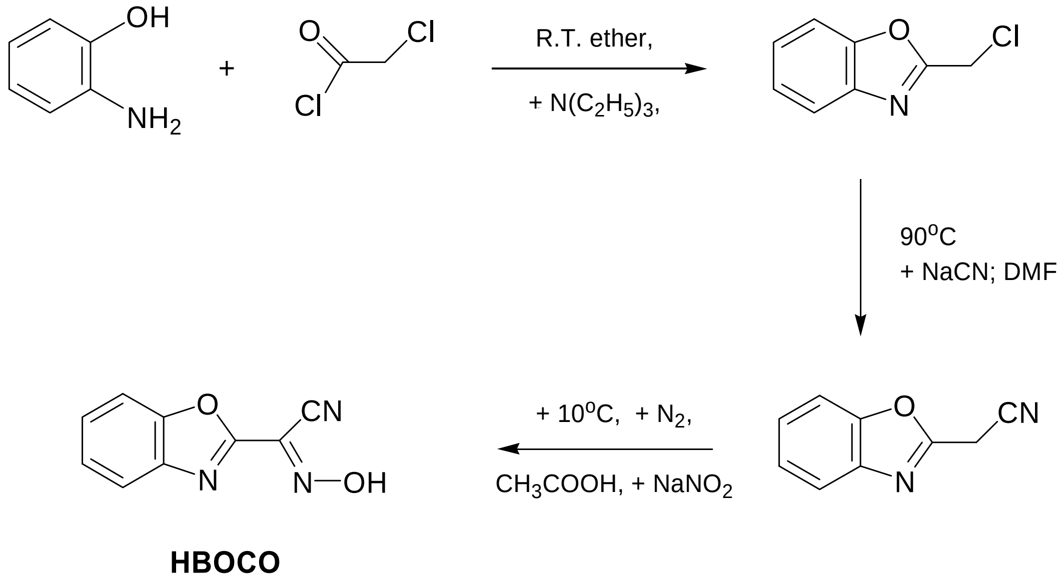
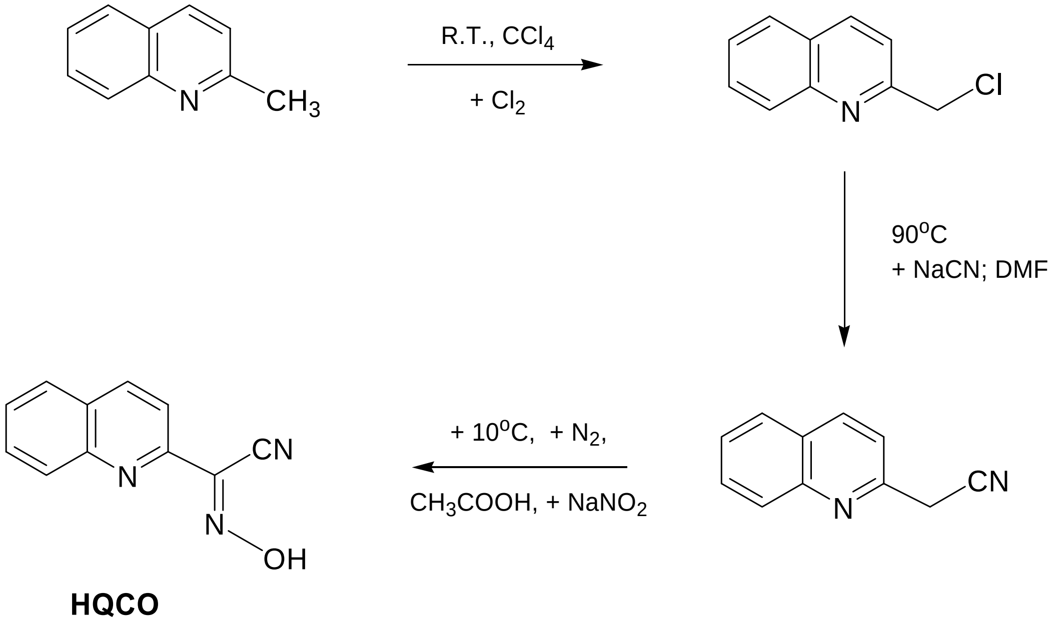
Preparation of HBOCO and HQCO ligands from respective substituted acetonitriles that are not commercially available.

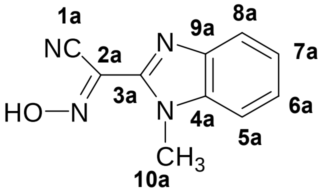
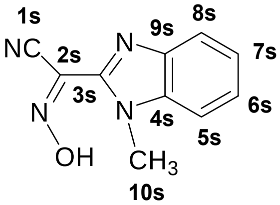
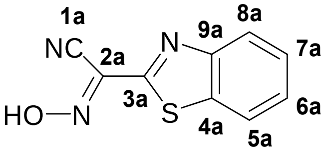
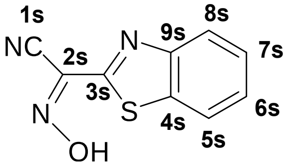
A



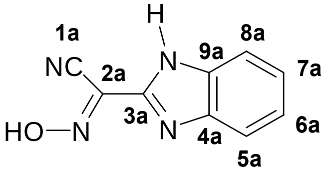
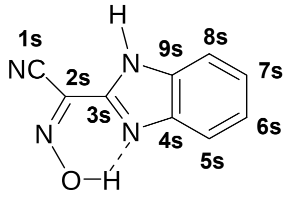
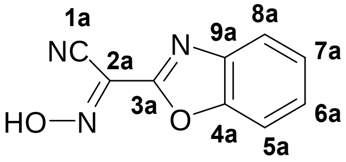
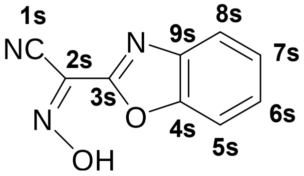
B



Results of $^{13}C\{^{1}H\}$ NMR spectroscopic investigations of benz(2-heteroaryl) cyanoximes.

Cyanoxime	Chemical shift, ppm
75 % *anti*- and 25% *syn*- isomers in dmso-d_6 solution at 298 K **HBIMCO**  	1a 109.92 2a 127.05 3a 143.76 4a 137.44 5a 111.52 6a 120.55 7a 123.55 8a 125.09 9a 142.58 10a 33.01 1s 115.08 2s 127.71 3s 141.95 4s 136.18 5s 111.76 6s 120.60 7s 123.61 8s 124.87 9s 142.58 10s 32.59
90 % *anti*- and 10% *syn*- isomers in dmso-d_6 solution at 298 K **HBTCO**  	1a 109.08 2a 160.17 3a 152.97 4a 134.25 5a 123.17 6a 127.81 7a 127.75 8a 124.31 9a 129.31 1s 129.26 2s 114.39 3s 150.96 4s 136.24 5s 123.31 6s 128.10 7s 127.93 8s 124.71 9s 131.93

Results of $^{13}C\{^{1}H\}$ NMR spectroscopic investigations of benz(2-heteroaryl) cyanoximes (continued).

Cyanoxime	Chemical shift, ppm
70 % *anti*- and 30% *syn*- isomers in dmso-d_6 solution at 298 K; anti- isomer exhibits dynamic proton exchange (tautomerism) between nitrogen atoms of the heterocycle **HBIHCO**  	1a 112.72 2a 135.17 3a 143.76 4a, 9a 123.16 5a, 8a 120.38 6a, 7a 124.79 1s 109.70 2s 140.74 3s 144.26 4s, 9s 128.59 5s, 8s 114.79 6s, 7s 125.99
50 % *anti*- and 50% *syn*- isomers in dmso-d_6 solution at 298 K **HBOCO**  	1a 109.11 2a 129.33 3a 160.24 4a 134.25 5a 124.32 6a 127.86 7a 127.81 8a 123.23 9a 152.98 1s 114.66 2s 128.11 3s 152.82 4s 132.00 5s 124.60 6s 127.27 7s 126.34 8s 123.18 9s 150.96

Results of $^{13}C\{^{1}H\}$ NMR spectroscopic investigations of benz(2-heteroaryl) cyanoximes (continued).

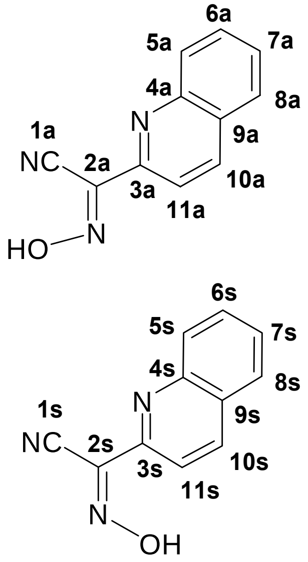
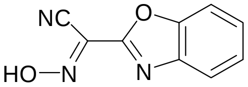
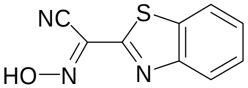
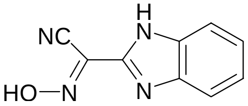
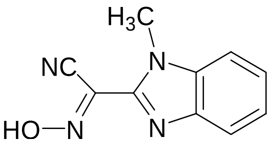
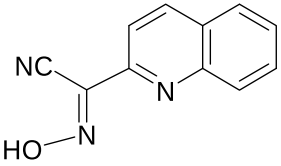
Cyanoxime	Chemical shift, ppm
Mixture of 87.5 % *anti*- and 12.5% *syn*- isomers in acetone-d_6 solution at 298 K **HQCO** 	1a 109.11 2a 137.68 3a 149.73 4a 147.71 5a 128.18 6a 128.21 7a 130.65 8a 129.71 9a 128.68 10a 117.21 11a 137.48 1s not found 2s not found 3s 150.30 4s 148.05 5s 127.01 6s 128.06 7s 130.20 8s 129.09 9s not found 10s 120.58 11s 134.68

Table. **Data of IR spectroscopic studies of synthesized benz(2-heteroaryl)cyanoximes and their Tl(I) complexes**.

