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The antielectrostatic effect of benzimidazolium salts

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Several new benzimidazolium chlorides were prepared by the reaction of 1-substituted benzimidazole with chloromethylalkyl ethers or sulphides. Benzimidazolium salts like iodides, tetrafluoroborates or perchlorates were obtained by a rapid and simple method.

44 benzimidazolium salts were examined according to their antielectrostatic effect: the surface resistance, half decay time and the maximum voltage induced on polyethylene film were measured. © 1997 Elsevier Science Ltd.

(Keywords: new benzimidazolium salts; antielectrostatic effect)

INTRODUCTION

3-alkoxymethyl-1-benzyl-, 3-alkylthiomethyl-1-benzyl-, 1-benzyl-3-cycloalkoxymethyl-, 3-alkoxymethyl-1-alkyl-, 3-alkylthiomethyl-1-alkyl-, 1-alkoxymethyl-3-alkyl-, 1,3-dialkoxymethyl-, 1-alkoxymethyl-3-alkylthiomethylbenzimidazolium salts tend to have various interesting properties. They may be used as bactericidal, fungicidal, surface active agents but we gave particular attention to the antielectrostatic effects which are shown only by a few of the aforementioned salts. The efficiency of their action depends on the presence of a benzyl group in position one and, in the rest of the compounds studied, on the length of the alkyl substituents in both positions one and three.

Ammonium salts have proved to be very effective antistatic agents and are the subject of many scientific dissertations[1–5].

In our study we have concentrated on benzimidazolium salts with alkyl chains included, from 2 to 12 carbon atoms.

EXPERIMENTAL

Melting points were determined by using an electrothermal digital-melting-point apparatus model JA 9100 and are corrected. ^{1}H-n.m.r. spectra were recorded with a Varian Model XL 300 spectrometer at 300 MHz with TMS as standard. ^{13}C-n.m.r. spectra were recorded on the same instrument at 75 MHz. Elemental analyses were performed at the Adam Mickiewicz University, Poznań.

Preparation of 1-substituted benzimidazole

Benzimidazole, m.p. 172–173°C (1 mol) was dissolved in anhydrous toluene or THF by boiling for 0.5 h and then sodium hydride (1.2 mol) was added very carefully because of the exothermal reaction. After dissolving the sodium hydride, benzyl chloride was added dropwise and the mixture was boiled for 4 h. The solid that separated out after cooling was filtered off and washed with hot hexane to yield 90% 1-benzylbenzimidazolium. The residue was recrystallized from toluene (m.p. 117–118°C). The rest of the 1-substituted benzimidazoles were obtained in the same way using alkyl halides or chloromethylalkyl ethers or sulphides instead of benzyl chloride (*Table 1*). Chloromethylalkyl ethers and sulphides were prepared by the chloromethylation of alcohols or thiols[6].

Preparation of benzimidazolium chlorides: general procedure

1-Substituted benzimidazole (0.2 mol) was dissolved in anhydrous toluene or acetone at about 60°C and quaternization agents such as chloromethylalkyl ethers or sulphides or alkyl halides were then added (0.25 mol). The reaction was carried out for 2 h and the product that separated was purified by extraction with hot hexane. Water was used for recrystallization. The final product was obtained mostly as crystals with a 75–95% yield when using ethers and a 57–85% yield in the reaction with sulphides. 3-Alkoxymethyl-1-dodecyloxymethyl- and 3-alkylthiomethyl-1-dodecyloxymethylbenzimidazolium chlorides were purified only by extraction with warm hexane.

1-benzyl-3-octylthiomethylbenzimidazolium chloride (**22**). ^{1}H n.m.r. ($CDCl_3$) δ (ppm): 11.84 (s, 1H), 7.92 (d, $J = 8$ Hz, 1H), 7.69 (m, 5H), 7.35 (m, 5H), 5.89 (s, 4H), 2.79 (t, $J = 7$ Hz, 2H), 1.52 (m, 2H), 1.24 (m, 10H), 0.86 (t, $J = 7$ Hz, 3H); ^{13}C n.m.r. ($CDCl_3$) δ (ppm): 142.8, 132.5, 131.2, 130.5, 129.1, 128.9, 128.0, 127.0, 126.7, 114.2, 113.7, 51.4, 49.8, 32.4, 31.6, 28.9, 28.8, 28.4, 22.5, 14.0.

