Supplementary Information

Facile one-pot synthesis of novel dicyanoanilines fused to thiopyran ring via Et₃N/H₂O catalyzed
pseudo four-component reactions

M. Saeed Abaee, Sodabeh Forghani, Mohammad M. Mojtahedi

Department of Organic Chemistry and Natural Products, Chemistry and Chemical Engineering Research Center of
Iran, Pajohesh Blvd., 17th km of Tehran-Karaj Highway, P.O.Box 14335-186, Tehran, Iran

Klaus Harms

Fachbereich Chemie der Philipps-Universitaet Marburg, Hans-Meerwein-Strasse, D-35032 Marburg, Germany

Table 1. Crystal data and structure refinement for **4c**.

Crystal data		
Identification code	4c	
Habitus, colour	plate, colorless	
Crystal size	0.42 x 0.24 x 0.06 mm ³	
Crystal system	Monoclinic	
Space group	P2 ₁ /c	Z = 4
Unit cell dimensions	a = 7.8313(3) Å	α = 90°.
	b = 17.4673(9) Å	β = 99.258(3)°
	c = 11.2292(4) Å	γ = 90°.
	1516.05(11) Å ³	
Volume	10711 peaks with Theta 2.9 to 27.2°.	
Cell determination	C ₁₈ H ₁₅ N ₃ O S	
Empirical formula	C ₁₈ H ₁₅ N ₃ O S	
Moiety formula	321.39	
Formula weight	1.408 Mg/m ³	
Density (calculated)	0.222 mm ⁻¹	
Absorption coefficient	672	
F(000)		
Data collection:		
Diffraction type	STOE IPDS 2T	
Wavelength	0.71073 Å	
Temperature	100(2) K	
Theta range for data collection	3.182 to 25.245°.	
Index ranges	-9<=h<=8, -20<=k<=19, -13<=l<=13	
Data collection software	STOE X-Area ^[1]	
Cell refinement software	STOE X-Area ^[1]	
Data reduction software	STOE X-RED ^[2]	
Solution and refinement:		
Reflections collected	8371	
Independent reflections	2732 [R(int) = 0.0319]	
Completeness to theta = 25.242°	99.8 %	
Observed reflections	2314[I>2sigma(I)]	
Reflections used for refinement	2732	
Absorption correction	Integration ^[2]	
Max. and min. transmission	0.9875 and 0.9611	
Largest diff. peak and hole	0.221 and -0.287 e.Å ⁻³	
Solution	Direct methods	
Refinement	Full-matrix least-squares on F ²	
Treatment of hydrogen atoms	CH geom., constr., NH located, isotr. ref.	
Programs used	SHELXS-97 ^[3]	
	SHELXL-2014/7 (Sheldrick, 2014) ^[3]	
	DIAMOND ^[4]	
Data / restraints / parameters	2732 / 0 / 217	
Goodness-of-fit on F ²	1.040	
R index (all data)	wR2 = 0.0703	
R index conventional [I>2sigma(I)]	R1 = 0.0287	

