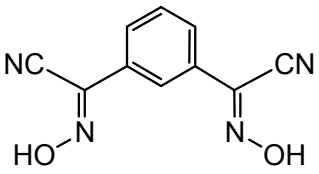
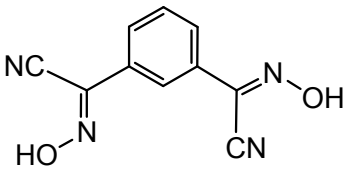
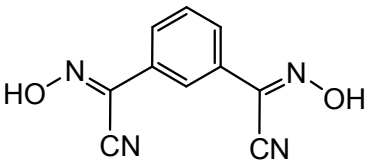
Possible geometrical isomers and conformers for 1,3-bis(cyanoxime)benzene.



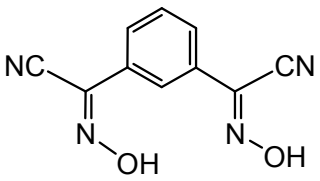
1, trans-trans, *anti-anti*



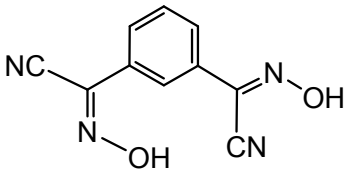
2, trans-cis, *anti-anti*



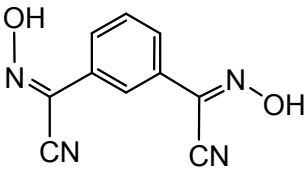
3, cis-cis, *anti-anti*



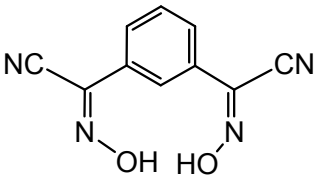
4, trans-trans, *syn-anti*



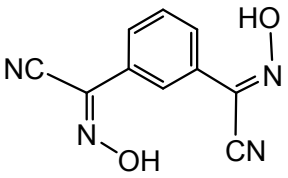
5, trans-cis, *syn-anti*



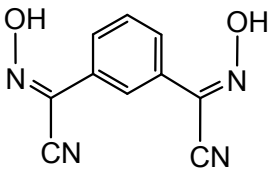
6, cis-cis, *syn-anti*



7, trans-trans, *syn-syn*

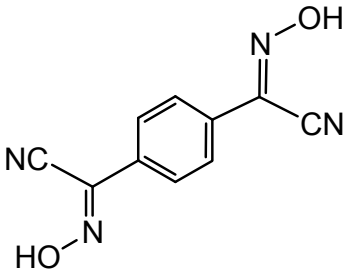


8, trans-cis, *syn-syn*

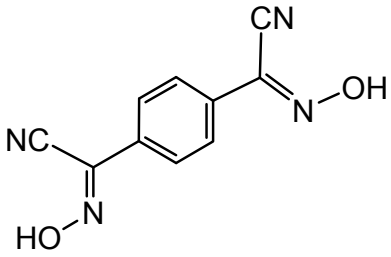


9, cis-cis, *syn-syn*

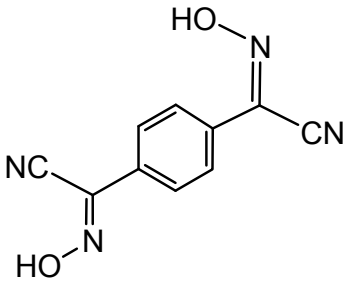
Possible geometrical isomers and conformers for 1,4-bis(cyanoxime)benzene.



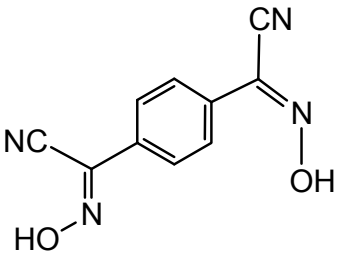
I, trans, *anti-anti*



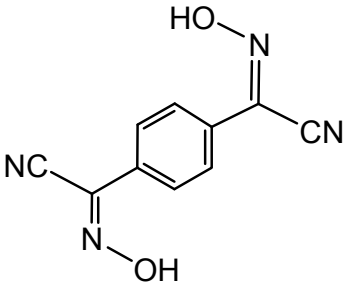
II. cis, *anti-anti*



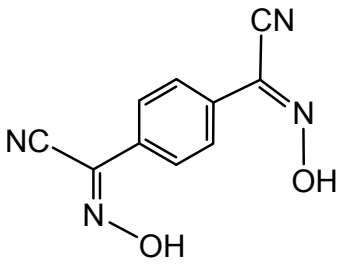
III, trans, *syn-anti*



IV, cis, *syn-anti*



V, trans, *syn-anti*



VI, cis, *syn-anti*

Crystal data and structure refinement for the 1,3-BCO-monooxime.

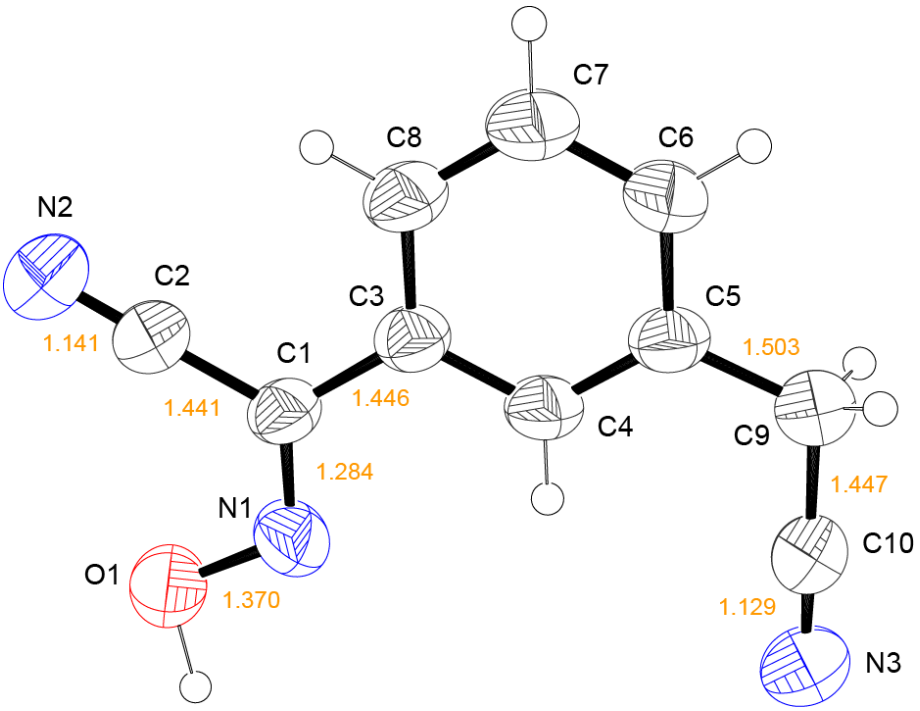
Empirical formula	$C_{10}H_7N_3O$	
Formula weight	185.19	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1, #2	
Unit cell dimensions	a = 5.676(4) Å	α= 102.487(7)°.
	b = 9.573(7) Å	β= 101.186(7)°.
	c = 9.600(7) Å	γ = 106.568(7)°.
Volume, Z	469.6(6) $Å^3$, 2	
Density (calculated)	1.310 Mg/m^3	
Absorption coefficient	0.090 mm^{-1}	
F(000)	192	
Index ranges	-6<=h<=6, -11<=k<=11, -11<=l<=11	
Reflections collected	3673	
Independent reflections	1764 [R(int) = 0.0462]	
Completeness to theta = 25.67°	98.7 %	
Max. and min. transmission	0.7454 and 0.4930	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1764 / 0 / 139	
Goodness-of-fit on F^2	0.997	
Final R indices [I>2sigma(I)]	R1 = 0.0696, wR2 = 0.1575	
R indices (all data)	R1 = 0.1390, wR2 = 0.1938	
Extinction coefficient	0.029(13)	
Largest diff. peak and hole	0.451 and -0.165 $e.Å^{-3}$	

Hydrogen bonds for 1,3-BCO-monooxime [Å and °].

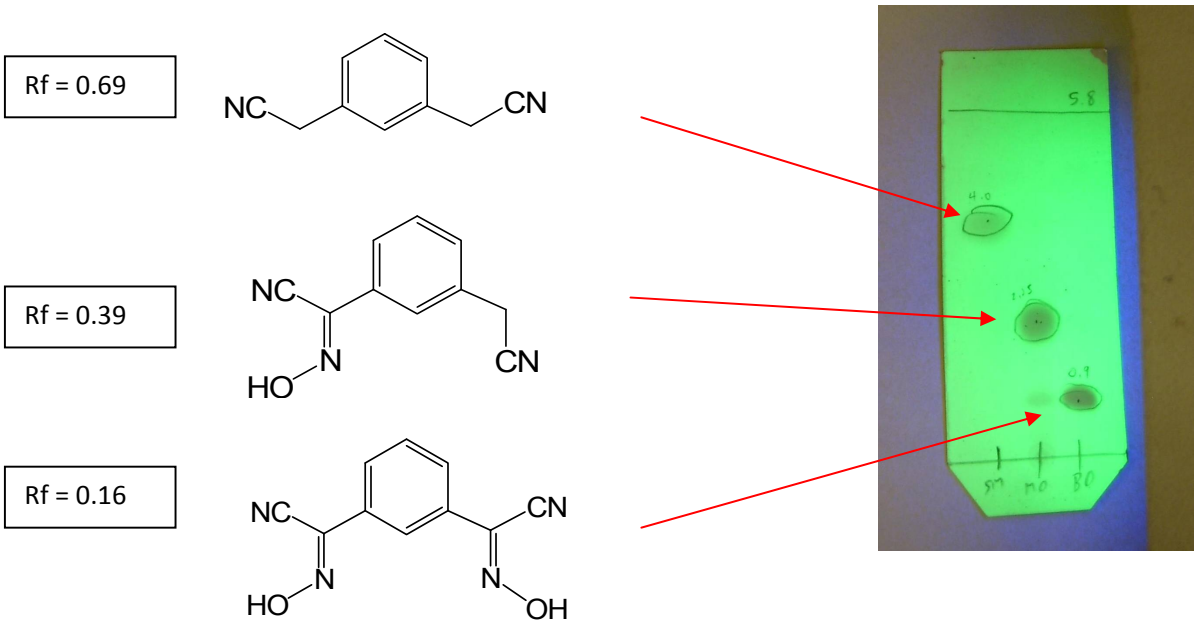
D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(1)-H(1O)...N(3)#1	1.09(6)	1.67(6)	2.749(4)	172(4)

