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(54) INSECTICIDAL AND ACARICIDAL BENZIMIDAZOLE COMPOSITIONS

(71) We, ELI LILLY AND COMPANY, a Corporation organised and existing under the laws of the State of Indiana, United States of America, of 307 East McCarty Street, City of Indianapolis, State of Indiana, United States of America, do hereby declare invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

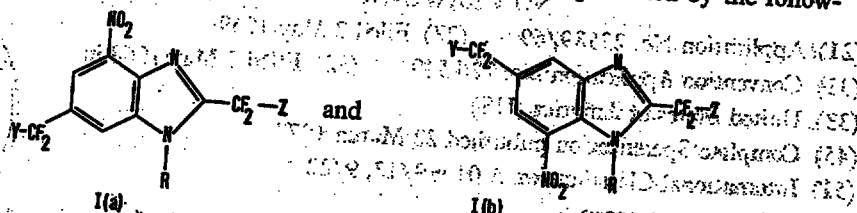
Benzimidazoles are known to be useful in combating intestinal parasites of mammals and birds. Furthermore, 2-trifluoromethylbenzimidazoles have been found to be useful as herbicides, nematocides, molluscicides, and insecticides. (British patent 1,087,561; U.S. patent 3,412,101; South African patent 65/5584; and Netherlands patent 67/13786 are exemplary.) The 2-trifluoromethyl derivatives most frequently employed as insecticides have been substituted in the benzene portion of the benzimidazole ring system with chlorine and nitro groups, with the most active compounds being: 2-trifluoromethyl-4,5,6,7-tetrachlorobenzimidazole, 2-trifluoromethyl-5,6-dichlorobenzimidazole, and phenyl 2-trifluoromethyl-4-nitro-6-chloro-1-benzimidazole-carboxylate. In general these compounds have shown their greatest activity against insects of the order Lepidoptera, such as Southern armyworm, and of the order Diptera, such as house flies and mosquitoes. For example, 2-trifluoromethyl-4,5-dichlorobenzimidazole gives a complete kill of Southern armyworm larvae at 250 ppm, but is without action against milkweed bugs, oriental roaches and boll weevils at that same concentration, and in fact, its activity against house flies is excellent only at 1000 ppm. The isomeric compound, 2-trifluoromethyl-5,6-dichlorobenzimidazole, has the same excellent activity against Southern armyworm larvae at 250 ppm, but no activity at the same level against milkweed bugs, house flies, oriental roach and boll weevil. In general, these chlorinated benzimidazoles do not approach, in absolute activity, the organic phosphate insecticides, nor do they have the same broad spectrum of action.

Two large classes of marketed insecticides which have been widely used and which have a reasonably broad spectrum against many orders of insects plus a low dosage range are the organic phosphates and the chlorinated hydrocarbons. Many of the most active of the organic phosphate insecticides are extremely toxic to humans and their toxicity by intradermal absorption is of the same order of magnitude as their toxicity by inhalation. Thus, these very toxic compounds are extremely dangerous to handle, even when using a gas mask or oxygen mask. The safest of the phosphorus insecticides, Malathion (Registered Trade Mark), is still widely used, but its spectrum is not as broad as would be desirable and many species of insects or mites have become resistant to it over the years.

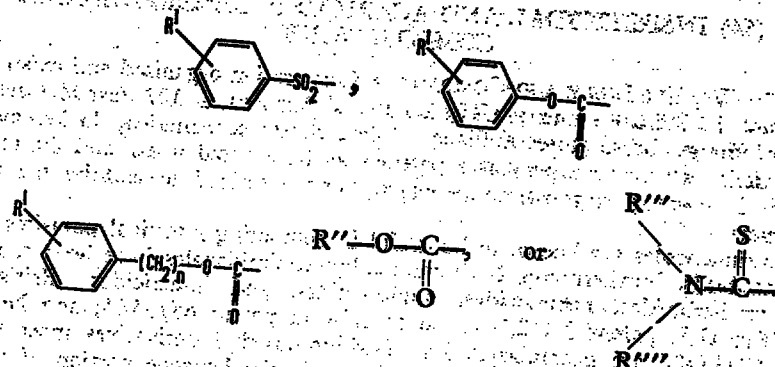
The deficiencies of the chlorinated hydrocarbons are of a different nature. Resistance is, of course, prevalent, but this problem is not as serious as might be expected because of the endless succession of new chlorinated hydrocarbons which have been produced. The chief drawback to the use of chlorinated hydrocarbons is their persistence in soil and water for many, many years, attributed chiefly to their metabolic stability. This persistence has now begun to affect other forms of life, including birds and fish.

Thus, there is a need for compounds with both insecticidal and acaricidal activity, which have a broad spectrum, are safe to handle and are non-persistent.

This invention provides an insecticidal and acaricidal composition which comprises, as its biocidally effective ingredient, a benzimidazole represented by the following formulae:



wherein R is hydrogen, an alkali or alkaline earth metal,



wherein n is 1 to 3; R' is hydrogen, fluorine, chlorine, bromine, C_1-C_6 alkoxy, C_1-C_6 alkyl or nitro; and R'' is C_1-C_6 alkyl, halo-substituted C_1-C_6 alkyl, halo-substituted C_2-C_6 alkenyl, C_2-C_6 alkynyl or C_2-C_6 alkenyl; R''' and R''' individually are hydrogen, C_1-C_6 alkyl or phenyl, or when taken together a pentamethylene or tetramethylene chain; and Y is F or H; Z is F, H, Cl, $-CF_3$, or $-CF_2-CF_3$; and halo is fluorine, chlorine or bromine.