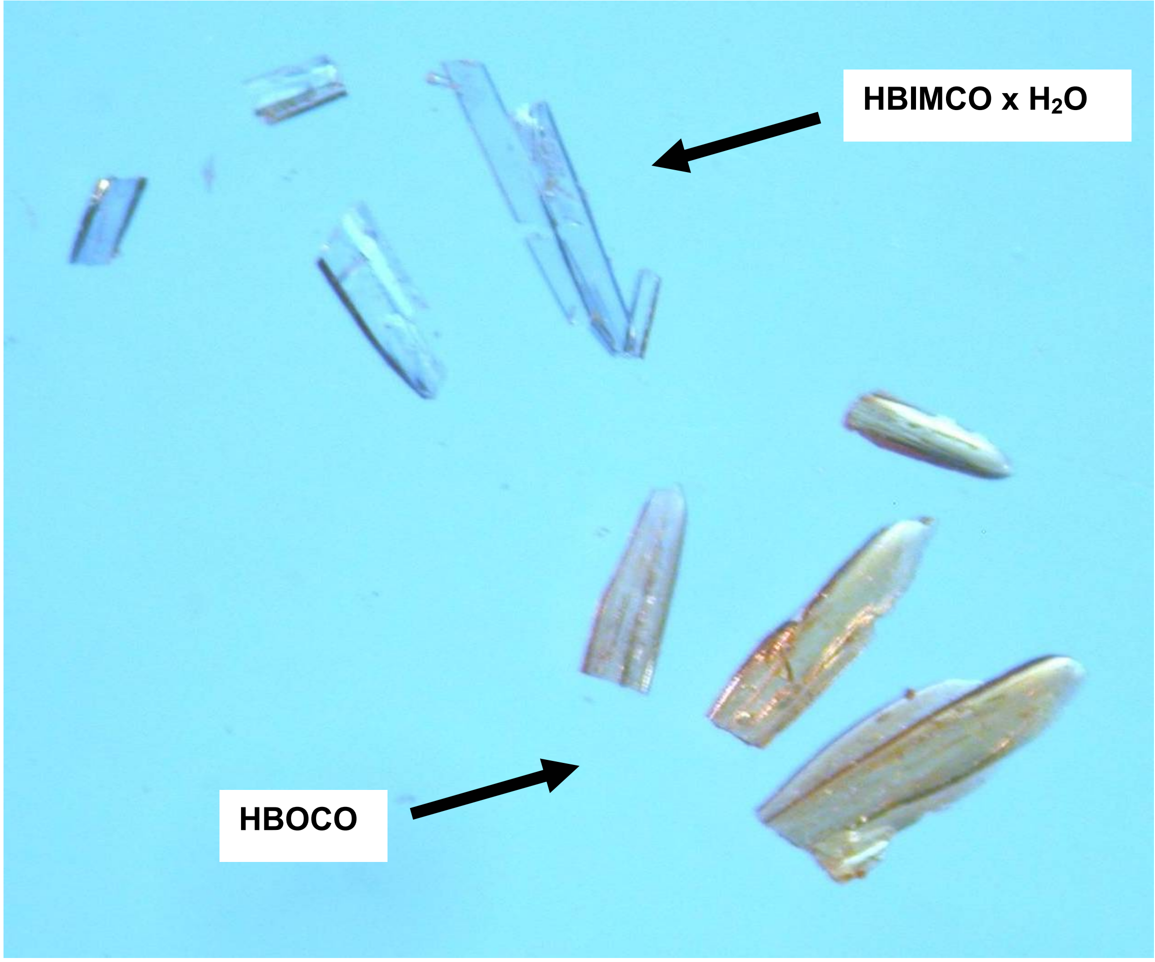
Ligand studied	Compound	Observed and assigned frequencies, cm^{-1}						
		ν(O-H)	ν(C-H)^{arom}	ν(C≡N)	ν(C=N)^{het}	ν(C=N)^{oxime}	ν(C=C)	ν(N-O)
	**HBOCO**	3433	3101	2243	1612	1585	1460	1045
	Tl(BOCO)	-	3094	2220	1610	1407	1455	1160
	**HBTCO**	3240	3075	2236	1590	1575	1510	1063
	Cs(BTCO)	-	3054	2207	1590	1372	1506	1209
	Tl(BTCO)	-	3060	2207	1590	1415	1507	1148
	**HBIHCO**	3345, 3284*	3061	2239	1614	1533	1441	1065
	Tl(BIHCO)	3411, 3287*	3054	2211	1610	1540, 1522	1449	1185, 1166 1103

∗ – ν^{as}(NH) and ν^{s}(NH) respectively

Table. **Data of IR spectroscopic studies of synthesized benz(2-heteroaryl)cyanoximes and their Tl(I) complexes (continued).**

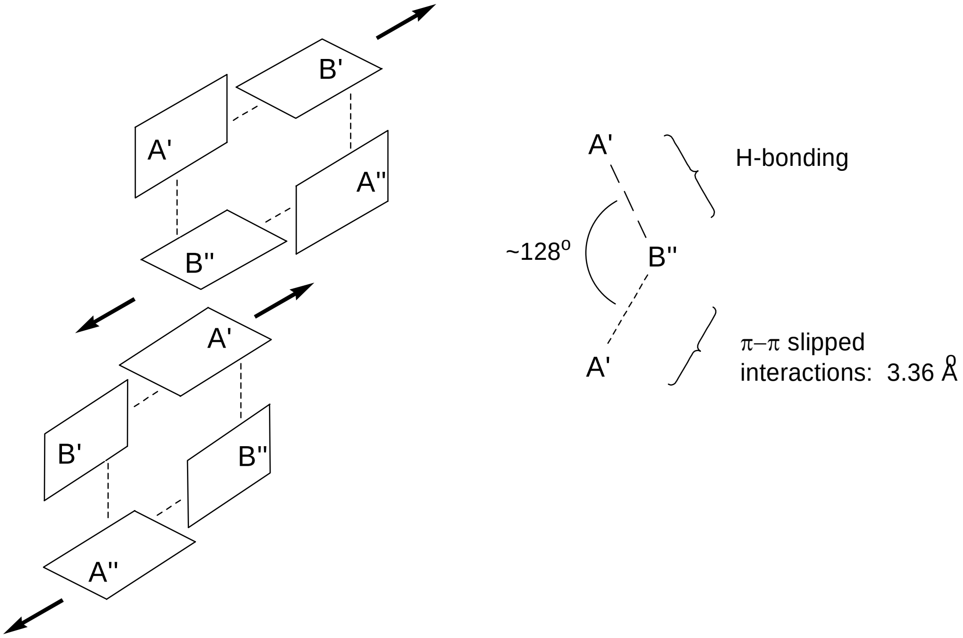
Ligand		Observed and assigned frequencies, cm^{-1}						
		ν(O-H)	ν(C-H)^{arom}	ν(C≡N)	ν(C=N)^{het}	ν(C=N)^{oxime}	ν(C=C)	ν(N-O)
	**HBIMCO**	3550	3023	2236	1610	1596	1478, 1451	1090
	Tl(BIMCO)	-	3050	2210	1610	1500, 1468	1468, 1447	1220,
	**HQCO**	3570	3030	2230	1596	1615	1508	1030
	Cs(QCO)	-	3042	2200	1604	1328	1505	1210
	Tl(QCO)	-	3060, 3042	2217, 2210	1596	1429	1503	1188

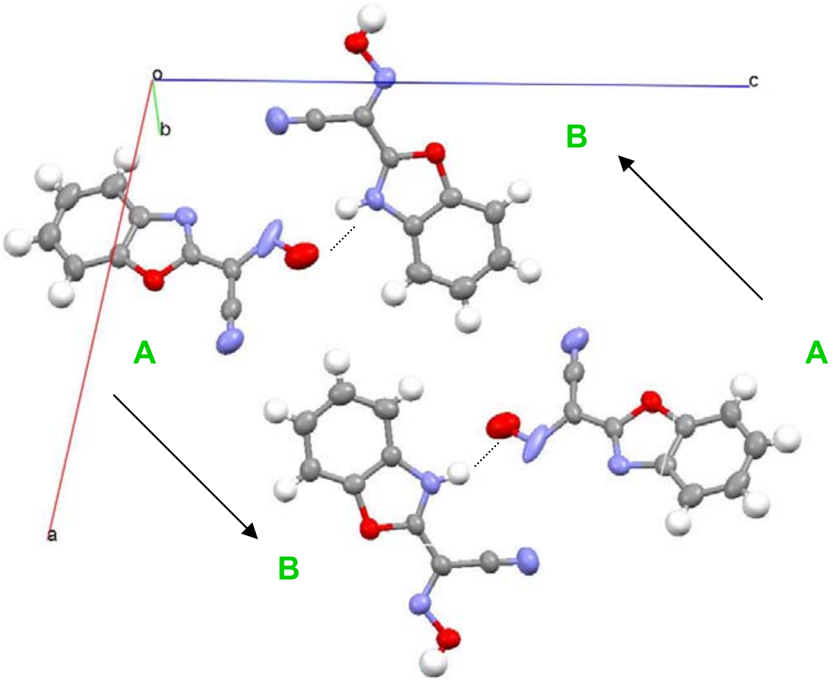
Side by side photographs of crystals of HBIMCO x H_2O and HBOCO showing difference in color between the two 2-benz(heteroarylcyanoximes) attributed to solid state autoionization of the latter.



Picture taken at ×60 magnification on the Nikon microscope equipped with digital camera.