Symmetry transformations used to generate equivalent atoms: #1 -x+1,-y+1,-z

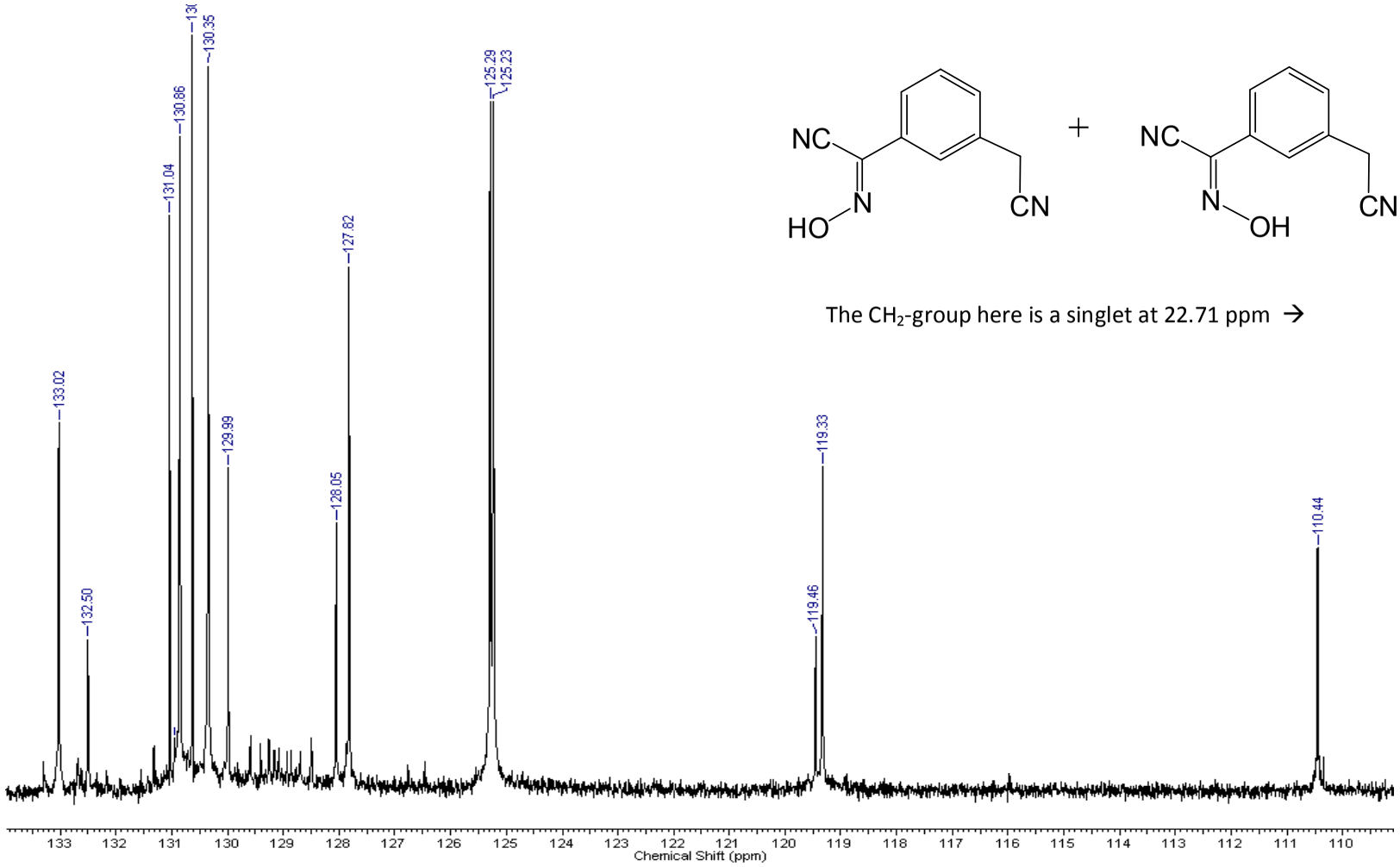
Molecular structure and numbering scheme for the 1,3-BCO-monooxime. An ORTEP drawing at 50% thermal ellipsoids probability level. Selected bonds lengths (Å) are indicated in yellow.



Actual TLC (MeOH/CHCl3) of all compounds involved into the synthesis of 1,3-BCO.

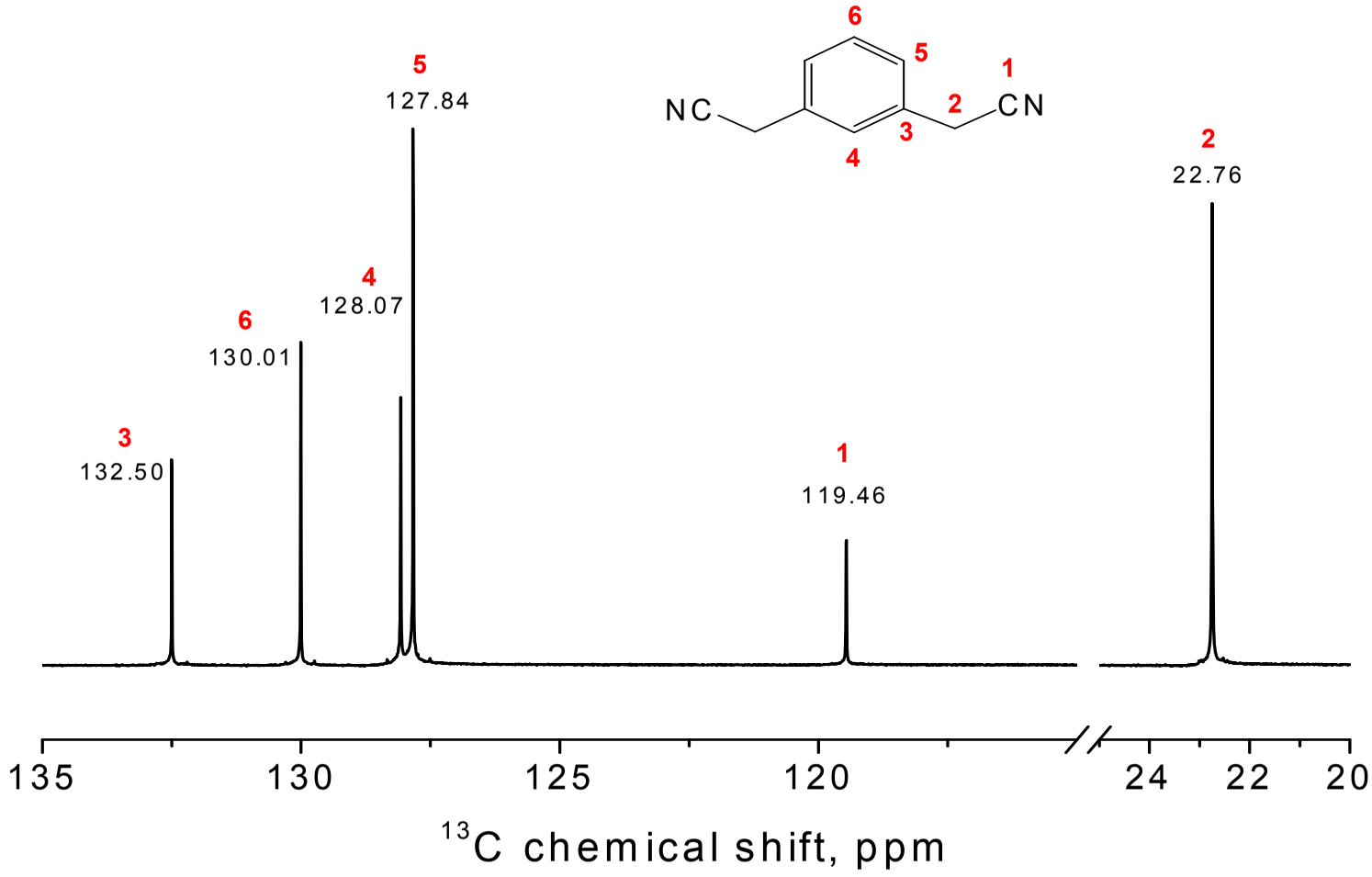


$^{13}C\{^{1}H\}$ NMR spectrum of pure, one TLC spot sample of the 1,3-BCO-monooxime in dmso-d_6 at 293 K in the *sp*, sp^2 carbons region. The 15 signals instead of 10 evidenced the presence of two geometrical isomers in solution.

