Table 2. *Selected geometric parameters (Å, °)*

O(1)—N(1)	1.213 (6)	O(2)—N(1)	1.208 (7)
O(3)—N(2)	1.220 (7)	O(4)—N(2)	1.230 (6)
O(5)—N(7)	1.225 (6)	O(6)—N(7)	1.211 (7)
O(7)—N(8)	1.209 (6)	O(8)—N(8)	1.232 (6)
N(1)—C(1)	1.457 (5)	N(2)—C(3)	1.457 (6)
N(3)—N(4)	1.384 (6)	N(3)—C(6)	1.343 (6)
N(4)—C(7)	1.283 (6)	N(5)—N(6)	1.370 (6)
N(5)—C(10)	1.291 (6)	N(6)—C(12)	1.357 (6)
N(7)—C(15)	1.461 (6)	N(8)—C(17)	1.448 (6)
C(7)—C(8)	1.485 (6)	C(7)—C(9)	1.508 (8)
C(9)—C(10)	1.489 (8)	C(10)—C(11)	1.489 (6)
N(3)···O(1)	2.612 (6)	N(6)···O(8)	2.618 (5)
O(1)—N(1)—O(2)	122.8 (5)	O(2)—N(1)—C(1)	117.7 (4)
O(1)—N(1)—C(1)	119.5 (5)	O(3)—N(2)—O(4)	123.3 (5)
O(4)—N(2)—C(3)	116.6 (5)	O(3)—N(2)—C(3)	120.1 (5)
N(4)—N(3)—C(6)	118.5 (4)	N(3)—N(4)—C(7)	116.2 (4)
N(6)—N(5)—C(10)	116.7 (4)	N(5)—N(6)—C(12)	118.9 (4)
O(5)—N(7)—O(6)	123.9 (5)	O(6)—N(7)—C(15)	117.7 (5)
O(5)—N(7)—C(15)	118.4 (5)	O(7)—N(8)—O(8)	120.9 (5)
O(8)—N(8)—C(17)	119.8 (4)	O(7)—N(8)—C(17)	119.3 (4)
N(1)—C(1)—C(6)	121.1 (4)	N(1)—C(1)—C(2)	116.9 (4)
N(2)—C(3)—C(2)	118.2 (5)	N(6)—C(12)—C(13)	120.7 (4)
N(2)—C(3)—C(4)	120.1 (4)	N(7)—C(15)—C(14)	119.3 (4)
N(3)—C(6)—C(5)	120.8 (4)	N(3)—C(6)—C(1)	123.7 (4)
N(4)—C(7)—C(9)	115.3 (4)	N(4)—C(7)—C(8)	126.8 (5)
C(8)—C(7)—C(9)	118.0 (4)	C(7)—C(9)—C(10)	113.9 (5)
N(5)—C(10)—C(9)	115.3 (4)	C(9)—C(10)—C(11)	118.1 (4)
N(5)—C(10)—C(11)	126.6 (4)	N(6)—C(12)—C(17)	122.5 (4)
N(7)—C(15)—C(16)	119.6 (4)	C(13)—C(12)—C(17)	116.8 (4)
N(8)—C(17)—C(12)	122.0 (4)		

The structure of the title compound was solved by direct methods using *SHELXS*86 (Sheldrick, 1985) and refined by full-matrix least squares using *SHELX*76 (Sheldrick, 1976). The positional parameters of the non-H atoms were refined anisotropically. The positional parameters of the H atoms were located from a difference Fourier map and their isotropic displacement parameters were set equivalent to those of the corresponding C atoms and included in the final cycles of refinement but not refined. All other geometrical calculations were carried out using *PARST* (Nardelli, 1983).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry, including least-squares-planes data, torsion angles and intermolecular contact distances less than 3.5 Å, have been deposited with the IUCr (Reference: HA1101). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Drew, M. G. B., Vickery, B. & Willey, G. R. (1984). *Acta Cryst.* C**40**, 304–306.
Edmonds, J. W. & Hamilton, W. C. (1972). *Acta Cryst.* B**28**, 1362–1366.
Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Nardelli, M. (1983). *Comput. Chem.* **7**, 95–98.
Pauling, L. (1960). In *The Nature of the Chemical Bond*, 3rd ed. Ithaca: Cornell University Press.
Sheldrick, G. M. (1976). *SHELX*76. *Program for Crystal Structure Determination*. University of Cambridge, England.
Sheldrick, G. M. (1985). *SHELXS*86. *Program for the Solution of Crystal Structures*. University of Göttingen, Germany.
Willey, G. R. & Drew, M. G. B. (1983). *Acta Cryst.* C**39**, 403–407.
Willey, G. R. & Drew, M. G. B. (1985). *Acta Cryst.* C**41**, 589–594.

