.0385 (12)	0.0046 (9)	0.0064 (9)	-0.0043 (9)
C4	0.0486 (13)	0.0364 (13)	0.0530 (14)	-0.0040 (10)	0.0100 (11)	-0.0029 (11)
C5	0.0496 (14)	0.0406 (14)	0.0610 (16)	-0.0088 (11)	0.0053 (12)	-0.0091 (12)
C6	0.0446 (13)	0.0519 (15)	0.0443 (14)	-0.0017 (11)	-0.0003 (10)	-0.0084 (11)

Geometric parameters (\AA , $^\circ$)

O1—C1	1.365 (3)	C2—C3	1.379 (3)
O1—H1	0.8200	C2—H2	0.9300
N31—C3	1.470 (3)	C3—C4	1.377 (3)
N31—H31A	0.88 (3)	C4—C5	1.376 (4)
N31—H31B	0.83 (4)	C4—H4	0.9300
N31—H31C	0.87 (4)	C5—C6	1.385 (4)
C1—C6	1.384 (3)	C5—H5	0.9300
C1—C2	1.389 (3)	C6—H6	0.9300
C1—O1—H1	109.5	C4—C3—C2	122.6 (2)
C3—N31—H31A	110.4 (18)	C4—C3—N31	118.4 (2)
C3—N31—H31B	110 (3)	C2—C3—N31	119.0 (2)
H31A—N31—H31B	108 (3)	C5—C4—C3	118.1 (2)
C3—N31—H31C	107 (2)	C5—C4—H4	120.9
H31A—N31—H31C	109 (3)	C3—C4—H4	120.9
H31B—N31—H31C	113 (3)	C4—C5—C6	121.2 (2)
O1—C1—C6	122.6 (2)	C4—C5—H5	119.4
O1—C1—C2	117.0 (2)	C6—C5—H5	119.4

C6—C1—C2	120.5 (2)	C1—C6—C5	119.5 (2)
C3—C2—C1	118.2 (2)	C1—C6—H6	120.3
C3—C2—H2	120.9	C5—C6—H6	120.3
C1—C2—H2	120.9		

Hydrogen-bond geometry (\AA , $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1—H1 \cdots Br1	0.82	2.52	3.222 (2)	145
N31—H31A \cdots Br1 ⁱ	0.88 (4)	2.42 (4)	3.279 (3)	168 (3)
N31—H31B \cdots Br1 ⁱⁱ	0.84 (4)	2.57 (5)	3.355 (3)	156 (4)
N31—H31C \cdots O1 ⁱⁱⁱ	0.87 (4)	2.01 (5)	2.833 (4)	158 (4)

Symmetry codes: (i) $x-1/2, -y+1/2, z-1/2$; (ii) $-x+3/2, y+1/2, -z+3/2$; (iii) $-x+1/2, y+1/2, -z+3/2$.

