

2-(Methoxycarbonyl)anilinium dihydrogen phosphate

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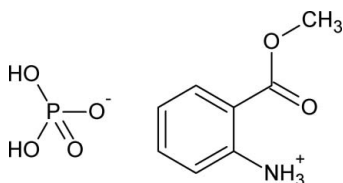
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Key indicators: single-crystal X-ray study; $T = 296$ K; mean $\sigma(\text{C}-\text{C}) = 0.002$ Å; R factor = 0.037; wR factor = 0.102; data-to-parameter ratio = 15.8.

The title compound, $\text{C}_8\text{H}_{10}\text{NO}_2^+\cdot\text{H}_2\text{PO}_4^-$, is a derivative of the naturally occurring compound methylantranilate. The asymmetric unit comprises the 2-(methoxycarbonyl)anilinium cation and the dihydrogen phosphate anion. In the cation, the dihedral angle between the benzene ring plane and that through the methyl ester substituent is $22.94(9)^\circ$. In the crystal, adjacent cations and anions form dimers through $\text{N}-\text{H}\cdots\text{O}$ and $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds, respectively. Additional $\text{N}-\text{H}\cdots\text{O}$ and $\text{C}-\text{H}\cdots\text{O}$ contacts result in a network of cation and anion dimers stacked down the b axis.

Related literature

For thiazine-related heterocycles see: Shafiq *et al.* (2009a). For related structures, see: Gel'mbol'dt *et al.* (2006); Ma *et al.* (2005); Shafiq *et al.* (2008, 2009b).



Experimental

Crystal data

$\text{C}_8\text{H}_{10}\text{NO}_2^+\cdot\text{H}_2\text{PO}_4^-$
 $M_r = 249.16$
 Monoclinic, $C2/c$
 $a = 20.939(3)$ Å
 $b = 4.7880(5)$ Å
 $c = 22.283(4)$ Å
 $\beta = 114.970(5)^\circ$

$V = 2025.2(5)$ Å³
 $Z = 8$
 Mo $K\alpha$ radiation
 $\mu = 0.29$ mm⁻¹
 $T = 296$ K
 $0.39 \times 0.21 \times 0.17$ mm

Data collection

Bruker Kappa APEXII CCD diffractometer
 Absorption correction: multi-scan (*SADABS*; Bruker, 2005)
 $T_{\min} = 0.928$, $T_{\max} = 0.958$

10812 measured reflections
 2413 independent reflections
 2078 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.035$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.037$
 $wR(F^2) = 0.102$
 $S = 1.07$
 2413 reflections
 153 parameters

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\max} = 0.29$ e Å⁻³
 $\Delta\rho_{\min} = -0.48$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{C4}-\text{H4}\cdots\text{O5}$	0.93	2.68	3.387 (2)	133
$\text{C4}-\text{H4}\cdots\text{O6}$	0.93	2.71	3.590 (2)	158
$\text{C3}-\text{H3}\cdots\text{O2}^{\text{i}}$	0.93	2.72	3.609 (2)	162
$\text{N1}-\text{H1A}\cdots\text{O3}^{\text{ii}}$	0.89	1.93	2.8218 (18)	178
$\text{N1}-\text{H1A}\cdots\text{O5}^{\text{ii}}$	0.89	2.68	3.190 (2)	118
$\text{N1}-\text{H1C}\cdots\text{O3}^{\text{iii}}$	0.89	2.01	2.9005 (18)	175
$\text{N1}-\text{H1B}\cdots\text{O3}^{\text{iv}}$	0.89	2.09	2.9400 (17)	160
$\text{O5}-\text{H5O}\cdots\text{O6}^{\text{v}}$	0.78 (2)	1.83 (2)	2.6021 (17)	170 (2)
$\text{O4}-\text{H4O}\cdots\text{O6}^{\text{vi}}$	0.72 (2)	1.88 (2)	2.6015 (17)	179 (2)

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

Data collection: *APEX2* (Bruker, 2007); cell refinement: *SAINT* (Bruker, 2007); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008) and *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *SHELXL97*, *enCIFer* (Allen *et al.*, 2004), *PLATON* (Spek, 2009) and *pubCIF* (Westrip, 2009).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BT2987).

