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# 2-[(Dimethylphenylphosphanylidene)-azaniumyl]-5-methylbenzenesulfonate benzene monosolvate

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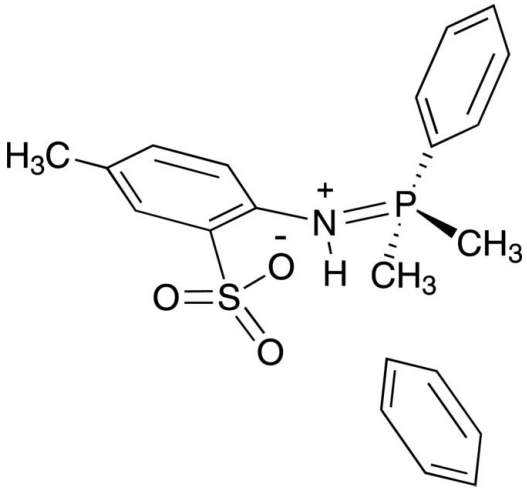
Key indicators: single-crystal X-ray study; $T$ = 100 K; mean $\sigma$(C–C) = 0.003 Å; $R$ factor = 0.041; $wR$ factor = 0.096; data-to-parameter ratio = 21.0.

The title compound, $C_{15}H_{18}NO_3PS\cdot C_6H_6$, is a rare example of a crystallographically characterized exocyclic phosphinimi-nium–arenesulfonate zwitterion, which crystallises as its benzene solvate. The crystal structure shows that the N atom is protonated and that the iminium H atom forms both intra- and intermolecular hydrogen bonds to the single-bonded sulfonate O atom in an $R_2^2(4)$ graph-set motif. The dihedral angle between the aromatic rings in the main molecule is 89.49 (8)°.

## Related literature

For background to this class of compound, see: Brown *et al.* (2007); Bruneau & Achard (2012); Drent *et al.* (2002); Lee & Hoveyda (2009); Lee *et al.* (2008, 2009); Nakamura *et al.* (2009). For related structures, see: Burns *et al.* (2012); Liu *et al.* (1995); Perrotin *et al.* (2011); Spencer *et al.* (2003); Wallis *et al.* (2009, 2010); Zhang *et al.* (2006); Zhou & Jordan (2011). For hydrogen-bonding details, see: Desiraju (1995).



## Experimental

### Crystal data

$C_{15}H_{18}NO_3PS\cdot C_6H_6$
$M_r$ = 401.44
Triclinic, $P\overline{1}$
$a$ = 9.3696 (2) Å
$b$ = 10.3141 (2) Å
$c$ = 11.7579 (3) Å
$\alpha$ = 68.665 (2)°
$\beta$ = 78.180 (2)°
$\gamma$ = 70.630 (2)°
$V$ = 993.89 (4) Å$^3$
$Z$ = 2
Mo $K\alpha$ radiation
$\mu$ = 0.27 mm$^{-1}$
$T$ = 100 K
0.41 × 0.31 × 0.25 mm

### Data collection

Agilent Xcalibur (Ruby, Gemini) diffractometer
Absorption correction: multi-scan (*CrysAlis PRO*; Agilent, 2010)
$T_{min}$ = 0.939, $T_{max}$ = 1.000
22626 measured reflections
5263 independent reflections
4918 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.017

### Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.041
$wR(F^2)$ = 0.096
$S$ = 1.05
5263 reflections
251 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 1.40 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.42 e Å$^{-3}$

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| N1—H1*N*···O2 | 0.80 (2) | 2.09 (2) | 2.7374 (17) | 139 (2) |
| N1—H1*N*···O2$^{i}$ | 0.80 (2) | 2.47 (2) | 3.0311 (17) | 128 (2) |

Symmetry code: (i) $-x+1, -y+1, -z+1$.

Data collection: *CrysAlis PRO* (Agilent, 2010); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis PRO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012) and *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *PLATON* (Spek, 2009) and *publCIF* (Westrip, 2010).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: PK2483).

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# supporting information

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## 2-[(Dimethylphenylphosphanylidene)azaniumyl]-5-methylbenzenesulfonate benzene monosolvate

