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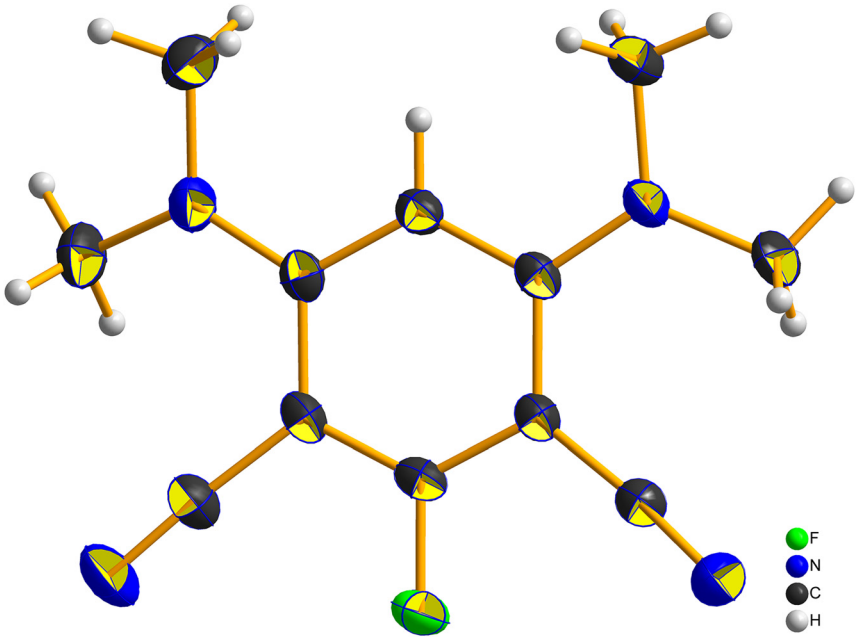
The crystal structure of 4,6-bis(dimethylamino)-2-fluoroisophthalonitrile, $C_{12}H_{13}FN_4$



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Abstract

$C_{12}H_{13}FN_4$, triclinic, $P\bar{1}$ (no. 2), a = 7.5580(3) Å, b = 8.4834(8) Å, c = 10.4451(7) Å, α = 71.478(7)°, β = 69.583(6)°, γ = 68.641(7)°, V = 570.42(8) Å^3, Z = 2, $R_{gt}(F)$ = 0.0565, wR_{ref} (F^2) = 0.1668, T = 296 K.

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The molecular structure is shown in the figure. Table 1 contains the crystallographic data and the list of the atoms including atomic coordinates and displacement parameters can be found in the cif-file attached to this article.

Table 1: Data collection and handling.

Crystal:	Colorless block
Size:	0.30 × 0.25 × 0.22 mm
Wavelength:	Cu$K\alpha$ radiation (1.54184 Å)
μ:	0.80 mm^{-1}
Diffractometer, scan mode:	Rigaku XtaLAB Synergy, ω scans
θ_{max}, completeness:	65.0°, 97 %
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	4145, 1879, 0.035
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\sigma(I_{obs})$, 1,647
$N(\text{param})_{refined}$:	159
Programs:	Rigaku,[1] Olex2,[2] SHELX [3]

1 Source of materials

The 1,3,5-trifluoro-2,4,6-triiodobenzene (1.02 g, 2 mmol) and copper(I) cyanide (1.08 g, 6 mmol) were placed in a 50 mL round bottomed flask with 20 mL of dry *N*,*N*-dimethylformamide

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(DMF). The mixture was refluxed for 24 h under N_2 atmosphere. When the reaction was finished, 10 mL of concentrated ammonia water and 20 mL of dichloromethane were sequentially added to the reaction. After separation, the aqueous phase was extracted three times with dichloromethane, and the organic phases were combined. The organic phases were then washed three times with water, and finally dried with anhydrous sodium sulfate. Most of the dichloromethane was removed using a rotary evaporator, and after cooling and standing overnight, colorless block crystals were obtained. After filtration, about 186 mg were obtained with a yield of approximately 40 %.

2 Experimental details

The data were collected and processed using CrysAlis^{PRO}.[1] The structures were solved using Olex2 software[2] and refined with the SHELXL.[3] The hydrogen atom positions were fixed geometrically at the calculated distances and allowed to ride on the parent atoms. The U_{iso} of the H-atoms were set to 1.2 and 1.5 times U_{eq} of the parent atoms with C–H = 0.96 Å (aliphatic) and C–H = 0.93 Å (aromatic).

