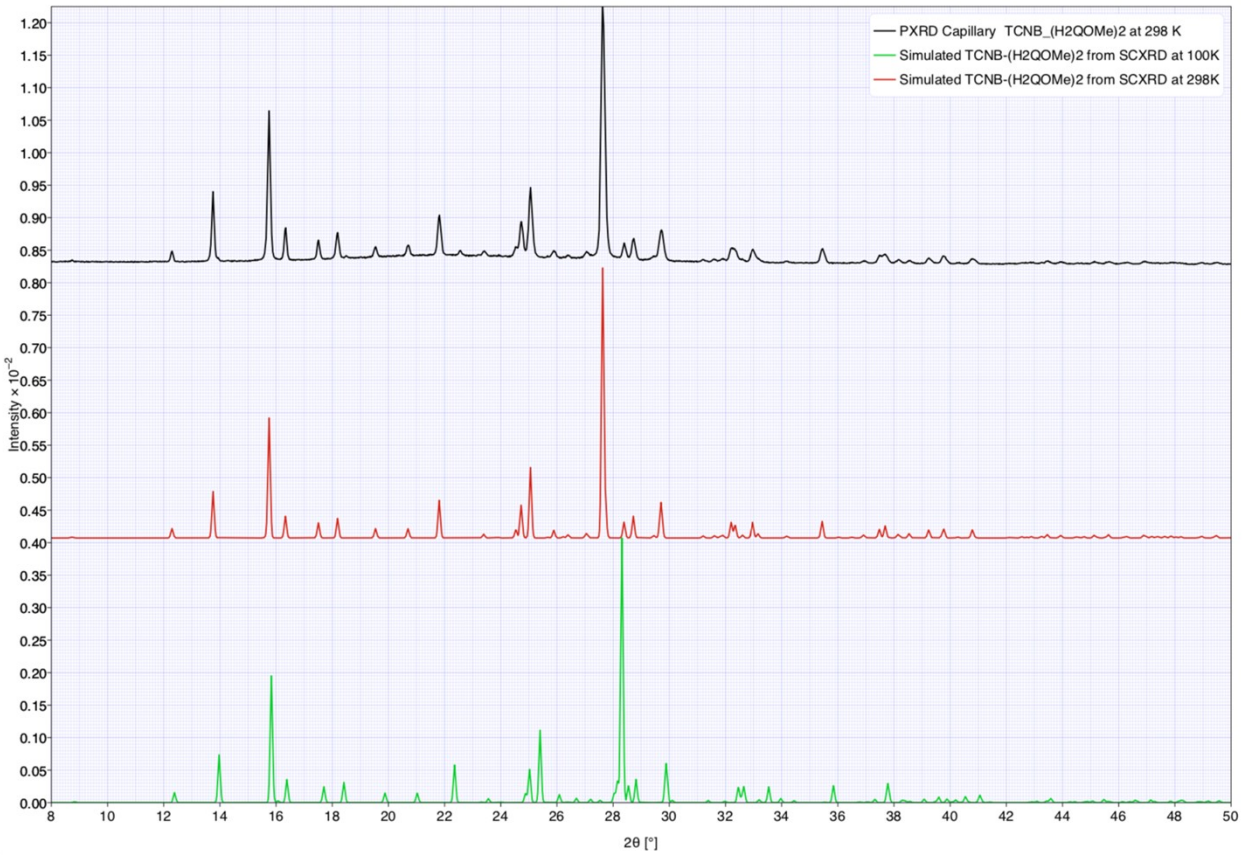
Series of charge transfer complexes obtained as crystals in a confined environment

Ali Sanda Bawa[a,b], Rita Meunier-Prest[a], Yoann Rousselin[a], Jean-Pierre Couvercelle[a], Christine Stern[a], Bernard Malézieux[c], Marcel Bouvet*[a]

Supporting Information



External Reference	PXRD TCNB_(H2QOMe)2	SCXRD TCNB_(H2QOMe)2
Temperature	298 K	100 K
Crystal system	Triclinic	Triclinic
Space group	*P* -1	*P* -1
a (Å)	7.1960(1)	7.0977(3)
b (Å)	7.7457(2)	7.7054(4)
c (Å)	10.3037(3)	10.1834(5)
α (°)	79.226(2)	79.516(2)
β (°)	86.831(1)	85.590(3)
γ (°)	70.689(1)	70.030(3)
Volume (Å³)	532(1)	515(1)
Rp	3.26	
wRp	4.49	

Figure S1. Powder XRD spectrum of TCNB-$(H_2Q_{OMe})_2$ compared to simulated spectra from single crystal XRD at 100 K and 298 K(top) and comparative crystallographic data obtained on PXRD and SCXRD (bottom).

PXRD Analysis:

Analyses are performed from 2θ = 3° to 50° by default. X-ray powder analysis diffraction were carried out in transmission mode unless mentioned otherwise. The samples (few milligrams) are introduced without being crushed in 1 mm diameter glass capillaries to avoid preferential orientation. The capillaries are sealed to avoid contact with air. The analysis is performed in transmission mode by using a focusing X-ray mirror with divergence slits and anti-scatter slits (aperture 0.5°), on an Empyrean diffractometer from PANalytical Company equipped with a copper anticathode tube (wavelength λ Kα1 = 1.54060 Å/Kα2 = 1.54443 Å) and with a PIXcel 1D detector with anti-scatter slits of 7.5 mm. The calibration of the analytical instrument is checked before each analytical batch according to quality system. The powder diffractograms were processed using the HighScore Plus software[1] or Jana Software.[2] Lattice parameters were performed using indexing methods included in TREOR,[3] ITO[4] and DICVOL.[3] Le Bail[5] refinement was performed with the most plausible unit cell (Table in Figure S1)

Bibliography

1 *Highscore Plus Software 4.8*, Malvern Panalytical B.V., 2018.
2 V. Petricek, M. Dusek and L. Palatinus, *Zeitschrift für Kristallographie - Crystalline Materials*, 2014, **229**, 345–352.
3 A. Boultif and D. Louer, *Journal of Applied Crystallography*, 2004, **37**, 724–731.
4 J. W. Visser, *Journal of Applied Crystallography*, 1969, **2**, 89–95.
5 A. Le Bail, H. Duroy and J. L. Fourquet, *Material Research Bulletin*, 1988, **23**, 447–452.

Table S1. TGA data of TCNB-$(H_2Q_{OMe})_2$ and TCNB-H_2Q CTC obtained in confined environments.

	ONSET (°C)	ENDSET (°C)	Weight loss (%)	ONSET (°C)	ENDSET (°C)	Weight loss (%)
TCNB				271.7	312.4	
Grinded TCNB				260.4	300.5	
H_2Q	186.0	222.3				
Grinded H_2Q	183.2	214.9				
TCNB-H_2Q CTC	**181.0**	**207.6**	**38**	**265.5**	**292.3**	
Grinded TCNB-H_2Q mixture	182.2	217.2	40	272.7	300.1	
H_2Q_{OMe}	179.6	217.6				
TCNB-$(H_2Q_{OMe})_2$ CTC	**180.2**	**218.9**	**68**	**253.1**	**274.3**	
Grinded TCNB-$(H_2Q_{OMe})_2$ mixture	158.7	195.5	69	246.0	274.3	

