Crystal structure of 4,4′-bipyridin-1-ium bi(trihydrogen-1,2,4,5-benzenetetracarboxylate), $C_{30}H_{20}N_2O_{16}$

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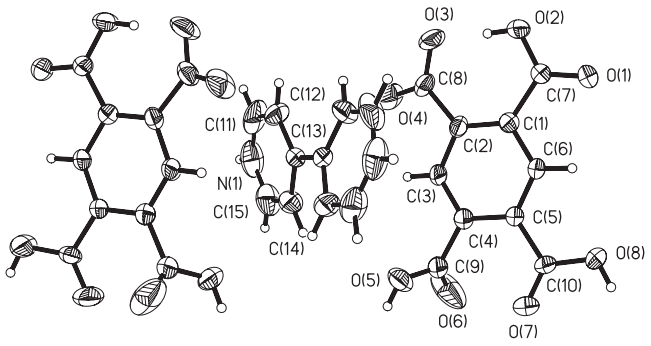

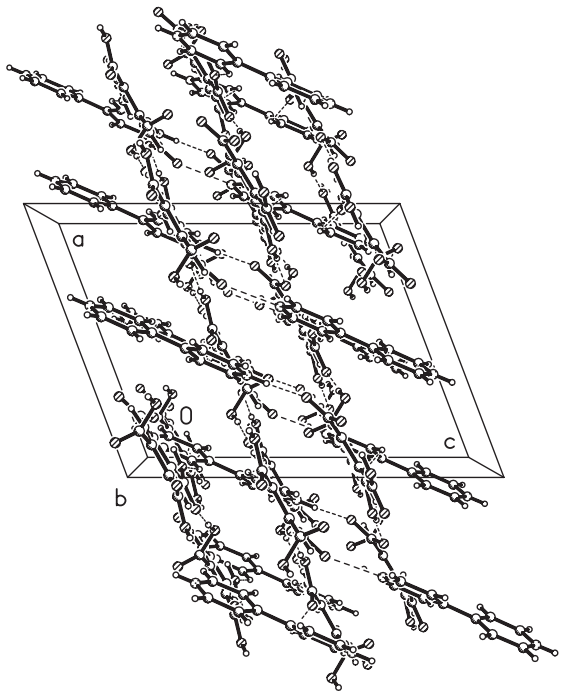

Abstract

$C_{30}H_{20}N_2O_{16}$, monoclinic, *C*12/*c*1 (No. 15), a = 12.021(6) Å, b = 15.469(7) Å, c = 15.436(7) Å, β = 110.806(7)°, V = 2683.2 Å^3, Z = 4, $R_{gt}(F)$ = 0.063, $wR_{ref}(F^2)$ = 0.143, T = 298 K.

Source of material

An ethanol solution (10 mL) of 4,4′-bipyridine (0.4 mmol) was added dropwise to a stirred aqueous solution (10 mL) of 1,2,4,5-benzenetetracarboxylic acid (0.8 mmol) at a temperature of 253 K . Then the reaction mixture was filtered and the filtrate stood for about two weeks until the colorless single crystals were obtained.

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Discussion

4,4′-Bipyridine, a spacer molecule, not only acts as a bridged ligand in the preparation of the metal complexes [1], but also as a kind of host molecules in the formation of the inclusion compounds [2]. Consequently, much interest has been focused on its complexes or inclusions [3]. However, to our knowledge, so far few charge transfer complexes of 4,4′-bipyridine used as a proton receptor have been reported. In order to better understand the behavior of proton transfer in charge transfer complexes, the synthesis and crystal structure of the title compound have been investigated.

As shown in top figure with 50 % probability displacement ellipsoids, the title compound comprises two trihydrogen 1,2,4,5-benzenetetracarboxylate anions and a 4,4′-bipyridin-1-ium cation. Moreover, the pyridinium conjugated cation can be confirmed by the distances of N1-C15, C11-N1, C11-C12, C12-C13, C13-C14 and C14-C15, which (1.321 Å – 1.391Å) are between single bond and double bond. Obviously, a pyridine-ring accepts a proton coming from a 1,2,4,5-benzenetetracarboxylic acid molecule to produce the pyridinium conjugated cation, so the two pyridine-rings of each 4,4′-bipyridine molecular accept two protons coming from two 1,2,4,5-benzenetetracarboxylic acid molecules to produce the two pyridinium conjugated cations. Furthermore, the two pyridinium conjugated cations are linked by a single bond [d(C13—C13) = 1.494(5) Å], and are not in the same plane with the dihedral angle 22.0°. It is noteworthy that π-π stacking interactions play an important role in the solid-state structure of the title compound [4], as shown in bottom figure. The interplanar distance between the two phenyl rings from neighboring unit is a 3.46 Å. Meanwhile, there are also π-π stacking interactions between pyridinium rings with the distance of 3.64 Å. Then, an extended three-dimensional network structure with π-π stacking between phenyl rings and between pyridinium rings is formed.

Table 1. Data collection and handling.