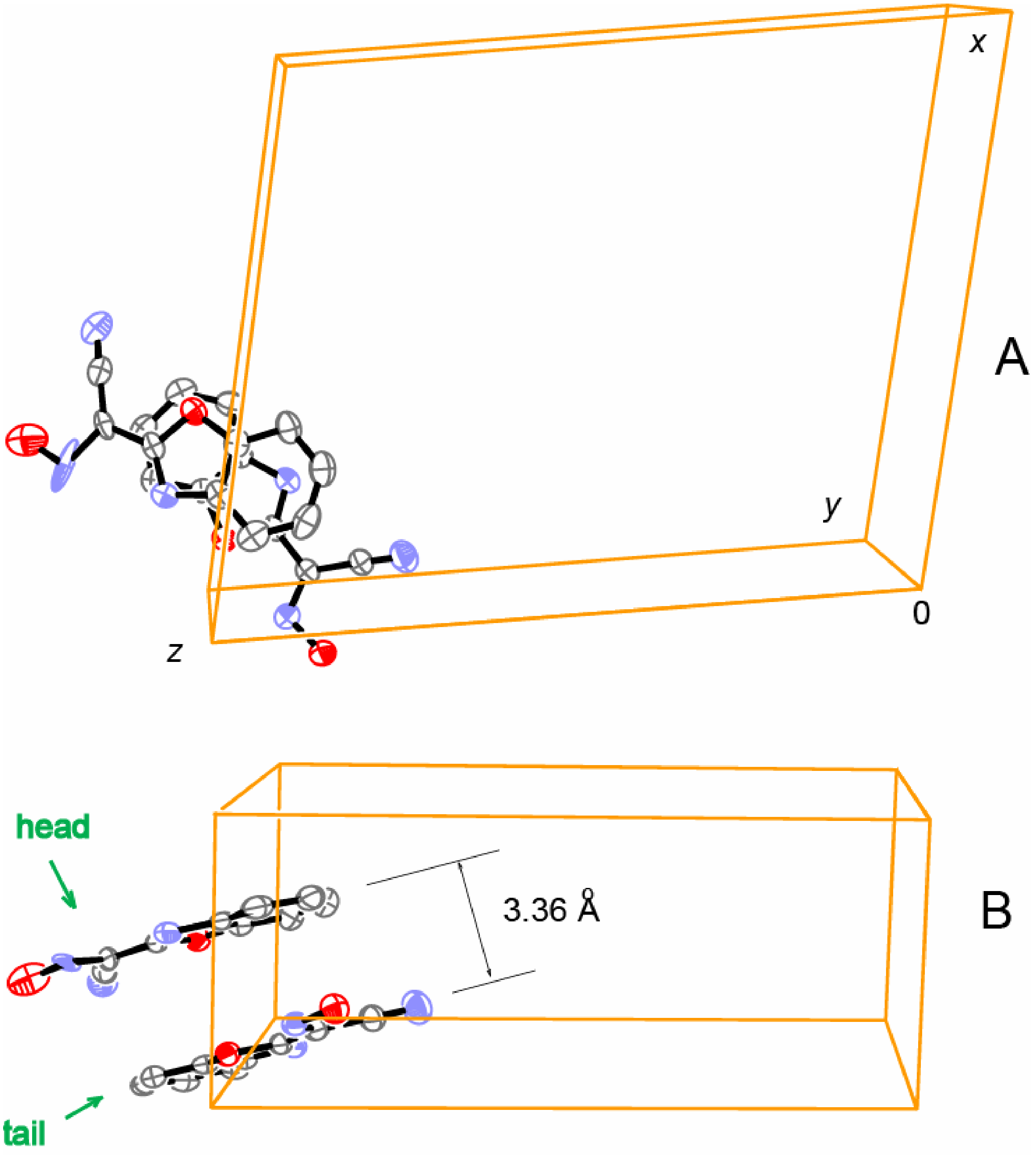
Crystal packing diagram for the structure of HBOCO: schematic representation, where A and B represent anionic (BOCO$^-$) and cationic (H$_2$BCO$^+$) portions respectively.



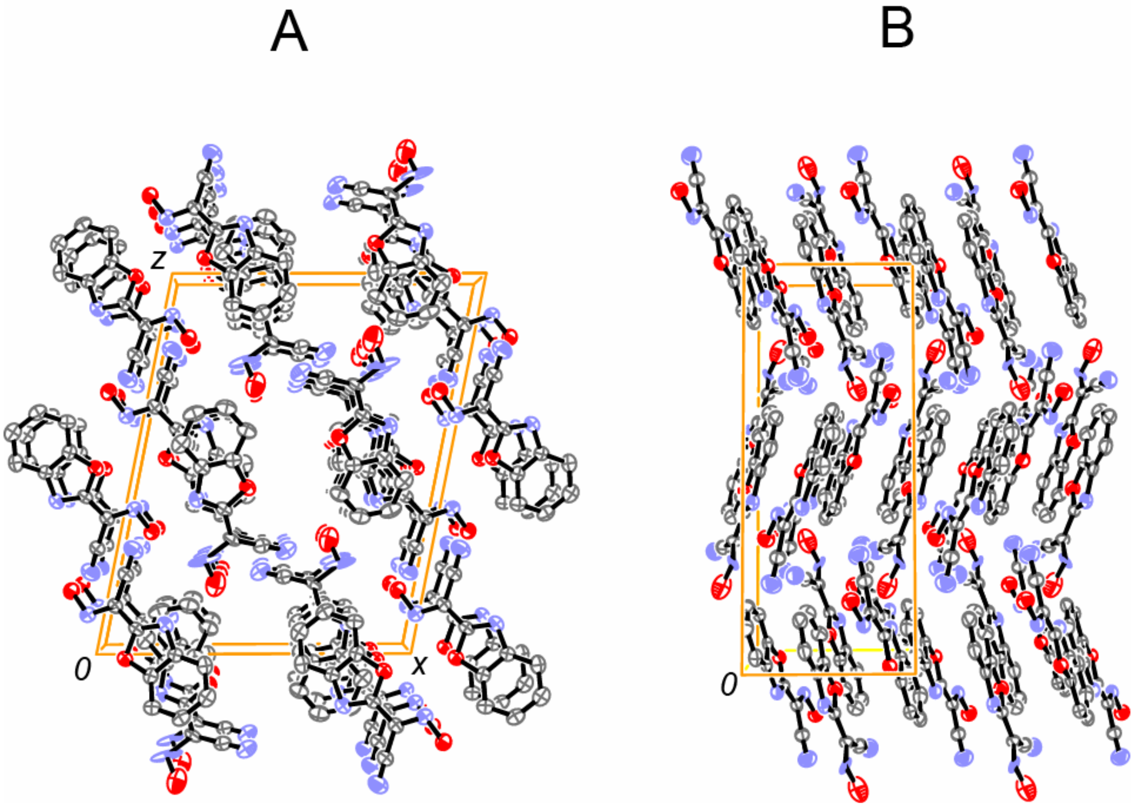


View along *b* direction showing only two isolated **HBOCO** dimers forming A-B "head-to-tail" H-bonded polymeric sheets.

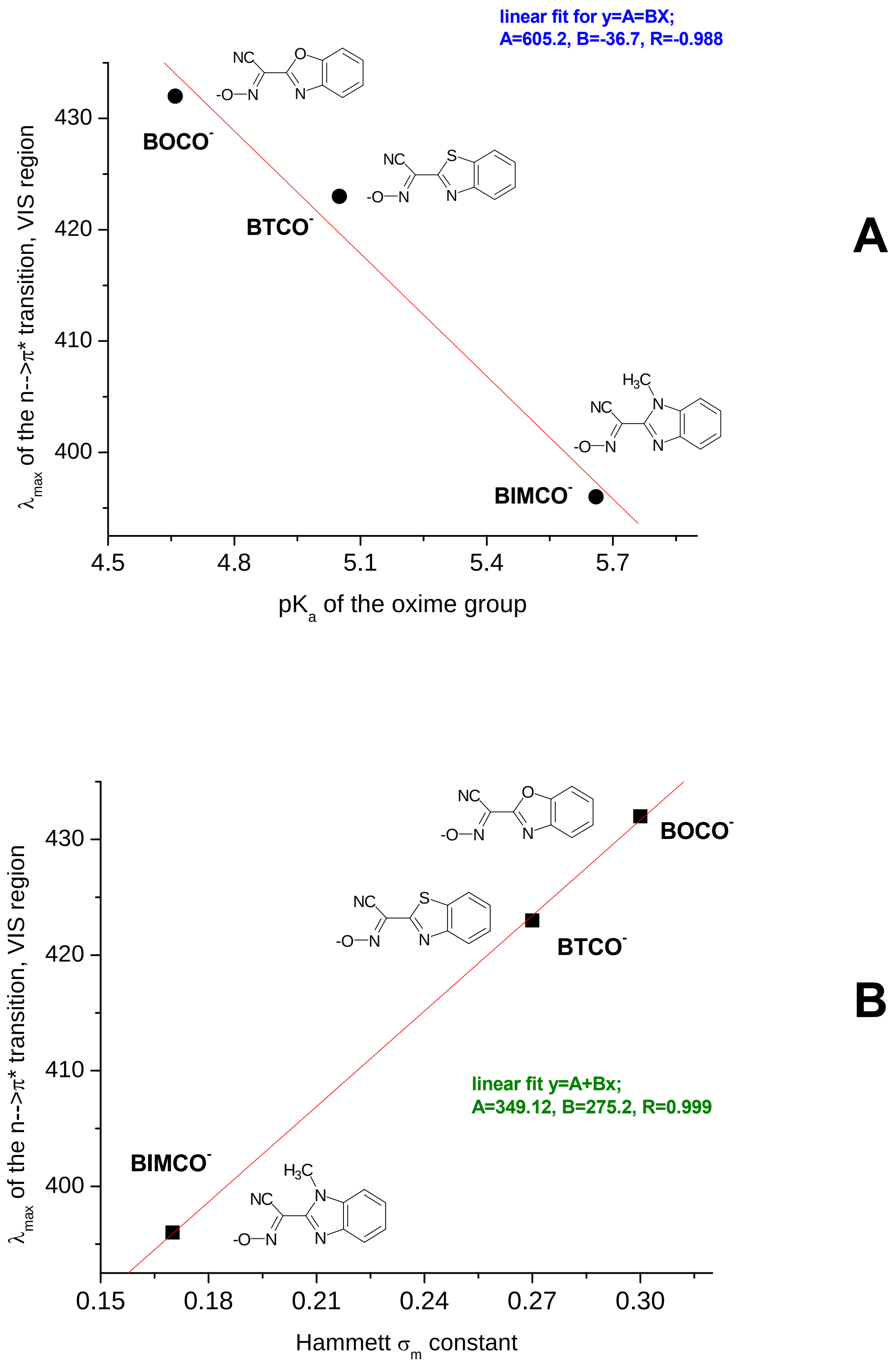
Fragment of crystal structure of HBOCO showing two isolated molecules (cationic H_2BCO^+ and anionic BCO^-) from two adjacent layers engaged into short "slipped" π–π interactions. Displayed are two orthogonal views (A and B) of the unit cell.