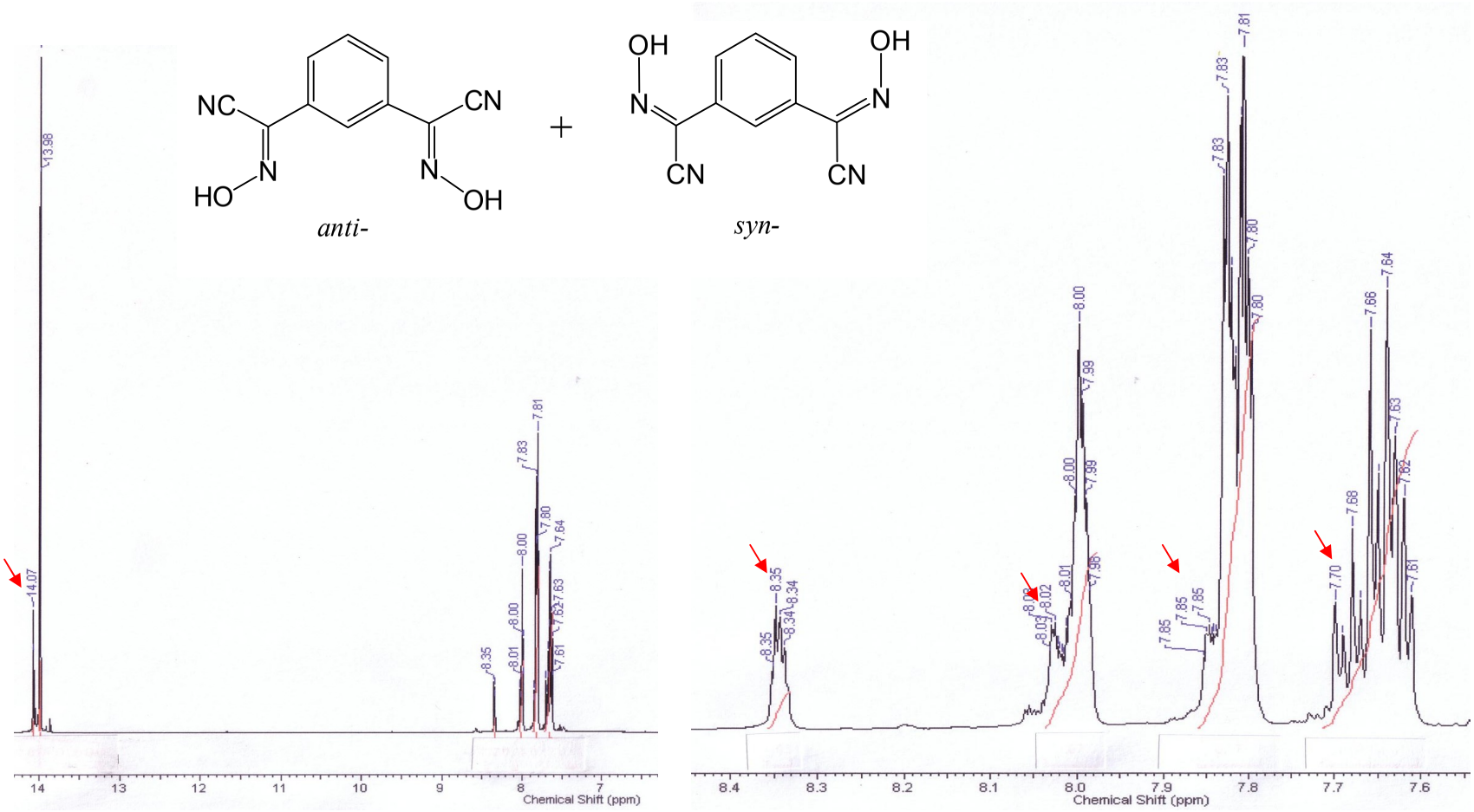


The CH_2-group here is a singlet at 22.71 ppm →

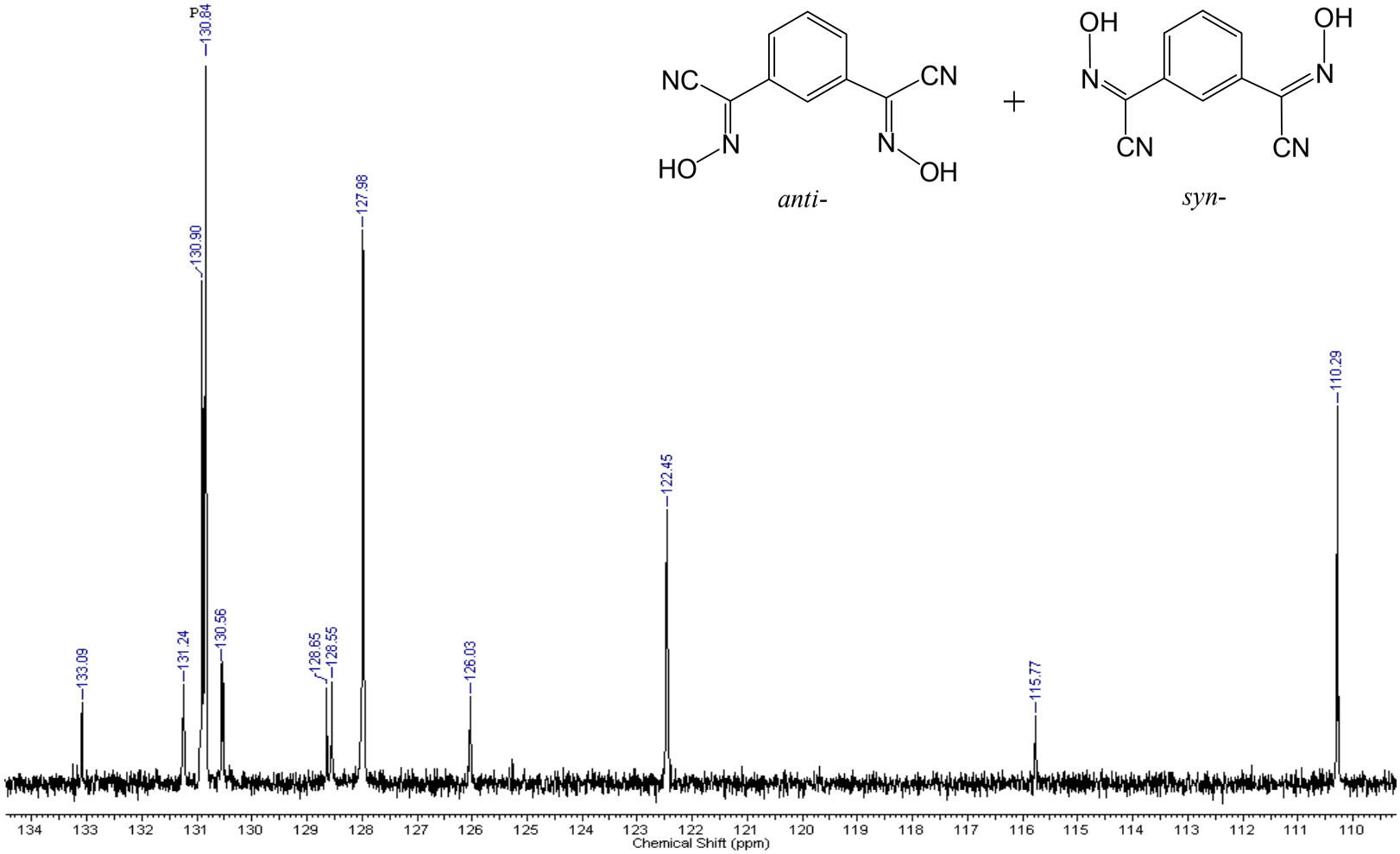
$^{13}C\{^{1}H\}$ NMR spectra of pure 1,3-dibenzylphenyl-dicyanide (starting bis-acetonitrile) in dmso-d_6 at 293 K.



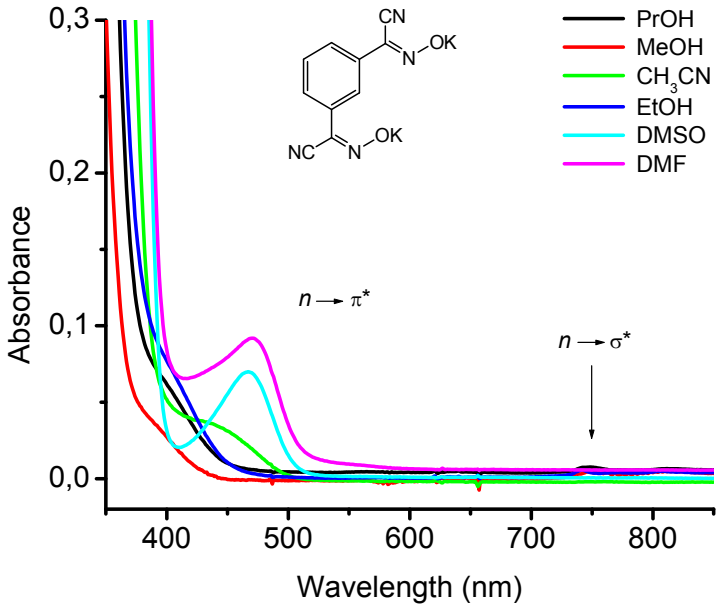
^{1}H NMR spectra of pure, one TLC spot sample of the 1,3-BCO in dmso-d_6 at 293 K: **A** – panoramic view, **B** – details. Red arrows indicate minor presence of the second geometrical isomer.

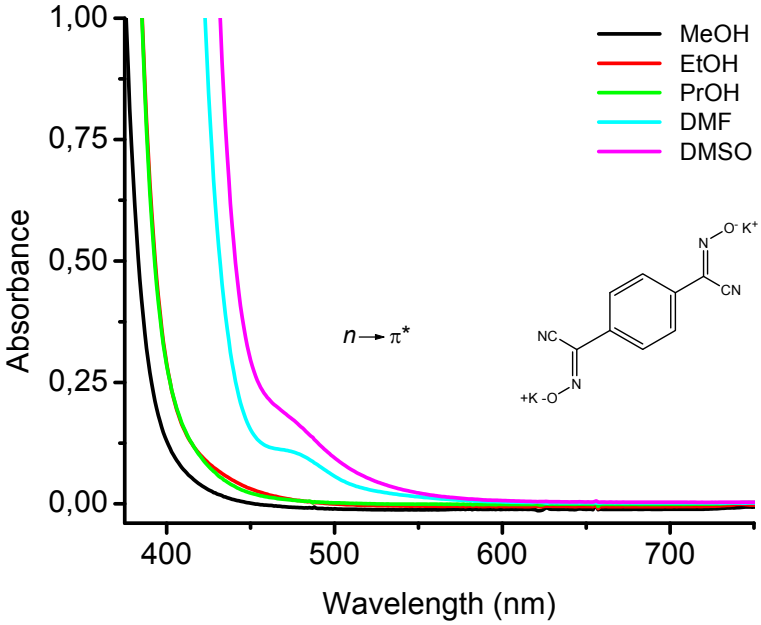


$^{13}C\{^{1}H\}$ NMR spectra of pure, one TLC spot sample of the 1,3-BCO in dmso-d_6 at 293 K. Double set of lines evidenced presence of two geometrical isomers in solution.



UV-visible spectra of 1,3-BCO (top) and 1,4-BCO (nbottom) in different solvents upon addition of KOH with the formation of dianion. Shown $n \rightarrow \pi^*$ and $n \rightarrow \sigma^*$ (only for 1,3-BCO) transitions in visible region of spectrum.





Tables of H-bonding for studied bis-cyanoximes.

1,4-BCO · H_2O [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(1)-H(1)...O(3S)#1	0.84	1.93	2.748(3)	165.5
O(3S)-H(1S)...N(4)#2	0.67(4)	2.20(4)	2.851(4)	167(5)

Symmetry transformations used to generate equivalent atoms:
#1 -x+3/4,y+1/4,z+3/4; #2 x,y,z+1

1,3-BCO · DMF [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(1)-H(1)...O(1S)	0.84	1.83	2.664(2)	169.7
O(1)-H(1)...O(1S)#2	0.84	1.83	2.664(2)	169.7

Symmetry transformations used to generate equivalent atoms:
#1 x,y,-z+3/2 #2 x,y,-z+1/2

1,4-BCO [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(1)-H(1)...N(2)#2	0.84	1.99	2.814(2)	165.6

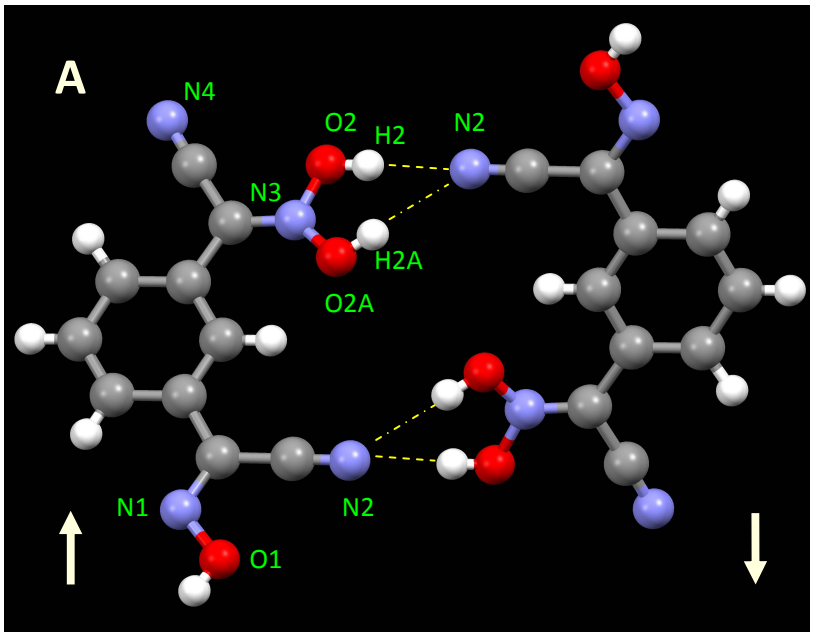
Symmetry transformations used to generate equivalent atoms:
#1 -x+1,-y,-z+1 #2 -x-1/2,y+1/2,z

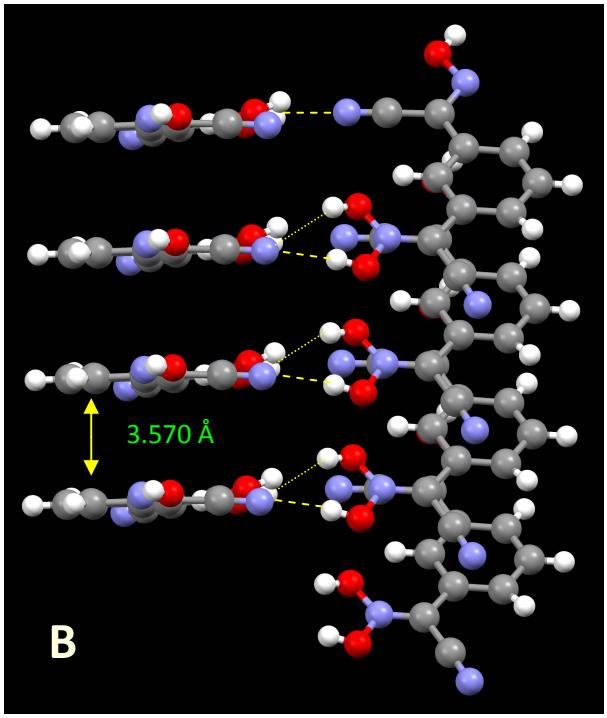
1,4-BCO · DMSO [Å and °].