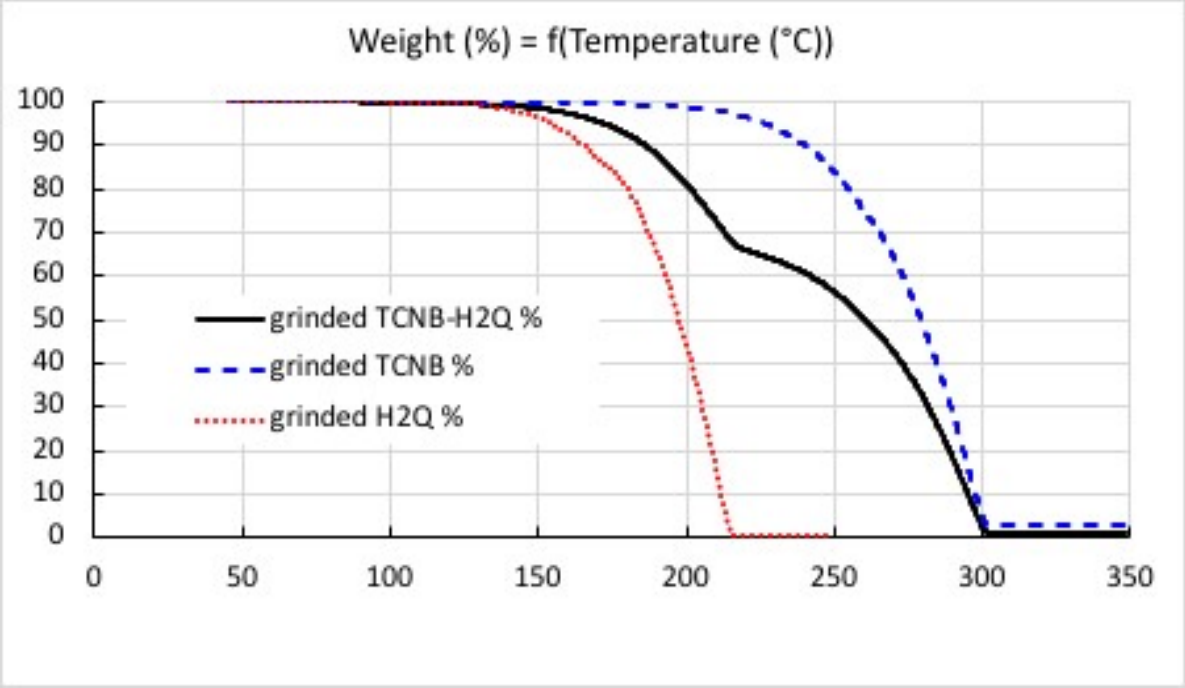
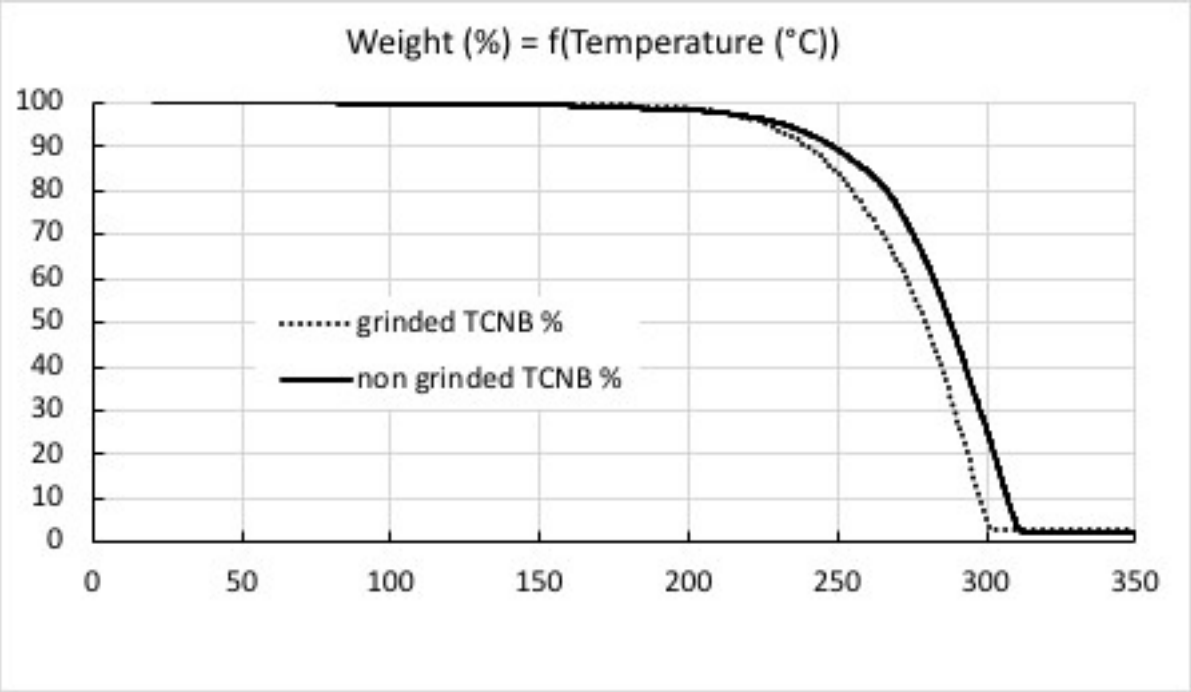


Figure S2. TGA traces of the grinded TCNB-H_2Q mixture (black line) and grinded crystalline H_2Q (dotted red line) and TCNB (dashed blue line).



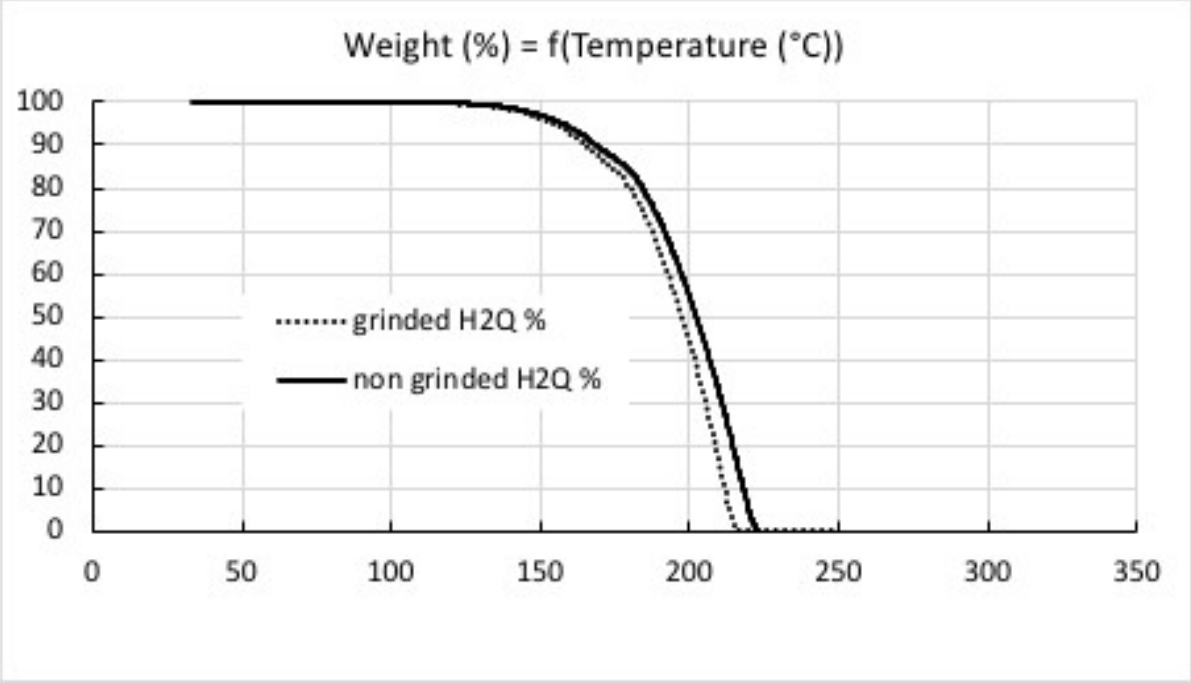


Figure S3. (top) TGA traces of grinded (dashed line) and non-grinded (black line) TCNB; (bottom) TGA traces of grinded (dashed line) and non-grinded (black line) H_2Q.

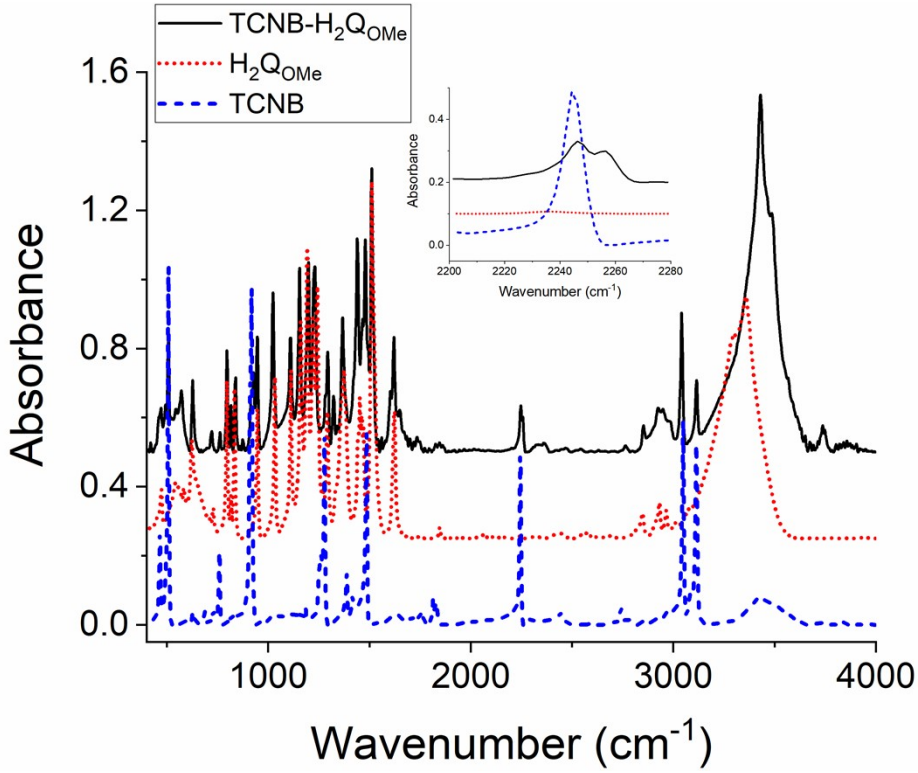


Figure S4. Infrared spectra of TCNB- H_2Q_{OMe} crystals compared to these of TCNB and H_2Q_{OMe}.

