2-Acyl-1,1,3,3-tetracyanopropenides (ATCN): structure characterization and luminescent properties of ammonia and alkali metal ATCN salts

Supporting Information

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Synthesis of ATCN salts

The starting compounds for preparation of ATCN salts are 3-aroylcyclopropane-1,1,2,2-tetracarbonitriles (ACT), which can be easily obtained using acetophenones, malonodinitrile, bromine and DMSO as precursores[1]. Reaction between ACT and metal or ammonia acetates results in ATCN formation, but we have found that using of carbonates instead of acetates leads to better yields of ATCN.

Synthesis of lithium ATCN **1-4 b** (general procedure)

3-Aroylcyclopropane-1,1,2,2-tetracarbonitrile (0.05 mol) and lithium carbonate (not acetate!) (0.07 mol) was added in water (10 mL) then stirred at 50-60 °C until the ACT had dissolved. The resulting yellow solution was filtered, the filtrate allowed to cool then extracted three times with ethyl acetate (3x5 mL). The combined organic phases were evaporated in vacuo and the residue was triturated with anhydrous diethyl ether. The resulting mixture was filtered, washed with diethyl ester and dryed in air. Yields are about 50-60%.
The single crystals were obtained by slowly evaporating of ethyl acetate solution in air.

Synthesis of sodium, potassium, rubidium and cesium ATCN **1-4 c-f** (general procedure)

3-Aroylcyclopropane-1,1,2,2-tetracarbonitrile (0.05 mol) and corresponding carbonate or acetate (0.05 mol) was added in water (5 mL), then stirred at 50-60 °C until the solids had dissolved. The resulting solution allowed to cool, formed precipitate (it may be necessary to initiate crystallization by using a glass rod to rub the inside surface of the crystallization vessel!) was filtered, washed with 3-5 mL of cold water and dryed in air. Yields of sodium ATCN are 70-80%, of other - almost quantitative.
Sodium 2-benzoyl-1,1,3,3-tetracyanopropenide **1c**: the single crystals of α-modification were obtained by slowly evaporating of water solution in air. β-form was obtained by slowly cooling of saturated at 70°C ethyl acetate solution.
Potassium 2-benzoyl-1,1,3,3-tetracyanopropenide **1d**: analogously **1c**.
Sodium 2-(4'-methylbenzoyl)-1,1,3,3-tetracyanopropenide **2c**: the single crystals of α-modification were obtained by slowly evaporating of water or ethyl acetate solution in air. β-form was obtained by rapid evaporation of saturated at ethyl acetate solution in vacuo.
Potassium 2-(4'-methoxybenzoyl)-1,1,3,3-tetracyanopropenide **3d**: the single crystals of α-modification were obtained by slowly evaporating of water solution in air. β-form was obtained by rapid evaporation of saturated at ethyl acetate solution in vacuo.
The single crystals of other salts were obtained by slowly evaporating of ethyl acetate solution in air.

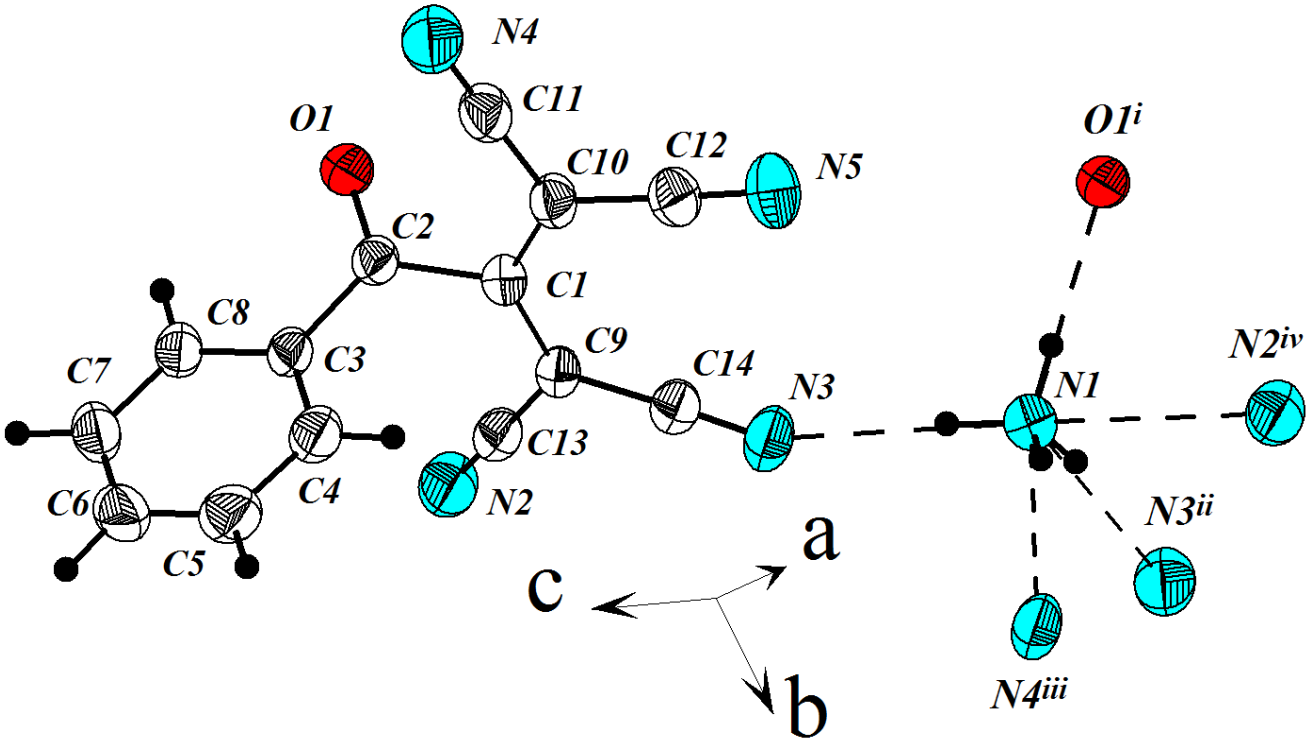
Synthesis of ammonia ATCN **1-4 a** (general procedure)

3-Aroylcyclopropane-1,1,2,2-tetracarbonitrile (0.05 mol) and ammonia acetate (0.2-0.35 mol) was added in water (5 mL), then stirred at 50-60 °C until the solids had dissolved. The resulting solution allowed to cool, formed precipitate (it is necessary to initiate crystallization by using a glass rod to rub the inside surface of the crystallization vessel!) was filtered, washed with 3-5 mL of cold water and dryed in air. Yields are about 50-60%.
The single crystals were obtained by slowly evaporating of ethyl acetate solution in air.

1 Sergey V. Karpov, Arthur A. Grigor'ev, Yakov S. Kayukov, Irina V. Karpova, Oleg E. Nasakin, Victor A. Tafeenko. *J. Org. Chem.* **2016**, *81*, 6402 − 6408.

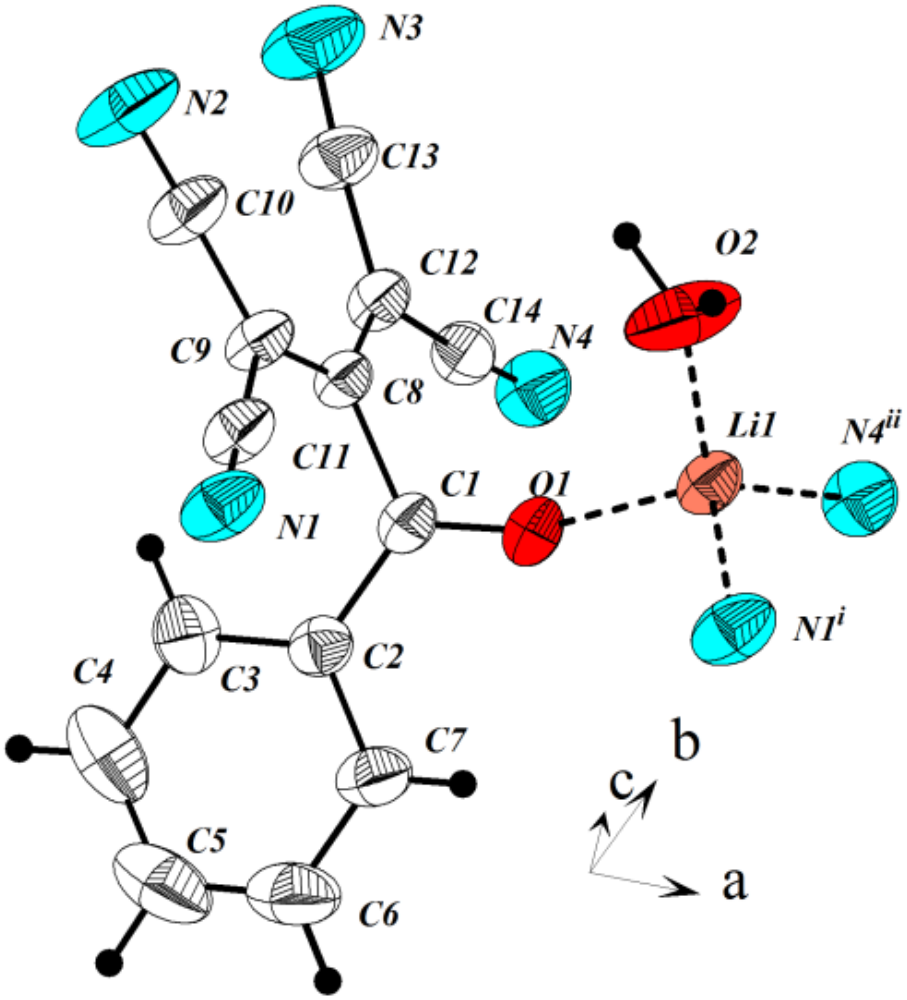
ORTEP images of ATCN with 50% probability ellipsoids

Ammonium 2-benzoyl-1,1,3,3-tetracyanopropenide **1a**



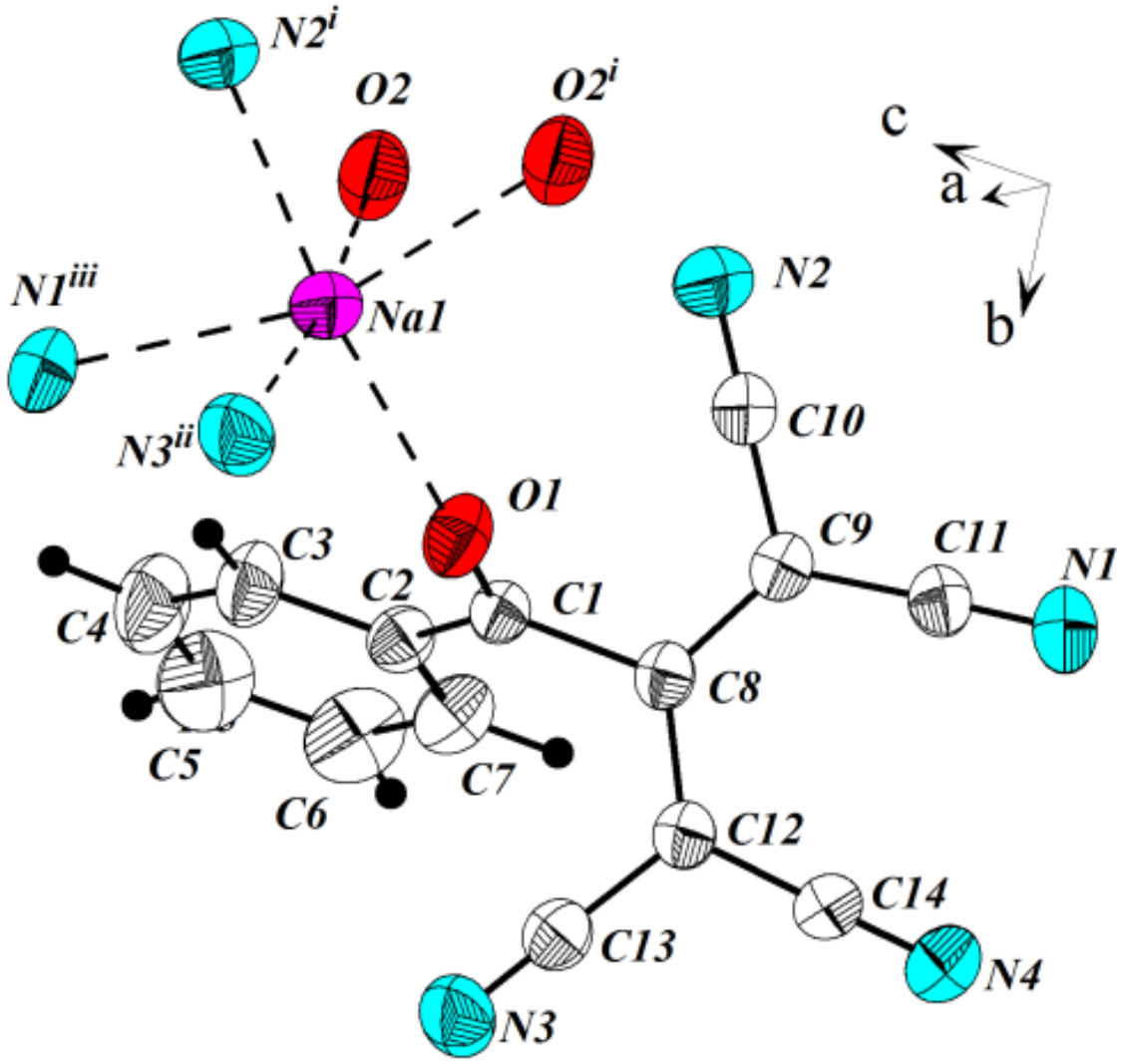
Bond lengths, Å	
N1N3	3.002
N1O1^{i}	2.871
N1N2^{iv}	3.011
N1N4^{iii}	2.982
N1N3^{ii}	3.098
Symmetry codes: *i* = 1-*x*, 2-*y*, -*z*; *ii*= 1-*x*, 3-*y*, -*z*; *iii* = 1+*x*, 1+*y*, -1+*z*; *iv* = 0.5+*x*, 0.5-*y*, -0.5+*z*.	
CCDC deposit number: 694326	

Lithium 2-benzoyl-1,1,3,3-tetracyanopropenide **1b**



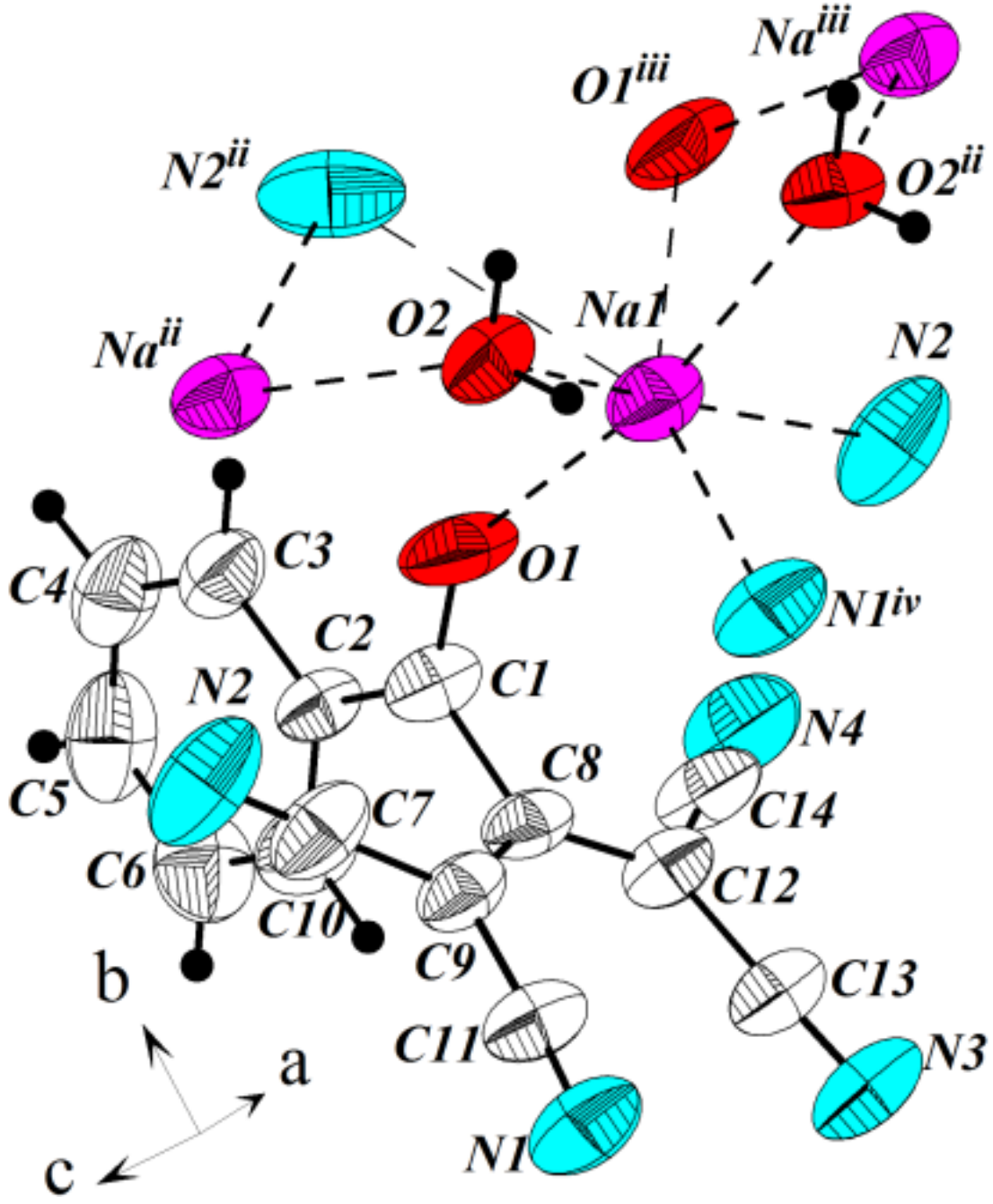
Bond lengths, Å	
Li*N1*	2.047
Li*N4*	2.043
Li*O2*	1.859
Li*O1*	1.946
Symmetry codes: *i=1-x, -y, 1-z; ii=1-x, 1-y, -z.*	
CCDC deposit number: 1452033	

Sodium 2-benzoyl-1,1,3,3-tetracyanopropenide **α-1c**



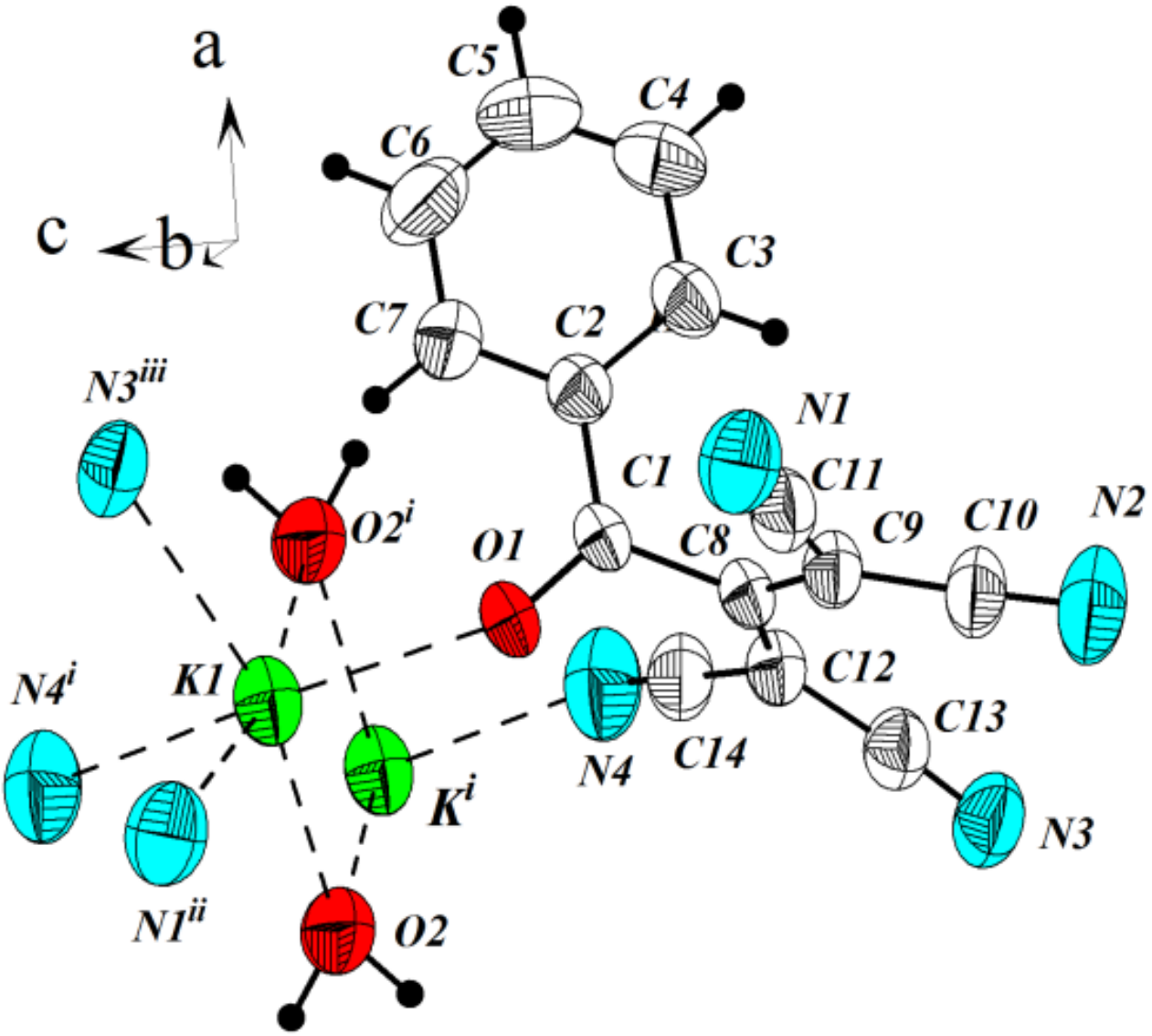
Bond lengths, Å	
NaO*1*	2.431
NaO*2*	2.504
NaO*2*^{i}	2.494
NaN*1*^{iii}	2.607
NaN*2*^{i}	2.452
NaN*3*^{ii}	2.493
Symmetry codes: *i= -x, 1-y, 1-z; ii= -x, 2-y,1-z; iii= 0.5+x, 1.5-y, 0.5+z.*	
CCDC deposit number: 1452034	

Sodium 2-benzoyl-1,1,3,3-tetracyanopropenide **β-1c**



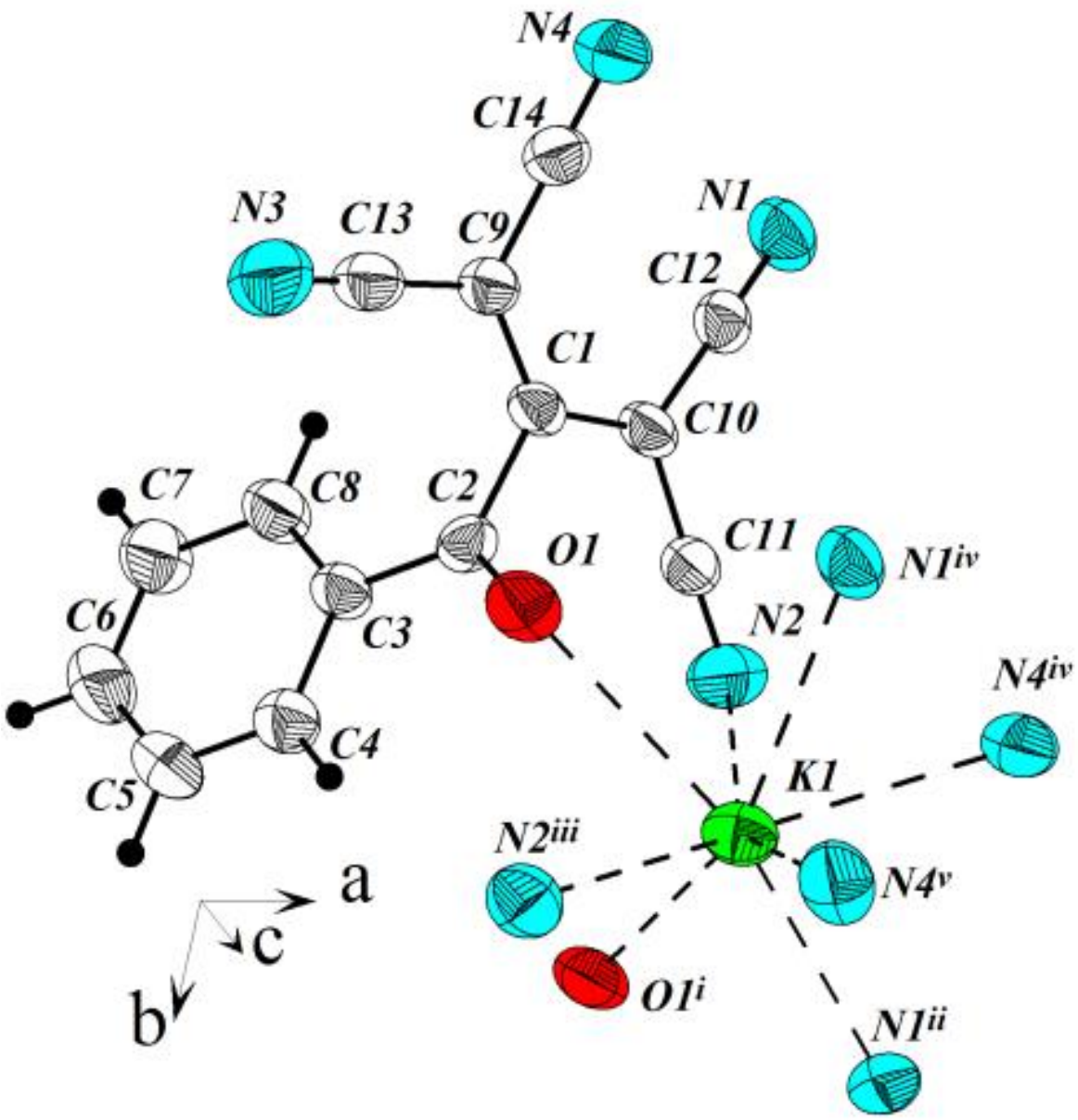
Bond lengths, Å	
NaO*1*	2.297
NaO*2*	2.447
NaO*2*^{ii}	2.366
NaN*2*	2.459
NaN*1*^{iv}	2.455
NaN*2*^{ii}	3.178
NaO*1*^{iii}	3.243
Symmetry codes: *i*= *x*, *y*, 1+*z*; *ii*= *x*, 0.5-*y*,0.5+*z*; *iii*= *x*, 0.5-*y*, -0.5+*z*; *iv*=1-*x*, -*y*, 2-*z*.	
CCDC deposit number: 1574996	