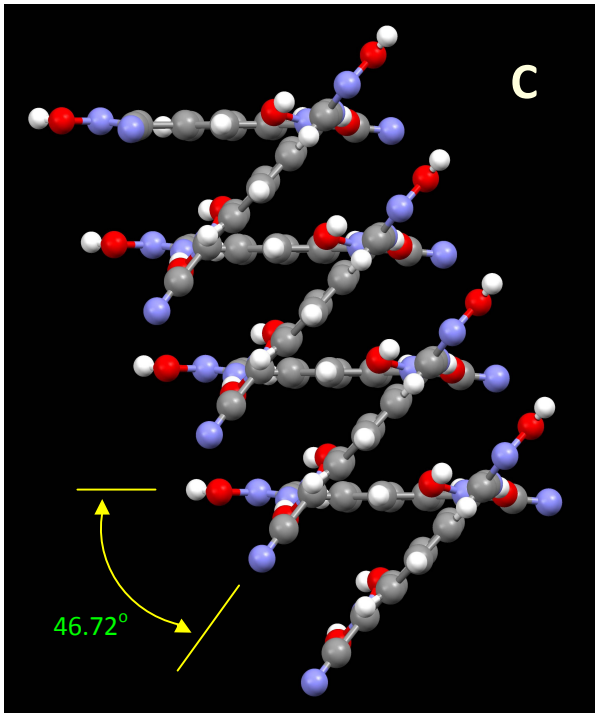
D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(1)-H(1)...O(1S)#2	0.92(2)	1.68(2)	2.6044(14)	176(2)

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,-y+2,-z+2 #2 x+1,y,z

H-bonding pattern in the structure of 1,3-BCOxH_2O viewed from a fragment of 4 unit cells. **A** – intermolecular dimer; **B** – π–π stacking between layers of bis-cyanoxime; **C** – "herring bone" motif betwee H-bonded and π-stacked layers.

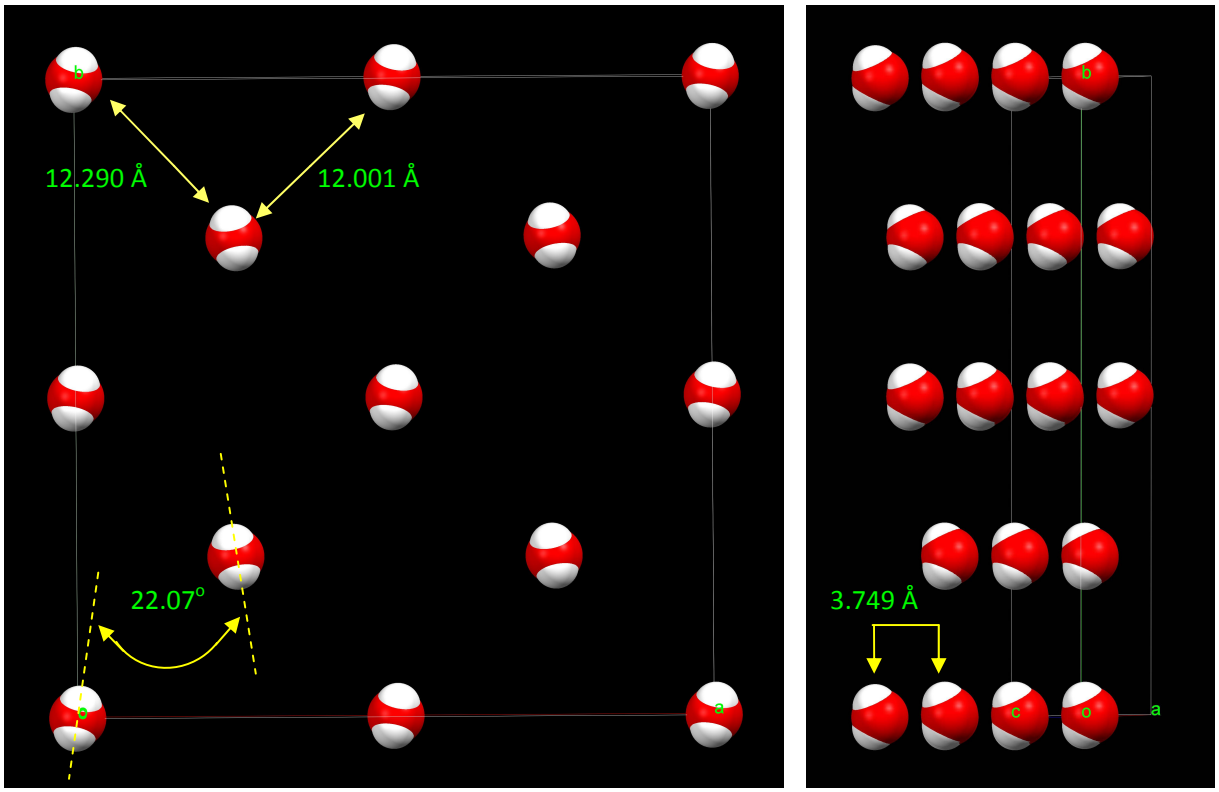




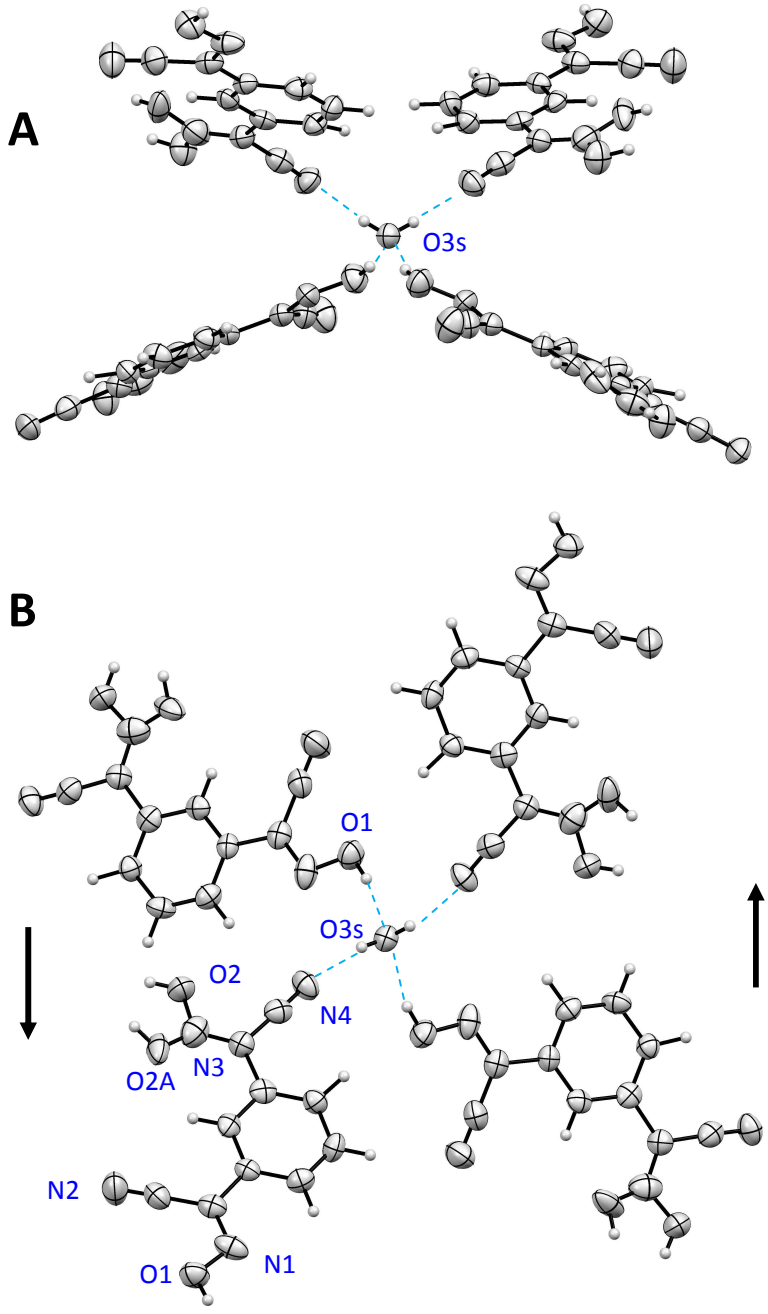


Two views of 3 unit cells showing only trapped water molecules in a space filling representation: **A** – view along *c*-direction, **B** – along cell diagonal. There are 13 channels in the unit cell which occupied with slightly tilted relatively to each other water molecules.

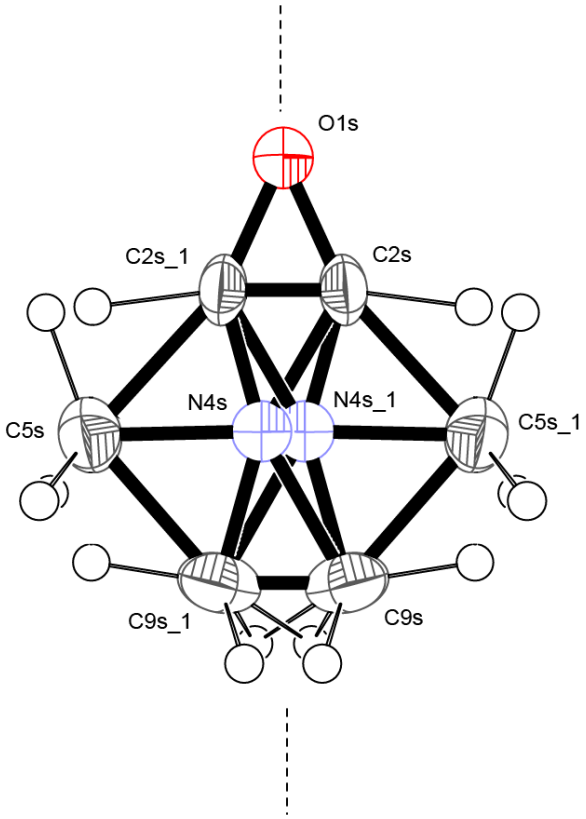
A **B**



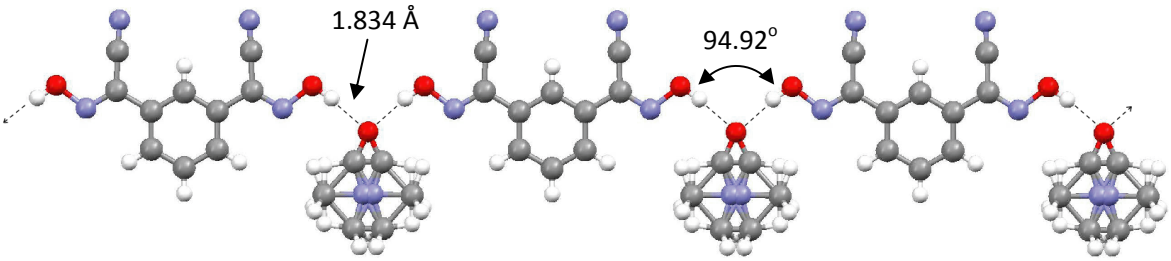
Fragment of crystal structure of 1,3-BCO showing trapped inside lattice water molecule. Two different views showing geometry of H-bonding.



