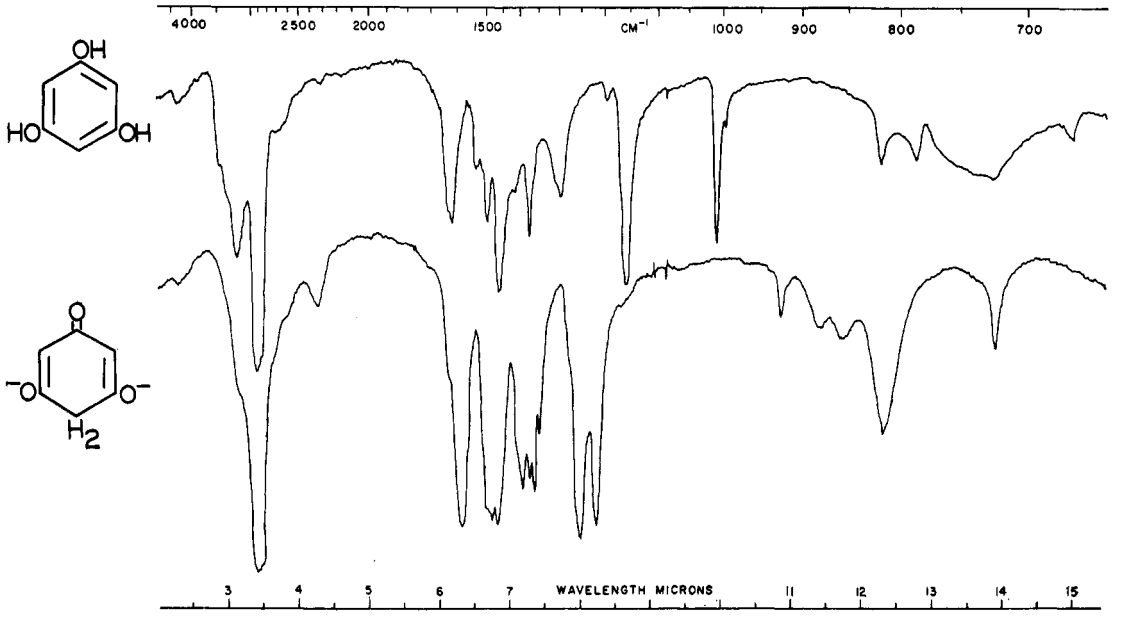

Figure 1.

benzoate and disodium phloroglucinolate shows peaks near τ 2.5 and 6.93 in the anticipated ratio of 5:2.

The chemical shift of the observed peaks is relatively insensitive to changes in concentration and temperature. Warming, however, produced the broadening to be expected of the increased rate of exchange, with the eventual disappearance of the separate peaks into the solvent peak at about 75°.[9] Addition of further sodium hydroxide increased the rate of exchange at room temperature, with the eventual disappearance of the C–H proton peak.

TABLE II

DISSOCIATION CONSTANTS OF SELECTED DIBASIC PHENOLS[a]

	$K_1 \times 10^9$	$K_2 \times 10^{12}$
Phloroglucinol	3.56	1320
Pyrogallol	9.67	2.30
Resorcinol	0.71	4.78
Catechol	0.75	0.84
Hydroquinone	0.12	0.92

[a] C. T. Abichandani and S. K. Jatkar, *J. Indian Inst. Sci.*, **A21**, 417 (1938).

These observations demonstrate clearly that phloroglucinol and its monosodium salt exist in an aromatic structure, while the disodium salt exists as the alicyclic tautomer (II).

The infrared spectra of Nujol mulls of phloroglucinol and the disodium salt both show strong absorption near 1600 cm.$^{-1}$ but differ markedly at lower frequencies (see Fig. 1). The strong aromatic oxygen peaks of the phloroglucinol are absent in the spectrum of the disalt, which evidently also exists in the alicyclic form (II) in the solid state.

The unusual structure of the dianion is associated with unusual acidity. As Table II shows, the second dissociation constant of resorcinol is approximately 300 times smaller than that of phloroglucinol, while those of other polyphenols are even smaller.

(9) *Cf.* J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p. 218.

The Ionization Constants, Ultraviolet and Infrared Spectra of Some Substituted Benzimidazoles

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The benzimidazole ring is of considerable chemical and biological interest and has been the subject of many papers. Review articles on benzimidazoles may be consulted for leading references in this field.[1a-c] A considerable amount of work on benzimidazole chemistry has been carried out in this laboratory by several workers. This interest in benzimidazole chemistry has prompted us to start a systematic study of various physical properties of substituted benzimidazoles in order to observe the effect of substituents on the physical properties of the ring. Because of the importance of the benzimidazole ring, more data on the ionization constants and spectroscopic characteristics of substituted benzimidazoles appeared desirable.

Experimental and Results

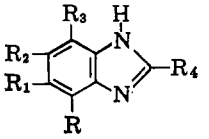
The benzimidazoles used in this study were either available commercially or prepared by well-known procedures. All compounds were recrystallized from the appropriate solvents to constant melting points. All melting points are uncorrected. Melting points and appropriate references are shown in Table I. The ionization constants of various substituted benzimidazoles are also listed in Table I.