1-benzyl-3-decyloxymethylbenzimidazolium chloride (**26**). ^{1}H n.m.r. ($CDCl_3$-d_6) δ (ppm): 11.73 (s, 1H), 7.89 (d, $J = 4$ Hz, 1H), 7.67 (d, $J = 6$ Hz, 1H), 7.64 (m, 4H), 7.37 (m, 3H), 6.13 (s, 2H), 5.93 (s, 2H), 3.67 (t, $J = 6$ Hz, 2H), 1.55 (t, $J = 7$ Hz, 2H), 1.22 (d, $J = 3$ Hz, 14H), 0.89 (t, $J = 7$ Hz, 3H); ^{13}C n.m.r. ($CDCl_3$-d_6) δ (ppm): 143.2, 132.5, 131.1, 130.7, 129.0, 128.8, 128.0, 127.0, 114.0, 113.6, 77.8, 77.4, 70.2, 51.4, 31.7, 29.3, 29.1, 29.0, 25.7, 22.5, 14.0.

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Table 1 The prepared benzimidazolium salts and their antielectrostatic effect

Salt number	R^1	R^2	Y	Melting point (°C)	Yield (%)	Antistatic effect
1	CH_2Ph	$CH_2OC_2H_5$	Cl	145.1–145.6	91	lack
2	CH_2Ph	$CH_2OC_3H_7$	Cl	120.7–122.3	90	lack
3	$CH_2OC_{12}H_{25}$	$CH_2OC_3H_7$	Cl	greasy subst.	80	excellent
4	C_9H_{19}	$CH_2OC_3H_7$	Cl	57.2–59.0	87	very good
5	CH_2Ph	$CH_2OC_4H_9$	Cl	108.7–110.1	88	lack
6	$CH_2OC_{12}H_{25}$	$CH_2OC_4H_9$	Cl	greasy subst.	70	excellent
7	CH_2Ph	$CH_2SC_4H_9$	Cl	126.4–128.2	68	lack
8	$CH_2OC_{12}H_{25}$	$CH_2SC_4H_9$	Cl	110.1–111.8	83	insufficient
9	C_2H_5	$CH_2SC_4H_9$	Cl	78.0–79.9	80	insufficient
10	C_9H_{19}	$CH_2SC_4H_9$	Cl	91.4–93.2	76	sufficient
11	$C_{12}H_{25}$	$CH_2SC_4H_9$	Cl	138.3–139.7	81	insufficient
12	CH_2Ph	$CH_2OC_5H_{11}$	Cl	96.7–97.5	90	lack
13	CH_2Ph	$CH_2OC_5H_9$	Cl	117.5–119.0	93	lack
14	CH_2Ph	$CH_2OC_6H_{13}$	Cl	108.2–109.5	89	lack
15	CH_2Ph	$CH_2OC_6H_{11}$	Cl	104.1–104.8	92	lack
16	CH_2Ph	$CH_2SC_6H_{13}$	Cl	134.4–136.1	90	lack
17	C_2H_5	$CH_2SC_6H_{13}$	Cl	155.2–156.7	76	insufficient
18	CH_2Ph	$CH_2OC_7H_{15}$	Cl	103.8–104.7	89	lack
19	CH_2Ph	$CH_2OC_7H_{13}$	Cl	88.9–90.7	88	lack
20	CH_2Ph	$CH_2OC_8H_{17}$	Cl	101.4–102.5	92	lack
21	C_2H_5	$CH_2OC_8H_{17}$	Cl	greasy subst.	78	excellent
22	CH_2Ph	$CH_2OC_8H_{15}$	Cl	84.8–86.5	91	lack
23	CH_2Ph	$CH_2SC_8H_{17}$	Cl	154.3–154.7	82	lack
24	C_2H_5	$CH_2SC_8H_{17}$	Cl	79.6–81.1	74	very good
25	CH_2Ph	$CH_2OC_9H_{19}$	Cl	90.5–91.8	87	lack
26	CH_2Ph	$CH_2OC_{10}H_{21}$	Cl	94.2–94.8	66	lack
27	C_2H_5	$CH_2OC_{10}H_{21}$	Cl	greasy subst.	73	excellent
28	CH_2Ph	$CH_2SC_{10}H_{21}$	Cl	138.2–139.7	58	lack
29	C_2H_5	$CH_2SC_{10}H_{21}$	Cl	83.2–84.9	75	excellent
30	CH_2Ph	$CH_2OC_{11}H_{23}$	Cl	94.3–95.8	79	lack
31	CH_2Ph	$CH_2OC_{12}H_{25}$	Cl	91.4–92.5	94	lack
32	CH_2Ph	$CH_2OC_{12}H_{23}$	Cl	113.4–113.9	92	lack
33	C_2H_5	$CH_2OC_{12}H_{25}$	Cl	67.1–68.5	79	very good
34	CH_2Ph	$CH_2SC_{12}H_{25}$	Cl	125.4–126.9	92	lack
35	CH_2Ph	$CH_2OC_3H_7$	I	151.0–152.5	75	lack
36	CH_2Ph	$CH_2OC_3H_7$	BF_4	102.2–103.1	70	lack
37	CH_2Ph	$CH_2OC_3H_7$	ClO_4	120.9–122.7	73	lack
38	C_2H_5	$CH_2SC_4H_9$	I	150.2–152.0	70	sufficient
39	CH_2Ph	$CH_2OC_6H_{13}$	I	96.0–97.6	78	lack
40	CH_2Ph	$CH_2OC_6H_{13}$	BF_4	80.4–82.1	73	lack
41	CH_2Ph	$CH_2OC_{12}H_{25}$	I	87.9–89.8	90	lack
42	CH_2Ph	$CH_2OC_{12}H_{25}$	BF_4	71.2–72.9	82	lack
43	C_5H_{11}	CH_3	I	70.0–71.7	80	sufficient
44	C_6H_{13}	CH_3	I	89.3–91.0	74	sufficient