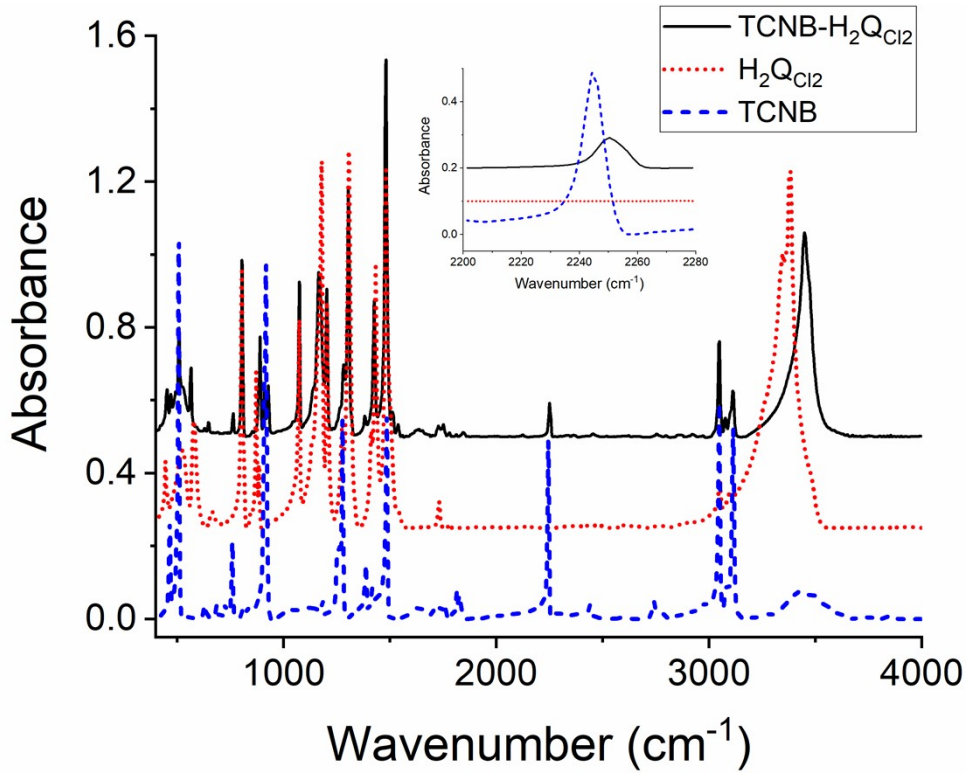
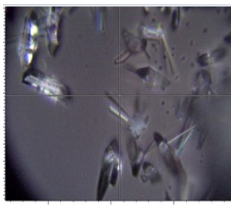


Figure S5. Infrared spectra of TCNB- H_2Q_{Cl2} crystals compared to these of TCNB and H_2Q_{Cl2}.



TCNB	H_2QF_4	TCNB- H_2QF_4
405 w		409 w
	448 m	
460 vw	457 m	
505 vw		
550 m		551 w
	568 VS	
723 m		724 w
1034 vw		
	1161 vw	
1260 S	1256 vw	1261 S
1540 m		1540 m
1598 m		1600 w
1607 sh		1608 w
	1667 w	
2239 VS		2240 VS
2249 sh		2250 w

Figure S6. Raman data of TCNB-H_2Q_{F4} crystals compared to these of TCNB and H_2Q_{F4}. A photograph of the crystals obtained in a confined environment is shown.

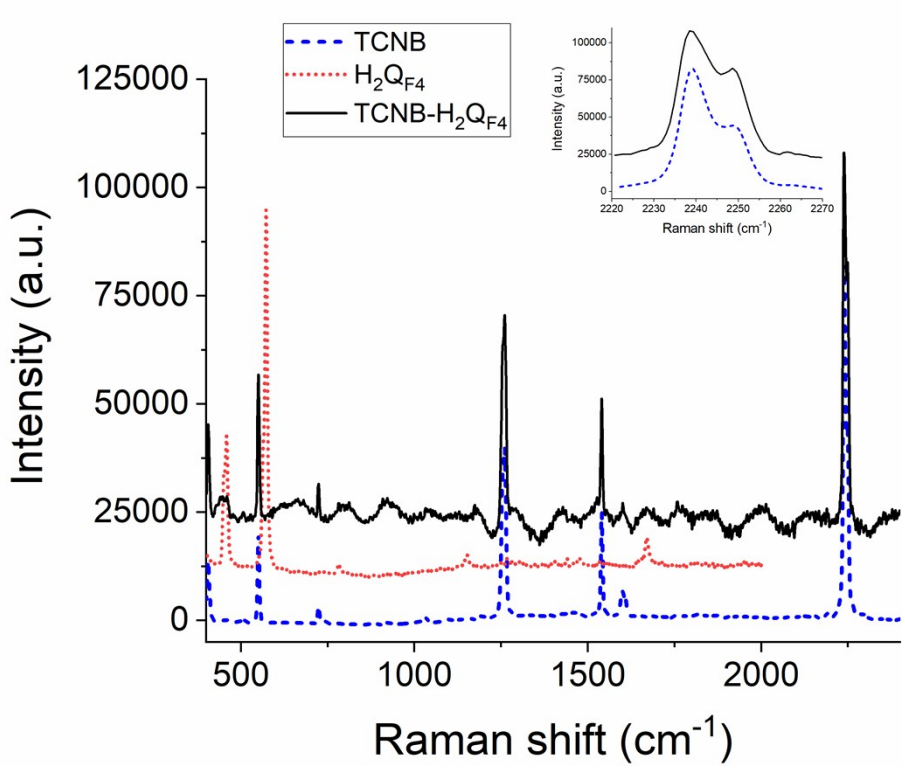
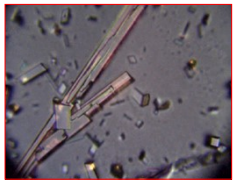


Figure S7. Raman spectra of TCNB-H_2Q_{F4} crystals compared to these of TCNB and H_2Q_{F4}.



TCNB	H_2Q_{OMe2}	TCNB-H_2Q_{OMe2}
405 w		406 vw
460 vw	471 m	468 m
505 vw		511 vw
	528 w	527 vw
550 m		550 vw
	590 S	587 vw
		618 vw
723 m		723 m
	807 VS	802 vw 812 vw
	916 vw	
	991 m	
1034 vw	1036 S	1038 w
	1150 w	
	1180 w	
	1218 w	
1260 S		1254 S
	1350 m	1348 S
		1364 vw
	1455 vw	
	1471 S	
		1513 S
1540 m		1544 VS
1598 m		
1607 sh	1611 m	1605 m
		1634 vw
2239 VS		2243 VS
2250		2260 w

Figure S8. Raman data of TCNB-H_2Q_{OMe2} crystals compared to these of TCNB and H_2Q_{OMe2}. A photograph of the crystals obtained in a confined environment is shown.

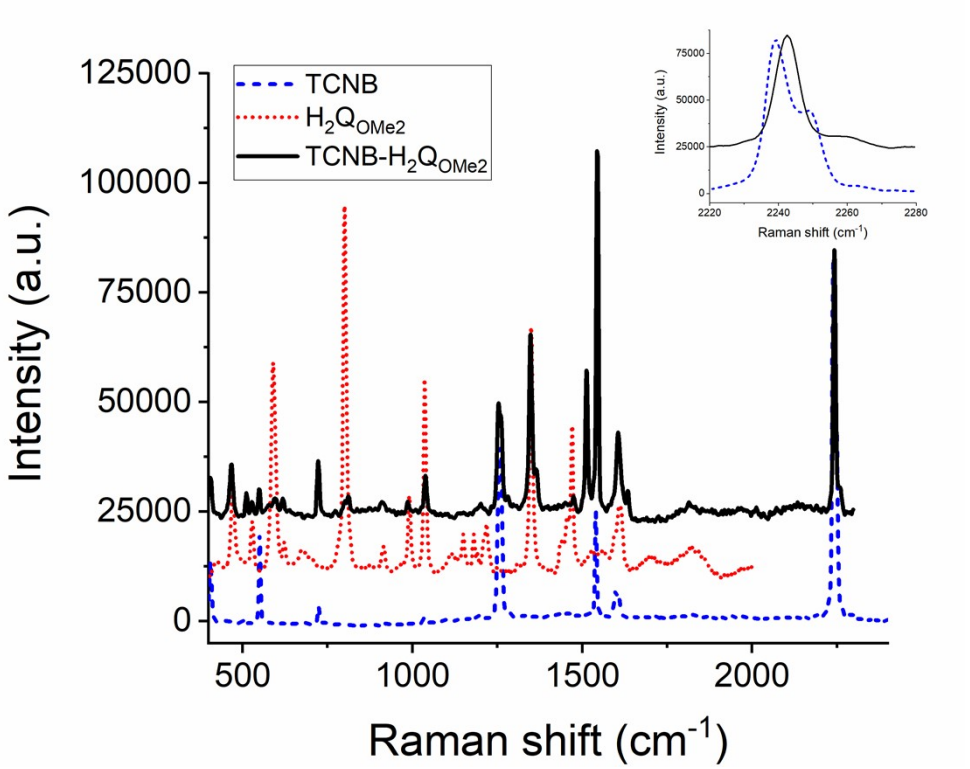
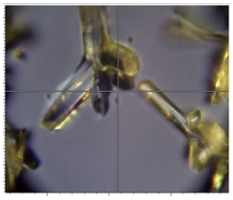


Figure S9. Raman spectra of TCNB-H_2Q_{OMe2} crystals compared to these of TCNB and H_2Q_{OMe2}.



TCNB	H_2Q_{Cl2}	TCNB- H_2Q_{Cl2}
405 w	409 vw	407 w
460 vw		
	476 S	477 w
505 vw		
550 m		550 w
	580 vw	
	709 VS	705 w
723 m		722 w
	977 S	974 vw
1034 vw		1038 vw
	1167 vw	1172 vw
1260 S		1260 S
	1310 w	
		1322 m
1540 m		1540 F
	1579 w	1572 m
1598 m	1603 w	1600 S
1607 sh	1611 w	
	1622 w	
	1669 vw	
2239 VS		2245 VS
2249 sh		2256 sh

Figure S10. Raman data of TCNB-H_2Q_{Cl2} crystals compared to these of TCNB and H_2Q_{Cl2}. A photograph of the crystals obtained in a confined environment is shown.

