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Crystal structure of dimethyl 2,2-dicyano-1-(4-nitrophenyl)propyl-phosphonate, $C_{13}H_{14}N_3O_5P$

Shoukang Wang, Li-Tao An*, Kunbo Shi and Lin Zhao

Huaiyin Normal University, Jiangsu Key Laboratory for Chemistry of Low-Dimensional Materials, Department of Chemistry, Huaian, Jiangsu 223300, P. R. China

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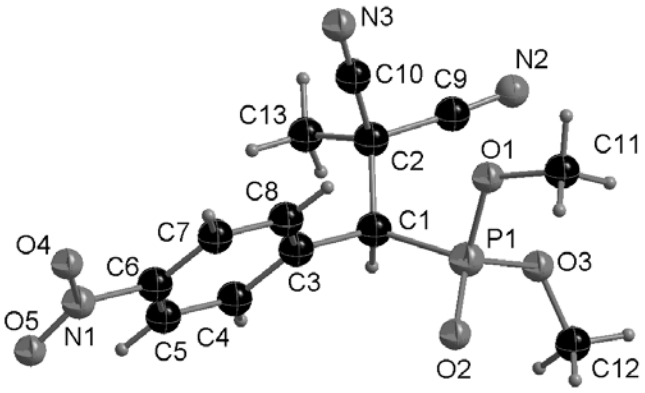

Abstract

$C_{13}H_{14}N_3O_5P$, monoclinic, $P12_1/c1$ (no. 14), a = 18.205(6) Å, b = 10.647(4) Å, c = 7.858(3) Å, β = 93.006(4)°, V = 1521.0 Å^3, Z = 4, $R_{gt}(F)$ = 0.048, $wR_{ref}(F^2)$ = 0.135, T = 296 K.

Source of material

A mixture of 2-(4-nitrobenzylidene)malononitrile (1 mmol) and trimethyl phosphite (2 ml) was heated at 90 °C for 5 h. After removal of excess trimethyl phosphate under vacuum, the residue was subjected to column chromatography, giving the pure title compound in 75 % yield. The suitable single crystals were obtained by slow evaporation from its acetone/petroleum solution. The ^{1}H NMR and ^{13}C NMR data are available in the CIF.

Experimental details

All H atoms were positioned geometrically and allowed to ride on their parent atoms, with d(C—H) = 0.93 Å; and U_{iso}(H) = 1.2 U_{eq}(C).

Discussion

Arylidene malononitriles are reactive compounds and valuable synthetic intermediates in the preparation of a wide variety of organic compounds [1-5]. Some of them have potential for biomedical and industrial applications. Although the adducts of arylidene malononitriles and trimethyl phosphite have been reported earliar, there have been few reports on the single crystal according to CCDC survey.

In the title crystal tructure, the plane (N1/O4/O5) is not coplanar with the benzene ring (C3-C8) with an angle between them of 9.0°, which may be due to the H-bond formation (C13–H13C···O4). Because of the steric hindrance between phosphate and nitrile groups, the angles of C2–C1–P1 and C1–C2–C9 are ca. 117.26° and 112.03°, respectively and are larger than the normal angle of sp^3 carbon (109.5°). The angle of nitrile group to the its linked carbon atom is 176.3° (N2–C9–C2). There were three types of intermolecular H bonds: C13–H13C···O4 (–x,2–y,1–z), C1–H1···O2 (x,$\frac{3}{2}$–y,$\frac{1}{2}$+z) and C13–H13A···N3 (x,$\frac{5}{2}$–y,$\frac{1}{2}$+z). Head-to-tail dimers are formed *via* intermolecular H bonds (C13–H13C···O4). In the dimer, the aromatic rings are parallel with the distance between the centroids of 5.06 Å. The dimers are further inter-connected *via* H bonds (C1–H1···O2, C13–H13A···N3) resulting in a 3-dimensional network.

Table 1. Data collection and handling.

Crystal:	colorless block, size 0.08 × 0.10 × 0.20 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	2.08 cm^{-1}
Diffractometer, scan mode:	Bruker SMART CCD Apex II, ω
$2\theta_{max}$:	51.98°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	11078, 2950
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 2107
$N(param)_{refined}$:	202
Programs:	SHELXS-97 [6], SHELXL-97 [7], SHELXTL [8]

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

Atom	Site	x	y	z	U_{iso}
H(1)	4*e*	0.2739	0.8381	0.6110	0.044
H(4)	4*e*	0.1553	0.7664	0.5916	0.063
H(5)	4*e*	0.0368	0.7690	0.4673	0.080
H(7)	4*e*	0.0852	1.0732	0.1978	0.071
H(8)	4*e*	0.2033	1.0706	0.3175	0.059
H(11A)	4*e*	0.4537	1.0644	0.2898	0.106
H(11B)	4*e*	0.4102	1.1899	0.2563	0.106
H(11C)	4*e*	0.3942	1.0731	0.1387	0.106
H(12A)	4*e*	0.4173	0.6855	0.5219	0.115
H(12B)	4*e*	0.4922	0.7477	0.4793	0.115
H(12C)	4*e*	0.4312	0.7252	0.3342	0.115
H(13A)	4*e*	0.2406	1.0456	0.9380	0.090
H(13B)	4*e*	0.2545	0.9038	0.8966	0.090
H(13C)	4*e*	0.1844	0.9719	0.8174	0.090