The invention moreover provides a method for killing insects and arachnids which comprises applying the above-mentioned insecticidal and acaricidal compositions to an insect or an arachnid habitat.

In the above formulae, it will be recognized that when R is hydrogen, the benzimidazole exists in two tautomeric forms, one of which is named (when Y and Z are F) 2,6-bis(trifluoromethyl)-4-nitrobenzimidazole and the other 2,5-bis(trifluoromethyl)-7-nitrobenzimidazole. Both of these structures exist in equilibrium in any preparation of the pure compound. When the hydrogen on the benzimidazole nitrogen is replaced by term "R" as defined above, there is no longer the possibility for tautomerism and each preparation of the N-derivative contains a mixture of two substances, one of which would be named, for example, using the same compound as above for illustrative purposes only, 2,6-bis(trifluoromethyl)-4-nitro-1-phenylsulfonylbenzimidazole and the other would be 2,5-bis(trifluoromethyl)-7-nitro-1-phenylsulfonylbenzimidazole. Only one of the two isomers may be readily isolatable. It should be understood that this invention includes within its scope both the 1-substituted-4-nitro-6-fluoromethyl-2-fluoroalkylbenzimidazoles and the 1-substituted-7-nitro-5-fluoromethyl-2-fluoroalkylbenzimidazoles.

In the above formulas, "halo" can be chlorine, bromine, or fluorine. When R' is C_1-C_6 alkoxy, it can be for example, methoxy, ethoxy, isopropoxy, *n*-propoxy, *sec*-butoxy, *n*-butoxy, isobutoxy, *n*-amyl, isobutyl, *sec*-butyl, *t*-amyl, *n*-amyl or *sec*-amyl. When R', R'', or R''' are C_1-C_6 alkyl, they can be, for example, methyl, ethyl, *n*-propyl, isopropyl, *n*-butyl, isobutyl, *sec*-butyl, *t*-amyl, *n*-amyl or *sec*-amyl. When R' and R''' together form a pentamethylene or tetramethylene chain, the resulting group is piperidino or pyrrolidino. Groups illustrating the scope of R'' include those specified for C_1-C_6 alkyl above as well as C_2-C_6 alkenyl groups including vinyl, 1-propenyl, isopropenyl, allyl, crotyl, methallyl and 2-pentenyl, and C_2-C_6 alkynyl groups including ethynyl, 1-propynyl, 1-butylnyl and 1-methyl-1-butylnyl. When R'' is halo-substituted C_1-C_6 alkyl or halo-substituted C_1-C_6 alkyl, it can be any of the above

groups used to illustrate the scope of the terms C_1-C_6 alkenyl or C_1-C_6 alkyl substituted with one or more halogens comprising chlorine, bromine, and fluorine. Typical groups illustrating the above terms include chloroalkyl, trifluoromethyl, chloromethyl, dichloromethyl, α -bromoethyl, 1,2-dichloro-2-methylbutyl and 3-bromo-1-pentenyl. When Y or Z are H or F, the resulting substituents are difluoromethyl and trifluoromethyl respectively. When Z is Cl, CF_3 , or C_2F_5 , the resulting 2-substituent is chlorodifluoromethyl, pentafluoroethyl or heptafluoropropyl.

In this invention, an insecticidal or acaricidal amount of a benzimidazole according to Formulae I (a) or I (b) above is applied to the insect or arachnid habitat, which habitat might be, for example, the foliage or other parts of a living plant when aphids, mites, milkweed bug or the like are to be combatted, or the soil in which a crop has been planted, as when it is desired to combat corn rootworm or the like. Again, the insect habitat might be the wall of a building when it is desired to combat flies or mosquitoes.

A benzimidazole according to the above formulae can be applied to the arachnid or insect habitat in pure or relatively pure form if desired; that is to say, unmixed with other constituents. Such a method of application is, however, wasteful inasmuch as the compounds are active at such extremely low rates, as will be delineated hereinafter. Thus, the insecticidal and acaricidal properties of 2-fluoroalkyl-6-fluoromethyl-4-nitrobenzimidazoles and their N-substituted derivatives are preferably secured by application of a formulation containing the benzimidazole as the active agent dispersed in a suitable inert carrier, with or without compatible fungicidal, bactericidal, insecticidal or herbicidal ingredients.

Benzimidazole containing compositions are most satisfactorily formulated as emulsifiable concentrates or dusts, although a granular formulation or wettable powder can also be used. Those compositions which are adapted for direct spraying or dusting upon the insect or arachnid habitat are prepared by methods well known to the art, as for example by mixing the benzimidazole with a non-phytotoxic diluent such as water plus a surface-active agent to provide an emulsifiable concentrate, or such as clay, bentonite, silica, hydrous alumina, kieselguhr, or diatomaceous earth to provide a dusting powder or wettable powder where a surfactant is included or with one of these latter ingredients followed by compression of the resulting mixture to provide a granular formulation. The dusting powder and granular formulations are customarily used as such, but wettable powders and emulsifiable concentrates are first prepared as a concentrate and then further diluted with a non-phytotoxic material prior to use. The insecticidally active benzimidazole is customarily present in the diluted dust or spray in a concentration varying from about 0.0025 percent to upwards of about 5 percent or preferably from 0.01 to 0.6 percent. The concentration of the benzimidazole in concentrates used for preparing wettable powders or emulsifiable concentrates is necessarily far higher and can vary from 5 percent up to as high as 80 or 90 percent if desired. The above insecticidally active compositions are applied to the insect or arachnid habitat by means of spray guns, dust guns, spreaders or the like.