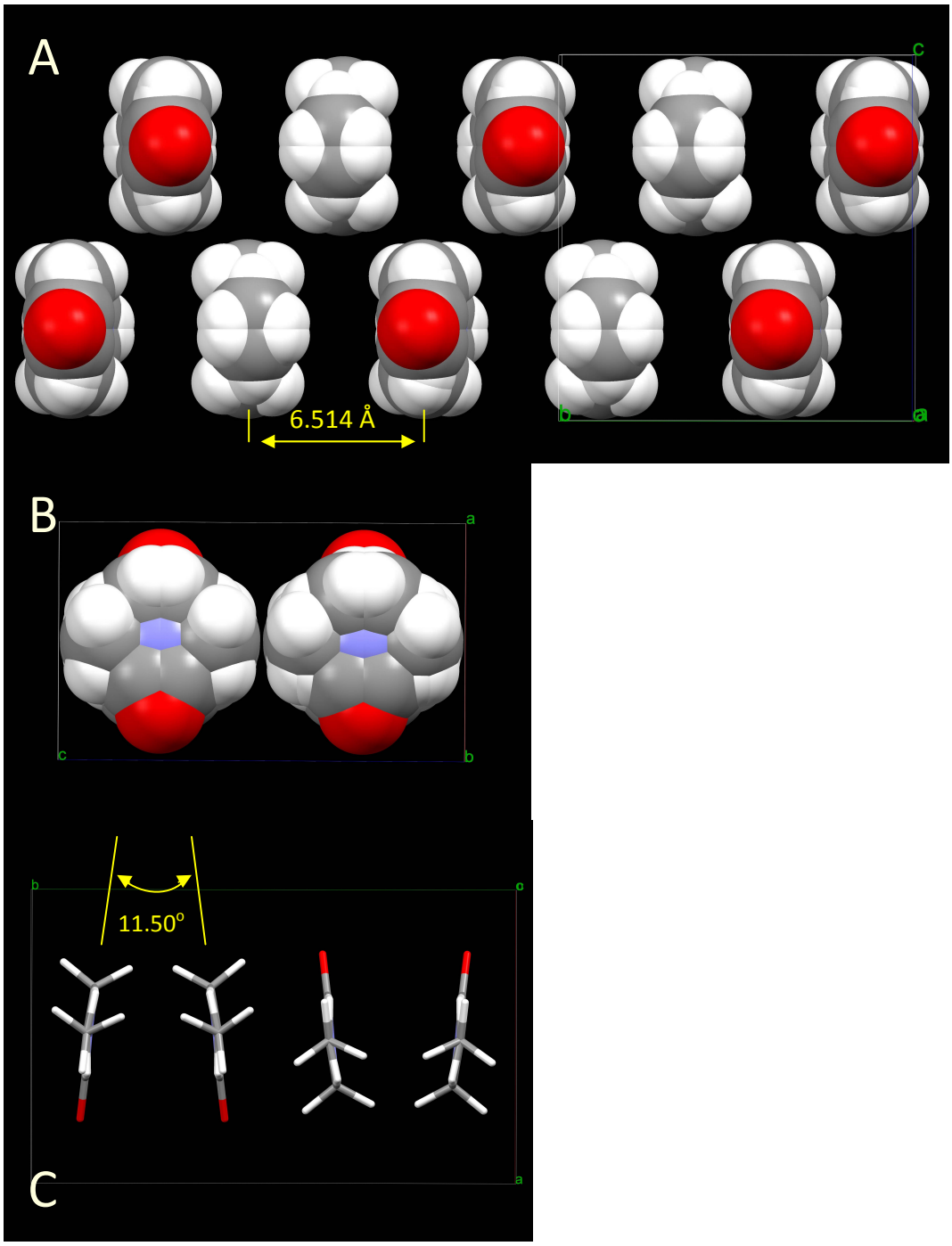
Successfully modeled two positional disorder of the solvent molecule in the structure of 1,3-BCO DMF. The mirror plane passes through O1s atom as shown with dotted line. Symmetry transformation for #1: x, y, ½ - z



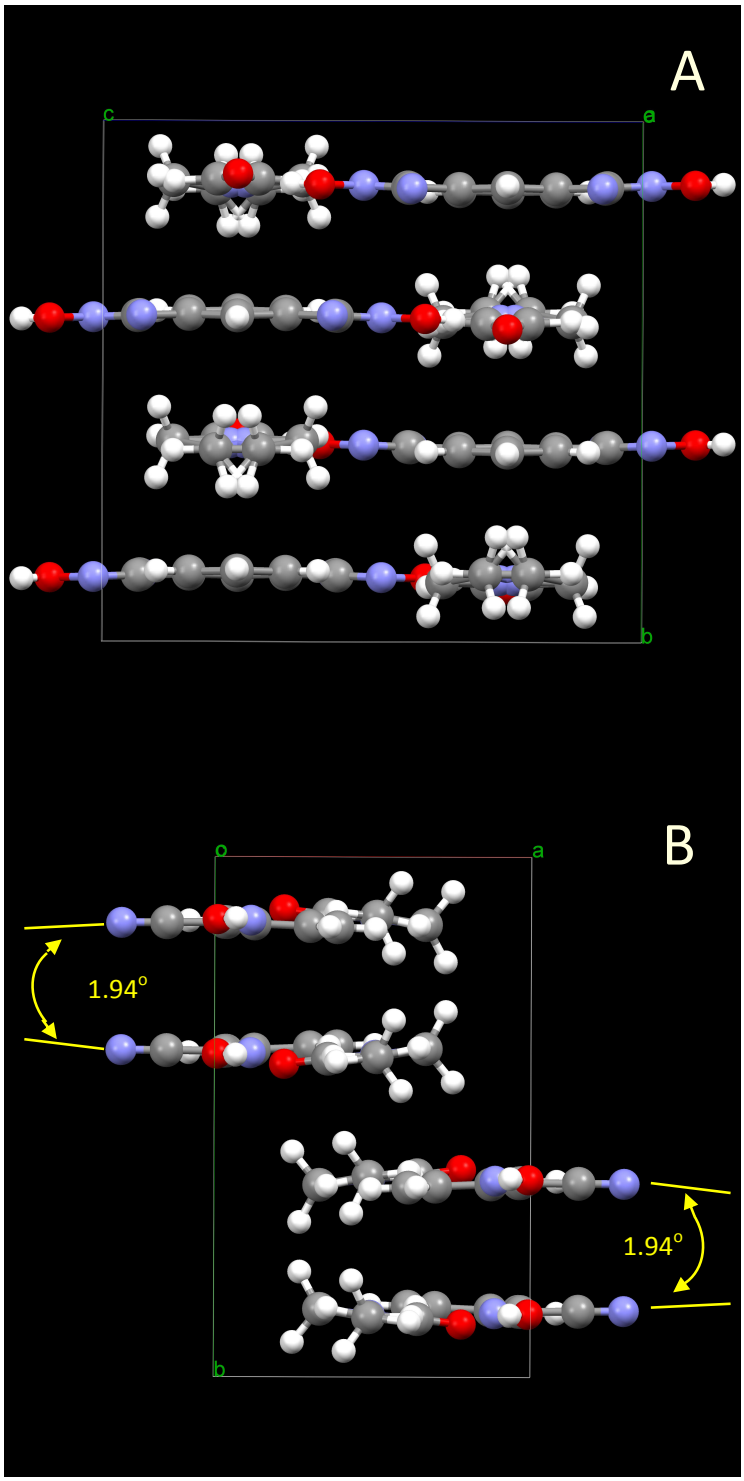
H-bonding in the structure involves two bis(cyanoximes) and one DMF molecule. A planar H-bonded sheet is formed along *c* direction.



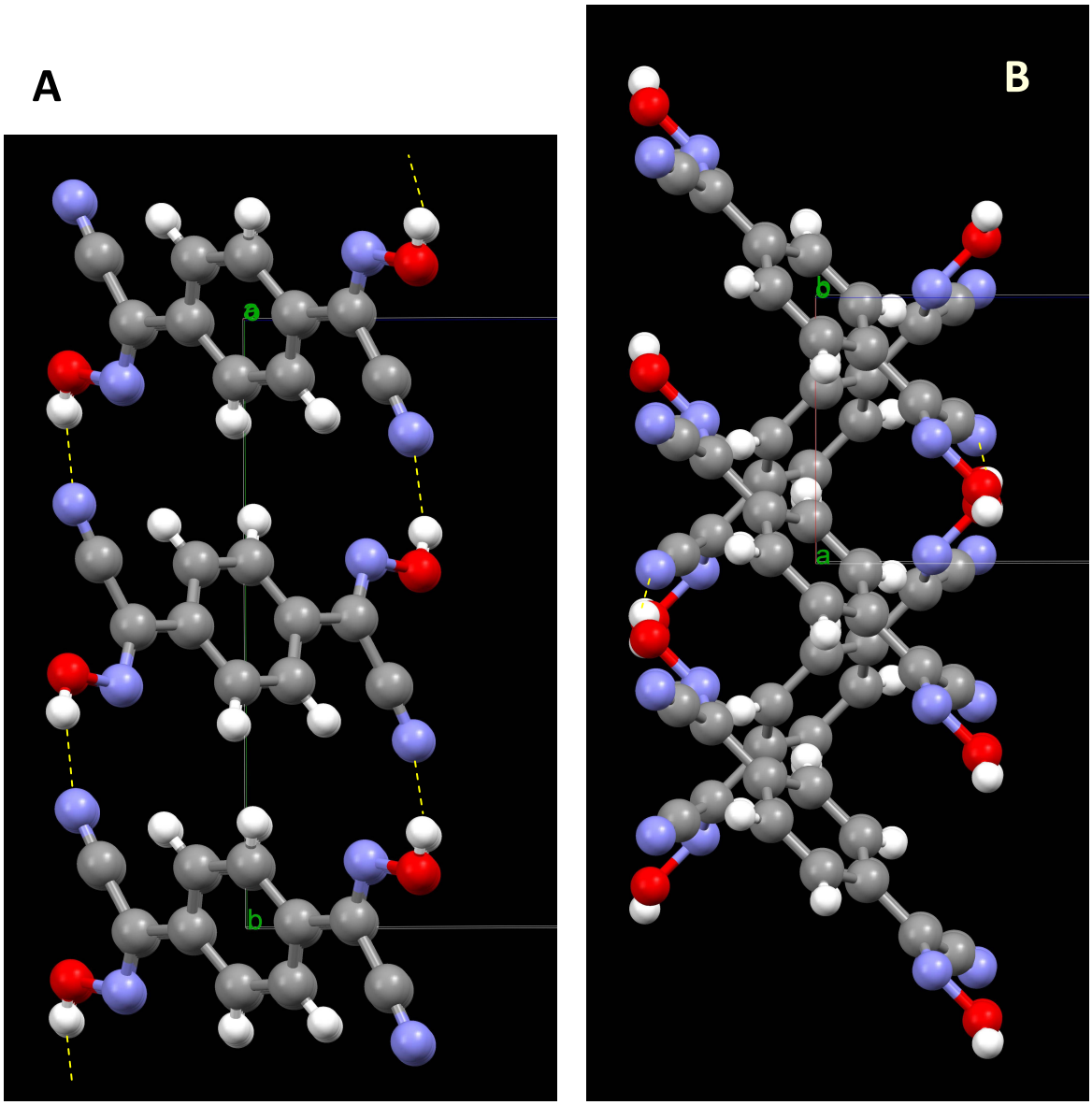
Two orthogonal views of 2.5 unit cells in the structure of 1,3-BCO DMF. Large channels along b axis are filled with the solvent molecules. Molecules of cyanoximes are omitted and only disordered solvent molecules are shown in space-filling representation. **A** – view along *a* direction, **B** – view along *b*, **C** – stick representation of DMF molecules to show the tilt angle between solvent molecules.



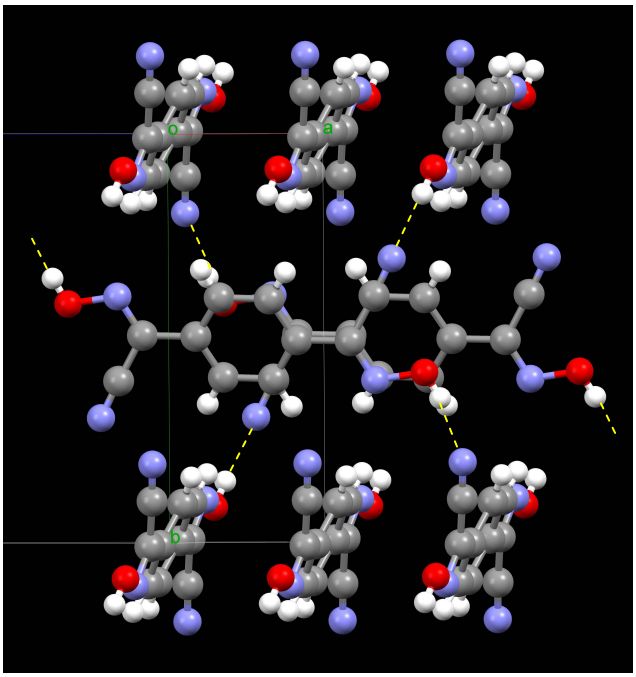
Two orthogonal views of the unit cell content in the layered structure of 1,3-BCO DMF: **A** – along *a* axis, **B** – along *c* direction.

