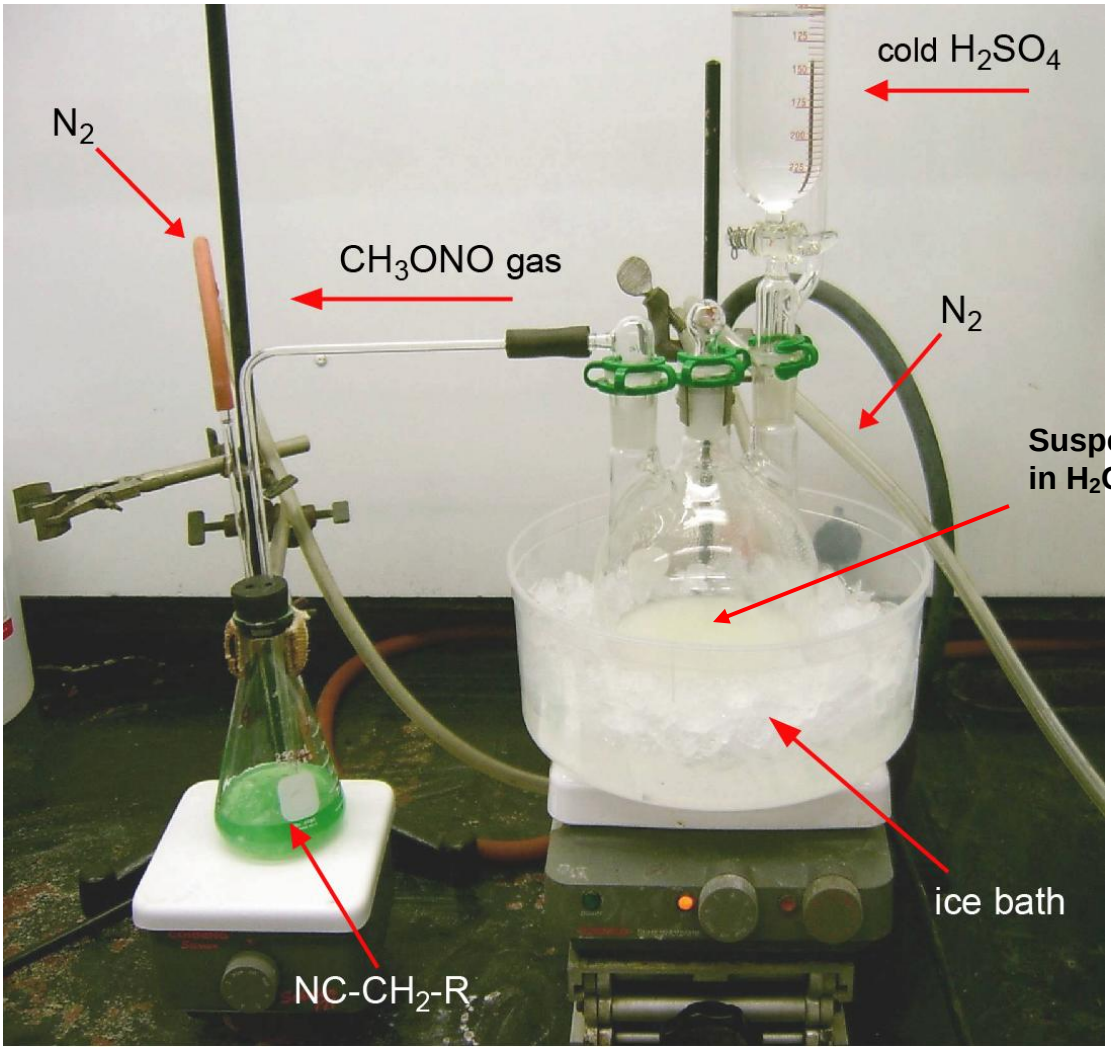
Used in our work experimental setup for generation of gaseous methylnitrite, CH_3ONO.

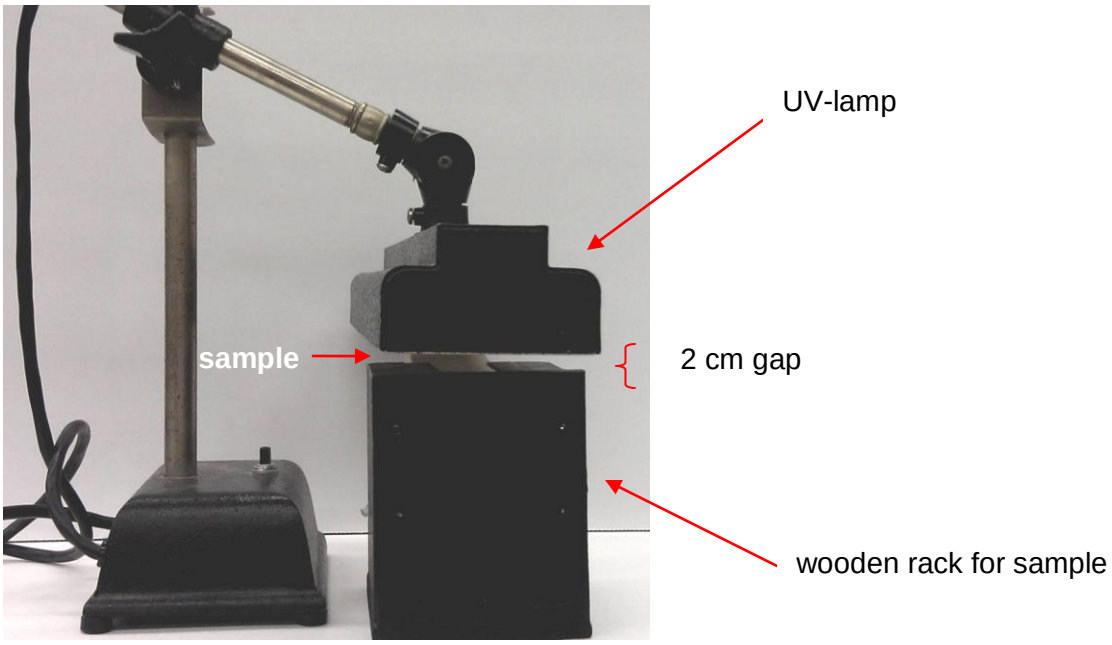


Sample holders were prepared from four strips of black cardboard, tape, and white paper. Next, the Ag(I)-cyanoximate salt was compressed into a uniform thickness on each sample holder (Figure 5.) The samples were then tested for “adhesiveness” via tapping to ensure they would not fall off mid-measurement in the spectrophotometer. The samples rested in a wooden apparatus that held them in place.

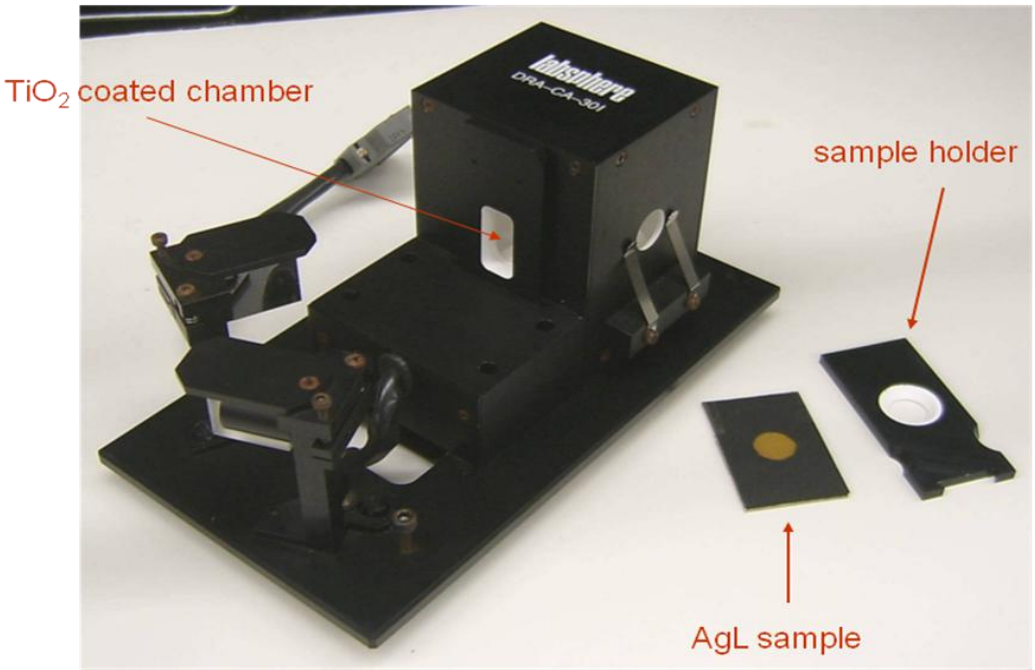
Preparation of solid samples of **3** and **6** for photophysical studies: **A** – placement and spreading of finely ground compounds onto the black cardboard; **B** – cardboard attached to the sample holder;

A **B**

The UV light was laid directly on top of the wooden holder, approximately 2 cm away from the samples. The samples were exposed to thirty minutes of 254 nm light. After each round of thirty minutes, the samples were removed from the UV light, photographed, and their reflectance spectra were recorded.



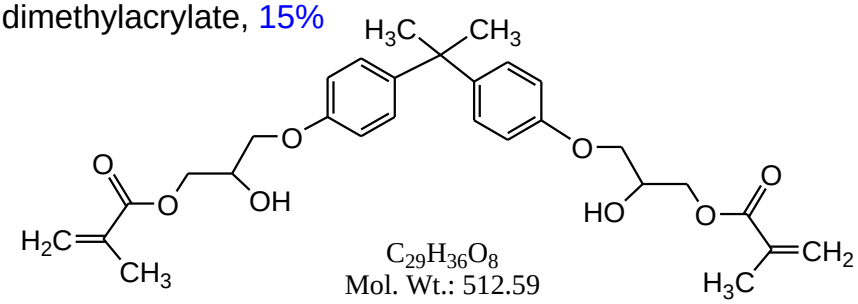
The integrating sphere (an accessory to the Cary 100 Bio UV-visible spectrometer).



Empirical trials with adjusting of percentage of ingredients for the polymer mixture resulted in optimized the following composition of a truly flowable acrylate composite that is displayed in Figure below along with mass % for each component.

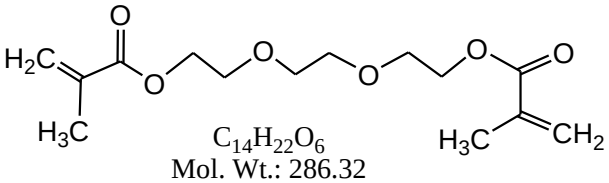
Bisphenol A glycerolate dimethylacrylate, 15%

Bis-GMA



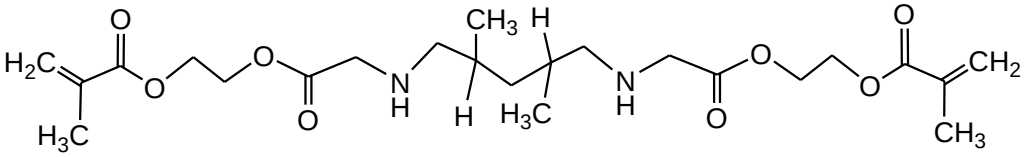
$C_{29}H_{36}O_8$
Mol. Wt.: 512.59

TEGMA, 20%



$C_{14}H_{22}O_6$
Mol. Wt.: 286.32

UDMA, 20%

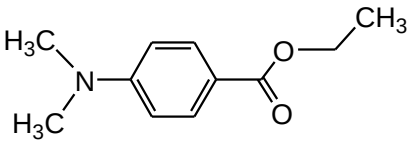


$C_{23}H_{38}N_2O_8$
Mol. Wt.: 470.56

SiO_2, 45%

EDMAB, 0.5%

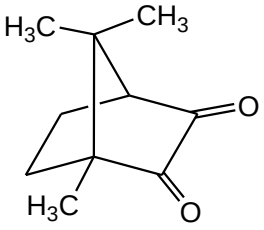
Ethyl-(4-dimethylamino)benzoate



$C_{11}H_{15}NO_2$
Mol. Wt.: 193.24

CPQ, 0.5%

Camphorquinone

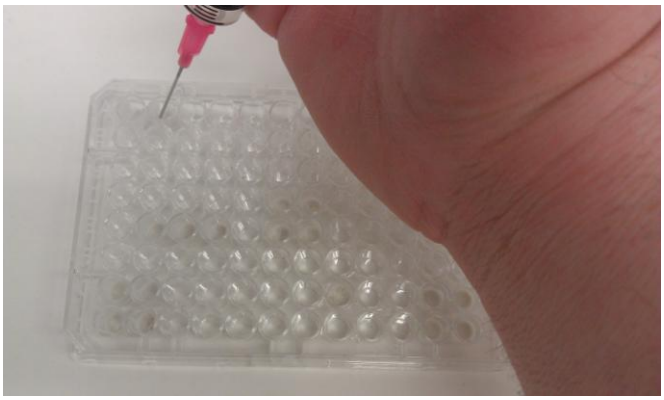


$C_{10}H_{14}O_2$
Mol. Wt.: 166.22

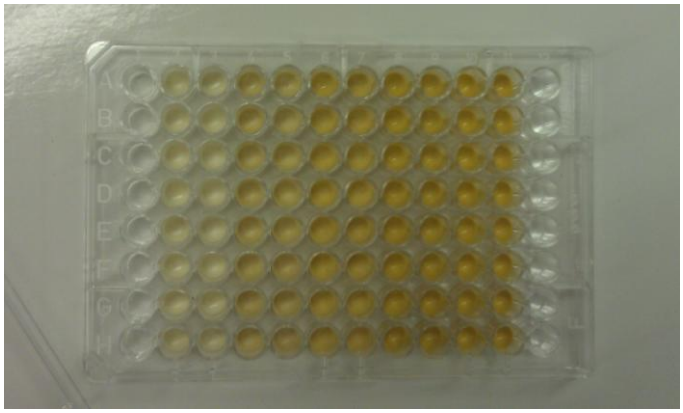
Actual protocol of making composite is the following (using abbreviations in Figure above):

1) Add TEGMA and UDMA ingredients into flask and mix them thoroughly for 2 minutes;
2) Add Bis-GMA and stir using mechanical stirrer at least 5 minutes at high speed;
3) Silica powder was added in 2 g increments and stirred for 5 minutes at high speed between additions of each portion;
4) Add dried, powdery Ag(I) cyanoximate and stir for 10 minutes;
5) Add CPQ and then separately EDMAB and mixed for 2 min at high speed between additions;
6) Final mixing of all components for additional 10 minutes.

