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LUMINESCENCE AND SCINTILLATION PROPERTIES OF SOME 1, 2-DISUBSTITUTION PRODUCTS OF BENZIMIDAZOLE

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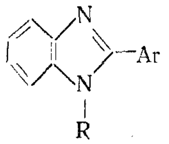
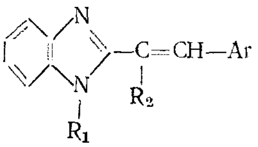
The absorption and photoluminescence spectra of 71 derivatives of benzimidazole have been studied. The relation between the chemical structure and the light yield in solution is discussed. The scintillation efficiency of the compounds in toluene solution has been measured. Several easily soluble derivatives of 2-arylbenzimidazole have the same scintillation efficiency as p-terphenyl (5 g/*l*).

This paper constitutes the extension of earlier work on spectral and scintillation properties in the benzazole series. Earlier [1-4] we studied these for the benz- and naphthoxazoles.

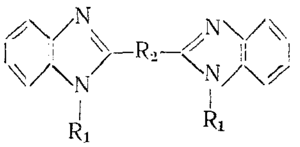
Here we present results on the luminescence, absorption spectra, and the scintillation properties in solution for some benzimidazoles. The aryl derivatives have not previously been studied as scintillators, although they possess (in analogy with the benzoxazoles) a conjugated system that extends to the pair of p-electrons on the nitrogen heteroatom. The H in the NH-group may be replaced by various radicals to produce more derivatives than in the benzoxazole series. In [5] we described the synthesis of the arylbenzimidazoles (I)-(VIII)*; the substituents in position 2 are the same as in the benzoxazole series [1, 3]:



$R=H$ (I), CH_3(II),
C_6H_5(III). CH_2Ar(IV)



$R_1=R_2=H$(V),
$R_1=H$, $R_2=C_6H_5$(VI),
$R_1=CH_3$, $R_2=H$(VII)



(VIII)

$R_1=H$, $R_2=—CH=CH—$, p—C_6H_4
$R_1=CH_3$, $R_2=—CH=CH—$

Measurements were made of the absorption and photoluminescence spectra in benzene solution, the quantum yield B_q^f relative to 2, 5-diphenyloxazole, the mean wavelength of the luminescence λ_m, and the scintillation efficiency s relative to p-terphenyl in toluene (5 g/*l*). The apparatus used and the measuring conditions have been described [2, 3]. The luminescence and scintillation properties of disubstituted benzoxazoles and benzimidazoles have been compared in [2], showing that the main effect on the absorption and luminescence spectra in the 1, 2-disubstituted benzimidazoles comes from the substituents in the 2-position, and that the substituent on N^1 in the imidazole ring has mainly an induction effect, or (for bulky substituents) a spatial interaction as well. Table 1 indicates the effects of various substituents in position 2 on the optical and scintillation properties of compounds (I)-(IV); these agree with the conclusions of [2, 3].

Measurement of s for the 2-arylbenzimidazoles showed that a series of very soluble compounds with CH_3, C_6H_5, or CH_2Ar in position 1 had the same scintillation properties as p-terphenyl. Of these, the easily accessible compounds (IV) deserve attention.

To the unsymmetrical benzimidazolylarylethylenes (V)-(VII) we may apply all that has been said of similar benzoxazoles [1, 3]. The absorption maxima of (V) and (VII) agree fairly well in position and ε (Tables 2 and 3). The optical characteristics of (VI) also suggest that the phenyl radical ($R_2 = C_6H_5$) is somewhat displaced from the plane of the molecule.

Compounds (V) and (VII) differ from the benzoxazolylarylethylenes in showing considerable luminescence; they show a considerably larger Stokes displacement than the 2-arylbenzimidazoles, especially the N-methyl derivatives of (VII). The B_q^f depend markedly on the substituent in the phenyl ring, as in the benzoxazolylarylethylenes [3]. B_q^f falls from 0.60 to 0.02, and the groups may be placed in the order: p-C_6H_4—C_6H_5, 1-$C_{10}H_7$, p-C_6H_4Cl, p-C_6H_4Br, C_6H_5, p-C_6H_4F, p-$C_6H_4CH_3$, p-$C_6H_4OCH_3$, 3,4-$C_6H_3(OCH_2O)$, 3,4-$C_6H_3(OCH_3)_2$ (Table 3). Photoluminescence is absent in the dialkylaminophenyl derivative (V).