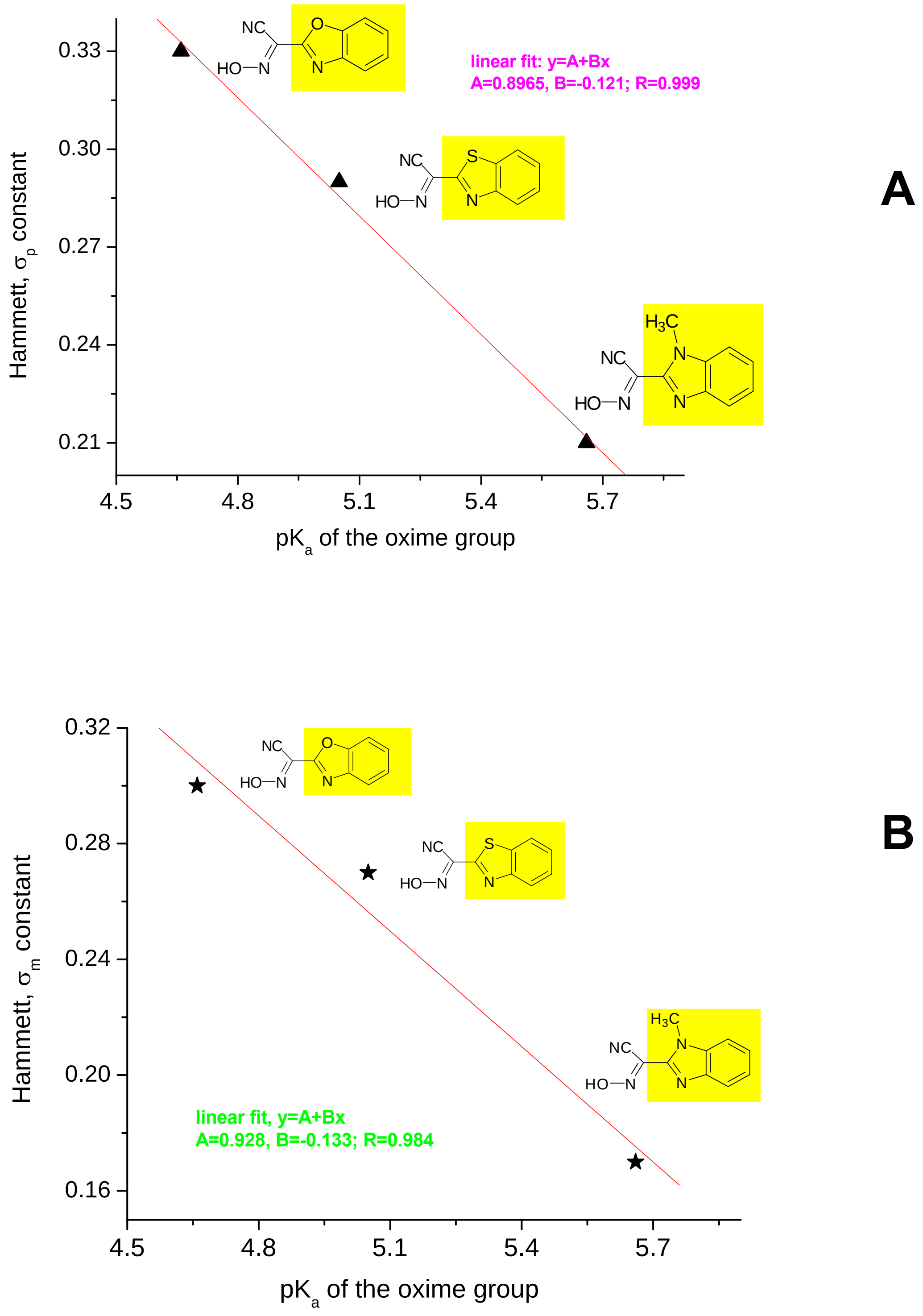
Organization of the crystal structure of HBOCO: views down *y* axis (A) and *x* axis (B) showing π–π stacking interactions between sheets of HBOCO dimers. Coloring scheme: C – grey, O – red, N – blue; hydrogen atoms are omitted for clarity.



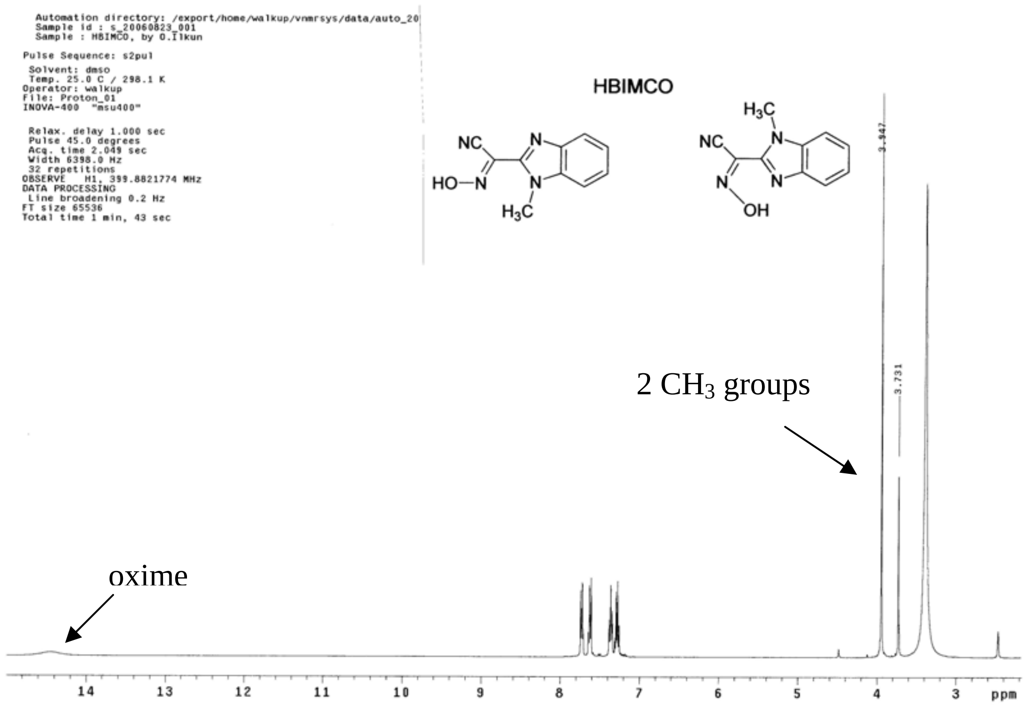
A - linear correlations between visible spectra of L$^-$ and pK$_a$ values of HL;
B – linear correlation between visible spectra of L$^-$ and Hammett σ constant for heteroaryl fragment.



Linear correlations between pK_a of the cyanoxime and Hammett constants σ_p (A) and σ_m (B) of the 2-heteroaryl group highlighted in yellow.



^{1}H NMR spectra of HBIMCO (A) and HBTCO (B) in dmso-d_6 at 298 K.



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  Sample : HBIMCO, by O.Ilkun

Pulse Sequence: s2pul

 Solvent: dmso
 Temp. 25.0 C / 298.1 K
Operator: walkup
File: Proton_01
INOVA-400  "msu400"

 Relax. delay 1.000 sec
 Pulse 45.0 degrees
 Acq. time 2.049 sec
 Width 6398.0 Hz
 32 repetitions
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DATA PROCESSING
 Line broadening 0.2 Hz
FT size 65536
Total time 1 min, 43 sec
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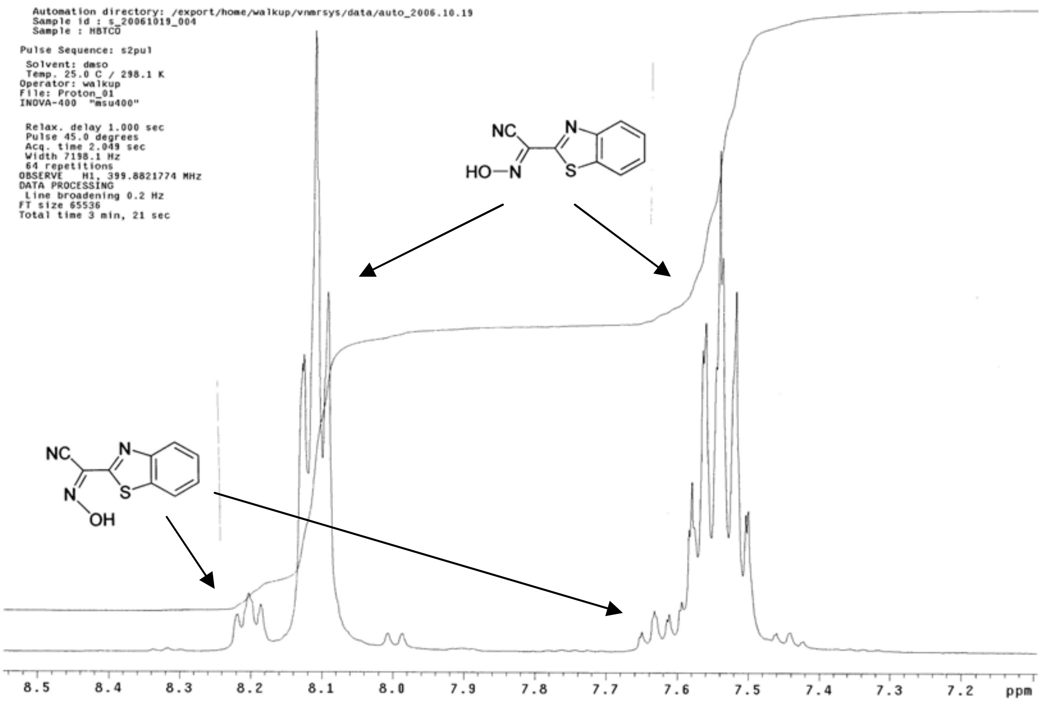
A