**Christopher T. Burns, Suisheng Shang and Mark S. Mashuta**

### S1. Comment

Exocyclic phosphinimine functionalized benzenesulfonate ligands have the potential to be used in the synthesis of new transition and main group metal catalysts with numerous applications. Few examples exist where an exocyclic phosphinimine has been incorporated into a mixed donor ligand system for use in the preparation of metal complexes (Liu *et al.*, 1995; Spencer *et al.*, 2003; Zhang *et al.*, 2006; Wallis *et al.*, 2009, 2010). There are also a very limited number of *ortho*-substituted arenesulfonate bidentate ligands used for catalytic reactions. 2-Phosphine-arenesulfonate chelates have received considerable attention in the last decade as ancillary ligands for group 10 olefin insertion polymerization catalysts (Drent *et al.*, 2002; Nakamura *et al.*, 2009; Perrotin *et al.*, 2011) and have also been used to stabilize ruthenium complexes that catalyze allylic alkylations of heterocycles and amines (Bruneau & Achard, 2012). Chiral and achiral *ortho*-*N*-heterocyclic-carbene-benzenesulfonate ligands have been used in the copper-catalyzed asymmetric conjugate addition, allylic alkylation, hydroboration and diboronation reactions (Brown *et al.*, 2007; Lee *et al.*, 2008, 2009; Lee & Hoveyda, 2009) as well as being explored as catalysts that promote insertion of unsaturated molecules into a palladium carbon bond (Zhou & Jordan, 2011). The title compound, (I), has been synthesized as an air-stable precursor of 2-dimethyl(phenyl)phosphinimine-5-methylbenzenesulfonate which is being explored as an ancillary ligand for metal mediated transformations.

The structures of the related 2-triphenylphosphiniminium-5-methylbenzenesulfonate and 2-diphenyl(methyl)-phosphiniminium-5-methylbenzenesulfonate (Burns *et al.*, 2012), have been reported recently and contain the same primary structural features as those found in (I). All three structures confirm the zwitterionic nature of these compounds *via* presence of the phosphiniminium group in which the nitrogen is protonated and the sulfonate anion is located *ortho* to the protonated phosphinimine. The P(1)—N(1) bond distance (Table 1) in (I) is statistically the same as the phosphiniminium P—N bonds in both 2-triphenylphosphiniminium-5-methylbenzenesulfonate [1.6327 (17) Å] and 2-diphenyl(methyl)phosphiniminium-5-methylbenzenesulfonate [1.6380 (12) Å] (Burns *et al.*, 2012) indicative of single bond character. The iminium hydrogen forms a strong intramolecular hydrogen bond to one sulfonate oxygen atom N1—H1n- - –O2 (Table 2), (Desiraju, 1995). This hydrogen is also involved in an intermolecular interaction with the nearest symmetry generated O2 atom N1—H1n- - –O2$^{i}$ (Table 2). The smaller phosphiniminium $Me_2PPh$ substituent in (I) has much less steric impact than the $Ph_3P$ and $Ph_2PMe$ groups in the two previously reported zwitterions. Comparison of relevant torsion angles in the three structures shows that the phosphorous atom of the phosphiniminium group in (I) is situated above the plane of the aryl ring of the 5-methylbenzenesulfonate fragment with a C5—C6—N1—P1 torsion angle of 29.7 (2)° whereas the phosphorous atom of the phosphiniminium group in the triphenylphosphiniminium and diphenyl(methyl)phosphiniminium zwitterion structures is located below the plane of the aryl ring with corresponding torsion angles of 39.2 (3)° and 14.9 (2)° respectively (Burns *et al.*, 2012).

## S2. Experimental

Compound (I) was synthesized following a previously reported procedure (Burns *et al.*, 2012). Dimethylphenylphosphine (11.1 mmol) was added dropwise to a toluene solution (40 ml) of propyl-2-azido-5-methylbenzenesulfonate (9.3 mmol) at 298 K. Effervescence was observed immediately after addition of the phosphine and the clear yellow solution was stirred under $N_2$. After 2 h the solvent was removed under vacuum. The resulting yellow oil was dissolved in $CH_2Cl_2$ (40 ml) and transferred *via* cannula to a suspension of pyridinium tetrafluoroborate (9.3 mmol) in $CH_2Cl_2$ (40 ml). Pyridine (14.0 mmol) was added to the white suspension in $CH_2Cl_2$ and the reaction mixture was stirred at 298 K for 48 h. A clear pale green solution was observed and the volatiles were removed under vacuum. The resulting residue was treated with diethyl ether (4 *x* 60 ml) followed by filtration to give a light yellow solid. The solid was purified *via* column chromatography using silica gel (160 g) and $CH_2Cl_2$. The column was eluted with $CH_2Cl_2$:MeOH 95:5 (500 ml), $CH_2Cl_2$:MeOH 90:10 (1 *L*) and $CH_2Cl_2$:MeOH 80:20 (1 *L*). The fractions (100 ml) were analyzed by UV-Vis, and those that contained the product were combined and dried under vacuum, affording a white solid. The solid was treated with $CH_2Cl_2$ (20 ml) and diethyl ether (100 ml) to afford a white precipitate. Filtration of the precipitate followed by diethyl ether washes (3 *x* 20 ml) afforded the title compound as a white powder (3.86 g, 70%). Crystals for X-ray analysis were obtained by slow diffusion of benzene into a $CHCl_3$ solution of the title compound in a sealed 5 mm tube at 298 K.