The pK_a values shown in Table I were determined by potentiometric titration. A Leeds and Northrup pH meter equipped with glass and saturated calomel electrodes was used to follow the pH of each solution during its titration. The pH meter was calibrated against two buffers: (1) 0.05 *M* potassium phthalate

(1) (a) J. B. Wright, *Chem. Rev.*, **48**, 437 (1951); (b) K. Hofmann, "The Chemistry of Heterocyclic Compounds," A. Weissberger, Ed., Interscience Publishers, Inc., New York, N. Y., 1953, p. 379; (c) E. S. Schipper and A. R. Day, "Heterocyclic Compounds," Vol. 5, Elderfield, Ed., John Wiley and Sons, Inc., New York, N. Y., 1957, p. 194.

TABLE I

IONIZATION CONSTANTS AND MELTING POINTS OF SUBSTITUTED BENZIMIDAZOLES



R	R_1	R_2	R_3	R_4	pK_a, in 5:95 ethanol–water (0.1 M in NaCl) at 30 ± 0.5°C.	Lit. pK_a In water	Lit. pK_a In 50% ethanol	M.p., °C.	Lit. m.p., °C.
H	H	H	H	H	5.52	5.53[a]	4.98[b]	169–170	170–172[b]
H	CH_3	H	H	H	5.65	5.81[b]	5.32[b]	116–118	114[b]
H	OCH_3	H	H	H	5.72		5.07[b]	123–124	123[b]
H	OC_2H_5	H	H	H	5.70			117–118	118–119[b]
H	NO_2	H	H	H	4.50	3.80[c]	2.68[b]	205	204–206[d]
H	H	H	NO_2	H	4.55	3.80[c]		247–248	248–249[d]
H	H	H	H	CH_3	6.10	6.19[b]	5.77[b]	175–176	178.5 179[b]
H	H	H	H	C_2H_5	6.15	6.20[b]	5.69[b]	172–173	177[b]
H	H	H	H	i-C_3H_7	6.08	6.23[b]	5.79[b]	232–233	225–226[e]
H	H	H	H	$CH(OH)CH_3$	5.55			178–180	178.5–179.5[f]
H	H	H	H	$CH_2C_6H_5$	5.70			187	189[b]
H	H	H	H	C_6H_5	5.33		4.51[b]	290	290[b]
H	H	H	H	$COCH_3$	4.61			190–193	188–189[g]
H	H	H	H	CF_3	4.51			209–210	210–210.5[h]
H	CH_3	CH_3	H	H	5.99	5.98[b]	5.48[b]	203–204	204–205[b]
OCH_3	H	H	OCH_3	H	5.63			228	218–222[i]
H	OCH_3	OCH_3	H	H	5.81			183–185	179–183[i]
H	Cl	Cl	H	H	4.74		3.26[b]	204–205	204–205[j]
H	NO_2	H	OCH_3	H	4.65			265–266	258–260[k]
H	Cl	H	H	CH_3	5.68			208–209	215–218[l]
H	Cl	H	NO_2	H	4.60			228–229	229–230[m]
H	CH_3	H	H	$CH(OH)CH_3$	5.70			183–184	183–184[f]
H	OCH_3	H	H	$CH(OH)CH_3$	5.59			160–161[n]	
H	NO_2	H	H	$CH(OH)CH_3$	4.65			200–202	204–205[f]
H	Cl	H	H	$CH(OH)CH_3$	5.08			175–176	178–179[f]
OCH_3	H	H	OCH_3	$CH(OH)CH_3$	5.10			171–172[o]	
H	CH_3	CH_3	H	CH_3	6.26		6.29[b]	233–234	233–234[b]
H	CH_3	CH_3	H	C_2H_5	6.39			223–224	223–224[p]
H	CH_3	CH_3	H	i-C_3H_7	6.35			206–207	206–207[p]
H	CH_3	CH_3	H	$CH_2C_6H_5$	6.07			104–105[q]	
H	OCH_3	NO_2	H	CH_3	4.88			172–173	172–174[r]
H	OCH_3	H	NO_2	CH_3	4.90			203–204	204–205[r]
OCH_3	Br	H	OCH_3	CH_3	5.18			176–177	177–181[s]

[a] G. Schwarzenbach and K. Lutz, *Helv. Chim. Acta*, **23**, 1162 (1940); A. Albert, R. J. Goldacre, and J. Phillips, *J. Chem. Soc.*, 2240 (1948). [b] K. Hofmann, "The Chemistry of Heterocyclic Compounds," A. Weissberger, Ed., Interscience Publishers Inc., New York, N. Y., 1953, p. 379. [c] J. L. Rabinowitz and E. C. Wagner, *J. Am. Chem. Soc.*, **73**, 3030 (1951). [d] E. C. Fisher and M. M. Joullié, *J. Org. Chem.*, **23**, 1944 (1958). [e] D. Jerchel, H. Fischer, and M. Kracht, *Ann.*, **575**, 162 (1952). [f] W. R. Siegart and A. R. Day, *J. Am. Chem. Soc.* **79**, 4391 (1957). [g] H. Matrick, Ph.D. thesis, University of Pennsylvania, 1960, p. 93. [h] W. T. Smith, Jr., and E. C. Steinle, Jr., *J. Am. Chem. Soc.*, **75**, 1292 (1953). [i] L. Weinberger and A. R. Day, *J. Org. Chem.*, **24**, 1451 (1959). [j] M. T. Davies, P. Mamalis, V. Petrow, and B. Sturgeon, *J. Pharm. Pharmacol.*, **3**, 420 (1951). [k] H. B. Gillespie, M. Engelman, and S. Graff, *J. Am. Chem. Soc.*, **76**, 3531 (1954). [l] E. J. VanLare, U. S. Patent 2,739,149 (March 20, 1956). [m] J. R. Hoover and A. R. Day, *J. Am. Chem. Soc.*, **77**, 4324 (1955). [n] *Anal.* Calcd. for $C_{10}H_{12}N_2O_2$: C, 62.50; H, 6.25; N, 14.58. Found: C, 62.67; H, 6.07; N, 14.38. [o] *Anal.* Calcd. for $C_{11}H_{14}N_2O_3$: C, 59.46; H, 6.31; N, 12.61. Found: C, 59.25; H, 6.39; N, 12.42. [p] Personal communication from Aldrich Chemical Co., Inc., Milwaukee 10, Wis. [q] *Anal.* Calcd. for $C_{12}H_{12}N_2$: C, 76.60; H, 8.51; N, 14.89. Found: C, 76.38; H, 8.36; N, 14.84. [r] H. B. Gillespie, M. Engelman, F. Spano, and S. Graff, *J. Am. Chem. Soc.*, **79**, 2245 (1957).