The amount of benzimidazole to be applied for insect or arachnid control purposes to a given area of plant life is, of course, dependent upon a variety of factors, such as the extent of vegetative surface to be covered, the severity of the insect infestation, the condition of the foliage treated, the temperature, the humidity etc. In general, however, the application of about 0.1 to about 5.0 pounds of a benzimidazole represented by the above formula per acre of insect-infested plant life provides effective insecticidal action. The application to plant foliage to the point of run-off of aqueous compositions containing from about 0.01 to about 0.6 percent on a weight-volume basis of a benzimidazole effectively controls the insecticidal or acaricidal life thereon. Alternatively, a light but complete dusting of plant foliage with a dusting composition containing, by weight, about 0.01 to about 0.6 percent of the benzimidazole also gives effective insecticidal or acaricidal control.

The compositions of this invention can also be formulated so as to contain other compatible insecticidal agents. Among these agents are included rotenone; natural or synthetic esters of chrysanthemic acid and its relatives including pyrethrin and allethrin; chlorinated hydrocarbons, including BHC, lindane, chlordane, heptachlor, toxaphene, aldrin, dieldrin, endrin, DDT (registered Trade Mark), TDE, and methoxychlor; organic phosphates, including TEPP, phosphamiden, demeton, Malathion, (Trade Mark), ethion, dimethoate, mecarbam, methyl parathion, parathion, O-2,4-dichlorophenyl-O-methyl isopropylphosphoramidothioate, Ronnel (registered Trade Mark), O-4-tert-butyl-2-chlorophenyl-O-methyl methylphosphoramidate, tepa, metepa, diazinon and Metasystox (Trade Mark), sulfites, including 2-(p-tert-butylphenoxy)-1-methyl-

ethyl 2-chloroethyl sulfite; and carbamates, including 4-dimethylamino-3,5-xylyl-methylcarbamate and carbaryl.

Illustrative formulations useful in this invention include the following:

I. WETTABLE POWDER

25 percent 2,6-bis(trifluoromethyl)-4-nitrobenzimidazole, 70.5 percent Kaolin
3 percent alkylaryl polyether alcohol,
1.5 percent sodium lignin sulfonate

II. GRANULES

An impregnating solution is prepared containing six parts of 2,6-bis(trifluoromethyl)-4-nitrobenzimidazole mixed with four parts of methyl Cellosolve (Trade Mark). Seventeen and two tenths grams of this solution is sprayed onto 82.8 g. of diatomaceous earth and the mixture is compressed into granules containing 10 percent of active ingredient.

III. GRANULES

An impregnating solution is prepared containing six parts of the sodium salt of 2,6-bis(trifluoromethyl)-4-nitrobenzimidazole and four parts tap water. Seventeen and two tenths grams of the solution is sprayed onto diatomaceous earth as before and the sprayed material compressed into granules containing 10 percent active ingredient.

IV. DUST

One part 2,6-bis(trifluoromethyl)-4-nitrobenzimidazole is mixed with 99 parts of talc after both ingredients have been ground finely enough to pass through a 325 mesh sieve.

Benzimidazoles represented by Formulae I (a) and I (b) above have an extremely broad insecticidal and acaricidal spectrum. The compounds are particularly active against insects belonging to the order Coleoptera: beetles including both larval and adult forms of Mexican bean beetle, boll weevil, corn rootworm, cereal leaf beetle, flea beetles, borers, Colorado potato beetle, grain beetles, alfalfa weevil, carpet beetle, flour beetle, powder post beetle, wireworms, rice weevil, rose beetle, plum curculio and white grubs. 2-Fluoroalkyl-6-fluoromethyl-4-nitrobenzimidazoles and their N-substituted derivatives are also extremely active against insects of the order Hemiptera, including melon aphid, rose aphid, white fly, grain aphid, corn leaf aphid, pea aphid, mealybugs, scales, leaf hoppers, citrus aphid, spotted alfalfa aphid, green peach aphid and bean aphid. The compounds also have an extremely high acaricidal activity, being effective against red spider mite (at application rates of 10 ppm or less), clover mite, rust mite, citrus mite, two-spotted spider mite, fowl mite and ticks. These compounds are also active against insects of the order Heteroptera, such as milkweed bug, tarnished plant bug, box elder bug, bed bug, squash bug and chinch bug; Diptera, such as house fly, yellow fever mosquito, stable fly, horn fly, cabbage maggot, and carrot rust fly; and Lepidoptera, such as Southern armyworm, codling moth, cutworm, clothes moth, Indianmeal moth, leafrollers, corn earworm, European corn borer, cabbage looper, cotton bollworm, bagworm, sod web worm and fall armyworm. Finally, the compounds have shown activity against roaches of the order Orthoptera at rates comparable to those employed with presently marketed insecticides for the purpose of roach control.

The insecticidal and acaricidal activity of the compounds of this invention is illustrated by the following tests against representative insects and mites.

TEST METHODS

Mexican Bean Beetle—

Epilachna varivestis (Coleoptera)

Cuttings of four six-day old Bountiful snap bean plants containing two leaves with approximately 5 square inches of leaf surface, are placed in water. The leaves are sprayed to wetting with about 5–10 ml. of a formulation containing a predetermined level of test compound. Half of the formulation is sprayed on the top surface and half on the bottom surface of the leaf using a Devilbiss (Trade Mark) atomizer at 10 psi held at a distance of about 18 inches from the leaf. After the leaves have dried, they are cut from the stem and placed separately in petri dishes. Ten third instar, non-molting Mexican bean beetle larvae grown on Bountiful snap beans are placed on each leaf. Controls consist of two leaves sprayed with 5 ml. of a 500 ppm Malathion formulation (reference standard), two leaves sprayed with the formulation without the active ingredient and two leaves held as untreated controls. After 48 hours a mortality count is made and the amount of feeding noted. Moribund larvae are counted as dead. The following rating scale is used:

	Percent dead	Rating	
	0—10	0	
	11—20	1	
	21—30	2	5
	31—40	3	
	41—50	4	
	51—60	5	
	61—70	6	
	71—80	7	10
	81—90	8	
	91—100	9	

SOUTHERN ARMYWORM

Prodenia eridania (Lepidoptera)

Ten uniform Southern Armyworm larvae about 1—1.5 cm. in length, grown on Henderson lima beans, are placed on excised bean leaves in petri dishes. The bean leaves are obtained and sprayed with the insecticide in the same way as are the snap bean leaves in the Mexican bean beetle test. The reference standards in this instance are leaves sprayed with 5 ml. 100 ppm DDT solution. Mortality counts are made 48 hours after spraying and again moribund larvae are counted as dead. Missing larvae which have probably been eaten are considered alive. The same rating scale is used as in the Mexican bean beetle test.

MELON APHID—

Aphis gossypii (Hemiptera)

Four blue hubbard squash seeds are planted per container in vermiculite and the containers watered from the bottom. After 6 days, the two weakest plants are cut off and one cotyledon and the primary leaves are removed from each of the two remaining plants. The remaining cotyledon is infested with 100 melon aphids from a stock colony by pinning the cotyledon against an aphid-infested squash cotyledon from the colony and allowing the aphids to transfer. After transfer, the colony leaf is removed. Forty-eight hours later, the infested leaves are sprayed to wetting with formulations containing graded amounts of the insecticide using a DeVilbiss atomizer at 10 psi held at 12—15 inches from the plant. Controls consist of two infested, unsprayed squash plants and two infested plants sprayed to wetting with a formulation containing 100 ppm Malathion as a reference standard. The mortality is estimated 24 hours after spraying by observation using a 10 power dissecting microscope. The same rating scale is used as before.

TWO-SPOTTED SPIDER MITE—

Tetranychus urticae (Acarina)

The procedure in this test is the same as that in the previous aphid test, except that about 100 two-spotted spider mites from a stock colony raised on squash plants are transferred to a cut squash cotyledon. The mortality is estimated 48 hours after spraying. The same rating scale is used.

MILKWEED BUG—

Oncopeltis fasciatus (Hemiptera)

Ten adult milkweed bugs are chilled and placed in a test cage. The cages containing the bugs are sprayed with 5 ml. of a test formulation containing a predetermined amount of the insecticide, using a DeVilbiss atomizer at 10 psi held 33 inches from the top of the cage. After the cage has been allowed to dry, the bugs are fed and watered for 48 hours. A formulation containing 500 ppm of Malathion is used as a reference standard and two unsprayed cages are kept as controls. Mortality counts are made 48 hours after spraying. Moribund adults are considered dead. The same rating scale is employed as before.

HOUSE FLY

Musca domestica (Diptera)

A. Contact

Rearing cages containing four-day adult house flies are chilled at 35—40°F. for about 1 hour. One hundred flies are transferred from the rearing cage to each test cage using a small scoop. The caged flies are kept for 1—2 hours at 70—80°F. The cages are sprayed in the same manner as described for the milkweed bug with 5 ml. of the test formulation. Two unsprayed cages are held as controls and two cages are sprayed with a 50 ppm DDT formulation as a reference standard. Mortality counts are made 24 hours after spraying. All flies that do not fly or do not walk up from the bottom of the cage are considered moribund. The same rating scale is employed as heretofore.

B. STOMACH

Ten chilled house flies are taken from the rearing cage and placed in a covered petri dish. Sugar cubes treated with 0.2 ml. of a formulation containing a specified level of the insecticide are placed in the petri dish one hour after the flies have been removed from the chill room. Controls consist of sugar cubes treated with 0.2 ml. of deionized water and cubes treated with 0.2 ml. of a formulation containing 500 ppm of Malathion. Mortality counts are made 24 hours later. The same rating scale is used as before.

ORIENTAL COCKROACH

Blattia orientalis (Orthoptera)

A rearing pan of late instar (3-4 months old) reaches is placed in a cold room for about 1 hour. Ten nymphs are taken from the pan and placed in each cage and the caged insects are kept at 70-80°F. for 1 hour. The test cages are then sprayed in the manner indicated above in the milkweed bug test using 5 ml. of a formulation containing a specified amount of the insecticide. The test cages are held for 72 hours during which time the cockroaches are neither fed nor watered. Controls consist of 2 unsprayed cages, two cages sprayed with the formulation alone and 2 cages with a formulation containing 1000 ppm of heptachlor. Mortality counts are made 24 hours after spraying by shaking the cages lightly. All cockroaches remaining in the bottom are counted as dead.

BOLL WEEVIL

Anthonomus grandis (Coleoptera)

The procedure is identical to that employed for the Mexican bean beetle and the Southern armyworm, except that 10 adult boll weevils are placed on cotton leaves that have dipped into formulations of the test compounds. The same rating scale is used.