Potassium 2-benzoyl-1,1,3,3-tetracyanopropenide **α-1d**



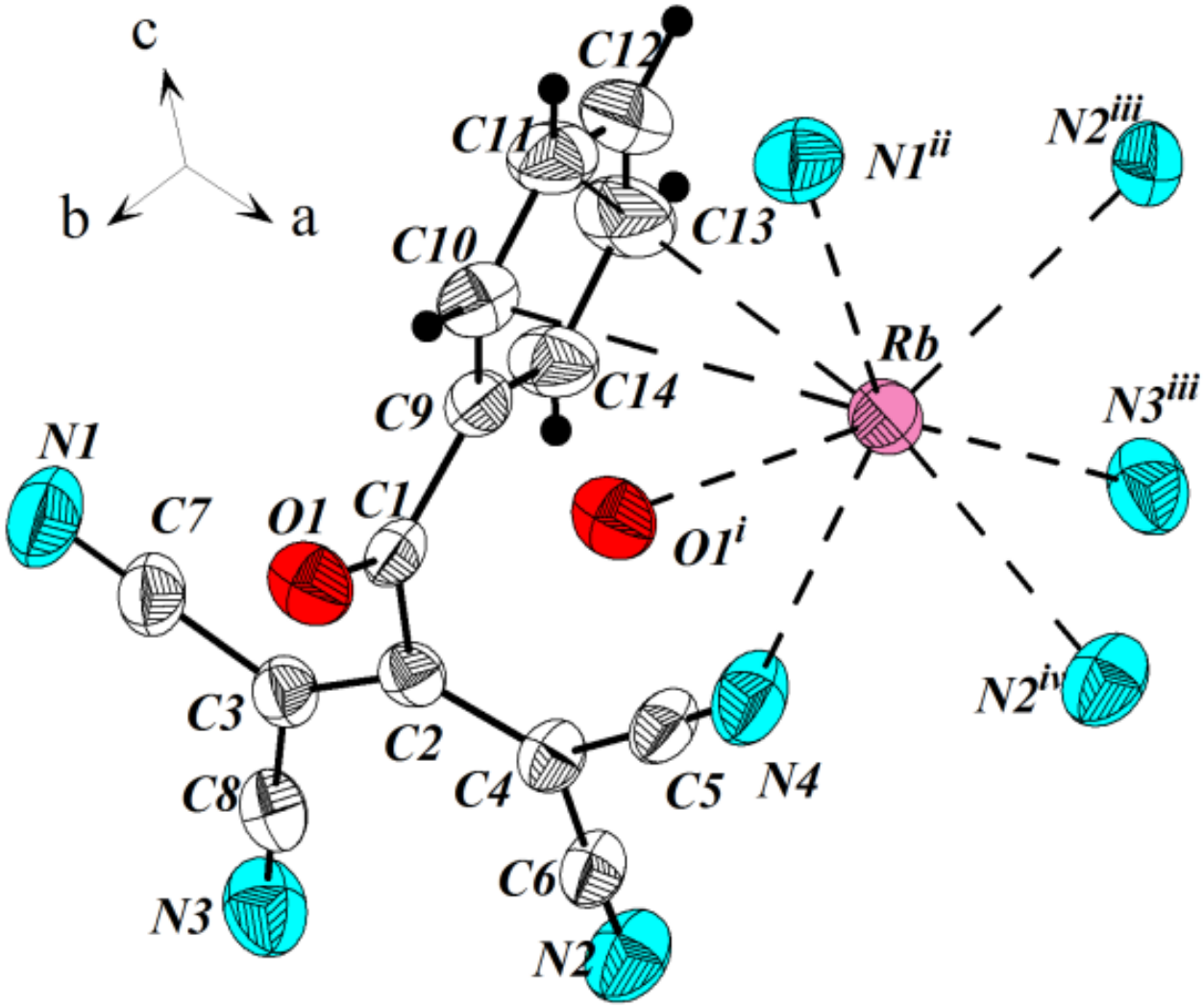
Bond lengths, Å	
KO*1*	2.708
KO*2*	2.765
KO*2*^{i}	2.805
KN*1*^{ii}	2.827
KN*3*^{iii}	2.891
KN*4*^{i}	2.808
Symmetry codes: *i= 1-x, 1-y, 1-z; ii= 1-x, -y,1-z; iii = 0.5+x, 0.5-y, 0.5+z.*	
CCDC deposit number: 1452031	

Potassium 2-benzoyl-1,1,3,3-tetracyanopropenide **β-1d**



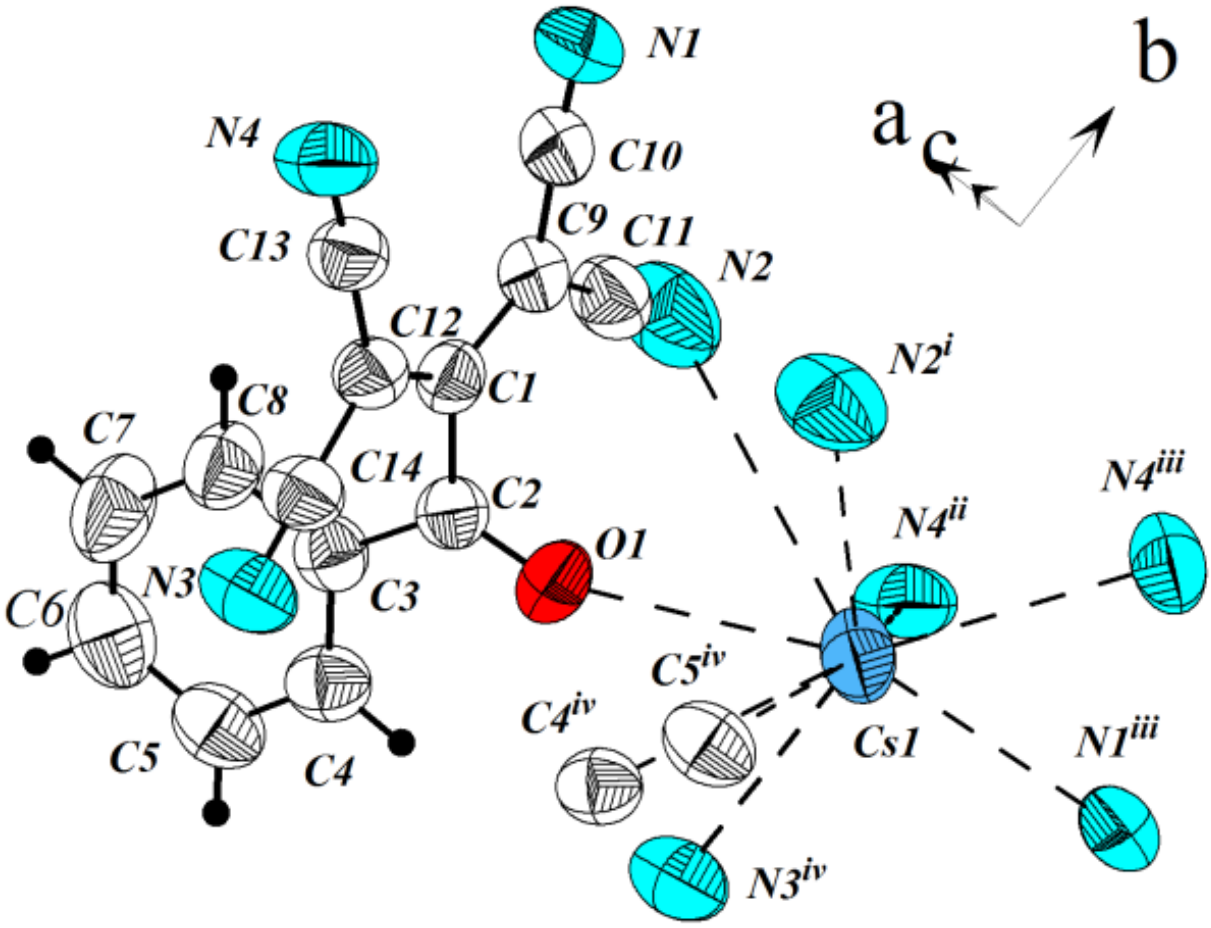
Bond lengths, Å	
K*1*O*1*	3.035
K*1*N*2*	3.020
K*1*O*1*^{i}	2.801
K*1*N*1*^{ii}	2.862
K*1*N*2*^{iii}	2.844
K*1*N*1*^{iv}	2.978
K*1*N*4*^{iv}	3.137
K*1*N*4*^{v}	2.944
Symmetry codes: *i = x, 0.5-y, 0.5+z; ii = 1-x, 0.5+y, 2.5-z; iii = x, 0.5-y, -0.5+z, iv = 1-x, -y, 2-z; vi = 1-x, 0.5+y, 1.5-z.*	
CCDC deposit number: 1574998	

Rubidium 2-benzoyl-1,1,3,3-tetracyanopropenide **1e**



Bond lengths, Å	
Rb*N4*	2.967
Rb*O1*^{i}	2.880
Rb*N1*^{ii}	2.965
Rb*N2*^{iii}	3.135
Rb*N3*^{iii}	3.120
Rb*N2*^{iv}	3.095
Rb*C11*	3.793
Rb*C10*	3.79(1)
Symmetry codes: *i= 1-x, 2-y,-z; ii= 1-x, -0.5+y, 0.5-z; iii= 2-x, -0.5+y, 0.5-z; iv = 2-x, 2-y,-z*	
CCDC deposit number: 1581463	

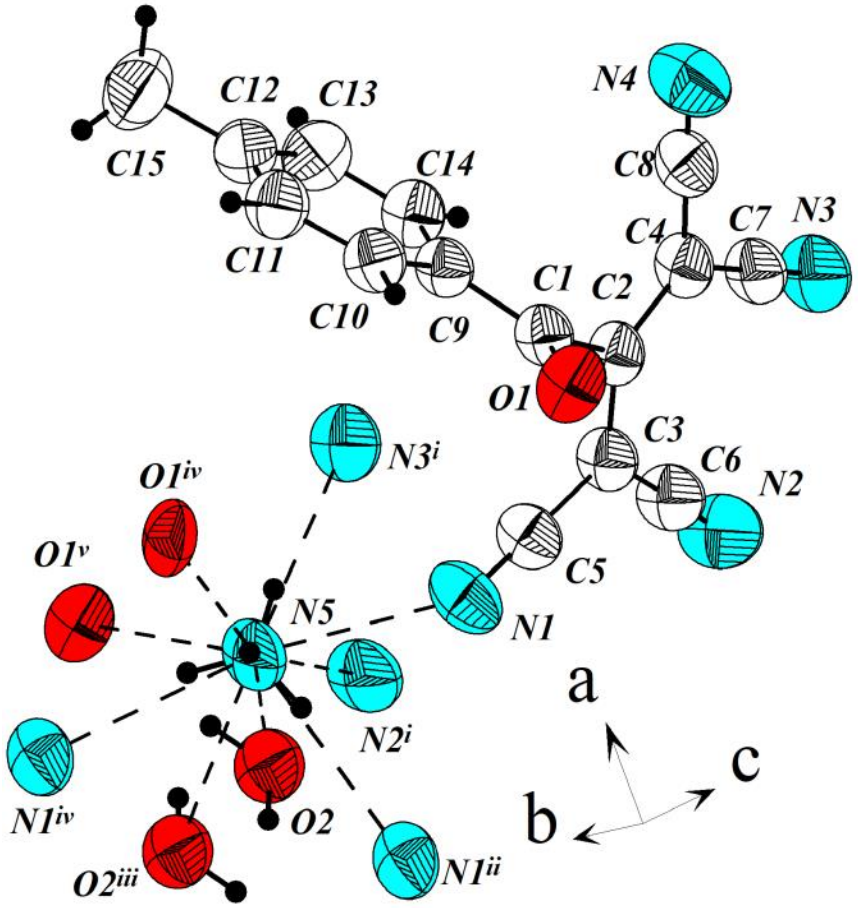
Cesium 2-benzoyl-1,1,3,3-tetracyanopropenide **1f**



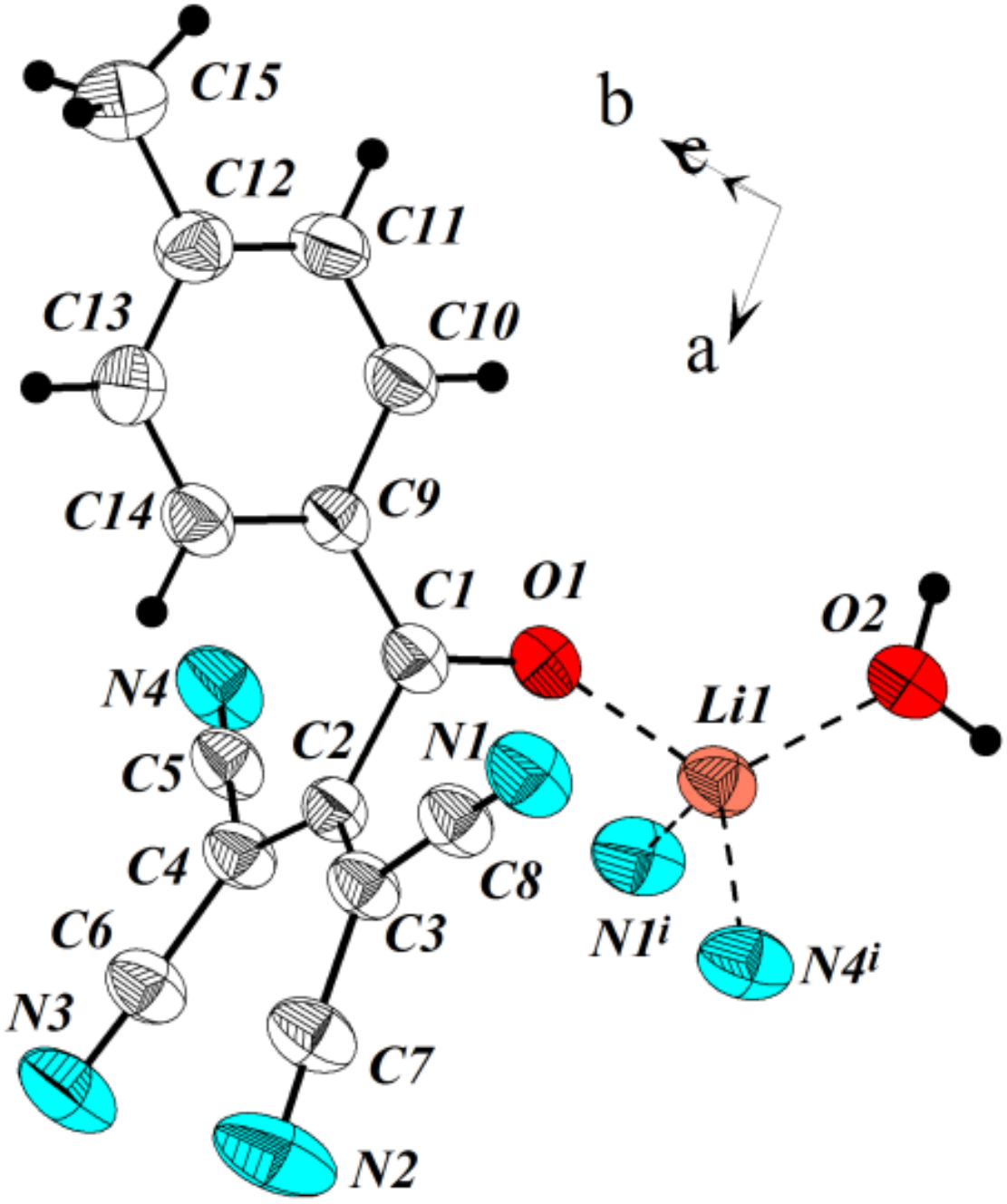
Bond lengths, Å	
CsO*1*	3.053
CsN*3*^{iv}	3.109
CsN*4*^{ii}	3.244
CsN*1*^{iii}	3.336
CsN*4*^{iii}	3.224
CsN*2*^{i}	3.172
CsC*4*^{iv}	3.882
CsC*5*^{iv}	3.821
Symmetry codes: *i= x, 0.5-y, -0.5+z; ii= -1+x, y, z; iii= -1+x, 0.5-y, -0.5+z*	
CCDC deposit number: 1580717	

Ammonium 2-(4'-methylbenzoyl)-1,1,3,3-tetracyanopropenide **2a**

Bond lengths, Å	
N5N1	3.077
N5N2^{i}	3.086
N5N1^{ii}	3.089
N5O2	3.487
N5O2^{iii}	3.116
N5N1^{iv}	3.073
N5O1^{v}	3.203
N5O1^{iv}	3.201
N5N3^{i}	2.943
Symmetry codes: *i=x, -y,-0.5+z; ii=-x, y, 0.5-z; iii=-x, 1-y,-z; iv=x, 1-y, -0.5+z; v= x, y, -1+z*	
CCDC deposit number: 1575039	

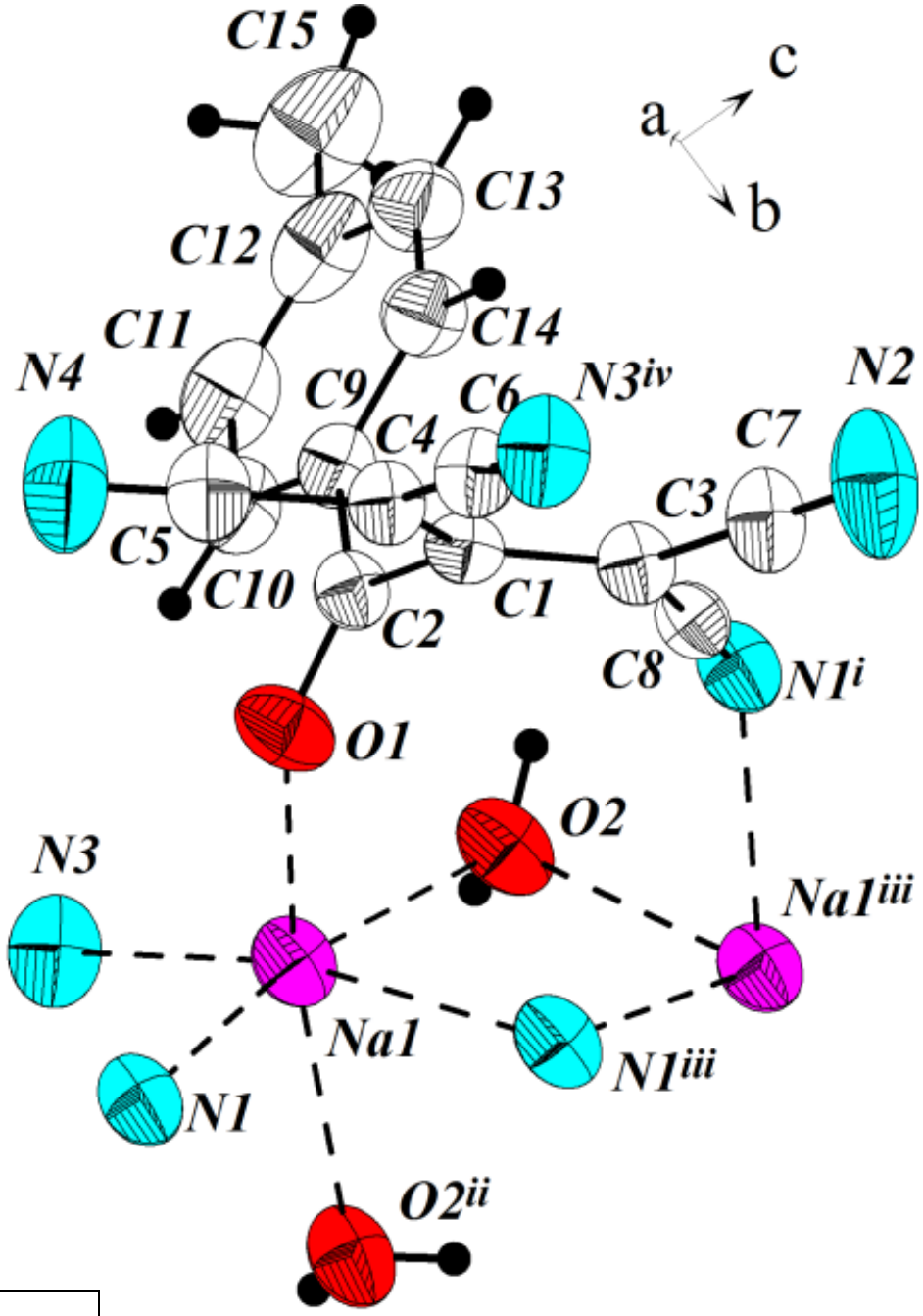


Lithium 2-(4'-methylbenzoyl)-1,1,3,3-tetracyanopropenide **2b**



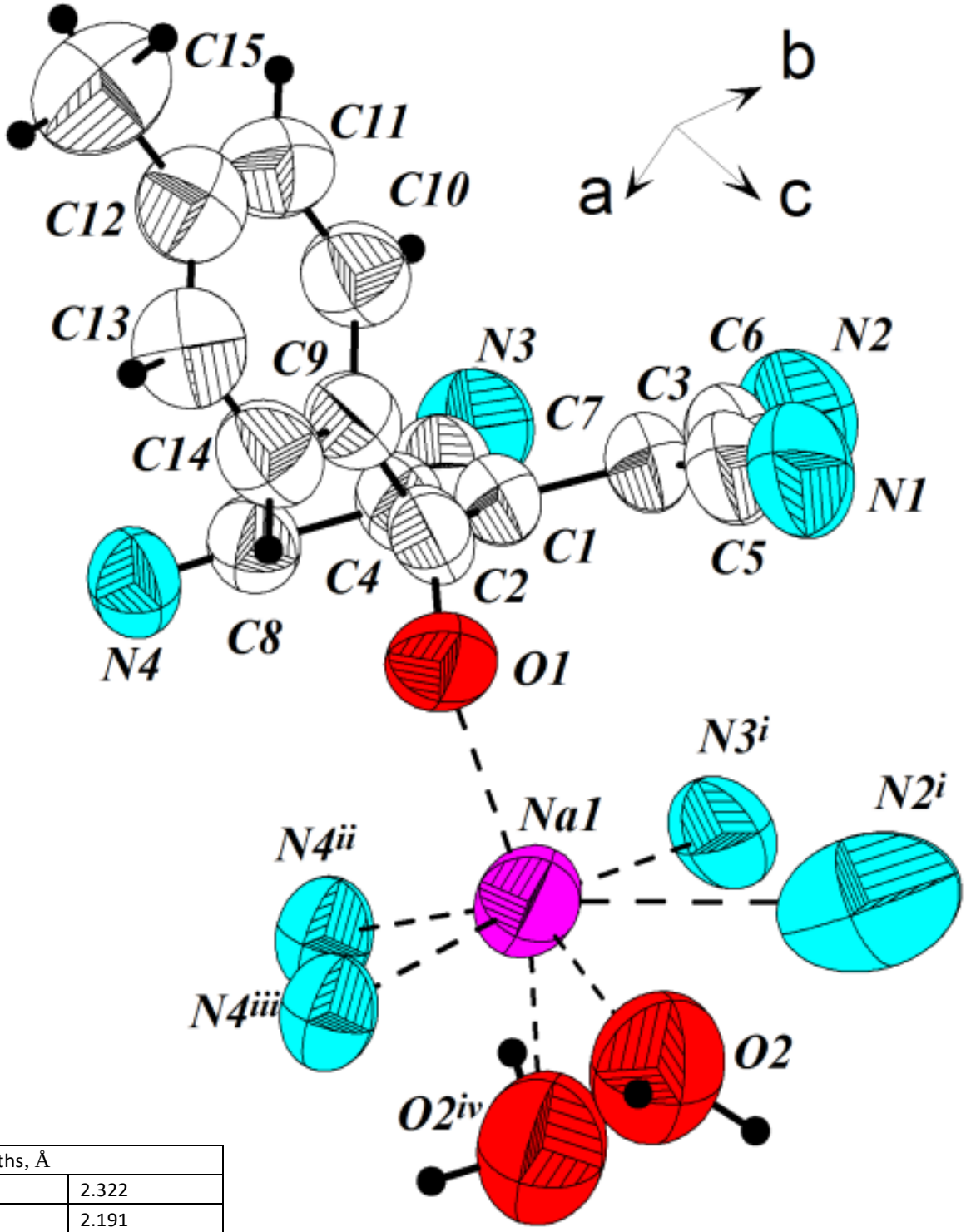
Bond lengths, Å	
Li*N1*	2.065
Li*N4*	2.041
Li*O2*	1.890
Li*O1*	1.939
Symmetry codes: *i*=*x*, 0.5-*y*, 0.5+*z*; *ii*=*x*, 0.5-*y*, -0.5+*z*	
CCDC deposit number: 1575056	

