

analogs to be spread over the paper chromatogram and rendered them difficult or impossible to detect. Eighty-three percent of the urinary metabolites isolated were 2-chloro analogs of cyprazine. The hydrolysis of the 2-chloro group by the rat cannot be ruled out, but it does not appear to be a major route of metabolism in the rat. These findings are consistent with those of Bohme and Barr (1967) and suggest that the 2-hydroxy metabolites isolated as atrazine metabolites (Bakke et al., 1972) were artifacts resulting from hydrolysis of the corresponding 2-chloro analogs during ion-exchange chromatography.

Total N-dealkylation, partial N-dealkylation, and N-dealkylation with N-alkyl oxidation are major routes of cyprazine metabolism in the rat.

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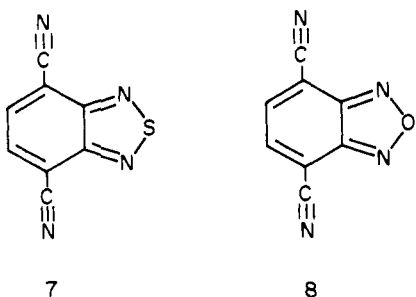
Herbicidal Activity of 2,1,3-Benzothiadiazolecarbonitriles and Related Cyanoheterocycles

Robert H. Schieferstein and Kurt Pilgram*

New carbonitriles of 2,1,3-benzothiadiazole and benzofurazan have been prepared and evaluated for herbicidal activity. 4,7-(and 4,5)-Dicyano-2,1,3-benzothiadiazole (7 and 4) and 4,7- (and 4,5)-dicyanobenzofurazan (8 and 5) were active pre- and postemergence at low rates. Substitution of one or both cyano groups by hydrogen, alkyl, chlorine, carboxy, alkoxy-carbonyl, carbox-amido, acylamido, and ureido reduced activity

significantly. High activity was maintained in the monomethyl analog of 7, whereas addition of two methyl groups or one amino or nitro group essentially eliminated activity. Annual ryegrass, wild oat, and corn have tolerance for 7 in relation to rates required for control of a wide range of weeds; other analogs do not appear as selective for corn as 7.

Earlier investigations in our laboratories showed that 2,1,3-benzothiadiazole-4,7-dicarbonitrile (7) was active as a herbicide (Slott et al., 1968). The related benzofurazan-4,7-dicarbonitrile (8) also showed herbicidal activity. A



number of related 2,1,3-benzothiadiazoles and benzofurazans have now been synthesized and their properties studied. As a result of these studies, some correlations have been made of the herbicidal activity with change of position and nature of substituents in the benzothiadiazoles and benzofurazans.

MATERIALS AND METHODS

Chemical Methods. Carbonitriles of 2,1,3-benzothiadiazoles and benzofurazans were prepared by reaction of the

respective bromoheterocycle with cuprous cyanide in dimethylformamide at elevated temperature. Cyanoheterocycles 3-20 and 23 were prepared by this method (Pilgram and Skiles, 1974; Pilgram and Zupan, 1974). The 2,1,3-benzothiadiazolecarbonitriles 1, 2, and 22 were conveniently prepared from the respective amino-2,1,3-benzothiadiazole using the Sandmeyer method (Pilgram and Skiles, 1974). Bis(thiocarboxamido)-2,1,3-benzothiadiazoles 25, 27, and 28, and 4,7-bis(thiocarboxamido)benzofurazan (26) were prepared by the base-catalyzed addition of hydrogen sulfide to the corresponding dicarbonitrile in dimethylformamide or alcohol solution (Slott et al., 1968). Dicarboxylic acid 24, prepared from 7 by alkaline hydrolysis, was converted, via the diacid chloride, into the diamides 29 and 30, the dihydrazide 31, and the dicarboxylic acid esters 32 and 33 (Pilgram, 1974). Nitration of 4-methyl-, 4-ethyl-, and 4-propyl-2,1,3-benzothiadiazole in concentrated sulfuric acid afforded the 7-nitro analogs 34, 36, and 38, respectively. Compounds 34 and 36 were reduced to the amines 35 and 37. The reduction was effected using iron filings in boiling water containing 3% of formic or acetic acid, or in aqueous sodium dithionite. Compound 39 was prepared by nitration with sodium nitrate in concentrated sulfuric acid by the method of Pesin et al. (1963). 4-Bromo-7-nitro-2,1,3-benzothiadiazole (Pilgram et al., 1970) with dimethylamine at 80° in methanol in an autoclave produced 40, which was reduced catalytically to 41. Chlorobenzothiadiazoles 21 and 43 were prepared by the methods of Pesin et al. (1963, 1964), whereas 4,7-dichlorobenzofurazan (44) was obtained following the