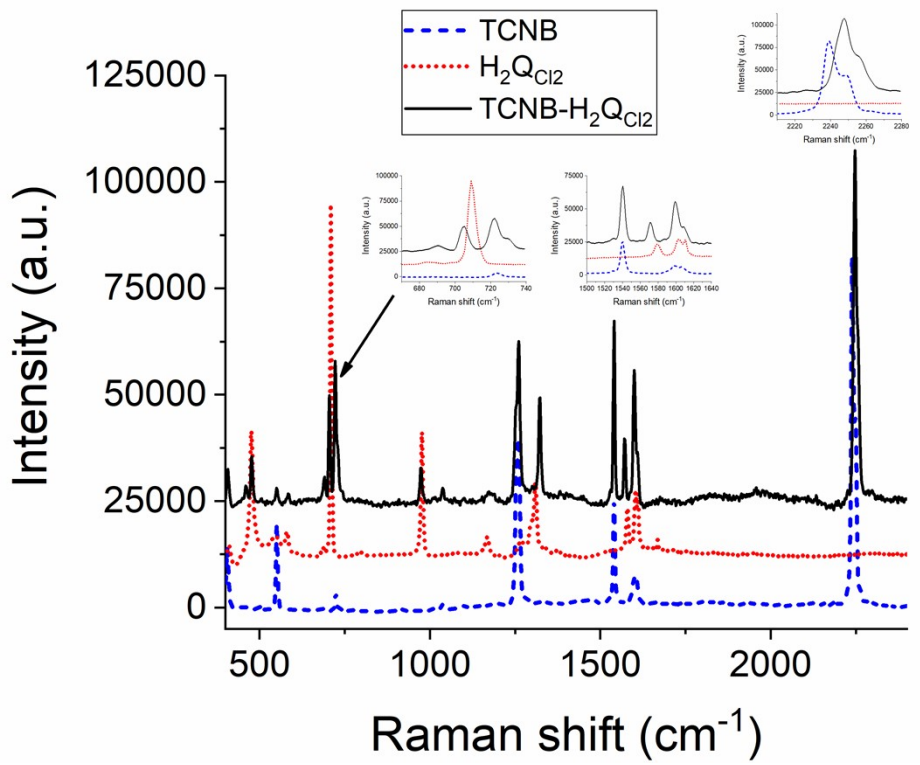


Figure S11. Raman spectra of TCNB- H_2Q_{Cl2} crystals compared to these of TCNB and H_2Q_{Cl2}.

TCNB	H_2Q_{OMe}	TCNB-H_2Q_{OMe}
405 w		408 m
460 vw	473 w	467 w
505 vw		507 vw
550 m	543 vw	547 w
		571 vw
	580 w	
	615 m	
		645 w
		675 vw
723 m		721 w
	729 F	
	796 VW	795 w
	812 vw	
		854 m
	945 F	946 vw
1034 vw	1036 m	1027 vw
	1168 F	
		1185 vw
	1242 m	1234 sh
		1250 F
1260 S		1260 F
	1289 m	1293 F
	1359 m	1365 m
	1467 w	
		1495 vw
		1511 vw
1540 m		1542 F
1598 m		1601 F
1607 sh		
	1622 w	
2239 VS		2239 VW
2249 sh		2247 VW
		2260 m

Figure S12. Raman data of TCNB-H_2Q_{OMe} crystals compared to these of TCNB and H_2Q_{OMe}. A photograph of the crystals obtained in a confined environment is shown.

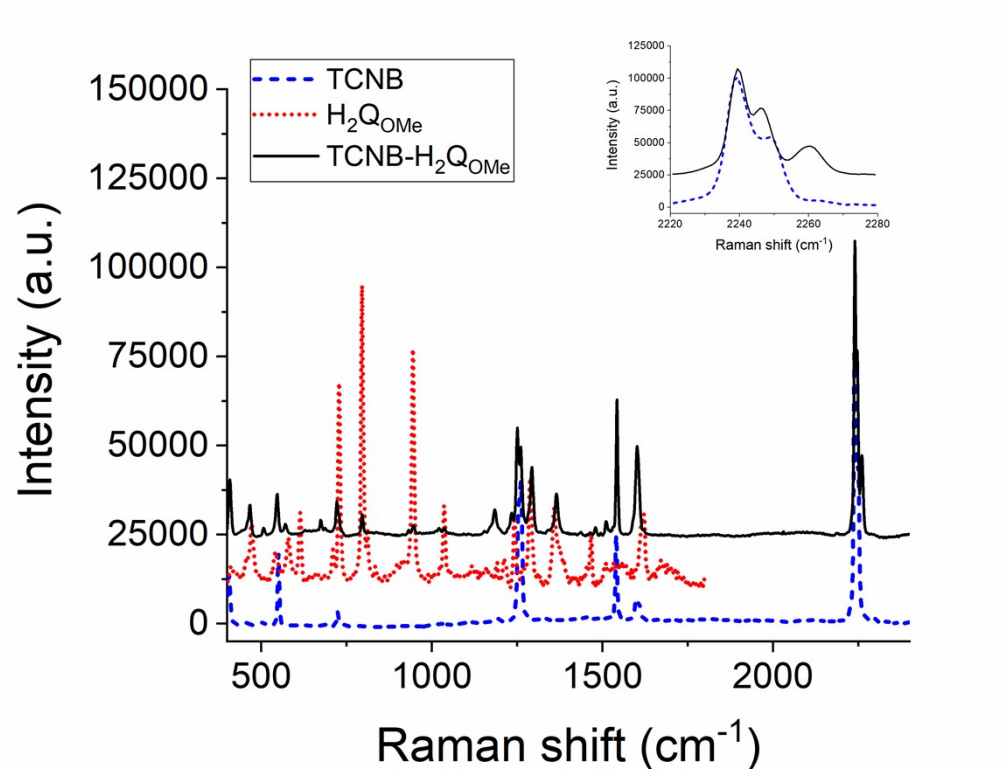
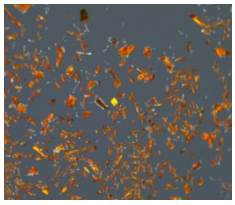


Figure S13. Raman spectra of TCNB-H_2Q_{OMe} crystals compared to these of TCNB and H_2Q_{OMe}.



TCNB	H_2Q	TCNB-H_2Q
405 w		409 m
460 vw	466 sh	460 w
	476 m	470 S
505 vw		505 w
550 m		548 m
		580 w
	645 m	645 w
	703 vw	709 sh
723 m		722 S
		730 S
	832 m	836 w
	854 VW	854 m
1034 vw		1035 w
	1168 F	1162 S
		1227 S
1260 S	1256 F	1261 VS
1540 m		1540 VS
1598 m		1598 VS
	1604 e	
1607 sh	1610 f	
	1626 f	1622w
		1635 sh
2239 VS		2236 S
2249 sh		2259 S

Figure S14. Raman data of TCNB-H_2Q crystals compared to these of TCNB and H_2Q. A photograph of the crystals obtained in a confined environment is shown.

TCNB-H2Q

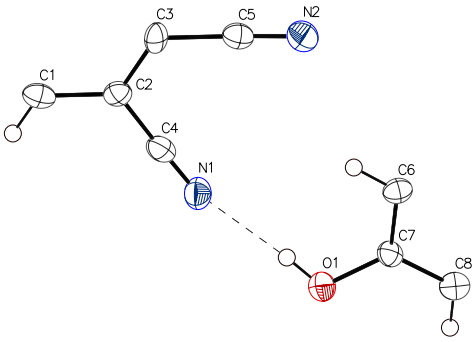
Report created with **ReportPlus**

Submitted by: **Ali SANDA BAWA**

Solved by: **Yoann Rousselin**

Sample ID: **20191118MBTCNBH2Q**

Crystal Data and Experimental



Experimental. Single clear light orange plate-shaped crystals of **TCNB-H2Q** were recrystallized by sublimation. A suitable crystal 0.16x0.09x0.06 mm^3 was selected and mounted on a MITIGEN holder oil on a Bruker D8 Venture diffractometer. The crystal was kept at a steady T = 100.0(1) K during data collection. The structure was solved with the **ShelXT** (Sheldrick, 2015) structure solution program using the Intrinsic Phasing solution method and by using **Olex2** (Dolomanov et al., 2009) as the graphical interface. The model was refined with version 2018/3 of **ShelXL** (Sheldrick, 2015) using Least Squares minimization.

Crystal Data. $C_{16}H_8N_4O_2$, M_r = 288.26, triclinic, P-1 (No. 2), a = 6.3120(4) Å, b = 7.4057(5) Å, c = 8.1661(5) Å, α = 108.309(5)°, β = 109.791(4)°, γ = 92.810(5)°, V = 335.79(4) Å^3, T = 100.0(1) K, Z = 1, Z' = 0.5, μ(CuK$_\alpha$) = 0.817, 2906 reflections measured, 1163 unique (R_{int} = 0.0615) which were used in all calculations. The final wR_2 was 0.1915 (all data) and R_1 was 0.0934 (I > 2(I)).