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supplementary materials

Acta Cryst. (2009). E65, o1786 [doi:10.1107/S1600536809025252]

2-(Methoxycarbonyl)anilinium dihydrogen phosphate

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Comment

Methylantranilite is a naturally occurring compound which has been used in food flavoring, as a fragrance additive and a bird repellent. Our group has been involved in the synthesis of heterocyclic molecules related to benzothiazine (Shafiq *et al.*, 2009a) in which the title compound has been used as a starting material (Shafiq *et al.*, 2008; Shafiq *et al.*, 2009b). Herein we report the structure of title compound which was obtained during the synthesis of methylantranilate Schiff base derivatives.

The asymmetric unit comprises the 2-(methoxycarbonyl)anilinium cation and the dihydrogen phosphate anion linked by bifurcated C4—H4 \cdots O5 and C4—H4 \cdots O6 interactions, Fig. 1. In the cation the dihedral angle between the C1 \cdots C6 benzene ring plane and that through the C2,C7(O1),O2,C8 atoms of the methyl ester substituent is 22.94 (9)°. Bond distances within the molecule are normal and similar to those observed in comparable structures (Gel'mbol'dt *et al.*, 2006; Ma *et al.*, 2005). In the crystal, adjacent cations and anions form dimers through N1—H1A \cdots O1 and O4—H4O \cdots O6 hydrogen bonds respectively, Fig. 2. Additional N—H \cdots O and C—H \cdots O contacts result in a network of cation and anion dimers stacked down the *b* axis, Fig. 3.

Experimental

The title compound was obtained during the synthesis of Schiff base of methyl anthranilate. Methyl anthranilite (0.5 g, 0.0 mol) was dissolved in methanol (5 ml). A few drops of polyphosphoric acid were added to the above solution to precipitate the product which was recrystallized from methanol.

Refinement

The H atoms bound to N1, O4 and O5 were located in a difference Fourier map and their coordinates were refined with $U_{\text{iso}} = 1.5U_{\text{eq}}$ (N) and $1.2U_{\text{eq}}$ (O). All other H-atoms were placed in calculated positions and refined using a riding model with $d(\text{C—H}) = 0.93 \text{ \AA}$, $U_{\text{iso}} = 1.2U_{\text{eq}}$ (C) for aromatic and 0.96 \AA , $U_{\text{iso}} = 1.5U_{\text{eq}}$ (C) for CH₃ H atoms.

Figures

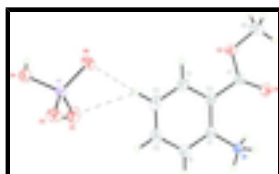


Fig. 1. The asymmetric unit of (I) with displacement ellipsoids for the non-hydrogen atoms drawn at the 50% probability level. Hydrogen bonds are drawn as dashed lines.

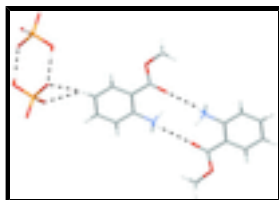


Fig. 2. Dimers formed by the cations and anions in the structure of (I) with hydrogen bonds drawn as dashed lines.

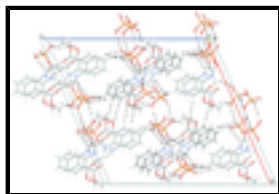
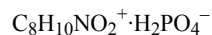


Fig. 3. Crystal packing of (I) viewed down the *b* axis

2-(Methoxycarbonyl)anilinium dihydrogen phosphate

Crystal data



$M_r = 249.16$

Monoclinic, *C2/c*

Hall symbol: -C 2yc

$a = 20.939 (3) \text{ \AA}$

$b = 4.7880 (5) \text{ \AA}$

$c = 22.283 (4) \text{ \AA}$

$\beta = 114.970 (5)^\circ$

$V = 2025.2 (5) \text{ \AA}^3$

$Z = 8$

$F_{000} = 1040$

$D_x = 1.634 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$

Cell parameters from 5124 reflections

$\theta = 2.2\text{--}27.9^\circ$

$\mu = 0.29 \text{ mm}^{-1}$

$T = 296 \text{ K}$

Needle, colourless

$0.39 \times 0.21 \times 0.17 \text{ mm}$

Data collection

Bruker Kappa APEXII CCD diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 296 \text{ K}$

φ and ω scans

Absorption correction: multi-scan (SADABS; Bruker, 2005)

$T_{\min} = 0.928$, $T_{\max} = 0.958$

10812 measured reflections

2413 independent reflections

2078 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.035$

$\theta_{\max} = 27.9^\circ$

$\theta_{\min} = 3.5^\circ$

$h = -27 \rightarrow 27$

$k = -4 \rightarrow 6$

$l = -29 \rightarrow 27$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.037$

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H atoms treated by a mixture of independent and constrained refinement