Table 2. Atomic coordinates and equivalent isotropic displacement parameters ($\text{\AA}^2$) for 4c. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	$U(\text{eq})$	Occupancy
C1	-0.1417(2)	0.24113(8)	0.85439(13)	0.0214(3)	1
C2	-0.18926(19)	0.19230(8)	0.74050(12)	0.0169(3)	1
C3	-0.03065(18)	0.17120(8)	0.68844(11)	0.0139(3)	1
C4	0.01418(18)	0.09499(8)	0.67148(11)	0.0140(3)	1
C5	0.16468(18)	0.07542(8)	0.62381(11)	0.0138(3)	1
C6	0.26940(18)	0.13676(8)	0.59623(11)	0.0136(3)	1
C7	0.22687(18)	0.21379(8)	0.61435(11)	0.0132(3)	1
C8	0.07528(18)	0.23072(8)	0.65939(11)	0.0135(3)	1
C9	0.01324(18)	0.31088(8)	0.67518(11)	0.0152(3)	1
C10	-0.09415(19)	0.03366(8)	0.70187(12)	0.0163(3)	1
C11	0.42143(18)	0.11786(8)	0.54603(12)	0.0158(3)	1
C12	0.34274(17)	0.27504(8)	0.58030(12)	0.0139(3)	1
C13	0.36304(18)	0.28308(8)	0.45964(12)	0.0157(3)	1
C14	0.47139(18)	0.33811(8)	0.42521(12)	0.0169(3)	1
C15	0.56470(18)	0.38612(8)	0.51122(13)	0.0166(3)	1
C16	0.54479(19)	0.37960(8)	0.63156(12)	0.0175(3)	1
C17	0.43336(19)	0.32461(8)	0.66485(12)	0.0164(3)	1
C18	0.7685(2)	0.48853(9)	0.55031(15)	0.0244(3)	1
N1	-0.17417(17)	-0.01740(7)	0.72637(12)	0.0238(3)	1
N2	0.20752(19)	0.00169(7)	0.60745(11)	0.0188(3)	1
N3	0.54126(17)	0.09948(7)	0.50599(12)	0.0231(3)	1
S1	-0.02262(5)	0.32780(2)	0.82945(3)	0.01549(11)	1
O1	0.66856(14)	0.43788(6)	0.46669(9)	0.0232(2)	1

Table 3. Bond lengths [$\text{\AA}$] and angles [$^\circ$] for 4c.

C1-C2	1.5325(19)	C9-H9B	0.9900
C1-S1	1.8233(15)	C10-N1	1.1486(19)
C1-H1A	0.9900	C11-N3	1.1496(19)
C1-H1B	0.9900	C12-C17	1.3921(19)
C2-C3	1.501(2)	C12-C13	1.3965(19)
C2-H2A	0.9900	C13-C14	1.378(2)
C2-H2B	0.9900	C13-H13	0.9500
C3-C4	1.3976(19)	C14-C15	1.394(2)
C3-C8	1.401(2)	C14-H14	0.9500
C4-C5	1.413(2)	C15-O1	1.3637(18)
C4-C10	1.441(2)	C15-C16	1.390(2)
C5-N2	1.3508(19)	C16-C17	1.389(2)
C5-C6	1.4136(19)	C16-H16	0.9500
C6-C7	1.4088(19)	C17-H17	0.9500
C6-C11	1.435(2)	C18-O1	1.4283(18)
C7-C8	1.395(2)	C18-H18A	0.9800
C7-C12	1.4919(19)	C18-H18B	0.9800
C8-C9	1.5019(18)	C18-H18C	0.9800
C9-S1	1.8232(13)	N2-H21	0.88(2)
C9-H9A	0.9900	N2-H22	0.83(2)
C2-C1-S1	113.30(10)	S1-C9-H9B	109.3
C2-C1-H1A	108.9	H9A-C9-H9B	108.0
S1-C1-H1A	108.9	N1-C10-C4	176.90(15)
C2-C1-H1B	108.9	N3-C11-C6	177.08(15)
S1-C1-H1B	108.9	C17-C12-C13	118.30(13)
H1A-C1-H1B	107.7	C17-C12-C7	122.39(12)
C3-C2-C1	110.89(12)	C13-C12-C7	119.31(12)
C3-C2-H2A	109.5	C14-C13-C12	120.91(13)
C1-C2-H2A	109.5	C14-C13-H13	119.5
C3-C2-H2B	109.5	C12-C13-H13	119.5
C1-C2-H2B	109.5	C13-C14-C15	120.20(13)
H2A-C2-H2B	108.0	C13-C14-H14	119.9
C4-C3-C8	120.26(13)	C15-C14-H14	119.9
C4-C3-C2	121.91(12)	O1-C15-C16	125.29(13)
C8-C3-C2	117.80(12)	O1-C15-C14	114.95(12)
C3-C4-C5	121.69(13)	C16-C15-C14	119.74(13)
C3-C4-C10	120.35(13)	C17-C16-C15	119.48(13)
C5-C4-C10	117.95(12)	C17-C16-H16	120.3
N2-C5-C4	121.52(13)	C15-C16-H16	120.3
N2-C5-C6	121.83(13)	C16-C17-C12	121.34(13)
C4-C5-C6	116.64(12)	C16-C17-H17	119.3
C7-C6-C5	122.23(12)	C12-C17-H17	119.3
C7-C6-C11	120.45(12)	O1-C18-H18A	109.5
C5-C6-C11	117.31(12)	O1-C18-H18B	109.5
C8-C7-C6	119.32(12)	H18A-C18-H18B	109.5
C8-C7-C12	121.94(12)	O1-C18-H18C	109.5
C6-C7-C12	118.71(12)	H18A-C18-H18C	109.5
C7-C8-C3	119.83(12)	H18B-C18-H18C	109.5
C7-C8-C9	123.42(12)	C5-N2-H21	120.9(13)
C3-C8-C9	116.71(12)	C5-N2-H22	121.8(12)
C8-C9-S1	111.44(9)	H21-N2-H22	117.1(18)
C8-C9-H9A	109.3	C9-S1-C1	99.91(6)
S1-C9-H9A	109.3	C15-O1-C18	117.74(11)
C8-C9-H9B	109.3		