Crystal:	colorless block, size 0.17 × 0.26 × 0.31 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	1.37 cm^{-1}
Diffractometer, scan mode:	Siemens SMART CCD, 450 frames, $\Delta\omega$ = 0.6°
$2\theta_{max}$:	55.76°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	7618, 2895
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 1604
$N(param)_{refined}$:	225
Programs:	SHELX-97 [5], ORTEP-II [6]

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

Atom	Site	x	y	z	U_{iso}
H(6)	8*f*	0.6548	0.0734	0.0358	0.079
H(3)	8*f*	0.0926	–0.1437	0.1423	0.076
H(4)	8*f*	0.3059	0.3199	0.1562	0.079
H(5)	8*f*	–0.1863	0.2744	0.1234	0.109
H(7)	8*f*	0.6503	–0.0517	0.1037	0.081
H(8)	8*f*	0.5700	–0.0559	0.2197	0.056
H(9)	8*f*	0.5057	0.1982	0.1838	0.051
H(10)	8*f*	0.5903	0.1960	0.0721	0.070
H(1)	8*f*	0.255(2)	0.099(2)	0.087(2)	0.032(7)
H(2)	8*f*	–0.096(2)	0.080(1)	0.138(1)	0.016(6)

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}
N(1)	8*f*	0.6251(2)	0.0725(3)	0.0789(2)	0.043(2)	0.110(3)	0.056(2)	–0.010(2)	0.030(2)	–0.011(2)
O(1)	8*f*	–0.1233(2)	–0.0712(1)	0.1444(2)	0.032(1)	0.035(1)	0.075(2)	–0.0030(8)	0.025(1)	0.005(1)
O(2)	8*f*	0.0265(2)	–0.1503(1)	0.1456(2)	0.046(1)	0.024(1)	0.095(2)	0.0017(9)	0.040(1)	0.001(1)
O(3)	8*f*	0.2119(2)	–0.1362(1)	0.1210(2)	0.059(1)	0.032(1)	0.112(2)	0.018(1)	0.056(1)	0.011(1)
O(4)	8*f*	0.2934(2)	–0.0415(1)	0.0557(2)	0.055(1)	0.054(2)	0.078(2)	0.015(1)	0.049(1)	0.007(1)
O(5)	8*f*	0.2798(2)	0.2735(1)	0.1662(2)	0.043(1)	0.038(1)	0.068(2)	–0.0124(9)	0.009(1)	0.009(1)
O(6)	8*f*	0.1459(2)	0.2969(2)	0.0277(2)	0.084(2)	0.098(2)	0.084(2)	–0.044(2)	–0.013(2)	0.054(2)
O(7)	8*f*	–0.0014(2)	0.3103(2)	0.1431(3)	0.058(2)	0.024(1)	0.291(5)	0.001(1)	0.070(2)	–0.006(2)
O(8)	8*f*	–0.1553(2)	0.2284(1)	0.1184(2)	0.042(1)	0.033(1)	0.156(3)	0.001(1)	0.050(2)	–0.020(1)
C(1)	8*f*	0.0384(2)	0.0051(2)	0.1263(2)	0.028(1)	0.029(2)	0.033(1)	–0.000(1)	0.009(1)	–0.002(1)
C(2)	8*f*	0.1458(2)	0.0120(2)	0.1087(2)	0.024(1)	0.034(2)	0.036(2)	0.005(1)	0.009(1)	0.000(1)
C(3)	8*f*	0.1879(2)	0.0948(2)	0.1003(2)	0.025(1)	0.032(2)	0.048(2)	0.001(1)	0.019(1)	0.006(1)
C(4)	8*f*	0.1306(2)	0.1690(2)	0.1086(2)	0.027(1)	0.031(2)	0.042(2)	0.000(1)	0.012(1)	0.004(1)
C(5)	8*f*	0.0216(2)	0.1623(2)	0.1228(2)	0.024(1)	0.026(1)	0.043(2)	0.000(1)	0.012(1)	0.001(1)
C(6)	8*f*	–0.0215(2)	0.0817(2)	0.1316(2)	0.023(1)	0.030(2)	0.042(2)	0.002(1)	0.014(1)	0.001(1)
C(7)	8*f*	–0.0250(2)	–0.0764(2)	0.1389(2)	0.029(1)	0.027(2)	0.042(2)	–0.001(1)	0.014(1)	0.000(1)
C(8)	8*f*	0.2216(2)	–0.0601(2)	0.0927(2)	0.031(1)	0.039(2)	0.043(2)	0.010(1)	0.015(1)	–0.002(1)
C(9)	8*f*	0.1841(2)	0.2540(2)	0.0965(2)	0.030(1)	0.033(2)	0.061(2)	0.001(1)	0.016(2)	0.008(1)
C(10)	8*f*	–0.0446(2)	0.2412(2)	0.1303(2)	0.036(2)	0.022(2)	0.068(2)	0.005(1)	0.023(1)	0.006(1)
C(11)	8*f*	0.6208(3)	–0.0015(3)	0.1207(3)	0.045(2)	0.089(3)	0.074(3)	0.018(2)	0.026(2)	–0.034(2)
C(12)	8*f*	0.5723(2)	–0.0041(2)	0.1898(2)	0.045(2)	0.037(2)	0.058(2)	0.010(1)	0.018(2)	–0.007(1)
C(13)	8*f*	0.5278(2)	0.0701(2)	0.2137(2)	0.026(1)	0.027(2)	0.037(2)	–0.002(1)	0.009(1)	–0.003(1)
C(14)	8*f*	0.5346(2)	0.1468(2)	0.1687(2)	0.045(2)	0.038(2)	0.049(2)	–0.003(1)	0.024(1)	0.008(1)
C(15)	8*f*	0.5846(3)	0.1450(3)	0.1020(2)	0.049(2)	0.079(3)	0.056(2)	–0.009(2)	0.029(2)	0.011(2)

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