



NOTE

Solvent Evaporation Method and Crystal Structure of 1,3-Dimethyl-3-(2,2,2-trifluoro-ethyl)-1*H*,3*H*-1-aza-phenalen-2-one

Y. ZHAO^{1,*} and L. ZHANG²

¹College of Physics and Electronic Information, Luoyang Normal University, Luoyang, Henan Province, P.R. China

²College of Chemistry and Chemical Engineering, Luoyang Normal University, Luoyang, Henan Province, P.R. China

*Corresponding author: Tel/Fax: +86 379 65515016, E-mail: luoyangchangchun@126.com

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One new compound [N-arylacrylamides (0.30 mmol), PhI(OAc) (0.6 mmol), NaOAc (0.6 mmol) in NMP (1 mL) was added TMSCF₃ (1.8 mmol)] has been successfully synthesized. Compound shows a one-dimensional framework. The 1D supramolecular structure is formed *via* hydrogen bonding connection.

Keywords: Trifluoromethylation, Crystal structure, PhI(OAc)₂.

The trifluoromethyl moiety is one of the key structural units found in pharmaceuticals, agrochemicals and functional materials mainly due to its excellent metabolic stability, elevated electronegativity and extremely high lipophilicity^{1,2}. Consequently, extensive efforts have been devoted to incorporation the trifluoromethyl group into a series of skeletal structures. Transition-metal-catalyzed trifluoromethylation reactions Starting from aryl halides³, boronic acids⁴, arenes substituted with directing groups⁵ alkynes⁶ and alkenes⁷ have been recognized as powerful methods for the preparation of CF₃-containing compounds.

All the reagents and solvents employed were commercially available and used as received without further purification.

A mixture of N-arylacrylamides (0.30 mmol), PhI(OAc) (0.6 mmol), NaOAc (0.6 mmol) in NMP (1 mL) was added TMSCF₃ (1.8 mmol). After stirring at room temperature for 12 h, the reaction mixture was diluted by adding EtOAc and brine. The aqueous layer was extracted with EtOAc The combined organic layer was dried over MgSO₄, filtered and concentrated. The residue was purified by flash column chromatography on silica gel to give the compound. Finally colourless crystals were formed Fig. 1.

Detection method: Diffraction intensity data of the single crystal of the compound was collected on a Bruker SMART APEX-II CCD diffractometer equipped with a graphite monochromated MoK_α radiation ($\lambda = 0.71073 \text{ \AA}$) by using a ω -scan mode. All the structures were solved by direct methods and refined by full-matrix least-squares methods on F² using the

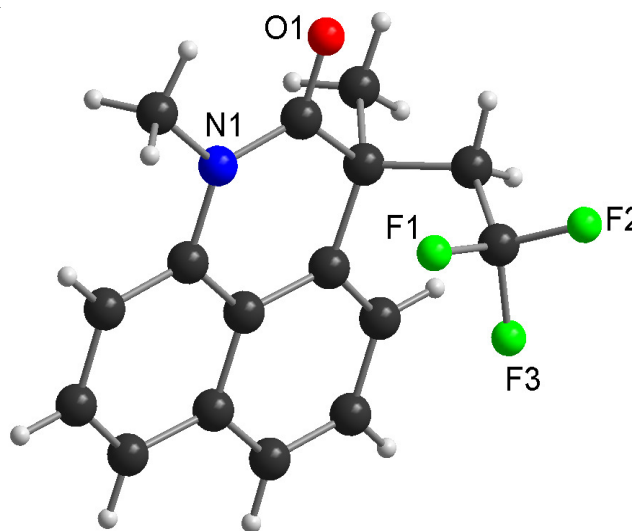


Fig. 1. Molecular structure of the title compound at 30 % probability displacement ellipsoids

program SHELXL 97⁸. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were located by geometrically calculations and their positions and thermal parameters were fixed during the structure refinement. The crystallographic data and experimental details of structural analyses for coordination polymers are summarized in Table-1. Selected bond and angle parameters are listed in Table-2. CCDC: 977359.