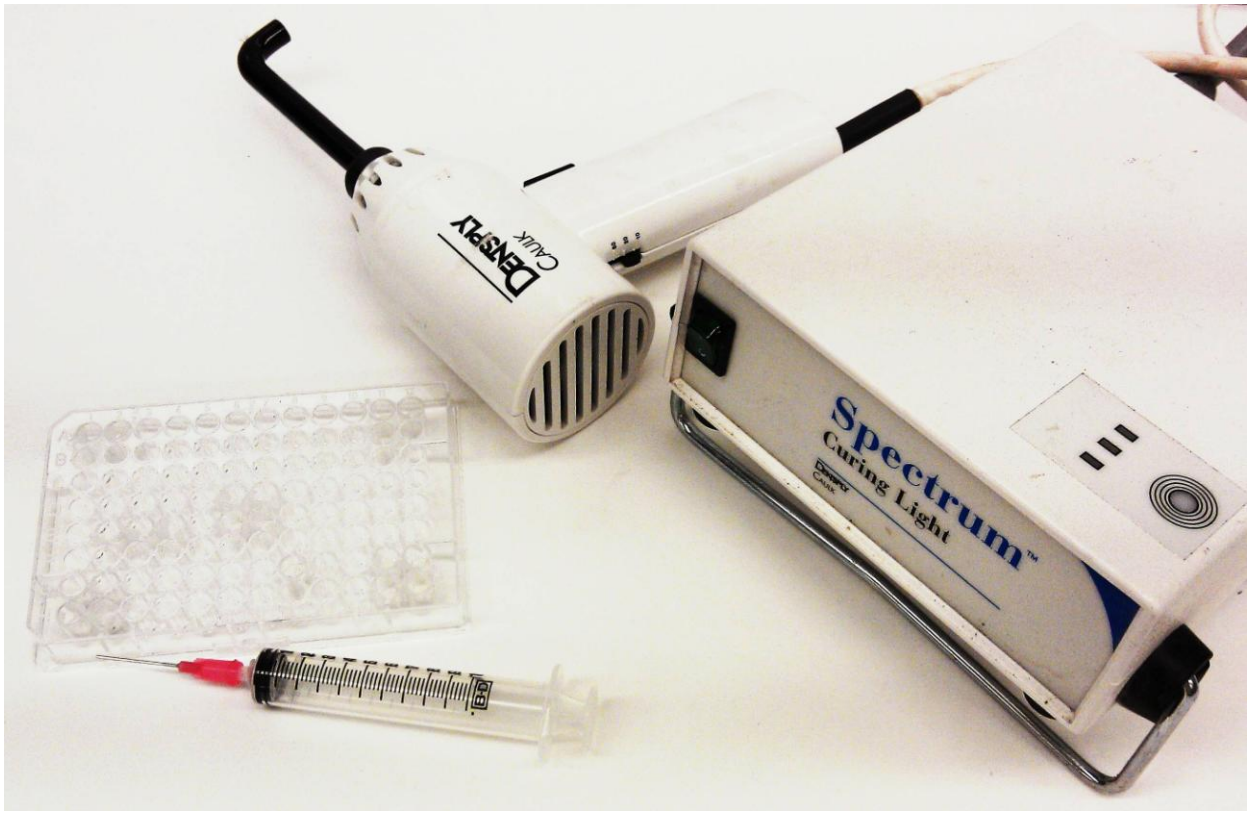
All these procedures were carried out in dark and under N_2 protection to prevent premature polymerization reactions and oxidation of susceptible ingredients. The mixture was loaded into the syringe, and then dispensed into the wells in the 96-wells plate as shown in Figure below.



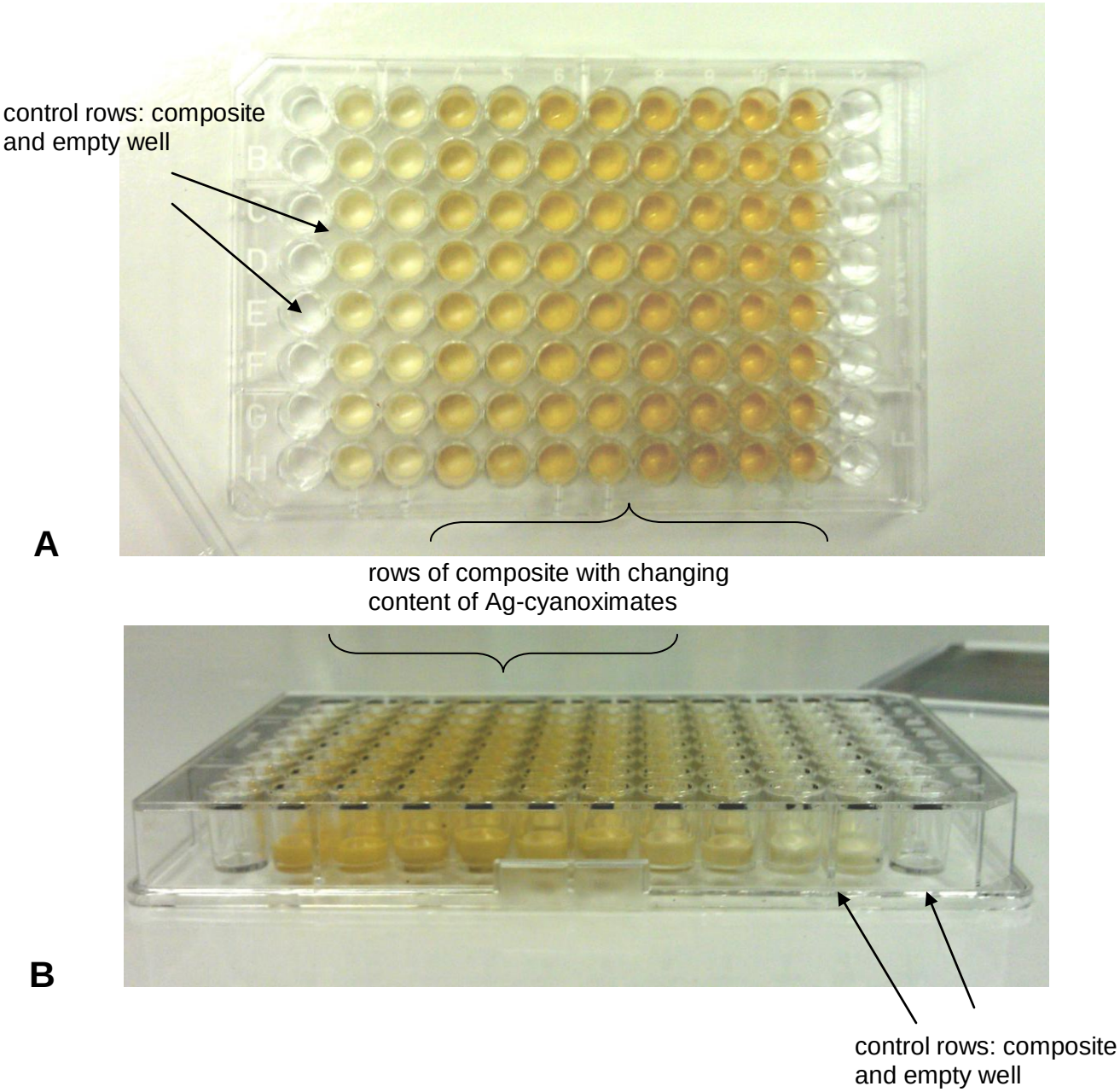
Actual appearance of prepared for microbiological testing polymeric composite (prior *to the light-induced polymerization!*) can be seen in here:



The process of extrusion was not very efficient and could not guarantee sufficient for our work homogeneity. Therefore, we explored several available receipts of dental polymeric composites and modified them to the extent of making the final mixture less viscous, so it should be possible to fill with it a syringe. The latter was used to deliver the mixture into the 96-wells plate that the co-PI Prof. Marianna Patrauchan has selected for the microbiological studies. The Spectrum© curing light source, with output at ~400 nm that is commonly used in dental practice, was selected for cross-linking the polymeric composite (Figure below).



Photographs of 96-wells plates with solid, light-polymerized composite containing embedded, homogenized Ag(I) cyanxoimates. A – top view; B – side view.

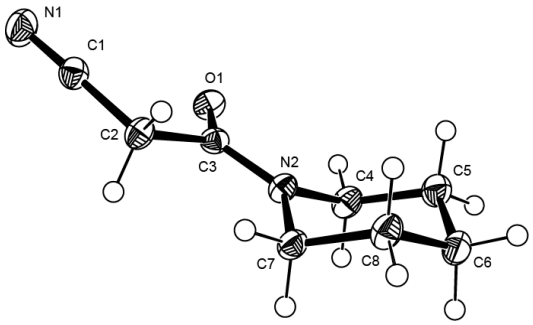


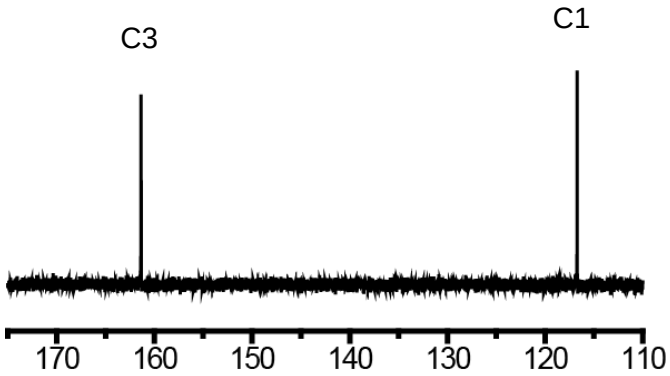
	Compound **1**, pre-PiPCO	Compound **4**, pre-MCO
Empirical formula	$C_8 H_{12} N_2 O$	$C_7 H_{10} N_2 O_2$
Formula weight	152.20	154.17
Temperature	120(2) K	120(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Orthorhombic
Space group	P 2_1/c	P b c a
Unit cell dimensions	a = 9.5392(6) Å b = 8.8975(5) Å c = 9.7075(6) Å α= 90° β= 101.6150(10)° γ = 90°	a = 8.8295(5) Å b = 7.0794(4) Å c = 23.7744(14) Å α= 90° α= 90° α= 90°
Volume	807.05(8) $Å^3$	1486.08(15) $Å^3$
Z	4	8
Density (calculated)	1.253 Mg/m^3	1.378 Mg/m^3
Absorption coefficient	0.085 mm^{-1}	0.103 mm^{-1}
F(000)	328	656
Crystal size, mm	0.55 · 0.09 · 0.09	0.50 · 0.30 · 0.30
Θ range for data collection	2.18 to 30.28°	1.71 to 30.50°
Index ranges	-13<=h<=13, -12<=k<=12, -13<=l<=13	-12<=h<=12 -10<=k<=10 -33<=l<=33
Reflections collected	17903	20206
Independent reflections	2413 [R(int) = 0.0446]	2256 [R(int) = 0.0304]
Completeness to Θ, %	30.28° (99.5 %)	30.50° (99.4 %)
Absorption correction	Numerical	Numerical
T_{max}. and T_{min}.	0.9925 and 0.9546	1.000 and 0.9655
Structure solution	Direct methods	
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	2413 / 0 / 100	2256 / 0 / 100
Goodness-of-fit on F^2	1.465	1.042
Final R indices [I>2s(I)]	R1=0.0490, wR2=0.1098	R1=0.0355, wR2=0.0870
R indices (all data)	R1=0.0792, wR2=0.1246	R1=0.0447, wR2= 0.0935
Largest diff. peak and hole	0.248 / -0.252 $e.Å^{-3}$	0.339 / -0.188 $e.Å^{-3}$

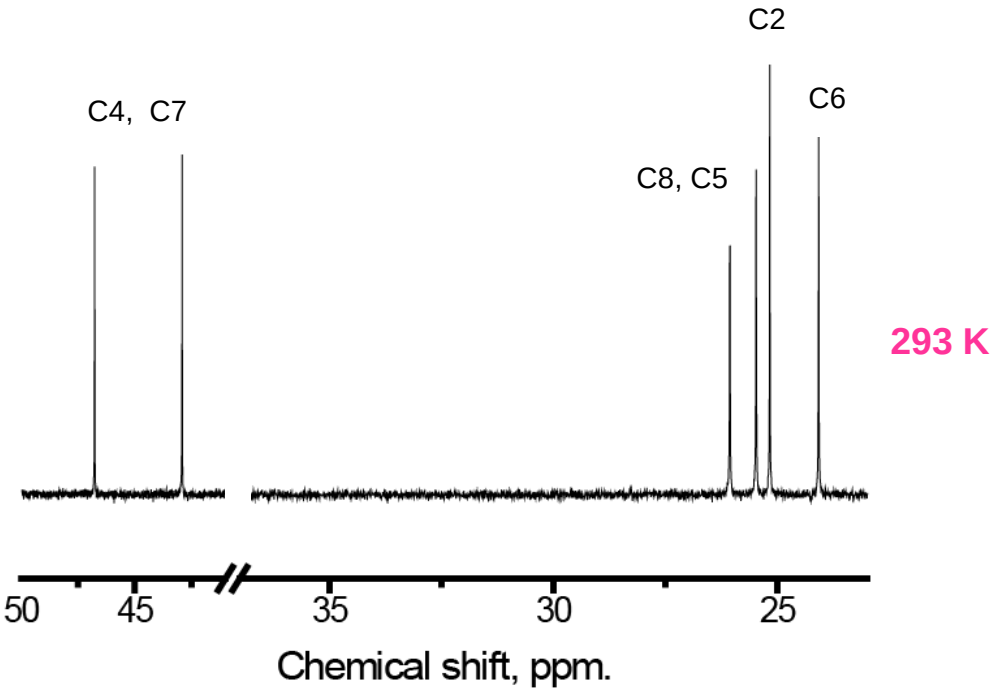
Selected bond lengths [Å] and angles [°] in the structures of N-morpholyl-amide acetonitrile (**4**), and N-piperidine-amide-acetonitrile, compound (**1**) – *precursors* for cyanoximes **HMCO** and **HPiPCO** respectively.