## S3. Refinement

The iminum hydrogen atom was located in a difference map and refined isotropically. Aromatic H atom positions were calculated, and included as fixed contributions with $U_{iso}(H) = 1.2\ x\ U_{eq}(C)$. Methyl H atoms were placed in calculated positions and allowed to ride (the torsion angle which defines its orientation was allowed to refine) on the attached C atom, and these atoms were assigned $U_{iso}(H) = 1.5\ x\ U_{eq}(C)$. The highest peak, 1.40 e/Å$^3$, and deepest trough, -0.42 e/Å$^3$, are located 0.75 Å and 0.73 Å from C16 and C20 respectively.

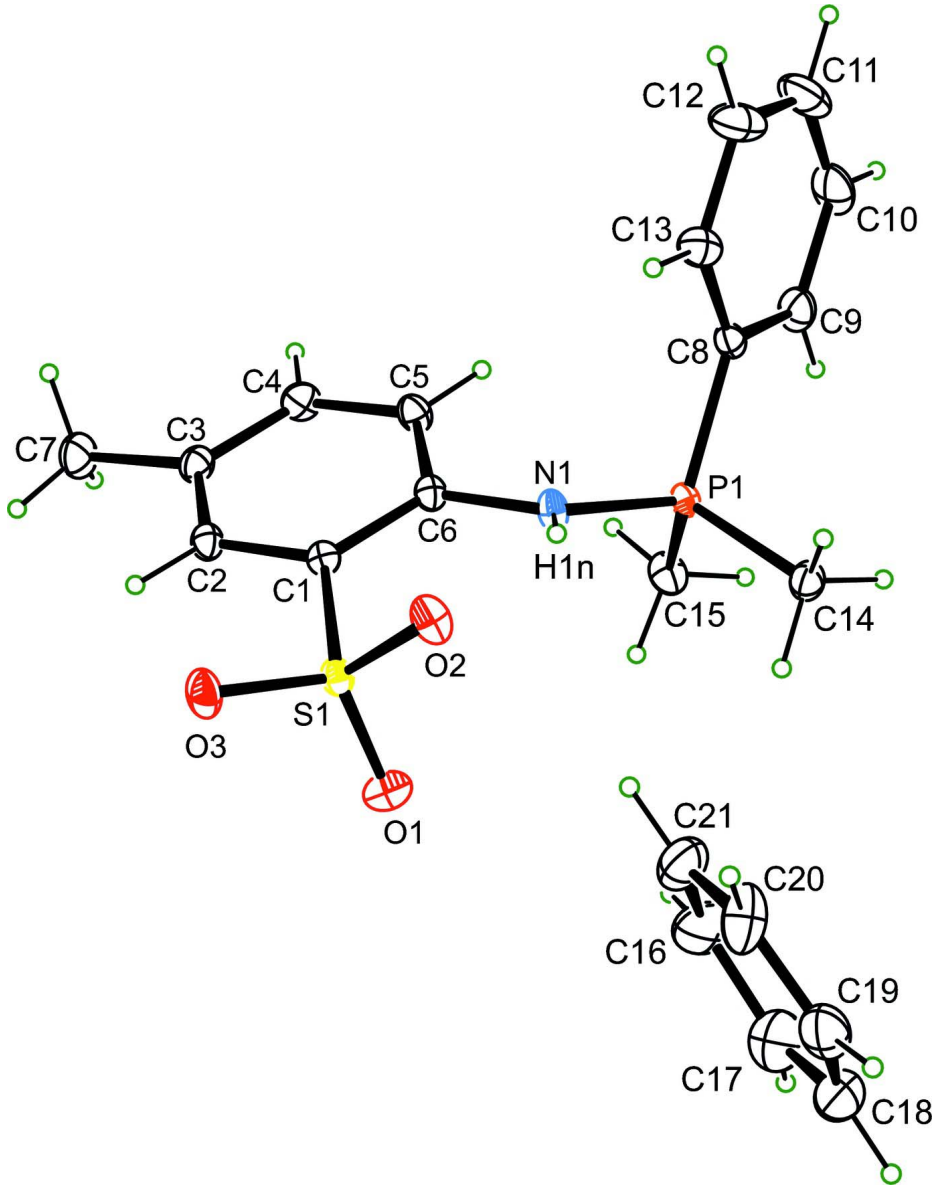


**Figure 1**

An ellipsoid plot of (I) showing 50% displacement ellipsoids. H atoms are shown as small spheres of arbitrary radii.