(pH 4.00 at 30°) and (2) 0.025 M potassium dihydrogen phosphate and 0.025 M disodium hydrogen phosphate (pH 6.85 at 30°). The solutions to be titrated were prepared by dissolving 1×10^{-5} mole of compound in 5 ml. of distilled water and 5 ml. of absolute ethanol to make 10 ml. of solution. This solution was then mixed with 25 ml. of 0.4 M sodium chloride solution and 65 ml. of distilled water. The resulting solution (100 ml.) was 1×10^{-4} M with respect to the compound analyzed and was titrated with 1×10^{-3} M of hydrochloric acid which had been standardized against sodium carbonate using methyl purple as the indicator. The sodium chloride was used to keep the ionic strength of the solution constant during the titrations.[2]

(2) J. L. Irwin and E. M. Irwin, *J. Am. Chem. Soc.*, **69**, 1091 (1947).

The ultraviolet spectra were obtained on a Beckman DU spectrophotometer modified by Process and Instruments Co. with an attached Leeds and Northrup Speedomax Type G recorder with 1-cm. quartz cells.

Solutions which were 1×10^{-4} M in absolute ethanol, 0.01 N hydrochloric acid (pH 2.02), and 0.01 N sodium hydroxide (pH 12.12) were prepared for each compound. The 0.01 N hydrochloric acid was prepared from 0.1 N hydrochloric acid purchased from Arthur H. Thomas Co. The 0.01 N sodium hydroxide was prepared accurately, and its normality was checked by titration with 0.01 N hydrochloric acid, using phenolphthalein as the indicator.

The optical densities used to calculate the molecular extinction coefficients were uncorrected values. The characteristic bands

TABLE II

CHARACTERISTIC BANDS IN THE ULTRAVIOLET SPECTRA OF SOME SUBSTITUTED BENZIMIDAZOLES

R	R_1	R_2	R_3	R_4	λ_{max}^{EtOH} (log ϵ), mμ	λ_{max}^{HCl} (log ϵ), mμ[a]	λ_{max}^{NaOH} (log ϵ), mμ[a]
H	H	H	H	C_2H_5	280 (3.89), 272 (3.91), 243 (3.80)	274 (3.91), 268 (3.92), 235 (3.61)	277 (3.75), 271 (3.74), 240 (3.63)
H	H	H	H	$CH(CH_3)_2$	280 (3.84), 272 (3.86), 241 (3.73)	274 (3.85), 267 (3.87)	278 (3.65), 270 (3.63), 240 (3.49)
H	CH_3	CH_3	H	C_2H_5	287 (3.78), 281 (3.85), 244 (3.65)	283 (3.93), 274 (3.93)	286 [3.71],[b] 280 [3.79], 243 [3.52]
H	CH_3	CH_3	H	$CH(CH_3)_2$	286 (3.81), 282 (3.88), 246 (3.71)	283 (3.91), 274 (3.92)	286 [3.68], 281 [3.75], 243 [3.41]
H	CH_3	CH_3	H	$CH_2C_6H_5$	287 (3.83), 283 (3.89), 246 (3.73)	285 (3.96), 277 (3.97)	286 [3.40]
H	H	H	H	$COCH_3$	300 (3.92), 235 (3.65)	300 (3.76), 275 (3.83), 267 (3.77), 234 (3.64)	320 (3.97), 237 (3.74)
H	H	H	H	CF_3	281 (3.72), 274 (3.79), 266 (3.76) 246–252 (3.71)		
H	Cl	H	H	CH_3	287 (3.76), 281 (3.86), 246 (3.74)	283 (3.86), 275 (3.89), 234–238 (3.56)	285 (3.70), 280 (3.69), 243 (3.42)
H	Cl	Cl	H	H	293 (3.70), 284 (3.80), 252 (3.61)	289 (3.74), 281 (3.84), 243–246 (3.50)	290 (3.55)
H	OC_2H_5	H	H	H	290 (3.71), 286 (3.74), 243 (3.58)	283 (3.84)	283 (3.76), 241 (3.49)
H	OCH_3	OCH_3	H	H	289 (3.84), 243 (3.48)		
OCH_3	H	H	OCH_3	H	251 (3.77)	263–266 (3.79)	249 (3.58)
OCH_3	Br	H	OCH_3	CH_3	251 (3.70)	260 (3.75)	251 (3.58)
OCH_3	NO_2	H	H	H	300 (3.81), 234 (3.97)	277 (3.88), 243 (3.91)	360–380 (3.89), 243–246 (3.91)
NO_2	OCH_3	H	H	H	366–372 (3.83), 306–309 (3.67)	349–352 (3.54), 280 (3.90)	380–400 [3.60]
NO_2	Cl	H	H	H	303–312 (3.74)	277 (3.87)	368–380 (3.88), 234 (3.83)
H	OCH_3	NO_2	H	CH_3	340 (3.57), 295 (3.60), 251–254 (3.90), 237 (3.94)	340 (3.40), 246–249 (3.90), 234–237 (3.87)	368–380 (3.94), 254–257 (3.79)
NO_2	OCH_3	H	H	CH_3	308–311 (3.76)	342–352 (3.56), 288–291 (3.76), 247 (3.67)	360–380 (3.78)
H	H	H	H	H	279 (3.81), 272 (3.82), 243 (3.68)	274 (3.88), 266 (3.90)	278 (3.67), 272 (3.66), 241 (3.40)
H	CH_3	H	H	H	284 (3.89), 278 (3.91), 244 (3.75)	280 (3.89), 272 (3.91)	283 (3.79), 277 (3.79), 243 (3.53)
H	Cl	H	H	H	286 (3.83), 281 (3.92), 246 (3.76)	284 (3.90), 275 (3.93), 240 (3.59)	286 (3.69)
H	NO_2	H	H	H	306 (3.89), 234–237 (3.99)	280 (3.95), 226–229 (3.95)	360–366 (3.94), 249 (3.93)
H	OCH_3	H	H	H	286–289 (3.79), 243–246 (3.57)	284 (3.93)	286–289 (3.71)
OCH_3	H	OCH_3	H	H	254 (3.80)	266 (3.79)	254 (3.47)