$wR(F^2) = 0.102$	$w = 1/[\sigma^2(F_o^2) + (0.0575P)^2 + 1.6713P]$
$S = 1.07$	where $P = (F_o^2 + 2F_c^2)/3$
2413 reflections	$(\Delta/\sigma)_{\max} = 0.001$
153 parameters	$\Delta\rho_{\max} = 0.29 \text{ e } \text{Å}^{-3}$
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{\min} = -0.48 \text{ e } \text{Å}^{-3}$
	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 $F^2 > \sigma(F^2)$ 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	$U_{\text{iso}}^*/U_{\text{eq}}$
N1	0.24287 (7)	0.4968 (3)	0.93401 (6)	0.0200 (3)
H1A	0.2695	0.3443	0.9473	0.030*
H1B	0.2127	0.5014	0.9526	0.030*
H1C	0.2702	0.6478	0.9460	0.030*
C1	0.20379 (8)	0.4920 (3)	0.86203 (7)	0.0202 (3)
C2	0.14685 (8)	0.3118 (3)	0.83134 (7)	0.0227 (3)
C3	0.11163 (9)	0.3157 (4)	0.76239 (8)	0.0300 (4)
H3	0.0730	0.1996	0.7412	0.036*
C4	0.13337 (10)	0.4893 (4)	0.72527 (9)	0.0326 (4)
H4	0.1102	0.4864	0.6793	0.039*
C5	0.18948 (10)	0.6671 (4)	0.75648 (9)	0.0322 (4)
H5	0.2038	0.7857	0.7315	0.039*
C6	0.22462 (9)	0.6700 (4)	0.82496 (8)	0.0273 (4)
H6	0.2622	0.7916	0.8459	0.033*
C7	0.12565 (8)	0.1075 (3)	0.86989 (8)	0.0225 (3)
C8	0.03453 (11)	-0.1887 (5)	0.86660 (11)	0.0433 (5)
H8A	0.0609	-0.1795	0.9138	0.065*
H8B	0.0402	-0.3700	0.8511	0.065*
H8C	-0.0144	-0.1566	0.8555	0.065*
O1	0.16391 (6)	0.0261 (3)	0.92428 (6)	0.0273 (3)
O2	0.05989 (7)	0.0218 (3)	0.83567 (7)	0.0380 (3)
P1	0.10739 (2)	0.56312 (8)	0.531833 (19)	0.01826 (13)
O3	0.17510 (6)	0.5066 (2)	0.52576 (6)	0.0248 (3)
O4	0.05239 (6)	0.6781 (3)	0.46425 (6)	0.0262 (3)
H4O	0.0163 (12)	0.681 (5)	0.4598 (10)	0.031*

supplementary materials

O5	0.12078 (7)	0.8011 (3)	0.58427 (6)	0.0323 (3)
H5O	0.1063 (13)	0.948 (5)	0.5709 (11)	0.039*
O6	0.07879 (6)	0.3146 (2)	0.55400 (6)	0.0255 (3)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0199 (6)	0.0202 (6)	0.0191 (6)	-0.0008 (5)	0.0075 (5)	-0.0015 (5)
C1	0.0202 (7)	0.0201 (7)	0.0196 (7)	0.0040 (6)	0.0076 (6)	-0.0003 (6)
C2	0.0230 (8)	0.0219 (7)	0.0215 (7)	0.0022 (6)	0.0079 (6)	0.0005 (6)
C3	0.0277 (9)	0.0334 (9)	0.0222 (8)	-0.0011 (7)	0.0038 (6)	-0.0010 (7)
C4	0.0353 (10)	0.0407 (10)	0.0194 (8)	0.0074 (8)	0.0091 (7)	0.0046 (7)
C5	0.0365 (10)	0.0354 (9)	0.0294 (9)	0.0048 (8)	0.0185 (7)	0.0085 (8)
C6	0.0277 (8)	0.0260 (8)	0.0295 (8)	-0.0016 (7)	0.0134 (7)	0.0009 (7)
C7	0.0219 (7)	0.0202 (7)	0.0235 (8)	-0.0008 (6)	0.0077 (6)	-0.0031 (6)
C8	0.0388 (11)	0.0397 (11)	0.0495 (12)	-0.0184 (9)	0.0167 (9)	0.0013 (9)
O1	0.0257 (6)	0.0293 (6)	0.0241 (6)	0.0007 (5)	0.0078 (5)	0.0036 (5)
O2	0.0268 (7)	0.0436 (8)	0.0329 (7)	-0.0137 (6)	0.0022 (5)	0.0073 (6)
P1	0.0173 (2)	0.0154 (2)	0.0226 (2)	0.00185 (14)	0.00890 (16)	0.00206 (14)
O3	0.0181 (6)	0.0250 (6)	0.0324 (6)	0.0032 (4)	0.0118 (5)	0.0025 (5)
O4	0.0179 (5)	0.0338 (7)	0.0261 (6)	0.0029 (5)	0.0086 (5)	0.0069 (5)
O5	0.0466 (8)	0.0189 (6)	0.0277 (6)	0.0072 (5)	0.0122 (6)	0.0001 (5)
O6	0.0234 (6)	0.0186 (5)	0.0363 (6)	0.0010 (4)	0.0142 (5)	0.0060 (5)