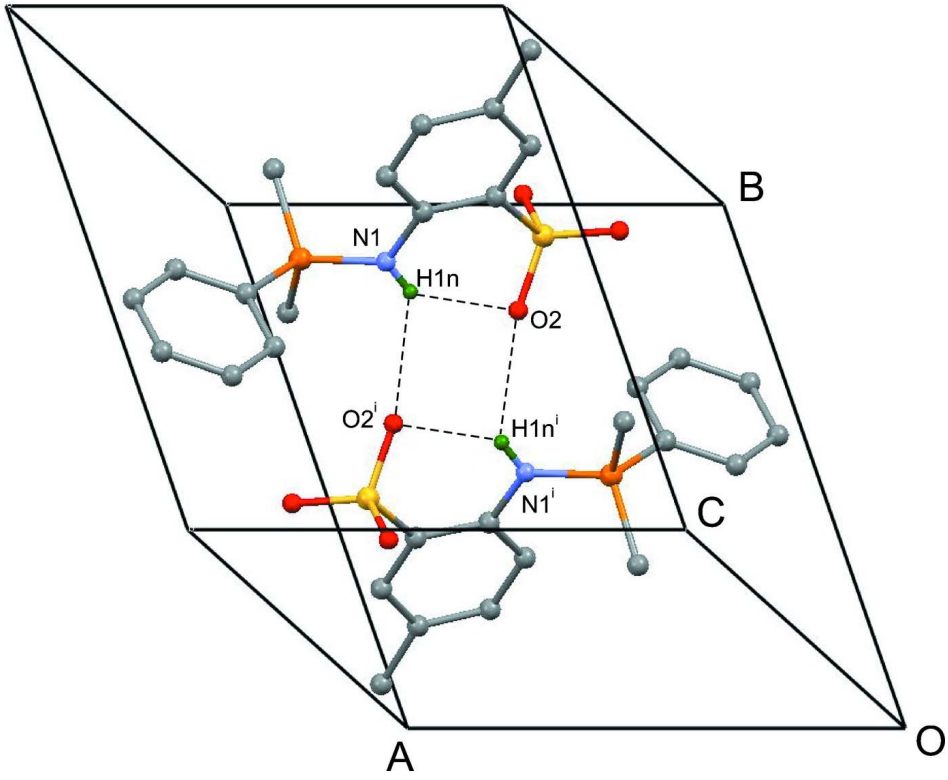


**Figure 2**

Packing diagram displaying intramolecular and intermolecular hydrogen-bonding interactions between H1n, O2 and O2$^{i}$. [Symmetry code: (i) 1 - *x*, 1 - *y*, 1 - *z*]

### 2-[(Dimethylphenylphosphanylidene)azaniumyl]-5-methylbenzenesulfonate benzene monosolvate

*Crystal data*

$C_{15}H_{18}NO_3PS{\cdot}C_6H_6$
$M_r$ = 401.44
Triclinic, $P\overline{1}$
Hall symbol: -P 1
*a* = 9.3696 (2) Å
*b* = 10.3141 (2) Å
*c* = 11.7579 (3) Å
*α* = 68.665 (2)°
*β* = 78.180 (2)°
*γ* = 70.630 (2)°
*V* = 993.89 (4) Å$^3$
*Z* = 2
*F*(000) = 424
$D_x$ = 1.341 Mg m$^{-3}$
Melting point: 490 K
Mo *Kα* radiation, *λ* = 0.71073 Å
Cell parameters from 16324 reflections
*θ* = 3.3–29.0°
*μ* = 0.27 mm$^{-1}$
*T* = 100 K
Prism, colorless
0.41 × 0.31 × 0.25 mm

*Data collection*

Agilent Xcalibur (Ruby, Gemini) diffractometer
Radiation source: Enhance (Mo) X-ray Source
Graphite monochromator
Detector resolution: 10.2836 pixels mm$^{-1}$
*ω* scans
Absorption correction: multi-scan (*CrysAlis PRO*; Agilent, 2010)
$T_{min}$ = 0.939, $T_{max}$ = 1.000
22626 measured reflections
5263 independent reflections
4918 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.017
$\theta_{max}$ = 29.1°, $\theta_{min}$ = 3.3°
*h* = −12→12
*k* = −13→13
*l* = −16→16

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.041$
$wR(F^2) = 0.096$
$S = 1.05$
5263 reflections
251 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
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
$w = 1/[\sigma^2(F_o^2) + (0.0264P)^2 + 1.4298P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 1.40$ e Å$^{-3}$
$\Delta\rho_{min} = -0.42$ e Å$^{-3}$

