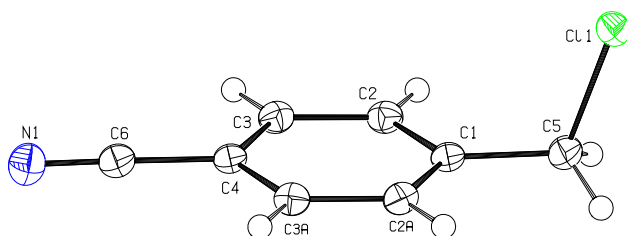


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# The crystal structure of 4-(chloromethyl) benzonitrile, C<sub>8</sub>H<sub>6</sub>ClN



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## Abstract

C<sub>8</sub>H<sub>6</sub>ClN, orthorhombic, *Pnma* (no. 62), *a* = 20.3965(7) Å, *b* = 7.8164(3) Å, *c* = 4.5015(2) Å, *V* = 717.66(5) Å<sup>3</sup>, *Z* = 4, *R*<sub>gt</sub>(*F*) = 0.0265, *wR*<sub>ref</sub>(*F*<sup>2</sup>) = 0.0670, *T* = 100.0 K.

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The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

## Source of material

4-(Chloromethyl)benzonitrile was obtained commercially from the Sigma–Aldrich company. Then the white powder (0.50 g) was solved in a 20.0 ml ethanol solution. Needle crystals were obtained at the bottom of the vessel after one week at ambient conditions.

## Experimental details

H atoms were initially located in difference maps and subsequently treated as riding, with C–H distances of

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Table 1: Data collection and handling.

|                                                                            |                                                       |
|----------------------------------------------------------------------------|-------------------------------------------------------|
| Crystal:                                                                   | Colourless block                                      |
| Size:                                                                      | 0.20 × 0.12 × 0.10 mm                                 |
| Wavelength:                                                                | Synchrotron radiation (1.34139 Å)                     |
| $\mu$ :                                                                    | 2.64 mm <sup>-1</sup>                                 |
| Diffractometer, scan mode:                                                 | Bruker Photon III, Profile data from $\theta/2\theta$ |
| $\theta_{\max}$ , completeness:                                            | 72.3°, 98%                                            |
| $N(hkl)_{\text{measured}}$ , $N(hkl)_{\text{unique}}$ , $R_{\text{int}}$ : | 9401, 1133, 0.033                                     |
| Criterion for $I_{\text{obs}}$ , $N(hkl)_{\text{gt}}$ :                    | $I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$ , 1088    |
| $N(\text{param})_{\text{refined}}$ :                                       | 56                                                    |
| Programs:                                                                  | Bruker [1], SHELX [2, 3, 6], Diamond [4], Olex2 [5]   |

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å<sup>2</sup>).

| Atom | <i>x</i>   | <i>y</i>    | <i>z</i>    | <i>U</i> <sub>iso</sub> <sup>*</sup> / <i>U</i> <sub>eq</sub> |
|------|------------|-------------|-------------|---------------------------------------------------------------|
| C1   | 0.66112(6) | 0.750000    | 0.7612(2)   | 0.0181(2)                                                     |
| C2   | 0.63468(4) | 0.59550(11) | 0.66214(19) | 0.01925(19)                                                   |
| H2   | 0.652284   | 0.490416    | 0.731977    | 0.023*                                                        |
| C3   | 0.58281(4) | 0.59428(11) | 0.46221(19) | 0.01922(19)                                                   |
| H3   | 0.565069   | 0.489089    | 0.393539    | 0.023*                                                        |
| C4   | 0.55707(6) | 0.750000    | 0.3634(3)   | 0.0175(2)                                                     |
| C5   | 0.71880(6) | 0.750000    | 0.9670(3)   | 0.0225(3)                                                     |
| H5   | 0.721030   | 0.852230    | 1.093672    | 0.027*                                                        |
| C6   | 0.50238(6) | 0.750000    | 0.1599(3)   | 0.0204(2)                                                     |
| Cl1  | 0.79446(2) | 0.750000    | 0.75268(6)  | 0.02108(12)                                                   |
| N1   | 0.45819(6) | 0.750000    | 0.0025(3)   | 0.0265(3)                                                     |

0.98 Å (methylene C) and 0.95 Å (aromatic C) and thermal factors being set 1.2 times of the parent atoms.

## Comment

In some organic synthesis processes, a series of medium or fine chemicals with high economic value can be derived from an organic intermediate, 4-(chloromethyl)benzonitrile. For instance, it is often used in the production of distyrene fluorescent brightener, dyes, pesticides, synthetic fragrances, detergents, dye aids, plasticizers, synthetic resins and so on [7–9]. Although some analogs of 4-(chloromethyl)benzonitrile have been synthesised and

reported in recent years [10–12] the crystallographic research of the title compound has not been reported so far.