TABLE-1
CRYSTALLOGRAPHIC DATA AND STRUCTURE
REFINEMENT SUMMARY FOR COMPLEX

Empirical formula	C ₁₆ H ₁₄ NOF ₃	Z, Calculated density (mg/m ³)	4, 1.419
Formula weight	293.28	Absorption coefficient (mm ⁻¹)	0.116
Crystal system	Monoclinic,	F(000)	608
space group	P2(1)/c		
Unit cell dimensions	a = 9.8366(19) Å b = 10.3480(19) Å c = 14.200(3) Å	Limiting indices	-11 ≤ h ≤ 11 -12 ≤ k ≤ 12 -17 ≤ l ≤ 17
Volume (Å ³)	1373.1(4)	Largest diff. peak and hole (e/Å ³)	0.207 and -0.233
θ range for data collection	2.48-25.50	Goodness-of-fit on F ²	1.033
Final R indices [I > 2σ(I)]	R ₁ = 0.0481 wR ₂ = 0.1168	R indices (all data)	R ₁ = 0.0684, wR ₂ = 0.1298

TABLE-2
SELECTED BOND LENGTHS (Å) AND ANGLES (°) FOR COMPLEX

F(1)-C(1)	1.314(3)	N(1)-C(5)	1.415(3)
N(1)-C(4)	1.359(3)	N(1)-C(15)	1.468(3)
F(3)-C(1)	1.326(3)	O(1)-C(4)	1.222(2)
O(1)-C(4)-N(1)	121.4(2)	F(1)-C(1)-F(2)	106.4(2)
C(4)-N(1)-C(15)	117.20(19)	F(3)-C(1)-F(2)	104.58(19)
C(5)-N(1)-C(15)	118.92(18)	F(1)-C(1)-C(2)	113.2(2)
F(1)-C(1)-F(3)	105.5(2)	F(3)-C(1)-C(2)	114.2(2)

The crystal structure determined by X-ray diffraction reveals that the asymmetric unit is composed of two moieties, one 1,3-dimethyl-1*H*-1-aza-phenalen-2-ol and 1,1,1-trifluoropropane. While in the 1,1,1-trifluoropropane, bond length of F(1)-C(1), F(2)-C(1) and F(3)-C(1) are found to be 1.314(3), 1.333 (3 Å and 1.326 (3) Å, respectively. The bond connecting the pyridine ring is a single bond, which can rotate and the bond length of N(1)-C(15), O(1)-C(4) and C(3)-C(16) are 1.468(3), 1.222(2) Å and 1.547(3) Å, in addition. The dihedral angle between the benzene ring C13 to C14 and the pyridine

ring N1 to C5 is 1.32°. The dihedral angle between the benzene ring C11 to C10 and the pyridine ring N1 to C5 is 1.08°. The chains are further assembled by the intermolecular hydrogen bonding interaction leading to the formation of a 1D framework (Fig. 2).

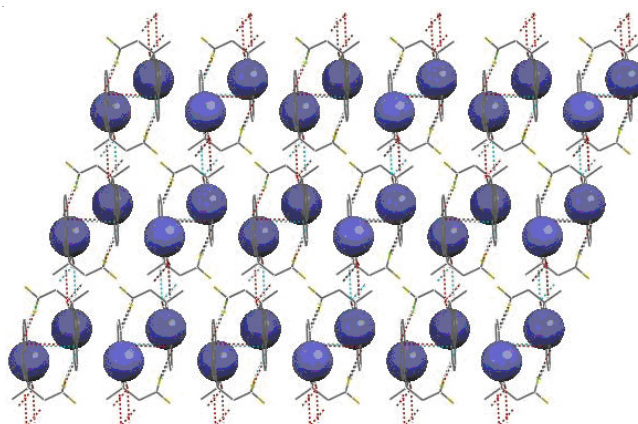


Fig. 2. 1D structure formed *via* hydrogen bonding interactions

REFERENCES

1. P. Kirsch, *Modern Fluoroorganic Chemistry*, Wiley-VCH, Weinheim, Germany (2004).
2. A. Studer, *Angew. Chem. Int. Ed.*, **51**, 8950 (2012).
3. A. Zanardi, M.A. Novikov, E. Martin, J. Benet-Buchholz and V.V. Grushin, *J. Am. Chem. Soc.*, **133**, 20901 (2011).
4. T.D. Senecal, A.T. Parsons and S.L. Buchwald, *J. Org. Chem.*, **76**, 1174 (2011).
5. X. Wang, L. Truesdale and J.-Q. Yu, *J. Am. Chem. Soc.*, **132**, 3648 (2010).
6. Z. Weng, H. Li, W. He, L.-F. Yao, J. Tan, J. Chen, Y. Yuan and K.-W. Huang, *Tetrahedron*, **68**, 2527 (2012).
7. Y. Miyake, S.-I. Ota and Y. Nishibayashi, *Chem. Eur. J.*, **18**, 13255 (2012).
8. G.M. Sheldrick, SHELXTL97, Program for the Refinement of Crystal Structure, University of Gottingen, Germany (1997).