*1-benzyl-3-cyclododecyloxymethylbenzimidazolium chloride (**32**).* ^1H n.m.r. ($CDCl_3$) δ (ppm0: 11.74 (s, 1H), 7.89 (dd, J = 7 Hz, 1H), 7.68 (dd, J = 5 Hz, 1H), 7.58 (m, 4H), 7.37 (m, 3H), 6.12 (s, 2H), 5.92(s, 2H), 3.77 (m, 1H), 1.67 (m, 2H), 1.49 (m, 2H), 1.32 (m, 12H); ^{13}C n.m.r. ($CDCl_3$) δ (ppm): 142.9, 132.5, 131.0, 130.8, 129.0, 128.8, 128.0, 127.04, 126.970, 114.1, 113.5, 78.0, 77.4, 75.8, 51.3, 28.2, 24.7, 24.5, 22.7, 22.6, 19.9.

Preparation of 1-benzylbenzimidazolium salts

Salts like iodides, tetrafluoroborates and perchlorates were prepared by the reaction of chloride with inorganic acid or salt. The appropriate benzimidazolium chloride (0.01 mol) was dissolved in water (200 cm^3), then an inorganic agent (0.03 mol) was added, with constant stirring, to yield 73–90%. The reaction was carried out for 1 h. The precipitation was crystallized from ethanol (*Table 1*).

We confirmed the structure of some new benzimidazolium salts by elemental analysis.

1-benzyl-3-propoxymethylbenzimidazolium iodide (m.p. 151–152.5°C) (35). Anal. C, H, N. Calcd.: C = 52.93, H = 5.19, N = 6.86. Found: C = 52.97, H = 4.87, N = 6.76.

*1-benzyl-3-propoxymethylbenzimidazolium tetrafluorborate (m.p. 102–103°C) (**36**).* Anal. C, H, N. Calcd.: C = 58.72, H = 5.75, N = 7.61. Found: C = 58.74, H = 5.66, N = 7.58.

*1-benzyl-3-propoxymethylbenzimidazolium perchlorate (m.p. 121–123°C) (**37**).* Anal. C, H, N. Calcd.: C = 56.77, H = 5.56, N = 7.36. Found: C = 56.81, H = 5.54, N = 7.43.

It should be underlined that the values show consistency and the differences between them are less then 0.4.