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  Sample : HBTCO

Pulse Sequence: s2pul

 Solvent: dmso
 Temp. 25.0 C / 298.1 K
Operator: walkup
File: Proton_01
INOVA-400  "msu400"

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 Pulse 45.0 degrees
 Acq. time 2.049 sec
 Width 7198.1 Hz
 64 repetitions
OBSERVE   H1, 399.8821774 MHz
DATA PROCESSING
 Line broadening 0.2 Hz
FT size 65536
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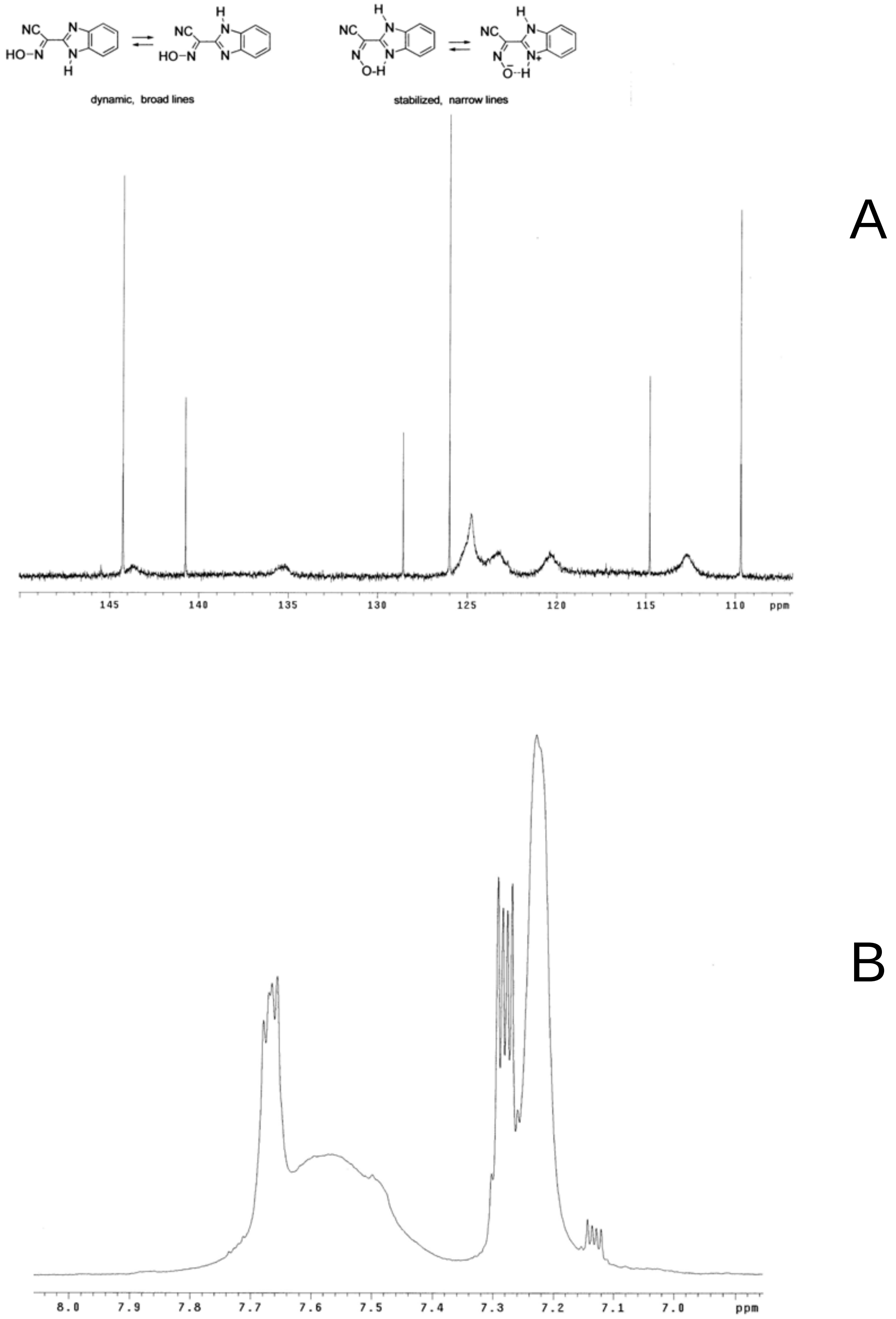
B

Fragments of ^{13}C (A) and ^{1}H (B) NMR spectra of benz(2-imidazolyl)cyanoxime in dmso-d_6 at 298K.



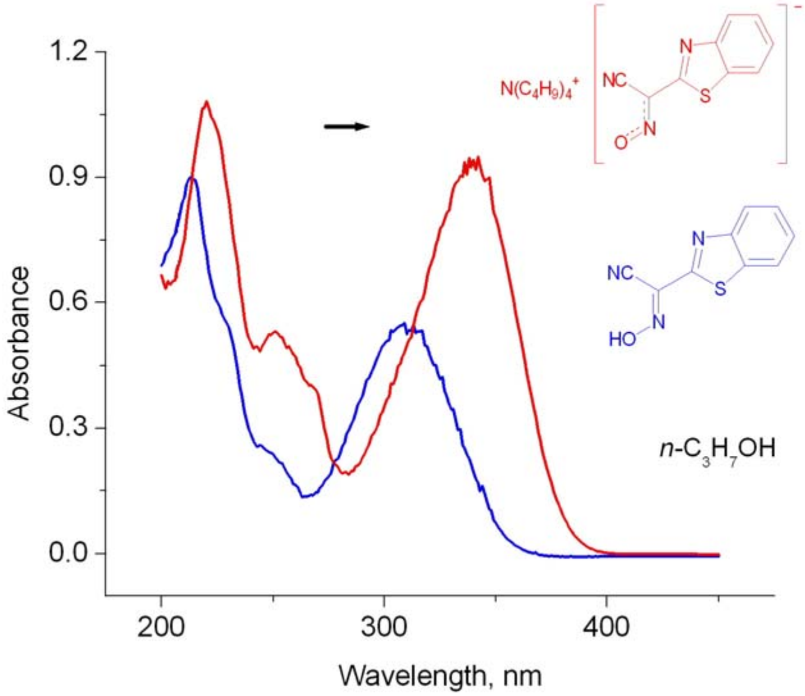
Results of solutions electric conductivity measurements for synthesized benz(2-heteroaryl)cyanoximes and organic salts used as standards.

Compound	Conductivity of 1 mM solutions Λ_M ($cm^2/mol\ \Omega$)		
		Solvent	
	DMSO[a]	acetone[b]	DMF[c]
$NBu_4^+Br^-$	21.1	130.7	73.3
$PPh_4^+Br^-$	28.8	145.1	66.0
HBOCO	**0.90**	**1.7**	**10.2**
HQCO	**4.47**	**10.5**	**14.2**
HBIHCO	0.37	0.5	7.0
HBIMCO	0.35	0.3	3.4
HBTCO	0.28	0.2	3.1

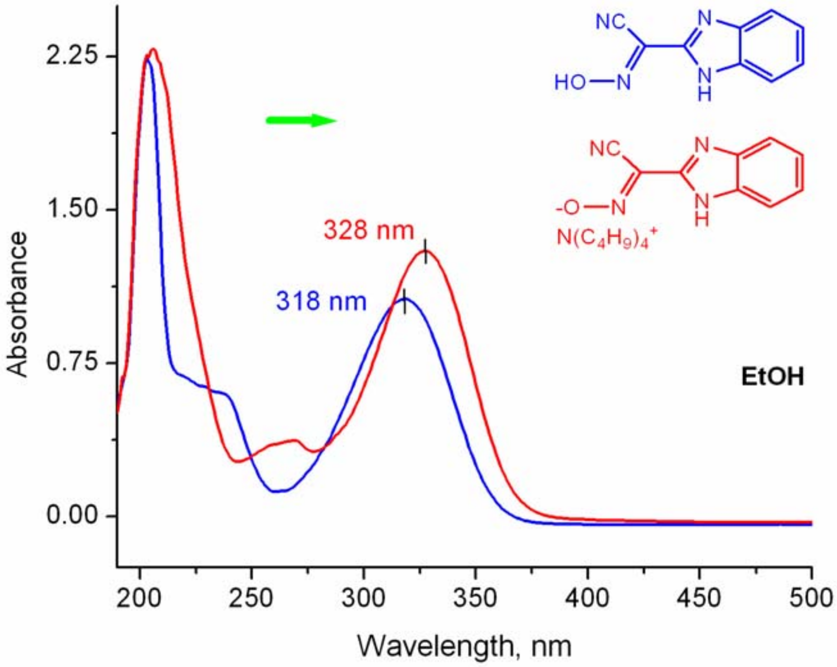
Tetrabutylammonium bromide and tetraphenylphosphonium bromide (both from ALDRICH) were used as standards for 1:1 type of electrolytes

[a] Conductivity of pure DMSO was 0.12
[b] Conductivity of pure acetone was 0.20
[c] Conductivity of pure DMF was 1.60

Fragments of UV-visible spectra of protonated (blue) and deprotonated (red) forms of the HBTCO (A) and HBIHCO (B), in EtOH at 296 K and 5x10^{-5} M concentration in 1 mm cuvettes. Clearly seen a batochromic shift of bands in anions.

