

КРАТКИЕ СООБЩЕНИЯ

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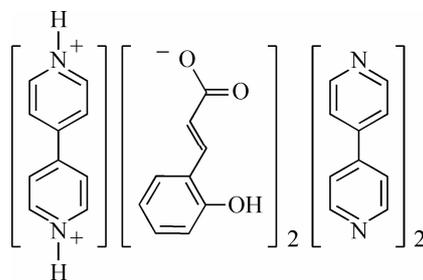
CRYSTAL AND MOLECULAR STRUCTURE OF
4,4'-BIPYRIDINIUM BIS(TRANS-2-HYDROXYCINNAMATE) BIS(4,4'-BIPYRIDINE)© 2009 Y.Y. Zhang¹, Y. Gio¹, H.X. Chen², W.J. Xu¹, Z.M. Jin^{1*}¹College of Pharmaceutical Sciences, Zhejiang University of Technology, Hangzhou, 310014, P. R. China²Analytical Center, Zhejiang Sci-Tech University, Hangzhou, 310018, P. R. China

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4,4'-Bipyridinium bis(trans-2-hydroxycinnamate) bis(4,4'-bipyridine), $0.5(\text{C}_{10}\text{H}_{10}\text{N}_2)^{2+} \cdot (\text{C}_9\text{H}_7\text{O}_3)^- \cdot \text{C}_{10}\text{H}_8\text{N}_2$, crystallizes in triclinic system, space group $P-1$, with $a = 7.4211(8)$, $b = 9.9516(11)$, $c = 13.8587(15)$ Å, $\alpha = 92.510(2)$, $\beta = 96.772(2)$, $\gamma = 99.164(2)^\circ$, $V = 1001.33(19)$ Å³, $\rho_{\text{calc}} = 1.321$ g/cm³, $Z = 2$. In the crystal, the whole trans-2-hydroxycinnamate is disordered over two sites with different occupancies. The molecular species are linked by O—H...N and N—H...O hydrogen bonds into five-molecule hydrogen bonded chain associates that are further linked by C—H...O hydrogen bonds into layers with the major orientation of the disordered 2-hydroxycinnamate. However such hydrogen bonds are not observed with the minor orientation.

Keywords: whole molecule disorder, hydrogen bond, co-crystal, hydroxycinnamate, ortho-coumaric acid, 4,4'-bipyridine.

Introduction. Disorder is a usual phenomenon in crystals; about 16.8 % structures in the Cambridge Structural Database show some form of disorder [1]. However the whole molecule disorder is not particularly common [2]. Very recently it was observed in the inclusion compounds of a tripeptide with pyridine and picolines, with the whole molecule disorder combined with twinning [3]. The new compound synthesized in this work, 4,4'-bipyridinium bis(trans-2-hydroxycinnamate) bis(4,4'-bipyridine), contains 4,4'-bipyridine which is frequently used to prepare novel structures due to its rigidity and ability to form strong hydrogen or coordination bonds via its two N atoms [4, 5]. In the structure reported, the whole trans-2-hydroxycinnamate (HCNMT) anion is disordered. The components that make the crystal and their stoichiometric ratio are presented in Scheme 1.



Scheme 1. 4,4'-Bipyridinium bis(trans-2-hydroxycinnamate) bis(4,4'-bipyridine)

Experiment. Hydroxycinnamic acid (3.32 g; 0.02 mol) and 4,4'-bipyridine (4.68 g; 0.03 mol) were combined and dissolved in 50 ml ethanol by heating to 365 K, to yield a clear solution. The crys-

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Table 1

Bond lengths (d , Å) and angles (ω , deg.) in the crystal of the title compound

Bond	d	Bond	d	Angle	ω	Angle	ω
C2—C3	1.314(6)	C4—C5	1.393(5)	C2—C3—C4	132.3(5)	C9—C4—C3	118.2(4)
C2'—C3'	1.326(9)	C4—C9	1.400(5)	C2'—C3'—C4'	127.4(10)	C9'—C4'—C3'	120.2(7)
C3—C4	1.456(6)	C5—C6	1.410(8)	C5—C4—C3	123.9(4)	C20—N3—C24	117.7(3)
C3'—C4'	1.464(9)	C6—C7	1.365(6)	C5'—C4'—C3'	121.8(7)	C17—N2—C18	114.4(3)
O3—C5	1.351(5)	C8—C9	1.382(7)				

Table 2

Parameters of hydrogen bonds in the crystal of the title compound: bond lengths (Å) and angles (deg.)

