Relationship between structure and photoinitiating abilities of selected bromide salts of 2-oxo-2,3-dihydro-1H-imidazo[1,2-a]pyridine (IMP): influence of the solvent and the substitution in benzaldehyde on the course of its reaction with IMP

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Table 1aS Comparison of bond lengths in the investigated molecules as obtained from DFT energy minimization procedure.

Bond lengths (Å)	(1)	(2a)	(3)
O1 - C7	1.198	1.202	1.216
N1 - C1	1.358	1.363	1.374
N1 - C5	1.365	1.357	1.366
N1 - C6	1.477	1.485	1.438
N2 - C1	1.366	1.365	1.357
N2 - C7	1.409	1.404	1.412
C1 - C2	1.396	1.395	1.396
C2 - C3	1.389	1.390	1.386
C3 - C4	1.410	1.408	1.410
C4 - C5	1.377	1.379	1.375

C6 - C7	1.535	1.539	1.471
C6 - C8	-	1.554	1.377
C8 - C9	-	1.531	1.426
O2 - C12	-	-	1.335
O2 - C15	-	-	1.438
O1R - C1R	-	1.434	-
O1R - C8	-	1.413	-
N3 - O2	-	1.247	-
N3 - O3	-	1.222	-
N3 - C10	-	1.470	-
C9 - C10	-	1.399	1.429
C9 - C14	-	1.413	1.422
C10 - C11	-	1.397	1.374
C11 - C12	-	1.392	1.415
C12 - C13	-	1.396	1.413
C13 - C14	-	1.397	1.383
N2 - H2A	1.01	1.01	1.01
C2 - H2	1.08	1.08	1.08
C3 - H3	1.08	1.08	1.08
C4 - H4	1.08	1.08	1.08
C5 - H5	1.08	1.08	1.08
C6 - H6A	1.09	1.09	-
C6 - H6B	1.09	-	-
C8 - H8	-	1.09	1.09
C10 - H10	-	-	1.09
C11 - H11	-	1.08	1.08
C12 - H12	-	1.08	-
C13 - H13	-	1.08	1.08
C14 - H14	-	1.08	1.08
C15 - H15A	-	-	1.09

C15 - H15B	-	-	1.09
C15 - H15C	-	-	1.09
C1R - H1R	-	1.09	-
C1R - H2R	-	1.09	-
C1R - H3R	-	1.09	-

Table 1bS Comparison of valence angles in the investigated molecules as obtained from DFT energy minimization procedure.

Valence angles (°)	(1)	(2a)	(3)
O1- C7 - N2	126.6	125.9	123.6
O1 - C7 - C6	128.3	128.4	131.7
N1 - C1 - N2	109.3	109.2	108.0
N1 - C1 - C2	120.3	120.4	121.3
N1 - C5 - C4	119.4	119.3	120.2
N1 - C6 - C7	102.7	101.6	105.4
N1 - C6 - C8	-	111.6	121.9
N2 - C1 - C2	130.4	130.4	130.6
N2 - C7 - C6	105.1	105.7	104.6
C1 - N1 - C5	122.3	122.4	120.4
C1 - N1 - C6	110.6	111.0	109.8
C1 - N2 - C7	112.3	112.2	112.1
C1 - C2 - C3	117.7	117.6	118.1
C2 - C3 - C4	121.1	121.0	120.1
C3 - C4 - C5	119.1	119.2	119.8
C5 - N1 - C6	127.1	126.5	129.8
C6 - C8 - C9	-	111.7	134.1
C7 - C6 - C8	-	112.7	132.6
O2 - N3 - O3	-	123.5	-