Fig. 1

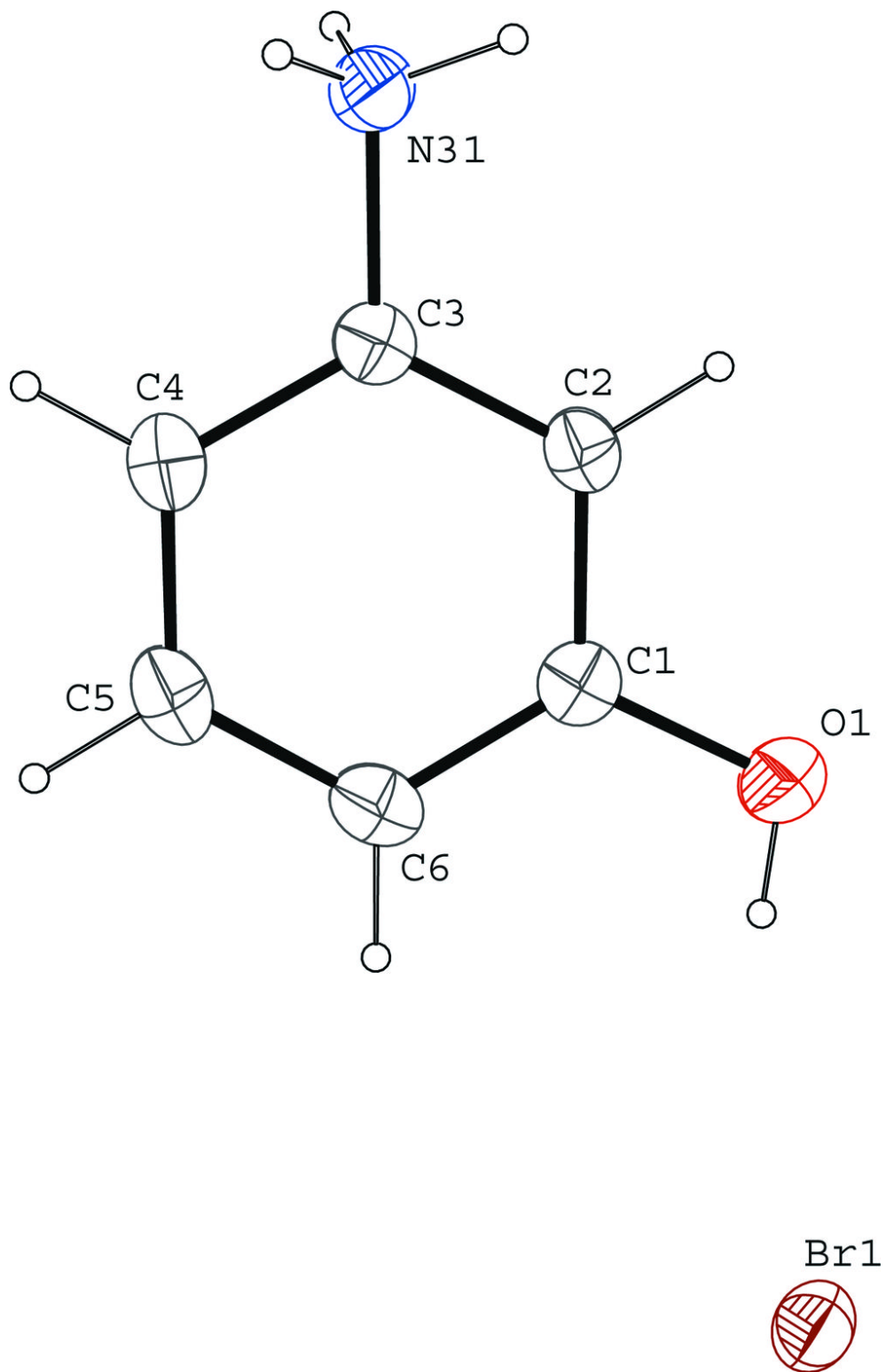


Fig. 2

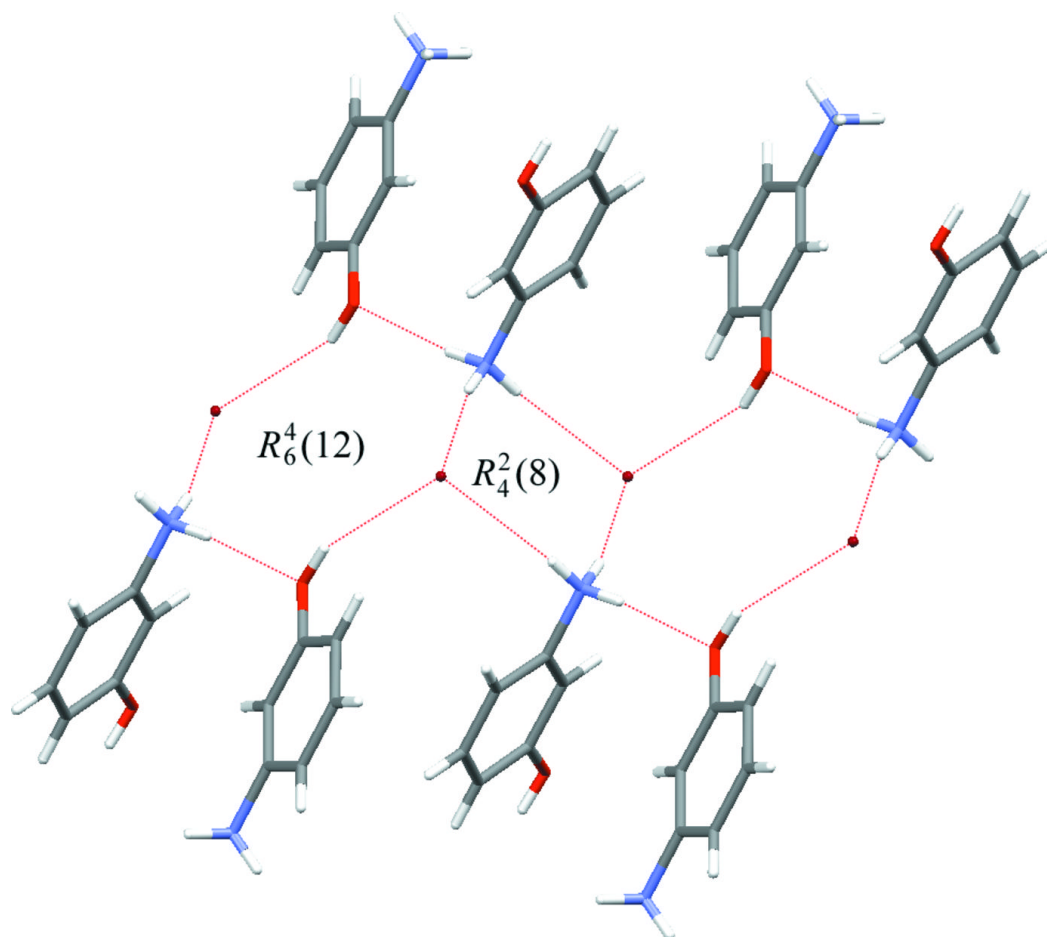


Fig. 3