TEST RESULTS

The following tables show the effect of the selected compounds of this invention against the above insect and mite species. In each of the following tables, the compound under test is indicated by a letter according to the following chart:

- A 2,6-bis(trifluoromethyl)-4-nitrobenzimidazole
- B 2,6-bis(trifluoromethyl)-4-nitrobenzimidazole sodium salt
- C Mixture of benzyl 2,6-bis(trifluoromethyl)-4-nitro-1-benzimidazolecarboxylate and benzyl 2,5-bis(trifluoromethyl)-7-nitro-1-benzimidazolecarboxylate
- D Mixture of methyl 2,6-bis(trifluoromethyl)-4-nitro-1-benzimidazolecarboxylate and methyl 2,5-bis(trifluoromethyl)-7-nitro-1-benzimidazolecarboxylate
- E n-hexyl 2,6-bis(trifluoromethyl)-4-nitro-1-benzimidazolecarboxylate
- F 2,6-bis(trifluoromethyl)-4-nitro-1-benzimidazolecarboxylate
- G ethyl 2,6-bis(trifluoromethyl)-4-nitro-1-phenylsulfonylbenzimidazole
- H Mixture of phenyl 2,6-bis(trifluoromethyl)-4-nitro-1-benzimidazolecarboxylate and phenyl 2,5-bis(trifluoromethyl)-1-benzimidazolecarboxylate
- I isopropyl 2,6-bis(trifluoromethyl)-4-nitro-1-benzimidazolecarboxylate
- K allyl 2,6-bis(trifluoromethyl)-4-nitro-1-benzimidazolecarboxylate
- L 2-chlorodifluoromethyl-4-nitro-6-trifluoromethylbenzimidazole
- M 2-trifluoromethyl-4-nitro-6-difluoromethylbenzimidazole
- N p-nitrophenyl-4-nitro-2,6-bis(trifluoromethyl)-1-benzimidazole
- O Mixture of N-ethyl-4-nitro-2,6-bis(trifluoromethyl)-benzimidazole-1-thiocarboxanilide and N-ethyl-7-nitro-2,5-bis(trifluoromethyl)-benzimidazole-1-thiocarboxanilide
- P Mixture of N,N-dimethyl-4-nitro-2,6-bis(trifluoromethyl)-benzimidazole-1-thiocarboxamide and N,N-dimethyl-7-nitro-2,5-bis(trifluoromethyl)-benzimidazole-1-thiocarboxamide

In the following tables, the insect or mite used as the test organism is indicated in the heading. Column 1 of the table itself gives the code letter for the test compound and columns 2 etc. the average rating using the above rating scale from 0-9 at decreasing concentrations beginning at 1000 ppm to the point where the insecticide shows virtually no activity. Included in each test are one or more standard insecticides.

TABLE 1

Mexican Bean Beetle Test

Compound	Ratings in ppm									
	1000	500	250	100	50	25	10	5	2.5	1
A	9	9	9	9	9	9	9	7	7	3
B	9	9	9	9	8	6	7	2	2	1
C	9	9	9	9	9	7	7	1	1	1
D	9	9	9	9	9	9	9	0	0	1
E	9	9	9	9	5	7	7.5	2.5	2.5	1
F	9	9	9	9	9	8	7	0	0	1
G	9	9	9	9	9	9	9	1	1	1
H	9	9	9	9	7	3	4	1	1	1
I	9	9	9	9	9	6.5	8	0	0	1
K	9	9	9	9	9	9	9	1	1	1
L	9	9	9	9	8.5	9	7	4	4	1
M	9	7.5	9	5.5	1.5	7	7	1	1	1
N	9	9	9	9	9	7	4	1	1	1
O	9	9	9	6.5	5.5	6	1.5	1	1	1
P	9	8.5	7.5	7	4.5	0	0	1	1	1

Malathion

7-8

TABLE 2

Southern Armyworm Test

Compound	Ratings in ppm									
	1000	500	250	100	50	25	10	5	2.5	1
A	9	9	9	9	9	9	9	7	7	3
B	9	9	9	9	9	9	9	7	7	3
C	9	9	9	9	9	9	9	7	7	3
D	9	9	9	9	9	9	9	7	7	3
E	9	9	9	9	9	9	9	7	7	3
F	9	9	9	9	9	9	9	7	7	3
G	9	9	9	9	9	9	9	7	7	3
H	9	9	9	9	9	9	9	7	7	3
I	9	9	9	9	9	9	9	7	7	3
K	9	9	9	9	9	9	9	7	7	3
L	9	9	9	9	9	9	9	7	7	3
M	9	9	9	9	9	9	9	7	7	3
P	9	9	9	9	9	9	9	7	7	3

Malathion

7-8

TABLE 3

TABLE 4

TABLE 4

Two-spotted Spider Mite

Ratings in ppm

Compound	1000	500	250	100	50	25	10	5	2.5	1
A	9	8	8	7	5	1	0	—	—	—
B	9	9	8	7	7	8	9	0	—	—
C	8	9	5	0	—	—	—	—	—	—
D	9	9	9	4	2	0	—	—	—	—
E	9	9	9	9.5	8	7	7	1.5	—	—
F	9	9	9	8	2	0	—	—	—	6.3
G	9	—	—	—	—	—	—	—	—	—
H	6	8	7	8	4	0	—	—	—	—
I	9	9	6.5	8	8.5	6	3	0	—	0
K	9	—	—	—	—	—	—	—	—	—
L	—	9	9	9	6	5.5	0	—	—	0
M	9	9	9	7	0	—	—	—	—	—
N	9	9	7.5	1	0	—	—	—	—	2.5
P	4.5	7.5	7	4	—	1.5	0	—	—	—
Malathion										
Aramite (registered Trade Mark)										
P	9	9	8.5	7.5	7.0	6	4	4	—	3

Aramite
(registered Trade Mark)

7-9

TABLE 5
Milkweed Bug Test

Compound	Ratings in ppm									
	1000	500	500	250	100	50	25	10	5	—
A	9	9	9	9	7	4	4	5	—	—
B	9	9	9	9	2	2	1	—	—	—
C	9	8.5	8	—	—	7	0	0	—	—
D	9	9	9	9	8	—	5	—	—	—
E	9	9	9	8	4	1.5	6.5	.5	—	—
F	9	9	9	9	7.5	6	0	0	—	—
G	9	—	—	—	—	—	—	—	—	—
H	9	9	1	—	—	—	—	—	—	—
I	8	9	9	9	8	1	0	0	—	—
K	9	—	—	—	—	—	—	—	—	—
L	—	9	9	9	4.5	6	0	0	—	—
M	9	9	9	9	3.5	.5	—	—	—	—
N	8	9	9	9	7	1	0	0	—	—
O	1	—	—	—	—	—	—	—	—	—
P	2	4	4	4	4.5	3.5	0	0	—	—

