Crystal Structure of 2-[(2-Chloro-5-methyl-3-pyridinyl)(hydroxy)-methyl]acrylonitrile

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The crystal structure of a novel Baylis-Hillman adduct, a 2,3,5-substituted derivative of pyridine, is reported here. The final *R*-value is 0.054. The structure has a chiral atom, and thus represents a racemic mixture. In the crystal packing, the molecules are linked by O-H...N intermolecular interactions.

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The Baylis-Hillman¹ is a well known method for coupling aldehydes and activated alkenes, and is catalyzed by tertiary amines or phosphines, emerging as a valuable carbon-carbon bond-forming reaction. These adducts have applications in biology.² Keeping in view the importance of such adducts, the crystal structure of the above compound has been carried out by crystallographic methods. A schematic view of the molecule is shown in Fig. 1.

The title compound (Fig.1) was prepared by the coupling of 2-chloro-5-methyl-pyridine-3-carbaldehyde (5 mmol) and acrylonitrile (5 mmol) in methanol, the reaction mixture being stirred at room temperature in the presence of 1,4-diazabicyclo[2.2.2]octane (5 mmol) for 15 min. This mixture was washed with water, extracted with chloroform and recrystallized from acetonitrile (yield 96%).

A summary of the key crystallographic information for the title compound is given in Table 1. Intensity data were collected on a Bruker SMART CCD area detector diffractometer with graphite-monochromated radiation ($\lambda = 0.71073$ Å). Cell constants and an orientation matrix for data collection were obtained from a least-squares refinement in the range (2θ) 2.413–27.404°, and corresponded to a primitive orthorhombic cell. The data were collected at a temperature of 293(2)K using the ω - 2θ scan technique to a maximum θ value of 28.01°. The collected data were reduced by using the program SAINT, and an empirical absorption correction was carried out by using the SADABS program. The structure was solved by direct methods using SHELXS-97, and anisotropic displacement parameters were applied to non-hydrogen atoms in a full-matrix least-squares refinement based on F^2 using SHELXL-97. All of the hydrogen atoms were positioned

geometrically and allowed to ride on their parent atoms, with C-H = 0.93 Å and O-H = 0.81 Å, and with Uiso(H) = 1.2Ueq(C) or 1.5Ueq(C,O) for methyl and hydroxy groups. The final cycle of refinement converged to $R = 0.054$. The geometrical parameters and molecular graphics were computed using programs PARST, ORTEP-3 and PLATON.

The crystal structure of the title compound together with the atom labeling scheme is shown in Fig. 2, while the final positional parameters of the non-hydrogen atoms with their equivalent temperature factors are presented in Table 2. The selected bond lengths and angles are listed in Table 3. The hydrogen bonding geometry is presented in Table 4.

The N-C, Cl-C and other bond distances are comparable to

Table 1 Crystal and experimental data

CCDCNo.	264448
Formula	C ₁₀ H ₉ ClN ₂ O
Formula weight	208.64
Temperature	273(2)K
Wavelength	0.71073 Å
Crystal system	orthorhombic
Space group	<i>Pccn</i>
Unit cell dimensions	<i>a</i> = 11.799(2)Å <i>b</i> = 12.094(1)Å <i>c</i> = 14.231(1)Å
Volume	2030.7(3)Å ³
Z	8
Calculated density	1.365 Mg/m ³
μ (Mo K α)	0.343 mm ⁻¹
<i>F</i> (000)	864
Crystal size	0.19 × 0.20 × 0.18 mm
θ range	2.41 to 28.01°
Limiting indices	−15 ≤ <i>h</i> ≤ 15, −15 ≤ <i>k</i> ≤ 15, −18 ≤ <i>l</i> ≤ 18
Reflections collected/unique	16174/2421
Absorption correction	none
Refinement method	full-matrix least-squares on F^2
Data/parameters	2421/132
Goodness-of-fit	1.114
Final <i>R</i> indices [$I > 2\sigma(I)$]	<i>R</i> 1 = 0.0535, <i>wR</i> 2 = 0.1367
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0613, <i>wR</i> 2 = 0.1423
Largest diff. peak and hole	0.425 and −0.208 e.Å ⁻³

Fig. 1 Chemical structure.