The fall in B_q^f of the ethylenes as compared with those when the aryl is directly connected to the heterocyclic ring must be due to an increased degree of free rotation around the additional single C—C bond, which is especially marked for systems such as solutions in benzene at ordinary temperatures. But the effects of the groups on B_q^f and s (Tables 2 and

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* Compounds not given in [5] and made for the first time are briefly characterized in Table 1.

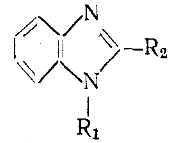

TABLE 1

Optical and scintillation characteristics of 1, 2-substituted benzimidazoles (I)-(IV)'

R_2	R_1	Maximum absorption, nm	lg ε	Photoluminescence spectra					S	
				λ_1, nm	λ_2, nm	λ_3, nm	λ_m, nm	B_q^f	concn. g/l	% of 5 g/l p-terphenyl in toluene
H	H	245**	3.76	less than 330 nm (outside range of instrument)					2.5*	17
"	C_6H_5	250**	4.29						5	39
"	p-$C_6H_4OCH_3$	247**	4.37						5	41
C_6H_5	H	302	4,40	345	360	—	365	0,82	0.45*	68
"	CH_3	295	4.28	347	358	—	364	0,84	5	95
"	$CH_2C_6H_5$	293	4,35	348	360	—	367	0,78	5	94
"	C_6H_5	295	4.36	349	360	—	365	0.65	5	87
p-C_6H_4F	H	304	4.18	343	357	—	366	0.76	0.5*	69
"	CH_3	295	4,35	345	360	—	367	0.78	4	83
"	—CH_2-p-C_6H_4F	295	4.64	348	361	—	369	0,70	5	87
"	C_6H_5	295	4,65	347	360	—	365	0.63	5	82
p-C_6H_4Cl	H	310	4,26	350	360	—	373	0,85	0.5*	69
"	CH_3	298	4.55	—	357	—	372	0.87	5	90
"	CH_2-p-C_6H_4Cl	297	4.46	352	368	—	370	0.80	5	86
"	C_6H_5	300	4,35	—	362	—	376	0,79	5	87
C_6H_4Br	H	310	4.40	352	370	—	372	0.25	0,3*	25
"	CH_3	302	4.31	348	365	—	373	0.29	5	33
"	CH_2-p-C_6H_4Br	299	4.54	353	370	—	372	0.22	5	29
"	C_6H_5	300	4.33	347	366	—	375	0.24	5	34
p-$C_6H_4CH_3$	H	306	4,52	352	360	—	370	0.73	0.4*	57
"	CH_3	296	4.39	352	360	—	370	0.73	5	97
"	CH_2-p-$C_6H_4CH_3$	295	4.36	348	363	—	369	0,75	5	94
"	C_6H_5	302	4.30	348	360	—	367	0.65	5	90
p-$C_6H_4OCH_3$	H	310	4,46	350	364	—	370	0.74	0.4*	70
"	CH_3	296	4.47	350	368	—	370	0.68	5	91
"	CH_2-p-$C_6H_4OCH_3$	296	4.45	350	367	—	372	0.77	5	94
"	C_6H_5	300	4.22	352	360	—	370	0.82	5	98
3,4-$C_6H_3(OCH_3)_2$	H	315	4.70	350	364	—	372	0,93	0,4*	68
"	CH_3	303	4,28	337	353	—	373	0,85	5	94
"	CH_2-3,4-$C_6H_3(OCH_3)_2$	302	4.52	—	355	—	373	1,02	5	95
"	C_6H_5	305	4,15	—	360	—	378	0.82	5	95
3,4-$C_6H_3(OCH_2O)$	H	313	4.48	—	357	—	372	0.94	5	93
"	CH_3	305	4.40	—	357	—	373	0,95	5	95
p-$C_6H_4N(CH_3)_2$	H	330	4,66	365	380	—	396	1.20	0,20*	57
"	CH_3***	317	4,59	363	382	—	390	1,13	5	108
"	C_6H_5	325	4,60	—	390	—	402	1.00	4	103
p-$C_6H_4N(C_2H_5)_2$	H	337	4.69	368	380	—	397	1.06	0.20*	53
"	CH_3****	317	4.58	364	383	—	396	0.92	4	107
"	C_6H_5	327	4.57	368	392	—	405	0,82	4	95
p-C_6H_4—C_6H_5	H	315	4.72	362	375	390	393	0.99	0.45*	68
"	CH_3	306	4.48	362	375	392	393	0.99	5	107
"	CH_2-p-C_6H_4—C_6H_5	305	5,55	362	375	395	391	0.98	5	100
"	C_6H_5	307	4.57	362	375	392	392	0,82	5	90
1-$C_{10}H_7$	H	318	4.35	362	382	405	400	0,70	0,7*	64
"	CH_3	297	4.22	—	382	—	407	0.50	5	93
"	CH_2-1-$C_{10}H_7$	285	4.38	363	375	398	398	0.73	5	91
"	C_6H_5	285	4,32	365	380	—	385	0.25	5	47