Sodium 2-(4'-methylbenzoyl)-1,1,3,3-tetracyanopropenide **α-2c**



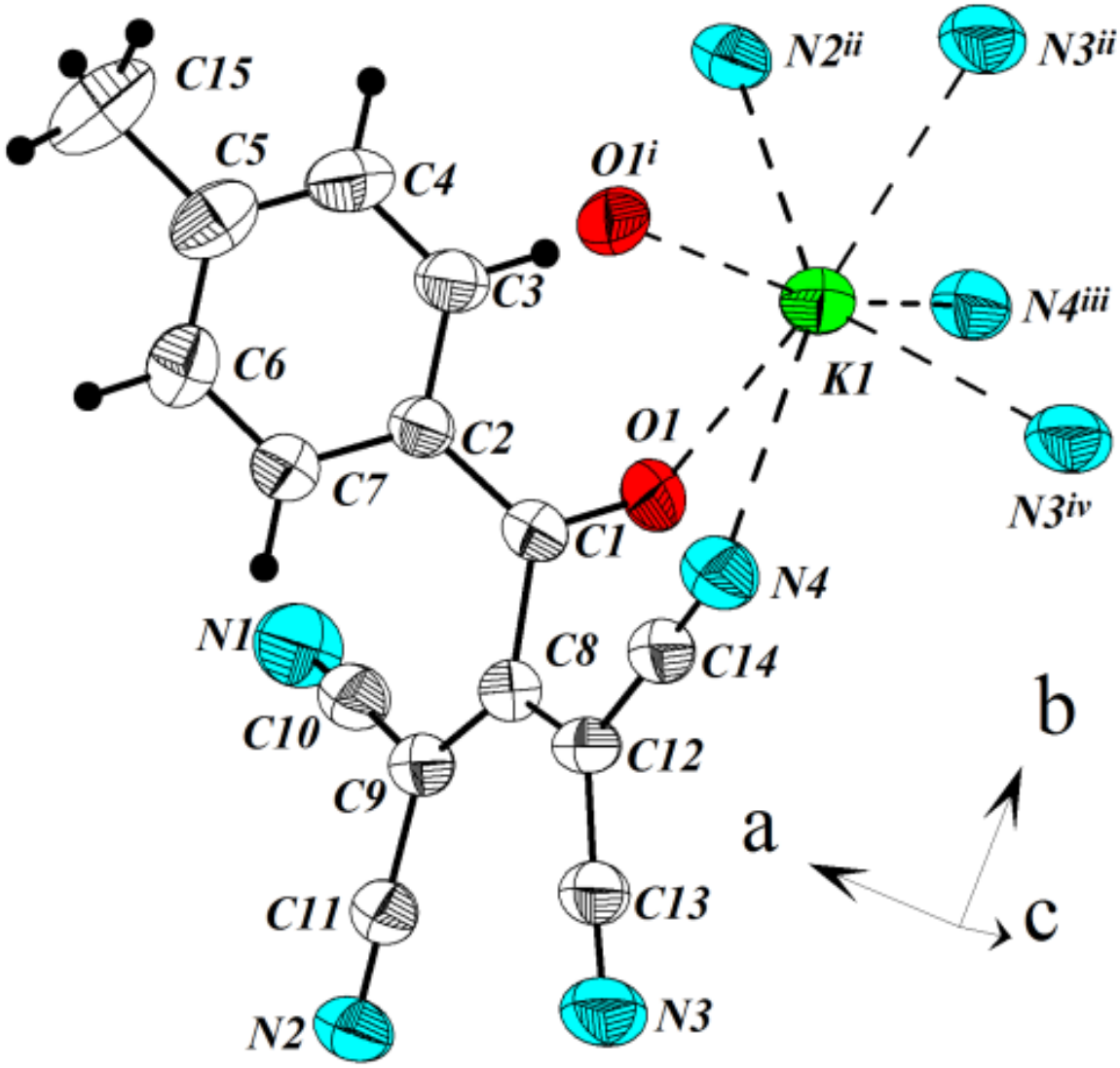
Bond lengths, Å	
NaO*1*	2.532
NaO*2*	2.385
NaO*2*^{ii}	2.425
NaN*1*	2.462
NaN*3*	2.533
NaN*1*^{iii}	2.542
NaNa	3.737
Symmetry codes: *i* = *x*, *y*, 1+*z*; *ii*= *x*, 1.5-*y*, -0.5+*z*; *iii* = *x*, 1.5-*y*, 0,5+*z*; *iv*=1+*x*, *y*, 1+*z*.	
CCDC deposit number: 1575015	

Sodium 2-(4'-methylbenzoyl)-1,1,3,3-tetracyanopropenide **β-2c**



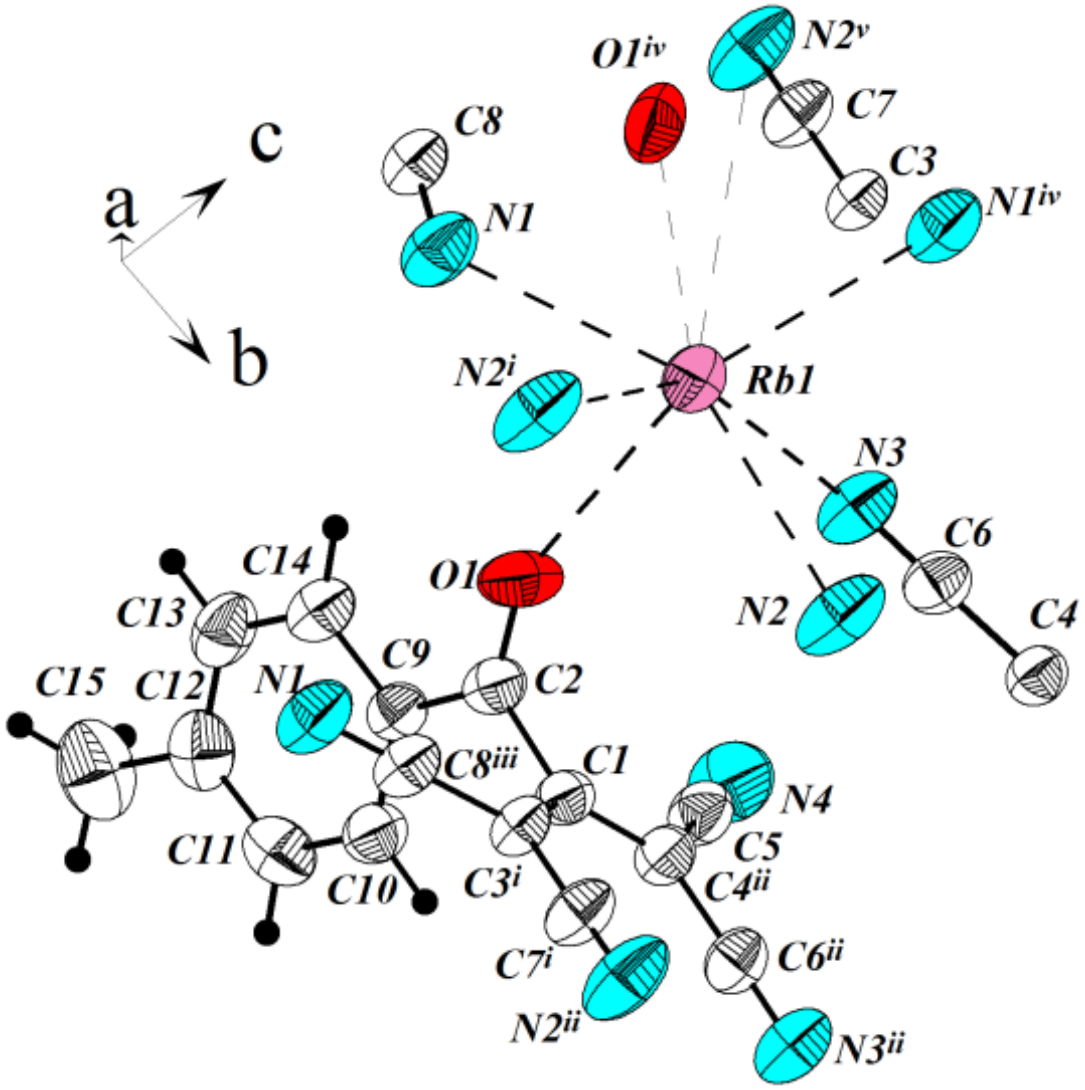
Bond lengths, Å	
NaO*1*	2.322
NaO*2*	2.191
NaO*2*^{iv}	2.272
NaN*2*^{i}	3.364
NaN*3*^{i}	2.425
NaN*4*^{ii}	2.653
NaN*4*^{iii}	2.696
Symmetry codes: *i = x, 1-y, 0.5+z; ii = 1-x, y, 0.5-z; iii = x, -y, 0.5+z; iv = 1-x, y, 1.5-z*	
CCDC deposit number: 1575014	

Potassium 2-(4'-methylbenzoyl)-1,1,3,3-tetracyanopropenide **2d**



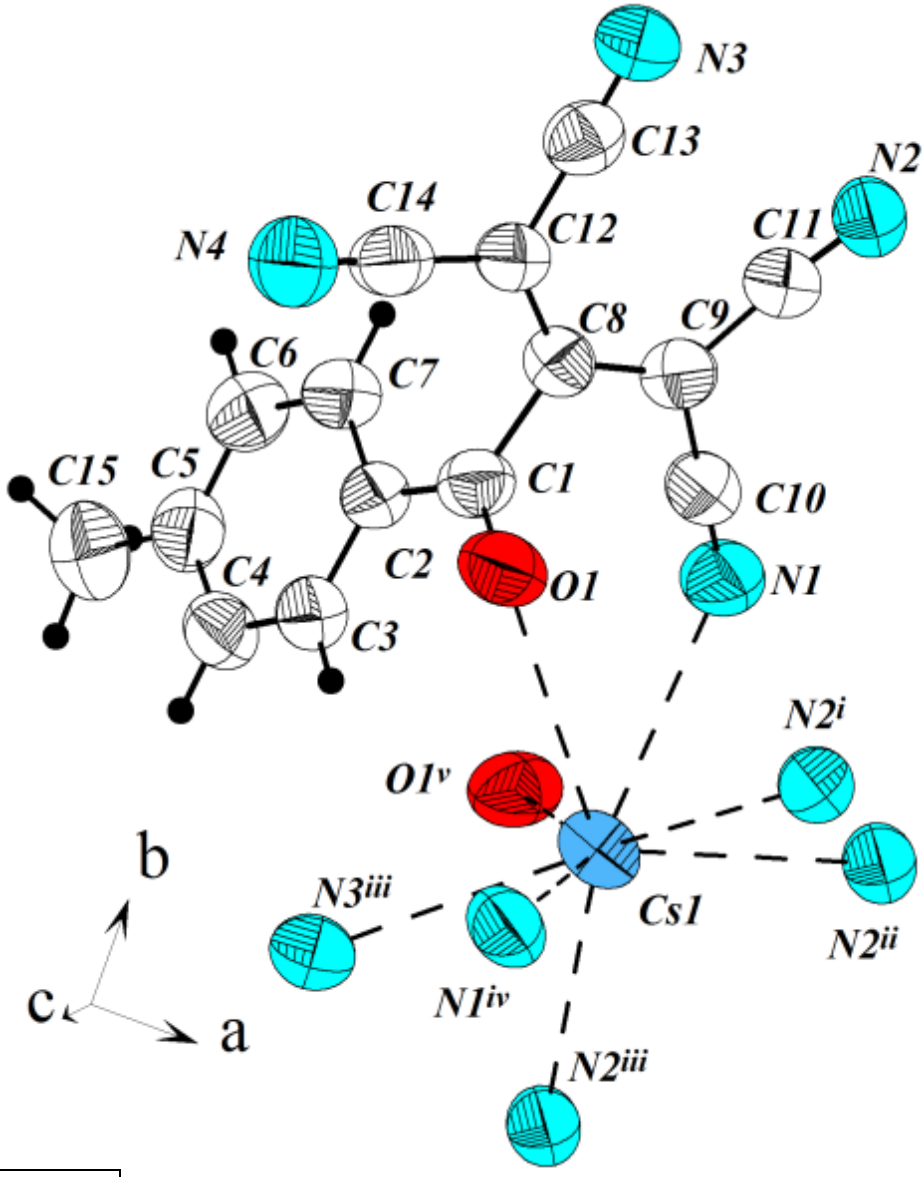
Bond lengths, Å	
KO*1*	3.206
KN*2*^{ii}	2.812
KN*3*^{ii}	2.977
KN*4*^{iii}	2.971
KN*3*^{iv}	2.874
KN*4*	2.928
KO*1*^{i}	2.800
Symmetry codes: *i = x, 1+y, z; ii = x, -1+y, z; iii = x, 0.5-y, -0.5+z; iv = -x, 1-y, -z*	
CCDC deposit number: 1575020	

Rubidium 2-(4'-methylbenzoyl)-1,1,3,3-tetracyanopropenide **2e**



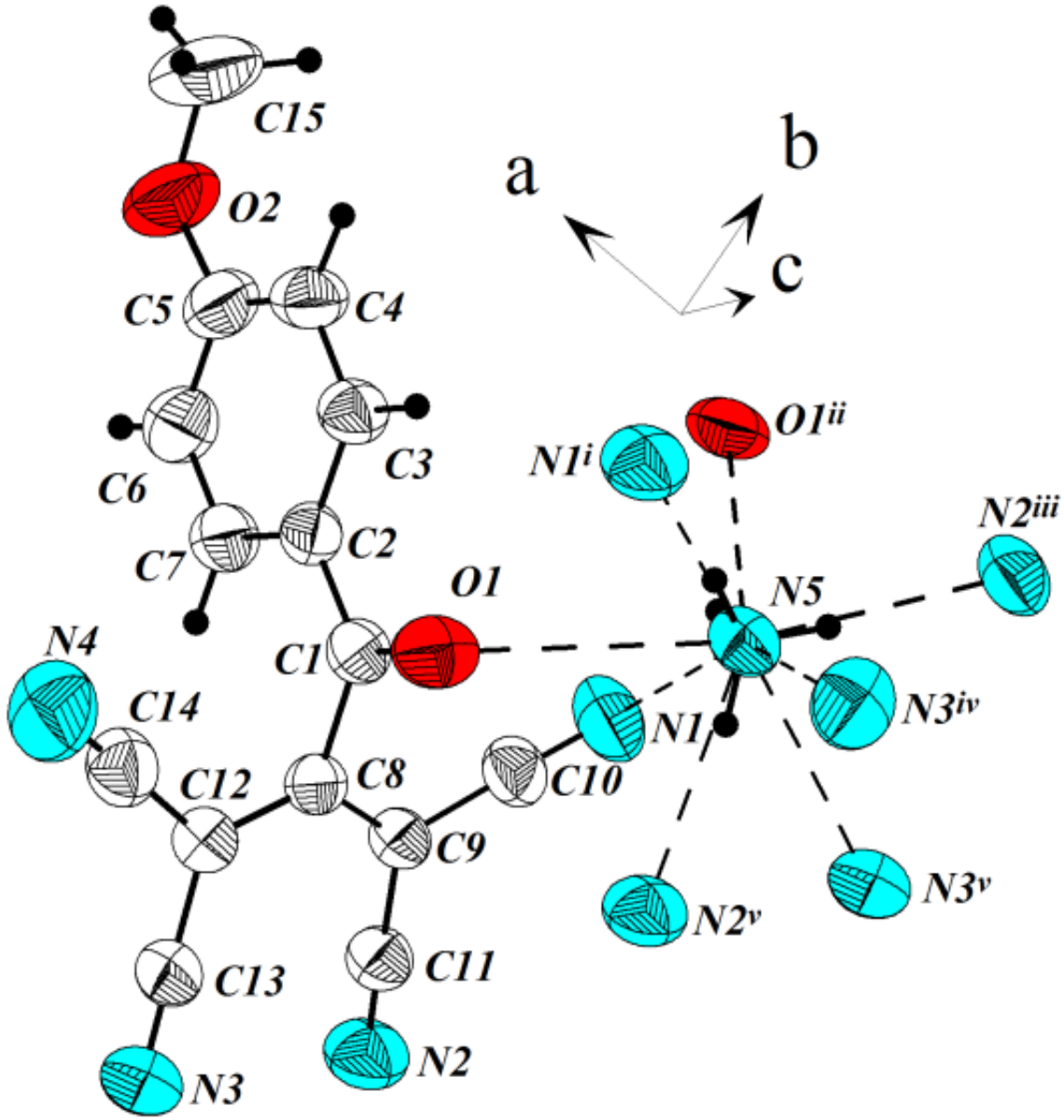
Bond lengths, Å	
Rb*1*O*1*	2.881
Rb*1*N*2*^{i}	3.181
Rb*1*N*1*	2.969
Rb*1*N*1*^{iv}	3.104
RbN*3*	2.981
RbN*2*	3.080
Rb*1*O*1*^{iv}	3.594
Rb*1*N*2*^{v}	3.746
Symmetry codes: *i = 1-x, 2-y, -z; ii = x, 2.5-y, -0.5+z; iii = x, 1.5-y, -0.5+z; iv = x, 1.5-y, 0.5+z; v = 1-x, -0.5+y, 0.5-z*	
CCDC deposit number: 1575001	

Cesium 2-(4'-methylbenzoyl)-1,1,3,3-tetracyanopropenide **2f**



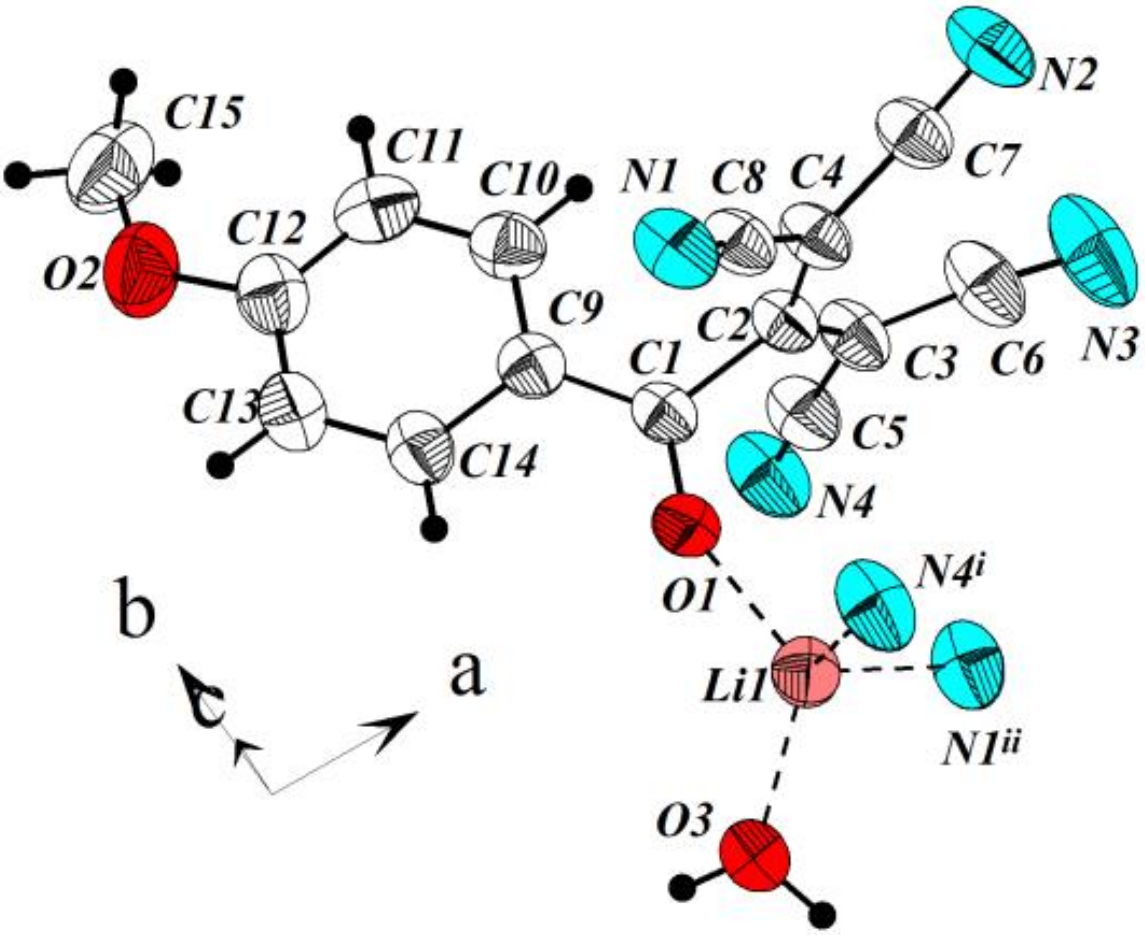
Bond lengths, Å	
CsO*1*	3.734
CsN*1*	3.139
CsN*2*^{i}	3.789
CsN*2*^{ii}	3.356
CsN*2*^{iii}	3.217
CsN*1*^{iv}	3.254
CsN*3*^{iii}	3.159
CsO*1*^{v}	3.067
Symmetry codes: *i = 2-x, -0.5+y, 0.5-z; ii = 2-x, 1-y, -z; iii = x, -1+y, z; iv = x, 0.5-y, 0.5+z; v= x, 0.5-y, -0.5+z*	
CCDC deposit number: 1575038	

Ammonium 1,1,3,3-tetracyano-2-(4'-methoxybenzoyl)propenide **3a**



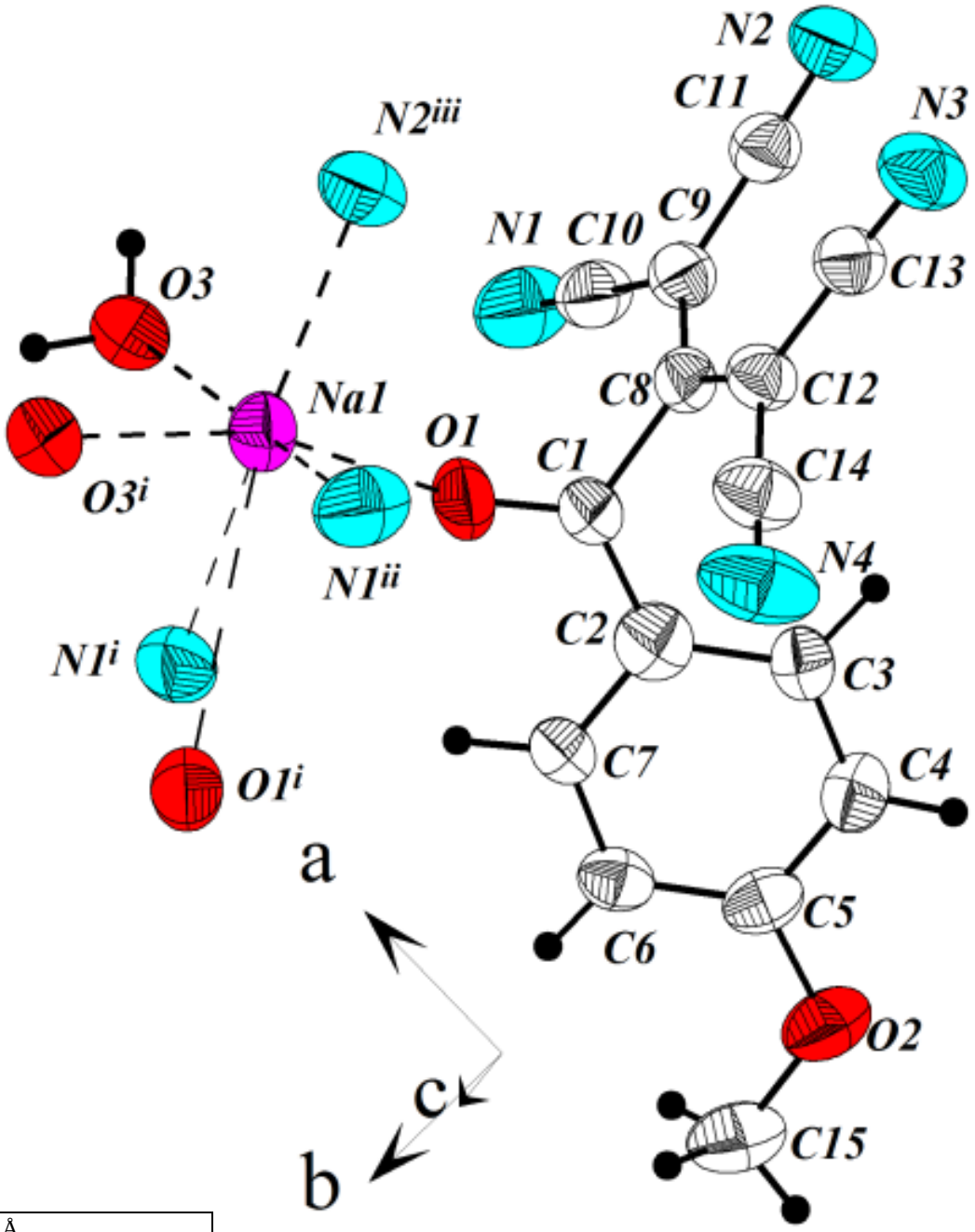
Bond lengths, Å	
N5O1	3.195
N5O1^{ii}	2.864
N5N1	3.122
N5N1^{i}	2.935
N5N2^{iii}	2.975
N5N2^{v}	3.045
N5N3^{iv}	3.011
N5N3^{v}	3.222
Symmetry codes: *i = x, 0.5-y, -0.5+z; ii= x, 0.5-y, 0.5+z; iii = -x, 0.5+y, 2.5-z; iv = -x, 0.5+y, 1.5-z; v = -x, -y, 2-z*	
CCDC deposit number: 1575023	

Lithium 1,1,3,3-tetracyano-2-(4'-methoxybenzoyl)propenide **3b**



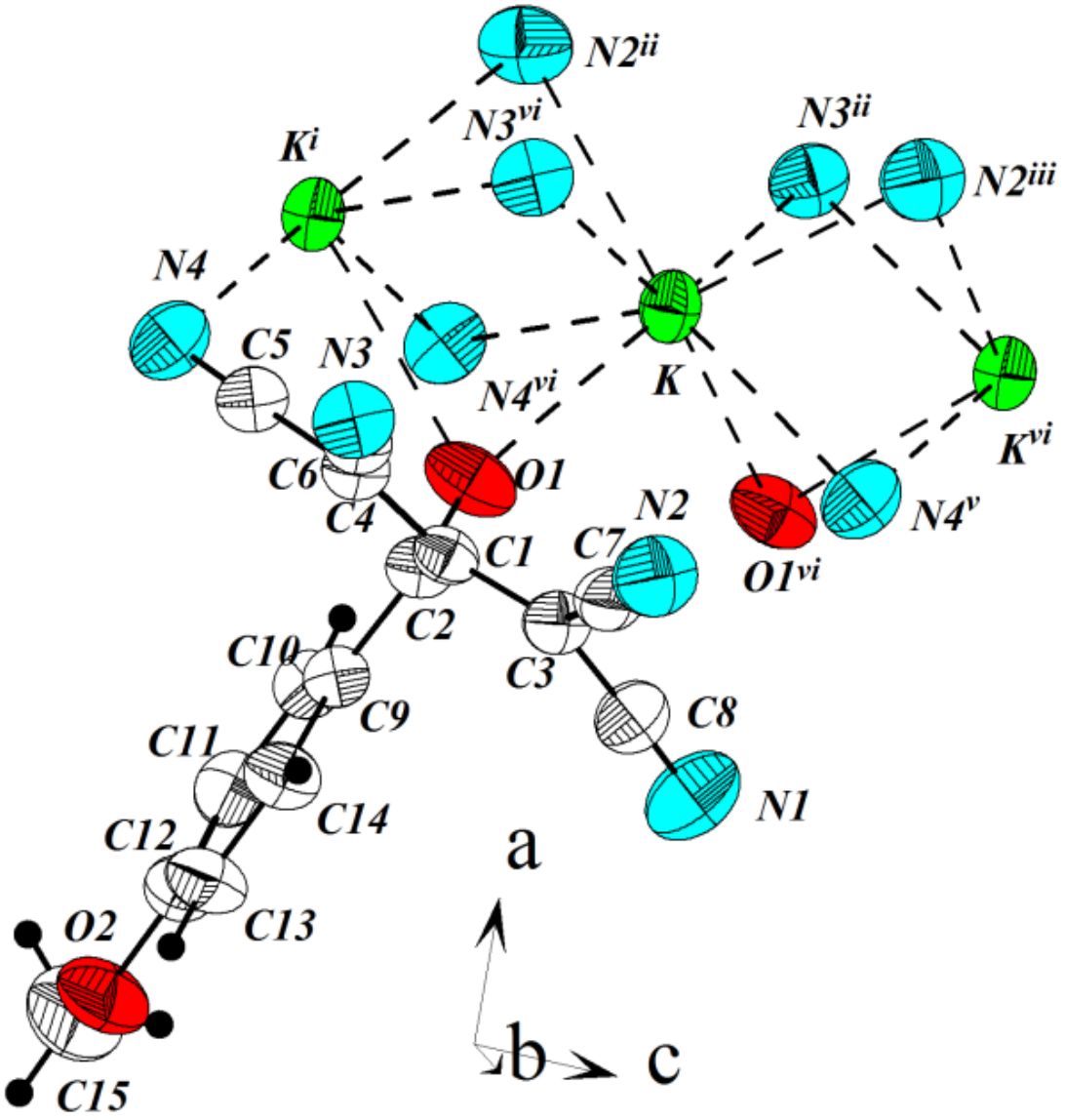
Bond lengths, Å	
Li*N1*	2.083
Li*N4*	2.03(1)
Li*O3*	1.917
Li*O1*	1.962
Symmetry codes: *i=x, 0.5-y, 0.5+z; ii=x, 0.5-y, -0.5+z*	
CCDC deposit number: 1575055	