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Fig. 2 ORTEP drawing of the title compound showing the atom numbering scheme. Thermal ellipsoids are drawn at the 30% probability level

Table 2 Fractional coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($\text{\AA}^2 \times 10^3$) for non-hydrogen atoms

Atom	x	y	z	U(eq)
C1	4215(2)	6469(2)	5652(1)	499(5)
C2	4839(2)	6565(2)	4837(1)	448(4)
C3	4265(2)	6397(2)	3999(1)	398(4)
C4	3128(1)	6119(1)	3986(1)	348(4)
C5	2610(2)	6035(2)	4858(1)	392(4)
C6	6067(2)	6894(3)	4854(2)	665(7)
C7	2501(2)	5958(1)	3062(1)	385(4)
C8	2246(2)	4744(2)	2878(1)	437(4)
C9	3211(2)	4089(2)	2602(1)	507(5)
C10	1228(2)	4288(2)	2919(2)	636(6)
O1	3192(1)	6390(1)	2345(9)	480(4)
N1	3118(1)	6207(2)	5671(1)	473(4)
N2	3972(2)	3576(2)	2380(2)	737(6)
Cl	1182(4)	5701(5)	4947(4)	606(2)

$$U(\text{eq}) = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* (a_i^* a_j^*)$$

related structures previously studied.^{3,4} Although the title compound belongs to a centrosymmetric space group, it contains a chiral atom [C7], and thus represents a racemic mixture.

The hydroxy oxygen is tilted away from the acrylonitrile group because the C8-C7-O1 bond angle is distinctly larger than that of C4-C7-O1. The chlorine atom is almost in the same plane with the pyridine ring. The cyano bond distance agrees well with the literature values.

In the crystal structure, the packing is dictated by intermolecular (O-H...N) hydrogen bonds into chains (C6 type)⁵

Table 3 Selected bond distances ($\text{\AA}$) and angles ($^\circ$)

C(1)-N(1)	1.333(3)	N(1)-C(1)-C(2)	123.78(16)
C(5)-N(1)	1.319(2)	N(1)-C(5)-C(4)	124.93(17)
C(5)-Cl	1.738(2)	O(1)-C(7)-C(8)	110.33(14)
C(7)-O(1)	1.407(2)	O(1)-C(7)-C(4)	107.28(15)
C(9)-N(2)	1.136(3)	N(2)-C(9)-C(8)	179.6(3)

Table 4 Hydrogen bonding geometry

D-H...A	D-A($\text{\AA}$)	H...A($\text{\AA}$)	D...A($\text{\AA}$)	DHA($^\circ$)
O1-H1'...N1 ⁱ	0.81	2.04	2.849(2)	179
C10-H10A...N2 ⁱⁱ	0.93	2.903	3.556(3)	176
C3-H3...O1	0.93	2.32	2.672(2)	102

Symmetry codes: (i) $3/2-x, y, 1/2+z$ (ii) $-x+1/2, -y+1/2, z$

along the *c*-axis. These chains are joined three dimensionally through C-H...N dimers. An intra-molecular C-H...O interaction is also observed. This interaction closes the five-membered pseudo-ring O1-C7-C4-C3-H3 according to the S(5) pattern. Similar interactions were observed in the literature.

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References

1. A. D. Baylis and M. E. D. Hillman, German Patent, **1972**, 2 155 113.
2. M. M. Kabat, J. Kiegel, N. Cohen, K. Toth, P. M. Wovkulich, and M. R. Uskokovic, *J. Org. Chem.*, **1996**, *61*, 118.
3. G. Y. S. K. Swamy, K. Ravikumar, P. Narender, and V. Jayathirtha Rao, *Acta Cryst.*, **2005**, *E61*, o706.
4. G. Y. S. K. Swamy, K. Ravikumar, P. Narender, and V. Jayathirtha Rao, *Acta Cryst.*, **2005**, *E61*, o708.
5. J. Bernstein, R. E. Davis, L. Shimoni, and N. L. Chang, *Angew. Chem. Int. Ed. Engl.*, **1995**, *34*, 1555.