7-8

Malathion

TABLE 6
Housefly (Contact) Test

[illegible]

Compound	Rating in ppm									
	7	4	5	0	—	—	25	50	100	150
A	7	4	5	0	—	—	—	—	—	—
B	9	6	2	3.5	1	—	—	—	—	—
C	9	1.5	.5	3	1.5	—	—	—	—	—
D	9	9	5.5	0	0	—	—	—	—	—
E	9	8.5	2	2	0	—	—	—	—	—
F	8	4	3	0	0	—	—	—	—	—
G	5.5	—	—	—	—	—	—	—	—	—
H	5	6.5	7	.5	0	—	—	—	—	—
I	9	6.5	5.5	1.5	0	—	—	—	—	—
K	9	—	—	—	—	—	—	—	—	—
L	—	5.5	1	0	0	—	—	—	—	—
M	9	1.5	0	—	—	—	—	—	—	—
N	5.5	4.5	0	0	0	—	—	—	—	—
O	0	—	—	—	—	—	—	—	—	—
P	8	9	5.5	2.5	0	—	—	—	—	—

Compound	Ratings in ppm									
	9	9	500	250	100	50	25	10	5	
A	9	9	9	9	7	2	—	—	—	
B	9	9	9	9	9	4	1	—	—	
C	9	4	0	—	—	—	—	—	—	
D	8.5	5.5	2	—	—	—	—	—	—	
E	9	9	8	7	1	—	—	—	—	
F	9	9	1	—	—	—	—	—	—	
G	0	—	—	—	—	—	—	—	—	
H	9	—	—	—	0	—	—	—	—	
I	9	—	—	9	9	6	0	—	—	
K	9	—	—	—	—	—	—	—	—	
L	—	9	9	7	.5	—	—	—	—	
M	9	—	—	—	5.5	0	0	0	—	
N	9	9	9	0	0	—	—	—	—	
O	1	—	—	—	—	—	—	—	—	
P	—	9	7	3	0	—	—	—	—	

Malathion
6-7

TABLE 9
Boll Weevil Test

Compound	Ratings in ppm							
	1000	500	250	100	50	25	10	5
A	9	9	9	9	8.5	8.8	6.7	7.5
B	9	9	8.5	9	9	8.5	6	6
C	9	9	9	9	7	8.5	4.5	—
D	9	9	9	9	9	8.5	5.5	0
E	9	9	9	9	9	6.5	8	2
F	9	9	8.5	9	6.5	7.5	4	—
G	9	—	—	—	—	—	—	—
H	9	9	9	9	8	5.5	1	—
I	9	9	9	7.5	8.5	8.5	8	6
K	9	—	—	—	—	—	—	—
L	—	9	9	9	9	1.5	.5	—
M	7.5	8.5	8.5	5	1.5	—	—	—
N	9	—	—	—	—	3.5	1.5	—
O	9	9	8.5	8	7.5	6.5	0	—
P	9	9	9	9	8	5	1.5	—
Malathion	7-8							

Compounds useful in the insecticidal processes of this invention are prepared in accordance with the procedure described in applicant's copending Applications Nos. 57611/70 (Serial No. 1267999) and 57613/70 (Serial No. 1268000).

Most of the compounds coming within the scope of Formulae I (a) and I (b) above are phytotoxic at application rates considerably higher than those at which the compounds are insecticidally active, and many are effective herbicides for a wide variety of plants at application rates of 8 pounds per acre or higher. However, the extreme effectiveness of the insecticides represented by Formulae I (a) and I (b) provides a sufficient margin of safety to enable their use, either in the soil in the presence of growing or seedling crops, or by a one-time application to the foliage, as agricultural insecticides.

While the compounds of this invention resemble the organic phosphates in being toxic upon ingestion, they differ from the organic phosphates in having a low toxicity when applied to the skin. The following charts give the estimated acute oral and acute dermal toxicities of 2,6-bis(trifluoromethyl)-4-nitrobenzimidazole in several species of mammals.

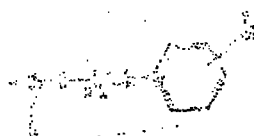
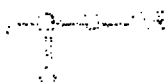
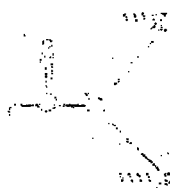


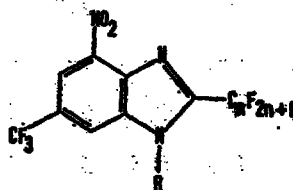
TABLE 10
Acute Oral Toxicity of 2,6-bis(trifluoromethyl)-
4-nitrobenzimidazole

Animals Used	Est. LD ₅₀ , mg./kg.
Mouse, female	27
Rat, male	16—20
Rat, female	19—22
Guinea Pig, male	15
Guinea Pig, female	15

TABLE 11
Acute Dermal Toxicity of 2,6-bis(trifluoromethyl)-
4-nitrobenzimidazole

Animals Used	Est. LD ₅₀ , mg./kg.
Rabbit, male	> 500
Rabbit, female	> 500

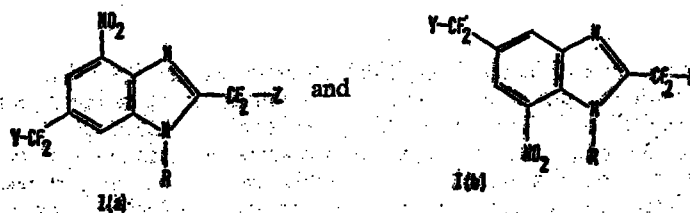
A group of highly active insecticides and arachnicides coming within the scope of Formulae I (a) and I (b) consists of 2,6(5)-bis(trifluoromethyl)-4(7)-benzimidazole and its N-substituted derivatives as represented by the formula:



wherein R, has the same meaning as hereinabove, and n is 1—3. The use of the compounds of the above formula as insecticides and arachnicides constitutes a preferred process of this invention.