* Correspondence author (e-mail: elite6860@sina.com)

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}
C(1)	4*e*	0.2691(1)	0.9189(2)	0.5519(3)	0.040(1)	0.029(1)	0.041(1)	–0.000(1)	0.003(1)	0.001(1)
C(2)	4*e*	0.2790(1)	1.0210(2)	0.6955(3)	0.042(2)	0.039(1)	0.041(2)	0.003(1)	–0.002(1)	–0.003(1)
C(3)	4*e*	0.1917(1)	0.9199(2)	0.4704(3)	0.038(1)	0.040(1)	0.039(1)	–0.001(1)	0.006(1)	–0.003(1)
C(4)	4*e*	0.1415(2)	0.8286(3)	0.5132(4)	0.050(2)	0.054(2)	0.055(2)	–0.010(1)	0.007(1)	–0.000(1)
C(5)	4*e*	0.0706(2)	0.8301(3)	0.4391(5)	0.046(2)	0.075(2)	0.080(2)	–0.021(2)	0.011(2)	–0.016(2)
C(6)	4*e*	0.0511(2)	0.9217(3)	0.3249(4)	0.037(2)	0.086(2)	0.060(2)	0.003(2)	–0.002(1)	–0.024(2)
C(7)	4*e*	0.0996(2)	1.0122(3)	0.2773(4)	0.049(2)	0.069(2)	0.059(2)	0.010(2)	–0.007(2)	–0.005(2)
C(8)	4*e*	0.1697(2)	1.0104(3)	0.3495(4)	0.042(2)	0.053(2)	0.052(2)	–0.001(1)	–0.003(1)	0.005(1)
C(9)	4*e*	0.3573(2)	1.0361(2)	0.7557(3)	0.048(2)	0.046(2)	0.041(2)	–0.000(1)	0.000(1)	–0.004(1)
C(10)	4*e*	0.2556(2)	1.1469(3)	0.6360(4)	0.054(2)	0.043(2)	0.052(2)	0.004(1)	–0.002(1)	–0.009(1)
C(11)	4*e*	0.4071(2)	1.0999(3)	0.2530(4)	0.069(2)	0.063(2)	0.084(2)	–0.010(2)	0.034(2)	0.008(2)
C(12)	4*e*	0.4402(2)	0.7466(3)	0.4521(4)	0.090(3)	0.070(2)	0.070(2)	0.043(2)	0.004(2)	–0.007(2)
C(13)	4*e*	0.2355(2)	0.9818(3)	0.8518(4)	0.062(2)	0.067(2)	0.052(2)	0.001(2)	0.011(2)	–0.005(2)
N(1)	4*e*	–0.0249(2)	0.9239(4)	0.2461(5)	0.041(2)	0.127(3)	0.105(3)	0.000(2)	–0.003(2)	–0.030(2)
N(2)	4*e*	0.4159(2)	1.0518(3)	0.8086(3)	0.053(2)	0.071(2)	0.069(2)	–0.006(1)	–0.008(1)	–0.013(1)
N(3)	4*e*	0.2380(2)	1.2453(2)	0.5986(4)	0.102(2)	0.047(2)	0.077(2)	0.016(2)	–0.011(2)	–0.006(1)
O(1)	4*e*	0.3518(1)	1.0585(2)	0.3640(2)	0.049(1)	0.039(1)	0.058(1)	–0.0021(8)	0.0155(9)	0.0018(8)
O(2)	4*e*	0.3133(1)	0.8421(2)	0.2417(2)	0.057(1)	0.055(1)	0.047(1)	–0.0011(9)	0.0008(9)	–0.0158(9)
O(3)	4*e*	0.41022(9)	0.8676(2)	0.4832(2)	0.042(1)	0.051(1)	0.061(1)	0.0115(8)	–0.0031(9)	–0.0124(9)
O(4)	4*e*	–0.0441(2)	1.0162(4)	0.1637(5)	0.058(2)	0.178(3)	0.120(3)	0.018(2)	–0.021(2)	0.000(2)
O(5)	4*e*	–0.0645(2)	0.8388(4)	0.2746(6)	0.064(2)	0.161(3)	0.247(4)	–0.030(2)	–0.040(2)	–0.015(3)
P(1)	4*e*	0.33703(4)	0.91538(6)	0.39135(8)	0.0384(4)	0.0361(4)	0.0417(4)	0.0003(3)	0.0034(3)	–0.0047(3)

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