Compound **4**		Compound **1**	
		Bonds:	
C(1)-N(1)	1.1422(12)	C(1)-N(1)	1.1437(15)
C(1)-C(2)	1.4636(12)	C(1)-C(2)	1.4610(17)
C(2)-C(3)	1.5281(12)	C(2)-C(3)	1.5283(17)
C(3)-O(2)	1.2263(11)	C(3)-O(1)	1.2332(14)
C(3)-N(2)	1.3507(11)	C(3)-N(2)	1.3437(15)
C(4)-N(2)	1.4628(11)	C(4)-N(2)	1.4669(15)
C(4)-C(5)	1.5181(13)	C(4)-C(5)	1.5228(18)
C(5)-O(1)	1.4319(11)		
C(6)-O(1)	1.4285(12)		
C(6)-C(7)	1.5178(13)		
C(7)-N(2)	1.4619(11)		
		Angles:	
N(1)-C(1)-C(2)	179.24(10)	N(1)-C(1)-C(2)	177.21(15)
C(1)-C(2)-C(3)	110.08(7)	C(1)-C(2)-C(3)	111.06(10)
O(2)-C(3)-N(2)	123.40(8)	O(1)-C(3)-N(2)	123.47(11)
O(2)-C(3)-C(2)	120.64(8)	O(1)-C(3)-C(2)	119.87(10)
N(2)-C(3)-C(2)	115.96(7)	N(2)-C(3)-C(2)	116.65(11)
N(2)-C(4)-C(5)	109.06(8)	N(2)-C(4)-C(5)	110.89(10)
O(1)-C(5)-C(4)	111.58(8)		
O(1)-C(6)-C(7)	111.58(8)		
N(2)-C(7)-C(6)	109.41(8)		
C(3)-N(2)-C(7)	120.31(8)		
C(3)-N(2)-C(4)	126.52(7)		
C(7)-N(2)-C(4)	112.70(7)		
C(6)-O(1)-C(5)	110.38(7)		

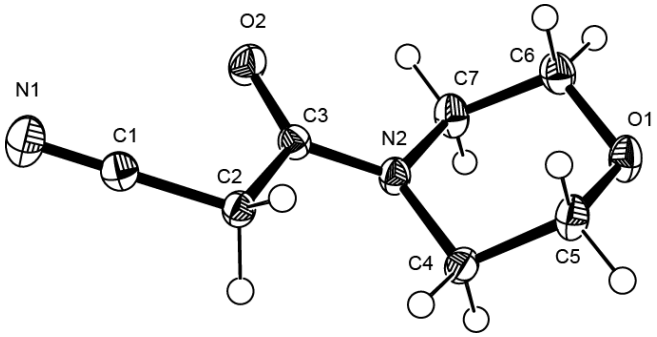
The $^{13}C\{^{1}H\}$ NMR spectrum (and numbering) of **1** in dmso-d_6.

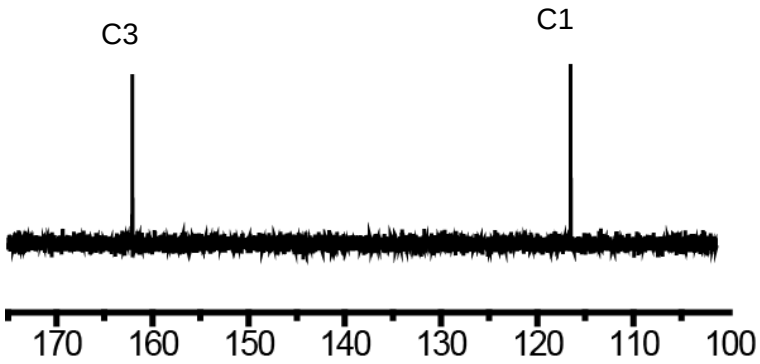


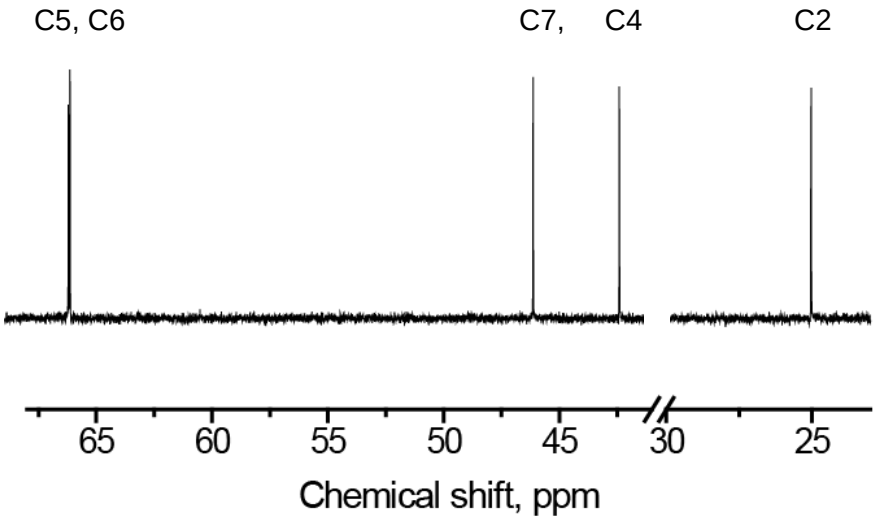




The $^{13}C\{^{1}H\}$ NMR spectrum (and numbering) of **4** in dmso-d_6.







293 K

checkCIF/PLATON report (publication check)

No syntax errors found.
Please wait while processing ....

CIF dictionary
Interpreting this report

Datablock: crystal-1 prePiPCO (1)

Bond precision: C-C = 0.0018 A Wavelength=0.71073

Cell: a=9.5392(6) b=8.8975(5) c=9.7075(6)
alpha=90 beta=101.615(1) gamma=90

Temperature: 120 K

	Calculated	Reported
Volume	807.05(8)	807.05(8)
Space group	P 21/c	P 21/c
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C8 H12 N2 O	C8 H12 N2 O
Sum formula	C8 H12 N2 O	C8 H12 N2 O
Mr	152.20	152.20
Dx,g cm-3	1.253	1.253
Z	4	4
Mu (mm-1)	0.085	0.085
F000	328.0	328.0
F000'	328.12	
h,k,lmax	13,12,13	13,12,13
Nref	2426	2413
Tmin,Tmax	0.991,0.992	0.955,0.993
Tmin'	0.954	

Correction method= NUMERICAL

Data completeness= 0.995 Theta(max)= 30.280

R(reflections)= 0.0490(1686) wR2(reflections)= 0.1246(2413)

S = 1.465 Npar= 100

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

PLAT230 ALERT 2 C Hirshfeld Test Diff for C1 -- C2 .. 6.21 su

Alert level G

PLAT710 ALERT 4 G Delete 1-2-3 or 2-3-4 Linear Torsion Angle ... # 1
N1 -C1 -C2 -C3 18.00 0.00 1.555 1.555 1.555 1.555

0 **ALERT level A** = In general: serious problem
0 **ALERT level B** = Potentially serious problem
1 **ALERT level C** = Check and explain

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   1 ALERT level G = General alerts; check

   0 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
   1 ALERT type 2 Indicator that the structure model may be wrong or
deficient
   0 ALERT type 3 Indicator that the structure quality may be low
   1 ALERT type 4 Improvement, methodology, query or suggestion
   0 ALERT type 5 Informative message, check
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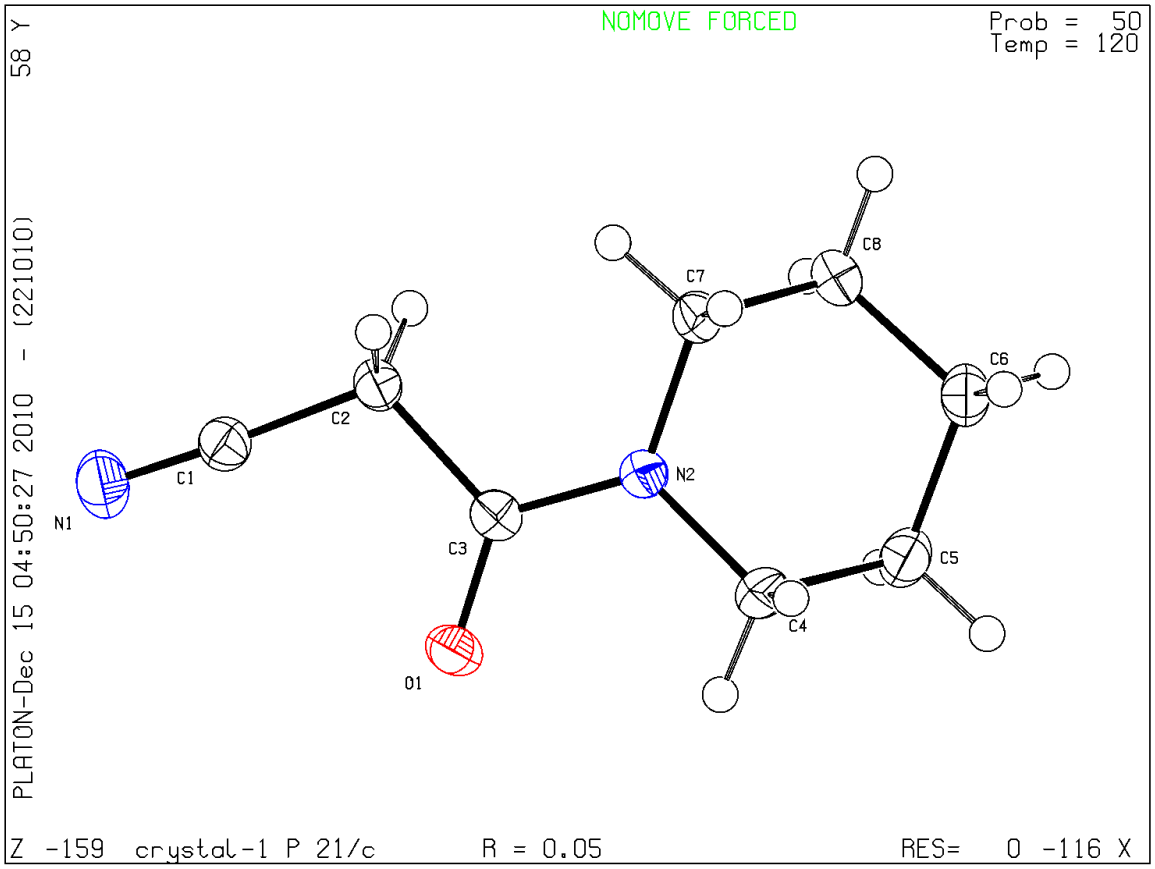
PLATON version of 22/10/2010; check.def file version of 11/10/2010

Datablock crystal-1 - ellipsoid plot



checkCIF/PLATON (full publication check)

Structure factors have been supplied for datablock(s) I

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary
Please wait while processing .... Interpreting this report
Structure factor report

Datablock: I preMCO (4)

Bond precision: C-C = 0.0013 A Wavelength=0.71073

Cell: a=8.8295(5) b=7.0794(4) c=23.7744(14)
alpha=90 beta=90 gamma=90

Temperature: 120 K

	Calculated	Reported
Volume	1486.08(15)	1486.08(15)
Space group	P b c a	P b c a
Hall group	-P 2ac 2ab	-P 2ac 2ab
Moiety formula	C7 H10 N2 O2	C7 H10 N2 O2
Sum formula	C7 H10 N2 O2	C7 H10 N2 O2
Mr	154.17	154.17
Dx,g cm-3	1.378	1.378
Z	8	8
Mu (mm-1)	0.103	0.103
F000	656.0	656.0
F000'	656.31	
h,k,lmax	12,10,33	12,10,33
Nref	2268	2256
Tmin,Tmax	0.964,0.970	0.965,1.000
Tmin'	0.950	

Correction method= NUMERICAL

Data completeness= 0.995 Theta(max)= 30.500

R(reflections)= 0.0355(1871) wR2(reflections)= 0.0935(2256)

S = 1.042 Npar= 100

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.

Click on the hyperlinks for more details of the test.

Alert level C

PLAT911_ALERT_3_C Missing # FCF Refl Between THmin & STh/L= 0.600 8

Alert level G

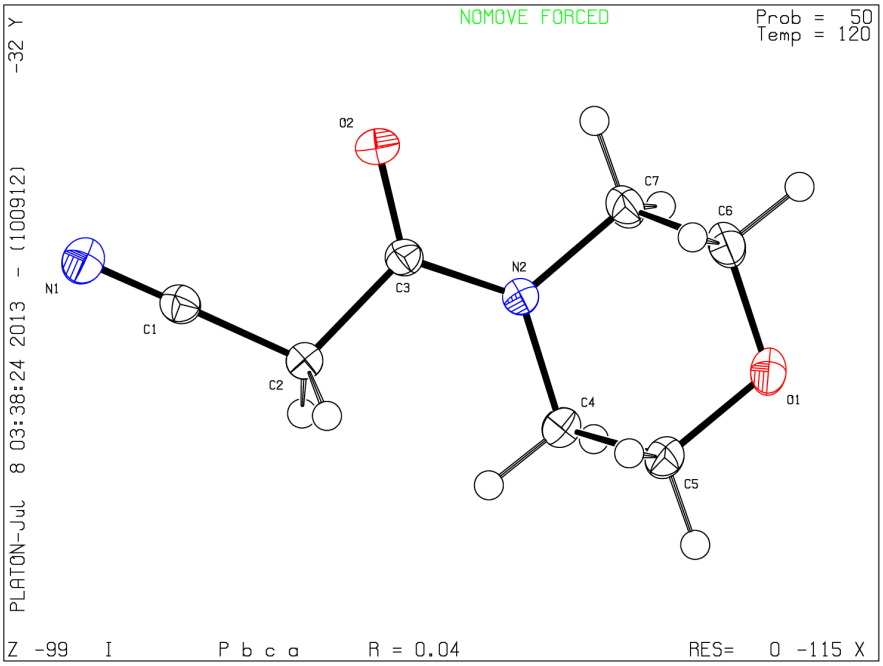
PLAT005_ALERT_5_G No _iucr_refine_instructions_details in the CIF ? Do !
PLAT230_ALERT_2_G Hirshfeld Test Diff for C1 -- C2 .. 7.8 su
PLAT912_ALERT_4_G Missing # of FCF Reflections Above STh/L= 0.600 5

0 **ALERT level A** = Most likely a serious problem - resolve or explain
0 **ALERT level B** = A potentially serious problem, consider carefully
1 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
3 **ALERT level G** = General information/check it is not something unexpected