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)*

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| S1 | 0.24462 (4) | 0.76594 (4) | 0.45953 (3) | 0.01262 (9) |
| P1 | 0.71909 (4) | 0.68470 (4) | 0.55802 (3) | 0.01128 (9) |
| O1 | 0.28714 (14) | 0.88299 (13) | 0.35938 (11) | 0.0211 (2) |
| O2 | 0.34682 (13) | 0.62271 (12) | 0.46153 (11) | 0.0181 (2) |
| O3 | 0.08543 (12) | 0.77151 (14) | 0.47013 (11) | 0.0200 (2) |
| N1 | 0.54554 (14) | 0.67514 (14) | 0.56918 (12) | 0.0135 (2) |
| H1N | 0.530 (3) | 0.632 (3) | 0.531 (2) | 0.027 (6)* |
| C1 | 0.27173 (16) | 0.78953 (15) | 0.59586 (13) | 0.0119 (3) |
| C2 | 0.14789 (16) | 0.86274 (16) | 0.65917 (14) | 0.0139 (3) |
| H2 | 0.0516 | 0.8904 | 0.6336 | 0.017* |
| C3 | 0.16470 (17) | 0.89556 (16) | 0.75995 (14) | 0.0155 (3) |
| C4 | 0.30965 (18) | 0.84905 (17) | 0.79818 (14) | 0.0171 (3) |
| H4 | 0.3235 | 0.8684 | 0.8658 | 0.021* |
| C5 | 0.43403 (17) | 0.77421 (17) | 0.73725 (14) | 0.0156 (3) |
| H5 | 0.5294 | 0.7428 | 0.7655 | 0.019* |
| C6 | 0.41761 (16) | 0.74565 (15) | 0.63435 (13) | 0.0125 (3) |
| C7 | 0.03151 (19) | 0.98321 (19) | 0.82218 (16) | 0.0221 (3) |
| H7A | 0.0137 | 0.9262 | 0.9060 | 0.033* |
| H7B | −0.0573 | 1.0103 | 0.7806 | 0.033* |
| H7C | 0.0532 | 1.0690 | 0.8195 | 0.033* |
| C8 | 0.81146 (16) | 0.56744 (16) | 0.69318 (13) | 0.0140 (3) |
| C9 | 0.92555 (18) | 0.6000 (2) | 0.72847 (15) | 0.0210 (3) |
| H9 | 0.9523 | 0.6850 | 0.6835 | 0.025* |
| C10 | 0.9990 (2) | 0.5043 (2) | 0.83147 (17) | 0.0296 (4) |
| H10 | 1.0755 | 0.5250 | 0.8552 | 0.036* |
| C11 | 0.9585 (2) | 0.3787 (2) | 0.89842 (18) | 0.0329 (4) |
| H11 | 1.0074 | 0.3155 | 0.9676 | 0.040* |
| C12 | 0.8455 (2) | 0.34585 (19) | 0.86339 (17) | 0.0286 (4) |
| H12 | 0.8190 | 0.2609 | 0.9090 | 0.034* |
| C13 | 0.77174 (19) | 0.43981 (17) | 0.76011 (15) | 0.0191 (3) |
| H13 | 0.6966 | 0.4177 | 0.7360 | 0.023* |
| C14 | 0.82093 (17) | 0.63095 (17) | 0.42977 (14) | 0.0169 (3) |
| H14A | 0.8261 | 0.5318 | 0.4443 | 0.025* |