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Table I. Substituted 2,1,3-Benzothiadiazole, Benzofurazan, and 2,1,3-Benzoselenadiazole Properties and Test Results

Compd	R ⁴	R ⁵	R ⁶	R ⁷	X	Mp, °C	Ref	Soil		Foliar spray	
								Water-grass	Cress	Crab-grass	Pig-weed
								1 2	1 2	1 2	1 2
1	CN				S	124–125	<i>b</i>	1 9	0 9	0 3	0 1
2		CN			S	112–113	<i>c</i>	0 5	5 9	0 0	0 0
3		CN			O	81–82	<i>d</i>	0 0	0 9	0 7	0 0
4	CN	CN			S	156–159	<i>c</i>	9 9	9 9	9 9	9 9
5	CN	CN			O	111–112	<i>d</i>	7 8	9 9	7 9	9 9
6	CN		CN		S	175–178	<i>c</i>	9 9	9 9	8 9	9 9
7	CN			CN	S	189–191	<i>c</i>	9 9	9 9	9 9	9 9
8	CN			CN	O	185–188	<i>d</i>	8 9	9 9	9 9	9 9
9		CN	CN		S	201–203	<i>c</i>	5 8	3 9	5 6	6 7
10	CN	CH ₃			S	150–153	<i>c</i>	1 9	6 9	0 4	1 3
11	CN	CH ₃			O	97–99	<i>d</i>	1 9	6 9	0 4	0 6
12	CN	Cl			S	172–175		0 8	5 9	7 9	9 9
13	CN			CH ₃	S	168–173	<i>c</i>	8 9	9 9	0 5	2 8
14	CN			C ₂ H ₅	S	94–95		0 8	3 8	0 0	0 2
15	CN			NO ₂	S	207–210		1 9	4 9	7 6	7 9
16	CN	CH ₃		CN	S	173–177	<i>c</i>	8 9	8 9	9 9	9 9
17	CN	NH ₂		CN	S	214–218	<i>c</i>	1 7	0 8	0 0	6 8
18	CN	CH ₃	CH ₃	CN	S	235–236	<i>c</i>	1 6	0 5	8 8	1 9
19	CN		CN	NO ₂	S	224–228	<i>c</i>	0 3	0 8	0 0	2 9
20	CN		CN	NH ₂	S	265–270		0 5	5 8	0 0	0 4
21	Cl	Cl		Cl	S	123–124	<i>c</i>	9 9	8 9	1 9	0 9
22	CN	Cl		Cl	S	188–192	<i>c</i>	0 1	0 5	0 4	1 8
23	CN	NO ₂		Br	S	190–193	<i>c</i>	1 9	2 9	2 7	8 9
24	C(=O)OH			C(=O)OH	S	325–329	<i>e</i>	3 8	0 9	0 0	0 2
25	C(=S)NH ₂			C(=S)NH ₂	S	261–262 ^a	<i>f</i>	8 9	8 9	8 9	9 9
26	C(=S)NH ₂			C(=S)NH ₂	O	~175 ^a	<i>f</i>	0 9	1 9	9 9	9 9
27	C(=S)NH ₂		C(=S)NH ₂	C(=S)NH ₂	S	220–223 ^a	<i>f</i>	8 9	8 9	2 9	8 9
28	C(=S)NH ₂	CH ₃	CH ₃	C(=S)NH ₂	S	~250 ^a	<i>f</i>	0 7	0 8	7 7	6 9
29	C(=O)NH ₂			C(=O)NH ₂	S	308–310	<i>e</i>	1 2	2 7	0 0	0 3
30	C(=O)NHCH ₃			C(=O)NHCH ₃	S	227–228	<i>e</i>	0 1	0 6	0 0	4 7
31	C(=O)NHNH ₂			C(=O)NHNH ₂	S	220–223	<i>e</i>	0 1	0 7	0 0	0 0
32	C(=O)OCH ₃			C(=O)OCH ₃	S	163–164	<i>e</i>	3 7	0 9	0 5	0 7
33	C(=O)OC ₂ H ₅			C(=O)OC ₂ H ₅	S	65	<i>e</i>	0 0	0 0	0 0	0 3
34	CH ₃			NO ₂	S	165–167	<i>g</i>	8 8	7 9	8 9	9 9
35	CH ₃			NH ₂	S	81–82		1 7	7 9	7 9	0 9
36	C ₂ H ₅			NO ₂	S	103–105	<i>e</i>	6 8	4 8	5 9	9 9
37	C ₂ H ₅			NH ₂	S	63–64	<i>e</i>	0 0	0 5	3 5	3 7
38	C ₃ H ₇			NO ₂	S	65–66.5	<i>e</i>	0 2	1 3	8 9	0 9
39	NO ₂			NO ₂	S	194–196	<i>h</i>	1 1	0 5	0 3	1 6
40	NO ₂			N(CH ₃) ₂	S	234–235	<i>e</i>	0 1	0 7	0 0	0 6
41	NH ₂			N(CH ₃) ₂	S	80–81	<i>e</i>	0 0	0 0	3 9	7 9
42	CH ₃			CH ₃	S	59	<i>e</i>	3 8	8 8	0 0	0 5
43	Cl			Cl	S	180–181	<i>b</i>	7 9	8 9	0 4	0 3
44	Cl			Cl	O	62–63	<i>i</i>	8 9	8 8	0 0	0 0
45	Cl			OH	O	132	<i>j</i>	0 0	0 0	0 0	1 2