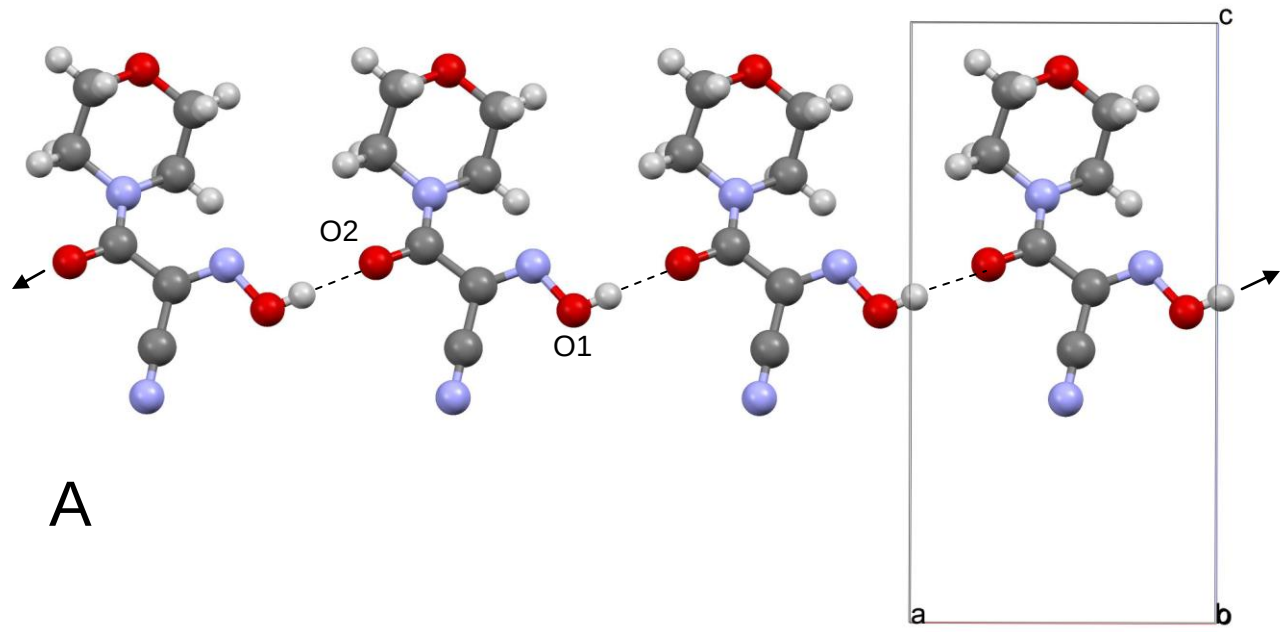
0 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
1 ALERT type 2 Indicator that the structure model may be wrong or deficient
1 ALERT type 3 Indicator that the structure quality may be low
1 ALERT type 4 Improvement, methodology, query or suggestion
1 ALERT type 5 Informative message, check

PLATON version of 01/06/2013; check.def file version of 24/05/2013

Datablock I - ellipsoid plot

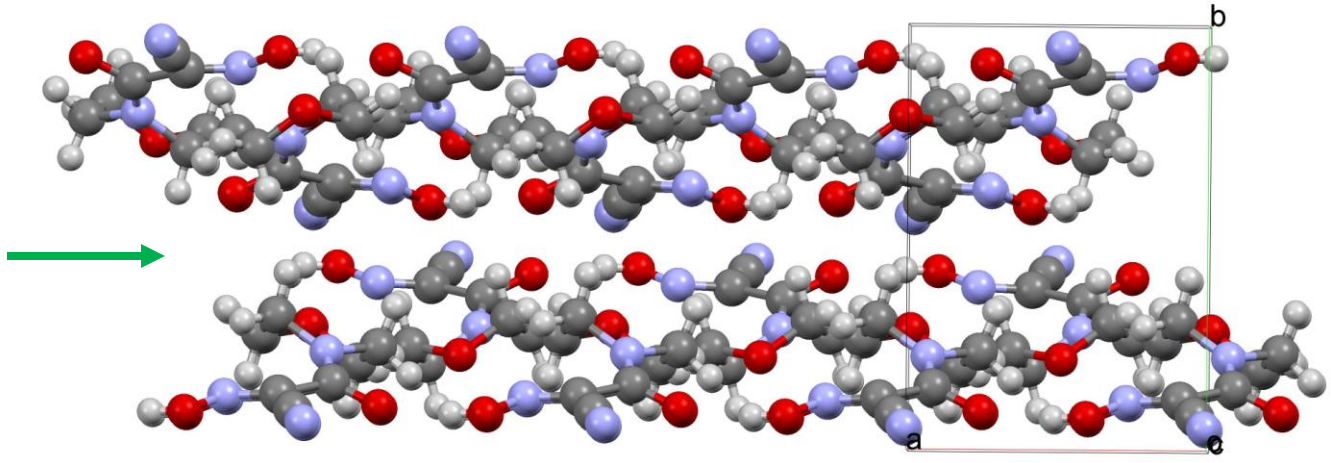


Packing diagram in the structure of HMCO (**5**): **A** – H-bonded chain of molecules (shown view along *b* direction); **B** – several unit cells viewed along *c* direction. The shearing plane of the crystal indicated with green arrow.

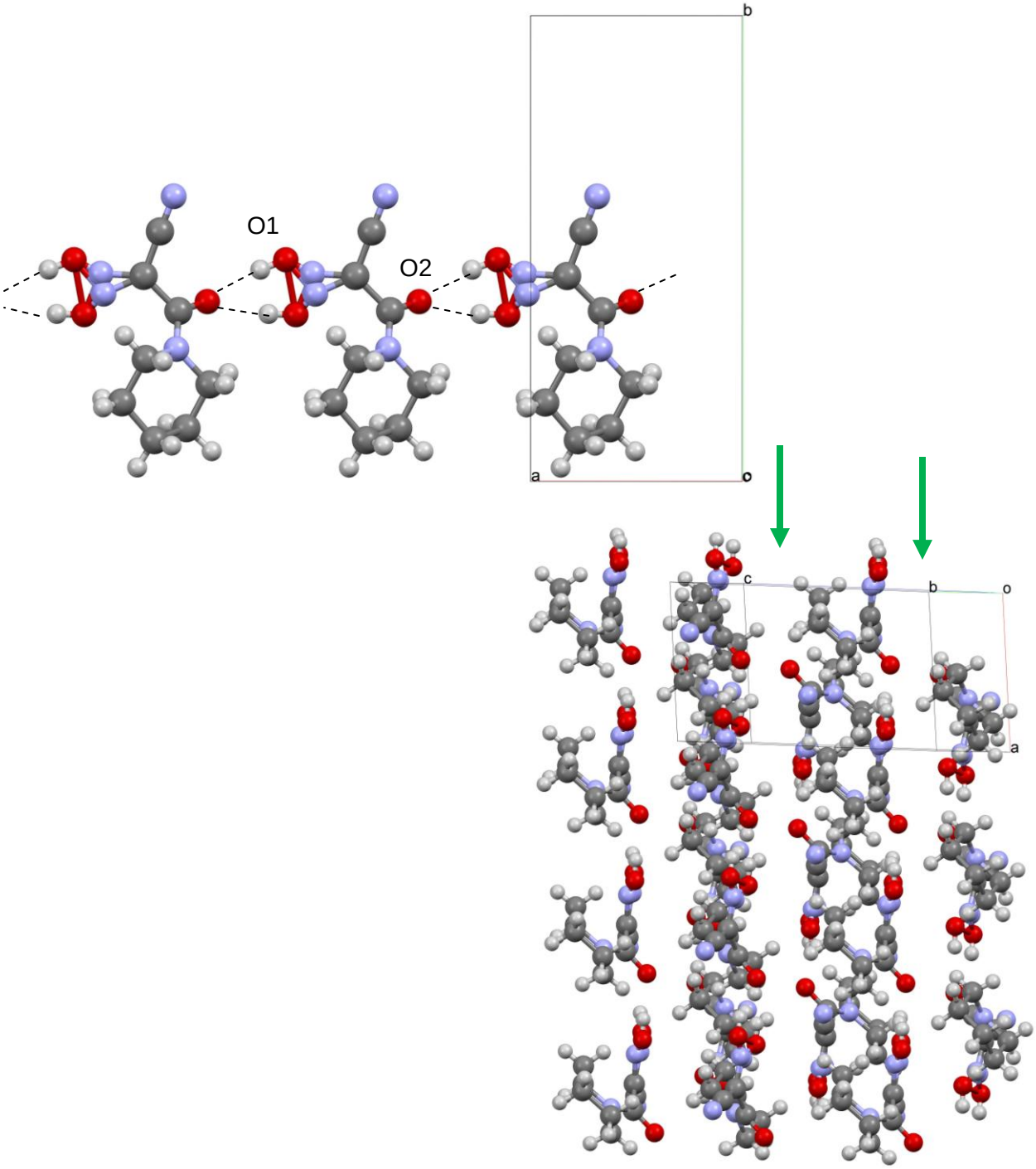


A

B

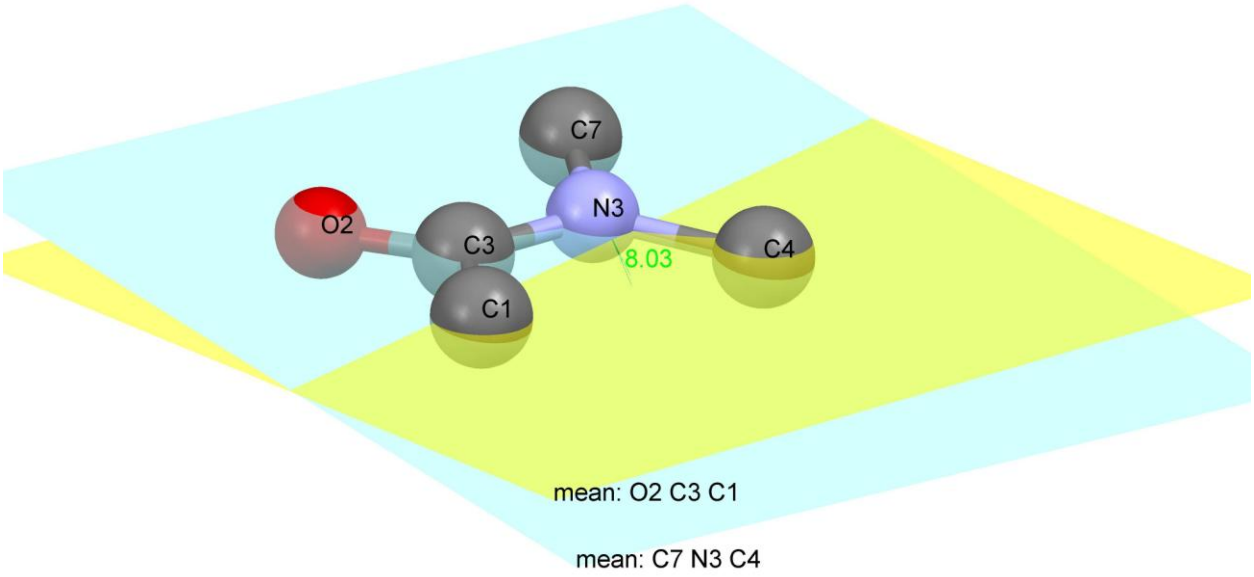


Packing diagram in the structure of HPiPCO (**2**): **A** – H-bonded chain of molecules (shown view along *c* direction); **B** – prospective view of several unit cells. The shearing plane of the crystal along *oa* direction is indicated with green arrow.

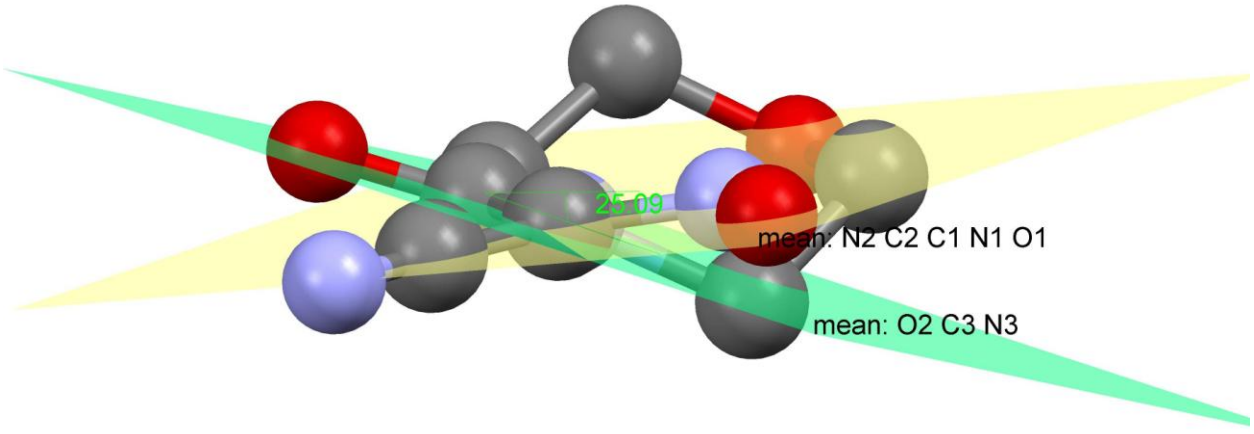


Planes in the structures of amide-cyanoxime 5.

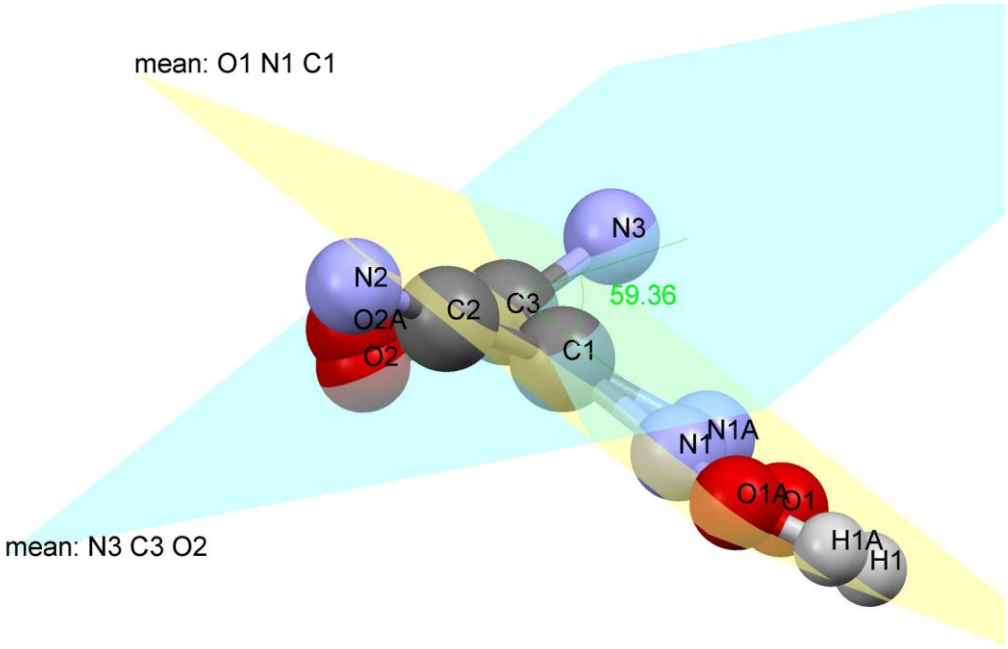
Selected fragments of the HMCO (**5**) structure are shown. **A** – the explanation for non-equivalence of carbon atoms in the $^{13}C\{^{1}H\}$ NMR spectrum is in the absence of rotation around C3-N3 amide bond; hence, all carbon atoms in both cyanoximes have different environment due to their different position relatively to the C=O bond.