| | | | | |
|---|---|---|---|---|
| H14B | 0.9220 | 0.6403 | 0.4181 | 0.025* |
| H14C | 0.7698 | 0.6918 | 0.3577 | 0.025* |
| C15 | 0.71858 (18) | 0.86602 (16) | 0.53121 (16) | 0.0186 (3) |
| H15A | 0.6603 | 0.9301 | 0.4637 | 0.028* |
| H15B | 0.8210 | 0.8728 | 0.5121 | 0.028* |
| H15C | 0.6741 | 0.8931 | 0.6034 | 0.028* |
| C16 | 0.6085 (3) | 0.8347 (2) | 0.14006 (19) | 0.0392 (5) |
| H16 | 0.5942 | 0.8883 | 0.1923 | 0.047* |
| C17 | 0.6651 (3) | 0.8839 (3) | 0.0207 (2) | 0.0363 (5) |
| H17 | 0.6838 | 0.9741 | −0.0092 | 0.044* |
| C18 | 0.6951 (2) | 0.8019 (2) | −0.05696 (18) | 0.0318 (4) |
| H18 | 0.7352 | 0.8361 | −0.1377 | 0.038* |
| C19 | 0.6647 (2) | 0.6685 (2) | −0.01315 (18) | 0.0296 (4) |
| H19 | 0.6886 | 0.6115 | −0.0639 | 0.035* |
| C20 | 0.6011 (2) | 0.6207 (2) | 0.1021 (2) | 0.0319 (4) |
| H20 | 0.5761 | 0.5336 | 0.1287 | 0.038* |
| C21 | 0.5720 (2) | 0.7022 (2) | 0.18328 (18) | 0.0311 (4) |
| H21 | 0.5297 | 0.6686 | 0.2634 | 0.037* |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| S1 | 0.01064 (16) | 0.01423 (17) | 0.01497 (16) | −0.00342 (12) | −0.00207 (12) | −0.00656 (13) |
| P1 | 0.00971 (16) | 0.01120 (16) | 0.01365 (17) | −0.00251 (12) | −0.00188 (12) | −0.00481 (13) |
| O1 | 0.0269 (6) | 0.0214 (6) | 0.0159 (5) | −0.0104 (5) | −0.0009 (4) | −0.0045 (4) |
| O2 | 0.0163 (5) | 0.0174 (5) | 0.0248 (6) | −0.0016 (4) | −0.0054 (4) | −0.0125 (4) |
| O3 | 0.0117 (5) | 0.0294 (6) | 0.0234 (6) | −0.0056 (4) | −0.0028 (4) | −0.0131 (5) |
| N1 | 0.0098 (5) | 0.0159 (6) | 0.0188 (6) | −0.0028 (4) | −0.0019 (4) | −0.0107 (5) |
| C1 | 0.0122 (6) | 0.0112 (6) | 0.0137 (6) | −0.0043 (5) | −0.0013 (5) | −0.0045 (5) |
| C2 | 0.0118 (6) | 0.0129 (6) | 0.0169 (7) | −0.0039 (5) | −0.0005 (5) | −0.0047 (5) |
| C3 | 0.0155 (7) | 0.0143 (6) | 0.0158 (7) | −0.0035 (5) | 0.0012 (5) | −0.0059 (5) |
| C4 | 0.0198 (7) | 0.0183 (7) | 0.0154 (7) | −0.0044 (6) | −0.0017 (6) | −0.0085 (6) |
| C5 | 0.0134 (6) | 0.0173 (7) | 0.0174 (7) | −0.0027 (5) | −0.0039 (5) | −0.0072 (6) |
| C6 | 0.0115 (6) | 0.0107 (6) | 0.0156 (6) | −0.0031 (5) | −0.0008 (5) | −0.0048 (5) |
| C7 | 0.0186 (7) | 0.0250 (8) | 0.0221 (8) | −0.0009 (6) | 0.0012 (6) | −0.0130 (6) |
| C8 | 0.0119 (6) | 0.0151 (7) | 0.0144 (6) | −0.0008 (5) | −0.0021 (5) | −0.0065 (5) |
| C9 | 0.0152 (7) | 0.0303 (9) | 0.0206 (7) | −0.0075 (6) | −0.0026 (6) | −0.0102 (7) |
| C10 | 0.0191 (8) | 0.0455 (11) | 0.0260 (9) | −0.0008 (7) | −0.0100 (7) | −0.0166 (8) |
| C11 | 0.0346 (10) | 0.0329 (10) | 0.0227 (9) | 0.0095 (8) | −0.0151 (7) | −0.0094 (7) |
| C12 | 0.0417 (11) | 0.0169 (8) | 0.0206 (8) | 0.0001 (7) | −0.0079 (7) | −0.0033 (6) |
| C13 | 0.0234 (8) | 0.0155 (7) | 0.0184 (7) | −0.0037 (6) | −0.0037 (6) | −0.0061 (6) |
| C14 | 0.0146 (7) | 0.0204 (7) | 0.0159 (7) | −0.0039 (6) | 0.0004 (5) | −0.0078 (6) |
| C15 | 0.0174 (7) | 0.0121 (7) | 0.0266 (8) | −0.0046 (5) | −0.0031 (6) | −0.0058 (6) |
| C16 | 0.0531 (13) | 0.0367 (11) | 0.0249 (9) | −0.0015 (10) | −0.0034 (9) | −0.0168 (8) |
| C17 | 0.0350 (11) | 0.0372 (11) | 0.0396 (11) | −0.0124 (9) | −0.0016 (9) | −0.0145 (9) |
| C18 | 0.0265 (9) | 0.0423 (11) | 0.0248 (9) | −0.0089 (8) | −0.0007 (7) | −0.0104 (8) |
| C19 | 0.0248 (9) | 0.0381 (10) | 0.0286 (9) | −0.0033 (8) | −0.0065 (7) | −0.0167 (8) |
| C20 | 0.0221 (9) | 0.0338 (10) | 0.0443 (11) | −0.0117 (7) | 0.0074 (8) | −0.0199 (9) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C21 | 0.0268 (9) | 0.0488 (12) | 0.0215 (8) | −0.0143 (8) | 0.0017 (7) | −0.0144 (8) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| S1—O1 | 1.4474 (12) | C9—H9 | 0.9300 |
| S1—O3 | 1.4547 (11) | C10—C11 | 1.380 (3) |
| S1—O2 | 1.4648 (11) | C10—H10 | 0.9300 |
| S1—O2 | 1.4648 (11) | C11—C12 | 1.387 (3) |
| S1—C1 | 1.7845 (15) | C11—H11 | 0.9300 |
| P1—N1 | 1.6373 (13) | C12—C13 | 1.391 (2) |
| P1—C14 | 1.7776 (15) | C12—H12 | 0.9300 |
| P1—C15 | 1.7783 (16) | C13—H13 | 0.9300 |
| P1—C8 | 1.7911 (15) | C14—H14A | 0.9600 |
| N1—C6 | 1.4155 (18) | C14—H14B | 0.9600 |
| N1—H1N | 0.80 (2) | C14—H14C | 0.9600 |
| C1—C2 | 1.395 (2) | C15—H15A | 0.9600 |
| C1—C6 | 1.4043 (19) | C15—H15B | 0.9600 |
| C2—C3 | 1.395 (2) | C15—H15C | 0.9600 |
| C2—H2 | 0.9300 | C16—C17 | 1.365 (3) |
| C3—C4 | 1.392 (2) | C16—C21 | 1.406 (3) |
| C3—C7 | 1.506 (2) | C16—H16 | 0.9300 |
| C4—C5 | 1.390 (2) | C17—C18 | 1.388 (3) |
| C4—H4 | 0.9300 | C17—H17 | 0.9300 |
| C5—C6 | 1.393 (2) | C18—C19 | 1.386 (3) |
| C5—H5 | 0.9300 | C18—H18 | 0.9300 |
| C7—H7A | 0.9600 | C19—C20 | 1.346 (3) |
| C7—H7B | 0.9600 | C19—H19 | 0.9300 |
| C7—H7C | 0.9600 | C20—C21 | 1.421 (3) |
| C8—C13 | 1.394 (2) | C20—H20 | 0.9300 |
| C8—C9 | 1.396 (2) | C21—H21 | 0.9300 |
| C9—C10 | 1.391 (2) | | |
| | | | |
| O1—S1—O3 | 114.14 (7) | C10—C9—C8 | 119.49 (17) |
| O1—S1—O2 | 112.97 (7) | C10—C9—H9 | 120.3 |
| O3—S1—O2 | 112.35 (7) | C8—C9—H9 | 120.3 |
| O1—S1—O2 | 112.97 (7) | C11—C10—C9 | 120.11 (17) |
| O3—S1—O2 | 112.35 (7) | C11—C10—H10 | 119.9 |
| O1—S1—C1 | 105.48 (7) | C9—C10—H10 | 119.9 |
| O3—S1—C1 | 106.09 (7) | C10—C11—C12 | 120.53 (17) |
| O2—S1—C1 | 104.84 (7) | C10—C11—H11 | 119.7 |
| O2—S1—C1 | 104.84 (7) | C12—C11—H11 | 119.7 |
| N1—P1—C14 | 107.43 (7) | C11—C12—C13 | 120.10 (18) |
| N1—P1—C15 | 110.52 (7) | C11—C12—H12 | 120.0 |
| C14—P1—C15 | 108.36 (8) | C13—C12—H12 | 120.0 |
| N1—P1—C8 | 111.53 (7) | C12—C13—C8 | 119.40 (16) |
| C14—P1—C8 | 109.37 (7) | C12—C13—H13 | 120.3 |
| C15—P1—C8 | 109.55 (7) | C8—C13—H13 | 120.3 |
| C6—N1—P1 | 125.47 (10) | P1—C14—H14A | 109.5 |