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1-(2,4-Dinitrophenyl)-3,5-dimethylpyrazole

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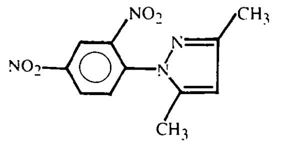
Abstract

The asymmetric unit of the title compound consists of two independent molecules of $C_{11}H_{10}N_4O_4$. The pyrazole and dinitrophenyl rings are individually planar and are twisted about the N—C_{sp^2} bond joining them by 64°. The two nitro groups attached to the phenyl ring show different degrees of rotation away from the plane of the phenyl ring, with those groups at the *para* positions rotated by 8.2 (3) and 14.8 (2)°, and those at the *ortho* positions rotated by 33.5 (1) and 33.2 (1)°. The crystal structure is stabilized by van der Waals interactions.

Comment

Pyrazole and several *N*-substituted pyrazoles are used as inhibitors and deactivators of liver alcohol dehydrogenase and many pyrazole derivatives constitute a family of interesting pharmaceutical agents such as analgesics, antipyretics and anti-inflammatories (Potts, 1986). In view of the wide biological applications of the pyrazole compounds, the crystal structure of 3,5-dimethyl-1-(2,4-dinitrophenyl)pyrazole, (I), has been determined.



(I)

The bond lengths and angles of the two molecules in the asymmetric unit are in agreement. The C_{sp^2}—N bonds associated with the nitro groups are clearly single bonds, while the C(6)—N(3) [1.408 (4) Å] and C(6′)—N(3′) [1.416 (3) Å] bonds show partial double-bond character. The nitro O(4) and O(4′) atoms have very high atomic displacement parameters (Table 1, Fig. 1). This accounts for the apparent shortening of the N(2)—O(4) [1.182 (6) Å] and N(2′)—O(4′) [1.185 (5) Å] bonds.

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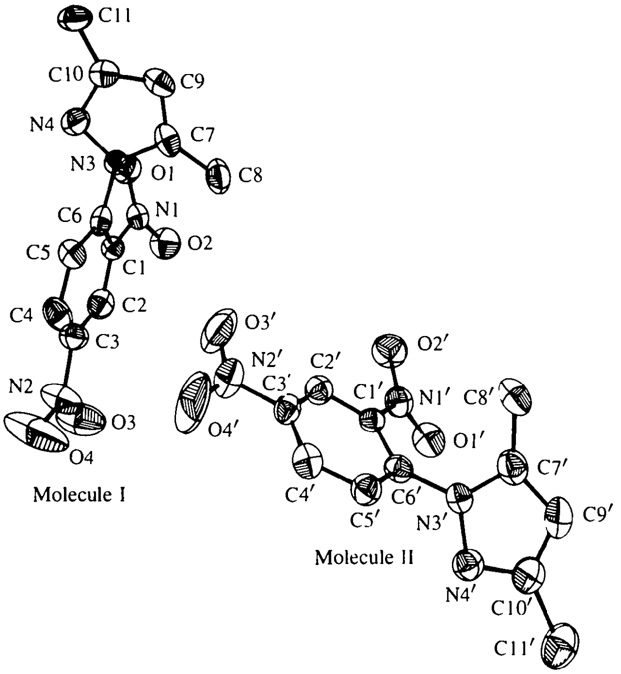

Fig. 1. An *ORTEP*II plot (Johnson, 1976) of the two molecules in the asymmetric unit showing the atom-numbering scheme. H atoms have been omitted for clarity.