Sodium 1,1,3,3-tetracyano-2-(4'-methoxybenzoyl)propenide **3c**



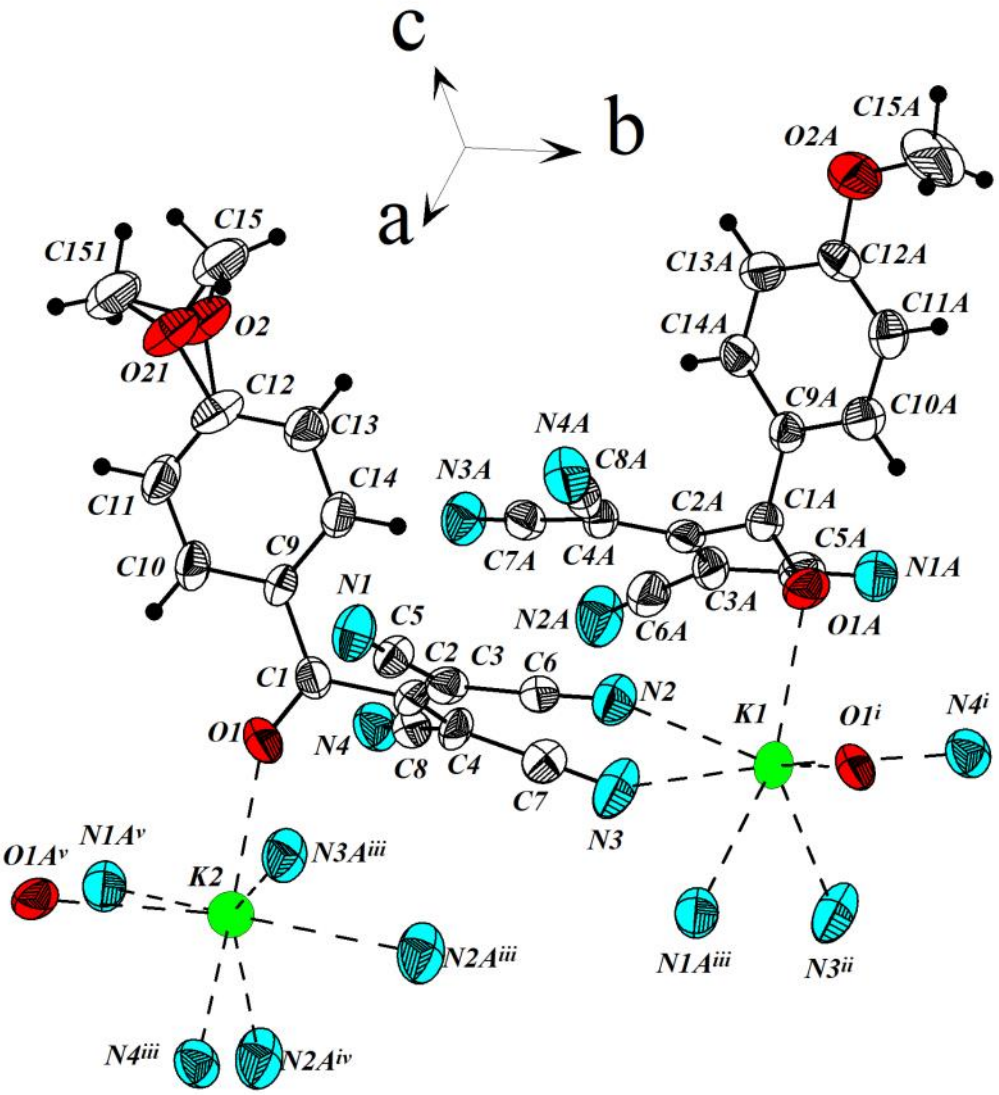
Bond lengths, Å	
NaO*1*	2.297
NaO*3*	2.431
NaO*3*^{i}	2.403
NaN*1*^{ii}	2.464
NaN*2*^{iii}	2.463
NaN*1*^{i}	3.254
NaO*1*^{i}	3.562
NaNa	3.871
Symmetry codes: *i = x, 0.5-y, 0.5+z; ii= x, y, 1+z;* *iii = 1-x, -y, -z; iv=1-x, -y, 2-z*	
CCDC deposit number: 1575016	

Potassium 1,1,3,3-tetracyano-2-(4'-methoxybenzoyl)propenide **α-3d**



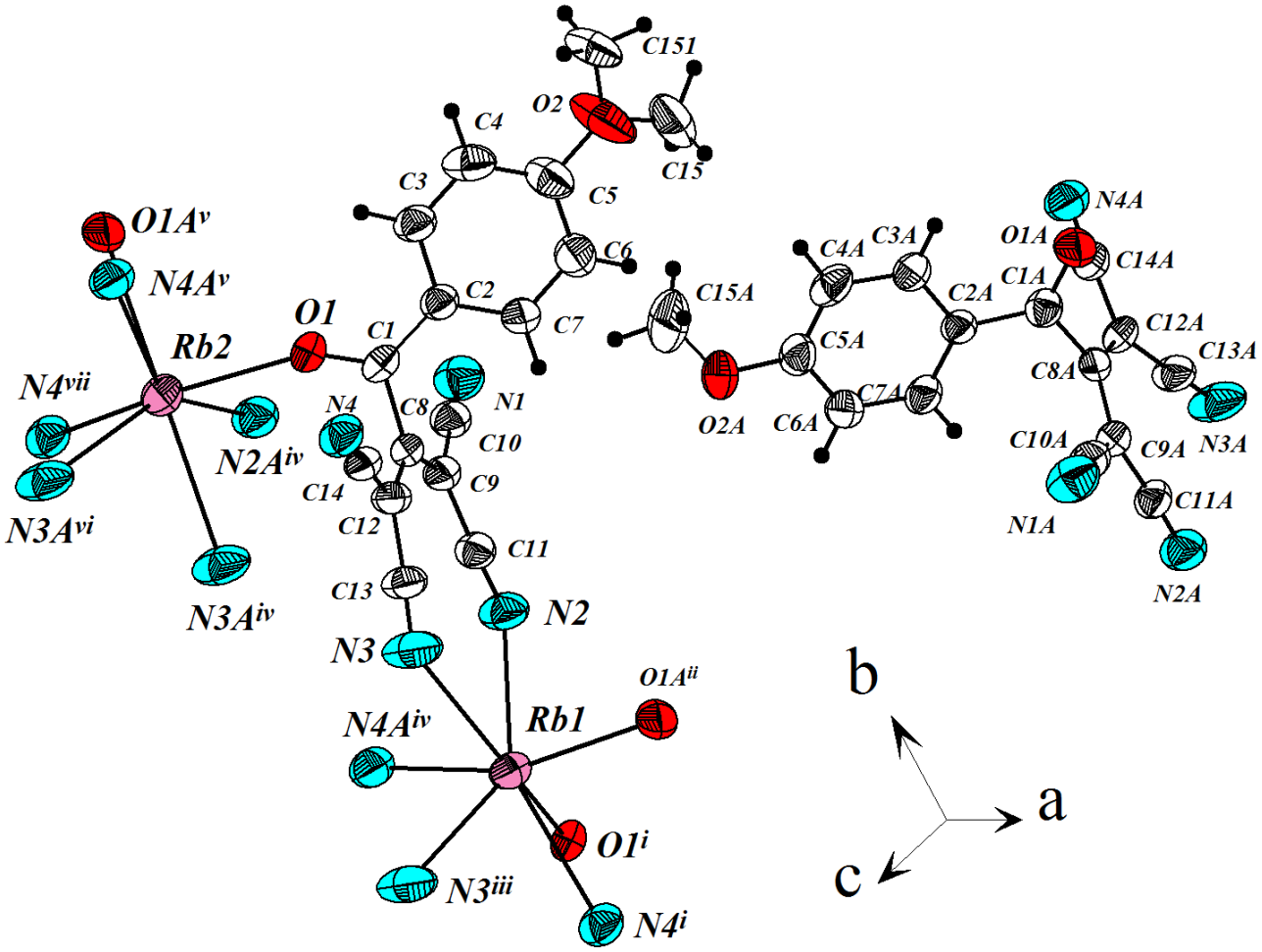
Bond lengths, Å	
KO*1*	2.750
KN*4*^{vi}	2.985
KN*3*^{vi}	2.840
KN*2*^{ii}	3.084
KN*3*^{ii}	2.940
KN*2*^{iii}	2.911
KN*4*^{v}	2.816
KO*1*^{vi}	3.110
Symmetry codes: *i = x, 0.5-y, -0.5+z; ii = 2-x, -0.5+y, 1.5-z; iii = 2-x, 1-y, 2-z; iv = 2-x, 1-y, 1-z; v = x, y, 1+z; vi = x, 0.5-y, 0.5+z*	
CCDC deposit number: 1575088	

Potassium 1,1,3,3-tetracyano-2-(4'-methoxybenzoyl)propenide **β-3d**



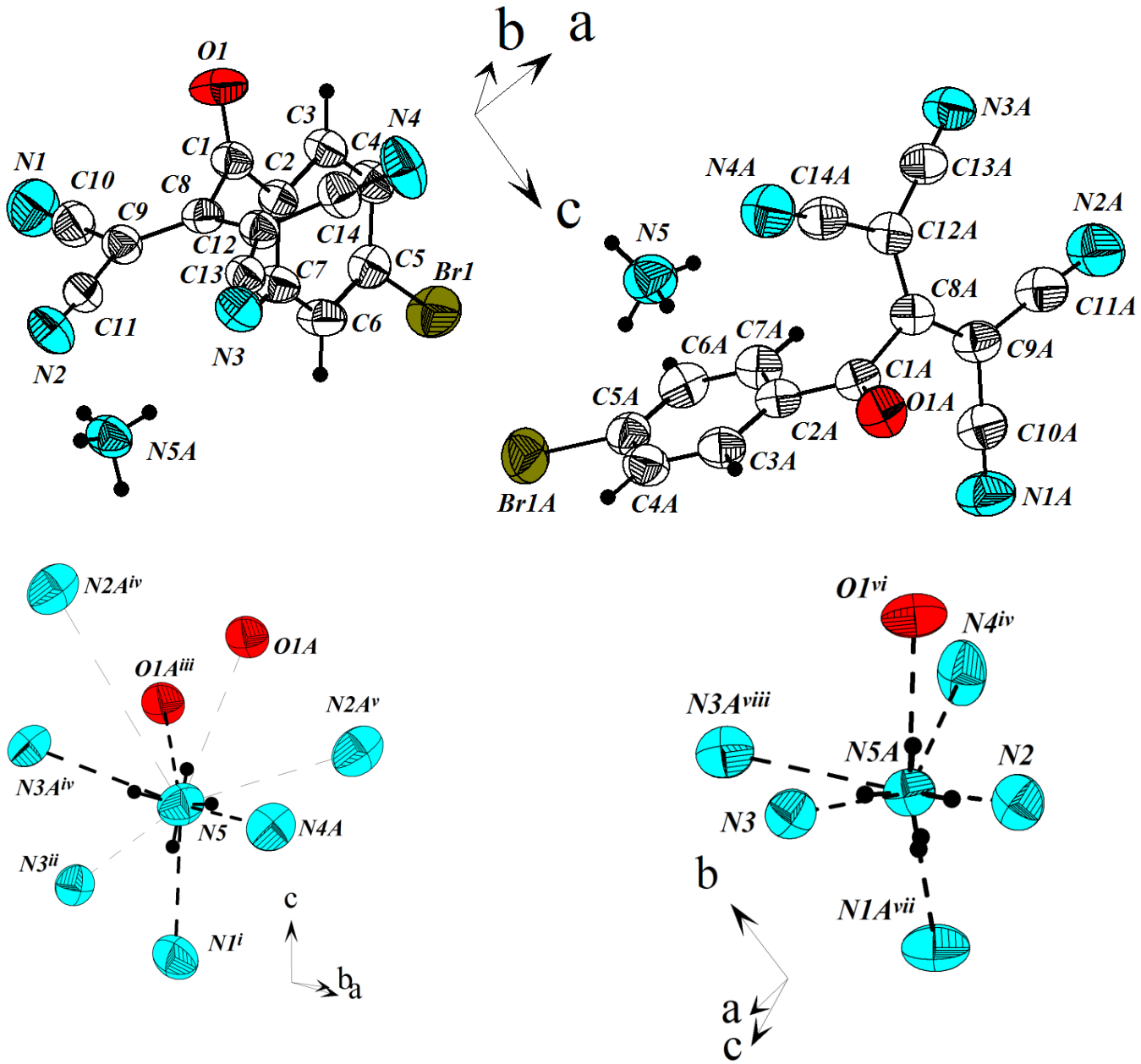
Bond lengths, Å	
K1O1A	2.814
K1O1^{i}	3.116
K1N4^{i}	2.920
K1N3^{ii}	2.870
K1N1A^{iii}	2.951
K1N3	2.966
K1N2	2.828
K2O1	2.792
K2O1A^{v}	3.122
K2N1A^{v}	2.920
K2N3A^{iii}	2.825
K2N2A^{iii}	2.956
K2N2A^{iv}	2.875
K2N4^{iii}	2.927
Symmetry codes: *i = x, 1+y, z; ii = 1-x, 1-y, -z.iii = 1+x, y,z;iv = 1-x, -y, -z;v = 1+x, -1+y, z.*	
CCDC deposit number: 1575000	

Rubidium 1,1,3,3-tetracyano-2-(4'-methoxybenzoyl)propenide **3e**



Bond lengths, Å	
Rb1O1^{i}	3.149
Rb1O1A^{ii}	2.932
Rb1N2	2.960
Rb1N3	3.035
Rb1N4A^{iv}	3.041
Rb1N3^{iii}	3.015
Rb1N4^{i}	3.016
Rb2O1	2.895
Rb2O1A^{v}	3.157
Rb2N2A^{iv}	2.960
Rb2N3A^{iv}	3.046
Rb2N3A^{vi}	3.026
Rb2N4^{vii}	3.038
Rb2N4A^{v}	3.023
Symmetry codes: *i = x, -1+y, z; ii = 2-x,1-y, 1-z; iii = 1-x, 1-y, 2-z; iv = 1-x, 1-y, 1-z; v = 1-x, 2-y, 1-z; vi = -1+x, 1+y, 1+z; vii = -1+x, y, z*	
CCDC deposit number: 1575021	

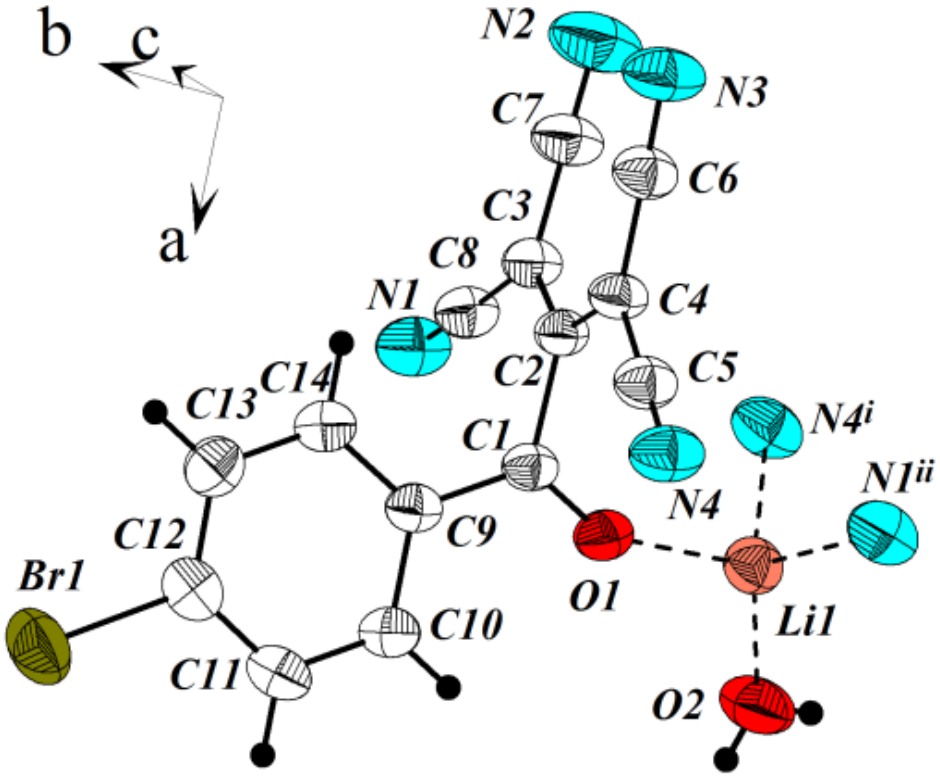
Ammonium 2-(4'-bromobenzoyl)-1,1,3,3-tetracyanopropenide **4a**



Bond lengths, Å	
N5O1A^{iii}	3.064
N5N1^{i}	2.943
N5N4A	3.034
N5N3A^{iv}	3.071
N5O1A	4.882
N5N2A^{v}	3.448
N5N2A^{iv}	4.818
N5N3^{ii}	3.357
Symmetry codes: *i = 1-x, 2-y, -z; ii= 1+x, -1+y, z; iii =2-x, 2-y, 1-z; iv = -1+x, y, z;v = 3-x, 2-y, 1-z; vi = -x, 3-y, -z; vii= 1-x, 2-y, 1-z; viii =-2+x, 1+y, z*	
CCDC deposit number: 1575024	

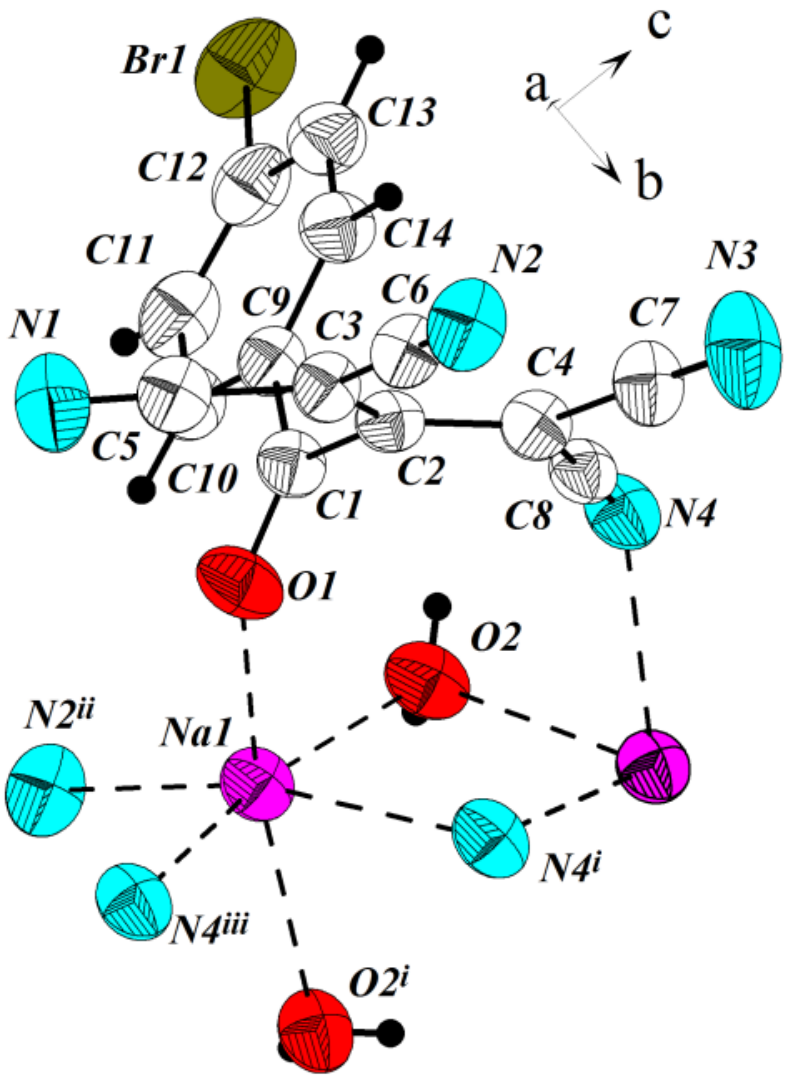
Bond lengths, Å	
N5AO1^{vi}	2.976
N5AN4^{iv}	2.868
N5AN2	2.907
N5AN1A^{vii}	3.045
N5AN3	3.016
N5AN3A^{iii}	3.092

Lithium 2-(4'-bromobenzoyl)-1,1,3,3-tetracyanopropenide **4b**



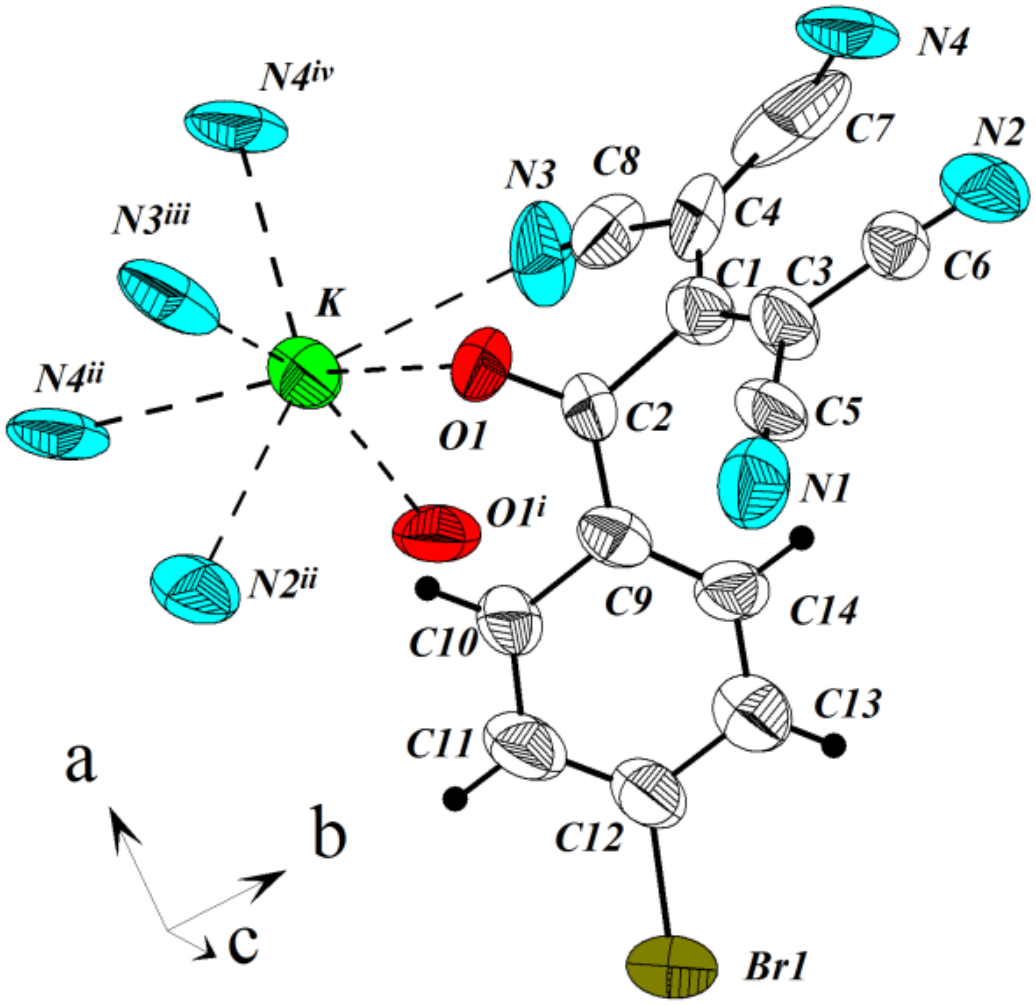
Bond lengths, Å	
LiN*1*	2.056
LiN*4*	2.064
LiO*2*	1.899
LiO*1*	1.946
Symmetry codes: *i=x, -0.5-y, 0.5+z; ii=x, -0.5-y, -0.5+z*	
CCDC deposit number: 1575057	

Sodium 2-(4'-bromobenzoyl)-1,1,3,3-tetracyanopropenide **4c**



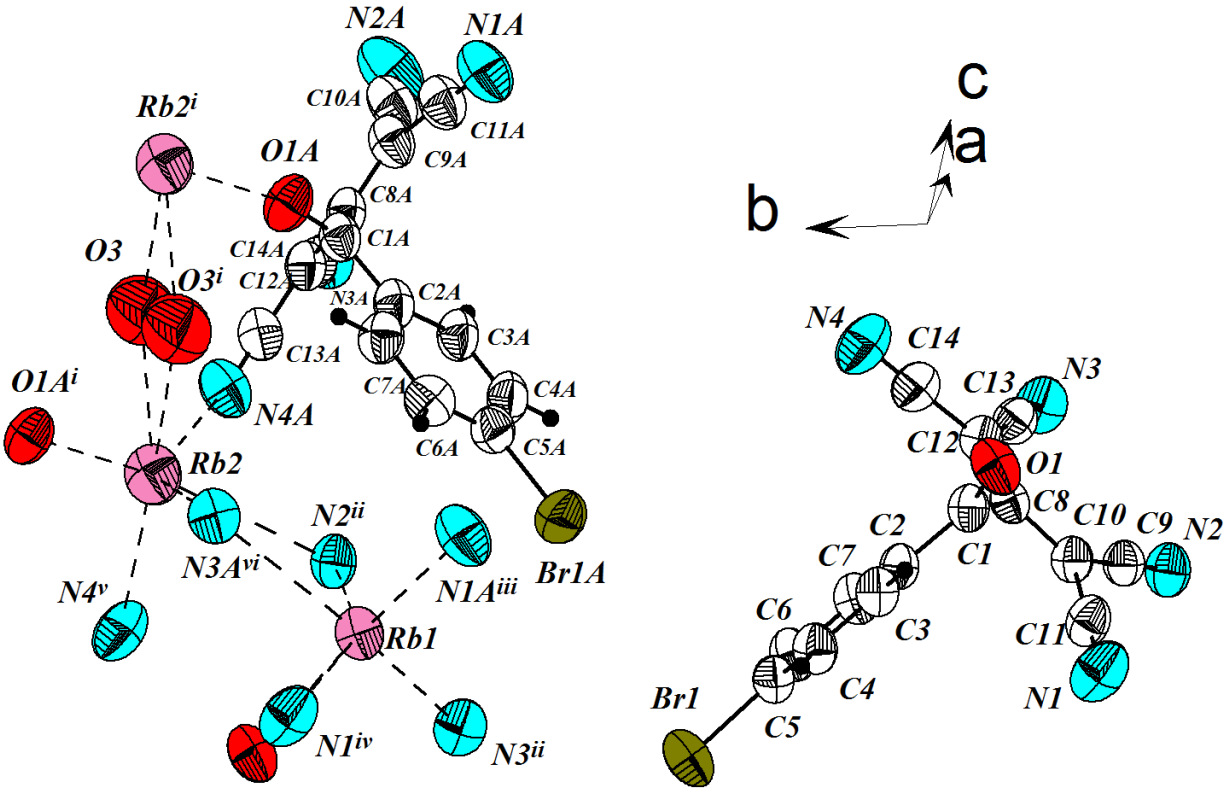
Bond lengths, Å	
NaO*1*	2.523
NaO*2*	2.384
NaO*2*^{i}	2.418
NaN*2*^{ii}	2.511
NaN*4*^{i}	2.544
NaN*4*^{iii}	2.459
NaNa	3.739
Symmetry codes: *i = x, 0.5-y, -0,5+z; ii= -1+x, y, -1+z; iii = x, y, -1+z*	
CCDC deposit number: 1575040	