O2 - N3 - C10	-	117.7	-
O2 - C12 - C11	-	-	124.6
O2 - C12 - C13	-	-	116.3
O3 - N3 - C10	-	118.7	-
N3 - C10 - C9	-	121.6	-
N3 - C10 - C11	-	116.1	-
C8 - C9 - C10	-	124.2	116.3
C8 - C9 - C14	-	118.8	126.1
C8 - O1R - C1R	-	114.8	-
C9 - C10 - C11	-	122.2	121.7
C9 - C14 - C13	-	121.5	121.1
C10 - C9 - C14	-	119.4	117.5
C10 - C11 - C12	-	116.9	119.7
C11 - C12 - C13	-	119.6	119.8
C12 - O2 - C15	-	-	120.3
C12 - C13 - C14	-	120.4	120.2
O1R - C8 - C6	-	105.4	
O1R - C8 - C9	-	113.7	
N1 - C5 - H5	116.4	116.2	117.0
N1 - C6 - H6A	111.0	109.1	
N1 - C6 - H6B	111.0	-	
C1 - N2 - H2A	124.9	124.9	125.5
C7 - N2 - H2A	122.7	122.7	122.4
C1 - C2 - H2	120.2	120.3	119.7
C2 - C3 - H3	119.3	119.3	119.8
C3 - C2 - H2	122.0	122.0	122.1
C3 - C4 - H4	121.2	121.2	121.1
C4 - C3 - H3	119.6	119.7	120.0
C4 - C5 - H5	124.1	124.5	122.7
C5 - C4 - H4	119.6	119.5	119.0

C6 - C8 - H8	-	107.1	114.0
C7 - C6 - H6A	111.0	111.0	
C7 - C6 - H6B	111.0	-	
H6A - C6 - H6B	109.8	-	
C8 - C6 - H6A	-	110.4	
C9 - C8 - H8	-	109.1	111.9
C9 - C10 - H10		-	119.3
C9 - C14 - H14	-	118.6	119.6
C10 - C11 - H11	-	119.2	121.7
C11 - C10 - H10		-	119.0
C11 - C12 - H12	-	119.8	
C12 - C11 - H11	-	121.4	118.6
C12 - C13 - H13	-	120.2	120.7
C13 - C12 - H12	-	120.6	
C13 - C14 - H14	-	119.9	119.3
C14 - C13 - H13	-	119.4	119.1
O2 – C15 - H15A		-	110.6
O2 – C15 - H15B		-	110.6
O2 – C15 - H15C		-	105.1
H15A - C15 - H15B		-	109.9
H15A - C15 - H15C		-	110.6
H15B - C15 - H15C		-	109.9
O1R – C8 - H8	-	109.5	
O1R - C1R - H1R	-	110.5	
O1R - C1R - H2R	-	111.3	
O1R - C1R - H3R	-	106.1	
H1R - C1R - H2R	-	109.5	
H1R - C1R - H3R	-	109.5	
H2R - C1R - H3R	-	109.6	

Table 2aS Comparison of bond lengths in the investigated molecules as obtained from X-ray Studies.

Bond lengths (Å)	(1)	(2a)	(3)
O1 - C7	1.202(2)	1.198(5)	1.229(5)
N1 - C1	1.356(2)	1.361(5)	1.342(6)
N1 - C5	1.345(2)	1.342(5)	1.394(6)
N1 - C6	1.470(2)	1.487(5)	1.437(6)
N2 - C1	1.361(2)	1.365(6)	1.357(5)
N2 - C7	1.379(3)	1.369(5)	1.369(6)
C1 - C2	1.384(3)	1.389(6)	1.382(7)
C2 - C3	1.368(3)	1.372(6)	1.376(8)
C3 - C4	1.395(3)	1.400(7)	1.395(9)
C4 - C5	1.370(3)	1.358(6)	1.330(8)
C6 - C7	1.519(3)	1.528(5)	1.475(6)
C6 - C8	-	1.529(5)	1.320(7)
C8 - C9	-	1.533(5)	1.462(8)
O2 - C12	-	-	1.376(6)
O2 - C15	-	-	1.439(8)
O1R - C1R	-	1.427(5)	-
O1R - C8	-	1.427(5)	-
N3 - O2	-	1.221(4)	-
N3 - O3	-	1.238(4)	-
N3 - C10	-	1.477(5)	-
C9 - C10	-	1.402(5)	1.384(7)
C9 - C14	-	1.387(5)	1.398(8)
C10 - C11	-	1.372(6)	1.368(8)
C11 - C12	-	1.366(7)	1.408(8)
C12 - C13	-	1.388(6)	1.357(8)
C13 - C14	-	1.387(6)	1.374(8)
N2 - H2A	0.80	0.81(4)	0.81