Compound	**TCNB-H2Q**
CCDC	**1994293**
Formula	$C_{16}H_8N_4O_2$
$D_{calc.}$/ g cm^{-3}	1.425
μ/mm^{-1}	0.817
Formula Weight	288.26
Color	clear light orange
Shape	plate
Size/mm^3	0.16x0.09x0.06
T/K	100.0(1)
Crystal System	triclinic
Space Group	P-1
a/Å	6.3120(4)
b/Å	7.4057(5)
c/Å	8.1661(5)
α/°	108.309(5)
β/°	109.791(4)
γ/°	92.810(5)
V/Å^3	335.79(4)
Z	1
Z'	0.5
Wavelength/Å	1.541840
Radiation type	CuK$_\alpha$
Θ_{min}/°	6.153
Θ_{max}/°	66.706
Measured Refl.	2906
Independent Refl.	1163
Reflections with I > 2(I)	927
R_{int}	0.0615
Parameters	101
Restraints	0
Largest Peak	0.279
Deepest Hole	-0.313
GooF	1.290
wR_2 (all data)	0.1915
wR_2	0.1831
R_1 (all data)	0.1149
R_1	0.0934

Structure Quality Indicators

Reflections:	d min (Cu) 0.84	I/σ 13.6	Rint 6.15%	complete 98%
Refinement:	Shift 0.000	Max Peak 0.3	Min Peak -0.3	GooF 1.290

A clear light orange plate-shaped crystal with dimensions 0.16x0.09x0.06 mm^3 was mounted on a MITIGEN holder oil. Data were collected using a Bruker D8 Venture diffractometer equipped with an Oxford Cryosystems low-temperature device operating at T = 100.0(1) K. Data were measured using ϕ and ω scans using CuK_α radiation. The total number of runs and images was based on the strategy calculation from the program **APEX3** (Bruker, 2015) The maximum resolution that was achieved was Θ = 66.706° (0.84 Å). The diffraction pattern was indexed. The total number of runs and images was based on the strategy calculation from the program **APEX3** (Bruker, 2015) and the unit cell was refined using **SAINT** (Bruker, V8.40A, after 2013) on 1700 reflections, 58% of the observed reflections. Data reduction, scaling and absorption corrections were performed using **SAINT** (Bruker, V8.40A, after 2013). The final completeness is 97.80 % out to 66.706° in Θ. A multi-scan absorption correction was performed using **SADABS**-2016/2 (Bruker, 2016) was used for absorption correction. wR_2(int) was 0.1231 before and 0.0720 after correction. The Ratio of minimum to maximum transmission is 0.7962. The absorption coefficient μ of this material is 0.817 mm^{-1} at this wavelength (λ = 1.542Å) and the minimum and maximum transmissions are 0.739 and 0.929. The structure was solved, and the space group P-1 (# 2) determined by the **ShelXT** (Sheldrick, 2015) structure solution program using Intrinsic Phasing and refined by Least Squares using version 2018/3 of **ShelXL** (Sheldrick, 2015). All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model. Hydrogen atom positions were calculated geometrically and refined using the riding model. The value of Z' is 0.5. This means that only half of the formula unit is present in the asymmetric unit, with the other half consisting of symmetry equivalent atoms.

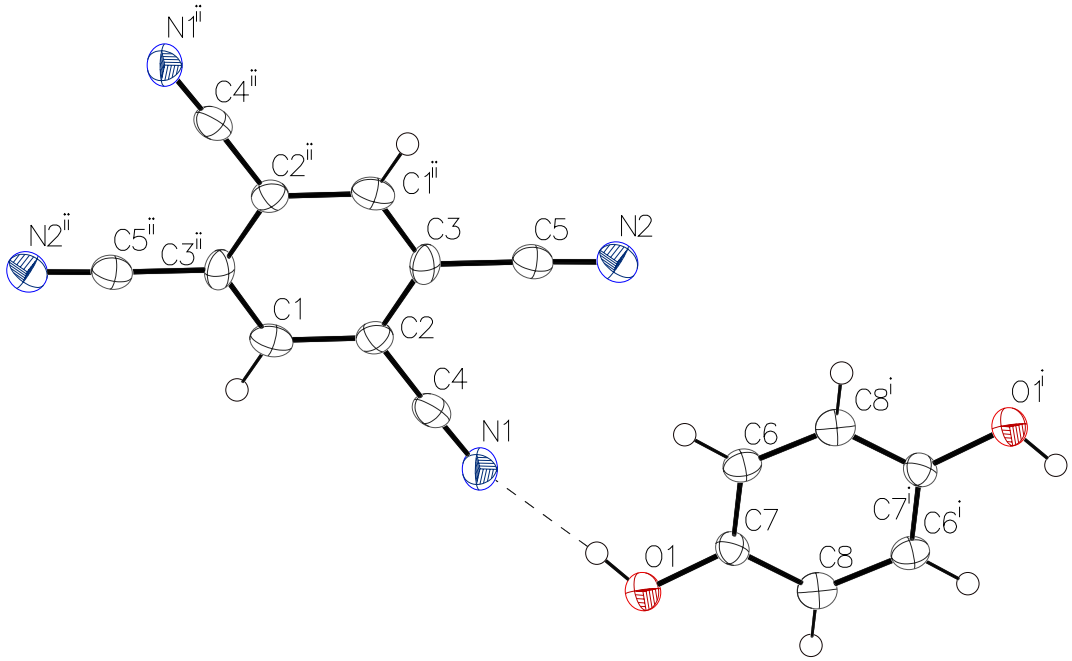


Figure 1: ORTEP view of compound **TCNB-H2Q** with symmetry element ([i]1-x,1-y,-z; [ii]1-x,2-y,2-z). Thermal ellipsoids are drawn at 50% probability plot.

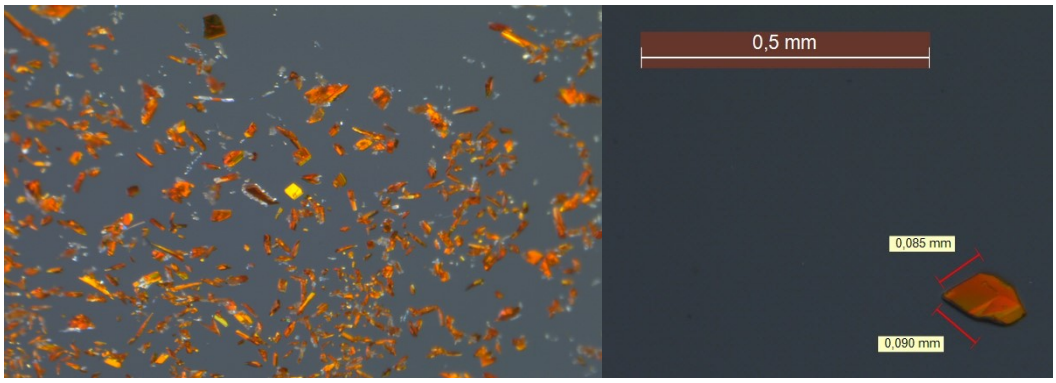


Figure 2: View of sample batch (left) and selected sample (right).

Table 1: Bond Lengths in Å for **TCNB-H2Q**.

Atom	Atom	Length/Å
O1	C7	1.370(5)
C6	C7	1.399(6)
C6	C8[1]	1.388(6)
C7	C8	1.399(6)
N1	C4	1.145(6)
N2	C5	1.143(6)
C1	C2	1.391(7)
C1	C3[2]	1.388(7)
C2	C3	1.400(6)
C2	C4	1.438(7)
C3	C5	1.450(7)

––––
[1]1-x,1-y,-z; [2]1-x,2-y,2-z

Table 2: Bond Angles in ° for **TCNB-H2Q**.

Atom	Atom	Atom	Angle/°
C8[1]	C6	C7	120.5(4)
O1	C7	C6	123.5(4)
O1	C7	C8	117.2(4)
C8	C7	C6	119.4(4)
C6[1]	C8	C7	120.1(4)
C3[2]	C1	C2	119.0(4)
C1	C2	C3	120.2(4)
C1	C2	C4	121.0(4)
C3	C2	C4	118.8(4)
C1[2]	C3	C2	120.7(4)
C1[2]	C3	C5	119.2(4)
C2	C3	C5	120.1(4)
N1	C4	C2	176.5(5)
N2	C5	C3	178.3(5)

––––
[1]1-x,1-y,-z; [2]1-x,2-y,2-z

Table 3: Torsion Angles in ° for **TCNB-H2Q**.