Potassium 2-(4'-bromobenzoyl)-1,1,3,3-tetracyanopropenide **4d**



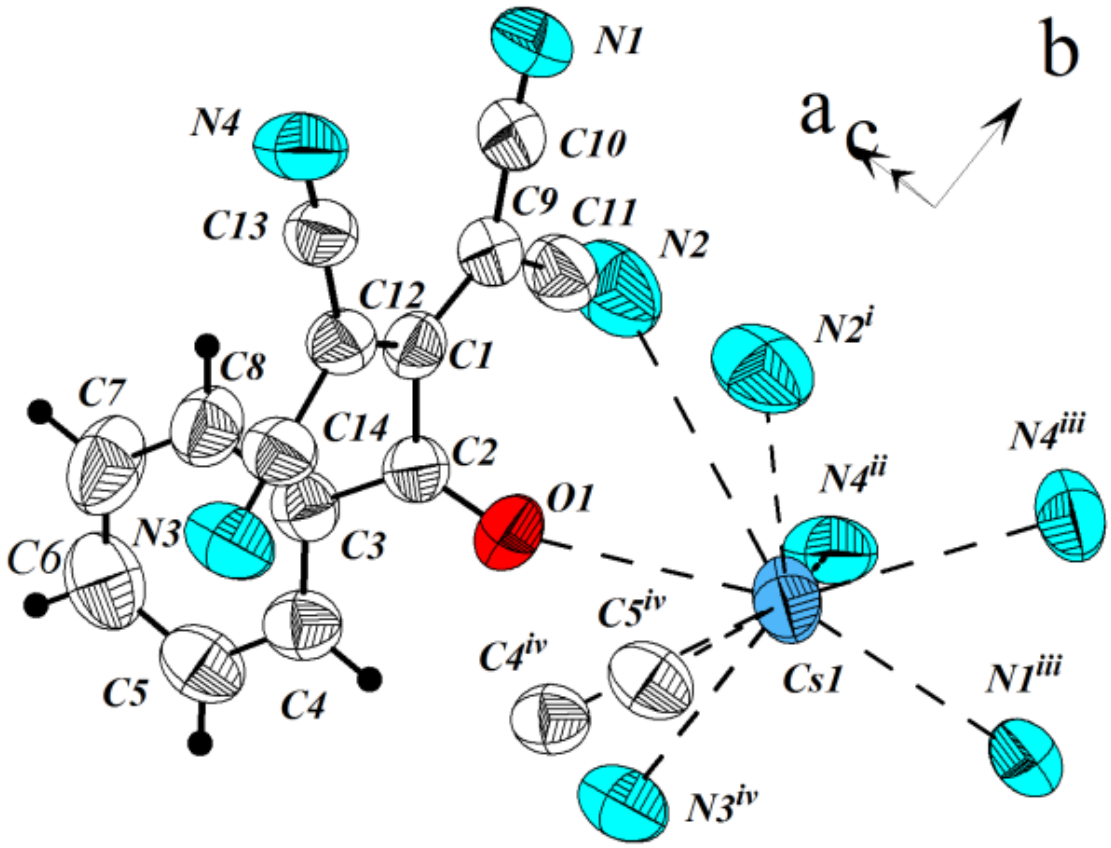
Bond lengths, Å	
KO*1*	3.096
KO*1*^{i}	2.839
KN*2*^{ii}	2.831
KN*4*^{ii}	2.928
KN*3*^{iii}	2.893
KN*4*^{iv}	2.883
KN*3*	2.880
Symmetry codes: *i = x, 0.5-y, 0.5+z; ii = x, -1+y, z; iii = x, 0.5-y, -0.5+z; iv = -x, 1-y, -z*	
CCDC deposit number: 1575041	

Rubidium 2-(4'-bromobenzoyl)-1,1,3,3-tetracyanopropenide **4e**



Bond lengths, Å	
RbBO1B^{v}	2.946
RbBN1B^{iv}	2.886
RbBN3B^{ii}	2.932
RbBN1A^{iii}	3.091
RbBN2B^{ii}	3.026
RbBN3A^{vi}	3.015
RbBN4B^{i}	3.016
RbAO1A^{i}	3.102
RbAO3	2.865
RbAN4A	3.064
RbAN2B^{ii}	3.280
RbAN3A^{vi}	3.104
RbAN4B^{v}	2.980
RbAO3^{i}	2.686
Symmetry codes: *i = 1-x, 2-y, 2-z; ii = 2-x, -y, 1-z; iii = 1-x, 1-y, 2-z; iv = 1-x, -y, 1-z; v = -1+x, 1+y, z; vi = -1+x, y, z*	
CCDC deposit number: 1575022	

Cesium 2-(4'-bromobenzoyl)-1,1,3,3-tetracyanopropenide **4f**



Bond lengths, Å	
CsO*1*	3.053
CsN*3*^{iv}	3.109
CsN*4*^{ii}	3.244
CsN*1*^{iii}	3.336
CsN*4*^{iii}	3.224
CsN*2*^{i}	3.172
CsC*4*^{iv}	3.882
CsC*5*^{iv}	3.821
Symmetry codes: *i= x, 0.5-y, -0.5+z; ii= -1+x, y, z; iii= -1+x, 0.5-y, -0.5+z*	
CCDC deposit number: 1575037	

Crystal data and structure refinement of new ATCN

Compound	**2a**	**3a**	**4a**	**2b**	**3b**
Empirical formula	$C_{30}H_{24}N_{10}O_3$	$C_{15}H_{11}N_5O_2$	$C_{14}H_8BrN_5O$	$C_{15}H_9LiN_4O_2$	$C_{15}H_9LiN_4O_3$
Formula weight	572.59	293.29	342.16	284.20	300.20
Crystal system	monoclinic	monoclinic	triclinic	monoclinic	monoclinic
Space group	C 2/c	P 21/c	P -1	P 21/c	P 21/c
a (Å)	33.875(2)	13.0933(4)	9.8525(3)	10.1025(5)	9.982(2)
b (Å)	9.8866(5)	16.1822(6)	10.3391(3)	14.6322(6)	15.469(2)
c (Å)	8.8250(5)	7.3295(2)	15.2660(4)	10.1353(5)	10.057(2)
α (deg)	90	90	107.694(2)	90	90
β (deg)	91.005(4)	93.538(3)	91.607(2)	107.709(4)	105.520(10)
γ (deg)	90	90	95.332(2)	90	90
Volume ($Å^3$)	2955.1(3)	1550.00(9)	1472.51(7)	1427.22(12)	1496.3(5)
Z	4	4	4	4	4
Temperature (K)	295(2)	295(2)	295(2)	295(2)	295(2)
D_c (g cm^{-3})	1.287	1.257	1.543	1.323	1.333
μ (mm-1)	0.725	0.730	3.866	0.746	0.792
diffrn_radiation_wavelength	1.54186	1.54186	1.54186	1.54186	1.54186
diffrn_radiation_type	CuK\a	CuK\a	Cu K\a	CuK\a	CuK\a
reflns_number_total	2592	2944	5512	2792	2942
reflns_number_gt	1858	2188	4658	1640	2197
Parameters	199	244	412	209	217
Goodness-of-fit on F^2	1.021	1.045	1.047	0.811	1.065
refine_ls_R_factor_all	0.0910	0.0545_	0.0476	0.0681	0.0705
refine_ls_R_factor_gt	0.0727	0.0409	0.0408	0.0345	0.0565
Max / min Δρ (e $Å^{-3}$)	0.294/-0.289	0.176/-0.167	0.981/-0.689	0.179/-0.170	0.647/-0.235

Compound	**4b**	**β-1c**	**α-2c**	**β-2c**	**3c**	**4c**
Empirical formula	$C_{14}H_6BrLiN_4O_2$	$C_{14}H_7N_4NaO_2$	$C_{15}H_9N_4NaO_2$	$C_{30}H_{16}N_8Na_2O_3$	$C_{15}H_9N_4NaO_3$	$C_{14}H_6BrN_4NaO_2$
Formula weight	349.08	286.23	300.25	582.49	316.25	365.13
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	P 21/c	P 21/c	P 21/c	C 2/c	P 21/c	P 21/c
a (Å)	10.1420(3)	11.7106(6)	9.5036(19)	29.668(3)	12.1923(3)	9.4244(3)
b (Å)	14.7088(4)	17.5383(7)	27.0995(12)	9.5151(7)	18.4186(6)	27.3787(10)
c (Å)	10.0556(3)	6.8408(3)	6.0260(2)	10.3581(8)	6.8235(2)	6.0595(2)
α (deg)	90	90	90	90	90	90
β (deg)	106.5590(10)	106.036(4)	105.992(2)	103.061(7)	92.312(2)	105.960(2)
γ (deg)	90	90	90	90	90	90
Volume ($Å^3$)	1437.85(7)	1350.32(11)	1491.9(3)	2848.4(4)	1531.07(8)	1503.25(9)
Z	4	4	4	4	4	4
Temperature (K)	295(2)	295(2)	295(2)	295(2)	295(2)	295(2)
D_c (g cm^{-3})	1.613	1.408	1.337	1.358	1.372	1.613
μ (mm-1)	3.997	1.097	1.017	1.023	1.071	4.125
diffrn_radiation_wavelength	1.54186	1.54186	1.54186	1.54186	1.54186	1.54186
diffrn_radiation_type	CuK\a	CuK\a	CuK\a	CuK\a	CuK\a	CuK\a
reflns_number_total	2752	2655	2644	2749	2728	2790
reflns_number_gt	2049	876	1949	1187	1578	2341
Parameters	208	197	209	207	234	208
Goodness-of-fit on F^2	1.040	0.983	0.908	0.951	0.924	1.050
refine_ls_R_factor_all	0.0487	0.1970	0.0471	0.1251	0.0848	0.0549
refine_ls_R_factor_gt	0.0343	0.0934	0.0334	0.0581	0.0794	0.0483
Max / min Δρ (e $Å^{-3}$)	0.328/-0.574	0.410/-0.278	0.175/-0.186	0.241/-0.325	0.161/-0.170	0.740/-0.815

Compound	**β-1d**	**2d**	**α-3d**	**β-3d**	**4d**	**2e**
Empirical formula	$C_{14}H_5KN_4O$	$C_{15}H_7KN_4O$	$C_{15}H_7KN_4O_2$	$C_{15}H_7KN_4O_2$	$C_{14}H_4BrKN_4O$	$C_{15}H_7N_4ORb$
Formula weight	284.32	298,35	314.35	314.35	363,22	344,72
Crystal system	monoclinic	monoclinic	monoclinic	triclinic	monoclinic	monoclinic
Space group	P 21/c	P 21/c	P 21/c	P -1	P 21/c	P 21/c
a (Å)	11.4796(4)	17.6593(8)	13.1407(5)	8.0354(8)	18.4561(9)	16.9587(6)
b (Å)	16.2292(10)	9.7349(3)	15.8712(4)	9.7076(10)	9.6685(4)	9.9439(3)
c (Å)	7.1308(2)	8.2353(4)	7.1612(2)	18.914(2)	8.1421(3)	8.5740(3)
α (deg)	90	90	90	87.341(8)	90	90
β (deg)	98.058(4)	90.419(4)	94.971(3)	89.785(8)	102.306(3)	97.445(3)
γ (deg)	90	90	90	89.833(10)	90	90
Volume ($Å^3$)	1315.39(10)	1415.71(10)	1487.91(8)	1445.6(3)	1419.52(11)	1433.69(8)
Z	4	4	4	4	4	4
Temperature (K)	295(2)	295(2)	295(2)	295(2)	295(2)	295(2)
D_c (g cm^{-3})	1.436	1.400	1.403	1.437	1.700	1.597
μ (mm-1)	3.545	3.320	3.240	3.335	6.610	4.785
diffrn_radiation_wavelength	1.54186	1.54186	1.54186	1.54186	1.54186	1.54186
diffrn_radiation_type	CuK\a	CuK\a	CuK\a	CuK\a	CuK\a	CuK\a
reflns_number_total	2316	2789	2932	4769	2456	2855
reflns_number_gt	946	1752	2147	1449	1755	1867
Parameters	182	207	201	407	207	191
Goodness-of-fit on F^2	0.688	1.045	1.010	0.679	0.994	0.882
refine_ls_R_factor_all	0.1430	0.0758	0.0504	0.1921	0.0716	0.0585
refine_ls_R_factor_gt	0.0426	0.0373	0.0338	0.0554	0.0509	0.0310
Max / min Δρ (e $Å^{-3}$)	0.250/-0.249	0.216/-0.361	0.177/-0.264	0.326/-0.359	0.664/-0.678	0.277/-0.290

Compound	**3e**	**4e**	**2f**	**4f**
Empirical formula	$C_{15}H_7N_4O_2Rb$	$C_{28}H_9Br_2N_8O_{2.5}Rb_2$	$C_{15}H_7CsN_4O$	$C_{14}H_4BrCsN_4O$
Formula weight	360,72	828,18	392,16	457,03
Crystal system	triclinic	triclinic	monoclinic	monoclinic
Space group	P -1	P -1	P 21/c	P 21/c
a (Å)	8.2743(3)	9.9306(3)	16.2580(10)	5.4897(2)
b (Å)	9.8536(4)	10.2782(3)	10.1991(5)	18.0253(7)
c (Å)	18.8581(8)	15.3731(4)	9.0735(6)	15.6406(5)
α (deg)	87.273(3)	107.505(3)	90	90
β (deg)	78.288(3)	92.216(2)	99.221(6)	94.225(3)
γ (deg)	89.663(3)	95.179(2)	90	90
Volume ($Å^3$)	1503.80(11)	1486.76(8)	1485.10(15)	1543.49(10)
Z	4	2	4	4
Temperature (K)	295(2)	295(2)	295(2)	295(2)
D_c (g cm^{-3})	1.593	1.850	1.754	1.967
μ (mm-1)	4.642	7.784	19.487	21.784
diffrn_radiation_wavelength	1.54186	1.54186	1.54186	1.54186
diffrn_radiation_type	CuK\a	CuK\a	CuK\a	CuK\a
reflns_number_total	5552	5336	2793	3005
reflns_number_gt	2990	4602	2037	2411
Parameters	409	395	191	190
Goodness-of-fit on F^2	0.863	1.060	0.958	0.985
refine_ls_R_factor_all	0.0967	0.0476	0.0820	0.0929
refine_ls_R_factor_gt	0.0392	0.0422	0.0695	0.0862
Max / min Δρ (e $Å^{-3}$)	0.435/-0.516	0.533/-0.964	2.237/-0.746	2.629/-1.087

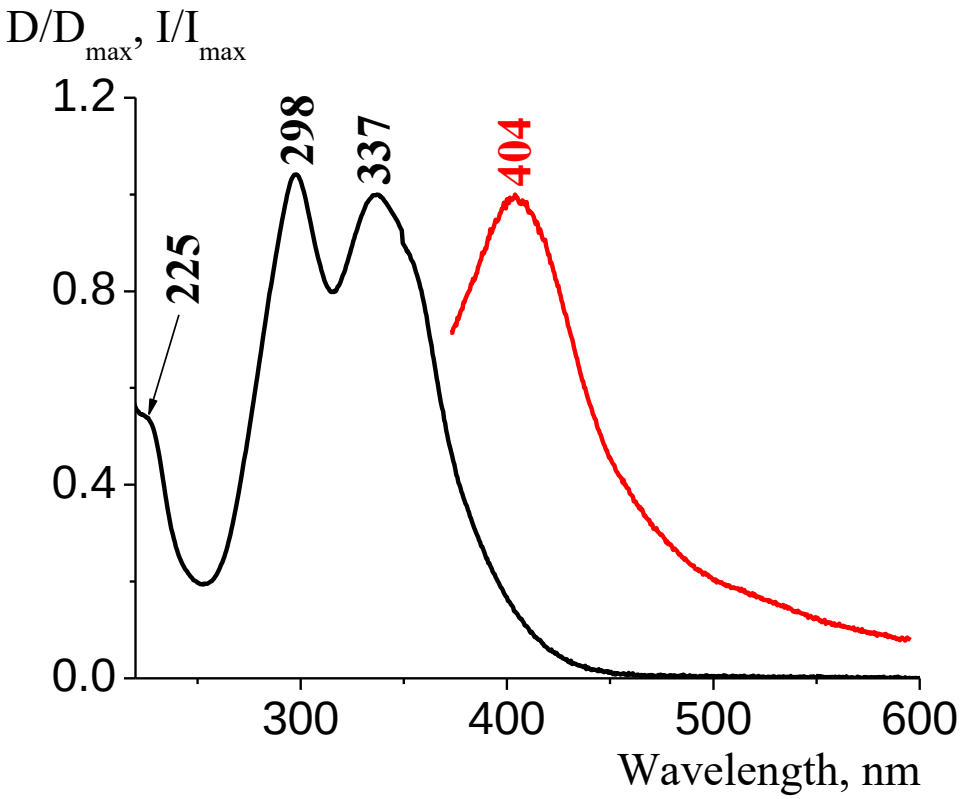


Fig. 1. ***3f*** *absorbance and emission spectra in ethanol; excitation wavelength is 320 nm.*

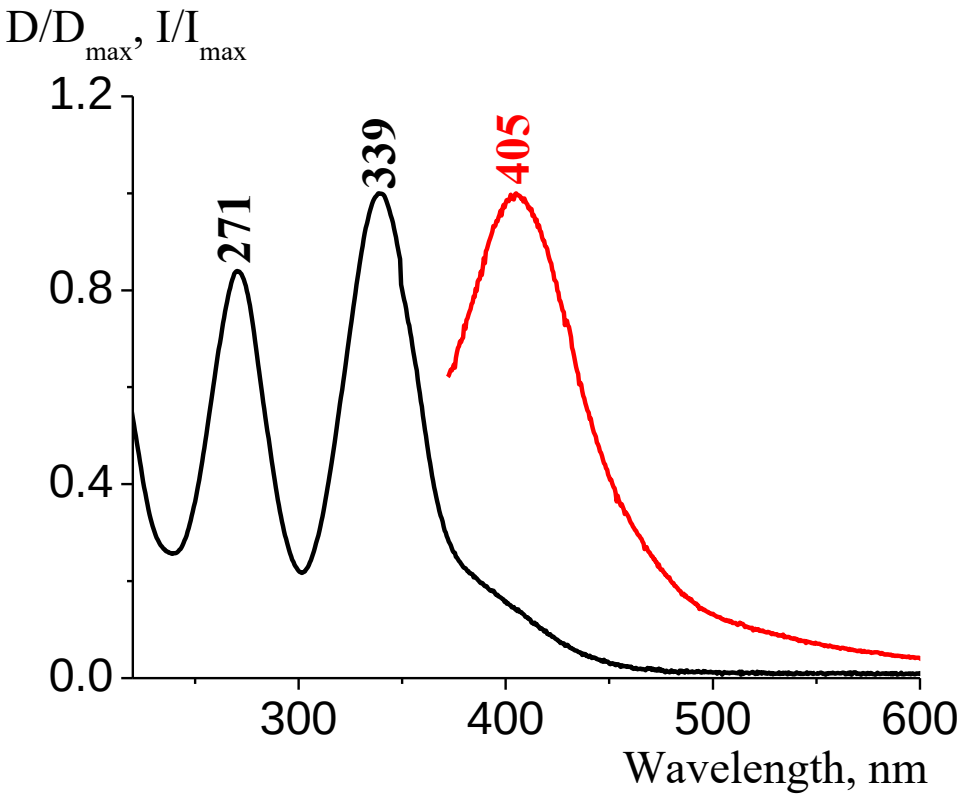


Fig. 2. ***4f*** *absorbance and emission spectra in ethanol; excitation wavelength is 320 nm.*

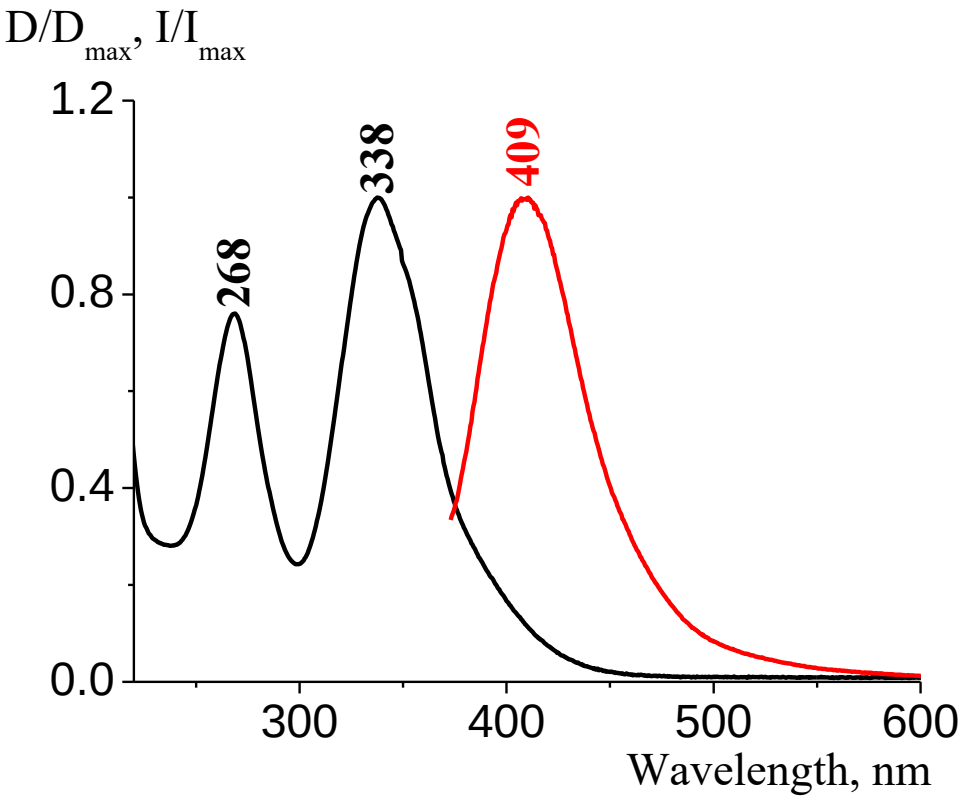


Fig. 3. ***2a*** *absorbance and emission spectra in ethanol; excitation wavelength is 320 nm.*

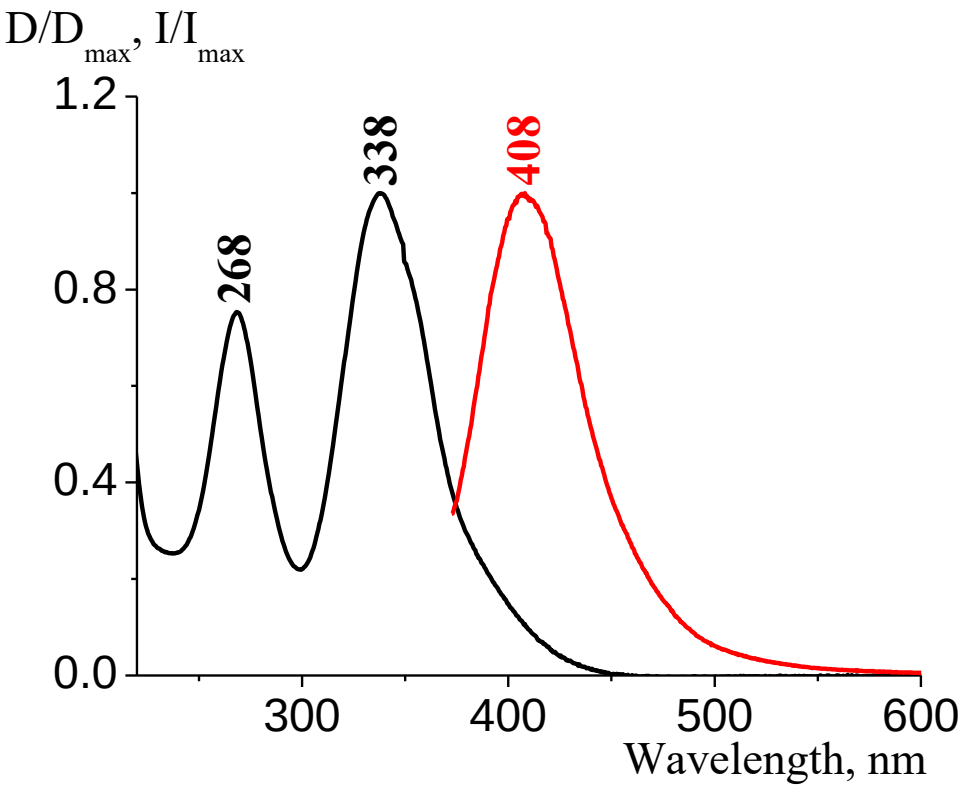


Fig. 4. ***2b*** *absorbance and emission spectra in ethanol; excitation wavelength is 320 nm.*