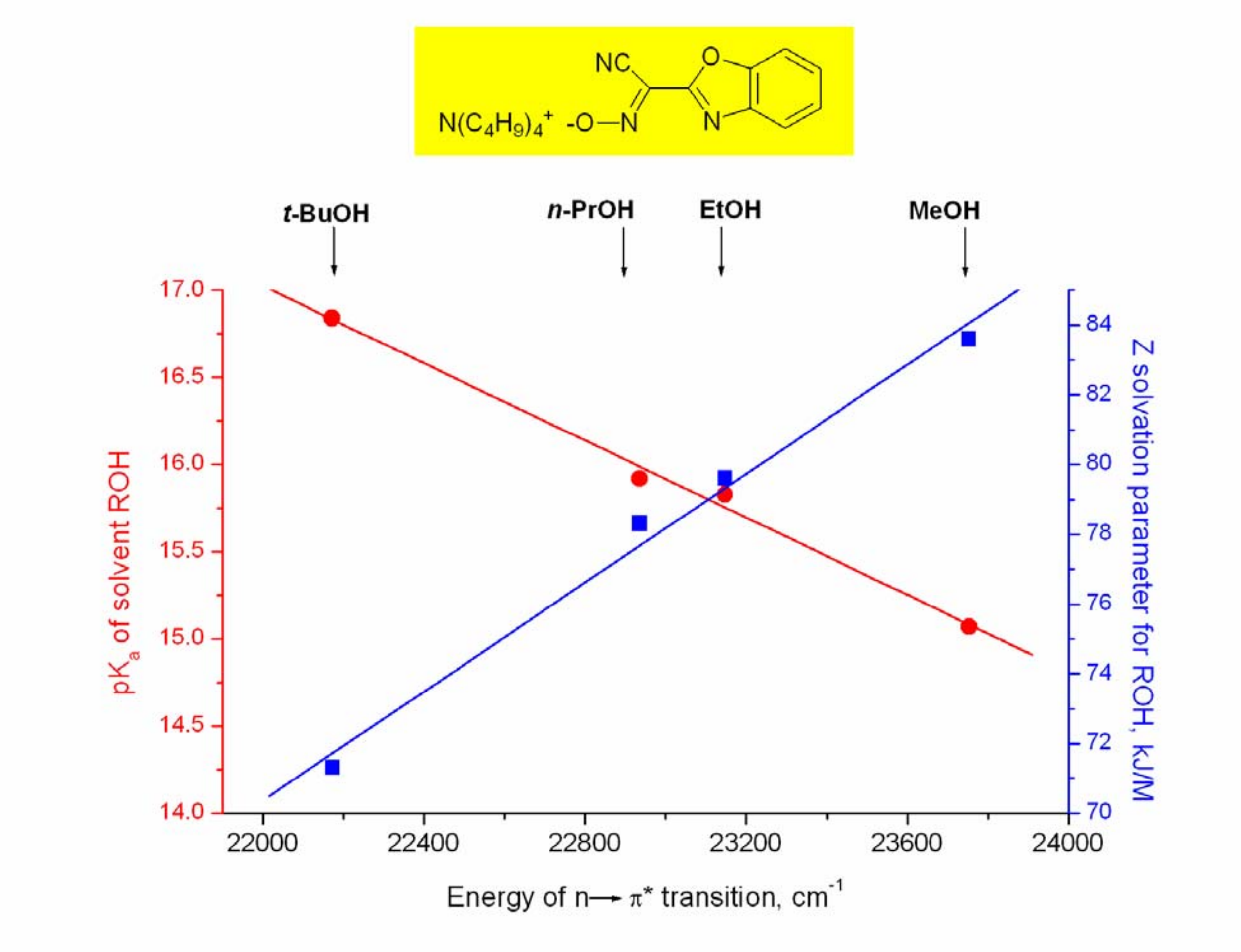


A



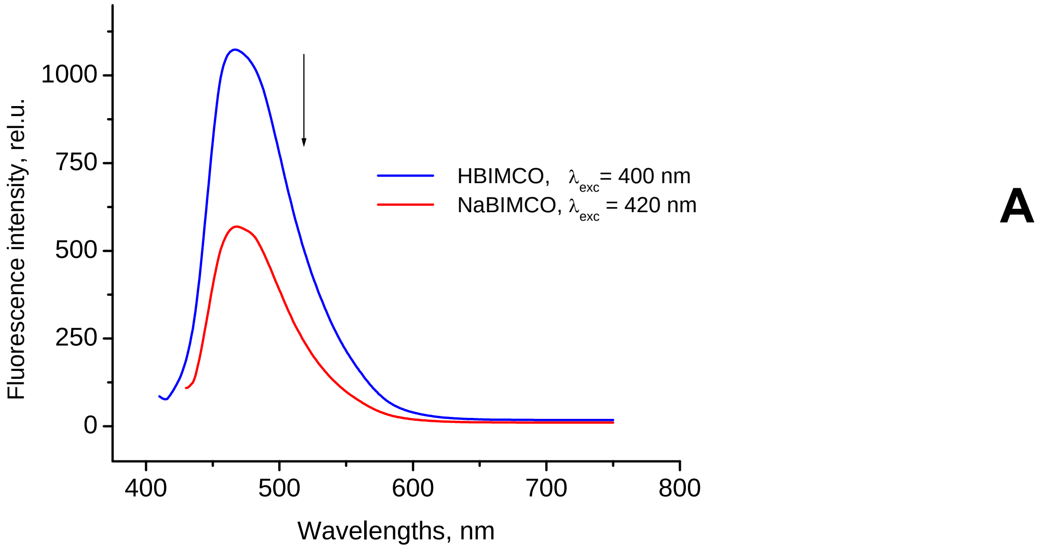
B

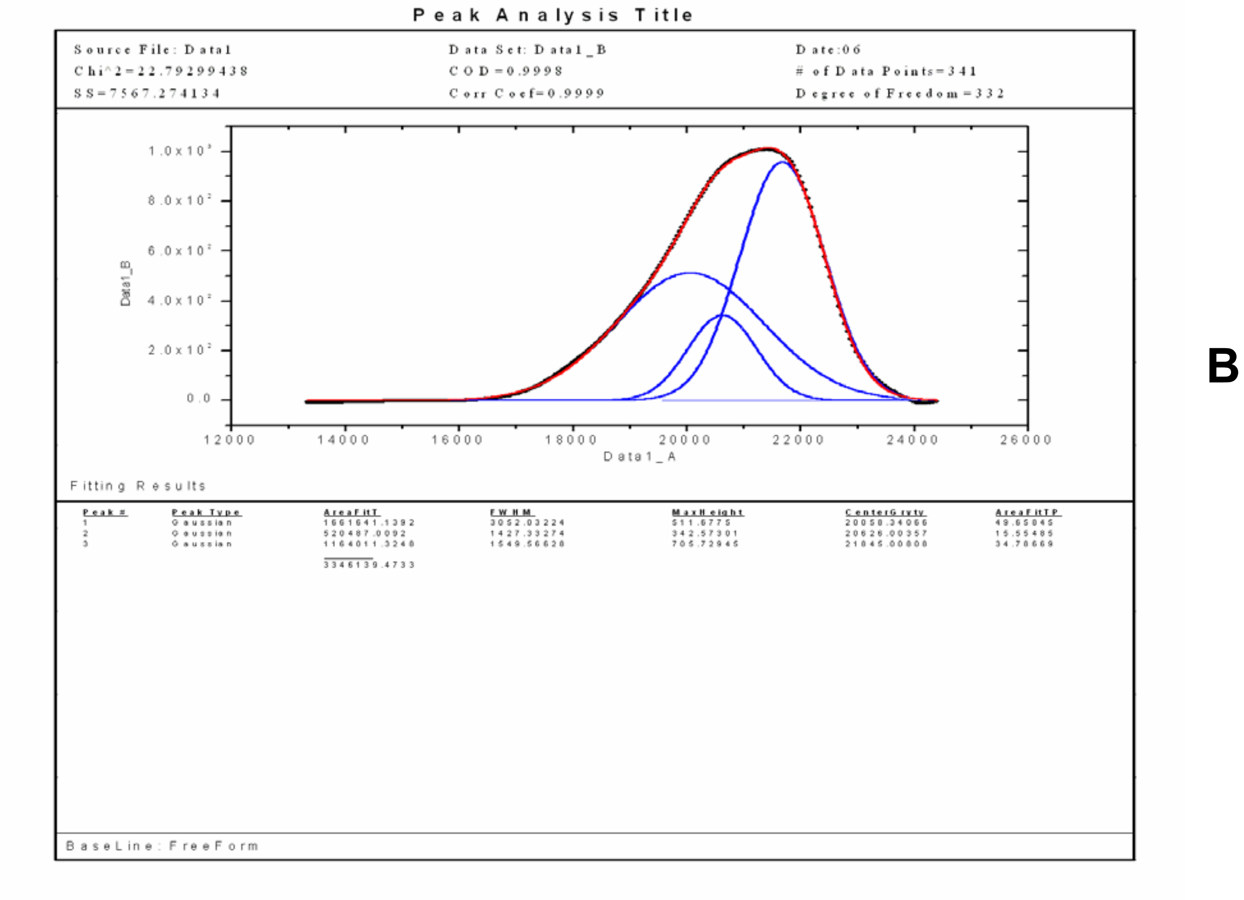
Linear correlations between the energy of n ⟶ π* transitions and solvent ROH parameters observed in UV-visible spectra of BOCO$^-$ anion at 5 mM concentrations. Red: energy of transition vs pK_a of the solvent; linear fir for $y = A+Bx$ with A = 41.39, B = -0.001 and R = -0.996. Blue: energy of transition vs Kosover[#] solvation energy Z; linear fit for $y = A+Bx$ with A = -101.5, B = 0.0078, R = 0.995.



[#] - Kosower, E.M.; Hoffmann, D.; Wallenfels, K. *J. Am. Chem. Soc.*, **1962**, *84*, p. 2755-2760; actual Z values taken from "*The chemist companion (Handbook)*", by Gordon, A.J.; Ford, R.A.; John Wiley & Sons: New York, 1972.

Fluorescence of 2.36 mM ethanol solutions of HBIMCO and NaBIMCO at 296 K in 1 cm cuvette (A), and deconvolution of spectroscopic envelope for HBIMCO as three Gaussian type lines which belong to $\pi^* \longrightarrow \pi$ transitions (B).