[a] The hydrochloric acid and sodium hydroxide were 0.01N. [b] The values in brackets are approximate due to insufficient solubility.

in the ultraviolet spectra of the substituted benzimidazoles studied are shown in Table II.

All infrared measurements were made on a Perkin-Elmer Model 421 spectrophotometer. The machine was calibrated against a polystyrene film and all values were corrected. All compounds were studied as potassium bromide disks. The characteristic bands in the infrared spectra of the substituted benzimidazoles studied are shown in Tables III, IV, V and VI.

Discussion

The pK_a values of various substituted benzimidazoles under various conditions have been reported in the literature. The most complete study of ionization constants of substituted benzimidazoles has been carried out by Davies, Mamalis, Petrow, and Sturgeon, who determined the pK_a values of a large number of substituted benzimidazoles both in water and 50% aqueous ethanol.[3] It is apparent from the literature that pK_a values obtained under different conditions vary considerably. In order to establish any correlation among various substituted benzimidazoles the same conditions must be used. The choice of water as a solvent is satisfactory, but too few benzimidazoles are sufficiently soluble in water. Although 50% aqueous ethanol is a good solvent for most benzimidazoles, pK_a determinations in organic solvents are not too accurate. To overcome this difficulty we have used just enough ethanol to dissolve all of the benzimidazoles studied, and the same small amount was used in all cases. These solutions were then diluted carefully with water to the same volume. The values obtained under these conditions appeared to be in good agreement with values previously determined in aqueous medium. Since our values were determined under identical conditions, they may be compared among themselves. Electron-donating groups such as alkyl groups and alkoxyl groups increase the basic character of the benzimidazole ring. Electron-withdrawing groups such as the nitro, trifluoromethyl, phenyl, and acetyl groups decrease the basicity of benzimidazole. Position is an important factor in determining basicity,

(3) M. T. Davies, P. Mamalis, V. Petrow, and B. Sturgeon, *J. Pharm. Pharmacol.*, **3**, 420 (1951).

TABLE III

CHARACTERISTIC BANDS IN THE SPECTRA OF SOME MONOSUBSTITUTED BENZIMIDAZOLES[a]

R = NO_2	R_1 = OCH_3	R_1 = OC_2H_5	R_1 = NO_2	R_4 = $CH_2C_6H_5$	R_4 = C_6H_5	R_4 = $COCH_3$[b]
1637 m	1633 s	1629 s	1625 m	1628 m	1624 m	1620 m
1585 m	1595 s	1593 m	1593 m	1605 w	1606 w	1584 m
1526 s	1509 m	1518 s	1514 s	1590 m	1595 ms	1509 s
1483 s	1473 s	1476 s	1480 w	1538 s	1543 m	1491 s
1416 s	1463 s	1461 s	1451 s	1498 s	1498 s	1445 s
1360 s	1428 w	1429 s	1406 s	1489 m	1480 s	1424 s
1335 s	1398 s	1398 m	1374 m	1459 s	1463 s	1389 s
1294 s	1350 s	1368 w	1349 s	1430 s	1444 s	1379 s
1259 s	1295 s	1350 m	1316 w	1389 m	1408 s	1358 s
1229 w	1285 s	1306 s	1300 m	1328 m	1378 s	1316 s
1210 w	1275 w	1291 s	1265 m	1319 m	1346 s	1283 m
1186 m	1245 s	1255 s	1244 m	1275 s	1318 s	1233 s
1164 m	1197 s	1202 s	1198 w	1228 m	1280 s	1148 s
1121 s	1190 s	1174 s	1182 w	1197 w	1231 s	1133 m
1066 m	1153 s	1110 s	1134 w	1177 w	1189 m	1123 m
1000 w	1132 m	1089 w	1108 w	1161 w	1161 w	1016 m
935 s	1116 w	1041 s	1068 s	1150 m	1150 m	1007 m
882 w	1027 s	962 s	953 s	1110 w	1121 s	990 m
857 m	950 s	952 s	897 m	1077 w	1115 s	956 m
808 m	917 w	905 m	839 m	1025 s	1075 w	903 w
798 m	880 m	810 s	829 m	1014 s	1028 m	856 w
728 s	832 s	764 w	817 s	1002 ms	1007 m	812 m
	792 s	748 w	794 s	990 w	969 s	772 m
	748 m		762 w	966 w	927 m	747 s
			740 s	928 ms	889 m	
				890 m	849 w	
				849 m	811 m	
				830 w	781 m	
				768 s	766 s	
				747 s	738 s	
				722 s	703 s	