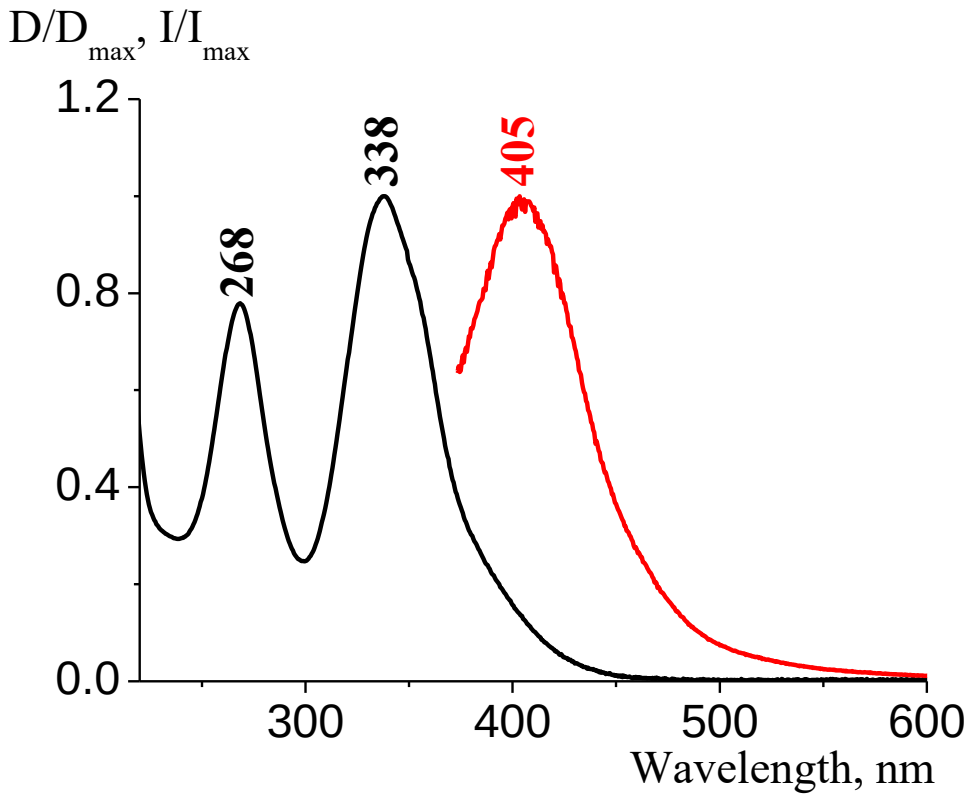


Fig. 5. ***α-2c*** *absorbance and emission spectra in ethanol; excitation wavelength is 320 nm.*

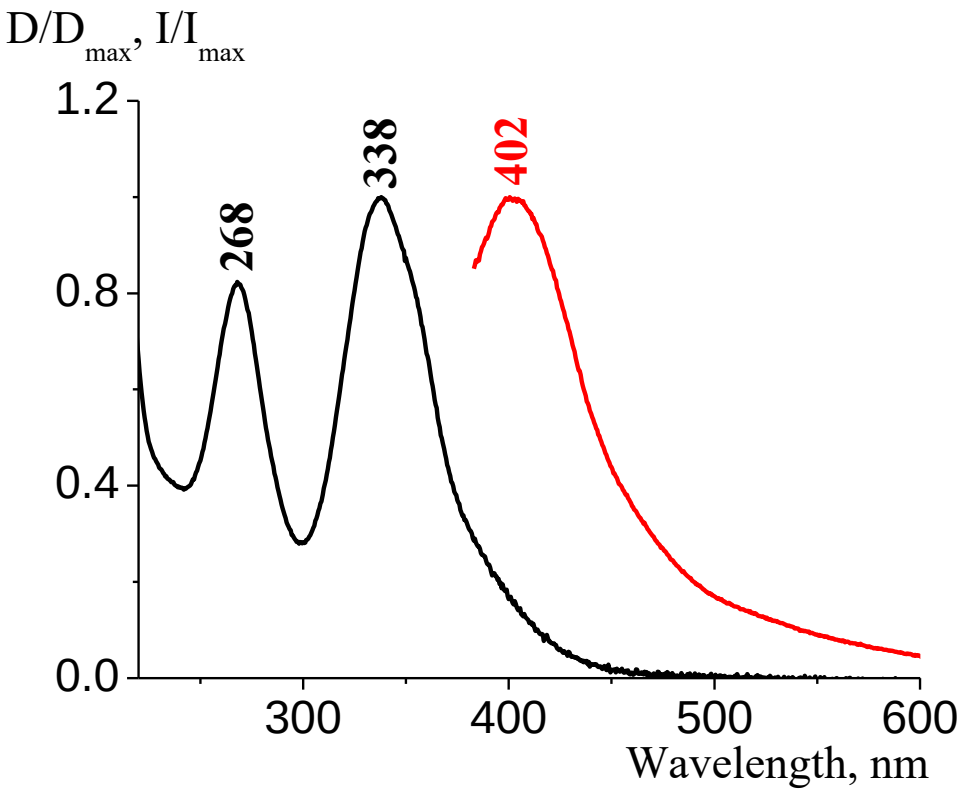


Fig. 6. ***β-2c*** *absorbance and emission spectra in ethanol; excitation wavelength is 340 nm.*

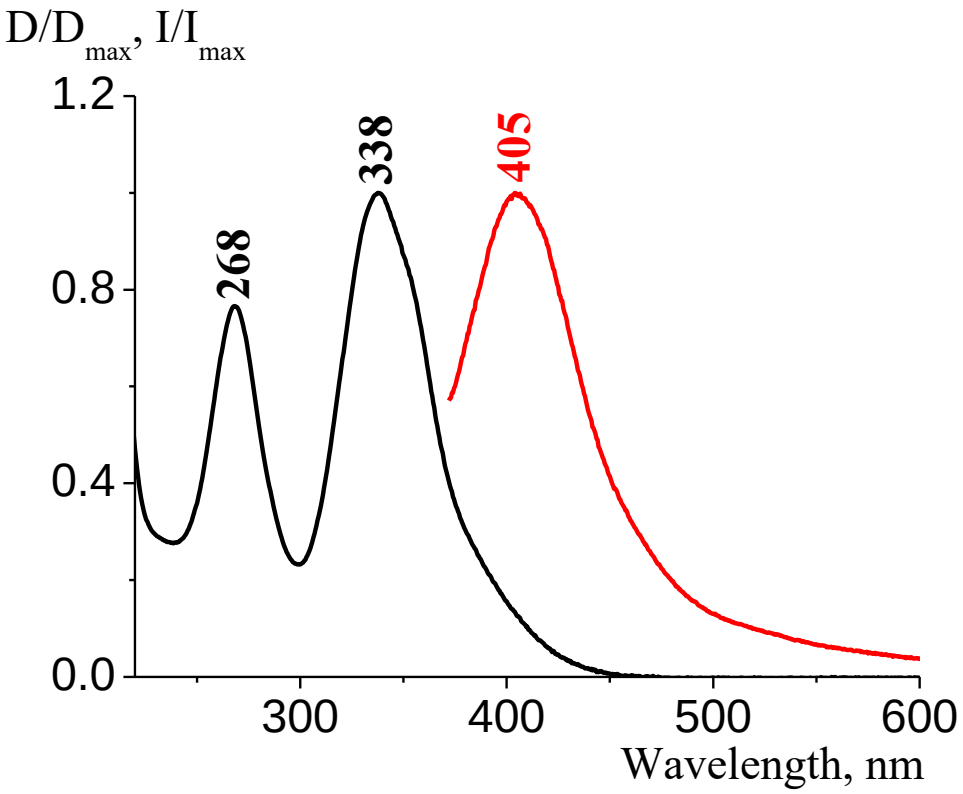


Fig. 7. ***2d*** *absorbance and emission spectra in ethanol; excitation wavelength is 320 nm.*

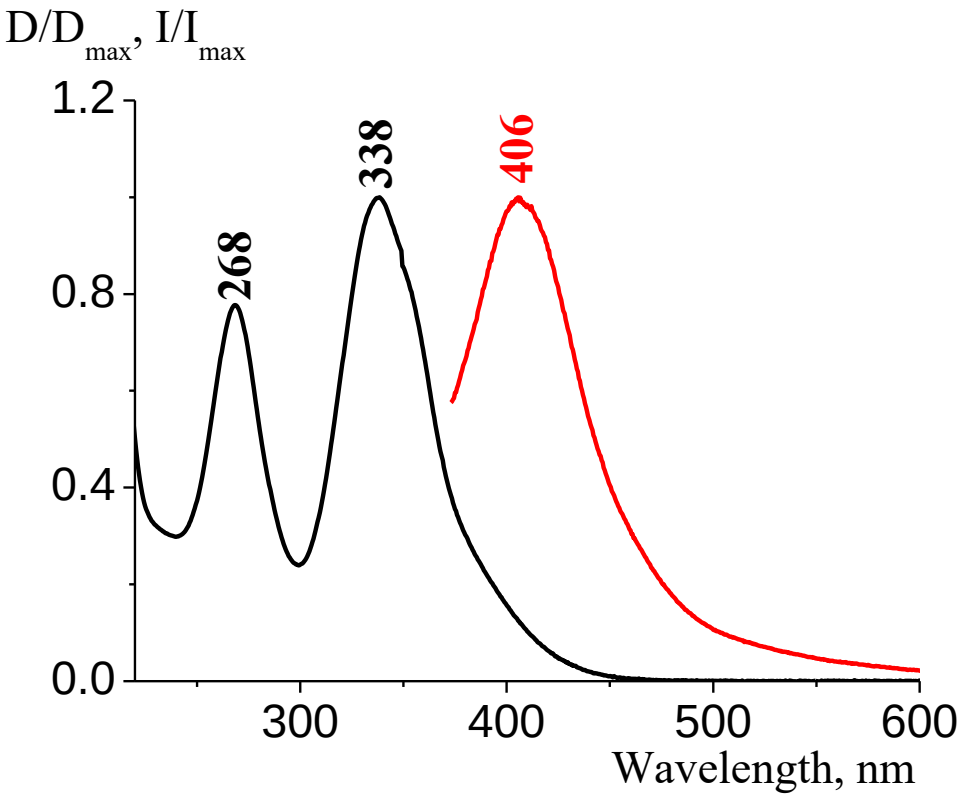


Fig. 8. ***2e*** *absorbance and emission spectra in ethanol; excitation wavelength is 320 nm.*

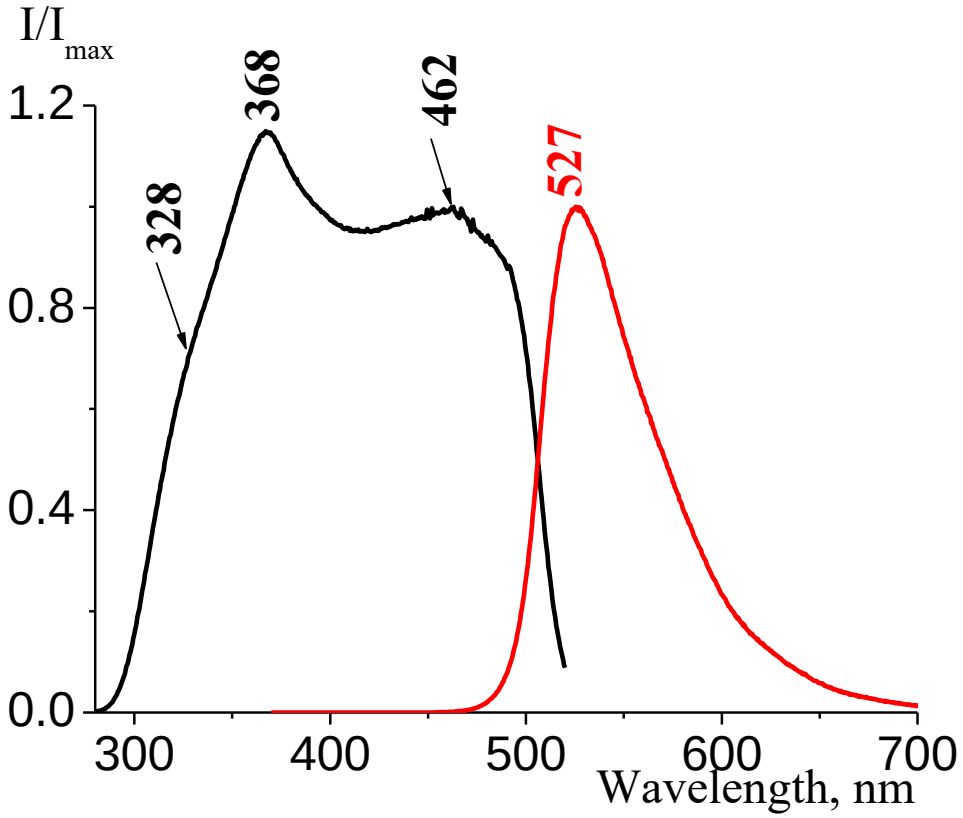


Fig. 9. *Solid state* ***1a*** *emission and excitation spectra; excitation wavelength is 365 nm (red curve), registration wavelength is 525 nm (black curve).*

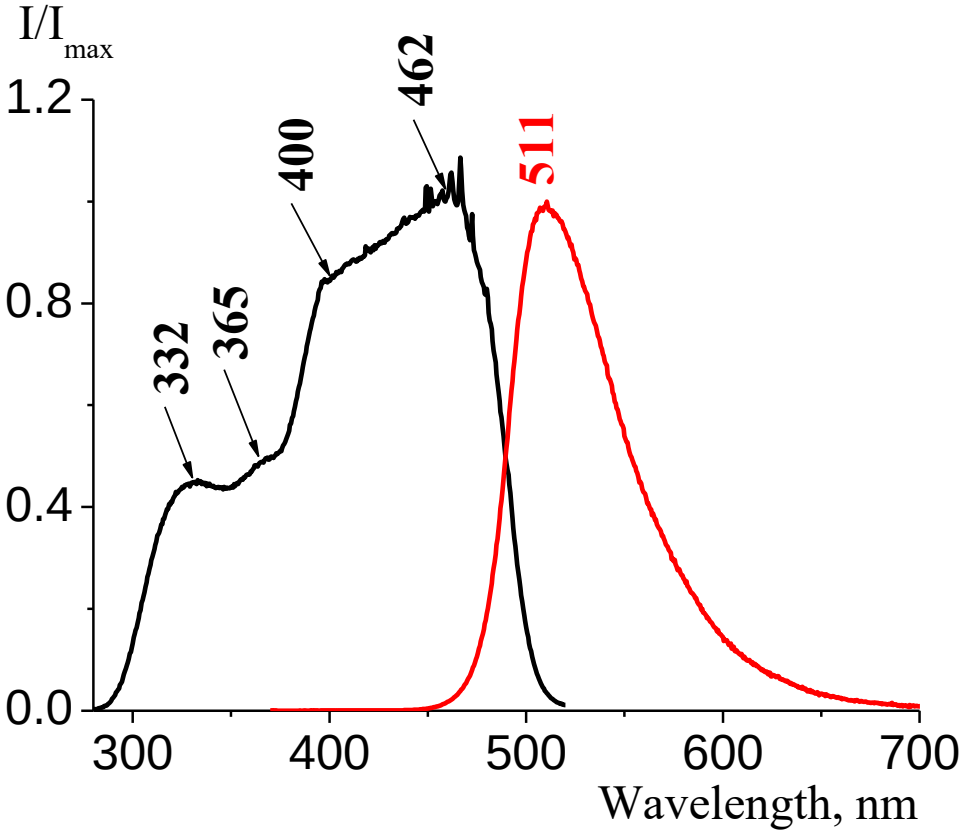


Fig. 10. *Solid state* ***1b*** *emission and excitation spectra; excitation wavelength is 365 nm (red curve), registration wavelength is 525 nm (black curve).*

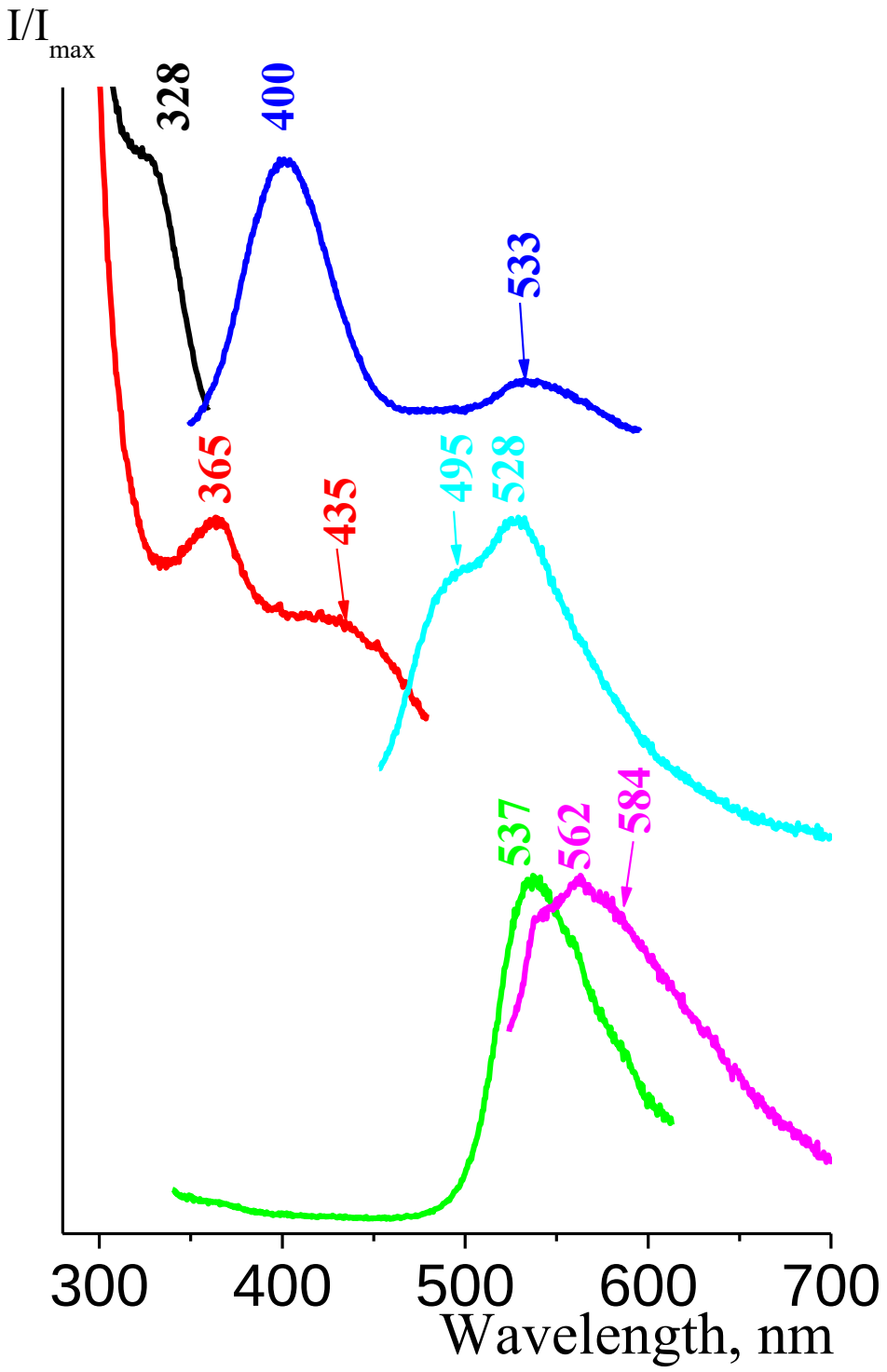


Fig. 11. *Solid state* ***α-1c*** *emission and excitation spectra; excitation wavelength is 320 nm (blue curve), 420 nm (cyan curve) and 500 nm (magenta curve), registration wavelength is 380 nm (black curve), 525 nm (red curve) and 640 nm (green curve).*

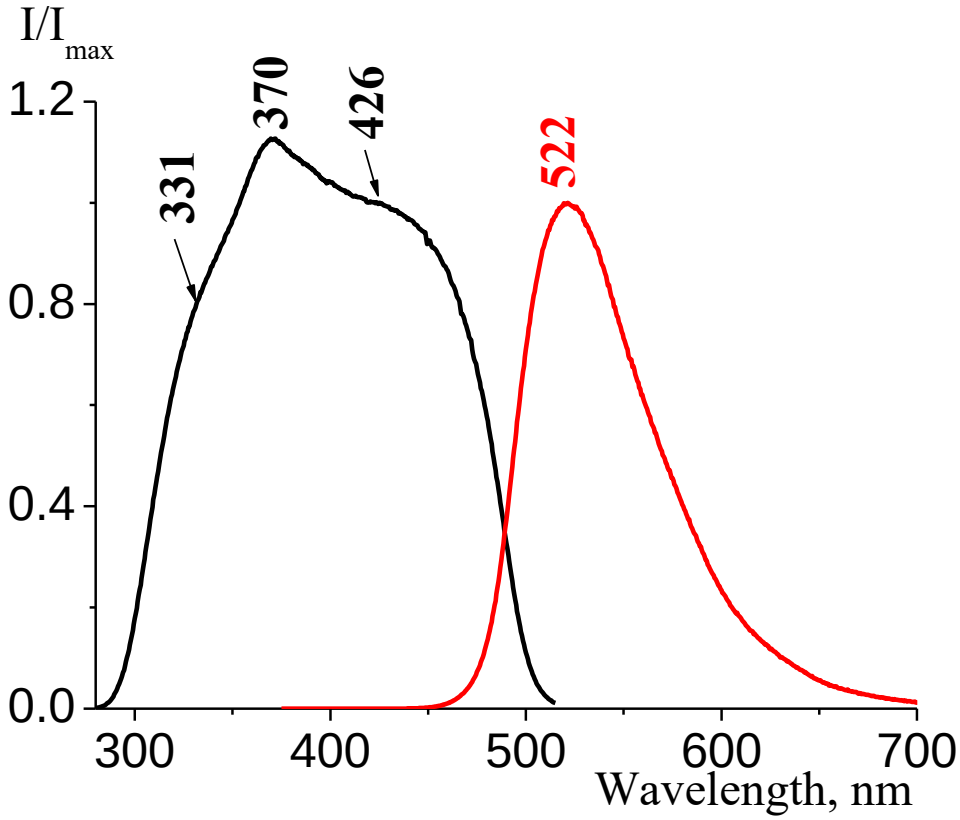


Fig. 12. *Solid state* ***β-1c*** *emission and excitation spectra; excitation wavelength is 365 nm (red curve), registration wavelength is 525 nm (black curve).*

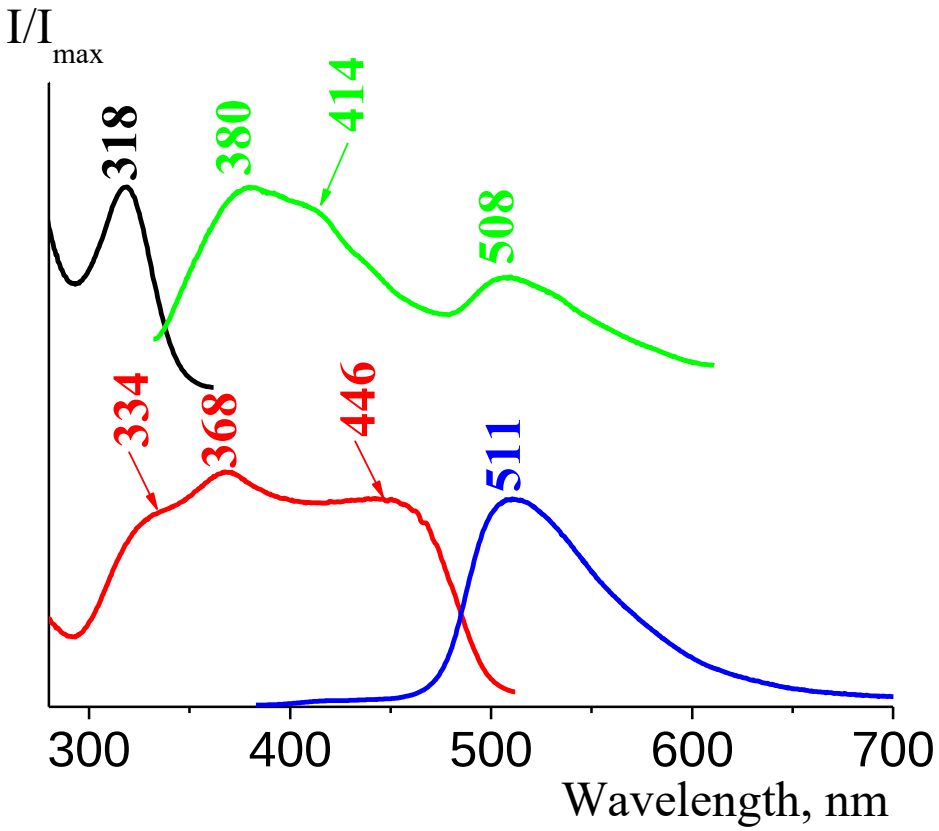


Fig. 13. *Solid state* ***1e*** *emission and excitation spectra; excitation wavelength is 320 nm (green curve) and 365 nm (blue curve), registration wavelength is 380 nm (black curve) and 525 nm (red curve).*

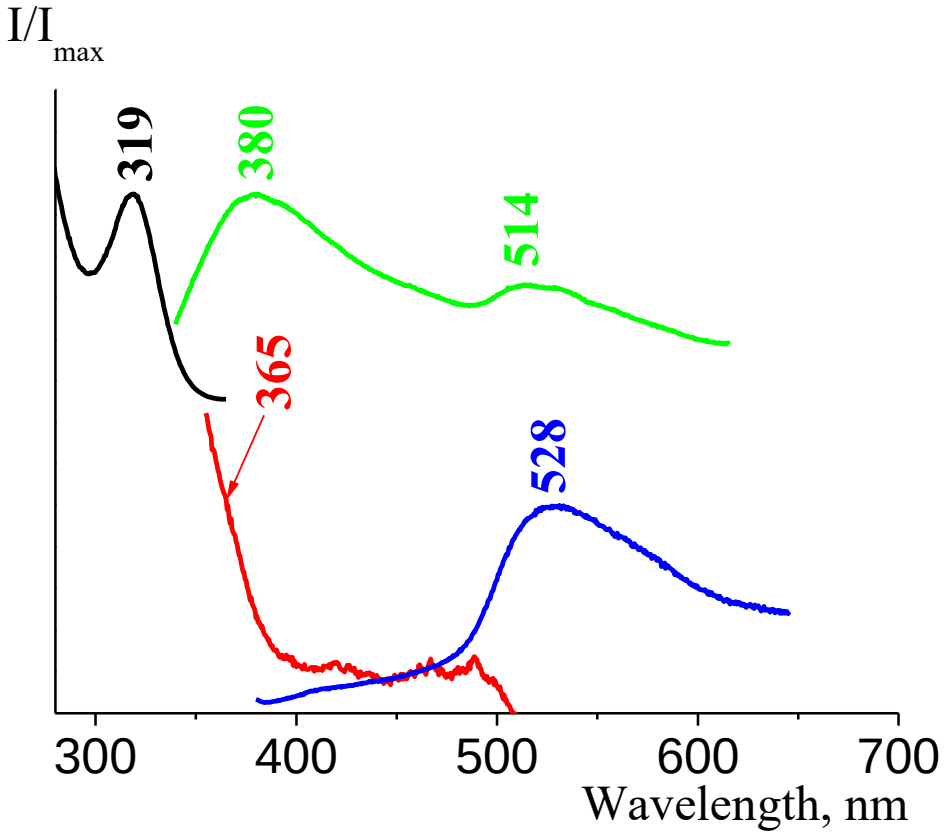


Fig. 14. *Solid state* ***1f*** *emission and excitation spectra; excitation wavelength is 320 nm (green curve) and 365 nm (blue curve), registration wavelength is 380 nm (black curve) and 525 nm (red curve).*