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

N1—C1	1.4609 (19)	C6—H6	0.9300
N1—H1A	0.8900	C7—O1	1.2010 (19)
N1—H1B	0.8900	C7—O2	1.326 (2)
N1—H1C	0.8900	C8—O2	1.443 (2)
C1—C6	1.379 (2)	C8—H8A	0.9600
C1—C2	1.395 (2)	C8—H8B	0.9600
C2—C3	1.396 (2)	C8—H8C	0.9600
C2—C7	1.488 (2)	P1—O3	1.5045 (12)
C3—C4	1.379 (3)	P1—O6	1.5062 (12)
C3—H3	0.9300	P1—O4	1.5597 (12)
C4—C5	1.378 (3)	P1—O5	1.5702 (13)
C4—H4	0.9300	O4—H4O	0.72 (2)
C5—C6	1.386 (2)	O5—H5O	0.78 (2)
C5—H5	0.9300		
C1—N1—H1A	109.5	C1—C6—C5	119.85 (16)
C1—N1—H1B	109.5	C1—C6—H6	120.1
H1A—N1—H1B	109.5	C5—C6—H6	120.1
C1—N1—H1C	109.5	O1—C7—O2	124.62 (16)
H1A—N1—H1C	109.5	O1—C7—C2	124.15 (15)
H1B—N1—H1C	109.5	O2—C7—C2	111.21 (14)
C6—C1—C2	120.64 (15)	O2—C8—H8A	109.5
C6—C1—N1	118.39 (14)	O2—C8—H8B	109.5

C2—C1—N1	120.97 (14)	H8A—C8—H8B	109.5
C1—C2—C3	118.45 (15)	O2—C8—H8C	109.5
C1—C2—C7	121.69 (14)	H8A—C8—H8C	109.5
C3—C2—C7	119.77 (15)	H8B—C8—H8C	109.5
C4—C3—C2	120.91 (17)	C7—O2—C8	116.33 (15)
C4—C3—H3	119.5	O3—P1—O6	114.06 (7)
C2—C3—H3	119.5	O3—P1—O4	108.44 (7)
C5—C4—C3	119.79 (16)	O6—P1—O4	111.21 (7)
C5—C4—H4	120.1	O3—P1—O5	108.56 (7)
C3—C4—H4	120.1	O6—P1—O5	107.47 (7)
C4—C5—C6	120.33 (17)	O4—P1—O5	106.83 (7)
C4—C5—H5	119.8	P1—O4—H4O	116.4 (17)
C6—C5—H5	119.8	P1—O5—H5O	117.1 (18)
C6—C1—C2—C3	0.1 (2)	N1—C1—C6—C5	178.83 (15)
N1—C1—C2—C3	-179.80 (15)	C4—C5—C6—C1	0.7 (3)
C6—C1—C2—C7	176.75 (15)	C1—C2—C7—O1	-21.1 (2)
N1—C1—C2—C7	-3.1 (2)	C3—C2—C7—O1	155.53 (17)
C1—C2—C3—C4	1.3 (3)	C1—C2—C7—O2	160.61 (16)
C7—C2—C3—C4	-175.43 (16)	C3—C2—C7—O2	-22.8 (2)
C2—C3—C4—C5	-1.7 (3)	O1—C7—O2—C8	-1.5 (3)
C3—C4—C5—C6	0.7 (3)	C2—C7—O2—C8	176.80 (16)
C2—C1—C6—C5	-1.1 (3)		