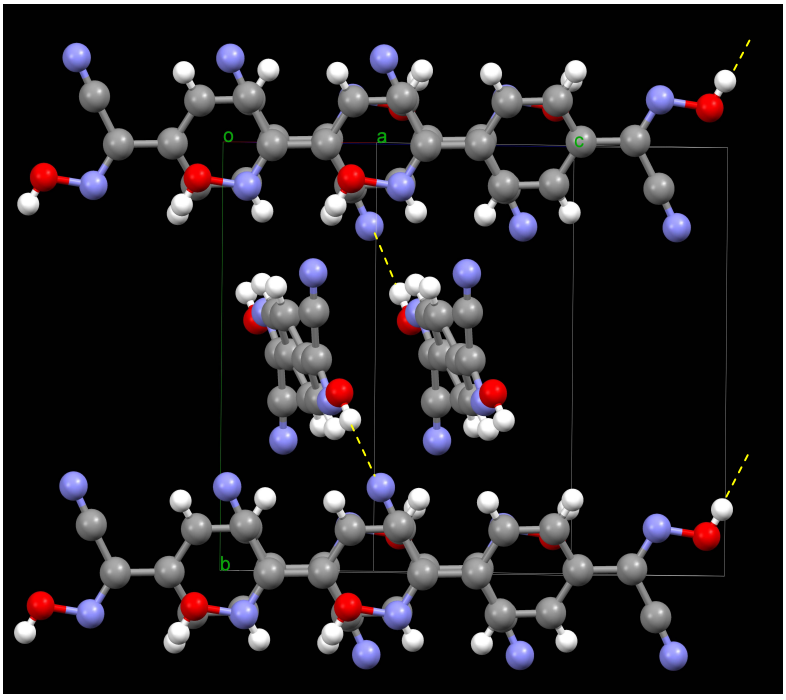


Organization of crystal lattice in the structure of 1,4-BCO. Two orthogonal views of the fragment in the structure showing only one selected column of H-bonded molecules in two adjacent two unit cells. **A** – view along *a* direction, **B** – view along *b* direction.

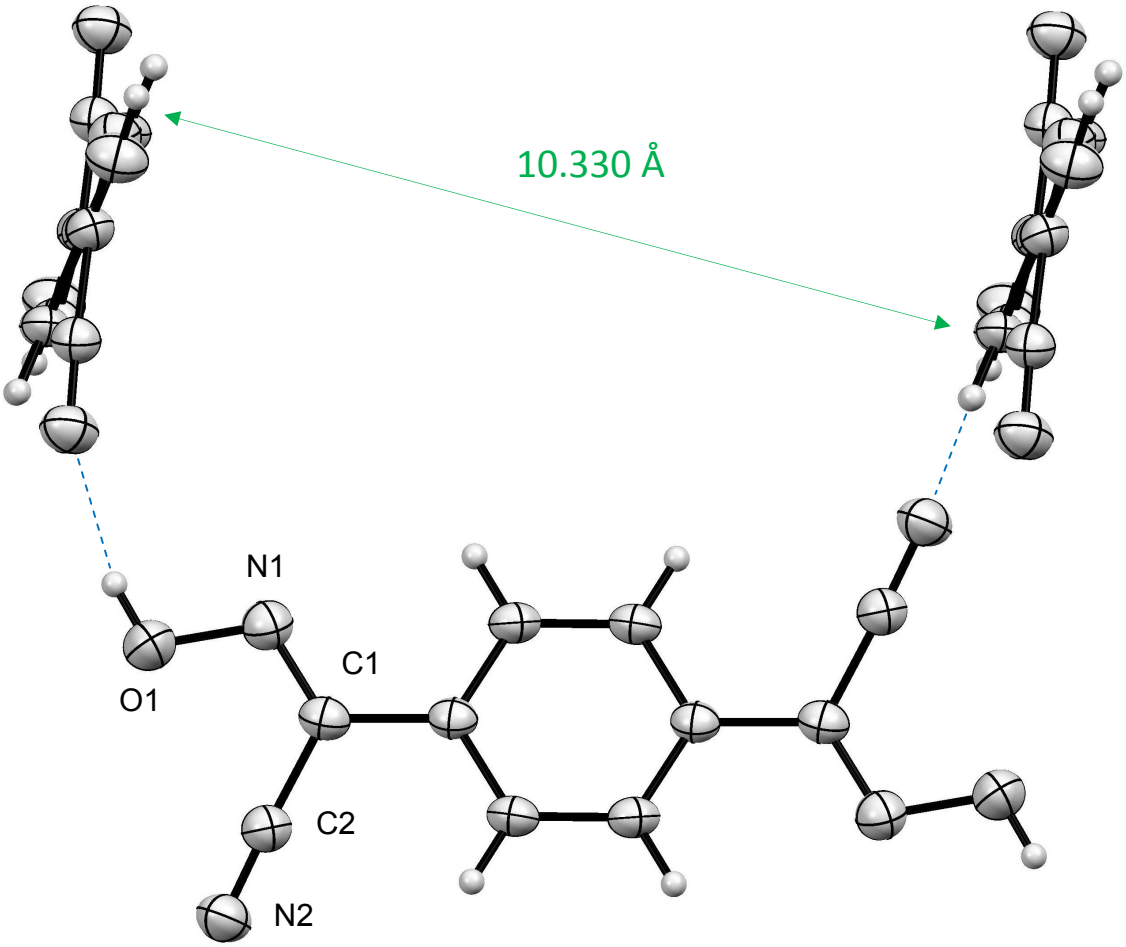


Organization of crystal lattice in the structure of 1,4-BCO: same fragment only shown at different projections to illustrate H-bonding pattern which represents “herring bone” type layers running along *b* direction. Hydrogen bonds are shown as dotted lines.

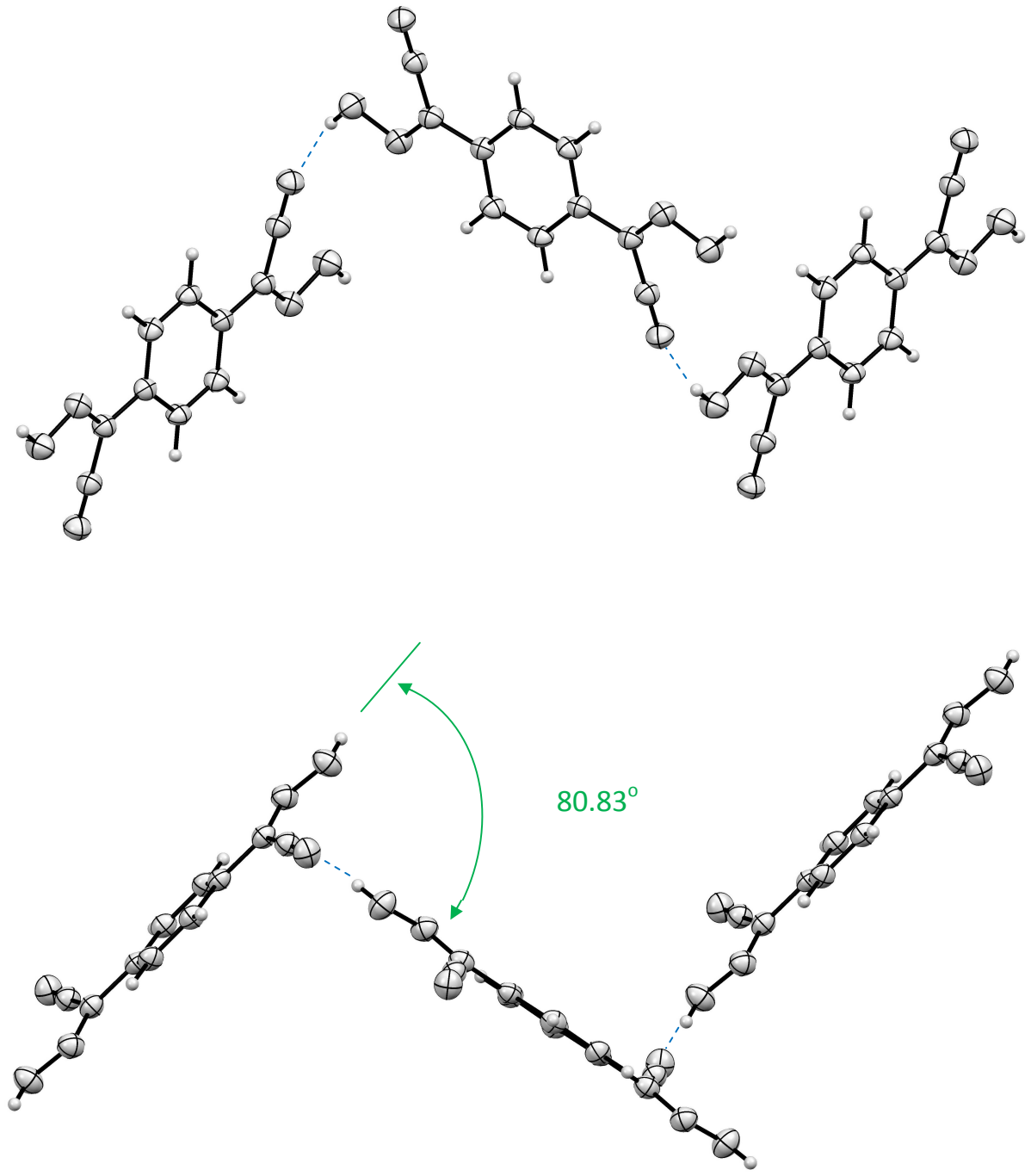




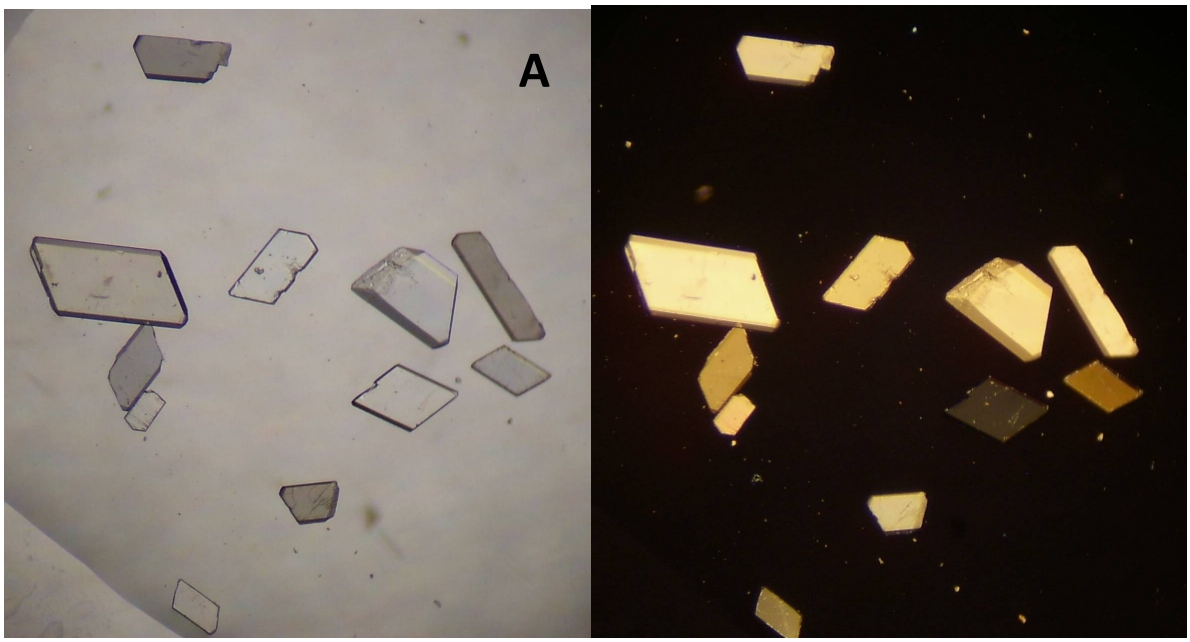
H-bonding in the structure of 1,4-BCO showing the shortest distance between two dioxime molecules separated by another one acting as a spacer.