The pyrazole ring is planar and the bond lengths agree well with those in 1-(2,4-dinitrophenyl)pyrazole (Fronczek, Parodi, Fischer, Hsieh & Chang, 1989), 1-(2,4-dinitrophenyl)-4-bromopyrazole (Galigne & Falgueirettes, 1969) and 1-(2,4-dinitrophenyl)-4-chloropyrazole (Galigne & Falgueirettes, 1970). The thermal vibrations of the O(3) and O(4) atoms of both molecules in the asymmetric unit are larger than those of the O(1) and O(2) atoms of the nitro groups. This may be due to the rotation of the nitro groups about the C—N bond.

Experimental

The title compound was prepared by the direct reaction of acetyl acetone with 2,4-dinitrophenylhydrazine and was recrystallized from methanol. The density D_m was measured by flotation in KI solution.

Crystal data

$C_{11}H_{10}N_4O_4$
$M_r = 262.22$
Monoclinic
$P2_1/c$
$a = 20.417\ (4)$ Å
$b = 7.711\ (2)$ Å
$c = 16.719\ (3)$ Å
$\beta = 113.71\ (2)°$
$V = 2410.0\ (9)$ Å^3
$Z = 8$
$D_x = 1.445$ Mg m^{-3}
$D_m = 1.50$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 20 reflections
$\theta = 10$–$15°$
$\mu = 0.11$ mm^{-1}
$T = 293$ K
Needle
0.4 × 0.3 × 0.3 mm
Golden yellow

Data collection

Syntex $P2_1$ diffractometer
θ–2θ scans
Absorption correction: none
3822 measured reflections
3693 independent reflections
2763 observed reflections [$F > 4\sigma(F)$]
$R_{\rm int} = 0.014$

$\theta_{\rm max} = 25°$
$h = 0 \rightarrow 24$
$k = 0 \rightarrow 9$
$l = -19 \rightarrow 19$
3 standard reflections monitored every 100 reflections intensity decay: <3%

Refinement

Refinement on F
$R = 0.055$
$wR = 0.061$
$S = 1.90$
2763 reflections
171 parameters
H-atom parameters not refined

$w = 1.2029/[\sigma^2(F_o) + 0.000722F_c]$
$(\Delta/\sigma)_{\rm max} = 0.003$
$\Delta\rho_{\rm max} = 0.22$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.29$ e Å^{-3}
Atomic scattering factors from *SHELX76* (Sheldrick, 1976)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$B_{\rm eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$B_{\rm eq}$
O(1)	0.5176 (1)	0.1593 (3)	0.0971 (1)	4.2 (1)
O(2)	0.6317 (1)	0.2026 (3)	0.1530 (2)	4.7 (1)
O(3)	0.7675 (2)	−0.1881 (4)	0.0559 (2)	7.6 (1)
O(4)	0.7351 (2)	−0.4469 (5)	0.0270 (3)	12.7 (2)
N(1)	0.5793 (2)	0.1091 (3)	0.1197 (1)	3.3 (1)
N(2)	0.7253 (2)	−0.3043 (5)	0.0457 (2)	5.8 (1)
N(3)	0.4905 (1)	−0.1789 (3)	0.1335 (1)	3.1 (1)
N(4)	0.4217 (1)	−0.2051 (3)	0.0737 (2)	3.6 (1)
C(1)	0.5923 (1)	−0.0722 (4)	0.1043 (2)	2.7 (1)
C(2)	0.6498 (2)	−0.1034 (4)	0.0841 (2)	3.2 (1)
C(3)	0.6617 (2)	−0.2711 (4)	0.0645 (2)	3.5 (1)
C(4)	0.6178 (2)	−0.4060 (4)	0.0643 (2)	3.9 (1)
C(5)	0.5618 (2)	−0.3729 (4)	0.0869 (2)	3.4 (1)
C(6)	0.5475 (1)	−0.2057 (4)	0.1078 (2)	2.8 (1)
C(7)	0.4933 (2)	−0.1208 (4)	0.2118 (2)	3.4 (1)
C(8)	0.5616 (2)	−0.0933 (5)	0.2887 (2)	4.6 (1)
C(9)	0.4242 (2)	−0.1088 (4)	0.2020 (2)	4.1 (1)
C(10)	0.3817 (2)	−0.1613 (4)	0.1170 (2)	3.8 (1)
C(11)	0.3021 (2)	−0.1772 (5)	0.0747 (3)	5.7 (1)
O(1′)	0.9800 (1)	0.1515 (3)	0.5787 (1)	4.4 (1)
O(2′)	0.8671 (1)	0.2048 (3)	0.5204 (2)	5.1 (1)
O(3′)	0.7290 (2)	−0.1827 (5)	0.2879 (2)	8.0 (1)
O(4′)	0.7708 (2)	−0.4266 (5)	0.2760 (2)	10.4 (1)
N(1′)	0.9182 (2)	0.1072 (3)	0.5393 (2)	3.5 (1)
N(2′)	0.7741 (2)	−0.2949 (5)	0.3140 (2)	5.1 (1)
N(3′)	1.0037 (1)	−0.1873 (3)	0.6389 (1)	3.0 (1)
N(4′)	1.0731 (1)	−0.2115 (3)	0.6479 (2)	3.5 (1)
C(1′)	0.9038 (1)	−0.0734 (4)	0.5094 (2)	2.8 (1)
C(2′)	0.8463 (2)	−0.1003 (4)	0.4315 (2)	3.3 (1)
C(3′)	0.8353 (2)	−0.2655 (4)	0.3977 (2)	3.4 (1)
C(4′)	0.8788 (2)	−0.4037 (4)	0.4391 (2)	3.7 (1)
C(5′)	0.9338 (2)	−0.3745 (4)	0.5190 (2)	3.4 (1)
C(6′)	0.9474 (1)	−0.2105 (4)	0.5556 (2)	2.9 (1)
C(7′)	0.9991 (2)	−0.13331 (4)	0.7140 (2)	3.5 (1)
C(8′)	0.9302 (2)	−0.1085 (5)	0.7223 (2)	4.8 (1)
C(9′)	1.0679 (2)	−0.1209 (4)	0.7732 (2)	4.2 (1)
C(10′)	1.1117 (2)	−0.1682 (4)	0.7308 (2)	3.9 (1)
C(11′)	1.1915 (2)	−0.1806 (5)	0.7681 (3)	5.8 (1)