[*] Concentration of saturated solution in toluene.

[**] In n-heptane.

[***] Obtained from N-methyl-o-phenylenediamine and p-dimethylaminobenzaldehyde [5], m. p. 154-156° (from mixture of n-heptane with benzene). Found %: C 76. 33; H 6. 70; N 16. 65. $C_{16}H_{17}N_3$. Calculated %: C 76. 49; H 6. 77; N 16. 73.

[****] Obtained by methylation of the silver salt of 2-(p-diethylaminophenyl)benzimidazole, as in [5]; m. p. 116-118° (from mixture of n-heptane with benzene). Found % C 77. 49; H 7. 34; N 15. 31. $C_{18}H_{21}N_3$. Calculated %: C 77. 42; H 7. 52; N 15. 06.

3) resemble those for the benzoxazolylarylethylenes [3] in being the opposite of those found for the 2-arylbenzimidazoles (Table 1) and 2-arylbenzoxazoles [3]. Methoxy, dimethoxy, and dialkylaminophenyl groups in the latter increase the photoluminescence and scintillation yield (relative to the phenyl derivative), but here they reduce these quantities considerably. On the other hand, bromine quenches the luminescence heavily in the benzoxazoles [3] and in benzimidazoles (I)-(IV) but here gives an emission considerably greater than that from the phenyl derivative.

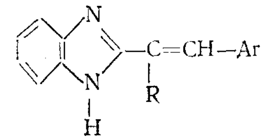

TABLE 2

Spectral characteristics of N-unsubstituted unsymmetrical benzimidazolylarylethylenes (V) and (VI)

R	Aryl	Absorption spectra		λ_{max} of luminescence, nm	s	
		λ_{max}, nm	lg ε		concn, g/l	% to n-terphenyl
H	C_6H_5	337	4.61	388	0.2*	37
"	p-C_6H_4F	335	4.58	390	"	36
"	p-C_6H_4Cl	346	4.60	392	"	41
"	p-C_6H_4Br	347	4.59	395	"	51
"	p-$C_6H_4OCH_3$	345	4.75	—	0.3*	20
"	p-$C_6H_4N(CH_3)_2$	375	4.88	—	0.1*	<10
"	p-C_6H_4—C_6H_5	350	4.81	415	0.2*	43
"	1—$C_{10}H_7$	350	4.60	420	0.3*	34
C_6H_5	p-C_6H_4F	332	4.54	386	0.2*	33
"	p-C_6H_4Cl	340	4.60	387	"	38
"	p-C_6H_4Br	340	4.58	390	"	46

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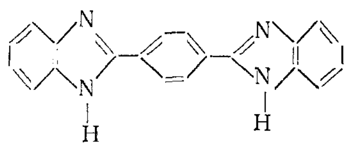
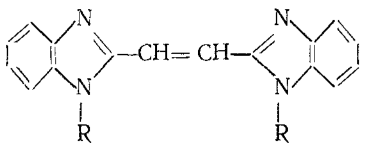
* Slightly soluble in toluene. Approximate concentration of saturated solution given.