D—H...A	D—H	H...A	D...A	DHA	D—H...A	D—H	H...A	D...A	DHA
N3—H3N...O2	0.86	1.84	2.692(7)	173	C8—H8...O3 [#]	0.93	2.60	3.449(6)	152
N3—H3N...O2'	0.86	1.79	2.639(8)	168	C9—H9...O2 [#]	0.93	2.57	3.421(7)	152
O3—H3O...N1	0.82	2.05	2.862(7)	173	C2—H2...O3	0.93	2.27	2.878(8)	122.8
O3'—H3'...N1	0.82	1.79	2.611(7)	175	C3'—H3'...O3'	0.93	2.41	2.756(9)	101

Symmetry code ([#]): $x, y, z+1$.

tals of the title compound formed upon gradual evaporation of excess ethanol over a period of one week at 293 K. A transparent colorless prismatic single crystal with dimensions 0.33×0.28×0.05 mm was studied at 273(2) K on a Bruker APEX area-detector diffractometer (MoK α radiation). The structure was solved by direct methods and refined in anisotropic approximation for non-hydrogen atoms using SHELXL-97 program [6]. Hydrogen atom positions were calculated on the basis of stereochemical considerations and refined by using a riding model isotropically. All calculations were performed with WinGX program package [7].

The hydroxycinnamate anion was disordered over two sites; their occupancies were refined and converged to 0.663(8) and 0.337(8). For Figure drawing and the analysis of intermolecular interactions the SHELXTL program package [8] was used. The crystal data of the title compound: 0.5(C₁₀H₁₀N₂)²⁺·(C₉H₇O₃)⁻·C₁₀H₈N₂; triclinic, $P-1$, $a = 7.4211(8)$, $b = 9.9516(11)$, $c = 13.8587(15)$ Å, $\alpha = 92.510(2)$, $\beta = 96.772(2)$, $\gamma = 99.164(2)^\circ$; $V = 1001.33(19)$, $\rho_{\text{calc}} = 1.321$ g/cm³, $Z = 2$. The θ -range was $1.48 < \theta < 25.30^\circ$. A total of 3569 independent reflections were collected including 2591 ones with $I \geq 2\sigma$. The final values of agreement factors were $R = 0.0800$ and $wR2 = 0.1779$ for 2591 reflections with $I \geq 2\sigma(I)$. GOOF on F^2 : 1.092. CIF file containing complete information on the studied structure was deposited with CCDC, deposition number 626122, and is freely available upon request from the following web site: www.ccdc.cam.ac.uk/data_request/cif. Selected bond lengths and angles are listed in Table 1. The parameters of hydrogen bonding are listed in Table 2.

Results and discussion. As shown in Fig. 1, *a*, the crystal structure of the title compound comprises a half of the centrosymmetric 4,4'-bipyridinium cation, one HCNMT anion and one neutral molecule of 4,4'-bipyridine in the asymmetric unit. In the bipyridine molecule, the dihedral angle between the two pyridine rings is 6.8°, while in the bipyridinium cation two pyridine rings are parallel (due to centrosymmetry). Compared with 4,4'-bipyridine [9], the geometry of the bipyridine components is within a reasonable range. However, it is of a great difference for the C—N—C angle of the bipyridinium cation: C20—N3—C24 [117.7(3)°] is obviously greater than those of C10—N1—C14 [115.1(3)°] and C17—N2—C18 [114.4(3)°]. The widening of C—N—C is due to protonation. The increase of this internal angle has been observed previously in other 4,4'-bipyridinium salts [10–12].