Table 2. *Selected bond distances (Å) and angles (°)*

	Molecule I	Molecule II
O(1)—N(1)	1.223 (4)	1.214 (4)
O(2)—N(1)	1.223 (4)	1.220 (4)
O(3)—N(2)	1.207 (5)	1.210 (5)

O(4)—N(2)	1.182 (6)	1.185 (5)
N(1)—C(1)	1.465 (4)	1.469 (4)
N(2)—C(3)	1.476 (6)	1.471 (4)
N(3)—N(4)	1.373 (3)	1.376 (3)
N(3)—C(6)	1.408 (4)	1.416 (3)
N(3)—C(7)	1.363 (4)	1.362 (4)
N(4)—C(10)	1.334 (5)	1.332 (4)
C(7)—C(8)	1.483 (4)	1.480 (6)
C(7)—C(9)	1.356 (6)	1.358 (5)
C(9)—C(10)	1.394 (4)	1.395 (6)
C(10)—C(11)	1.494 (5)	1.495 (5)
O(1)—N(1)—O(2)	123.9 (3)	124.1 (3)
O(2)—N(1)—C(1)	117.1 (3)	117.6 (3)
O(1)—N(1)—C(1)	119.0 (3)	118.3 (3)
O(3)—N(2)—O(4)	122.7 (5)	123.3 (4)
O(4)—N(2)—C(3)	118.3 (4)	119.0 (4)
O(3)—N(2)—C(3)	118.7 (4)	117.7 (4)
C(6)—N(3)—C(7)	128.4 (3)	128.0 (3)
N(4)—N(3)—C(7)	112.5 (3)	113.0 (2)
N(4)—N(3)—C(6)	119.0 (2)	118.9 (2)
N(3)—N(4)—C(10)	103.8 (3)	103.4 (3)
N(1)—C(1)—C(6)	121.9 (3)	122.2 (3)
N(1)—C(1)—C(2)	116.5 (3)	116.3 (3)
N(2)—C(3)—C(2)	117.9 (4)	118.0 (3)
N(2)—C(3)—C(4)	119.8 (3)	119.1 (3)
N(3)—C(6)—C(5)	119.5 (3)	119.3 (3)
N(3)—C(6)—C(1)	122.8 (3)	122.2 (3)
N(3)—C(7)—C(9)	105.5 (3)	105.0 (3)
N(3)—C(7)—C(8)	122.8 (3)	123.1 (3)
C(8)—C(7)—C(9)	131.6 (3)	131.8 (3)
C(7)—C(9)—C(10)	107.1 (4)	107.3 (3)
N(4)—C(10)—C(9)	111.1 (4)	111.2 (3)
C(9)—C(10)—C(11)	128.2 (3)	128.2 (3)
N(4)—C(10)—C(11)	120.6 (3)	120.5 (3)