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($\text{\AA}^2$) for 4c.
The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C1	0.0259(8)	0.0199(7)	0.0211(7)	-0.0034(6)	0.0116(6)	-0.0032(6)
C2	0.0162(7)	0.0149(7)	0.0209(7)	-0.0018(5)	0.0068(6)	-0.0004(6)
C3	0.0145(7)	0.0160(7)	0.0107(6)	-0.0005(5)	0.0005(5)	0.0013(6)
C4	0.0158(7)	0.0140(7)	0.0122(6)	0.0002(5)	0.0023(5)	-0.0005(5)
C5	0.0159(7)	0.0131(7)	0.0119(6)	-0.0002(5)	0.0007(5)	0.0019(5)
C6	0.0144(7)	0.0155(7)	0.0112(6)	0.0000(5)	0.0027(5)	0.0016(5)
C7	0.0149(7)	0.0145(7)	0.0095(6)	0.0000(5)	0.0003(5)	0.0004(5)
C8	0.0159(7)	0.0135(6)	0.0108(6)	-0.0004(5)	0.0013(5)	0.0014(5)
C9	0.0168(7)	0.0153(7)	0.0140(6)	0.0001(5)	0.0044(5)	0.0014(6)
C10	0.0172(7)	0.0154(7)	0.0169(7)	-0.0008(5)	0.0042(5)	0.0045(6)
C11	0.0185(8)	0.0119(6)	0.0169(6)	-0.0007(5)	0.0024(6)	-0.0011(6)
C12	0.0127(7)	0.0129(6)	0.0167(6)	0.0007(5)	0.0040(5)	0.0034(5)
C13	0.0152(7)	0.0164(7)	0.0157(7)	-0.0026(5)	0.0031(5)	0.0008(6)
C14	0.0166(7)	0.0197(7)	0.0154(7)	0.0013(5)	0.0061(5)	0.0013(6)
C15	0.0130(7)	0.0142(7)	0.0232(7)	0.0031(5)	0.0044(5)	0.0011(6)
C16	0.0168(7)	0.0151(7)	0.0195(7)	-0.0024(5)	-0.0005(5)	-0.0002(6)
C17	0.0183(7)	0.0164(7)	0.0146(6)	0.0006(5)	0.0030(5)	0.0021(6)
C18	0.0189(8)	0.0171(7)	0.0361(9)	0.0026(6)	0.0011(6)	-0.0044(6)
N1	0.0232(7)	0.0176(7)	0.0326(7)	0.0022(5)	0.0105(6)	0.0002(6)
N2	0.0199(7)	0.0125(6)	0.0266(7)	-0.0003(5)	0.0117(6)	0.0010(5)
N3	0.0217(7)	0.0202(7)	0.0293(7)	-0.0029(5)	0.0103(6)	0.0016(5)
S1	0.01827(19)	0.01397(18)	0.01460(17)	-0.00214(13)	0.00380(13)	0.00117(13)
O1	0.0227(6)	0.0226(5)	0.0250(5)	0.0017(4)	0.0063(4)	-0.0089(4)

Table 5. Hydrogen coordinates and isotropic displacement parameters ($\text{\AA}^2$) for 4c.

