Crystal structure of *N*,*N*′,*N*″,*N*‴-tetrakis(4-methylphenyl)-diphosphoric tetraamide, $C_{28}H_{32}N_4O_3P_2$

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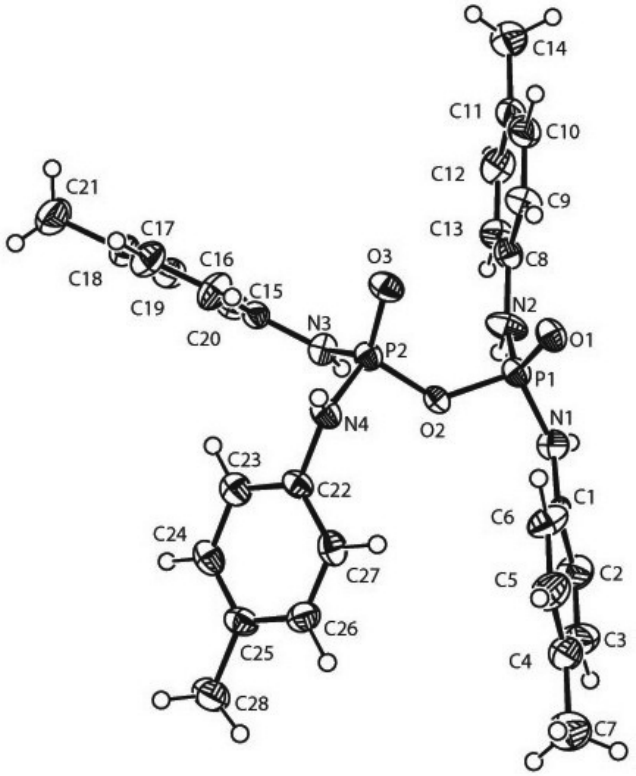

Abstract

$C_{28}H_{32}N_4O_3P_2$, monoclinic, $P12_1/c1$ (no. 14), a = 13.0365(5) Å, b = 9.6142(2) Å, c = 22.3704(8) Å, β = 106.080(1)°, V = 2694.1 Å^3, Z = 4, $R_{gt}(F)$ = 0.107, $wR_{ref}(F^2)$ = 0.187, T = 173 K.

Source of material

The title compound was obtained fortuitously from the reaction between phosphoryl chloride (20 mmol) and *p*-toluidine (80 mmol) in $CHCl_3$, after stirring for 3 h at 268 K, removing the solvent in vacuum and crystallization from $CHCl_3$ after slow evaporation at room temperature.

Experimental details

The structure was solved by the direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. The H atoms were included at geometrically idealized positions and were not refined. The final cycle of full-matrix least-squares refinement was performed using SHELXL-97 [1]. The weighting scheme was based on counting statistics and the final difference Fourier map was essentially featureless.

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Discussion

Previous works have reported on diphosphoric tetraamide compounds containing a $[HN]_2(O)P–O–P(O)[NH]_2$ skeleton ($[C_6H_4(2\text{-}CH_3)NH]_2(O)P–O–P(O)[NHC_6H_4(2\text{-}CH_3)]_2$, [2,3]).

In the title crystal structure, two $(C_6H_4(4\text{-}CH_3)NH)_2P(O)$ moieties are bridged *via* an oxygen atom [∠P1–O2–P2 = 130.8(2)°]; the bond lengths of *d*(P1—O2) =1.615(3) Å and *d*(P2—O2) = 1.596(3) Å are standard for the P–O–P moiety [4]. The P atoms adopt a distorted tetrahedral environment. The bond angles around the P atoms are in the range of 102.2(2)° to 117.8(2)° for P1 and 99.8(2)° to 117.0(2)° for P2. The P=O bond lengths (*d*(P1—O1) = 1.465(3) Å, *d*(P2—O3) = 1.472(3) Å) and the P—N bond lengths (1.623(4), 1.618(4), 1.635(4) and 1.623(4) Å) are standard for this type of compounds [5]. In the $[HN]_2(O)POP(O)[NH]_2$ moiety of the title compound, the two phosphoryl groups are in *syn* position relative to one another. One of them (P1=O1) adopts only the *anti* orientations with respect to both corresponding N–H units; whereas, the other phosphoryl group (P2=O3) adopts a *syn* orientation with respect to one of the N–H units and an *anti* orientation relative to the other N–H. So, the N4 atom bonded to P2 atom is not involved in any N–H···O hydrogen bond. In the crystal, molecules are linked *via* N–H···O(P) hydrogen bonds into extended chains parallel to the *b* axis.

Table 1. Data collection and handling.