[a] Bands are in cm.$^{-1}$. [b] ν_{max} 1664 cm.$^{-1}$ (C=O for the ketone group).

TABLE IV

CHARACTERISTIC BANDS IN THE SPECTRA OF SOME SUBSTITUTED 2-(1-HYDROXYMETHYL)BENZIMIDAZOLES[a]

R = H	R_1 = CH_3	R_1 = Cl	R_1 = NO_2	R_1 = OCH_3	R = R_3 = OCH_3
1625 m	1632 m	1624 m	1628 s	1629 s	1632 w
1593 m	1596 m	1588 m	1598 m	1598 m	1528 s
1535 m	1533 m	1530 m	1540 m	1530 m	1450 m
1488 m	1456 s	1473 s	1510 s	1491 s	1424 s
1458 s	1443 s	1447 s	1468 s	1460 s	1405 m
1439 s	1421 m	1424 s	1413 s	1429 s	1371 m
1372 s	1375 m	1414 s	1378 w	1376 m	1349 w
1321 s	1314 s	1378 m	1335 s	1309 s	1310 w
1305 s	1301 s	1316 s	1304 s	1279 s	1270 m
1274 s	1282 m	1296 m	1245 m	1239 m	1255 s
1224 m	1232 m	1279 m	1218 m	1202 s	1230 m
1146 m	1145 s	1243 w	1106 m	1149 s	1192 w
1122 s	1132 m	1219 m	1079 s	1109 s	1172 m
1111 s	1102 s	1106 s	1064 m	1086 m	1119 m
1088 s	1086 s	1086 m	1028 m	1029 s	1092 s
1044 m	1049 w	1061 m	990 m	997 m	1072 m
1009 m	1040 m	992 s	948 m	954 m	1053 m
990 s	993 s	927 m	895 m	912 m	994 w
971 w	948 m	902 m	845 m	835 m	984 m
916 m	907 m	856 m	825 m	801 s	898 w
814 s	869 m	798 s	755 m	768 w	787 m
766 m	831 m	755 w	735 m	724 w	723 m
737 s	791 s	706 m			
	759 m				
	728 w				
	703 w				

[a] Bands are in cm.$^{-1}$.

particularly in the case of substituents which act predominantly through an inductive effect. Since the effect of a substituent on the basicity of benzimidazole is stronger the closer this group is to the nitrogen atom, groups in the 2-position are more effective in modifying the basic nature of the imidazole ring than similar groups in the 5(6)-position. This is illustrated by the fact that 2-methylbenzimidazole is more basic than either 5(6)-methyl- or 5,6-dimethylbenzimidazole.

4,7-Dimethoxybenzimidazole is more basic than benzimidazole but less basic than 5(6)-methoxy- and 5(6)-ethoxybenzimidazoles. The 2-(1-hydroxyethyl)-benzimidazoles follow the expected changes by introduction of substituents in the 5(6)-position. However, 4,7-dimethoxy-2-(1-hydroxyethyl)benzimidazole is less basic than either 2-(1-hydroxyethyl)benzimidazole or 4,7-dimethoxybenzimidazole. All 2,5,6-trialkylbenzimidazoles show approximately the same basicity and are more basic than the mono- or disubstituted compounds. The other trisubstituted benzimidazoles have pK_a values which are in agreement with the expected effects of the substituents involved.

The ultraviolet spectra of many substituted benzimidazoles, measured under a variety of conditions, have been reported in the literature. The most comprehensive study of ultraviolet spectra of substituted benzimidazoles has been carried out by Leandri, Mangini, Montanari, and Passerini.[4] The ultraviolet spec-

(4) G. Leandri, A. Mangini, F. Montanari, and R. Passerini, *Gazz. chim. ital.*, **85**, 769 (1955).

TABLE V

CHARACTERISTIC BANDS IN THE SPECTRA OF SOME DISUBSTITUTED BENZIMIDAZOLES[a]