4-(Chloromethyl)benzonitrile crystallized in the orthorhombic *Pnma* space group with only half a molecule in its asymmetric unit (located on a mirror plane; see the figure). In the benzene ring of the molecular structure, these three pairs of symmetric intracyclic bond lengths and angles are ranging from 1.389(1) to 1.398(2) Å and 119.08(8)° to 121.05(11)°, respectively, indicating a nearly regular hexagon. The nitrile group is almost located on the benzene plane with two respective deviations of only 0.020(1) Å and 0.061(1) for C6 and N1 atoms. For the chloromethyl group, C5 atom is only away from the benzene plane by 0.057(1) Å. Another noteworthy bond length is the C5–Cl1 (1.8199(13) Å) which is slightly longer than its analogs [13].

The interactions between separated molecules were considered by geometrical calculations using the program Platon within the sum of the atomic van der Waals radii [14]. Although there are no classical hydrogen bonds, there is each one weak C3–H3...N1 (1 – *x*, *y* – 1/2, –*z*, *d*<sub>C3...N1</sub> = 3.510(2) Å) and one C–H... $\pi$  interaction, respectively. The C–H... $\pi$  interaction originates from the methylene group and directs to neighbouring benzene ring with the C5...Cg distance of 3.494(2) Å which is similar to its analog, benzyl chloride [13]. There is also another intermolecular  $\pi$ ... $\pi$  stacking interaction between the small  $\pi$  conjugate system of nitrile and the adjacent benzene rings at (*x*, *y*, *z* – 1). The sp hybridized C6 atom is distanced from the centroid of the hexa-membered ring only 3.458(2) Å away. By a combination of these two types of interactions, the molecules are linked into a three-dimensional network.

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## References

1. Bruker. *Apex 3*, v2018.1–0, SAINT V8.40B; Bruker AXS Inc.: Madison, 2018.
2. Sheldrick G. M. *SHELXTL* – integrated space-group and crystal-structure determination. *Acta Crystallogr.* 2015, *A71*, 3–8.
3. Sheldrick G. M. Crystal structure refinement with SHELXL. *Acta Crystallogr.* 2015, *C71*, 3–8.
4. Brandenburg K. *DIAMOND*; Crystal Impact GbR: Bonn Germany, 2006.
5. Dolomanov O. V., Bourhis L. J., Gildea R. J., Howard J. A. K., Puschmann H. OLEX2: a complete structure solution, refinement and analysis program. *J. Appl. Crystallogr.* 2009, *42*, 339–341.
6. Sheldrick G. M. A short history of SHELX. *Acta Crystallogr.* 2008, *A64*, 112–122.
7. Li J., Gao F., Wen J., Xu Z., Zhang C., Hua X., Cai X., Li Y., Shi B., Han Y., Ren X., Liu S. Effective surface passivation with 4-bromobenzonitrile to enhance the performance of perovskite solar cells. *J. Mater. Chem.* 2021, *C9*, 17089–17098.
8. Zhao G., Zhang K., Wang L., Li J., Zou D., Wu Y., Wu Y. Efficient synthesis of diarylmethane derivatives by PdCl<sub>2</sub> catalyzed cross-coupling reactions of benzyl chlorides with aryl boronic acids in aqueous medium. *Tetrahedron Lett.* 2015, *56*, 6700–6703.
9. Qiu X., Wang X., Hou S., Zhang J., Zhou J., Tan Y. Tunable fluorescence-responsive double hydrophilic block polymers induced by the formation of pseudopolyrotaxanes with cucurbit [7]uril. *Polymers* 2019, *11*, 1470.
10. Zang Y.-L., Wu G.-L., Xu W.-J., Yang C.-H. 4-(Chloromethyl) benzophenone. *Acta Crystallogr.* 2007, *E63*, o3339.
11. Betz R., Britten-Kelly M., McClelland C., Hosten E. Refinement of the crystal structure of 1-chloromethyl-4-nitrobenzene, C<sub>7</sub>H<sub>6</sub>ClNO<sub>2</sub>, at 200 K. *Z. Kristallogr. N. Cryst. Struct.* 2011, *226*, 583–584.
12. Aziz-ur-Rehman, Yasir A., Akkurt M., Abbasi M. A., Jahangir M., Khan I. U. 1-chloromethyl-4-nitrobenzene. *Acta Crystallogr.* 2010, *E66*, o1667.
13. Nayak S. K., Sathishkumar R., Row T. N. G. Directing role of functional groups in selective generation of C–H... $\pi$  interactions: *in situ* cryo-crystallographic studies on benzyl derivatives. *CrystEngComm* 2010, *12*, 3112–3118.
14. Spek A. L. Structure validation in chemical crystallography. *Acta Crystallogr.* 2009, *D65*, 148–155.