C2 - H2	0.96	0.94(5)	0.87(5)
C3 - H3	0.96	0.89(4)	1.03(6)
C4 - H4	0.96	0.96(4)	0.84(5)
C5 - H5	0.96	0.90(5)	0.98(5)
C6 - H6A	0.96	0.96	-
C6 - H6B	0.96	-	-
C8 - H8	-	0.93(4)	0.82(5)
C10 - H10	-	-	1.11(6)
C11 - H11	-	0.96	0.87(6)
C12 - H12	-	0.97(4)	-
C13 - H13	-	0.93(4)	1.05(6)
C14 - H14	-	0.89(4)	0.92(6)
C15 - H15A	-	-	0.92
C15 - H15B	-	-	0.92
C15 - H15C	-	-	0.92
C1R - H1R	-	0.98	-
C1R - H2R	-	0.92	-
C1R - H3R	-	0.91	-

Table 2bS Comparison of valence angles in the investigated molecules as obtained from X-ray studies.

Valence angles (°)	(1)	(2a)	(3)
O1- C7 - N2	126.2(2)	126.5(4)	124.2(4)
O1 - C7 - C6	128.1(2)	126.7(4)	128.9(5)
N1 - C1 - N2	109.2 (1)	108.9(4)	108.2(4)
N1 - C1 - C2	120.4(2)	119.8(4)	122.4(4)
N1 - C5 - C4	118.9(2)	119.2(4)	118.2(5)
N1 - C6 - C7	102.6(1)	101.1(3)	102.5(4)
N1 - C6 - C8	-	111.5(3)	122.8(4)
N2 - C1 - C2	130.4(2)	131.4(4)	129.4(5)

N2 - C7 - C6	105.7(1)	106.8(3)	106.9(4)
C1 - N1 - C5	122.4(1)	122.7(4)	120.5(4)
C1 - N1 - C6	110.1(1)	110.6(3)	111.2(4)
C1 - N2 - C7	112.4 (1)	112.5(4)	111.2(4)
C1 - C2 - C3	117.6(2)	117.7(4)	117.0(5)
C2 - C3 - C4	121.2 (2)	121.1(4)	120.0(5)
C3 - C4 - C5	119.4 (2)	119.4(4)	122.0(5)
C5 - N1 - C6	127.5(1)	126.5(3)	128.3(4)
C6 - C8 - C9	-	111.4(3)	133.2(5)
C7 - C6 - C8	-	111.5(3)	134.3(4)
O2 - N3 - O3	-	124.3(3)	-
O2 - N3 - C10	-	117.4(3)	-
O2 – C12 - C11	-	-	114.0(5)
O2 – C12 - C13	-	-	126.2(5)
O3 - N3 - C10	-	118.3(3)	-
N3 - C10 - C9	-	120.6(3)	-
N3 – C10 - C11	-	116.0(4)	-
C8 - C9 - C10	-	123.5(4)	117.5(5)
C8 - C9 - C14	-	120.6(4)	124.7 (5)
C8 – O1R - C1R	-	113.5(3)	-
C9 – C10 - C11	-	123.4(4)	121.2(5)
C9 – C14 - C13	-	121.9(4)	121.4(5)
C10 - C9 - C14	-	115.7(4)	117.8(6)
C10 - C11 - C12	-	119.1(4)	119.7(5)
C11 - C12 - C13	-	120.2(5)	119.7(5)
C12 - O2 - C15	-	-	115.9(5)
C12 - C13 - C14	-	119.7(4)	120.2(5)
O1R - C8 - C6	-	105.2(3)	
O1R - C8 - C9	-	112.8(3)	
N1 - C5 - H5	120	110(3)	114(3)