3 Comment

The potential of organic cyanates in synthetic chemistry is extensive, with a wide range of applications in the production of carboxylic acid compounds,[3] amides,[4] aldehyde compounds,[5] ketone compounds,[6] and some heterocyclic compounds[7] under specific conditions. Furthermore, cyanoaromatic compounds, such as polycyanobenzenes, have been in the focus of extensive research due to their significant photophysical and electron transfer properties.[8] These compounds are frequently employed as photocatalysts in various applications.[9,10]

In the asymmetric unit, there is one complete 4,6-bis(dimethylamino)-2-fluoroisophthalonitrile molecule. In this molcule the dimethylamine group is the decomposition product of DMF molecules under heat condition, which subsequently undergoes nucleophilic substitution to obtain the product. Cyan group is generated through the Rosenmund von Braun reaction between iodobenzene and cuprous cyanide.[11] The departure reaction of iodine atoms on the benzene ring occurred under copper catalysis during the reaction process.[12] After undergoing the above chemical reactions, the target product was finally obtained. The C–C bond distances on the aromatic ring range from 1.382(2) to 1.436(2) Å. $C_{(sp2)}$–N bond distances are 1.359(2) and 1.361(2) Å. And $C_{(sp3)}$–N bond distances range from 1.444(3) to 1.460(3) Å. C–N bond distances of cyano group are 1.153(2) and 1.148(2) Å. $C_{(sp2)}$–F bond distance is 1.3526(19) Å. All bond distances are within the normal range.[13,14]

References

1. Agilent Technologies. CrysAlis^{PRO} *Software System (Version 171.38.43f)*; Agilent Technologies UK Ltd: Oxford, UK, 2015.
2. 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.
3. Sheldrick, G. M. Crystal Structure Refinement with SHELXL. *Acta Crystallogr.* **2015**, *C71*, 3–8.
4. Daw, P.; Sinha, A.; Rahaman, S. M. W.; Dinda, S.; Bera, J. K. Bifunctional Water Activation for Catalytic Hydration of Organonitriles. *Organometallics* **2012**, *31* (9), 3790–3797.
5. Paul, B.; Maji, M.; Kundu, S. Atom-Economical and Tandem Conversion of Nitriles to N-Methylated Amides Using Methanol and Water. *ACS Catal.* **2019**, *9* (11), 10469–10476.
6. Wang, K. Z.; Jiang, P. B.; Yang, M.; Ma, P.; Qin, J. H.; Huang, X. K.; Ma, L.; Li, R. Metal-Free Nitrogen-Doped Carbon Nanosheets: A Catalyst for the Direct Synthesis of Imines Under Mild Conditions. *Green Chem.* **2019**, *21*, 2448–2461.
7. Hatano, M.; Kuwano, K.; Asukai, R.; Nagayoshi, A.; Hoshihara, H.; Hirata, T.; Umezawa, M.; Tsubaki, S.; Yoshikawa, T.; Sakata, K. Zinc Chloride-Catalyzed Grignard Addition Reaction of Aromatic Nitriles. *Chem. Sci.* **2024**, *15*, 8569–8577.
8. Yan, L. W.; Gou, S. H.; Ye, Z. B.; Zhang, S. H.; Ma, L. H. Self-Healing and Moldable Material with the Deformation Recovery Ability from Self-Assembled Supramolecular Metallogels. *Chem. Commun.* **2014**, *50*, 12847–12850.
9. Li, Y.; Ren, T.; Dong, W.-J. Tuning Photophysical Properties of Triphenylamine and Aromatic Cyano Conjugate-Based Wavelength-Shifting Compounds by Manipulating Intramolecular Charge Transfer Strength. *J. Photochem. Photobiol. A: Chem.* **2013**, *251*, 1–9.
10. Bryden, M. A.; Millward, F.; Matulaitis, T.; Chen, D.; Villa, M.; Cetin, S.; Ceroni, P.; Zysman-Colman, E. Moving Beyond Cyanoarene Thermally Activated Delayed Fluorescence Compounds as Photocatalysts: An Assessment of the Performance of a Pyrimidyl Sulfone Photocatalyst in Comparison to 4CzIPN. *J. Org. Chem.* **2023**, *88* (10), 6364–6373.
11. Chen, S. P.; Pan, T.; Jiang, Q.; Li, J.; Chen, J. M.; Sheng W. B. Regioselectivity for Nucleophilic Substitutions of Aryl Halides with DMF in Deep Eutectic Solvent. *Tetrahedron* **2025**, *176*, 134543.
12. Leadbeater, N. E.; Torenius, H. M.; Tye H. Ionic Liquids as Reagents and Solvents in Conjunction with Microwave Heating: Rapid Synthesis of Alkyl Halides from Alcohols and Nitriles from Aryl Halides. *Tetrahedron* **2003**, *59* (13), 2253–2258.
13. Nguyen, T. T.; Phan, N. T. S. A Metal-Organic Framework $Cu_2(BDC)_2(DABCO)$ as an Efficient and Reusable Catalyst for Ullmann-Type N-Arylation of Imidazoles. *Catal. Lett.* **2014**, *144* (11), 1877–1883.
14. Matthew, R.; Cargill, A.; Katharine, E.; Linton, A.; Graham, S. A.; Dmitrii, S.; Yufit, B.; Judith, A. K.; Howard, B. Annelation Reactions of Pentafluorobenzonitrile. *Tetrahedron* **2010**, *66* (13), 2356–2362.