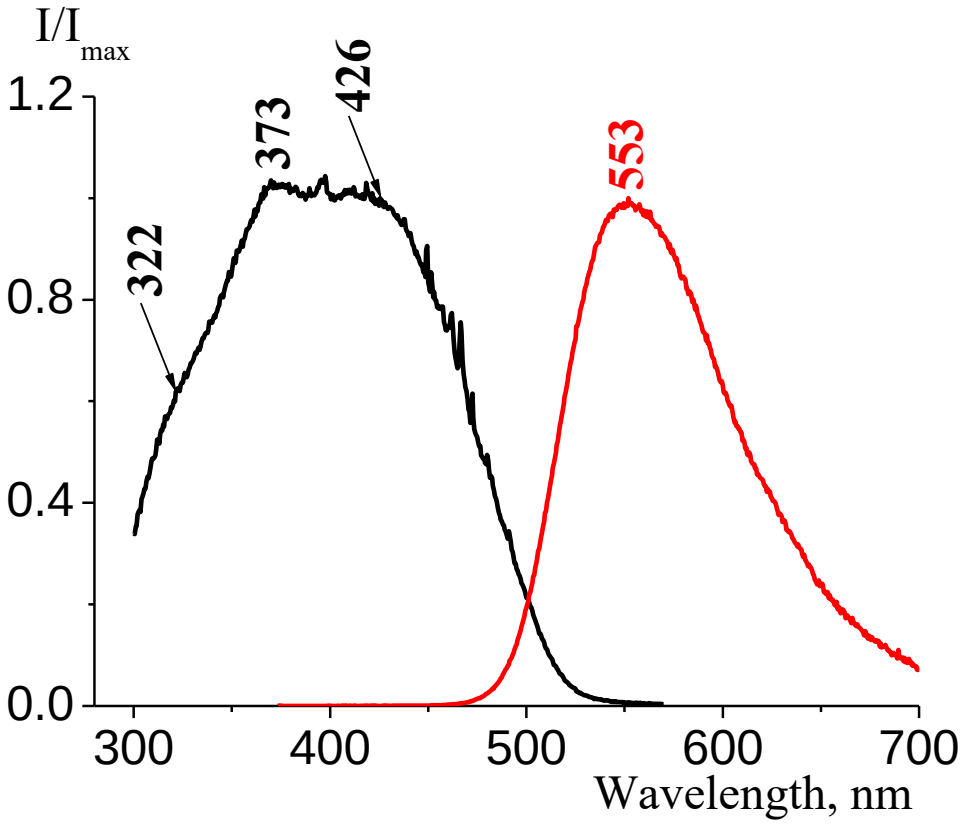


Fig. 15. *Solid state* ***2a*** *emission and excitation spectra; excitation wavelength is 365 nm (red curve), registration wavelength is 580 nm (black curve).*

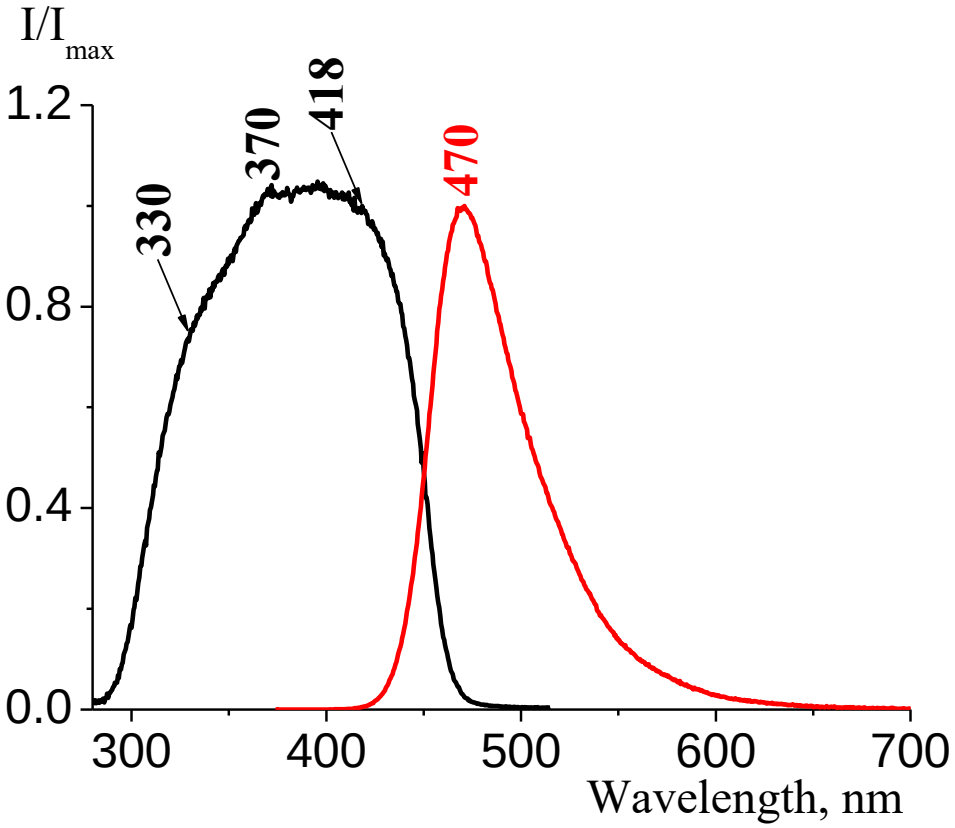


Fig. 16. *Solid state* ***2b*** *emission and excitation spectra; excitation wavelength is 365 nm (red curve), registration wavelength is 525 nm (black curve).*

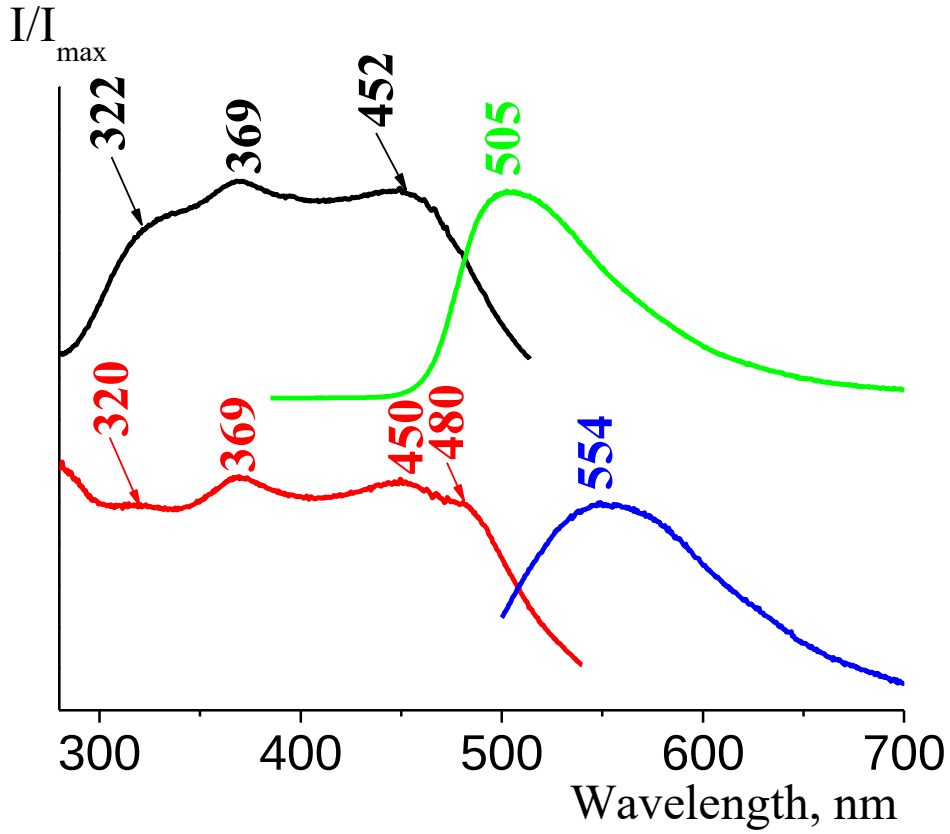


Fig. 17. *Solid state **α-2c** emission and excitation spectra; excitation wavelength is 365 nm (green curve) and 490 nm (blue curve), registration wavelength is 525 nm (black curve) and 550 nm (red curve).*

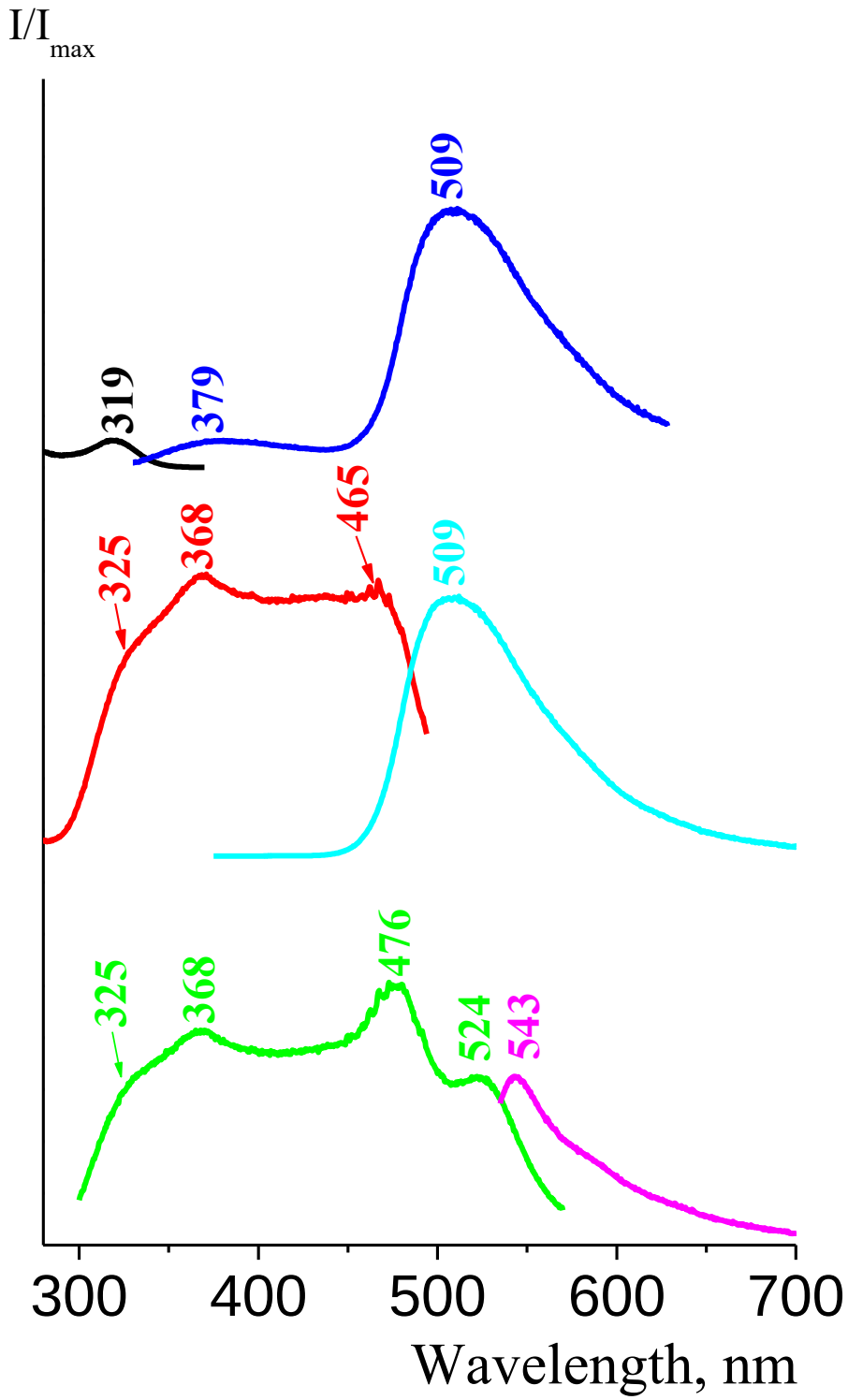


Fig. 18. *Solid state* ***β-2c*** *emission and excitation spectra; excitation wavelength is 320 nm (blue curve), 365 nm (cyan curve) and 525 nm (magenta curve), registration wavelength is 380 nm (black curve), 525 nm (red curve) and 580 nm (green curve).*

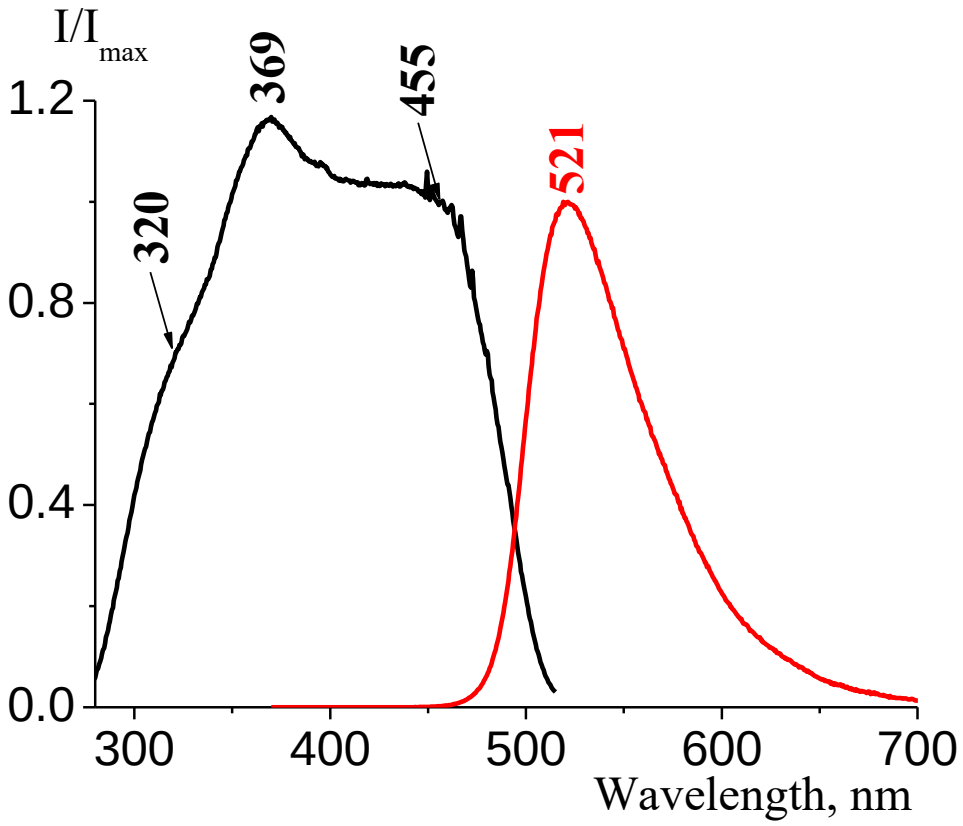


Fig. 19. *Solid state* ***2d*** *emission and excitation spectra; excitation wavelength is 365 nm (red curve), registration wavelength is 525 nm (black curve).*

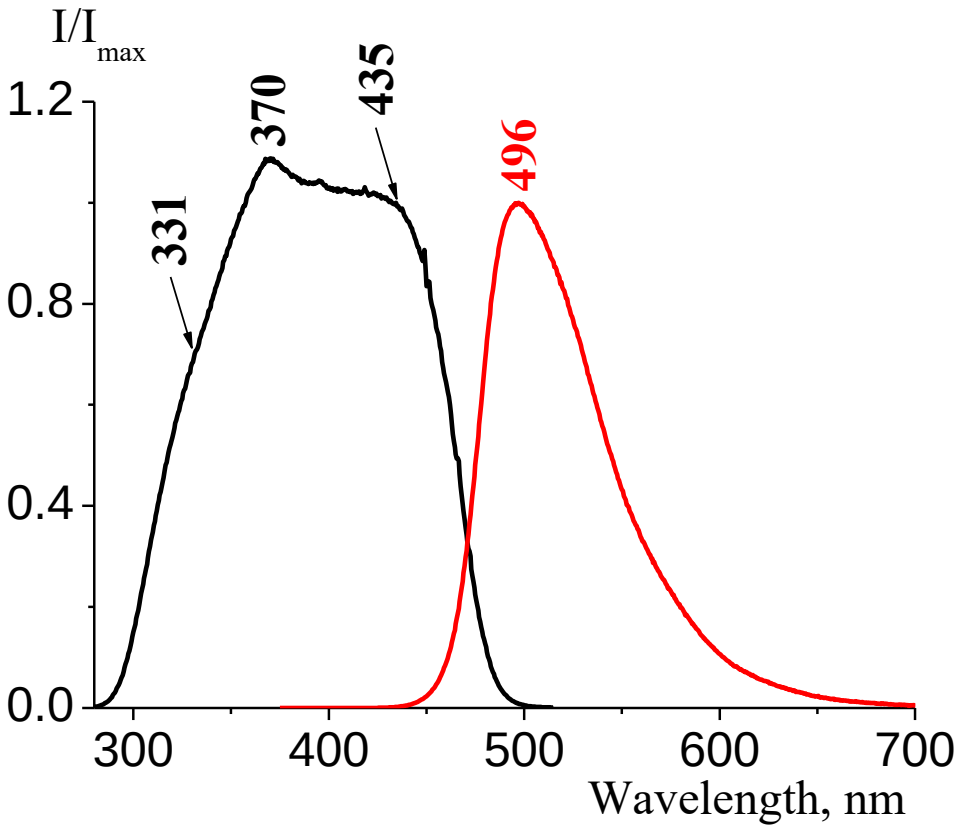


Fig. 20. *Solid state* ***2e*** *emission and excitation spectra; excitation wavelength is 365 nm (red curve), registration wavelength is 525 nm (black curve).*

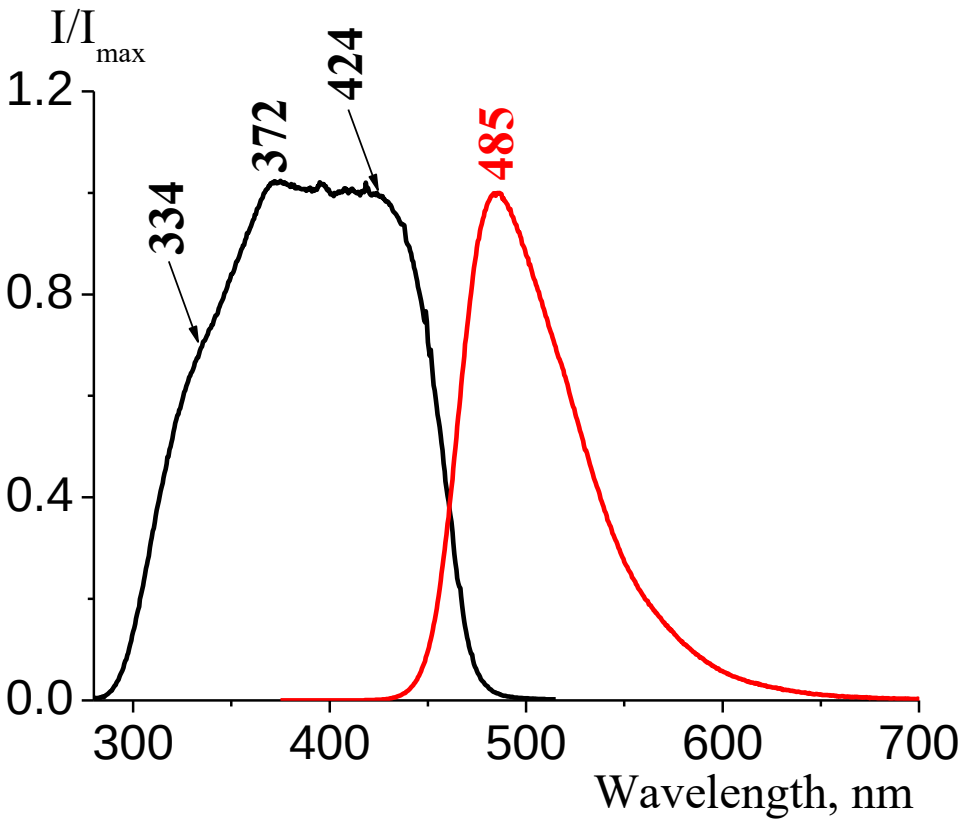


Fig. 21. *Solid state* ***2f*** *emission and excitation spectra; excitation wavelength is 365 nm (red curve), registration wavelength is 525 nm (black curve).*

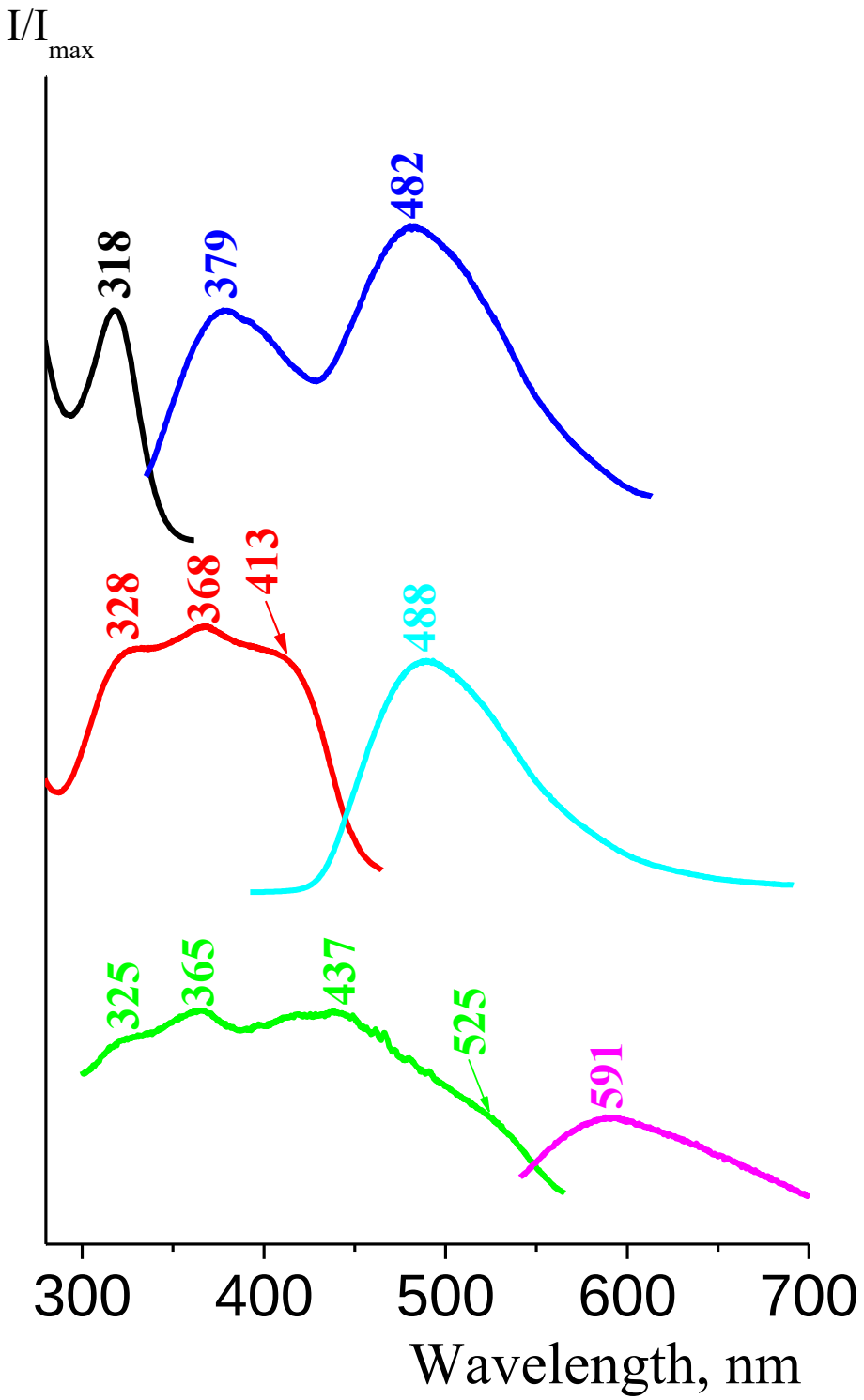


Fig. 22. *Solid state* ***3a*** *emission and excitation spectra; excitation wavelength is 320 nm (blue curve), 365 nm (cyan curve) and 525 nm (magenta curve), registration wavelength is 380 nm (black curve), 480 nm (red curve) and 580 nm (green curve).*

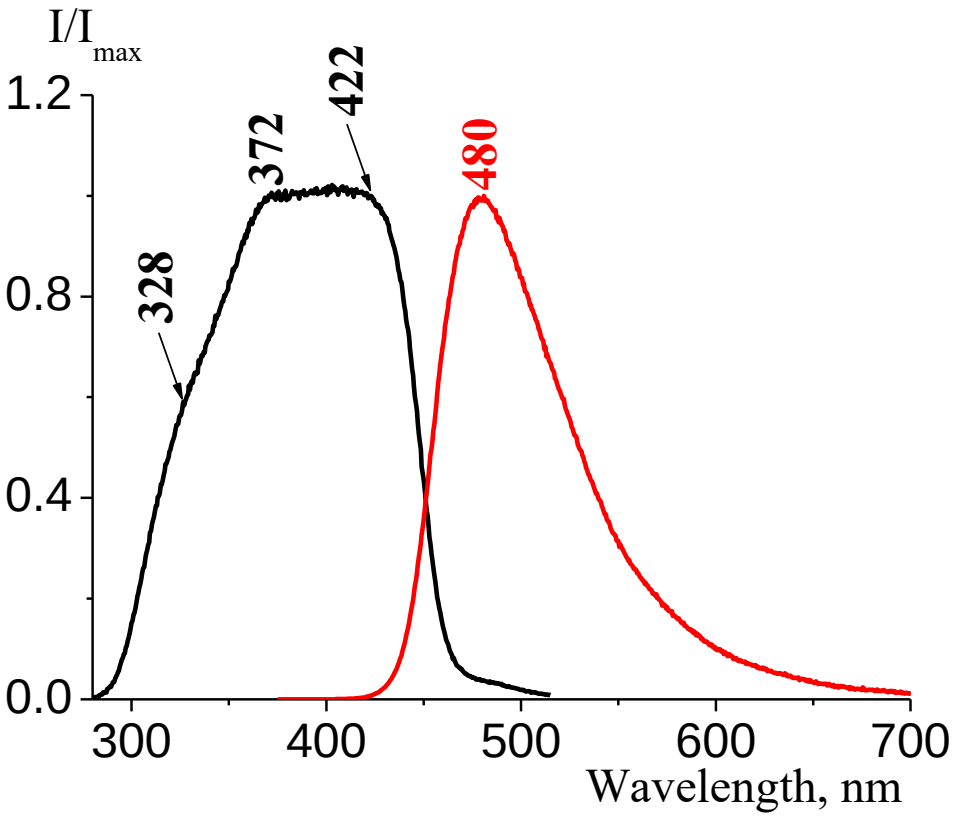


Fig. 23. *Solid state* ***3b*** *emission and excitation spectra; excitation wavelength is 365 nm (red curve), registration wavelength is 525 nm (black curve).*