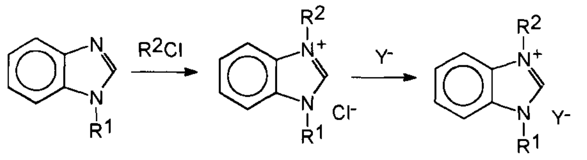
ANTIELECTROSTATIC PROPERTIES

The antielectrostatic effect of the salts in this study was measured on a polyethylene film (LDPE II 003/GO) which did not contain any lubricants or antioxidants. Thin films of quaternary benzimidazolium salts were deposited on disks of PE film. The PE disks of 0.125 m diameter were washed in acetone, then dried by placing them in an air-conditioned room. The disks were then immersed in a 0.5% chloroform solution of quaternary salt for 60 s. Then they were hung up so that the solvent could evaporate spontaneously. For each salt two disks were prepared in the manner mentioned above, the third disc was rubbed on the surface with a cotton-bud soaked with the solution of quaternary salt to affirm that the surface was covered thoroughly. The disks were stored for 24 h in an air-conditioned room at a temperature of 20°C and relative humidity of 65%.

Finally, the surface resistance, half charge decay time and the maximum voltage induced on the film surface were examined. The measuring apparatus, the method of measurement and the measurement conditions were described by Pernak *et al.*[7].

RESULTS AND DISCUSSION

The new benzimidazolium chlorides such as: 3-alkoxymethyl-1-benzyl-, 3-alkylthiomethyl-1-benzyl-, 1-benzyl-3-cycloalkoxymethylbenzimidazolium chlorides were obtained from the reaction of 1-benzylbenzimidazole with chloromethylalkyl ethers or sulphides in toluene or THF and the new salts like iodides, tetrafluoroborates and perchlorates were prepared by mixing the salts, given above, with inorganic acids or their salts in water (*Scheme 1*). The structure of the new compounds were established on the basis of their spectral properties and elemental analysis.



Scheme 1

The ^{1}H-n.m.r. spectra of 3-alkylthiomethyl-1-benzylbenzimidazolium chloride shows a singlet at δ 11.84 ppm due to the CH group of the imidazole ring. The second singlet at δ 5.89 ppm, from resonations of the two CH_2 groups and two protons of the CH_2 group attached directly to the atom of sulphur, appears as a multiplet at 2.29–2.74 ppm. The ^{13}C-n.m.r. spectra of the same chloride shows typical peaks at 51.4 ppm for the carbon atom attached to the phenyl group and at 49.8 ppm for the second CH_2 group next to the quaternary nitrogen atom.

The ^{1}H-n.m.r. spectra of 3-alkoxymethyl-1-benzylbenzimidazolium chloride shows a singlet at 11.69 ppm for the proton of benzimidazole group, the two characteristic singlets peak at 6.13 ppm and 5.95 ppm for the CH_2 groups attached to the benzimidazole ring and a multiplet in the region of 3.66–3.62 ppm for the first CH_2 group of the alkyl chain attached to the oxygen atom. Examination of ^{13}C-n.m.r. spectra of this compound shows the absorption peak for the carbon atom of $N-CH_2-O$ group at 77.6 ppm and for the carbon directly attached to the oxygen atom at 70.0 ppm. At 51.2 ppm the C–H bond from the benzyl group shows its absorption peak.

The ^{1}H-n.m.r. spectra of 1-benzyl-3-cycloalkoxymethylbenzimidazolium chloride shows characteristic absorption peaks: a singlet at 11.74 ppm of the hydrogen atom of the benzimidazole ring, two singlet peaks at 6.12 ppm and 5.92 ppm of the two CH_2 groups directly attached to the benzimidazolium ring and finally a multiplet in the region of 3.77 ppm from the C–H bond attached to the oxygen atom and the cycloalkyl group. The ^{13}C-n.m.r. spectra of chloride given above shows a peak at 78.0 ppm for the carbon atom attached to the quaternary nitrogen atom, at 75.6 ppm for the carbonyl carbon atom and at 51.2 ppm for the carbon atom of the CH_2 group attached to the phenyl ring in the benzyl group.