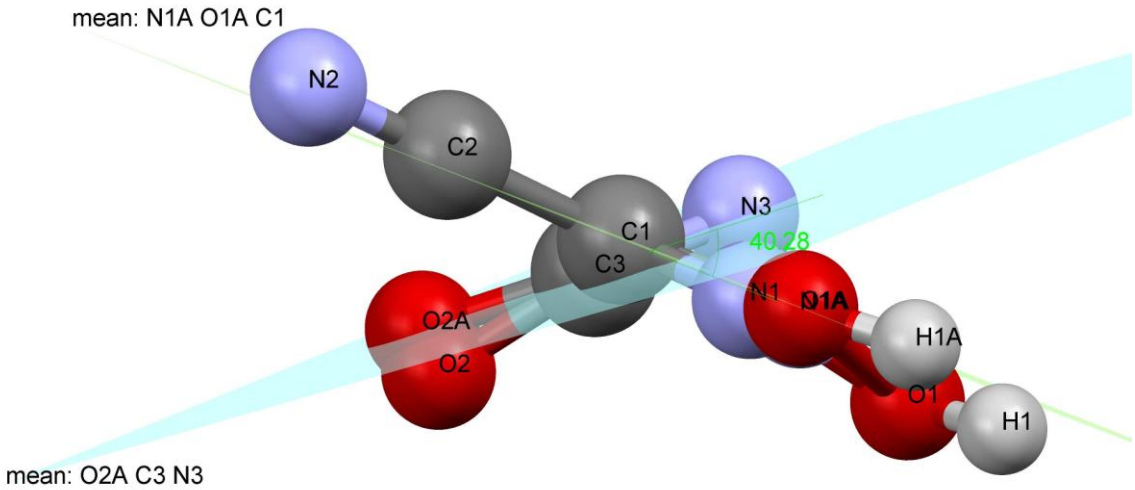


B - The ligand's core is not planar as well: the dihedral angle between the cyanoxime and amide fragments is shown (29.09^{o}). H-atoms are omitted for clarity.

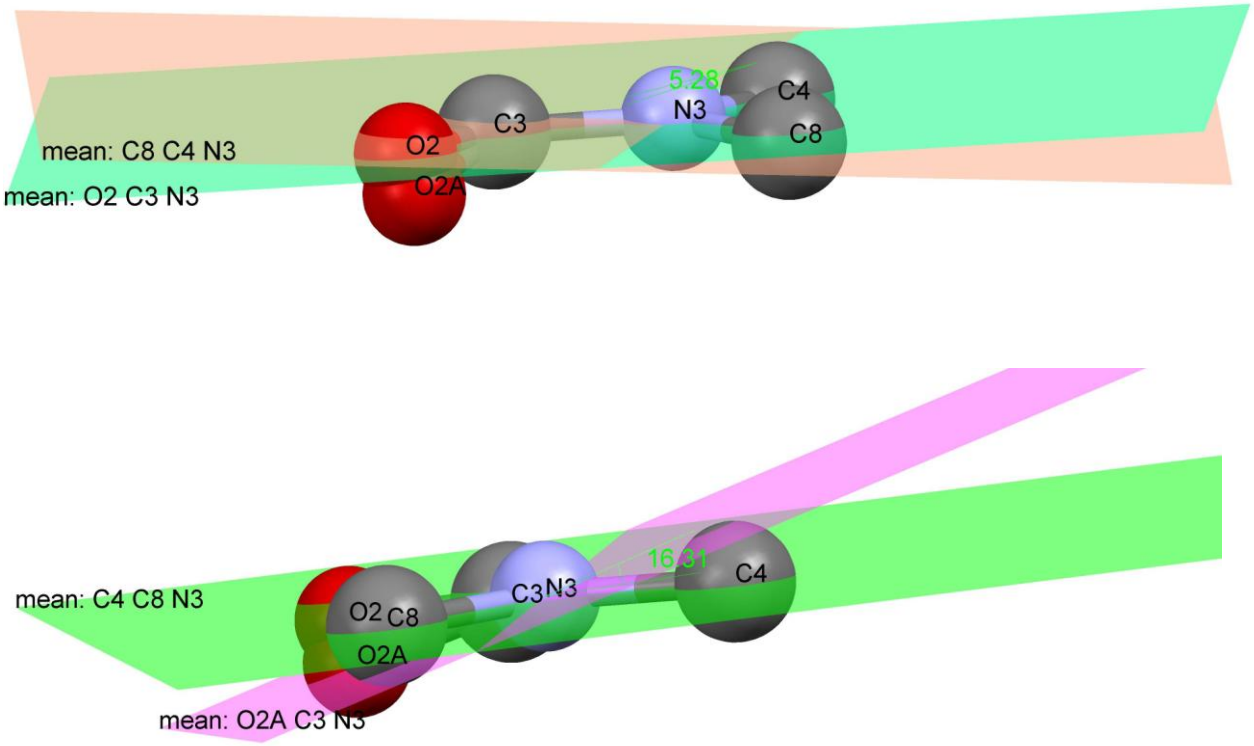


Planes in the structures of amide-cyanoxime 2.





Planes in the structures of amide-cyanoxime 2.



Hydrogen bonding for cyanoxime 5 (HMCO),

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(1)-H(1)...O(2)#1	0.84	1.77	2.6028(13)	173.4

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

and

cyanoxime 2 (HPipCO) [Å and °]

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(1A)-H(1A)...O(2A)#1	0.84	1.67	2.500(19)	167.7
O(1A)-H(1A)...O(2)#1	0.84	1.90	2.722(11)	164.6
O(1)-H(1)...O(2A)#1	0.98(7)	1.58(7)	2.55(2)	173(6)
O(1)-H(1)...O(2)#1	0.98(7)	1.74(7)	2.714(12)	177(6)

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

checkCIF/PLATON (full publication check)

Structure factors have been supplied for datablock(s) I

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary
Please wait while processing .... Interpreting this report
Structure factor report

Datablock: I HPipCO (2)

Bond precision: C-C = 0.0042 A Wavelength=0.71073

Cell: a=6.3640(9) b=13.8997(19) c=10.3185(14)
alpha=90 beta=95.059(2) gamma=90

Temperature: 120 K

	Calculated	Reported
Volume	909.2(2)	909.2(2)
Space group	P 21/c	P 21/c
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C8 H11 N3 O2	C8 H11 N3 O2
Sum formula	C8 H11 N3 O2	C8 H11 N3 O2
Mr	181.20	181.20
Dx,g cm-3	1.324	1.324
Z	4	4
Mu (mm-1)	0.098	0.098
F000	384.0	384.0
F000'	384.17	
h,k,lmax	8,19,14	8,19,14
Nref	2526	2512
Tmin,Tmax	0.971,0.981	0.792,1.000
Tmin'	0.971	

Correction method= NUMERICAL

Data completeness= 0.994 Theta(max)= 29.490

R(reflections)= 0.0500(1905) wR2(reflections)= 0.1177(2512)

S = 1.039 Npar= 145

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

CRYSC01_ALERT_1_C The word below has not been recognised as a standard identifier: coloreless
CRYSC01_ALERT_1_C No recognised colour has been given for crystal colour.

PLAT340_ALERT_3_C Low Bond Precision on C-C Bonds ..... 0.0042 Ang.
PLAT906_ALERT_3_C Large K value in the Analysis of Variance 4.271
PLAT911_ALERT_3_C Missing # FCF Refl Between THmin & STh/L= 0.600 2

Alert level G

PLAT002_ALERT_2_G Number of Distance or Angle Restraints on AtSite 6
PLAT005_ALERT_5_G No _iucr_refine_instructions_details in the CIF ? Do !
PLAT007_ALERT_5_G Note: Number of Unrefined Donor-H Atoms 1
PLAT301_ALERT_3_G Note: Main Residue Disorder ..... 23 %
PLAT311_ALERT_2_G Isolated Disordered Oxygen Atom (No H's ?) O2
PLAT710_ALERT_4_G Delete 1-2-3 or 2-3-4 Linear Torsion Angle ... # 1
N1 -C1 -C2 -N2 17.00 0.00 1.555 1.555 1.555 1.555
And 2 other PLAT710 Alerts
Less ...

PLAT710_ALERT_4_G Delete 1-2-3 or 2-3-4 Linear Torsion Angle ... # 2

N1A -C1 -C2 -N2 18.00 0.00 1.555 1.555 1.555 1.555

PLAT710_ALERT_4_G Delete 1-2-3 or 2-3-4 Linear Torsion Angle ... # 3

C3 -C1 -C2 -N2 -4.00 39.00 1.555 1.555 1.555 1.555

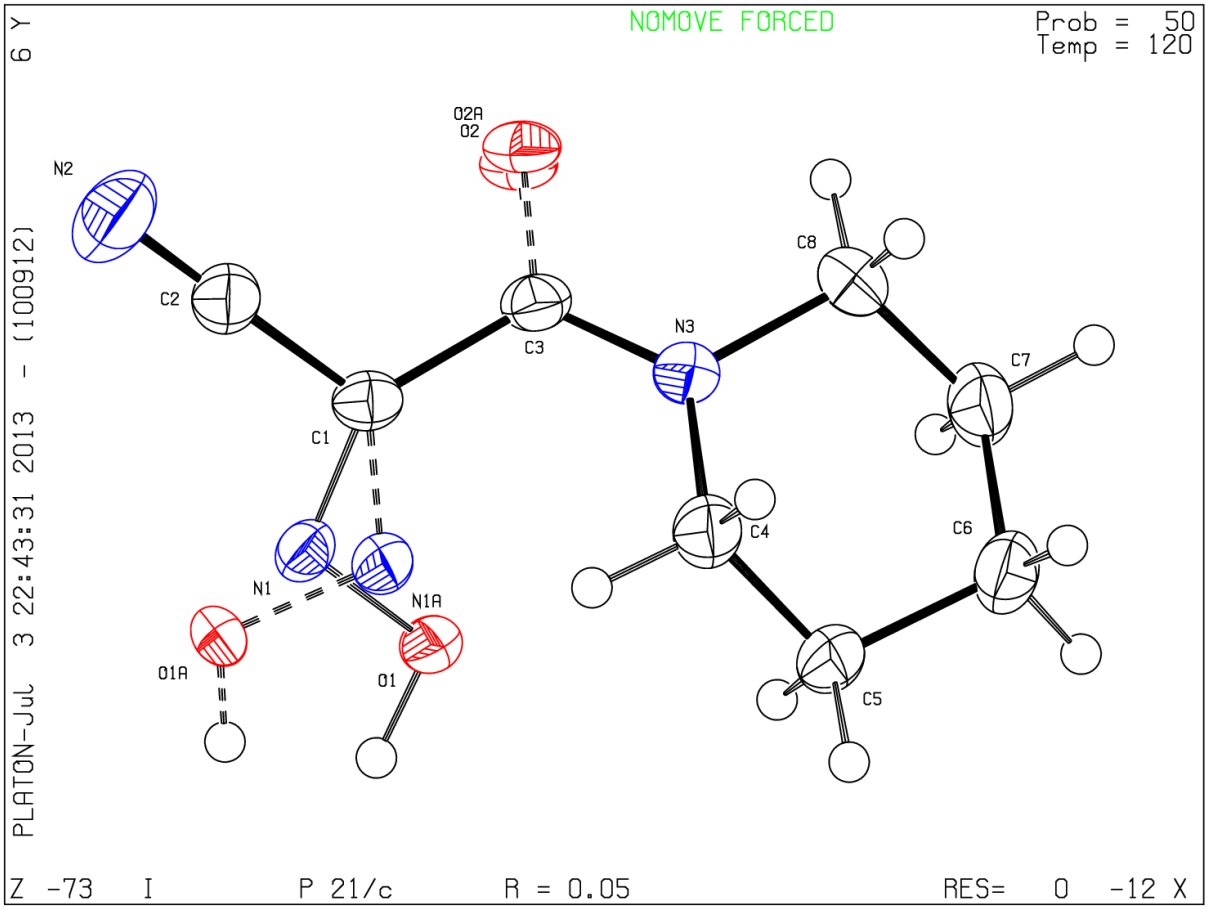
PLAT764_ALERT_4_G Overcomplete CIF Bond List Detected (Rep/Expd) . 1.14 Ratio
PLAT779_ALERT_4_G Suspect or Irrelevant (Bond) Angle in CIF .... # 1
N1 -C1 -N1A 1.555 1.555 1.555 26.60 Deg.
PLAT779_ALERT_4_G Suspect or Irrelevant (Bond) Angle in CIF .... # 8
O2A -C3 -O2 1.555 1.555 1.555 14.10 Deg.
PLAT811_ALERT_5_G No ADDSYM Analysis: Too Many Excluded Atoms .... ! Info
PLAT860_ALERT_3_G Note: Number of Least-Squares Restraints 4
PLAT912_ALERT_4_G Missing # of FCF Reflections Above STh/L= 0.600 10

0 **ALERT level A** = Most likely a serious problem - resolve or explain
0 **ALERT level B** = A potentially serious problem, consider carefully
5 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
14 **ALERT level G** = General information/check it is not something unexpected

2 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
2 ALERT type 2 Indicator that the structure model may be wrong or deficient
5 ALERT type 3 Indicator that the structure quality may be low
7 ALERT type 4 Improvement, methodology, query or suggestion
3 ALERT type 5 Informative message, check

PLATON version of 01/06/2013; check.def file version of 24/05/2013

Datablock I - ellipsoid plot



checkCIF/PLATON (full publication check)

Structure factors have been supplied for datablock(s) I

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary
Please wait while processing .... Interpreting this report

Datablock: I HMCO (5)