Atom	Atom	Atom	Atom	Angle/°
O1	C7	C8	C6[1]	-177.8(4)
C6	C7	C8	C6[1]	2.6(7)
C8[1]	C6	C7	O1	177.8(4)
C8[1]	C6	C7	C8	-2.7(7)
C1	C2	C3	C1[2]	0.3(7)
C1	C2	C3	C5	-179.9(4)
C3[2]	C1	C2	C3	-0.3(7)
C3[2]	C1	C2	C4	178.8(4)
C4	C2	C3	C1[2]	-178.9(4)
C4	C2	C3	C5	0.9(7)

––––
[1]1-x,1-y,-z; [2]1-x,2-y,2-z

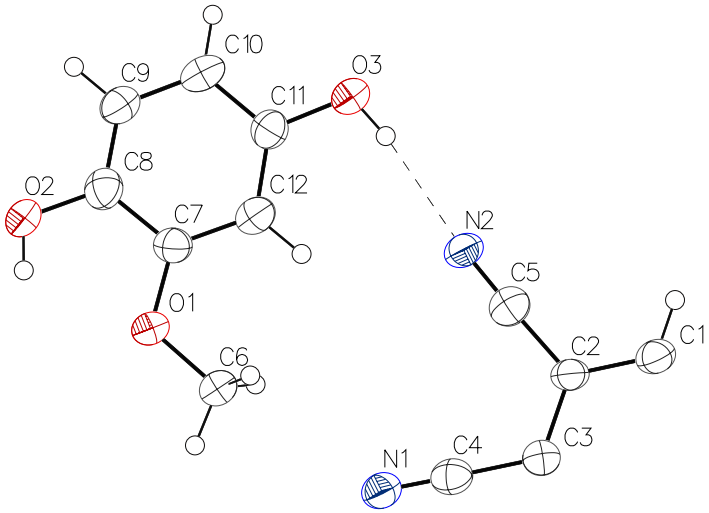
Table 4: Hydrogen Bond information for **TCNB-H2Q**.

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/deg
O1	H1A	N1	0.84	2.02	2.854(5)	176.2

TCNB-(H2QOMe)2

Submitted by: **Marcel Bouvet**
Solved by: **Yoann Rousselin**
Sample ID: **MB2101**

Crystal Data and Experimental



Experimental. Single clear light orange plate crystals of **20210125MB2101** recrystallised by sublimation. A suitable crystal with dimensions 0.56 x 0.41 x 0.09 mm^3 was selected and mounted on a MITIGEN holder oil on a Bruker D8 Venture (Cu) diffractometer. The crystal was kept at a steady T = 100.0(1) K during data collection. The structure was solved with the **ShelXT** (Sheldrick, 2015) solution program using dual methods and by using Olex2 (Dolomanov et al., 2009) as the graphical interface. The model was refined with **ShelXL 2018/3** (Sheldrick, 2015) using full matrix least squares minimisation on $\boldsymbol{F^2}$.

Crystal Data. $C_{24}H_{18}N_4O_6$, M_r = 458.42, triclinic, P-1 (No. 2), a = 7.0977(3) Å, b = 7.7054(4) Å, c = 10.1834(5) Å, α = 79.516(2)°, β = 85.590(3)°, γ = 70.030(3)°, V = 514.64(4) Å^3, T = 100.0(1) K, Z = 1, Z' = 0.5, μ(CuK$_\alpha$) = 0.910, 11444 reflections measured, 1824 unique (R_{int} = 0.0994) which were used in all calculations. The final wR_2 was 0.2917 (all data) and R_1 was 0.1137 (I≥2 σ(I)).

Compound	**TCNB-(H2QOMe)2**
CCDC	**2063384**
Formula	$C_{24}H_{18}N_4O_6$
$D_{calc.}$/ g cm^{-3}	1.479
μ/mm^{-1}	0.910
Formula Weight	458.42
Colour	clear light orange
Shape	plate
Size/mm^3	0.56x0.41x0.09
T/K	100.0(1)
Crystal System	triclinic
Space Group	P-1
a/Å	7.0977(3)
b/Å	7.7054(4)
c/Å	10.1834(5)
α/°	79.516(2)
β/°	85.590(3)
γ/°	70.030(3)
V/Å^3	514.64(4)
Z	1
Z'	0.5
Wavelength/Å	1.54178
Radiation type	CuK$_\alpha$
Θ_{min}/°	4.416
Θ_{max}/°	66.792
Measured Refl's.	11444
Indep't Refl's	1824
Refl's I≥2 σ(I)	1358
R_{int}	0.0994
Parameters	157
Restraints	0
Largest Peak	0.557
Deepest Hole	-0.323
GooF	1.125
wR_2 (all data)	0.2917
wR_2	0.2756
R_1 (all data)	0.1391
R_1	0.1137

Structure Quality Indicators

Reflections:	d min (Cu\a) 2θ=133.6° 0.84	I/σ(I) 17.6	Rint 9.94%	Full 133.6° 99.9
Refinement:	Shift 0.000	Max Peak 0.6	Min Peak -0.3	GooF 1.125

A clear light orange plate-shaped crystal with dimensions 0.56 x 0.41 x 0.09 mm^3 was mounted on a MITIGEN holder oil. Data were collected using a Bruker D8 Venture (Cu) diffractometer equipped with an Oxford Cryosystems low-temperature device operating at T = 100.0(1) K. Data were measured using ϕ and ω scans using CuK_α radiation. The maximum resolution that was achieved was Θ = 66.792° (0.84 Å). The unit cell was refined using **SAINT** (Bruker, V8.40B, after 2013) on 7283 reflections, 64% of the observed reflections. Data reduction, scaling and absorption corrections were performed using SAINT (Bruker, V8.40B, after 2013). The final completeness is 99.90 % out to 66.792° in Θ. A multi-scan absorption correction was performed using **SADABS-2016/2** (Bruker, 2016) was used for absorption correction. wR_2(int) was 0.1405 before and 0.1049 after correction. The Ratio of minimum to maximum transmission is 0.7764. The absorption coefficient μ of this material is 0.910 mm^{-1} at this wavelength (λ = 1.54178Å) and the minimum and maximum transmissions are 0.671 and 0.864. The structure was solved, and the space group P-1 (# 2) determined by the **ShelXT** (Sheldrick, 2015) structure solution program using dual methods and refined by full matrix least squares minimisation on F^2 using version 2018/3 of **ShelXL 2018/3** (Sheldrick, 2015). All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model. Hydrogen atom positions were calculated geometrically and refined using the riding model. The value of Z' is 0.5. This means that only half of the formula unit is present in the asymmetric unit, with the other half consisting of symmetry equivalent atoms.

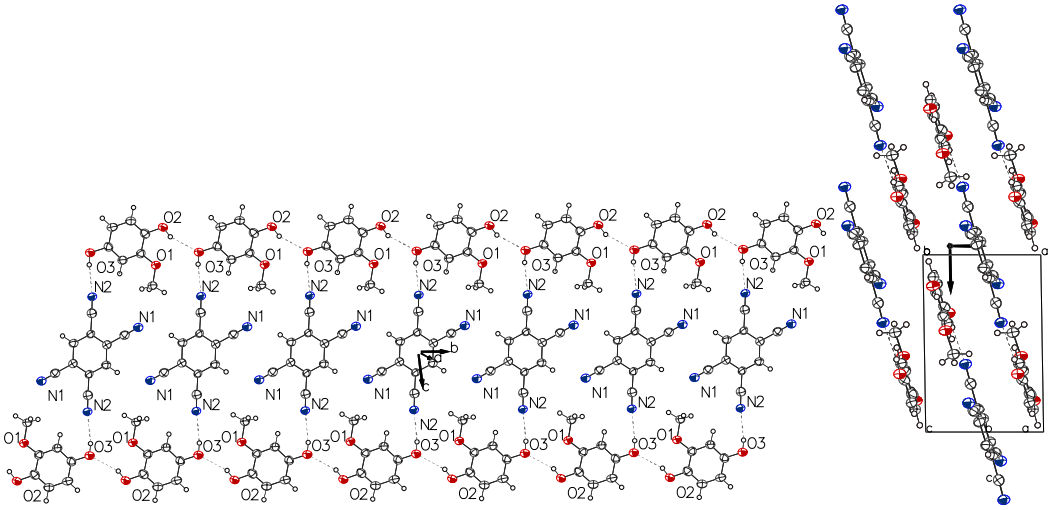


Figure 3: ORTEP view of crystal packing along b axis (left) and along c axis (right).

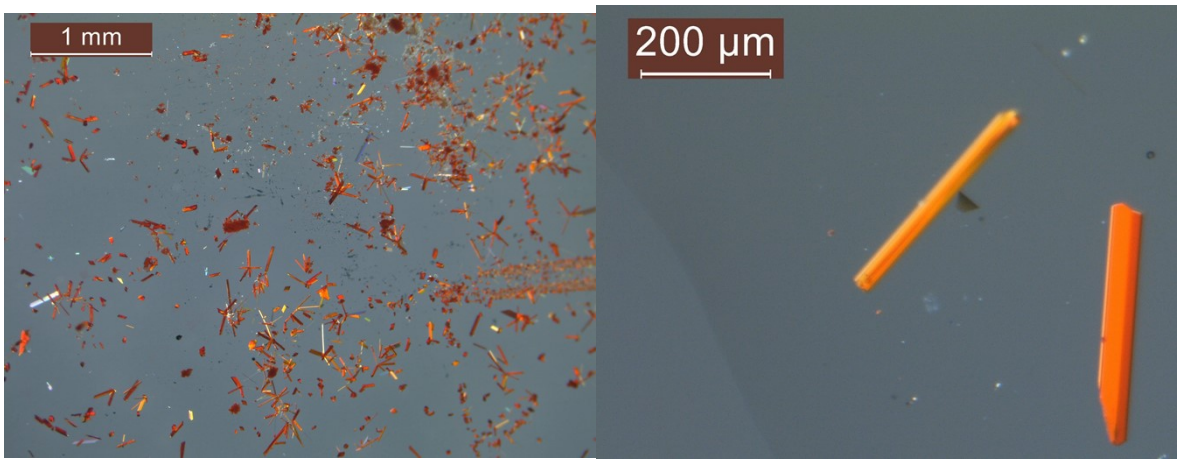


Figure 4: View of sample batch (left) and selected crystal (right).