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|---|---|---|---|
| C6—N1—H1N | 116.5 (17) | P1—C14—H14B | 109.5 |
| P1—N1—H1N | 117.9 (17) | H14A—C14—H14B | 109.5 |
| C2—C1—C6 | 119.74 (13) | P1—C14—H14C | 109.5 |
| C2—C1—S1 | 119.26 (11) | H14A—C14—H14C | 109.5 |
| C6—C1—S1 | 120.80 (11) | H14B—C14—H14C | 109.5 |
| C1—C2—C3 | 121.75 (14) | P1—C15—H15A | 109.5 |
| C1—C2—H2 | 119.1 | P1—C15—H15B | 109.5 |
| C3—C2—H2 | 119.1 | H15A—C15—H15B | 109.5 |
| C4—C3—C2 | 117.74 (14) | P1—C15—H15C | 109.5 |
| C4—C3—C7 | 121.16 (14) | H15A—C15—H15C | 109.5 |
| C2—C3—C7 | 121.05 (14) | H15B—C15—H15C | 109.5 |
| C5—C4—C3 | 121.29 (14) | C17—C16—C21 | 119.3 (2) |
| C5—C4—H4 | 119.4 | C17—C16—H16 | 120.3 |
| C3—C4—H4 | 119.4 | C21—C16—H16 | 120.3 |
| C4—C5—C6 | 120.79 (14) | C16—C17—C18 | 121.3 (2) |
| C4—C5—H5 | 119.6 | C16—C17—H17 | 119.4 |
| C6—C5—H5 | 119.6 | C18—C17—H17 | 119.4 |
| C5—C6—C1 | 118.64 (13) | C19—C18—C17 | 119.44 (19) |
| C5—C6—N1 | 120.69 (13) | C19—C18—H18 | 120.3 |
| C1—C6—N1 | 120.67 (13) | C17—C18—H18 | 120.3 |
| C3—C7—H7A | 109.5 | C20—C19—C18 | 120.70 (19) |
| C3—C7—H7B | 109.5 | C20—C19—H19 | 119.7 |
| H7A—C7—H7B | 109.5 | C18—C19—H19 | 119.7 |
| C3—C7—H7C | 109.5 | C19—C20—C21 | 120.49 (19) |
| H7A—C7—H7C | 109.5 | C19—C20—H20 | 119.8 |
| H7B—C7—H7C | 109.5 | C21—C20—H20 | 119.8 |
| C13—C8—C9 | 120.36 (15) | C16—C21—C20 | 118.63 (18) |
| C13—C8—P1 | 118.82 (12) | C16—C21—H21 | 120.7 |
| C9—C8—P1 | 120.78 (12) | C20—C21—H21 | 120.7 |