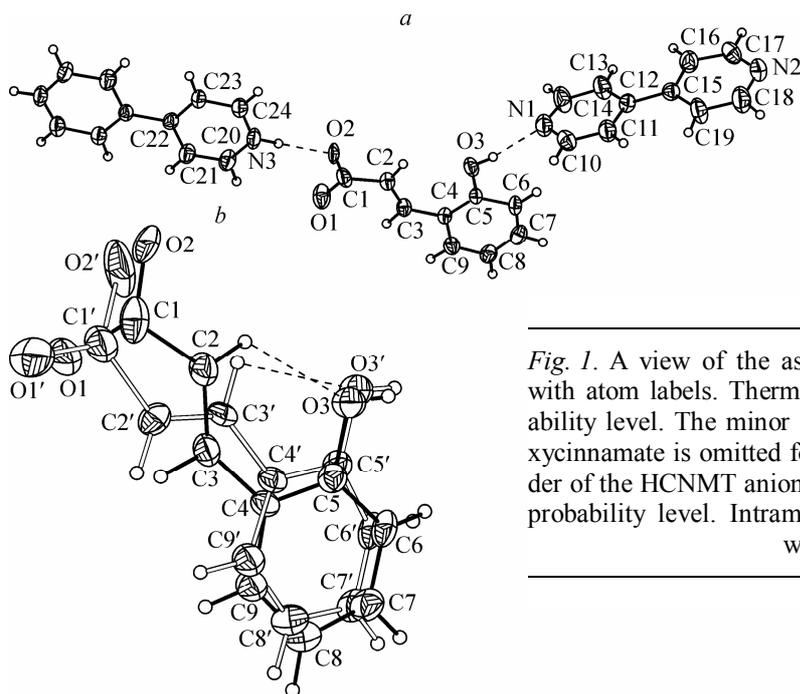


Fig. 1. A view of the asymmetric unit of the title compound with atom labels. Thermal ellipsoids are drawn at 40 % probability level. The minor orientation of the disordered 2-hydroxycinnamate is omitted for clarity — *a*. Whole molecule disorder of the HCNMT anion; thermal ellipsoids are drawn at 40 % probability level. Intramolecular hydrogen bonding is shown with dashes — *b*

The whole HCNMT anion is disordered, with the major orientation populated by 66.3(8) % (Fig. 1, *b*). The structure of HCNMT is almost planar, the dihedral angle between the plane of —CH—COO⁻ and the phenyl ring is 8.1(9)° in the major orientation, and 9.3(8)° in the minor one. This indicates a high degree of conjugation that causes a strong push-pull effect between the hydroxyl and carboxylate group through the coumaric acid skeleton. As a consequence of this conjugation, in the major orientation the C6—C7 and C8—C9 bond lengths are significantly shorter than those of C4—C5, C5—C6 and C4—C9, and the length of O3—C5 bond in the major orientation is much shorter than that of O—C bond in phenol, revealing the delocalization of the lone pair of the O3 atom. For the same reason, the geometric features in the minor orientation are similar to those in the major orientation.

The two orientations of the disordered carboxylate group reside inversely across the C3—C4 axis, mainly due to the rotation of the C3—C4 bond. A theoretical calculation indicates that the conformation of the major orientation is only about 5 kcal/mol different by energy from the minor one. The energy barrier is easy to overcome at room temperature so the carboxylate group is capable of adopting both conformations. The arrangement of the carboxylate in the major orientation is similar to those observed previously [13, 14], however the conformation of the minor orientation has not ever been reported. The dihedral angle between the two disordered carboxylate groups is 17.0(9)°. In the benzene ring, the separations between the corresponding atoms of the two parts of disorder are small but the atom positions are resolved. The C—H...O (C2—H2...O3 or C3'—H3'...O3') intramolecular hydrogen bond is observed in both major and minor orientations (Fig. 1, *b*).

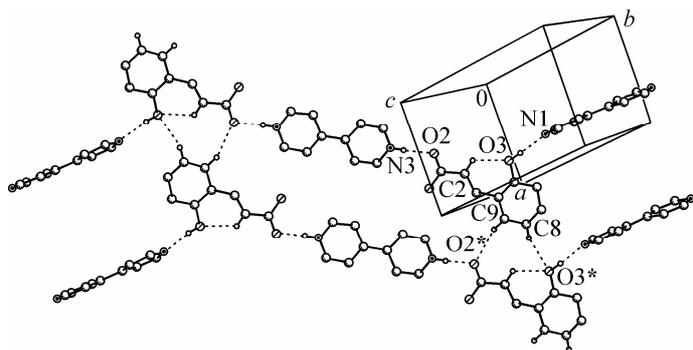


Fig. 2. A fragment of the crystal structure showing the hydrogen-bonded chains. Hydrogen bonds are indicated by dashed lines. For clarity, the minor orientation of the disordered HCNMT and all H atoms not involved in hydrogen bonding have been omitted. Atoms with (*) are generated by the symmetry operation ($x+1, y, z$)

As shown in Fig. 2, the molecules in the crystal are linked by O3—H3O...N1 and N3—H3N...O2 hydrogen bonds into five-molecule H-bonded chain associate, which could be described by the graph set $C_3^3(20)$ [15]. Surprisingly, in the bipyridine molecule N2 does not act as a hydrogen bond acceptor. Thus the centrosymmetric 4,4'-bipyridinium cation acts as a chain builder, while the bipyridine molecule as a chain terminator. For the major orientation, the five-molecule H-bonded chains are connected to one another via weak C8—H8...O3[#] and C9—H9...O2[#] hydrogen bonds [symmetry code (#): $x+1, y, z$] in an $R_2^2(11)$ ring [15] to form a layer. However, for the minor orientation there are no hydrogen bonds between the neighboring chains. The 4,4'-bipyridinium is almost coplanar with HCNMT, but the 4,4'-bipyridine is practically perpendicular to the benzene ring. Such an arrangement permits no $\pi\cdots\pi$ interactions in the crystal.

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