Peak Analysis Title

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SS=7567.274134

Data Set: Data1_B
COD=0.9998
Corr Coef=0.9999

Date:06
# of Data Points=341
Degree of Freedom=332

Fitting Results

Peak #	Peak Type	AreaFitT	FWHM	MaxHeight	CenterGrvty	AreaFitTP
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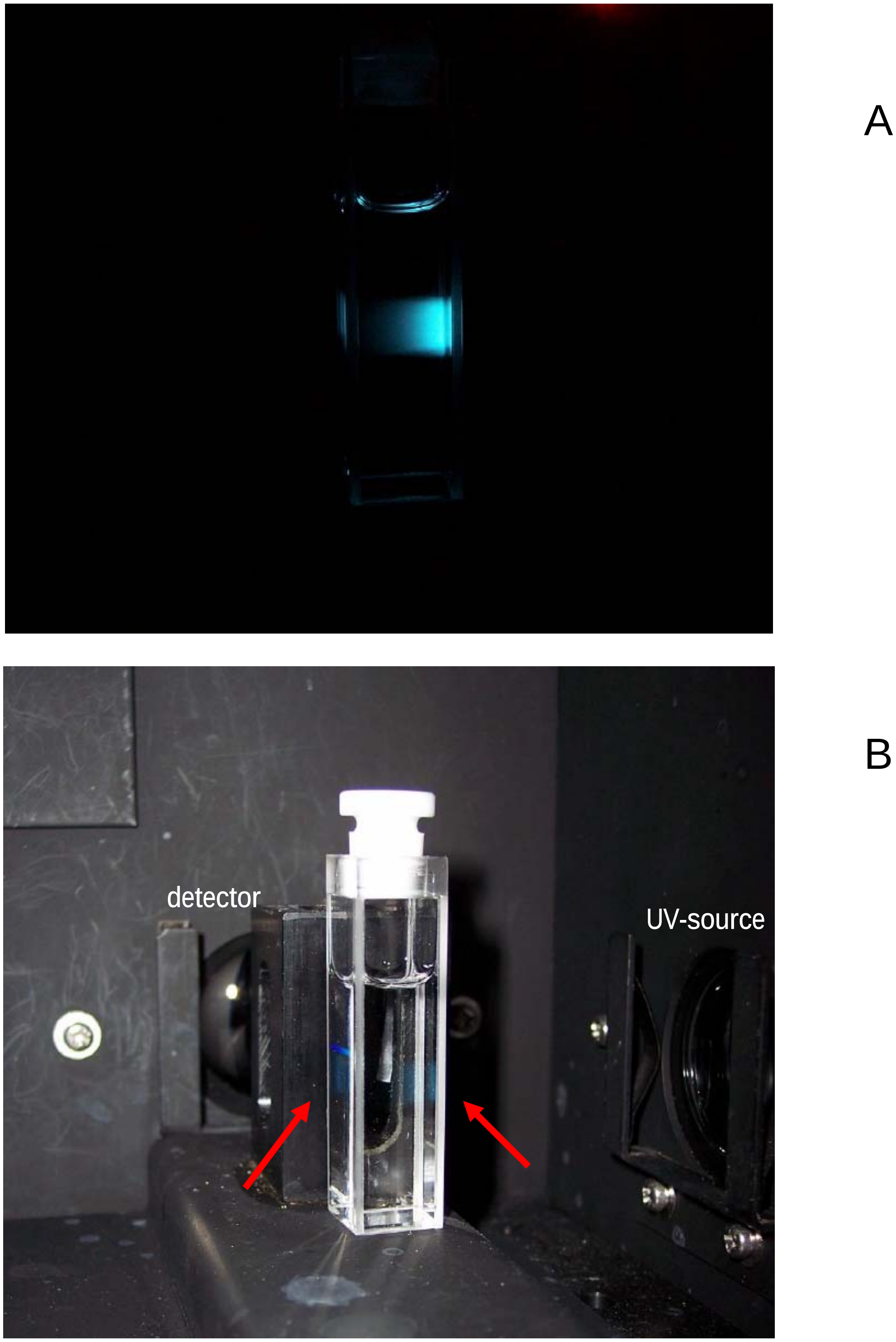
2	Gaussian	520487.0092	1427.33274	342.57301	20626.00357	15.55485
3	Gaussian	1164011.3248	1549.56628	705.72945	21845.00800	34.78669
		3346139.4733				

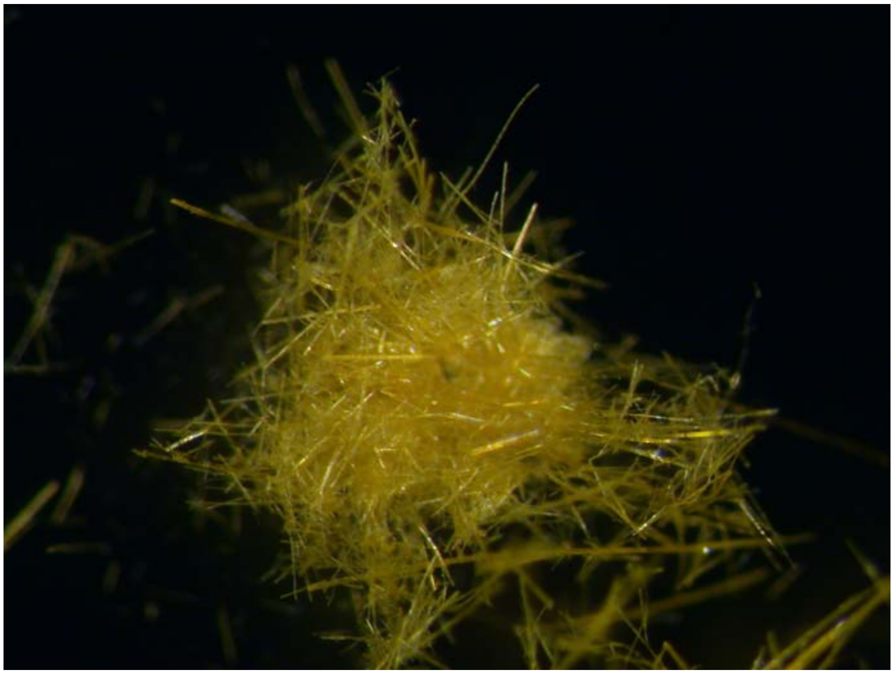
BaseLine: FreeForm

Photographs of 1 cm cuvette with bright blue fluorescent 2 mM solution of HBIHCO in EtOH; λ_{exc}=350 nm. A - in the dark; B - with open to a day light compartment (fluorescence is still visible and shown with red arrows)



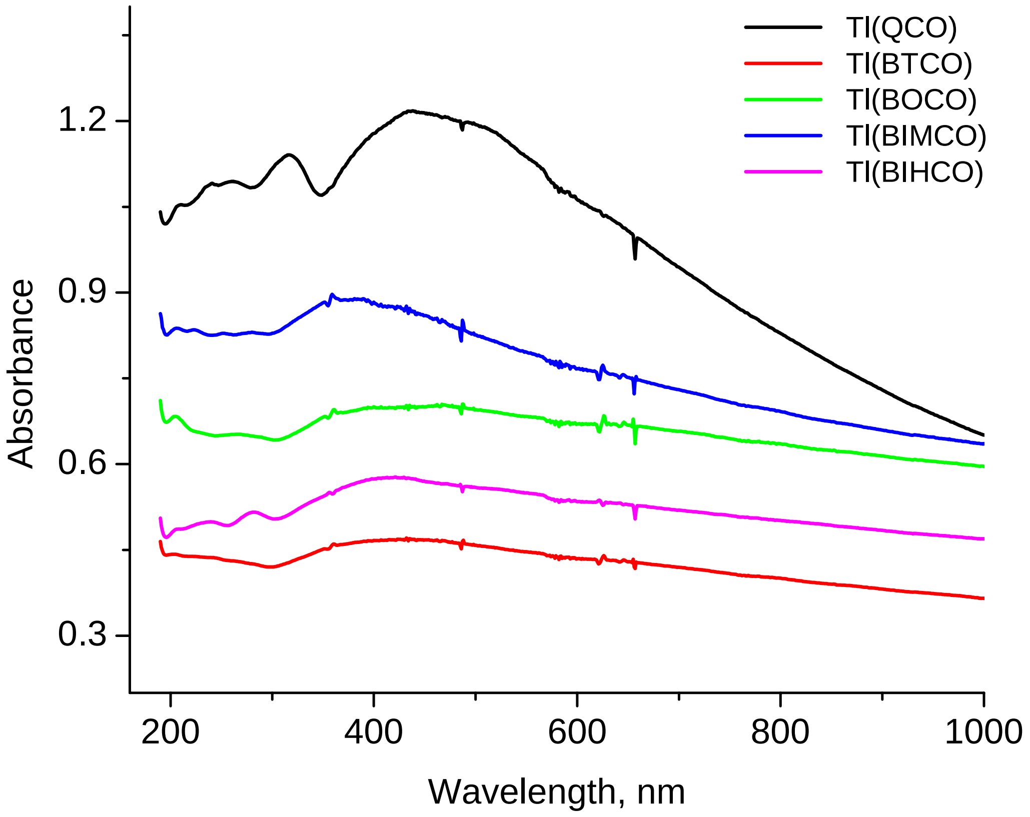
Actual photographs of polycrystalline samples of synthesized thallium(I) cyanoximates taken in reflected light with dark background at 60 x magnification. Clearly seen very fine fibrous, almost wool-like, texture of the Tl(BIMCO) and needles of Tl(BOCO).