| | | | |
|---|---|---|---|
| O1—S1—O2—O2 | 0.00 (7) | C2—C1—C6—N1 | −178.06 (13) |
| O3—S1—O2—O2 | 0.00 (4) | S1—C1—C6—N1 | −3.16 (19) |
| C1—S1—O2—O2 | 0.00 (6) | P1—N1—C6—C5 | −29.7 (2) |
| C14—P1—N1—C6 | −160.95 (12) | P1—N1—C6—C1 | 149.70 (12) |
| C15—P1—N1—C6 | −42.91 (15) | N1—P1—C8—C13 | 30.59 (14) |
| C8—P1—N1—C6 | 79.22 (14) | C14—P1—C8—C13 | −88.10 (13) |
| O1—S1—C1—C2 | 96.24 (13) | C15—P1—C8—C13 | 153.27 (12) |
| O3—S1—C1—C2 | −25.20 (13) | N1—P1—C8—C9 | −151.94 (12) |
| O2—S1—C1—C2 | −144.27 (12) | C14—P1—C8—C9 | 89.38 (14) |
| O2—S1—C1—C2 | −144.27 (12) | C15—P1—C8—C9 | −29.26 (15) |
| O1—S1—C1—C6 | −78.68 (13) | C13—C8—C9—C10 | −0.3 (2) |
| O3—S1—C1—C6 | 159.88 (12) | P1—C8—C9—C10 | −177.74 (13) |
| O2—S1—C1—C6 | 40.81 (13) | C8—C9—C10—C11 | −0.4 (3) |
| O2—S1—C1—C6 | 40.81 (13) | C9—C10—C11—C12 | 0.5 (3) |
| C6—C1—C2—C3 | 0.7 (2) | C10—C11—C12—C13 | −0.1 (3) |
| S1—C1—C2—C3 | −174.27 (11) | C11—C12—C13—C8 | −0.6 (3) |
| C1—C2—C3—C4 | −1.8 (2) | C9—C8—C13—C12 | 0.8 (2) |
| C1—C2—C3—C7 | 175.96 (14) | P1—C8—C13—C12 | 178.27 (13) |

| | | | |
|---|---|---|---|
| C2—C3—C4—C5 | 0.9 (2) | C21—C16—C17—C18 | −3.6 (4) |
| C7—C3—C4—C5 | −176.87 (15) | C16—C17—C18—C19 | 1.1 (3) |
| C3—C4—C5—C6 | 1.1 (2) | C17—C18—C19—C20 | 2.6 (3) |
| C4—C5—C6—C1 | −2.2 (2) | C18—C19—C20—C21 | −3.7 (3) |
| C4—C5—C6—N1 | 177.15 (14) | C17—C16—C21—C20 | 2.5 (3) |
| C2—C1—C6—C5 | 1.3 (2) | C19—C20—C21—C16 | 1.1 (3) |
| S1—C1—C6—C5 | 176.21 (11) | | |

*Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N1—H1*N*···O2 | 0.80 (2) | 2.09 (2) | 2.7374 (17) | 139 (2) |
| N1—H1*N*···O2$^{i}$ | 0.80 (2) | 2.47 (2) | 3.0311 (17) | 128 (2) |

Symmetry code: (i) −*x*+1, −*y*+1, −*z*+1.