WHAT WE CLAIM IS:—

1. An insecticidal and acaricidal composition which comprises, as its biocidally effective ingredient, a benzimidazole represented by the following formulae:



wherein R is hydrogen, an alkaline or alkaline earth metal,

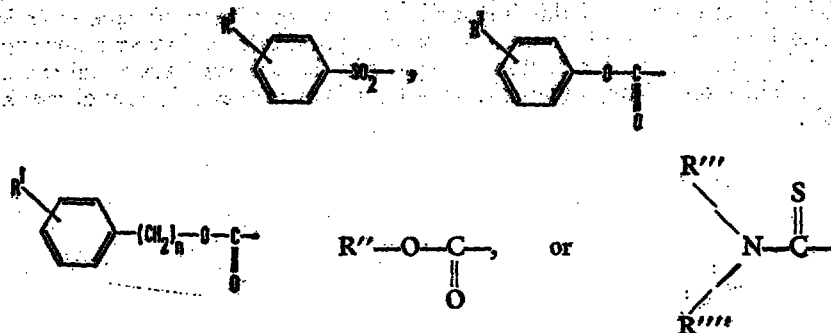


TABLE 10
Acute Oral Toxicity of 2,6-bis(trifluoromethyl)-
4-nitrobenzimidazole

Animals Used	Est. LD ₅₀ , mg./kg.
Mouse, female	27
Rat, male	16—20
Rat, female	19—22
Guinea Pig, male	15
Guinea Pig, female	15

10

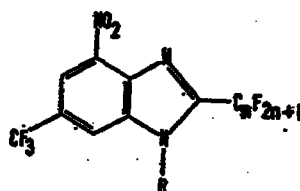
TABLE 11
Acute Dermal Toxicity of 2,6-bis(trifluoromethyl)-
4-nitrobenzimidazole

Animals Used	Est. LD ₅₀ , mg./kg.
Rabbit, male	> 500
Rabbit, female	> 500

15

15

A group of highly active insecticides and arachnides coming within the scope of Formulae I (a) and I (b) consists of 2,6(5)-bis(trifluoromethyl)-4(7)-benzimidazole and its N-substituted derivatives as represented by the formula:



20

wherein R, has the same meaning as hereinabove, and n is 1—3. The use of the compounds of the above formula as insecticides and arachnides constitutes a preferred process of this invention.

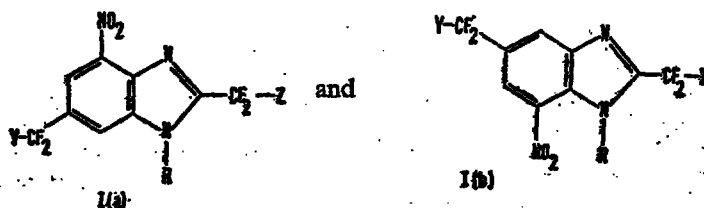
20

WHAT WE CLAIM IS:—

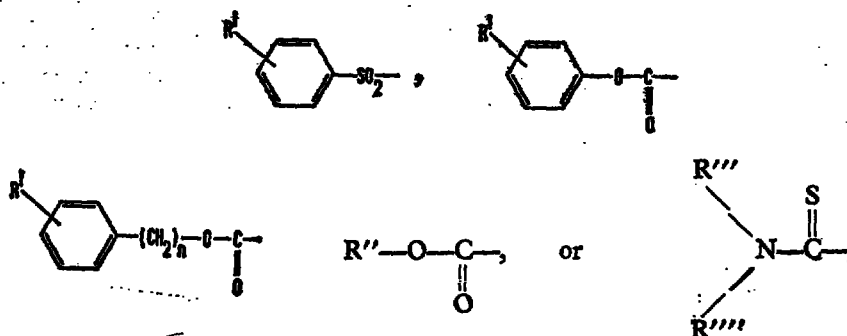
25

1. An insecticidal and acaricidal composition which comprises, as its biocidally effective ingredient, a benzimidazole represented by the following formulae:

25



wherein R is hydrogen, an alkaline or alkaline earth metal,



wherein n is 1 to 3, R' is hydrogen, fluorine, chlorine, bromine, C_1-C_5 alkoxy, C_1-C_5 alkyl or nitro; and R'' is C_1-C_5 alkyl, halo-substituted C_1-C_5 alkyl, halo-substituted C_2-C_5 alkenyl, C_2-C_5 alkynyl or C_2-C_5 alkenyl; R''' and R'''' individually are hydrogen, C_1-C_5 alkyl or phenyl, or when taken together a pentamethylene or tetramethylene chain; and Y is F or H; Z is F, H, Cl, $-CF_3$ or $-CF_2-CF_3$; and halo is fluorine, chlorine or bromine.

2. The composition of claim 1 wherein the biocidally effective ingredient is 2,6-bis(trifluoromethyl)-4-nitro-benzimidazole.

3. The composition of claim 1 wherein the biocidally effective ingredient is 2,6-bis(trifluoromethyl)-4-nitro-benzimidazole sodium salt.