N1 – C6 - H6A	111	113	
N1 – C6 - H6B	111	-	
C1 – N2 - H2A	122	123(3)	120
C7 – N2 - H2A	126	124(3)	128
C1 - C2 - H2	121	114(3)	120(3)
C2 - C3 - H3	119	116(3)	114(3)
C3 - C2 - H2	120	129(3)	123(3)
C3 - C4 - H4	119	119(3)	126(4)
C4 - C3 - H3	119	123(3)	126(3)
C4 - C5 - H5	120	131(3)	127(3)
C5 - C4 - H4	120	122(3)	112(4)
C6 - C8 - H8	-	105(2)	115(3)
C7 – C6 - H6A	111	108	-
C7 – C6 - H6B	111	-	-
H6A - C6 - H6B	109	-	-
C8 – C6 - H6A	-	110.6	-
C9 - C8 - H8	-	110(2)	111(3)
C9 – C10 - H10			116(3)
C9 – C14 - H14	-	119(3)	116(3)
C10 – C11 - H11	-	118	123(4)
C11 – C10 - H10			123(3)
C11 – C12 - H12	-	121(2)	-
C12 – C11 - H11	-	122(2)	118(4)
C12 – C13 - H13	-	122(2)	114(3)
C13 – C12 - H12	-	118(2)	-
C13 – C14 - H14	-	119(3)	122(3)
C14 – C13 - H13	-	119(2)	124(3)
O2 – C15 - H15A	-	-	104
O2 – C15 - H15B	-	-	113
O2 – C15 - H15C	-	-	106

H15A - C15 - H15B	-	-	113
H15A - C15 - H15C	-	-	106
H15B - C15 - H15C	-	-	113
O1R - C8 - H8	-	112(2)	-
O1R - C1R - H1R	-	104	-
O1R - C1R - H2R	-	109	-
O1R - C1R - H3R	-	112	-
H1R - C1R - H2R	-	106	-
H1R - C1R - H3R	-	112	-
H2R - C1R - H3R	-	112	-

Table 3S Point Charges derived from Natural and Mulliken Population Analyses for (1), (2a) and (3).

	(1)		(2a)		(3)	
Atom	NPA	Mulliken	NPA	Mulliken	NPA	Mulliken
O1	-0.487	-0.404	-0.510	-0.392	-0.563	-0.522
N1	-0.349	-0.061	-0.340	0.245	-0.323	-0.010
N2	-0.631	-0.617	-0.524	-0.485	-0.612	-0.682
H2NA	0.483	0.471	0.478	0.471	0.476	0.466
C1	0.453	0.432	0.458	1.053	0.433	0.227
C2	-0.273	0.015	-0.279	-0.905	-0.273	-0.030
H2	0.292	0.251	0.287	0.244	0.284	0.237
C3	-0.116	-0.410	-0.122	-0.392	-0.150	-0.342
H3	0.289	0.252	0.284	0.244	0.280	0.238
C4	-0.267	-0.028	-0.273	-0.131	-0.268	-0.340
H4	0.294	0.252	0.290	0.246	0.285	0.237
C5	0.080	-0.081	0.081	0.063	0.050	0.098

H5	0.280	0.256	0.291	0.291	0.261	0.231
C6	-0.346	-0.276	-0.146	-1.079	-0.016	0.012
H6A	0.308	0.304	0.324	0.323	-	-
H6B	0.308	0.304	-	-	-	-
C7	0.682	0.345	0.706	0.217	0.644	0.734
C8	-	-	0.085	0.626	-0.077	-0.342
H8	-	-	0.256	0.214	0.239	0.174
C9	-	-	-0.078	1.273	-0.118	0.972
C10	-	-	0.067	-0.336	-0.169	-0.732
H10	-	-	-	-	0.284	0.199
C11	-	-	-0.198	0.241	-0.371	-0.372
H11	-	-	0.287	0.248	0.263	0.223
C12	-	-	-0.213	-0.428	0.400	0.135
H12	-	-	0.269	0.220	-	-
C13	-	-	-0.184	-0.106	-0.313	-0.621
H13	-	-	0.267	0.218	0.263	0.208
C14	-	-	-0.208	-1.206	-0.150	-0.994
H14	-	-	0.273	0.236	0.284	0.271
N3	-	-	0.502	-0.512	-	-
O2	-	-	-0.454	0.087	-0.492	-0.343
O3	-	-	-0.322	0.030	-	-
C15			-	-	-0.336	-0.324
H15A			-	-	0.226	0.226
H15B			-	-	0.256	0.238
H15C			-	-	0.226	0.226
O1R			-0.607	-0.234	-	-
C1R			-0.325	-0.250	-	-
H1RA			0.248	0.230	-	-
H1RB			0.210	0.207	-	-

H1RC		0.220	0.230	-	-