$R_1 = R_2 = Cl$	$R_1 = Cl$, $R_4 = CH_3$	$R_1 = Cl$, $R_3 = NO_2$	$R = R_3 = OCH_3$	$R_1 = R_2 = OCH_3$	$R_1 = OCH_3$, $R_3 = NO_2$	$R_1 = NO_2$, $R_3 = OCH_3$
1633 m	1629 m	1639 m	1634 m	1632 m	1649 w, br	1632 m
1581 m	1588 m	1575 m	1628 w	1598 m	1589 m	1614 m
1489 s	1550 m	1521 s	1549 s	1511 s	1534 s	1520 s
1478 s	1470 s	1490 s	1531 s	1489 s	1474 s	1452 m
1449 s	1450 s	1457 s	1511 s	1464 s	1429 s	1419 m
1392 s	1441 s	1401 m	1463 s	1442 s	1362 s	1394 m
1327 s	1394 s	1350 s	1448 s	1415 s	1336 s	1340 s
1283 s	1342 m	1339 s	1429 s	1363 w	1309 s	1310 s
1267 s	1297 s	1269 s	1418 s	1322 s	1287 s	1290 m
1186 w	1282 s	1213 w	1391 s	1269 s	1226 m	1275 m
1156 w	1241 m	1192 w	1334 s	1247 s	1200 m	1238 w
1151 w	1228 s	1123 s	1287 m	1217 s	1191 m	1210 m
1099 s	1186 w	1089 m	1273 m	1197 s	1150 s	1172 w
960 s	1128 w	1081 m	1252 s	1167 s	1122 m	1106 s
948 s	1058 s	1011 m	1212 m	1156 s	1032 m	1066 m
865 s	1025 s	941 s	1166 s	1113 s	1019 w	974 m
852 s	920 s	894 s	1156 w	1034 m	948 m	961 m
819 s	850 s	873 s	1094 s	999 s	929 ms	859 m
751 w	804 s	806 s	1024 s	953 s	871 w	833 w
734 w	755 w	762 m	990 s	932 w	838 m	754 m
	727 w	741 m	971 m	861 s	820 w	739 m
	706 m		920 w	849 s	781 w	
	702 m		782 s	819 s	762 w	
			774 s	796 s		
			716 s	780 s		
				737 w		
				704 w		

[a] Bands are in cm.$^{-1}$.

TABLE VI

CHARACTERISTIC BANDS[a] IN THE SPECTRA OF SOME TRISUBSTITUTED[b] BENZIMIDAZOLES

$R_1 = R_2$, $R_4 = CH_3$	$R_1 = R_2 = CH_3$, $R_4 = C_2H_5$	$R_1 = R_2 = CH_3$, $R_4 = CH(CH_3)_2$	$R_1 = R_2 = CH_3$, $R_4 = CH_2C_6H_5$	$R = NO_2$, $R_1 = OCH_3$, $R_4 = CH_3$	$R_1 = NO_2$, $R_2 = OCH_3$, $R_4 = CH_3$
1651 s	1637 m	1630 m	1635 m	1630 s	1630 s
1594 m	1589 w	1589 m	1608 w	1581 s	1591 m
1541 m	1544 s	1543 m	1589 w	1547 w	1551 w
1520 m	1469 s	1464 s	1538 m	1499 s	1514 s
1467 s	1444 s, br	1454 s	1499 m	1451 m	1468 s
1452 s	1410 s	1441 s	1463 s	1430 w	1440 m
1434 s	1385 s	1420 m	1444 s	1380 s	1409 s
1392 s	1370 m	1381 m	1422 s	1342 s	1364 m
1310 s	1311 s	1371 m	1387 w	1324 s	1340 s
1267 m	1238 m	1312 s	1377 w	1299 s	1332 s
1249 w	1222 w	1290 m	1359 w	1274 s	1284 s
1236 m	1192 w	1260 w	1313 s	1233 s	1240 w
1164 m	1165 ms	1243 m	1281 w	1197 ms	1205 s
1104 w	1107 ms	1220 w	1230 w	1176 w	1171 m
1022 m	1071 ms	1168 m	1197 w	1153 w	1065 m
1002 m	1038 s	1111 m	1181 w	1086 s	1044 w
869 m	1026 s	1089 m	1167 m	1076 s	1027 w
857 m	1001 s	1073 m	1144 m	1029 m	1002 m
775 w	968 m	1028 m	1103 w	1013 w	904 w
751 w	859 s	1007 s	1076 w	952 w	880 w
739 w	797 m	898 w	1034 m	822 s	831 m
		852 m	1017 m	813 s	762 w
		776 w	1002 m	777 w	
		738 w	923 w	716 w	
			856 m		
			806 w		
			781 m		
			757 w		
			738 m		
			721 s		

[a] Bands are in cm.$^{-1}$. [b] One tetrasubstituted benzimidazole was studied, 2-methyl-5(6)-bromo-4,7-dimethoxybenzimidazole. The characteristic bands in the spectrum of this compound are 1624 m, 1539 m, 1500 s, 1484 m, 1464 m, 1424 s, 1383 m, 1363 m, 1329 m, 1292 s, 1262 s, 1227 s, 1183 m, 1149 s, 1077 s, 1028 m, 971 m, 816 s, 773 w, 749 m, and 709 m cm.$^{-1}$.

trum of benzimidazole resembles that of a substituted benzene. The band of shorter wave length has been related to excitations whose site is the amidine ring and the bands of longer wave length have been related to excitations involving the benzene ring. Some transitions may arise from excitations which include both rings, and in those cases it may be expected that they would produce bands of greater intensity at longer wave lengths. Substitution of simple alkyl groups in the benzimidazole ring causes small bathochromic wave length displacements for all bands. The ultraviolet spectra of 2-ethyl- and 2-isopropylbenzimidazole are very similar to the spectrum of benzimidazole. All the 2,5,6-trialkylbenzimidazole show increased bathochromic displacements of all bands. An electron-withdrawing group such as the acetyl group when in the 2-position modifies the ultraviolet spectrum of the benzimidazole ring considerably. An intense band around 300 mμ replaces the fine structure bands and the band at 240 mμ shows a hypsochromic displacement. The trifluoromethyl group is also an electron-withdrawing group, but it can only act through an inductive effect. When in the 2-position this substituent increases the degree of resolution of the fine structure and causes broadening and a bathochromic displacement of the 240-mμ band. Alkoxyl groups are well-known electron-donating groups and may be expected to cause bathochromic shifts. The spectrum of 5,6-dimethoxybenzimidazole shows loss of fine structure, but the bands present are similar in position to those of the monosubstituted compounds. The ultraviolet spectrum of the 4,7-dimethoxy compound has completely lost the fundamental character of the benzimidazole spectrum. A similar change has been reported in the ultraviolet spectrum of 4(7)-methoxybenzimidazole.[4]