^a With decomposition. ^b Pesin et al. (1963). ^c Pilgram and Skiles (1974). ^d Pilgram and Zupan (1974). ^e Pilgram (1974). ^f Slott et al. (1968). ^g Pesin and Muravnik (1964). ^h Pesin et al. (1964). ⁱ Boulton et al. (1967). ^j Shell International Research Maatschappij (1966).

procedure given by Boulton et al. (1967). Demethylation of 7-chloro-4-methoxybenzofurazan gave 7-chlorobenzofurazan-4-ol (45) following a literature procedure (Shell Internationale Research Maatschappij, 1966).

Structures and purities were confirmed by GC, TLC, NMR, and ir analyses; satisfactory elemental analyses ($\pm 0.4\%$ for N and S) were obtained.

One method for the preparation of a bis(thioamido) compound is described below for the synthesis of 25; this method was applicable for the synthesis of compounds 26, 27, and 28.

Preparation of 2,1,3-Benzothiadiazole-4,7-bis(thio-

carboxamide) (25). Hydrogen sulfide was introduced through a gas-inlet tube into a solution of 166 g (0.89 mol) of 7 in 610 ml of dimethylformamide containing 94 g (0.89 mol) of diethanolamine. The exothermic reaction was controlled at 55° with an ice bath. Hydrogen sulfide was added until the internal temperature dropped (ca. 1.5 hr). The dark reaction mixture was stirred for 15 min and poured in ice water. The solid product was collected, washed with ethanol, and sucked dry to give 157 g (69%) of maroon solid, mp 261–262° dec.