	x	y	z	U(eq)	Occupancy
H1A	-0.0708	0.2100	0.9175	0.026	1
H1B	-0.2491	0.2557	0.8847	0.026	1
H2A	-0.2487	0.1451	0.7606	0.020	1
H2B	-0.2699	0.2212	0.6798	0.020	1
H9A	-0.0960	0.3196	0.6190	0.018	1
H9B	0.1002	0.3477	0.6548	0.018	1
H13	0.3013	0.2502	0.4005	0.019	1
H14	0.4825	0.3433	0.3426	0.020	1
H16	0.6069	0.4125	0.6906	0.021	1
H17	0.4187	0.3207	0.7470	0.020	1
H18A	0.8536	0.4590	0.6053	0.037	1
H18B	0.6918	0.5158	0.5968	0.037	1
H18C	0.8285	0.5256	0.5062	0.037	1
H21	0.141(3)	-0.0361(12)	0.6247(17)	0.034(5)	1
H22	0.292(3)	-0.0100(10)	0.5755(16)	0.022(5)	1

Table 6. Torsion angles [°] for 4c.

S1-C1-C2-C3	56.57(15)	C2-C3-C8-C7	177.99(11)
C1-C2-C3-C4	122.22(13)	C4-C3-C8-C9	177.32(11)
C1-C2-C3-C8	-56.30(16)	C2-C3-C8-C9	-4.13(17)
C8-C3-C4-C5	-0.73(19)	C7-C8-C9-S1	-125.19(12)
C2-C3-C4-C5	-179.22(12)	C3-C8-C9-S1	57.01(14)
C8-C3-C4-C10	179.69(12)	C8-C7-C12-C17	65.93(18)
C2-C3-C4-C10	1.20(19)	C6-C7-C12-C17	-116.36(15)
C3-C4-C5-N2	-179.95(12)	C8-C7-C12-C13	-114.59(15)
C10-C4-C5-N2	-0.36(19)	C6-C7-C12-C13	63.13(17)
C3-C4-C5-C6	1.14(18)	C17-C12-C13-C14	0.7(2)
C10-C4-C5-C6	-179.27(12)	C7-C12-C13-C14	-178.82(13)
N2-C5-C6-C7	-179.22(12)	C12-C13-C14-C15	0.9(2)
C4-C5-C6-C7	-0.31(18)	C13-C14-C15-O1	179.50(13)
N2-C5-C6-C11	2.01(19)	C13-C14-C15-C16	-1.6(2)
C4-C5-C6-C11	-179.09(12)	O1-C15-C16-C17	179.47(13)
C5-C6-C7-C8	-0.93(19)	C14-C15-C16-C17	0.7(2)
C11-C6-C7-C8	177.81(12)	C15-C16-C17-C12	0.9(2)
C5-C6-C7-C12	-178.71(11)	C13-C12-C17-C16	-1.6(2)
C11-C6-C7-C12	0.03(18)	C7-C12-C17-C16	177.89(13)
C6-C7-C8-C3	1.36(18)	C8-C9-S1-C1	-46.11(11)
C12-C7-C8-C3	179.07(12)	C2-C1-S1-C9	-7.28(12)
C6-C7-C8-C9	-176.37(12)	C16-C15-O1-C18	1.5(2)
C12-C7-C8-C9	1.33(19)	C14-C15-O1-C18	-179.66(12)
C4-C3-C8-C7	-0.56(19)		

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for 4c [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N2-H21...S1#1	0.88(2)	2.63(2)	3.4863(14)	163.2(17)
N2-H22...N3#2	0.83(2)	2.32(2)	3.0695(19)	151.4(16)

Symmetry transformations used to generate equivalent atoms:

#1 -x,y-1/2,-z+3/2 #2 -x+1,-y,-z+1

- [1] *X-Area*, STOE & Cie GmbH, Darmstadt, Germany, **2011**.
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- [3] G. M. Sheldrick, *Acta crystallographica. Section A, Foundations of crystallography* **2008**, 64, 112–122.
- [4] K. Brandenburg, *Diamond - Crystal and Molecular Structure Visualization*, Crystal Impact - Dr. H. Putz & Dr. K. Brandenburg GbR, Bonn, Germany, **2014**.