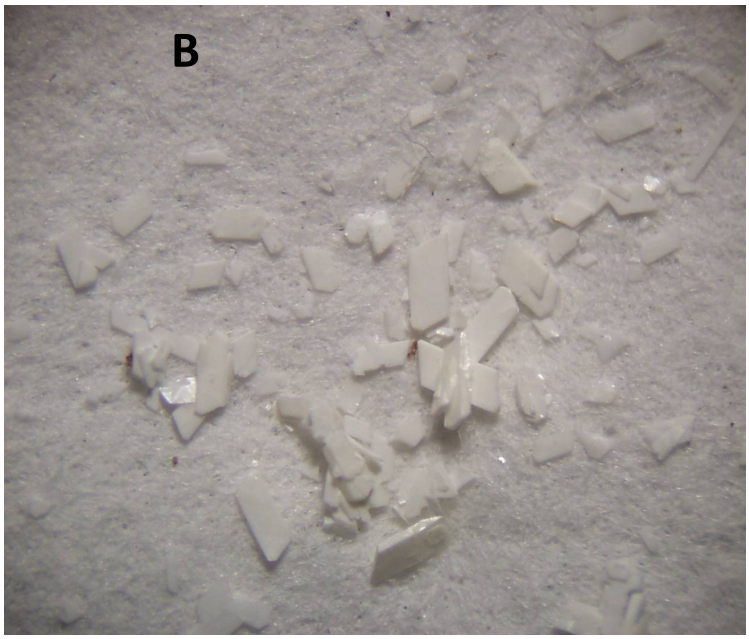


Building block in the structure: zigzag chain of 1,4-bis(cyanoxime)benzene connected via H-bonds.



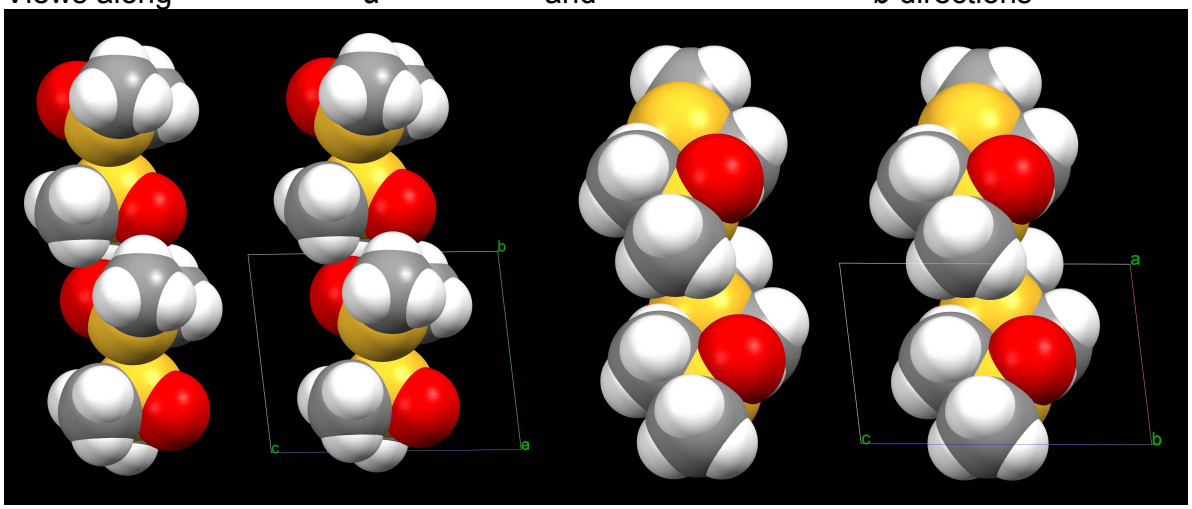
Actual microscope photographs of clear, suitable for the X-ray analysis crystals of 1,4-BCO x DMSO (**A**; ambient and polarized light) that grew up in dimethylsulfoxide, and opaque, non-suitable for crystallographic studies crystals of the dioxime when the solvent left after a week of exposure to air on a paper filter (**B**).



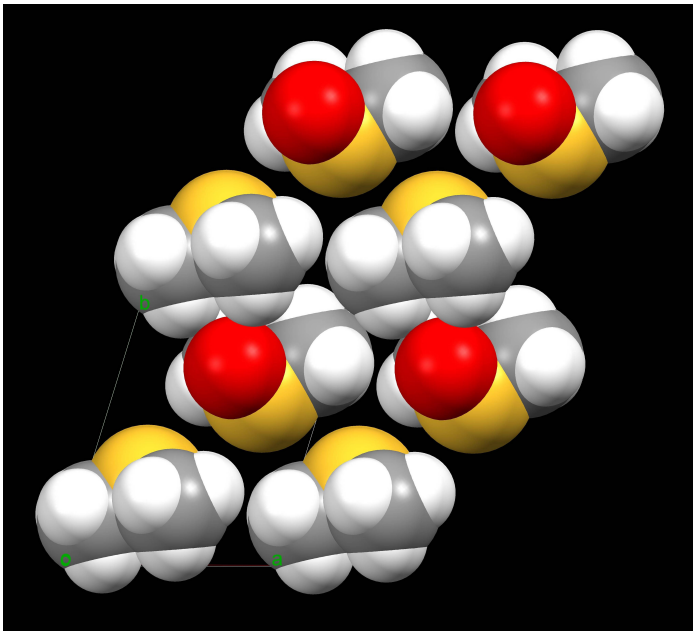


Details of the solvent packing into the crystal of 1,4-BCO x DMSO. Only solvent molecules occupying channels in the structure are shown; the dioxime molecules are omitted for clarity.