The symmetrical bis-benzimidazoles (VIII) are separated by p-phenyl and ethylene groups, and have strong fluorescence, as in the benzoxazole series:





λ_{max} abs. =340 nm

" lum.=372,392 nm

R=H; λ_{max} abs. =342 nm

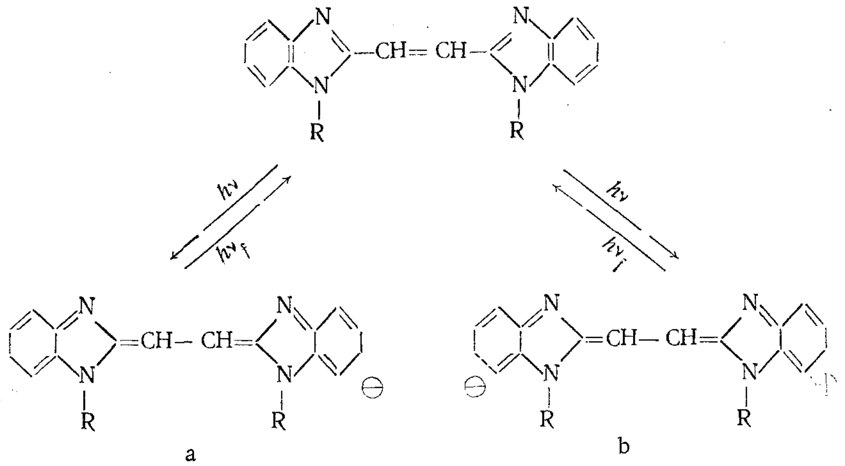
" lum.=390,415 nm

R=CH_3; " abs. =350 nm

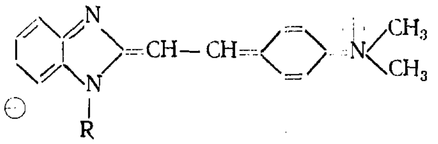
" lum.=415 nm

Their failing is poor solubility. The most soluble 1, 2-di[2'(1'-methyl)benzimidazolyl]ethylene (s = 76% for 0.5 g/l relative to 5 g/l p-terphenyl) may be of interest as a second solute.

Symmetrical structure is advantageous, as in the ethylene of benzimidazole and benzoxazole [3], perhaps because the electron distribution tends towards the equivalent a and b structures on excitation:



The unsymmetrical 2-styrylbenzimidazole has the phenyl ring as an electron acceptor relative to the benzimidazole system [6], which reduces the basicity of the nitrogen ring and so produces a more uniform electron-density distribution over the molecule. The acceptor properties of the halogens have an analogous effect; the 2-benzimidazolyl-(p-halophenyl)-ethylenes (even the bromine derivatives) show higher light yield than does 2-styrylbenzimidazole. The methoxy and dialkylamino groups act with the phenyl ring as electron donors with respect to the benzimidazole system, which results in a very nonuniform electron distribution even in the ground state, in which the δ^+ charge is on the methoxy or dialkylamino group and δ^- on the benzimidazole ring. The molecular structure in the excited state will most probably approach the limiting one:



This impediment to free electron migration along the molecule on excitation may be a cause of the internal quenching in this kind of compound.

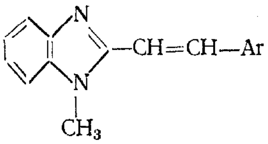


TABLE 3

Spectral characteristics of 1-[2'-(1'-methyl)benzimidazolyl] -2-arylethylenes (VII)

Aryl	Absorption spectra		Photo luminescence spectra					s	
	λ_{max}, nm	lg ε	λ_1, nm	λ_2, nm	λ_3, nm	λ_m, nm	B_q^f	concn. g/l	% to n-terphenyl
C_6H_5	337	4,56	390	410	435	432	0,24	5	54
p-C_6H_4F	337	4,57	390	412	430	430	0,13	6	41
p-C_6H_4Cl	343	4,60	393	416	442	435	0,37	5	78
p-C_6H_4Br	345	4,56	395	417	443	437	0,32	4	78
p-$C_6H_4CH_3$	342	4,58	390	413	440	430	0,09	5	33
p-$C_6H_4OCH_3$	346	4,61	390	420	—	439	0,03	6	16
3,4—$C_6H_3(OCH_3)_2$	355	4,59	390	422	—		0,02	5	15
3,4—$C_6H_3(OCH_2O)$	353	4,68	395	420	—		0,03	5	22
p-C_6H_4—C_6H_5	352	4,68	410	432	(460)	451	0,60	5	87
1-$C_{10}H_7$	350	4.56	420	443	(467)	462	0.46	5	75

The authors are indebted to Professor I. Ya. Postovskii for attention to the work and discussion of the results.

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