The antielectrostatic properties of the obtained

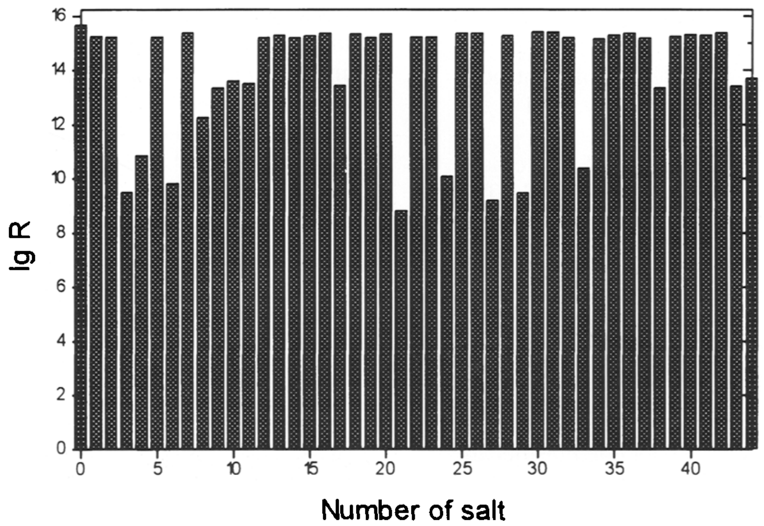


Figure 1 Values of logarithm of the surface resistance for the examined benzimidazolium salts (see *Table 1*)

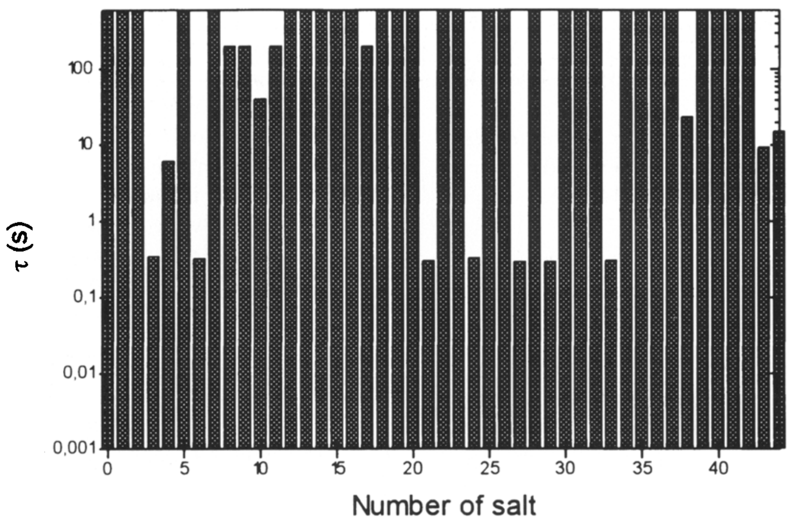


Figure 2 Values of half charge decay time for the examined benzimidazolium salts (see *Table 1*)

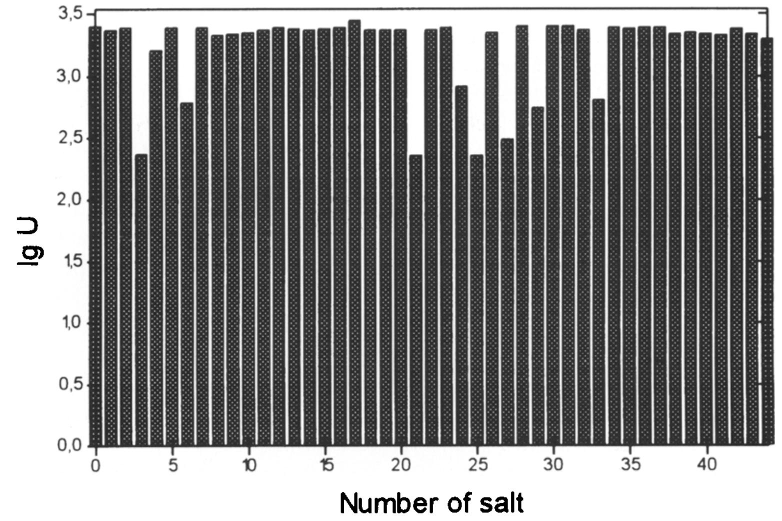


Figure 3 Values of maximum voltage induced for the examined benzimidazolium salts (see *Table 1*)

benzimidazolium salts used in the experiments are the resultant of three quantities: the surface resistance, the half charge decay time and the maximum voltage induced.