Bond precision: C-C = 0.0019 A Wavelength=0.71073
Cell: a=6.7259(4) b=9.4836(6) c=13.2127(9)
alpha=90 beta=90 gamma=90
Temperature: 120 K

	Calculated	Reported
Volume	842.78(9)	842.78(9)
Space group	P 21 21 21	P 21 21 21
Hall group	P 2ac 2ab	P 2ac 2ab
Moiety formula	C7 H9 N3 O3	C7 H9 N3 O3
Sum formula	C7 H9 N3 O3	C7 H9 N3 O3
Mr	183.17	183.17
Dx,g cm-3	1.444	1.444
Z	4	4
Mu (mm-1)	0.115	0.115
F000	384.0	384.0
F000'	384.20	
h,k,lmax	7,11,15	7,11,15
Nref	1479[884]	1478
Tmin,Tmax	0.951,0.966	0.909,1.000
Tmin'	0.938	

Correction method= NUMERICAL
Data completeness= 1.67/1.00 Theta(max)= 24.990
R(reflections)= 0.0249(1428) wR2(reflections)= 0.0633(1478)
S = 1.082 Npar= 118

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

STRVA01_ALERT_4_C Flack test results are meaningless.
From the CIF: _refine_ls_abs_structure_Flack -0.200
From the CIF: _refine_ls_abs_structure_Flack_su 1.000

PLAT089_ALERT_3_C Poor Data / Parameter Ratio (Zmax < 18) 7.48

Alert level G

PLAT005_ALERT_5_G No _iucr_refine_instructions_details in the CIF ? Do !
PLAT007_ALERT_5_G Note: Number of Unrefined Donor-H Atoms 1
PLAT032_ALERT_4_G Std. Uncertainty on Flack Parameter Value High . 1.000
PLAT230_ALERT_2_G Hirshfeld Test Diff for C1 -- C2 .. 5.6 su
PLAT371_ALERT_2_G Long C(sp2)-C(sp1) Bond C1 - C2 ... 1.45 Ang.
PLAT710_ALERT_4_G Delete 1-2-3 or 2-3-4 Linear Torsion Angle ... # 1
N1 -C1 -C2 -N2 -22.00 6.00 1.555 1.555 1.555 1.555
PLAT710_ALERT_4_G Delete 1-2-3 or 2-3-4 Linear Torsion Angle ... # 2
C3 -C1 -C2 -N2 165.00 6.00 1.555 1.555 1.555 1.555
PLAT909_ALERT_3_G Percentage of Observed Data at Theta(Max) still 91 %
PLAT916_ALERT_2_G Hooft y and Flack x Parameter values differ by . 0.80

0 **ALERT level A** = Most likely a serious problem - resolve or explain
0 **ALERT level B** = A potentially serious problem, consider carefully
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9 **ALERT level G** = General information/check it is not something unexpected
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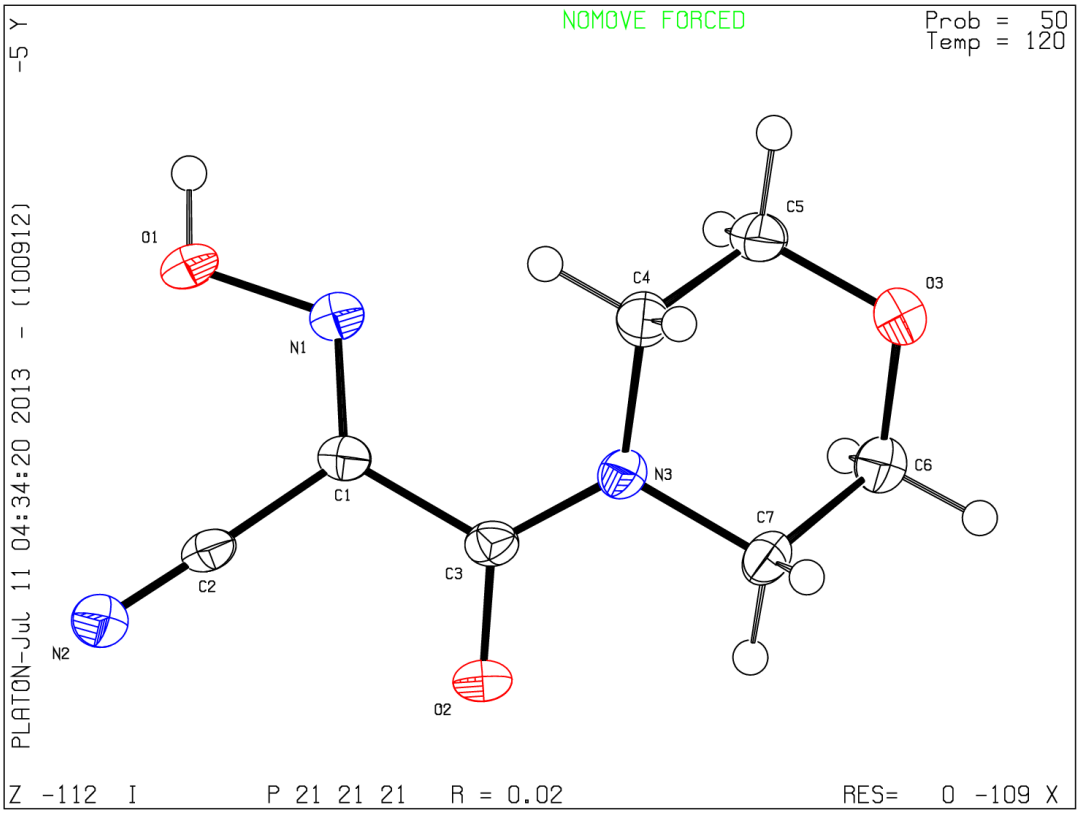
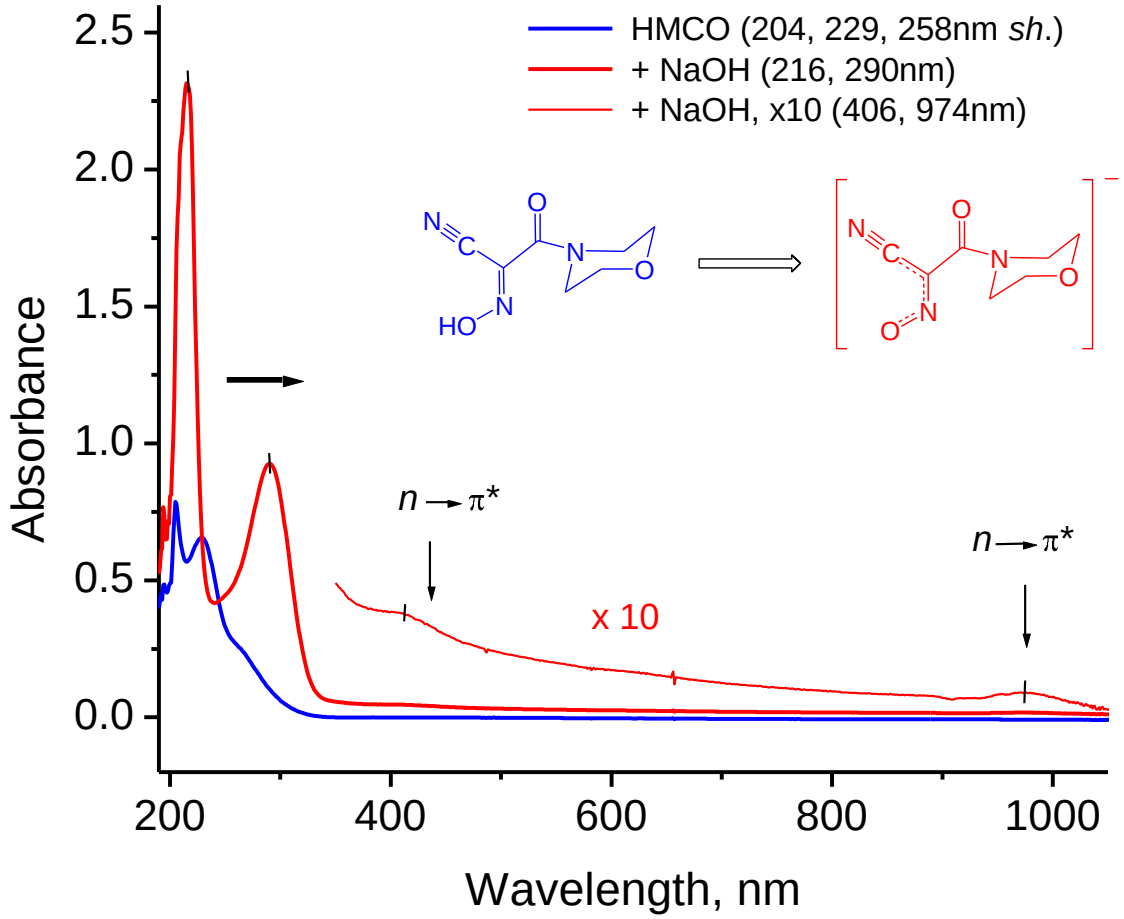
3 ALERT type 2 Indicator that the structure model may be wrong or deficient
2 ALERT type 3 Indicator that the structure quality may be low
4 ALERT type 4 Improvement, methodology, query or suggestion
2 ALERT type 5 Informative message, check