Anal. Calcd for C₈H₆N₄S₃: N, 22.1; S, 37.8. Found: N, 22.2; S, 37.5.

Table II. Response of Ten Plant Species to Pre- and Postemergence Applications of Substituted 2,1,3-Benzothiadiazoles and Benzofurazans

Compd	Preemergence (LD ₉₅), lb/acre						Postemergence (LD ₉₅), lb/acre					
	Rye-grass	Cheat-grass	Crab-grass	Curly dock	Pig-weed	Mustard	Wild oat	Water-grass	Crab-grass	Fiddle-neck	Field cress	
1	5.5	2.5	8.5	2.5	3.5	3.5	10+	10+	10+	10+	10+	
4	2.5	2.0	0.9	1.7	0.9	4.5	2.0	0.9	0.4	1.7	1.7	
5	5+	5+	5+	5+	3.5	5+	5.0	4.5	2.5	1.7	10+	
6	2+	2+	1.4	2+	1.4	2+	2+	1.2	1.0	2+	1.8	
7	10+	2.6	1.1	1.8	0.3	2.3	10+	1.0	0.3	0.5	1.1	
8	10.0	1.3	3.0	3.5	1.7	7.5	10+	1.5	0.2-	0.4	0.1	
13	2.5	1.3	5.0	0.5	3.5	6.0	10+	10+	10+	3.0	10+	
16	2+	2+	1.5	2+	1.1	2+	2+	1.2	0.5	2+	2.0	
25	10+	10.0	1.3	3.5	0.4	5.5	10.0	7.5	1.0	3.0	6.0	
42	4.5	6.0	10+	1.0-	5.0	8.5	10+	10+	10+	10+	10+	

Table III. Postemergence Crop Selectivity

Compd	Min effective dose, GI ₉₀ , lb/acre					Max tolerated dose, GI ₁₀ , lb/acre							
	Crab-grass	Pig-weed	Corn	Peas	Lettuce	Soy-bean	Wheat	Barley	Flax	Cotton	Sugar-beet	Alfalfa	
4	0.3	0.1-	0.1-	0.1-	0.1-	0.1-	1.0	0.3	0.1-	0.1-	0.1-	0.1-	
6	1.0	0.3	0.03-	1.0	0.1	0.1	3.0	0.1	0.1-	0.1-	0.1	0.1	
7	0.2	0.06	3.0	0.3	0.06	0.03	0.03-	0.1	0.06	0.03-	0.03	0.03-	
8	0.06	0.03-	0.03-	0.03-	0.03	0.03-	0.03	0.03-	0.03-	0.03-	0.03	0.03-	
16	0.3	0.01-	0.1-	0.1-	0.1	0.1-	0.3	0.1	0.1-	0.1-	1.0	0.3	
25	3.0	0.3-		0.3	0.3-	0.3-	0.3	0.3-	0.3-	0.3-	0.3-		
Atrazine ^a	5.0+	0.05-	5.0+	0.05-	0.05-	0.05-	5.0-	5.0-	0.1-	0.5-	0.05-	0.05-	

^a For comparison.

Biological Methods. The herbicidal properties were determined in various tests taking into account three potential ways of uptake of the test compounds: via the seeds, the roots, or the green parts of the plants (mainly the leaves).

Experimental compounds were tested preemergence on watergrass and cress as one of the initial screening tests for candidate herbicides. Seeds of watergrass and cress were planted in test tubes, nominally measuring 25 × 200 mm, containing soil treated with the test compounds at the rate of 0.1 and 1.0 mg of active ingredient per tube designated in Table I as rates 1 and 2, respectively. The planted soil was held under controlled conditions of temperature, moisture, and light for 13 to 14 days. Toxicity ratings were 0 to 9, with 0 indicating no effect, 9 indicating complete kill or no germination.