The structure of the title compound was solved by direct methods using *SHELXS*86 (Sheldrick, 1985) and refined by full-matrix least squares using *SHELX*76 (Sheldrick, 1976). The H-atom positions were located from difference Fourier maps. The positional parameters of the non-H atoms were refined anisotropically, whereas the positional and isotropic displacement parameters, set equal to those of the corresponding attached C atoms, of the H atoms were included in the final cycles of refinement but were not refined. The geometrical calculations for the structure were carried out using *PARST* (Nardelli, 1983).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry, including least-squares-planes data, torsion angles and intermolecular contact distances less than 3.5 Å, have been deposited with the IUCr (Reference: HA1102). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Fronczek, F. R., Parodi, F. J., Fischer, N. H., Hsieh, T. C.-Y. & Chang, B.-Y. (1989). *Acta Cryst.* C**45**, 2027–2028.
Galigne, J. L. & Falgueirettes, J. (1969). *Acta Cryst.* B**25**, 1637–1643.
Galigne, J. L. & Falgueirettes, J. (1970). *Acta Cryst.* B**26**, 380–386.
Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Nardelli, M. (1983). *Comput. Chem.* **7**, 95–98.
Potts, K. T. (1986). In *Comprehensive Heterocyclic Chemistry*, Vol. 5, part 4A. Oxford: Pergamon Press.
Sheldrick, G. M. (1976). *SHELX*76. *Program for Crystal Structure Determination*. University of Cambridge, England.
Sheldrick, G. M. (1985). *SHELXS*86. *Program for the Solution of Crystal Structures*. University of Göttingen, Germany.

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3-Hydroxy-6-methyl-2-pyridylmethyl Isopropylphosphonate Sesquihydrate

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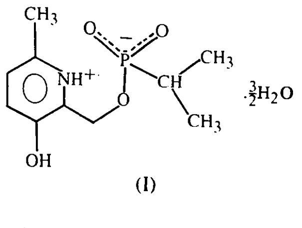
Abstract

The title compound, $C_{10}H_{16}NO_4P.\frac{3}{2}H_2O$, contains a zwitterion with a negative charge on the unsubstituted phosphonate O atoms and a positive charge on the N atom of the pyridine ring. The distances between the P and the two unsubstituted phosphonate O atoms [1.503 (2) and 1.483 (2) Å] lie between P—O single- and double-bond distances. The bond angle at the P atom between these O atoms [116.4 (1)°] is larger than the other O—P—O angles. Hydrogen bonds link the unsubstituted phosphonate O atoms through water molecules to the pyridyl N atoms of neighbouring molecules. The presence of the H atom on the N atom of the pyridine ring is associated with a large C—N—C bond angle [124.6 (2)°].

Comment

Organic phosphates are the components of many biologically important molecules, such as nucleic acids, enzymes and vitamins, performing important biochemical functions, such as participation in genetic processes and catalyzed metabolic reactions. This has prompted numerous structural studies of which the present study of 3-hydroxy-6-methyl-2-pyridylmethyl isopropylphosphonate sesquihydrate, (I), is one.



(I)

We find that the P—O(1) bond [1.601 (2) Å] is longer than the P—O(2) and P—O(3) bonds [1.503 (2) and 1.483 (2) Å, respectively], which is in agreement with the proposals of Cruickshank (1961) for monoionic phosphates, *i.e.* P—OC > P—OH > P—$O^{\frac{1}{2}-}$, and is also seen in other phosphate structures (Reddy & Viswamitra, 1975; Emerson & Sundaralingam, 1980).

The presence of an H atom on the pyridine N atom was indicated by difference Fourier synthesis and the

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