The ultraviolet spectra of 5(6)- and 4(7)-nitrobenzimidazoles have been reported by other investigators. The nitro group causes a regression of the shorter wave length band, disappearance of the fine structure, and appearance of a new band at around 300 mμ. In contrast with the behavior of the other substituents, a larger bathochromic displacement is noted for the 4(7) isomer. For methyl-substituted benzimidazoles, the greater bathochromic displacement of the 5(6) isomers is considered characteristic of substitution in this position.[5] The behavior of 4(7)-nitrobenzimidazole was first ascribed to chelation.[6] Although chelation may be important in the ground state, Leandri, *et al.*,[4] have shown that it cannot be used to explain the ultraviolet data. The 315-mμ band of 4(7)-nitrobenzimidazole shifts to a shorter wave length in acid solution but undergoes a further bathochromic displacement in alkaline solution. Chelation would not be possible under these conditions. Further support against chelation is given by the fact that the methylated products obtained by methylation of the 4(7) isomer have an almost identical spectrum with that of the original 4(7) isomer. Leandri, *et al.*,[4] associate the band in the 300-mμ region with the nitro group and consider the nitrobenzimidazoles as a nitrobenzene system slightly modified by the amidine chain. The large bathochromic shift in alkali is attributed to the increased acidity of the N–H bond since this shift is not nearly so pronounced in the methylated products. The ultraviolet spectra of the various nitro substituted benzimidazoles studied resemble those of the parent nitro compounds. A methyl group in the 2-position increases the resolution of the fine structure bands. The ultraviolet spectra of substituted 2-(1-hydroxyethyl)benzimidazoles resemble the spectra of similarly substituted benzimidazoles except for slight bathochromic shifts due to the presence of the hydroxyethyl group.

In dilute acid solution the benzimidazole ring is protonated, and this reaction immobilizes the unshared pair of electrons on the basic nitrogen, making it less available for resonance and forming a benzimidazolium ion which is best represented as a symmetrical resonance hybrid. The ultraviolet spectra of the compounds studied in 0.01 *N* hydrochloric acid showed shifts towards shorter wave lengths, as compared with their spectra in ethanol. The only shift towards longer wave lengths observed in dilute acid solution was in the case of 4,7-dimethoxybenzimidazole and its derivatives.

In dilute basic solution salt formation should occur, and since resonance should be greater in the salt, bathochromic displacements should be expected. This has not been found to be the case for several compounds. Loss of fine structure is sometimes observed. The ultraviolet spectra of substituted 4(7)- and 5(6)-nitrobenzimidazoles and 2-acetylbenzimidazole show bathochromic displacements in alkali. In these cases, a salt is certainly formed, and the greater mobility of electrons in the salt facilitates the formation of an electronic excited state.

Although some infrared absorption values for substituted benzimidazoles may be found in the literature, little systematic work has been done in this field until a recent study of the infrared spectra of simple alkyl- and perfluoroalkylbenzimidazoles.[7]

The infrared spectra of benzimidazoles are very complex. Benzimidazoles are not very soluble in the common solvents used in infrared work, and their spectra are best determined as potassium bromide disks. Because of the low solubility of the compounds studied in suitable solvents, all spectra were determined as potassium bromide disks in spite of the fact that in this medium certain bands originate from some type of crystal interaction rather than from a vibration of the molecule itself.

Benzimidazoles are known to be strongly associated through intermolecular hydrogen bonding. The spectra of all compounds studied show strong broad bands from 3300 to 2800 cm.$^{-1}$ which indicate polymeric association through intermolecular hydrogen bonding. The CH stretching vibrations of the ring also occur in this range (3300–3100 cm.$^{-1}$) and cannot be distinguished from the NH stretching frequencies.

Bands derived primarily from aromatic C=C and C=N stretching modes are found in the same region and cannot be distinguished. The C=C skeletal in-plane vibrations of benzene give rise to four bands near 1600, 1580, 1500, and 1450 cm.$^{-1}$. The infrared spectrum of benzimidazole has two bands of medium intensity at 1622 and 1591 cm.$^{-1}$ and a weak band at 1604 cm.$^{-1}$. The 1650–1500-cm.$^{-1}$ region is a very

(5) G. H. Beaven, E. R. Holiday, and E. A. Johnson, *Spectrochim. Acta*, **4**, 338 (1951).

(6) J. L. Rabinowitz and E. C. Wagner, *J. Am. Chem. Soc.*, **73**, 3030 (1951).