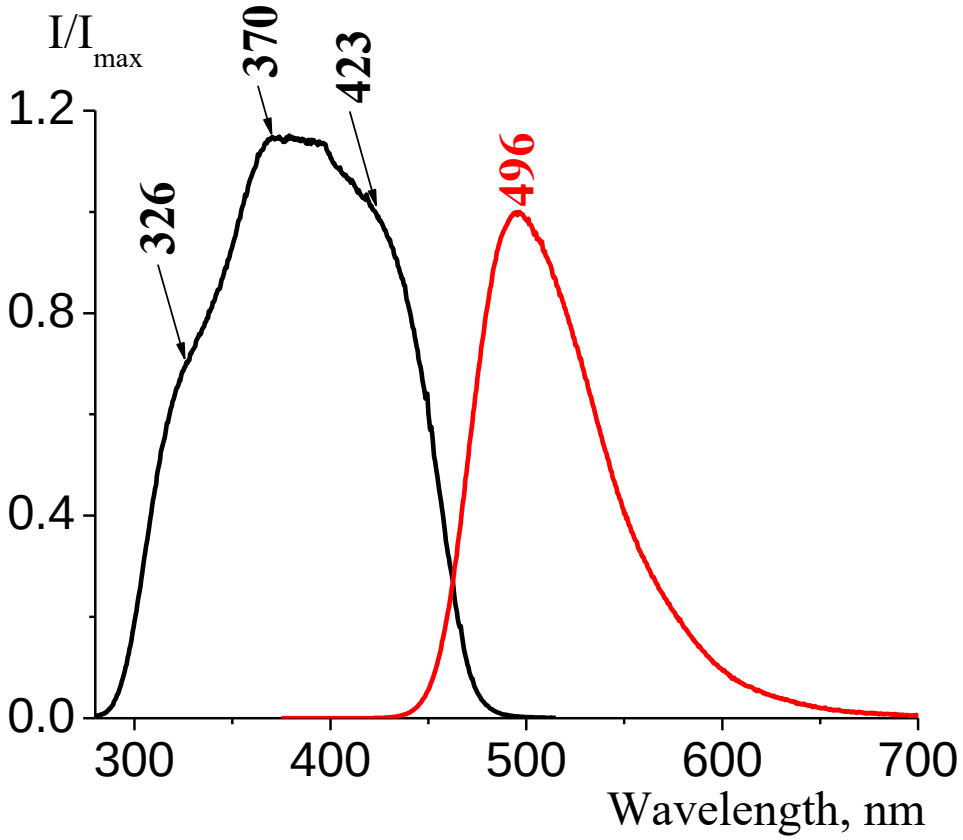


Fig. 24. *Solid state* ***3c*** *emission and excitation spectra; excitation wavelength is 365 nm (red curve), registration wavelength is 525 nm (black curve).*

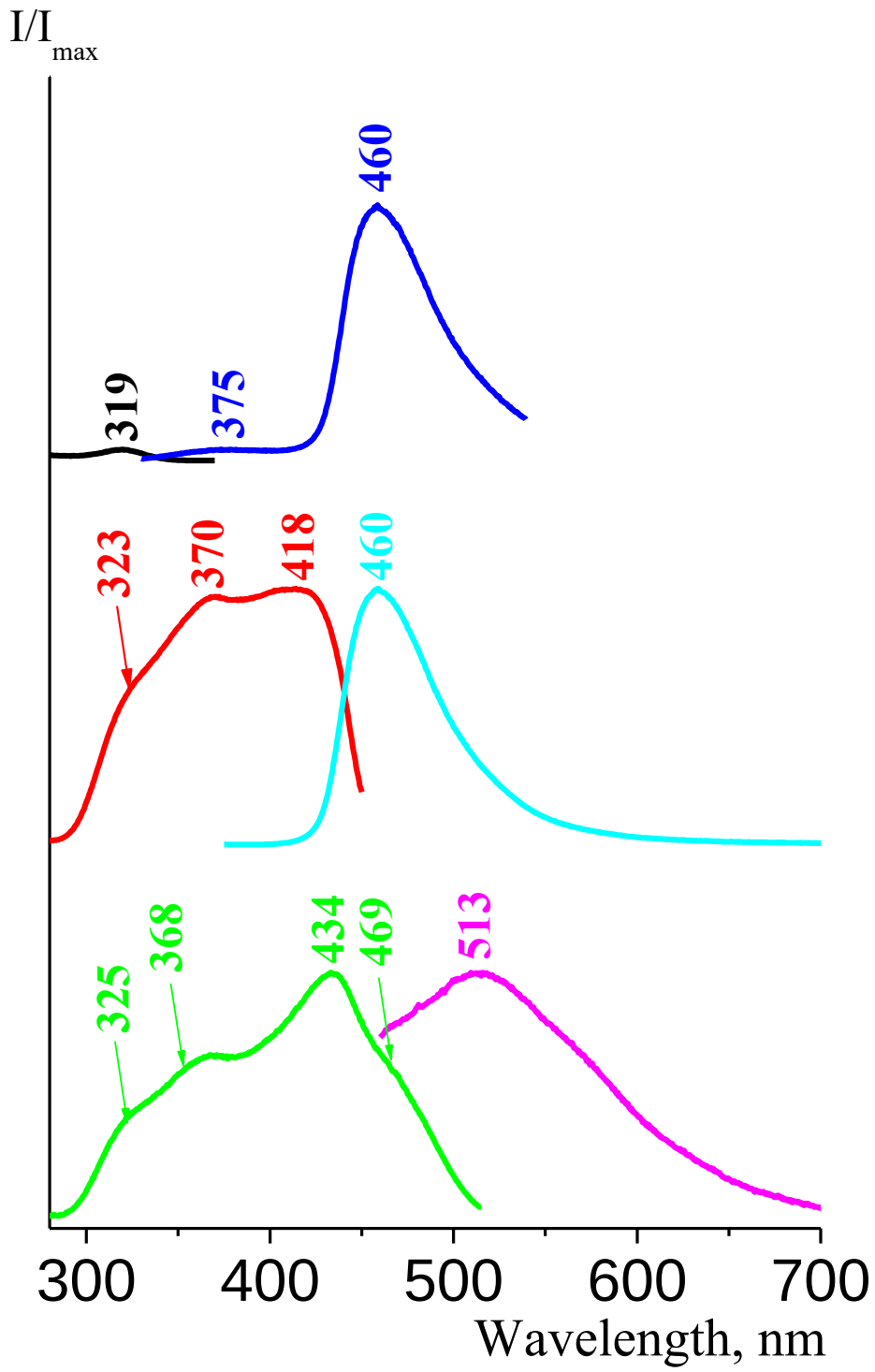


Fig. 25. *Solid state* ***α-3d*** *emission and excitation spectra; excitation wavelength is 320 nm (blue curve), 365 nm (cyan curve) and 450 nm (magenta curve), registration wavelength is 380 nm (black curve), 460 nm (red curve) and 525 nm (green curve).*

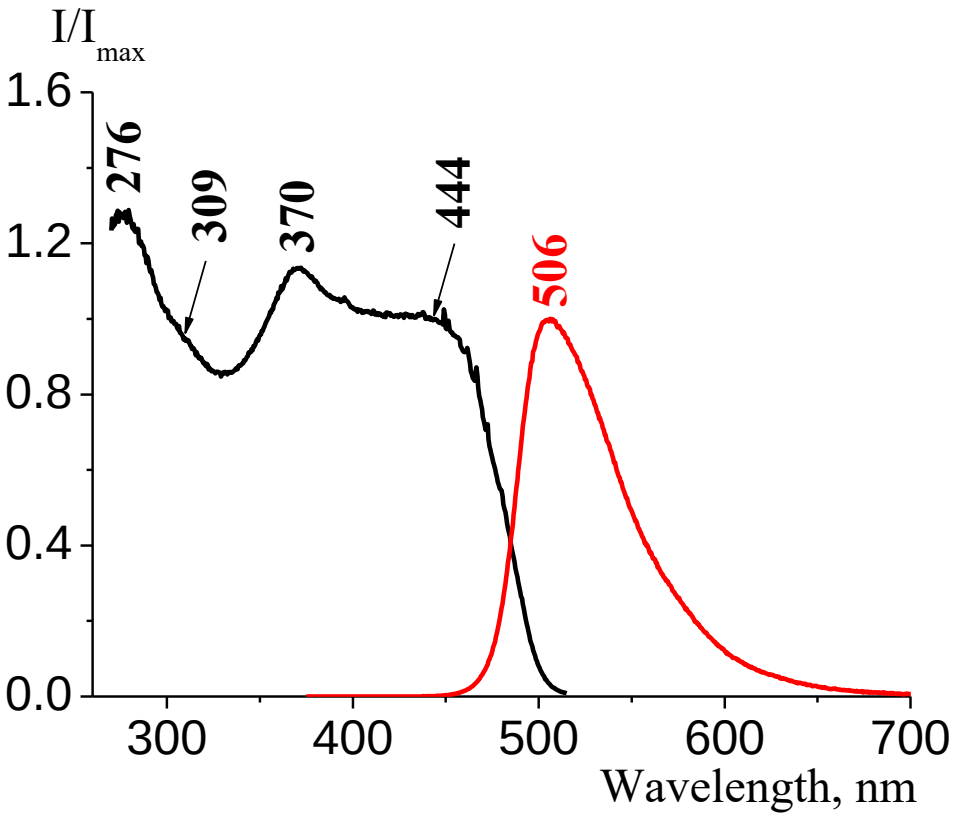


Fig. 26. *Solid state* ***β-3d*** *emission and excitation spectra; excitation wavelength is 365 nm (red curve), registration wavelength is 525 nm (black curve).*

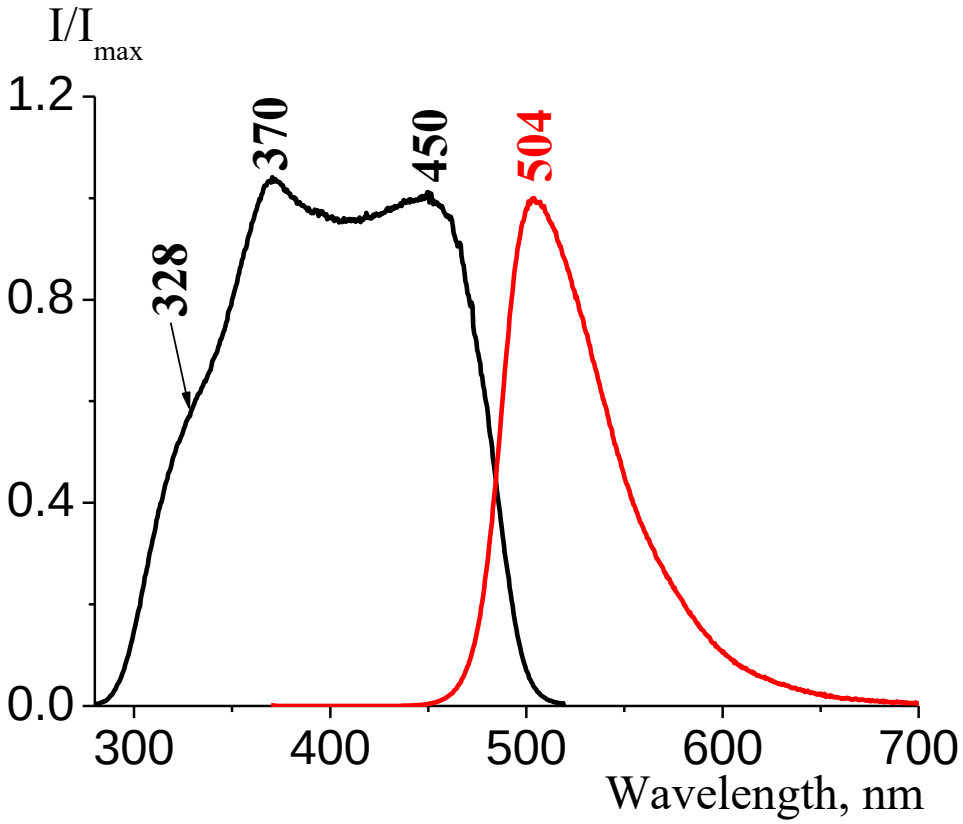


Fig. 27. *Solid state* ***3e*** *emission and excitation spectra; excitation wavelength is 365 nm (red curve), registration wavelength is 525 nm (black curve).*

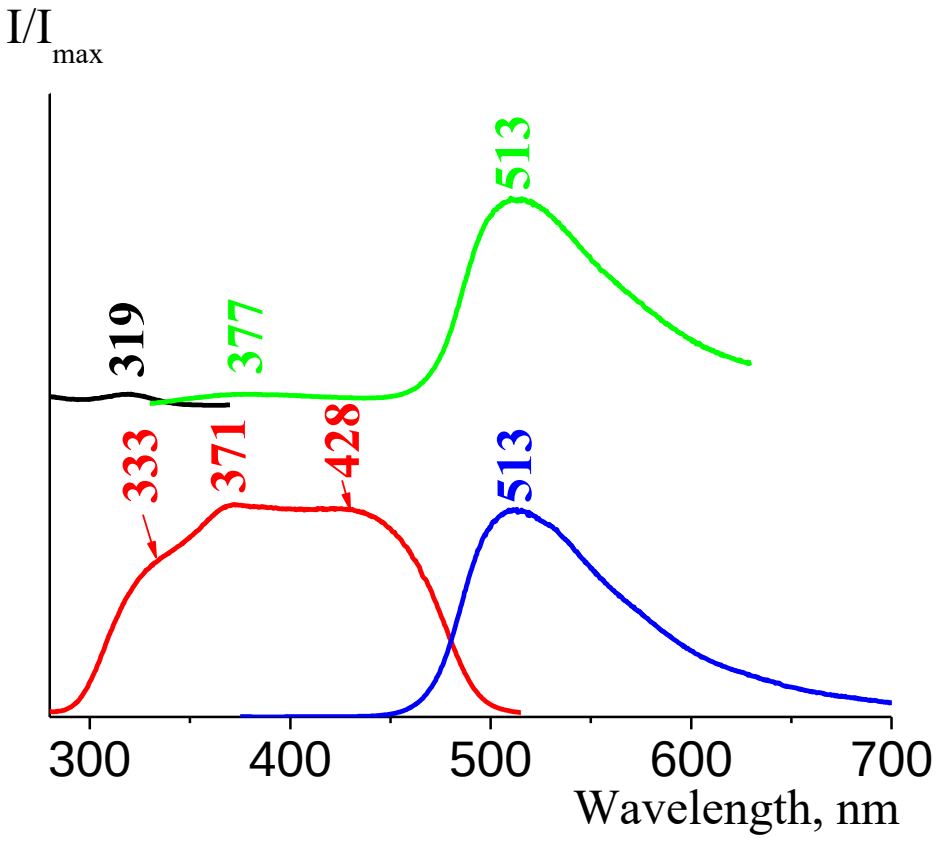


Fig. 28. *Solid state* ***4a*** *emission and excitation spectra; excitation wavelength is 320 nm (green curve) and 365 nm (blue curve), registration wavelength is 380 nm (black curve) and 525 nm (red curve).*

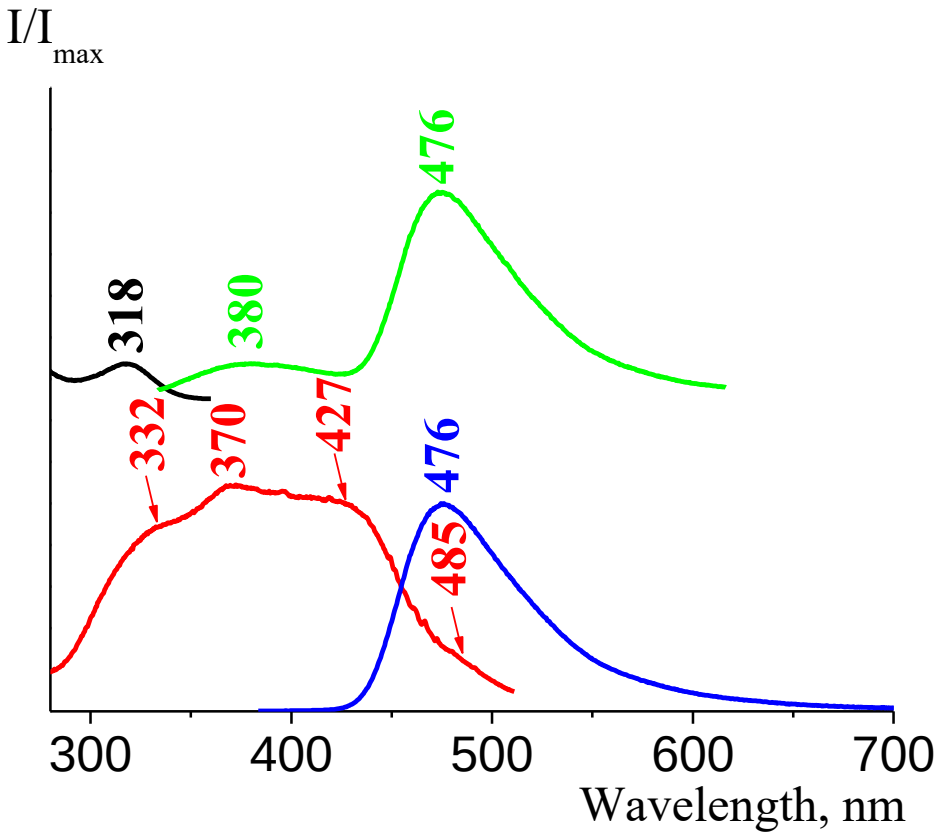


Fig. 29. *Solid state* ***4b*** *emission and excitation spectra; excitation wavelength is 320 nm (green curve) and 365 nm (blue curve), registration wavelength is 380 nm (black curve) and 525 nm (red curve).*

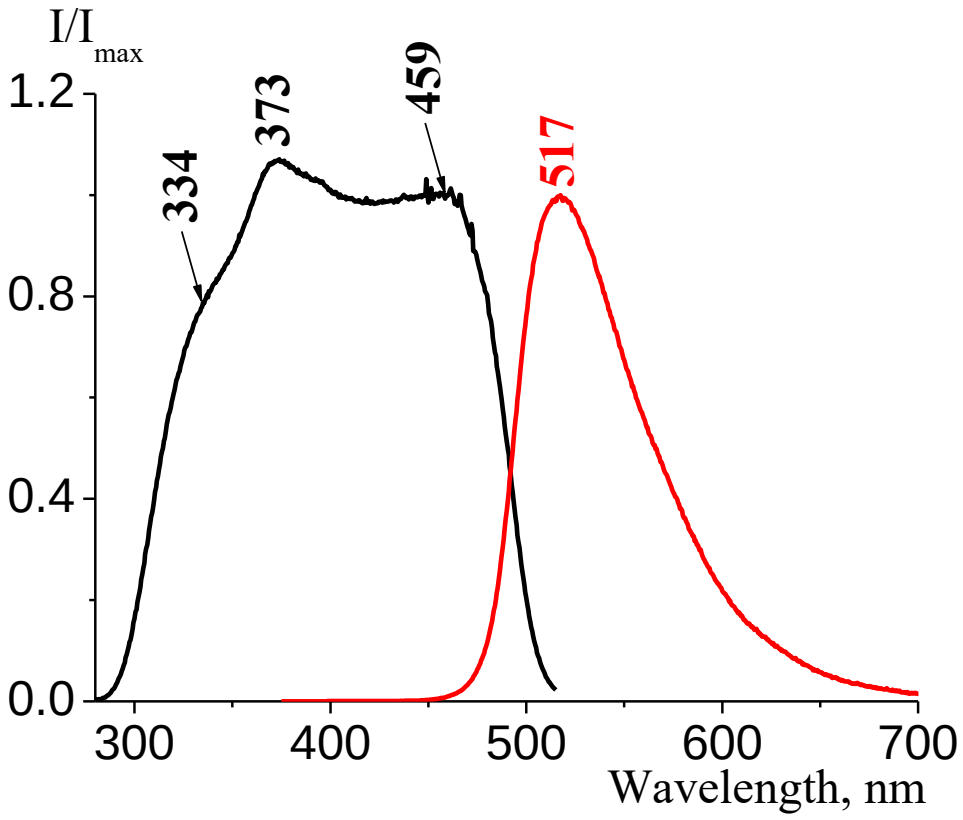


Fig. 30. *Solid state* ***4c*** *emission and excitation spectra; excitation wavelength is 365 nm (red curve), registration wavelength is 525 nm (black curve).*

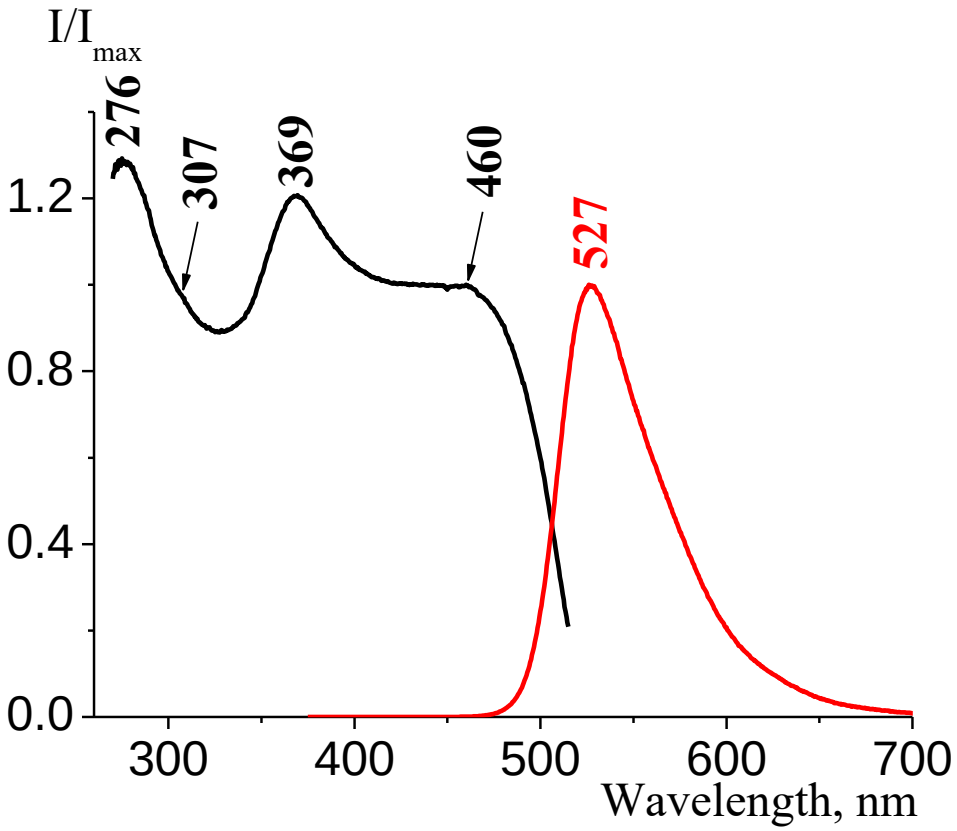


Fig. 31. *Solid state* ***4d*** *emission and excitation spectra; excitation wavelength is 365 nm (red curve), registration wavelength is 525 nm (black curve).*

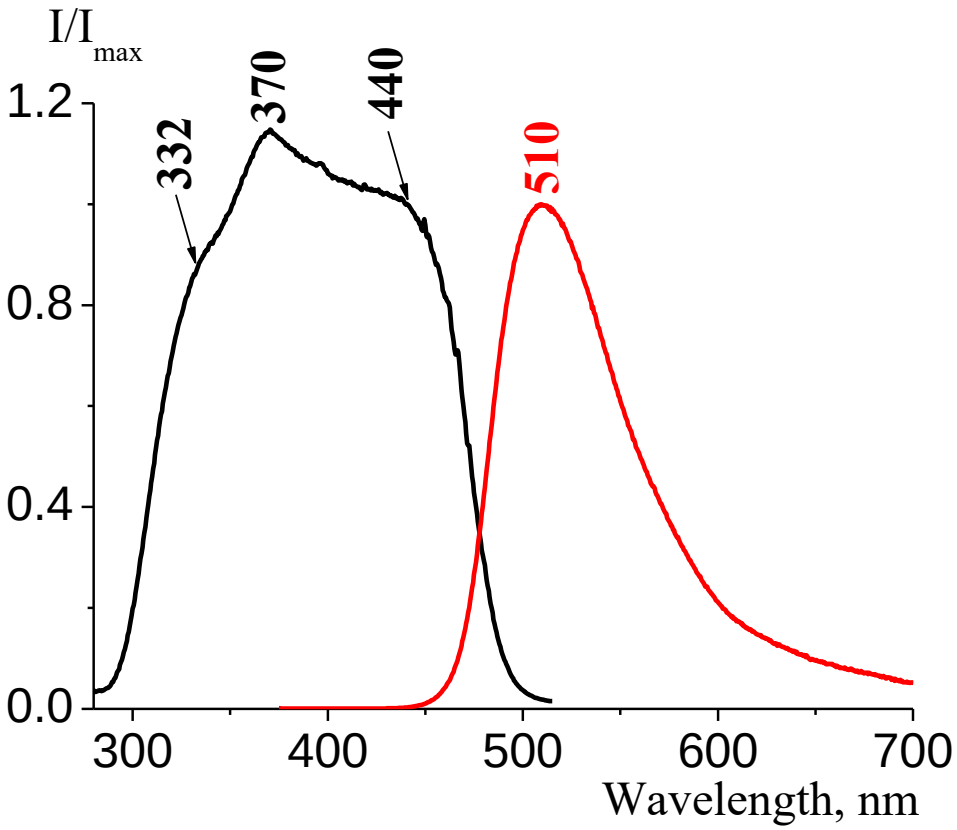


Fig. 32. *Solid state* ***4e*** *emission and excitation spectra; excitation wavelength is 365 nm (red curve), registration wavelength is 525 nm (black curve).*