4. The composition of claim 1 wherein the biocidally effective ingredient is isopropyl 2,6-bis(trifluoromethyl)-4-nitro-1-benzimidazolecarboxylate.

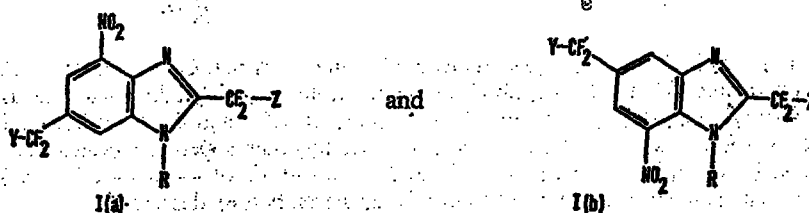
5. The composition of claim 1 wherein the biocidally effective ingredient is 2,6-bis(trifluoromethyl)-4-nitro-1-phenylsulfonylbenzimidazole.

6. The composition of claim 1 wherein the biocidally effective ingredient is allyl 2,6-bis(trifluoromethyl)-4-nitro-1-benzimidazolecarboxylate.

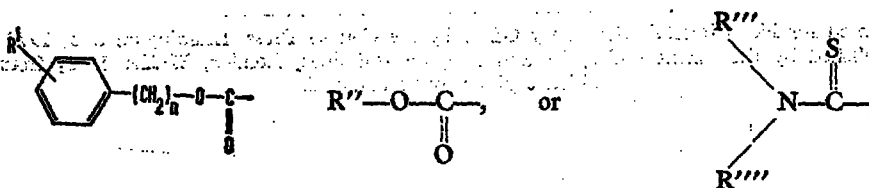
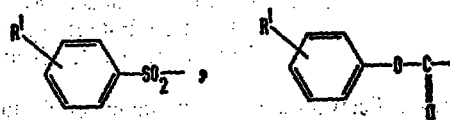
7. The composition of claim 1 wherein the biocidally effective ingredient is 2-chlorodifluoromethyl-4-nitro-6-trifluoromethylbenzimidazole.

8. The composition of claim 1 wherein the biocidally effective ingredient is 2-trifluoromethyl-4-nitro-6-difluoromethylbenzimidazole.

9. An insecticidal and acaricidal composition which comprises, as its biocidally effective ingredient, a benzimidazole represented by the following formulae:



wherein R is hydrogen,

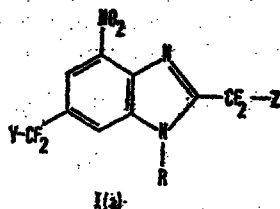


wherein n is 1 to 3, R' is hydrogen, fluorine, chlorine, bromine, C_1-C_5 alkoxy, C_1-C_5 alkyl or nitro; and R'' is C_1-C_5 alkyl, halo-substituted C_1-C_5 alkyl, halo-substituted C_2-C_5 alkenyl, C_2-C_5 alkynyl or C_2-C_5 alkenyl; R''' and R'''' individually are hydrogen, C_1-C_5 alkyl or phenyl, or when taken together a pentamethylene or tetramethylene chain; and Y is F or H; Z is F, H, Cl, $-CF_3$ or $-CF_2-CF_3$; and halo is fluorine, chlorine or bromine; substantially as hereinbefore described with particular reference to the examples.

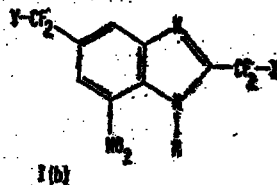
10. A method for killing insects and arachnids comprising the application to an insect or arachnid habitat of the composition of any of claims 1 to 9.



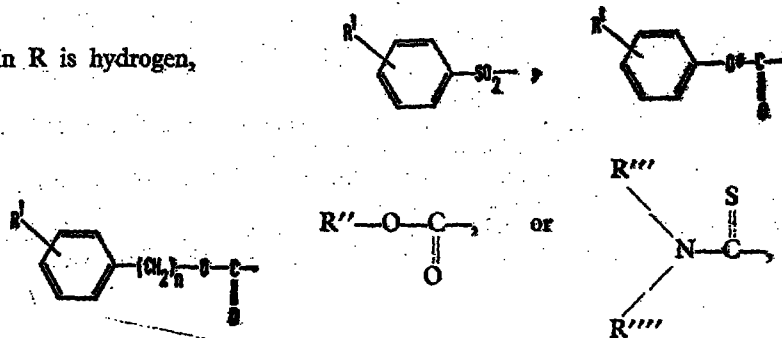
11. A method for killing insects and arachnids comprising the application to an insect or arachnid habitat of a composition containing, as its biocidally effective ingredient, a benzimidazole represented by the following formulae:



and



5 Wherein R is hydrogen,



10 wherein n is 1 to 3, R' is hydrogen, fluorine, chlorine, bromine, C₁-C₅ alkoxy, C₁-C₅ alkyl or nitro; and R'' is C₁-C₅ alkyl, halo-substituted C₁-C₅ alkyl, halo-substituted C₂-C₅ alkenyl, C₂-C₅ alkynyl or C₂-C₅ alkenyl; R''' and R''' individually are hydrogen, C₁-C₅ alkyl or phenyl, or when taken together a pentamethylene or tetramethylene chain; and Y is F or H; Z is F, H, Cl, -CF₃ or -CF₂-CF₃; and halo is fluorine, chlorine or bromine; substantially as hereinbefore described.

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Reference has been directed in pursuance of Section 9, subsection (1) of the Patents Act, 1949, to patent Nos: 1,170,737, 1,151,424, 1,104,936, and 1,087,561.

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