(7) K. J. Morgan, *J. Chem. Soc.*, 2343 (1961).

characteristic region of the benzimidazole spectrum. All substituted benzimidazoles have bands in this region which vary in position and intensity with the nature and position of the substituent. The spectra of most substituted benzimidazoles only have two bands, one around 1620 cm.$^{-1}$ and the other around 1590 cm.$^{-1}$. The band around 1590 cm.$^{-1}$ is in general fairly intense because of the conjugation between the benzene and imidazole rings. In the infrared spectrum of 4,7-dimethoxybenzimidazole and its 2-(1-hydroxyethyl) analog this band is absent. The frequencies of these bands also vary with the electronegativity of the substituent. The 2-substituted benzimidazoles show the least variation in frequency for these two bands since groups in this position are less apt to influence the vibrations of the benzene ring. Substitution in the 2-position is accompanied by the appearance of a rather intense band around 1550 cm.$^{-1}$. This band has been reported to be characteristic of 2-substitution.[7] Our data appears to support this although the band is absent in the infrared spectrum of 2-acetylbenzimidazole.

All benzimidazoles show strong bands in the 1500–1400-cm.$^{-1}$ region which could be attributed to skeletal in-plane vibrations. 5(6)- and 4(7)-substituted benzimidazoles show intense and sometimes broad bands around 1480, 1450, and 1420 cm.$^{-1}$. Similar bands are observed for the 2-substituted compounds. In the 1400–1300-cm.$^{-1}$ region, 5(6)-substituted benzimidazoles usually show two bands around 1370 and 1350 cm.$^{-1}$. The spectra of the 2-substituted benzimidazoles have a strong band around 1320 cm.$^{-1}$, and a medium to strong band around 1380 cm.$^{-1}$. In the case of the nitro substituted benzimidazoles, it is difficult to distinguish the bands in the 1570–1500- and 1370–1300-cm.$^{-1}$ regions from the nitro group absorptions.

Heterocyclic compounds also show a series of characteristic bands in the 1250–1000-cm.$^{-1}$ region which may be assigned to in-plane CH deformations and ring-breathing modes. The position of these bands is reported to be similar for compounds with the same number of hydrogen atoms in the same orientation. Similarly, substituted benzimidazoles also show a number of bands in this region which are similarly located. The C–O vibrations of aralkyl ethers are reported to cause strong absorption around 1250 and 1150 cm.$^{-1}$. Strong bands in these regions are noted when alkoxy groups are present.

Bands which appear regularly in the spectra of the simple benzimidazoles near 1000 and 960 cm.$^{-1}$ may be associated with benzenoid ring-breathing modes, and bands near 760 and 880 cm.$^{-1}$ with the heterocyclic ring-breathing modes.[7] Out-of-plane CH deformations and in-plane ring deformations cause absorption in the 1000–650-cm.$^{-1}$ region. The out-of-plane CH bending frequencies of substituted benzenes also fall in this region. The spectra of all 5(6)- and 4(7)-substituted compounds have an intense band around 950 cm.$^{-1}$ which is the strongest band in the region. The pattern found in the spectra of 2-substituted benzimidazoles is less constant although a band of medium intensity is sometimes present around 960 cm.$^{-1}$.

The out-of-plane CH bending frequencies of some substituted benzimidazoles have been assigned[8] as follows: 735 cm.$^{-1}$ for 2-methylbenzimidazole; 870, 812, and 800 cm.$^{-1}$ for 5(6)-methylbenzimidazole; 900, 830, and 820 cm.$^{-1}$ for 5(6)-nitrobenzimidazole. These values were derived by considering the 2-position as that of an *o*-disubstituted benzene (770–735 cm.$^{-1}$) and the 5(6)-position as having one isolated pair of hydrogens and one isolated hydrogen (850–800 cm.$^{-1}$, 900–830 cm.$^{-1}$). All bands were strong, although there were medium bands of doubtful identity.[8]

The spectra of 5(6)-substituted benzimidazoles show broad strong bands in the 900–800-cm.$^{-1}$ region and it is hard to make specific assignments. The spectra of 2-substituted benzimidazoles show a fairly constant band around 850 cm.$^{-1}$ of variable intensity. The spectra of all 2-substituted benzimidazoles have a very intense band between 747–733 cm.$^{-1}$. This band is the most intense in this region and one of the most intense in the spectra. It may be ascribed to the out-of-plane CH bending frequency. A medium to weak band is also present around 760 cm.$^{-1}$. The spectra of the 5(6)-substituted compounds show two intense bands around 790 and 740 cm.$^{-1}$. The out-of-plane CH bending frequencies of 4(7)-substituted benzimidazoles should cause absorption in the 800–700- and 720–685-cm.$^{-1}$ regions. The infrared spectrum of the 4(7)-nitrobenzimidazole shows two intense bands at 798 and 728 cm.$^{-1}$ which could be ascribed to the out-of-plane bending frequencies of a 4(7)-substituted benzimidazole.

In addition to vibrations typical of the benzimidazole ring, the vibrations typical of the groups attached to the ring must be considered. In general, substituents show the same characteristic bands regardless of whether they are attached to a benzene or benzimidazole ring. However, some of these vibrations may be modified by the heterocyclic nucleus if a strong electronic interaction occurs between the ring and the substituent. For instance, in the case of 2-acetylbenzimidazole, conjugation of the keto group with the heterocyclic ring is evidenced by its absorption at 1664 cm.$^{-1}$, typical of α,β-unsaturated ketones.

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Reactions of Free Radicals with Olefins. Thermal Decomposition of *t*-Butyl Peracetate in the Presence of 4-Vinylcyclohexene

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To obtain additional information on free radicals and their reactions with specific olefins, a study was undertaken complementing work previously published from this laboratory.[1,2] These earlier studies involved

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