The surface resistance R was calculated from the formula:

$$R=\frac{U\cdot l}{i\cdot s}[\Omega]$$

where U is the measured voltage, l the length of electrodes ($l = 100$ mm), i the electric current intensity, and s the distance between electrodes ($s = 10$ mm).

The obtained surface resistance values for 45 quaternary benzimidazolium salts are submitted in *Figure 1*. The surface resistance value for LDPE II 003/GO polyethylene film was $\log R = 15.67$.

The half charge decay time was found from relation:

$$\tau=\sqrt{\frac{\tau_{+}^{2}+\tau_{-}^{2}}{2}}[s]$$

where τ_+ and τ_- are the mean half decay times of positive and negative charges, respectively. The obtained results are shown at *Figure 2*. The half charge decay time for LDPE II 003/GO polyethylene film was 600 s.

The maximum voltage induced on the surface of the air-conditioned disks:

$$U=\sqrt{\frac{U_{+}^{2}+U_{-}^{2}}{2}}[V]$$

where U_+ and U_- are the voltages induced by positive and negative charges, respectively. *Figure 3* presents the values obtained for the studied salts.

The antielectrostatic effect was determined following the criteria given by Bukala *et al.*[8] and listed in *Table 2*. *Tables 1, and 3* shows the results of antielectrostatic properties according to the data of *Table 2*.

From 44 salts studied, eight showed an excellent or very good effect. The best results were given by: 3-alkoxymethyl-1-dodecyloxymethylbenzimidazolium chlorides with three and four carbon atoms in the alkoxymethyl chains, 3-alkoxymethyl-1-ethyl- and 3-alkylthiomethyl-1-ethylbenzimidazolium chlorides containing 8–12 carbon atoms in the substituent's chains, and finally 3-nonyl-1-propoxymethylbenzimidazolium chloride although its half charge decay time is rather long. Four more of the examined salts, 3-butylthiomethyl-1-ethyl-, 3-methyl-1-pentyl-, 1-hexyl-3-methylbenzimidazolium iodides and 3-butylthiomethyl-1-nonylbenzimidazolium chloride, showed 'sufficient' effects.

Table 2 Criteria for the estimation of the antielectrostatic effect based on the surface resistance and half decay time

Surface resistance, log *R*	Half charge decay time (s)	Antielectrostatic effect
< 9	< 0.5	excellent
9–10	1	very good
10–11	2 to 10	good
11–12	10 to 100	sufficient
12–13	> 100	insufficient
> 13	lack of antielectrostatic properties	lack of antielectrostatic properties

Table 3 The antielectrostatic effect of benzimidazolium salts studied

Antielectrostatic effect	Quaternary benzimidazolium salts	Total number of salts
Excellent	3, 6, 21, 27, 29	5
Very good	4, 24, 33	3
Sufficient	10, 38, 43, 44	4

The whole set of benzimidazolium salts containing a phenyl substituent in position one gave a lack of antielectrostatic effects because of the presence of two big groups such as the benzene ring and benzimidazole condensed ring and their spacial orientation. The antielectrostatic effect improves as the carbon chain shortens in position three in 3-alkoxymethyl-1-ethylbenzimidazolium chlorides and worsens in 3-alkylthiomethyl-1-ethylbenzimidazolium chlorides.

All of the benzimidazolium compounds studied (except four) had a crystal form and their chloroform solutions were carefully placed on the whole surface of polyethylene disks. The lack of antistatic effects in the examined salts is the resultant of the crystal structure of the studied salts and not a function of the experimental procedure.

The microbiological investigations of 3-alkoxymethyl- and 3-alkylthiomethyl-1-benzylbenzimidazolium salts indicate that they are active compounds. For the first time we have obtained quaternary ammonium salts possessing biological activity but lacking antielectrostatic properties.

CONCLUSIONS

A study of the antielectrostatic properties of benzimidazolium salts has indicated that the structure of a compound, the type of substituent and the length of carbon chains were dependent on various qualities. It was shown that the following conditions must be met for an ideal antistatic agent in the studied group of benzimidazolium salts.

(1) The substituent in position one cannot be from the benzyl group because of too large a spacial structure in connection with the benzimidazole ring.
(2) If the substituent in position one has a long alkyl chain, the second in position three must be rather shorter.

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