Table 5: Fractional Atomic Coordinates (x10^4) and Equivalent Isotropic Displacement Parameters (Å^{2}x10^3) for **20210125MB2101**. U_{eq} is defined as 1/3 of the trace of the orthogonalized U_{ij}.

Atom	x	y	z	U_{eq}
O2	814(6)	10116(5)	1748(3)	42.1(10)
O1	1818(6)	8560(5)	4271(3)	40.6(10)
O3	2116(6)	2537(5)	3279(3)	40.6(10)
C12	1978(8)	5483(8)	3864(5)	39.7(13)
C8	1097(9)	8268(8)	2138(6)	42.2(13)
C7	1669(8)	7383(8)	3462(5)	37.7(13)
C9	863(8)	7217(8)	1270(5)	39.5(13)
C6	2460(9)	7721(8)	5613(5)	39.1(13)
C11	1751(8)	4447(8)	2943(5)	38.3(13)
C10	1154(8)	5298(9)	1652(5)	41.6(14)
N2	3465(7)	1594(6)	6172(4)	39.2(11)
N1	3680(7)	5365(7)	8367(4)	40.6(12)
C2	4428(8)	573(7)	8671(5)	35.6(12)
C5	3872(8)	1176(8)	7280(5)	40.5(13)
C3	4563(8)	1869(8)	9422(5)	37.3(13)
C1	4846(8)	-1299(8)	9236(5)	39.1(13)
C4	4089(8)	3830(8)	8833(5)	39.1(13)

Table 6: Anisotropic Displacement Parameters (x10^4) for **20210125MB2101**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2} \times U_{11} + \ldots + 2hka^* \times b^* \times U_{12}]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O2	56(2)	40(2)	29.1(19)	-0.1(16)	-5.1(17)	-16.5(18)
O1	55(2)	41(2)	29.0(19)	-6.4(15)	-4.6(16)	-17.8(18)
O3	49(2)	43(2)	29.9(19)	-4.9(15)	-2.1(17)	-15.9(18)
C12	41(3)	47(3)	32(3)	-5(2)	-2(2)	-17(3)
C8	44(3)	43(3)	38(3)	-4(2)	6(2)	-15(3)
C7	41(3)	38(3)	35(3)	-10(2)	-1(2)	-12(2)
C9	38(3)	45(3)	32(3)	-7(2)	-1(2)	-9(2)
C6	46(3)	41(3)	30(3)	-5(2)	-4(2)	-14(2)
C11	40(3)	41(3)	35(3)	-5(2)	5(2)	-17(2)
C10	38(3)	58(4)	30(3)	-8(2)	-2(2)	-17(3)
N2	47(3)	47(3)	28(2)	-4.9(19)	-3.7(19)	-22(2)
N1	46(3)	45(3)	32(2)	-7(2)	-1(2)	-17(2)
C2	45(3)	42(3)	28(3)	-9(2)	2(2)	-23(3)
C5	38(3)	46(3)	38(3)	-7(2)	1(2)	-15(3)
C3	41(3)	38(3)	35(3)	-7(2)	-3(2)	-14(2)
C1	46(3)	46(3)	29(3)	-8(2)	1(2)	-20(3)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C4	39(3)	47(3)	34(3)	-12(2)	6(2)	-17(3)

Table 7: Bond Lengths in Å for **20210125MB2101**.

Atom	Atom	Length/Å
O2	C8	1.356(6)
O1	C7	1.366(6)
O1	C6	1.437(6)
O3	C11	1.386(6)
C12	C7	1.391(7)
C12	C11	1.388(8)
C8	C7	1.417(8)
C8	C9	1.357(8)
C9	C10	1.405(8)
C11	C10	1.386(8)

Atom	Atom	Length/Å
N2	C5	1.147(7)
N1	C4	1.136(7)
C2	C5	1.449(7)
C2	C3	1.394(7)
C2	C1	1.390(7)
C3	C1[1]	1.408(8)
C3	C4	1.453(8)

––––
[1]1-x,-y,2-z

Table 8: Bond Angles in ° for **20210125MB2101**.

Atom	Atom	Atom	Angle/°
C7	O1	C6	116.4(4)
C11	C12	C7	119.1(5)
O2	C8	C7	120.7(5)
O2	C8	C9	120.9(5)
C9	C8	C7	118.4(5)
O1	C7	C12	124.9(5)
O1	C7	C8	114.2(5)
C12	C7	C8	120.9(5)
C8	C9	C10	121.9(5)
O3	C11	C12	121.4(5)
C10	C11	O3	117.9(5)
C10	C11	C12	120.8(5)

Atom	Atom	Atom	Angle/°
C11	C10	C9	118.9(5)
C3	C2	C5	119.7(5)
C1	C2	C5	119.4(5)
C1	C2	C3	120.8(5)
N2	C5	C2	177.7(6)
C2	C3	C1[1]	120.6(5)
C2	C3	C4	120.6(5)
C1[1]	C3	C4	118.9(5)
C2	C1	C3[1]	118.6(5)
N1	C4	C3	178.6(6)

––––
[1]1-x,-y,2-z

Table 9: Torsion Angles in ° for **20210125MB2101**.

Atom	Atom	Atom	Atom	Angle/°
O2	C8	C7	O1	2.3(8)
O2	C8	C7	C12	-179.4(5)
O2	C8	C9	C10	179.8(5)
O3	C11	C10	C9	-177.2(5)
C12	C11	C10	C9	2.7(8)
C8	C9	C10	C11	-1.8(8)
C7	C12	C11	O3	177.5(5)
C7	C12	C11	C10	-2.3(8)
C7	C8	C9	C10	0.6(8)
C9	C8	C7	O1	-178.4(5)
C9	C8	C7	C12	-0.2(9)
C6	O1	C7	C12	3.9(8)
C6	O1	C7	C8	-178.0(5)
C11	C12	C7	O1	179.1(5)
C11	C12	C7	C8	1.1(8)
C5	C2	C3	C1[1]	-178.2(5)
C5	C2	C3	C4	2.0(8)
C5	C2	C1	C3[1]	178.3(5)
C3	C2	C1	C3[1]	-0.9(9)
C1	C2	C3	C1[1]	0.9(9)
C1	C2	C3	C4	-178.9(5)

––––
[1]1-x,-y,2-z

Table 10: Hydrogen Fractional Atomic Coordinates ($x10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2x10^3$) for **20210125MB2101**. U_{eq} is defined as 1/3 of the trace of the orthogonalized U_{ij}.

Atom	x	y	z	U_{eq}
H2	1119.56	10543.35	2372.08	63
H3	2376.54	2193.52	4095.88	61
H12	2339.75	4902.47	4756.77	48
H9	491.09	7794.96	378.03	47
H6A	3788.28	6765.13	5590.06	59
H6B	1501.96	7139.26	6065.22	59
H6C	2527.06	8685.99	6097.37	59
H10	944.47	4595.24	1035.16	50
H1	4735.25	-2176.62	8726	47

Table 11: Hydrogen Bond information for **20210125MB2101**.

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/deg
O2	H2	O3[1]	0.84	2.25	3.037(5)	155.6
O3	H3	N2	0.84	2.22	3.050(6)	169.1

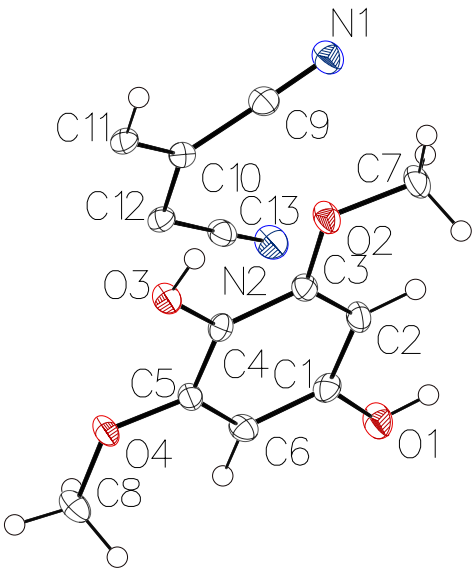
––––

[1]+x,1+y,+z

TCNB-(H2Q(OMe)2)2

Submitted by: **Elodie Grail**
Solved by: **Yoann Rousselin**
Sample ID: **09eg01**

Crystal Data and Experimental



Experimental. Single metallic dark black prism-shaped crystals of **TCNB-(H2Q(OMe)2)2** were recrystallized from by sublimation. A suitable crystal 0.17x0.12x0.12 mm^3 was selected and mounted on a mylar loop with grease on a Nonius Kappa Apex II diffractometer. The crystal was kept at a steady T = 115.0(1) K during data collection. The structure was solved with the **SIR92** (Altomare et al., 1993) structure solution program using the direct methods solution method and by using **Olex2** (Dolomanov et al., 2009) as the graphical interface. The model was refined with version 2018/3 of **ShelXL** (Sheldrick, 2015) using Least Squares minimization.

Crystal Data. $C_{26}H_{22}N_4O_8$, M_r = 518.47, monoclinic, $C2/c$ (No. 15), a = 18.7810(12) Å, b = 7.6668(5) Å, c = 17.9141(8) Å, β = 112.728(3)°, α = γ = 90°, V = 2379.2(2) $Å^3$, T = 115.0(1) K, Z = 4, Z' = 0.5, μ(MoK_α) = 0.109, 4818 reflections measured, 2698 unique (R_{int} = 0.0377) which were used in all calculations. The final wR_2 was 0.1134 (all data) and R_1 was 0.0540 (I > 2(I)).