Crystal:	colorless needle, size 0.03 × 0.04 × 0.30 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	1.99 cm^{-1}
Diffractometer, scan mode:	Nonius APEX2 CCD, φ/ω
$2\theta_{max}$:	55.08°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	10099, 5863
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 3514
$N(param)_{refined}$:	334
Programs:	SHELXL-97 [1], SIR92 [6], ORTEP-3 [7]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	*x*	*y*	*z*	U_{iso}
H(1N)	4*e*	0.1760	0.2233	0.8247	0.038
H(2N)	4*e*	–0.0073	0.2458	0.8016	0.047
H(3N)	4*e*	–0.1184	0.2579	0.6569	0.036
H(4N)	4*e*	–0.0325	–0.0618	0.5668	0.036
H(2)	4*e*	0.3287	0.3388	0.8107	0.054
H(3)	4*e*	0.4782	0.3331	0.7717	0.069
H(5)	4*e*	0.3776	–0.0268	0.6847	0.056
H(6)	4*e*	0.2336	–0.0296	0.7276	0.050
H(7A)	4*e*	0.5358	0.0732	0.6719	0.081
H(7B)	4*e*	0.6024	0.1522	0.7313	0.081

Table 2. Continued.

Atom	Site	*x*	*y*	*z*	U_{iso}
H(7C)	4*e*	0.5370	0.2363	0.6732	0.081
H(9)	4*e*	–0.0915	–0.0978	0.8113	0.044
H(10)	4*e*	–0.2381	–0.1567	0.8480	0.048
H(12)	4*e*	–0.2889	0.2475	0.8769	0.053
H(13)	4*e*	–0.1437	0.3078	0.8387	0.044
H(14A)	4*e*	–0.4065	0.0849	0.8966	0.063
H(14B)	4*e*	–0.3560	–0.0594	0.9211	0.063
H(14C)	4*e*	–0.4279	–0.0448	0.8524	0.063
H(16)	4*e*	–0.2458	0.0176	0.5443	0.047
H(17)	4*e*	–0.4165	0.0503	0.4723	0.053
H(19)	4*e*	–0.4482	0.4105	0.5562	0.048

Table 2. Continued.

Atom	Site	*x*	*y*	*z*	U_{iso}
H(20)	4*e*	–0.2797	0.3835	0.6255	0.042
H(21A)	4*e*	–0.5860	0.3414	0.4675	0.073
H(21B)	4*e*	–0.6028	0.1798	0.4631	0.073
H(21C)	4*e*	–0.5485	0.2555	0.4177	0.073
H(23)	4*e*	–0.1142	0.2292	0.5126	0.040
H(24)	4*e*	–0.0334	0.3930	0.4602	0.042
H(26)	4*e*	0.2526	0.2108	0.5312	0.041
H(27)	4*e*	0.1738	0.0479	0.5842	0.039
H(28A)	4*e*	0.2413	0.4061	0.4663	0.056
H(28B)	4*e*	0.1557	0.5161	0.4719	0.056
H(28C)	4*e*	0.1335	0.4183	0.4136	0.056

Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
P(1)	4*e*	0.0657(1)	0.0711(1)	0.77113(6)	0.0341(8)	0.0215(7)	0.0269(7)	–0.0002(6)	0.0094(6)	0.0002(6)
P(2)	4*e*	–0.0691(1)	0.0458(1)	0.64347(6)	0.0307(7)	0.0223(7)	0.0272(7)	–0.0007(6)	0.0081(6)	0.0008(6)
O(1)	4*e*	0.0739(3)	–0.0791(3)	0.7826(2)	0.042(2)	0.020(2)	0.032(2)	0.003(2)	0.010(2)	0.004(2)
O(2)	4*e*	0.0313(3)	0.0992(3)	0.6971(1)	0.030(2)	0.024(2)	0.025(2)	0.000(2)	0.008(2)	0.005(1)
O(3)	4*e*	–0.1164(3)	–0.0840(3)	0.6587(2)	0.043(2)	0.027(2)	0.036(2)	–0.005(2)	0.016(2)	0.002(2)
N(1)	4*e*	0.1737(3)	0.1633(4)	0.7947(2)	0.035(3)	0.031(3)	0.031(2)	–0.002(2)	0.011(2)	–0.006(2)
N(2)	4*e*	–0.0180(4)	0.1553(4)	0.7992(2)	0.056(3)	0.021(2)	0.052(3)	–0.007(2)	0.032(3)	–0.004(2)
N(3)	4*e*	–0.1438(3)	0.1852(4)	0.6336(2)	0.031(3)	0.026(2)	0.030(2)	0.003(2)	0.006(2)	–0.003(2)
N(4)	4*e*	–0.0255(3)	0.0224(4)	0.5829(2)	0.041(3)	0.023(2)	0.027(2)	–0.001(2)	0.011(2)	–0.000(2)
C(1)	4*e*	0.2653(4)	0.1569(6)	0.7717(2)	0.025(3)	0.037(3)	0.026(3)	0.000(2)	–0.002(2)	0.001(2)
C(2)	4*e*	0.3393(5)	0.2629(6)	0.7852(3)	0.045(4)	0.040(4)	0.046(4)	–0.013(3)	0.008(3)	–0.011(3)
C(3)	4*e*	0.4257(5)	0.2605(7)	0.7612(3)	0.043(4)	0.054(4)	0.075(5)	–0.014(3)	0.018(4)	0.003(4)
C(4)	4*e*	0.4433(5)	0.1540(7)	0.7233(3)	0.034(3)	0.055(4)	0.051(4)	0.010(3)	0.014(3)	0.016(3)
C(5)	4*e*	0.3690(4)	0.0478(7)	0.7115(3)	0.037(3)	0.049(4)	0.054(4)	0.005(3)	0.013(3)	–0.008(3)
C(6)	4*e*	0.2823(4)	0.0475(6)	0.7354(3)	0.028(3)	0.034(3)	0.062(4)	–0.005(3)	0.011(3)	–0.009(3)
C(7)	4*e*	0.5382(5)	0.1539(8)	0.6976(3)	0.051(4)	0.082(5)	0.075(5)	0.010(4)	0.027(4)	0.017(4)
C(8)	4*e*	–0.1053(4)	0.1109(5)	0.8205(2)	0.037(3)	0.034(3)	0.024(3)	0.003(2)	0.012(2)	–0.002(2)
C(9)	4*e*	–0.1327(4)	–0.0266(6)	0.8240(2)	0.044(4)	0.030(3)	0.041(3)	–0.002(3)	0.021(3)	–0.002(2)
C(10)	4*e*	–0.2191(4)	–0.0608(6)	0.8457(2)	0.044(4)	0.038(3)	0.035(3)	–0.007(3)	0.009(3)	0.001(3)
C(11)	4*e*	–0.2796(4)	0.0386(6)	0.8646(2)	0.034(3)	0.044(4)	0.032(3)	0.002(3)	0.012(3)	0.004(3)
C(12)	4*e*	–0.2496(5)	0.1766(6)	0.8626(3)	0.040(4)	0.044(4)	0.048(4)	0.006(3)	0.011(3)	–0.007(3)
C(13)	4*e*	–0.1632(4)	0.2120(6)	0.8406(2)	0.039(3)	0.030(3)	0.043(3)	0.002(3)	0.015(3)	0.001(3)
C(14)	4*e*	–0.3761(5)	0.0011(7)	0.8856(3)	0.046(4)	0.058(4)	0.056(4)	0.000(3)	0.015(3)	0.006(3)
C(15)	4*e*	–0.2463(4)	0.1985(5)	0.5905(2)	0.027(3)	0.027(3)	0.028(3)	0.002(2)	0.008(2)	0.005(2)
C(16)	4*e*	–0.2871(4)	0.0995(6)	0.5459(3)	0.032(3)	0.030(3)	0.049(3)	0.001(2)	0.000(3)	–0.009(3)
C(17)	4*e*	–0.3865(5)	0.1185(6)	0.5036(3)	0.037(4)	0.047(4)	0.044(3)	–0.010(3)	0.002(3)	–0.009(3)
C(18)	4*e*	–0.4479(4)	0.2345(6)	0.5054(3)	0.030(3)	0.046(4)	0.043(3)	–0.003(3)	0.001(3)	0.012(3)
C(19)	4*e*	–0.4063(4)	0.3305(6)	0.5525(3)	0.027(3)	0.042(3)	0.052(4)	0.010(3)	0.014(3)	0.013(3)
C(20)	4*e*	–0.3072(4)	0.3148(5)	0.5940(2)	0.041(3)	0.029(3)	0.038(3)	–0.002(3)	0.016(3)	0.001(2)
C(21)	4*e*	–0.5562(5)	0.2545(7)	0.4592(3)	0.037(4)	0.066(5)	0.068(5)	–0.005(3)	–0.004(3)	0.020(4)
C(22)	4*e*	0.0231(4)	0.1248(5)	0.5529(2)	0.036(3)	0.025(3)	0.024(3)	–0.003(2)	0.014(2)	–0.001(2)
C(23)	4*e*	–0.0391(4)	0.2257(5)	0.5162(2)	0.041(3)	0.030(3)	0.030(3)	–0.003(3)	0.010(3)	–0.004(2)
C(24)	4*e*	0.0089(5)	0.3221(5)	0.4858(2)	0.051(4)	0.027(3)	0.027(3)	–0.002(3)	0.012(3)	–0.001(2)
C(25)	4*e*	0.1163(4)	0.3182(5)	0.4909(2)	0.040(3)	0.033(3)	0.030(3)	–0.008(3)	0.017(3)	–0.005(2)
C(26)	4*e*	0.1775(4)	0.2150(6)	0.5275(2)	0.029(3)	0.039(3)	0.036(3)	–0.002(3)	0.011(3)	–0.003(3)
C(27)	4*e*	0.1313(4)	0.1186(5)	0.5586(2)	0.039(3)	0.030(3)	0.028(3)	0.007(2)	0.008(2)	0.003(2)
C(28)	4*e*	0.1662(5)	0.4244(6)	0.4576(3)	0.054(4)	0.047(4)	0.042(3)	–0.009(3)	0.019(3)	0.004(3)

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