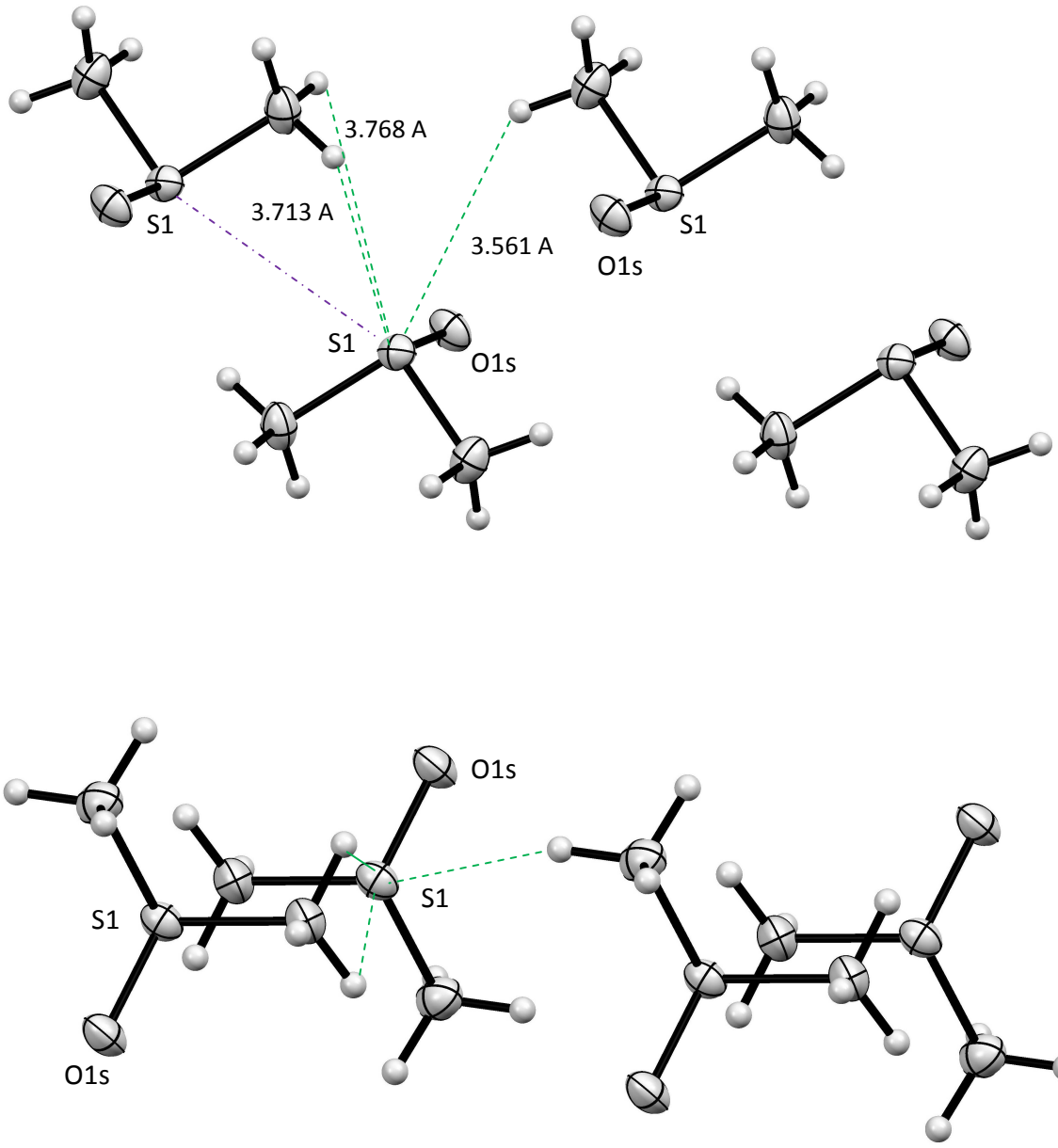
Views along *a* and *b* directions



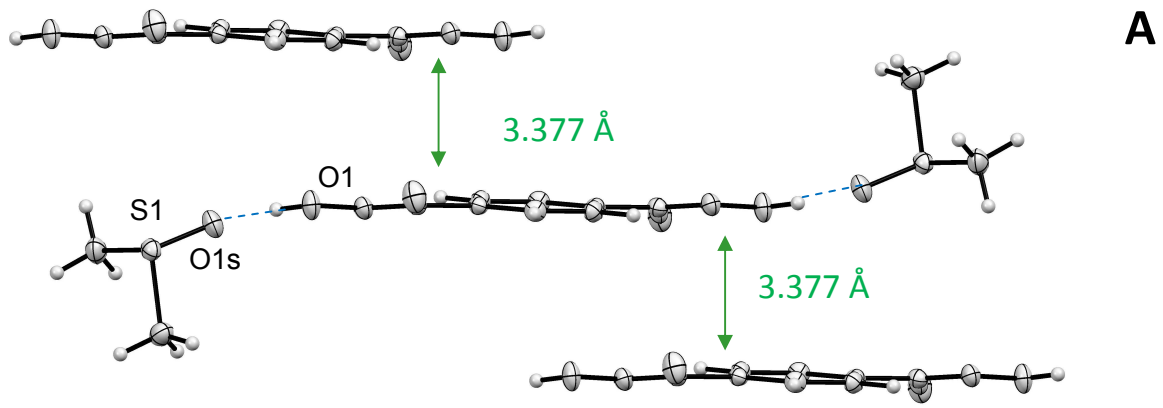
View along *c*



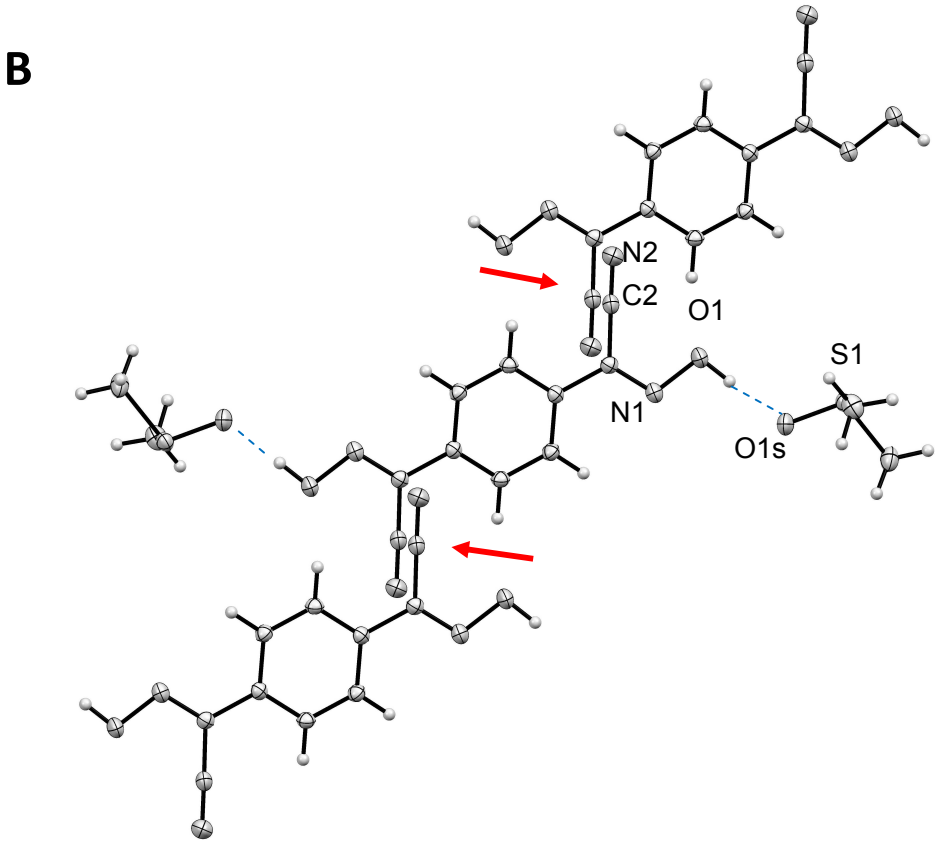
Two views of 4 DMSO molecules trapped between layers of the 1,4-BCO in the structure showing distant electrostatic C-H---S contacts.



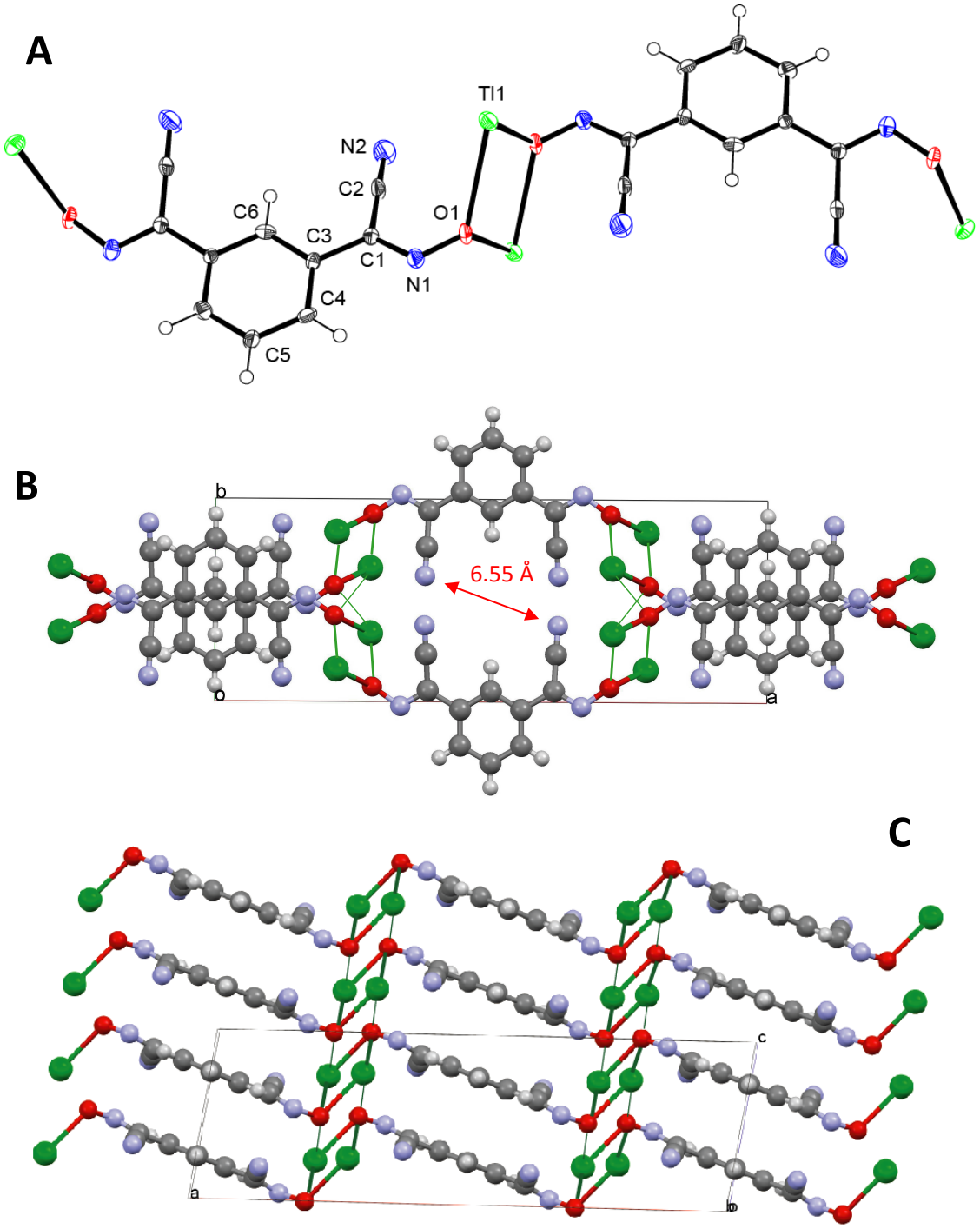
Two orthogonal views of the fragment of structure of 1,4-BCO x DMSO showing layers of molecules (**A**) with solvent connected to the dioxime via H-bonds (**B**).



A little overlap between π-systems of the C-C≡N fgragments (red arrows) contributes to stabilization of this structure that otherwise does not exhibit any significant π-stacking:

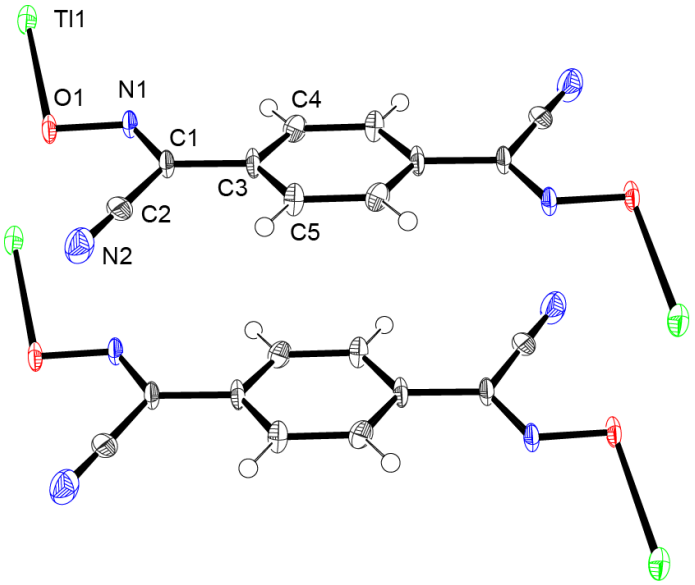


The GROW fragment in the structure of Tl_2(1,3-BCO) (**A**) that is a centrosymmetric dimer, and two views of two unit cells along *c* (**B**) and *b* directions (**C**). Cell volume: 1165.32 Å^3, structure occupies 830.18 Å^3 (71.2%); accessible volume – 29.8%.

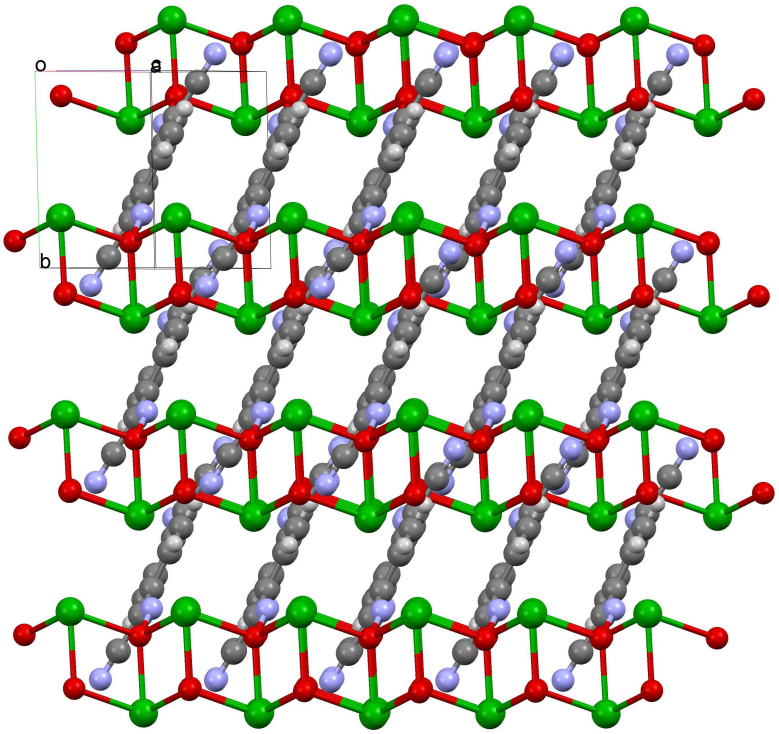


The GROW fragment in the structure of Tl_2(1,4-BCO) (**A**), which is a centrosymmetric dimer, and prospective views of three unit cells along *ac* diagonal (**B**) showing elegant Tl_2O_2 rhombs assmbled in a ladder-type motif. Cell volume: 290.73 $Å^3$, structure occupies 205.83 $Å^3$ (70.8%); accessible volume – 29.2%.

A



B



Selected the most important crystal data for structures of two based on Tl(I) and new bis-cyanoximes complexes that form metal-organic-frameworks.

	Tl_2(1,3-BCO)	**Tl_2(1,4-BCO)**
Empirical formula	C_{10} H_4 N_4 O_2 Tl_2	C_5 H_2 N_2 O Tl
Formula weight	620.91	310.46
Temperature	120(2) K	120(2) K
Crystal system	Monoclinic	Triclinic
Space group	C2/c	P-1
Unit cell dimensions	a = 21.672(4) Å;	a = 3.9696(15) Å;
	b = 7.8698(13) Å;	b = 6.672(2) Å;
	c = 6.9082(11) Å;	c = 11.149(4) Å;
	α= 90°	α= 83.551(5)°
	β= 98.487(2)°	β= 82.254(5)°
	γ = 90°	γ = 89.516(5)°
Volume	1165.3(3) $Å^3$	290.73(17) $Å^3$
Z	4	2
Density (calculated)	3.539 Mg/m^3	3.546 Mg/m^3
Absorption coefficient	27.619 mm^{-1}	27.675 mm^{-1}
F(000)	1080	270
Θ range for data collection	1.90 to 30.51°	1.86 to 26.20°
Reflections collected	8280	3208
Independent reflections	1757 [R(int) = 0.0474]	1158 [R(int) = 0.0418]
Absorption correction	Semi-empirical from equivalents	
Refinement method	Full-matrix least-squares on F^2	
GOF on F^2	1.073	1.035
Final R indices [I>2σ(I)]	R1 = 0.0388, wR2 = 0.0813	R1 = 0.0402, wR2 = 0.0972
R indices (all data)	R1 = 0.0480, wR2 = 0.0862	R1 = 0.0464, wR2 = 0.0998
Largest diff. peak and hole, $e.Å^{-3}$	4.628 and -2.785	4.161 and -2.118