PLATON version of 01/06/2013; check.def file version of 24/05/2013

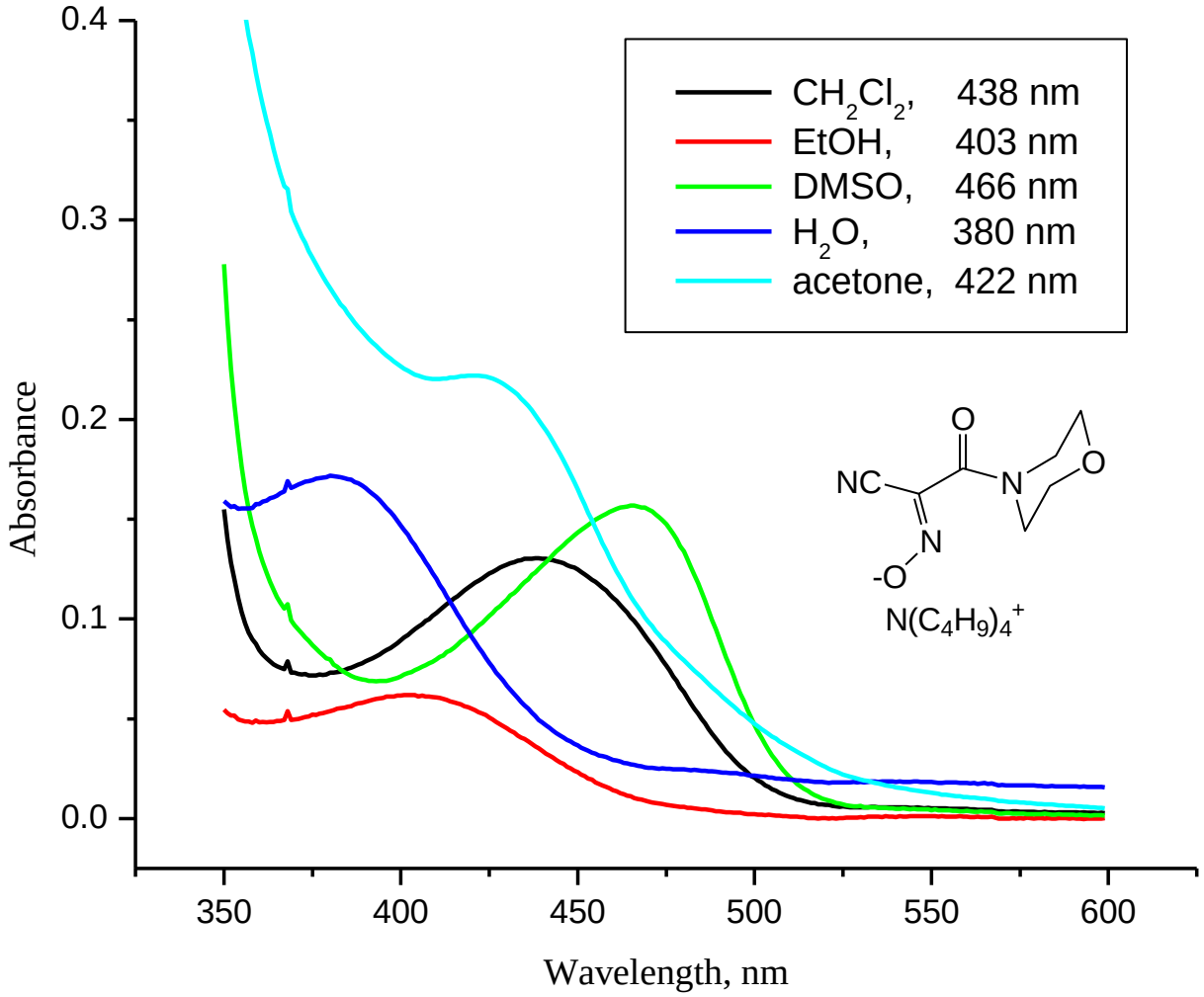
Datablock I - ellipsoid plot



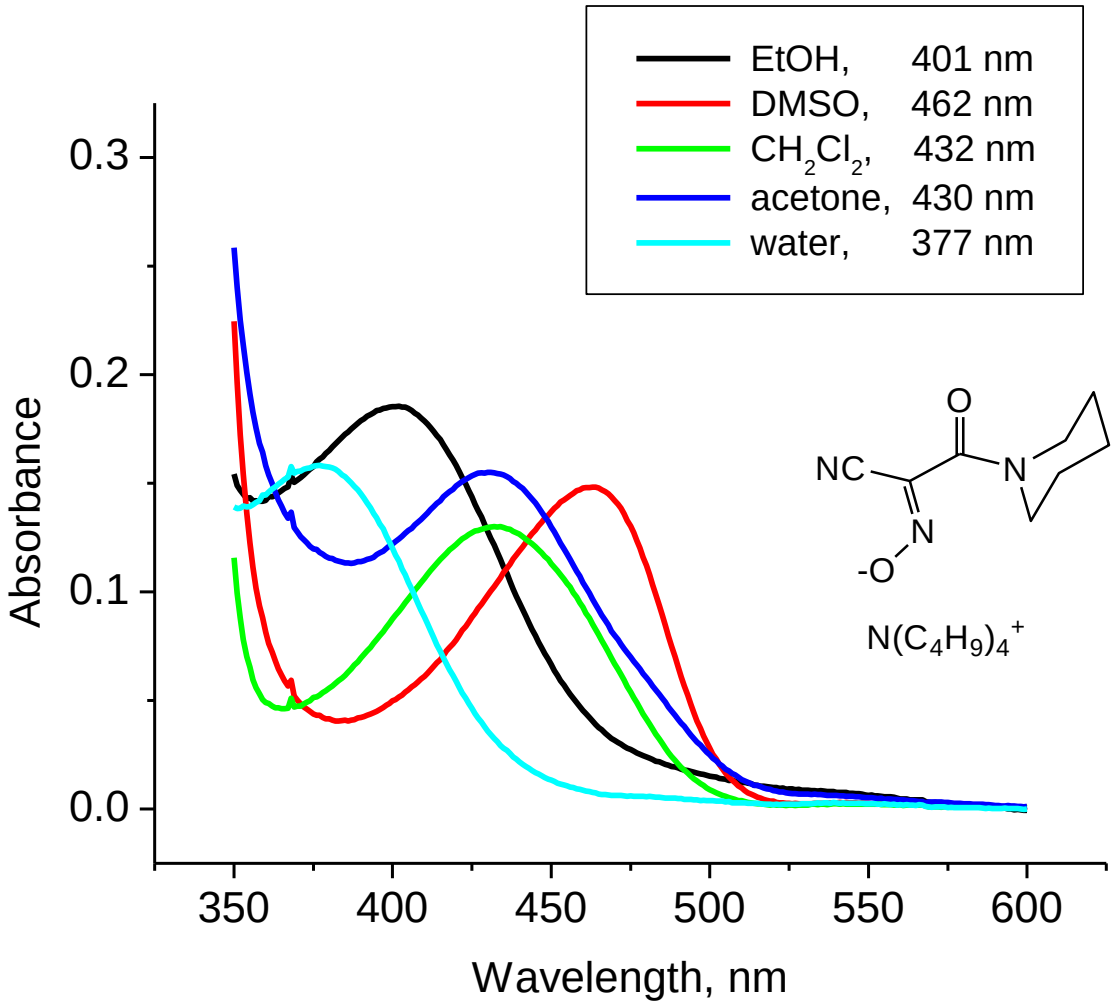
UV-visible spectra of protonated cyanoxime HMCO (**5**, blue), and its anion (**5**$^{-}$, red) in aqueous solutions. Clearly seen bathochromic shifts of bands, and an intensity increase in the **5**$^{-}$ due to the delocalization of negative charge in formed conjugated anion.



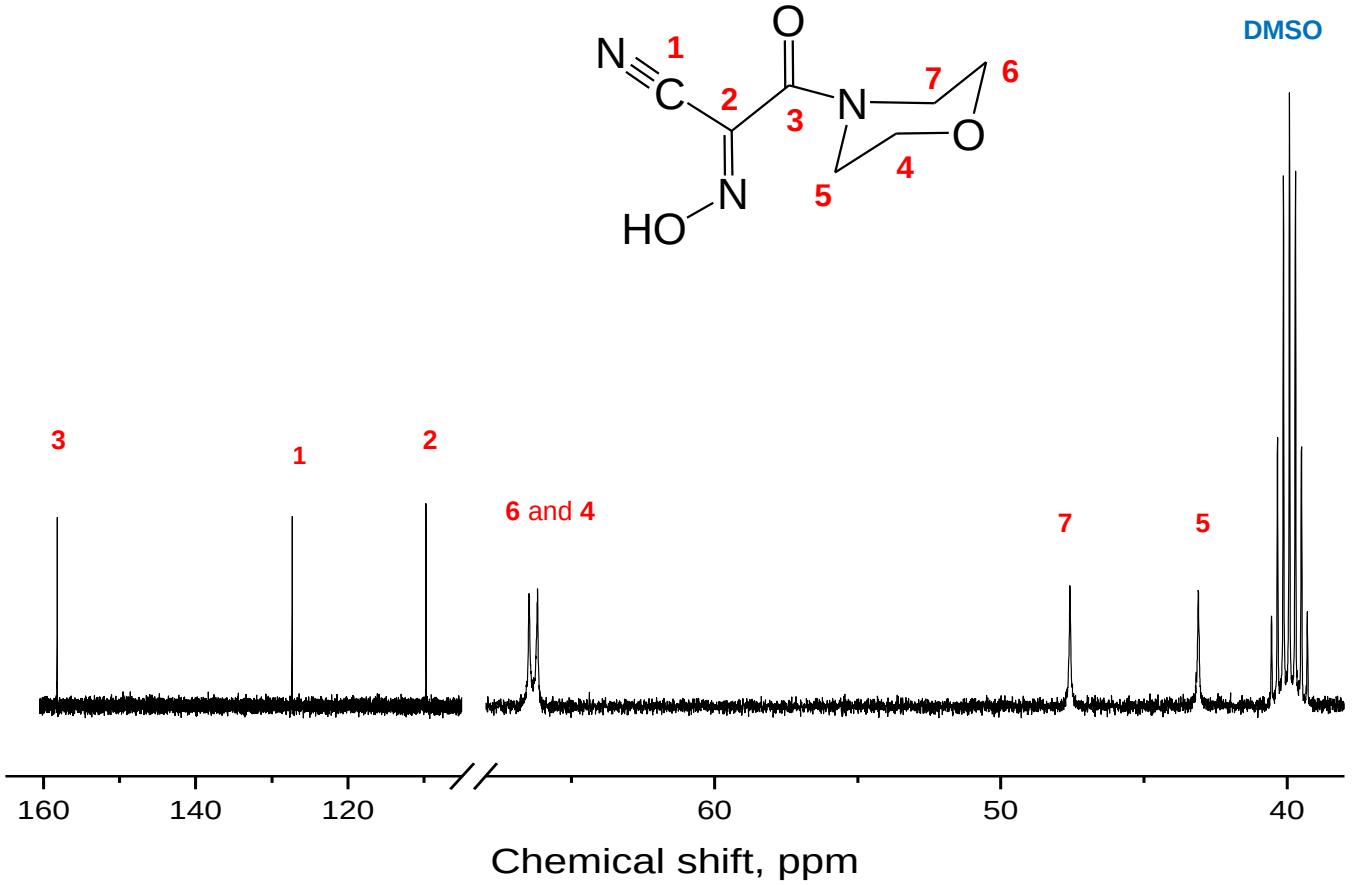
Solvatochromic series for MCO^- anion (**5**$^-$) in different solvents.



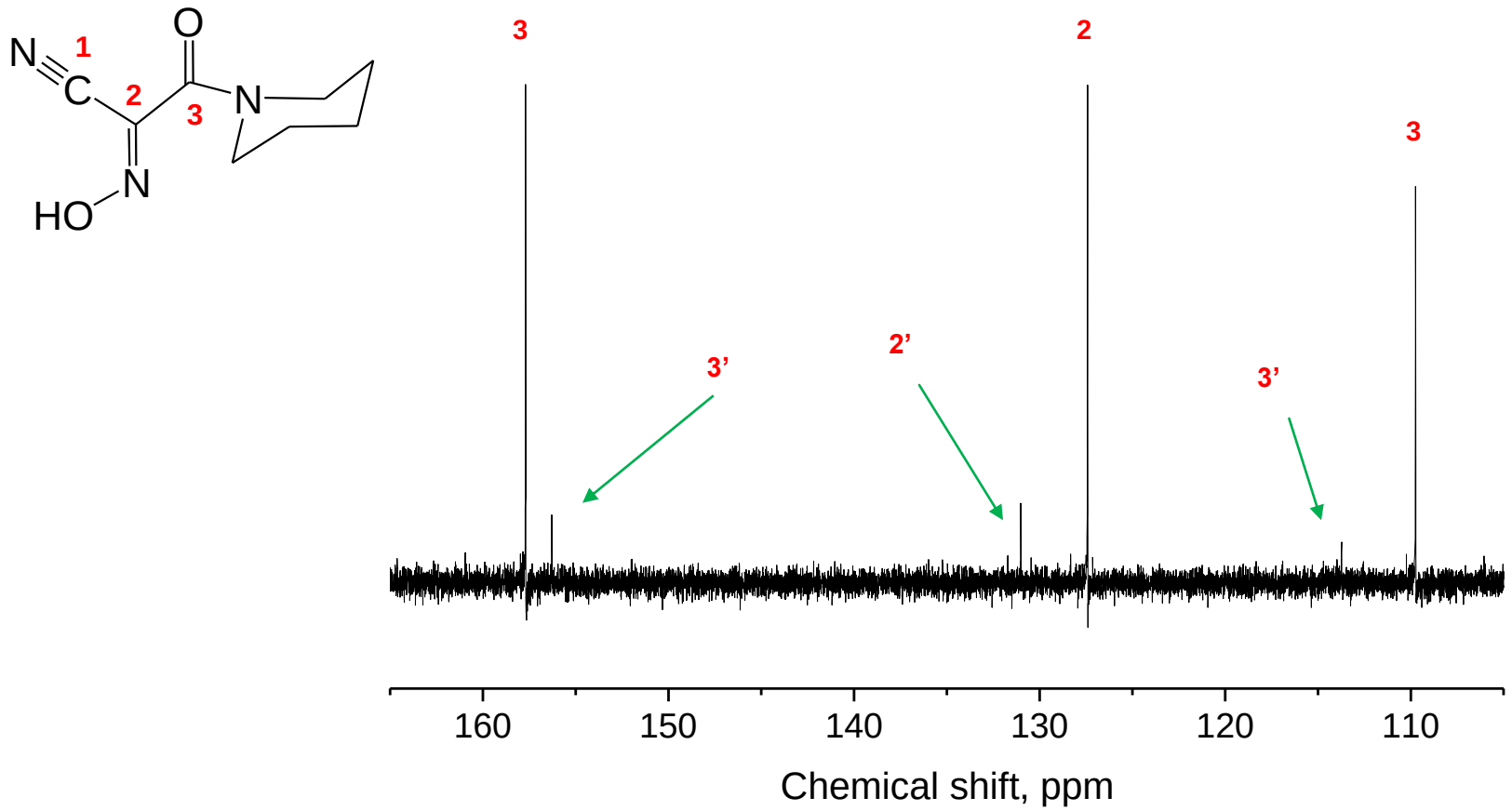
Solvatochromic series for PiPCO$^-$ anion (**2**$^-$) in different solvents.



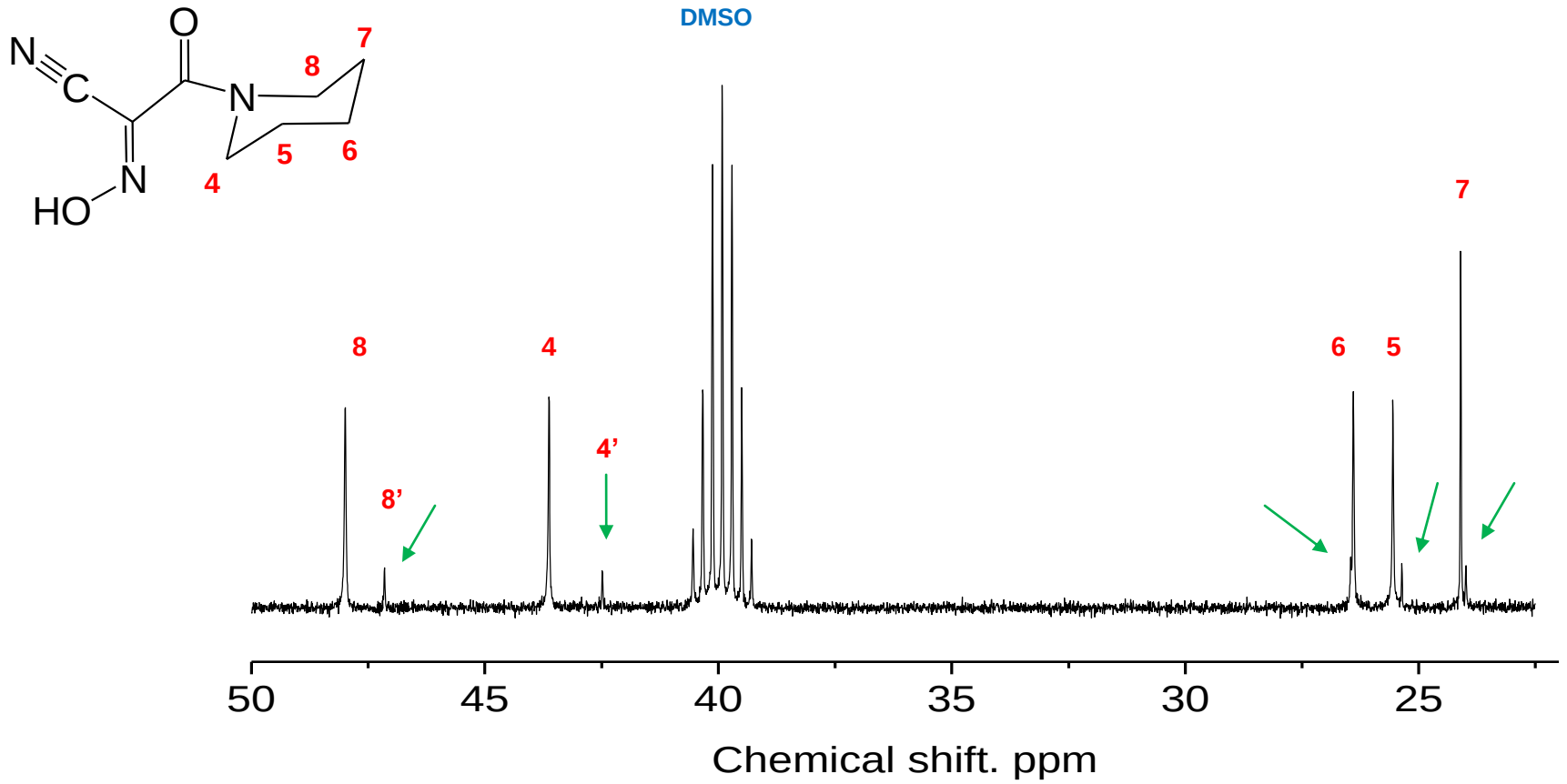
$^{13}C\{^{1}H\}$ NMR spectra of **5** in dmso-d_6 at 293 K.