The postemergence activity was evaluated by spraying 10-day-old pigweed plants and 7-day-old crabgrass plants to run-off with a liquid formulation of the test compound at the rates of 0.62 ml of a 0.04% solution designated rate 1, and 0.56 ml of a 0.5% solution designated rate 2 in Table I. The sprayed plants were held under controlled conditions of temperature, light, and moisture for 10-11 days and the effect of the test compound on the plant was then evaluated visually, the results being rated on the 0-9 scale described above.

Those compounds that showed appreciable activity in either the preemergence or postemergence screens have been followed up in additional tests which utilize log dilution, variable rate spray applications. Each chemical is applied in a logarithmic dilution either to the soil surface (preemergence) or to the foliage (postemergence) of seedlings grown in standard 6 × 24 in. trays. This log dilution screen is designed to determine approximate threshold ef-

fective rates (LD₉₅) on several important weed species for a test compound. With these "point-of-equal-response" data, compounds may be compared directly for level of activity either for individual species or as averages of several species. Results with these tests, which are evaluated 2 weeks after foliar treatment and 3 weeks after preemergence treatment, are presented in Table II.

Postemergence crop selectivity was determined on several test compounds by similar application to ten crop and two weed species grown in growth chambers in 2 × 2 in. pots under controlled temperature, light, and moisture conditions. Compounds are sprayed using the log dilution technique so that a 100-fold difference is obtained between the high and low rates. After 2 weeks in the growth chamber, the plants are harvested and weighed. Check plants are grown to establish the GI₁₀ tolerance limit for crop species and the GI₉₀ limit for crabgrass and pigweed. The results of postemergence crop selectivity tests are summarized in Table III.

Weed species mentioned in this paper include: watergrass (*Echinochloa crusgalli*), cress (*Lepidium sativum*), crabgrass (*Digitaria sanguinalis*), pigweed (*Amaranthus* sp. (mixture of species)), ryegrass (*Lolium multiflorum*), cheatgrass (*Bromus tectorum*), curly dock (*Rumex crispus*), mustard (*Brassica arvensis*), wild oat (*Avena fatua*), and fiddleneck (*Amsinkia douglasiana*).

RESULTS AND DISCUSSION

The results in Table I show that highest activity in the 2,1,3-benzothiadiazole series is associated with the dicyano-substituted compounds 7 (4,7-dicyano) and 4 (4,5-dicyano). High activity was maintained in the 4,6-dicyano isomer 6, whereas the 5,6-dicyano isomer 9 was considerably less active.

Within the isoelectronic benzofurazancarbonitrile series, highest pre- and postemergence activity of a comparable order of magnitude was found in 8 (4,7-dicyano) and 5 (4,5-dicyano). Being not only isoelectronic but also isomeric, these latter compounds are directly comparable with 7 and 4.

Substitution of one of the two cyano groups in 4, 7, and 8 by hydrogen (compounds 1, 2, and 3), chlorine (compound 12), methyl (compounds 10, 11, and 13), ethyl (compound 14), or a nitro group (compound 15) reduced activity significantly. However, high activity was maintained in the monomethyl derivative of 7, e.g. 16, while addition of an amino group, as in 17, or of two methyl groups (compound 18) essentially eliminated activity of the 4,7-dicyano compound. Note also the loss of activity produced when a nitro or amino group is added in the 7 position of the 4,6-dicyano isomer 6 as evidenced by the data recorded for 19 and 20.

While 4,5,7-trichloro-2,1,3-benzothiadiazole (21) (Philips Duphar N.V.'s Experimental Herbicide PH-40-21 (TH-052-H); common name, TCBT) (Koopman et al., 1967) was rated as highly active in the preemergence test, the 4-cyano-5,7-dichloro analog 22 and 4-cyano-5-nitro-7-bromo-2,1,3-benzothiadiazole (23), which are close to isomeric with 21, were surprisingly inactive.