Tl(BIMCO)



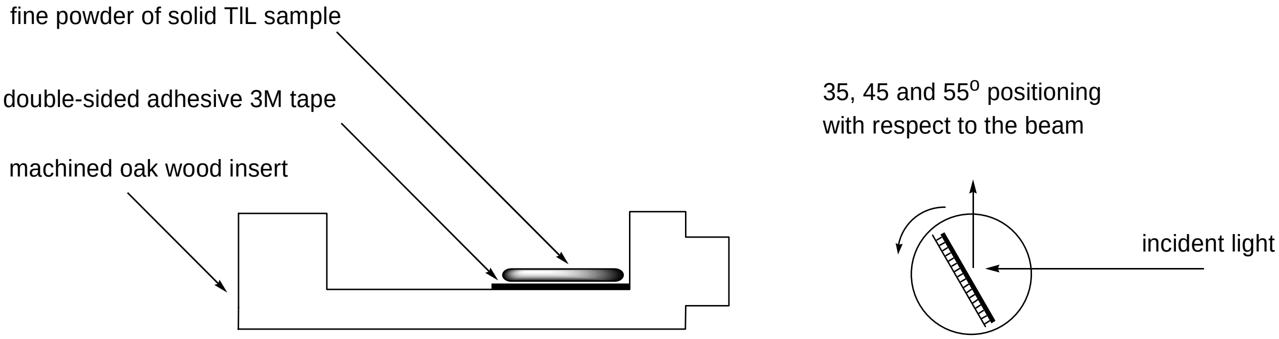
Tl(BOCO)

UV-visible spectra of solid samples of monovalent thallium benz(2-heteroaryl) cyanoximates obtained from fine suspensions of compounds in silicon oil. Spectra recorded at room temperature from paste-like samples squeezed between two quartz plates of 40 x 10 x 1 mm dimensions.

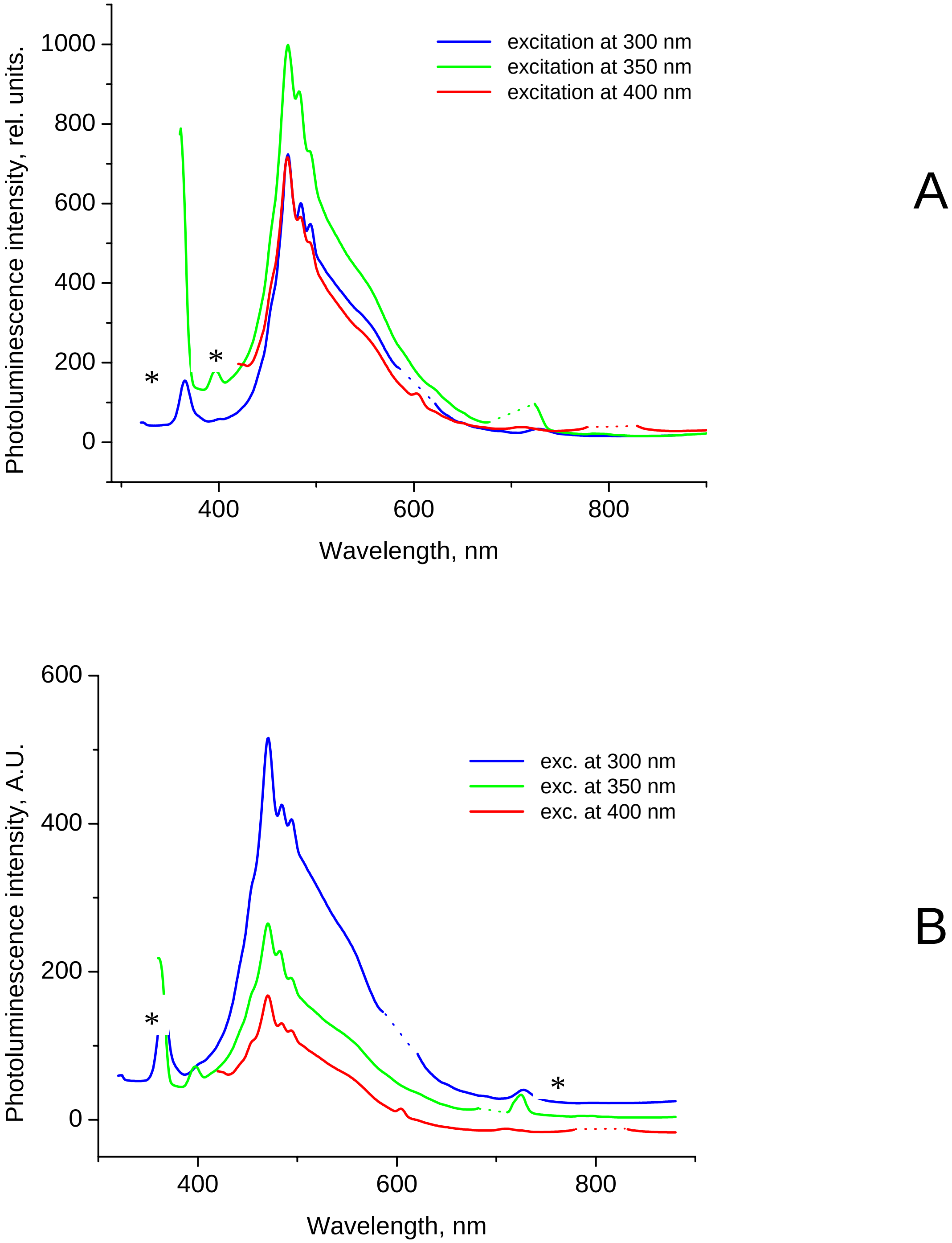


TlL samples preparation prior to room temperature photoluminescence measurements.

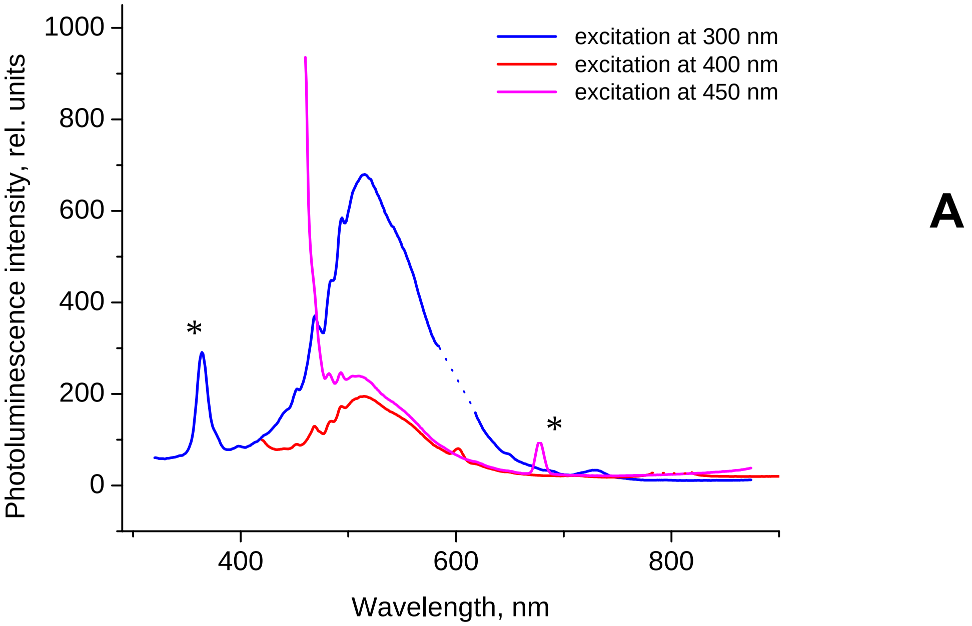
An insert (oak wood) into the cuvette holder for solid state photoluminescence measurements.

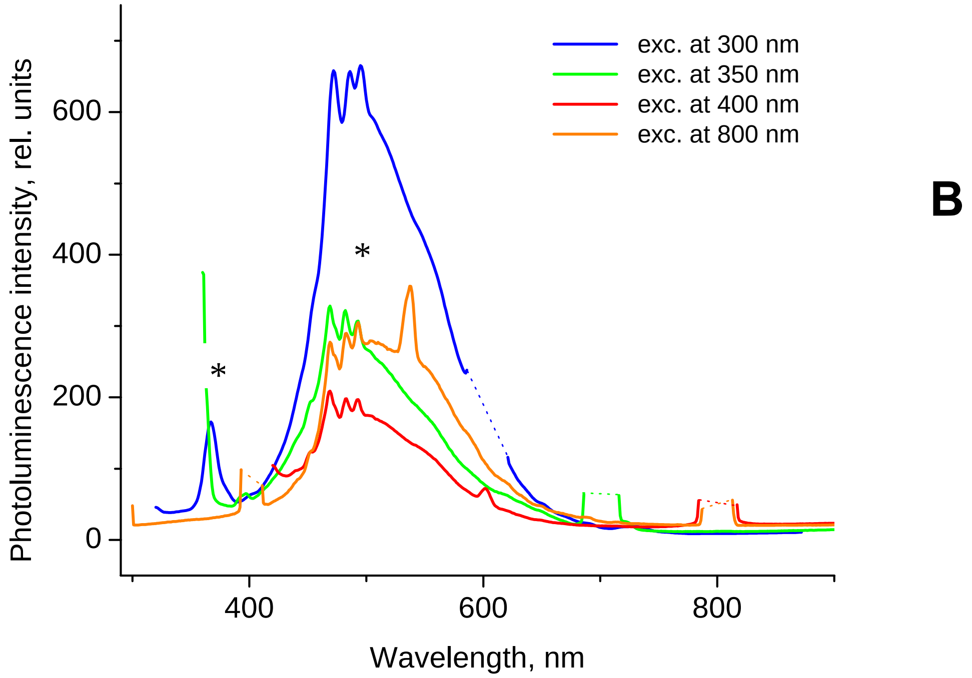


Solid state room temperature emission spectra of Tl(BIHCO) (A), and Tl(BIMCO), (B) obtained using different excitation wavelengths. Dotted lines indicate cut-offs the instrument emission/excitation lines including second harmonics, while asterisks show the instrument artifacts.



Solid state room temperature emission spectra of Tl(BOCO) (A), and Tl(BTCO), (B) obtained using different excitation wavelengths. Dotted lines indicate cut-offs the instrument emission/excitation lines including second harmonics, while asterisks show the instrument artifacts.





Solid state room temperature emission spectra of Tl(QCO) obtained using different excitation wavelengths. Dotted lines indicate cut-offs the instrument emission / excitation lines including second harmonics, while asterisks show the instrument artifacts.