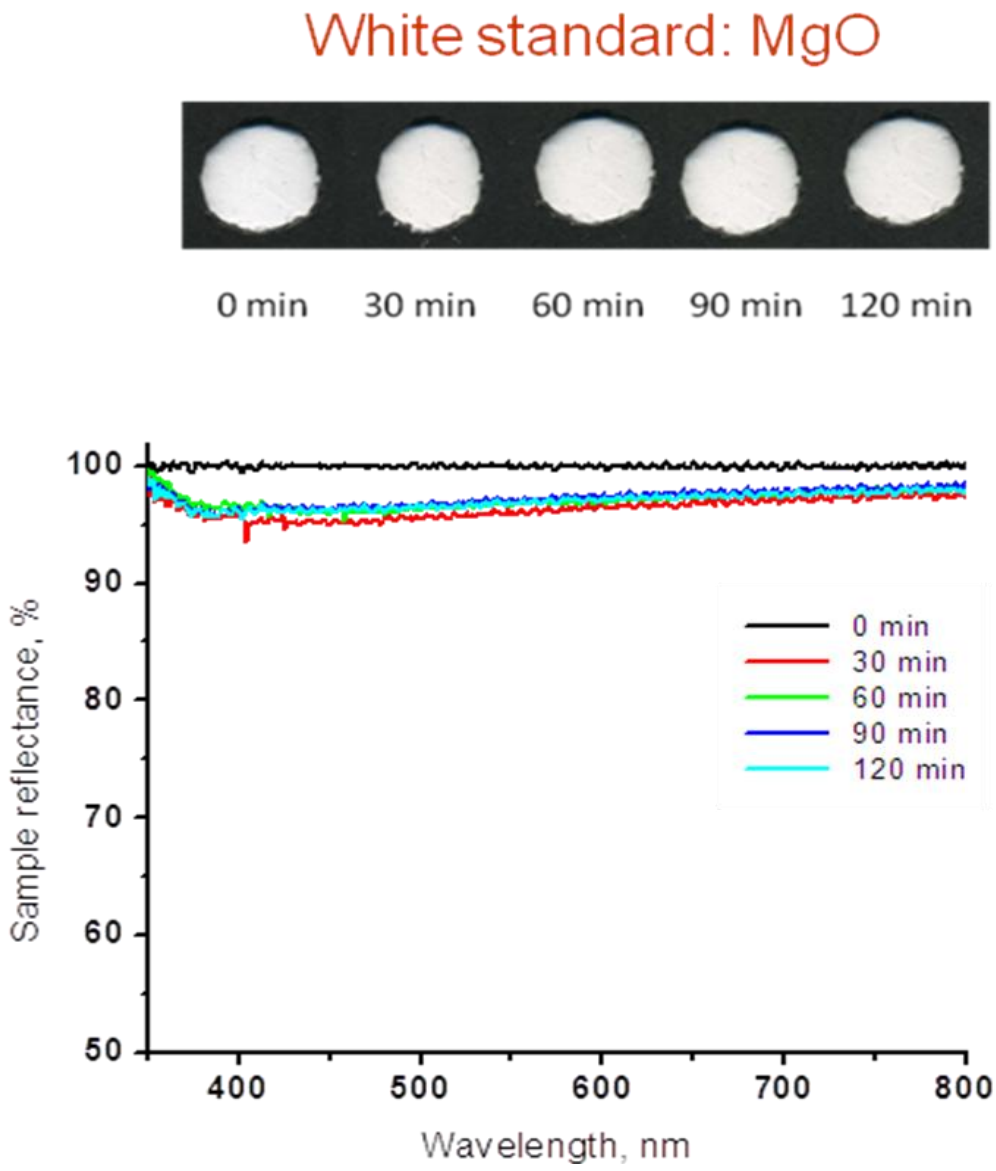
$^{13}C\{^{1}H\}$ NMR spectra of **2** in dmso-d_6 at 293 K. Shown sp, sp^2 carbons region only; second diastereomer (anti) is indicated by arrows.



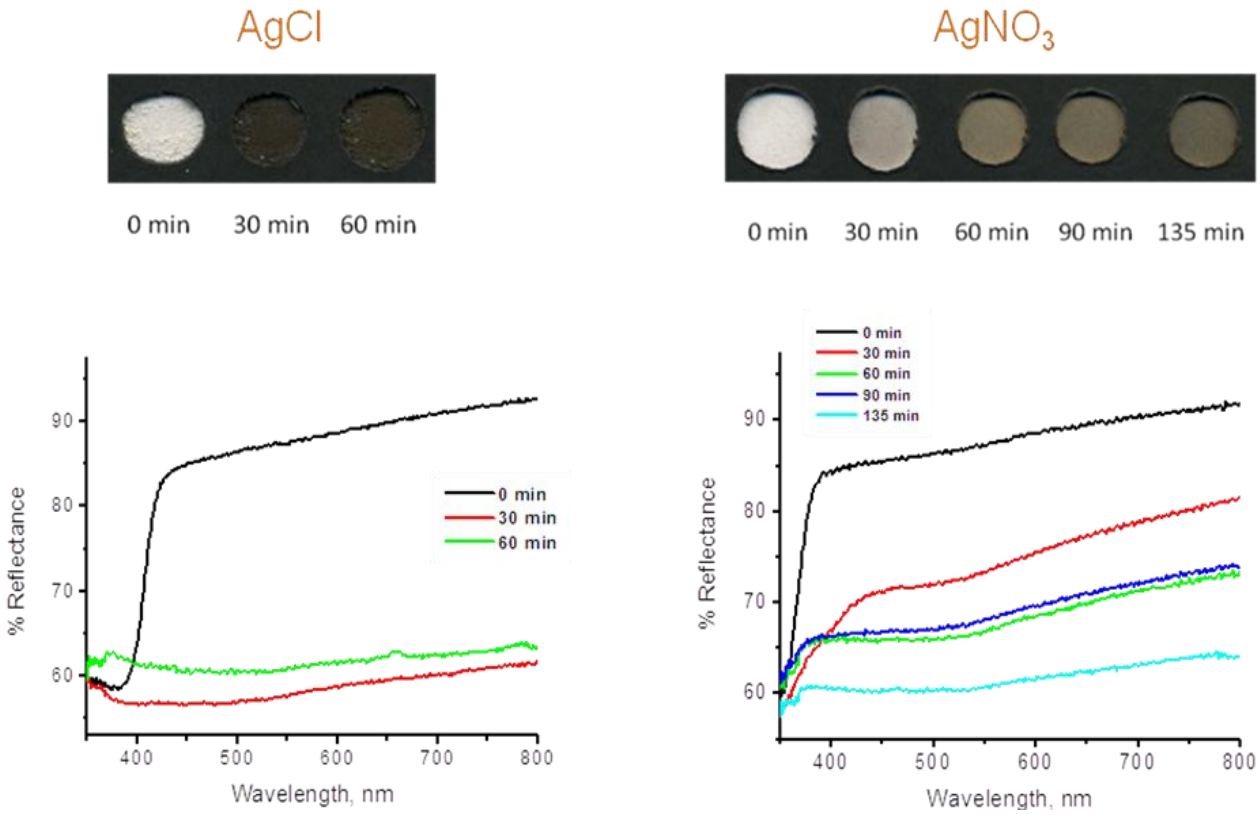
$^{13}C\{^{1}H\}$ NMR spectra of **2** in dmso-d_6 at 293 K. Shown aliphatic sp^3 carbons region only; second diastereomer (anti) is indicated by arrows.



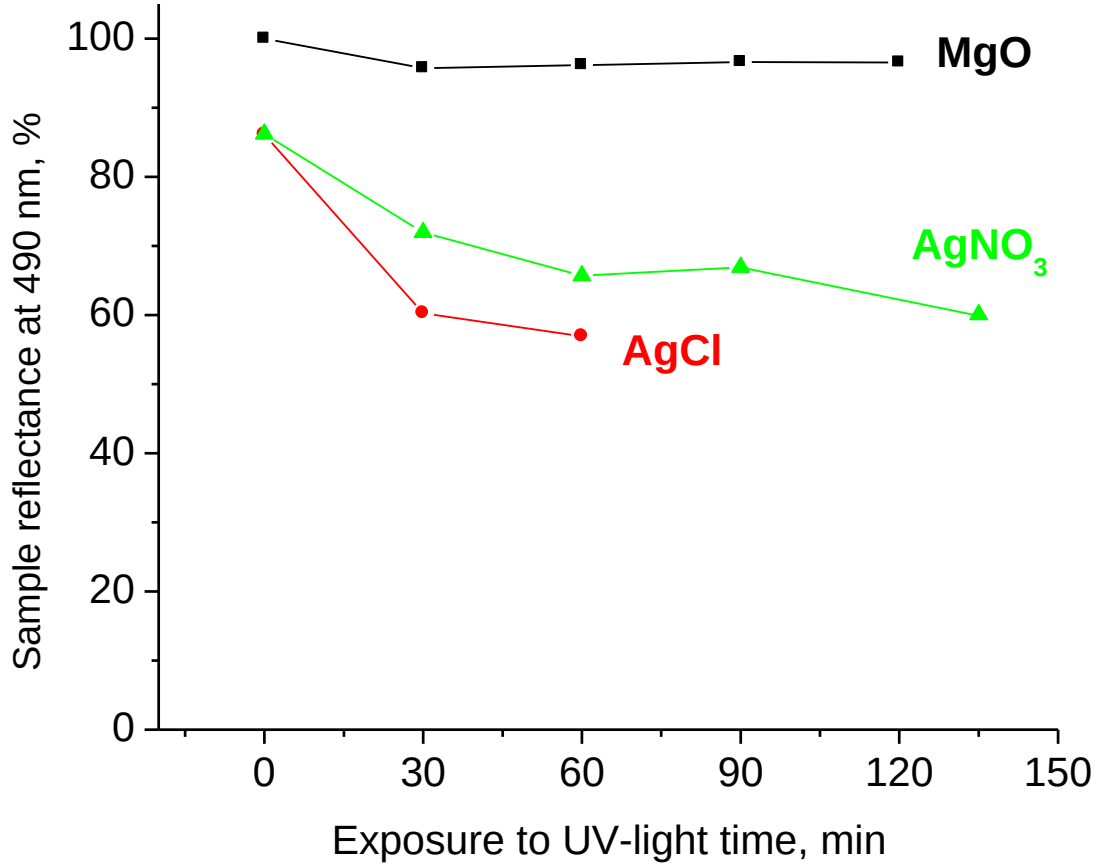
Results of studies of reflectance of MgO white standard subjected to UV-radiation. Slight dip at ~400 nm in reflectance profile is due to formation of point defects.



Reflectance spectra and actual photographs of samples of conventional light-sensitive inorganic salts AgCl (**A**) and $AgNO_3$ (**B**) recorded at different time intervals.



Time profiles of % reflectance of MgO, AgCl and $AgNO_3$ samples.



We empirically determined that the polymerization process has to be carried out using two different setups depending on the nature of used silver(I) cyanoximate (Figures 1 and 2 below). Thus, if we employ for the preparation of polymeric composite mostly *yellow* AgL complexes, the photo-polymerization reaction can be done quickly using an intense metal-halide lamp (Figure 1), where the 96-wells plate was placed directly onto the protective glass cover on the lamp. Such operation resulted in the formation of a solidified composite within sevreal minutes. No visible signs of photodegradation of silver(I) cyanoximates was observed during the curing process.

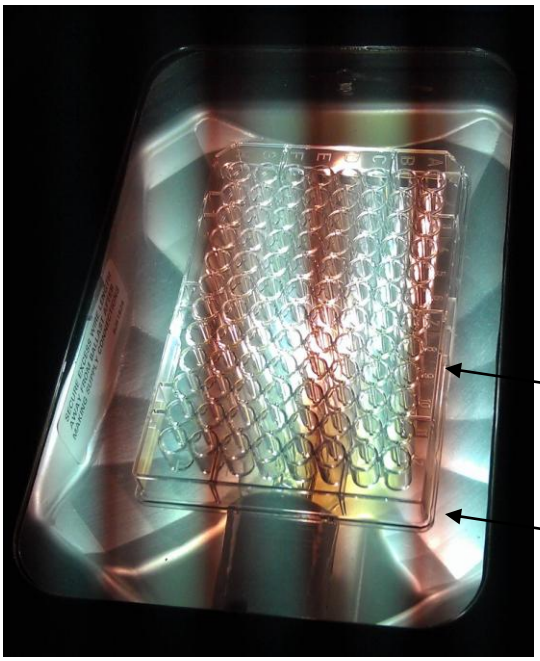


Figure 1.

A powerful metal-halide air-cooled lamp that was successfully used for polymerization of mixtures that contain yellow complexes. In order to exclude heat induced polymerization an intense air flow was applied to keep temperature in the plate at 296 K.

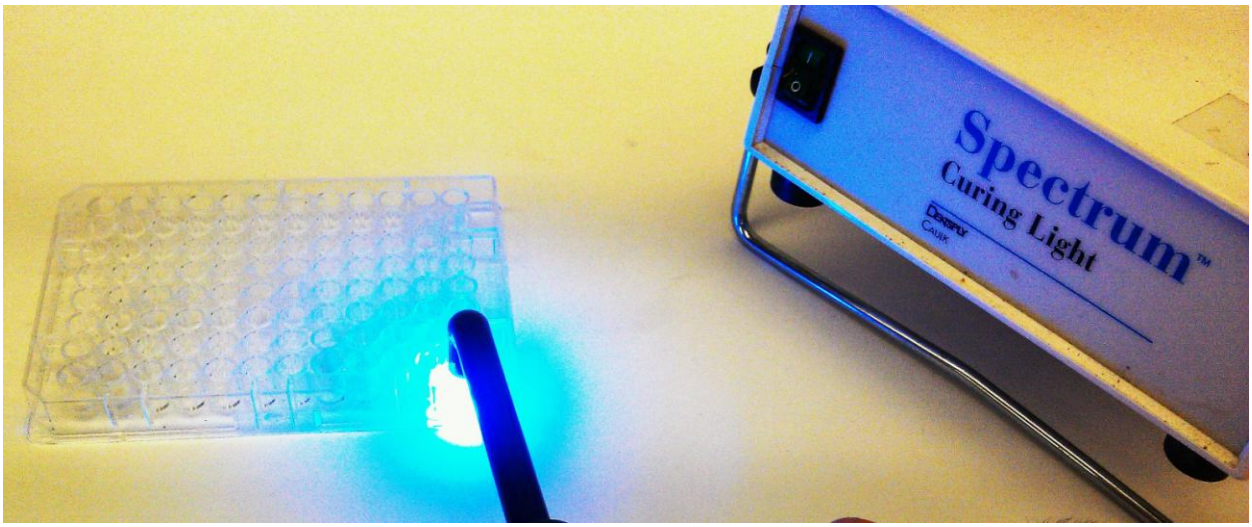


Figure 2. Mixtures with darker more *brownish* AgL complexes required manual irradiation.