Hydrogen-bond geometry (Å, °)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
C4—H4...O5	0.93	2.68	3.387 (2)	133
C4—H4...O6	0.93	2.71	3.590 (2)	158
C3—H3...O2 ⁱ	0.93	2.72	3.609 (2)	162
N1—H1A...O3 ⁱⁱ	0.89	1.93	2.8218 (18)	178
N1—H1A...O5 ⁱⁱ	0.89	2.68	3.190 (2)	118
N1—H1C...O3 ⁱⁱⁱ	0.89	2.01	2.9005 (18)	175
N1—H1B...O3 ^{iv}	0.89	2.09	2.9400 (17)	160
O5—H5O...O6 ^v	0.78 (2)	1.83 (2)	2.6021 (17)	170 (2)
O4—H4O...O6 ^{vi}	0.72 (2)	1.88 (2)	2.6015 (17)	179 (2)

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

Fig. 1

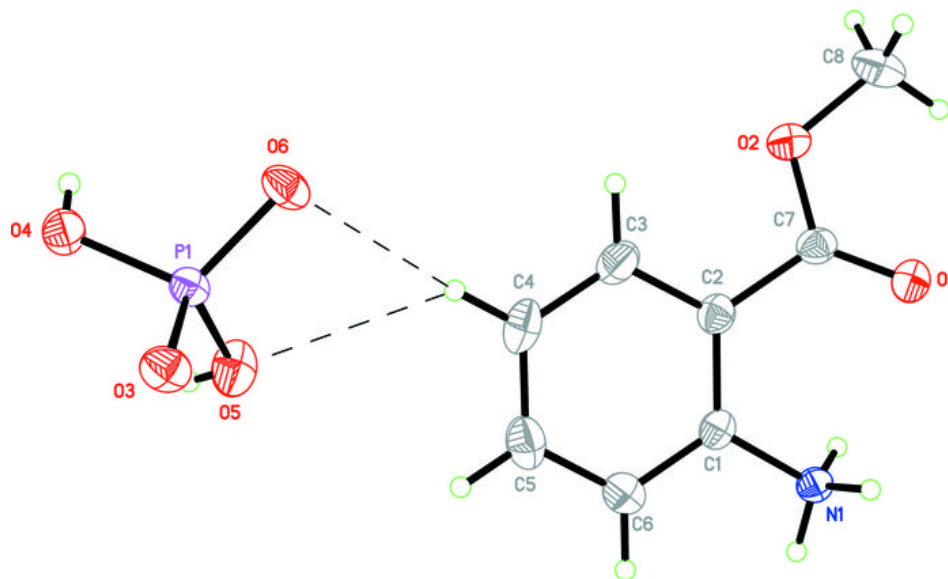


Fig. 2

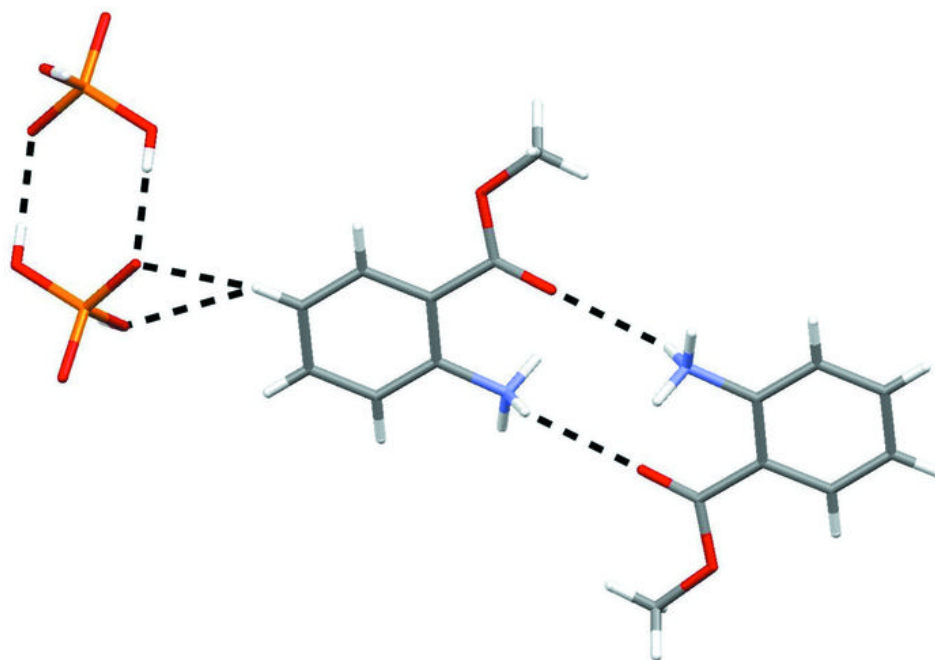


Fig. 3