Among the dicarboxylic acid derivatives, e.g. 24 which itself was inactive, only bis(thiocarboxamido) compounds such as 25, 26, and 27 were active, and none of the related amides (compounds 29 and 30), hydrazide (compound 31), and esters (compounds 32 and 33) were active. The activity of 25, 26, and 27 may be explained by the fact that these bis(thiocarboxamides) by loss of hydrogen sulfide generate the active dicarbonitrile precursors 7, 8, and 6, respectively.

Substitution of both cyano groups in 7 by other groups led to compounds with reduced activity. Where one of these substituents was either methyl, ethyl, or nitro, e.g. compounds 34 and 36, pre- and postemergence activity was highest. Activity was lowest where one substituent was amino (compounds 35 and 37) or where both substituents were either amino (compound 41) or nitro (compound 39) or a combination of amino and nitro (compound 40). Acylated and carbamoylated derivatives of 35 and 37 (Pilgram, 1974) were also found to be inactive.

Other symmetrically 4,7-disubstituted 2,1,3-benzothiadiazoles and benzofurazans such as 42 (4,7-dimethyl), 43 (4,7-dichloro), and 44 (4,7-dichloro) exhibited comparable preemergence activities, being inactive postemergence. Replacement of one chlorine atom in 44 by the hydroxy group essentially eliminated activity (compound 45).

One of the most promising features of 7 has been its wide differential level of activity between species. Annual ryegrass (Table II), wild oat (Table II), and corn (Table III), for example, appear to have tolerance for this compound in relation to rates required for control of a wide range of weeds. The results of the postemergence crop selectivity studies indicate that other analogs of 7 do not appear as selective for corn as 7.

Two modes of action are evident in carbonitriles derived from 2,1,3-benzothiadiazole and benzofurazan. The gross symptomatology of most of the 2,1,3-benzothiadiazolecarbonitriles, e.g. 7, is typical of many photosynthesis inhibitors. Others, like 8, appear to have two modes of action—they are growth inhibitors acting on the roots in preemergence tests, as well as photosynthesis inhibitors. There is no obvious correlation between structure, pattern of sub-

stituent groups, and apparent mode of action. However, antiphotosynthesis activity appears dependent on at least one cyano group in the 4 or 7 position and an additional electron-withdrawing substituent in either of the remaining positions of the benzene ring. Where two cyano groups are present, the 4,7- and 4,5-substituent pattern gave a somewhat higher level of antiphotosynthesis activity than the 4,6-substituent pattern.

In soil applications of near marginal dosages, photosynthesis inhibition takes the form of early seedling chlorosis followed by tip or marginal necrosis, which becomes general resulting in death to the plant. Following foliar treatment, there is an olive drab discoloration becoming rapidly necrotic. However, compound 7 has a very low level of activity in inhibiting the Hill reaction in isolated spinach chloroplasts (35% inhibition at 10^{-3} M). Therefore, 7 is acting at some other point to block photosynthesis. Treated plants kept in the light developed these symptoms within a few hours. In contrast, those plants that were immediately transferred to a dark environment were unaffected until subsequent exposure to light. The light-mediated action suggests a mode of action related to that of diquaternary bipyridyls such as diquat and paraquat. Their mode of action is connected with their ability to be reduced to stable radical cations by electrons from photosystem I of illuminated chloroplasts in a one-electron transfer which is reversed by air. Although cyano compounds such as 7 can be reduced and oxidized in a reversible one-electron step to their respective radical anion (Sherman et al., 1974), it is not known at this time whether they interfere in the oxidative metabolic pathway. Additional studies will be needed to determine the possible significance and generality of the formation of stable radical anions in plants and the mode of action of these cyanoheterocycles.

Root growth inhibition caused by compounds such as 8 and 42 does not result in a bulbous swelling of the inhibited root tips. The meristem of the root tip appears normal, but nearby tissues show a higher degree of differentiation than normal. This effect may simply reflect that cell division has ceased or greatly slowed, but cell differentiation has proceeded at a more nearly normal rate until cells remaining to be differentiated are exhausted. Such a picture could be caused by any one of a number of biochemical actions.

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