Compound	**TCNB-(H2Q(OMe)2)2**
CCDC	**1994294**
Formula	$C_{26}H_{22}N_4O_8$
$D_{calc.}$/ g cm^{-3}	1.447
μ/mm^{-1}	0.109
Formula Weight	518.47
Colour	metallic dark black
Shape	prism
Size/mm^3	0.17x0.12x0.12
T/K	115.0(1)
Crystal System	monoclinic
Space Group	$C2/c$
a/Å	18.7810(12)
b/Å	7.6668(5)
c/Å	17.9141(8)
α/°	90
β/°	112.728(3)
γ/°	90
V/$Å^3$	2379.2(2)
Z	4
Z'	0.5
Wavelength/Å	0.71073
Radiation type	MoK_α
Θ_{min}/°	2.351
Θ_{max}/°	27.456
Measured Refl.	4818
Independent Refl.	2698
Reflections with I > 2(I)	2129
R_{int}	0.0377
Parameters	176
Restraints	0
Largest Peak	0.346
Deepest Hole	-0.274
GooF	1.104
wR_2 (all data)	0.1134
wR_2	0.1018
R_1 (all data)	0.0746
R_1	0.0540

Structure Quality Indicators

Reflections:	d min (Mo) 0.77	I/σ 24.1	Rint 3.77%	complete 99%
Refinement:				GooF 1.104

A metallic dark black prism-shaped crystal with dimensions 0.17x0.12x0.12 mm^3 was mounted on a mylar loop with grease. Data were collected using a Nonius Kappa Apex II diffractometer equipped with an Oxford Cryosystems low-temperature device operating at T = 115.0(1) K. Data were measured using ϕ and ω scans using MoK_α radiation. The total number of runs and images was based on the strategy calculation from the program **XS** (Sheldrick, 2008) The maximum resolution that was achieved was Θ = 27.456° (0.77 Å). The diffraction pattern was indexed. The total number of runs and images was based on the strategy calculation from the program **XS** (Sheldrick, 2008) and the unit cell was refined using **DENZO** (Otwinowski & Minor, 1997) on 2695 reflections, 56% of the observed reflections. Data reduction, scaling and absorption corrections were performed using **DENZO** (Otwinowski & Minor, 1997). The final completeness is 99.40 % out to 27.456° in Θ. No absorption correction was performed. The absorption coefficient μ of this material is 0.109 mm^{-1} at this wavelength (λ = 0.711Å). The structure was solved, and the space group $C2/c$ (# 15) determined by the **SIR92** (Altomare et al., 1993) structure solution program using direct methods and refined by Least Squares using version 2018/3 of **ShelXL** (Sheldrick, 2015). All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model. Hydrogen atom positions were calculated geometrically and refined using the riding model. The value of Z' is 0.5. This means that only half of the formula unit is present in the asymmetric unit, with the other half consisting of symmetry equivalent atoms.

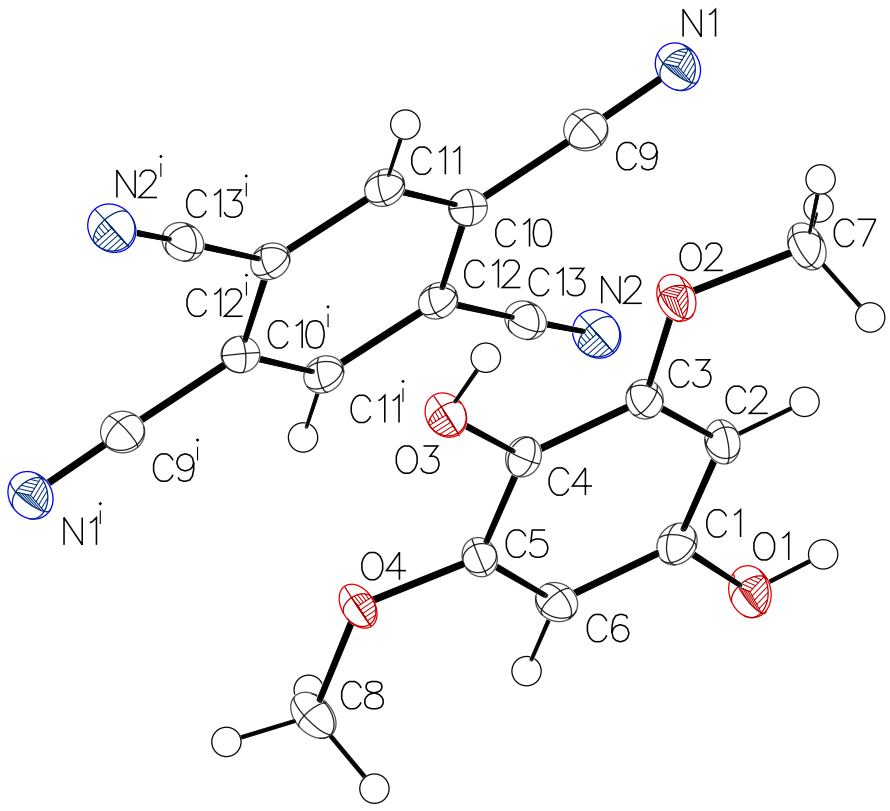


Figure 5: ORTEP view of compound **TCNB-(H2Q(OMe)2)2** with symmetry element ([i]3/2-x,1/2-y,1-z)

Table 12: Bond Lengths in Å for **TCNB-(H2Q(OMe)2)2**.

Atom	Atom	Length/Å
C1	C2	1.387(3)
C1	C6	1.386(3)
C1	O1	1.383(2)
C2	C3	1.395(3)
C3	C4	1.397(3)
C3	O2	1.367(2)
C4	C5	1.388(3)
C4	O3	1.375(2)
C5	C6	1.400(3)
C5	O4	1.374(2)
C7	O2	1.438(2)
C8	O4	1.434(2)
C9	C10	1.446(3)
C9	N1	1.144(3)
C10	C11	1.389(3)
C10	C12	1.402(3)
C11	C12[1]	1.393(3)
C12	C13	1.441(3)
C13	N2	1.145(3)

––––
[1]3/2-x,1/2-y,1-z

Table 13: Bond Angles in ° for **TCNB-(H2Q(OMe)2)2**.

Atom	Atom	Atom	Angle/°
C6	C1	C2	121.70(19)
O1	C1	C2	121.28(18)
O1	C1	C6	117.01(18)
C1	C2	C3	118.41(19)
C2	C3	C4	121.29(19)
O2	C3	C2	124.28(18)
O2	C3	C4	114.41(18)
C5	C4	C3	118.91(19)
O3	C4	C3	121.70(18)
O3	C4	C5	119.38(17)
C4	C5	C6	120.76(18)
O4	C5	C4	115.45(18)
O4	C5	C6	123.79(18)
C1	C6	C5	118.91(18)
N1	C9	C10	178.7(2)
C11	C10	C9	119.16(19)
C11	C10	C12	120.71(18)
C12	C10	C9	120.13(19)
C10	C11	C12[1]	119.15(19)
C10	C12	C13	120.05(18)
C11[1]	C12	C10	120.14(19)
C11[1]	C12	C13	119.81(18)
N2	C13	C12	178.6(2)
C3	O2	C7	116.68(16)
C5	O4	C8	116.81(16)

––––
[1]3/2-x,1/2-y,1-z

Table 14: Torsion Angles in ° for **TCNB-(H2Q(OMe)2)2**.

Atom	Atom	Atom	Atom	Angle/°
C1	C2	C3	C4	-0.3(3)
C1	C2	C3	O2	-178.49(19)
C2	C1	C6	C5	-0.8(3)
C2	C3	C4	C5	-0.9(3)
C2	C3	C4	O3	-179.74(18)
C2	C3	O2	C7	-9.7(3)
C3	C4	C5	C6	1.3(3)
C3	C4	C5	O4	-178.20(17)
C4	C3	O2	C7	172.00(17)
C4	C5	C6	C1	-0.4(3)
C4	C5	O4	C8	-176.34(17)
C6	C1	C2	C3	1.2(3)
C6	C5	O4	C8	4.2(3)
C9	C10	C11	C12[1]	179.21(18)
C9	C10	C12	C11[1]	-179.21(18)
C9	C10	C12	C13	0.6(3)
C11	C10	C12	C11[1]	0.2(3)
C11	C10	C12	C13	179.93(19)
C12	C10	C11	C12[1]	-0.2(3)
O1	C1	C2	C3	-179.42(19)
O1	C1	C6	C5	179.75(18)
O2	C3	C4	C5	177.46(17)
O2	C3	C4	O3	-1.4(3)
O3	C4	C5	C6	-179.87(18)
O3	C4	C5	O4	0.7(3)
O4	C5	C6	C1	179.00(18)

––––
[1]3/2-x,1/2-y,1-z

Table 15: Hydrogen Bond information for **TCNB-(H2Q(OMe)2)2**.

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/deg
O1	H1	N1[2]	0.84	2.40	3.224(2)	169.1
O3	H3	O1[1]	0.84	2.16	2.943(2)	155.3

––––
[1]+x,1+y,+z; [2]2-x,-y,1-z

Citations

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