1,182,132

PATENT SPECIFICATION

NO DRAWINGS

1,182,132

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International Classification:—C 07 d 107/02

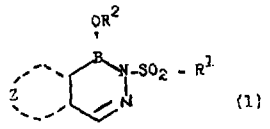
COMPLETE SPECIFICATION

Novel Heterocyclic Compounds containing Boron, and a process for their production

We, CHEMIE GRUNENTHAL G.M.B.H., a body corporate organised under the laws of Germany, of 5190 Stolberg im Rheinland, Germany, do hereby declare the 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:—

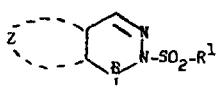
This invention relates to novel boron-containing heterocyclic compounds exhibiting valuable properties and to processes for the preparation of these compounds.

The present invention provides boron-containing heterocyclic compounds and salts thereof, which compounds have the general formula



(1)

wherein Z represents a fused *o*-phenylene, naphthylene or thienylene ring which may optionally be substituted by one or more alkyl radicals, halogen atoms, etherified hydroxy or mercapto groups, alkyl, aralkyl or aryl sulphonyl groups, amino groups, acylamino groups, or nitro groups, R^1 represents a mono- or polynuclear aromatic or heterocyclic radical, optionally substituted by one or more alkyl radicals, etherified hydroxy or mercapto groups, halogen atoms, amino or acyl amino groups or nitro groups, and R^2 represents a hydrogen atom, a monovalent cation or the radical



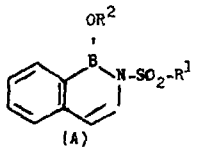
wherein R^1 and Z have the meanings given above.

If, in formula I, R^1 represents an aromatic radical (in particular a phenyl or naphthyl radical) any substituents present in it, advantageously alkyl radicals or etherified hydroxy or mercapto groups, are preferably in the *ortho*- and/or *para*-position to the SO_2-group. If RZ represents a heterocyclic radical, this substituent can be, for example, a thienyl (advantageously thienyl-2), furyl, thiozolyl pyridyl, pyrimidyl, imidazolyl or quinolyl radical, optionally substituted in the same manner as the aromatic radical, or can be a radical in which the SO_2-group is attached to a benzene ring which is in turn attached to a heterocyclic ring system, for example, a benzimidazolyl-4-(7)- or -5-(6)-radical, a quinazolyl-5- or -6- radical or a quinolyl-5-, -6-, 7- or -8-radical.

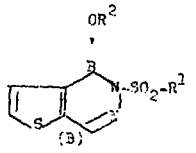
If Z and/or R^1 comprise one or more alkyl radicals, these radicals preferably contain one to five carbon atoms each.

Compounds in which R^1 represent a phenyl radical substituted by one or two methyl, ethyl, methoxy, ethoxy, methylmercapto or ethyl mercapto groups, are of particular interest.

Z preferably represents an o-phenylene- or a thienylene-2,3-or -3,4- radical, in which instance the compounds of general formula (I) will have one of the following formulae:

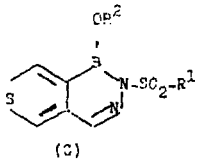


(A)



(B)

or



(C)

in which R^1 and R^2 have the meanings given above.

The basic structure present in formula (A) is known in the literature as "benzo-2,3,1-diazaborine". In the following Examples, the basic structures from formulae (B) and (C) are referred to as "thieno-[2,3-e]-2,3,1-diazoborine" and "thieno-[3,4-e]-2,3,1-diazoborine", respectively.

Where Z represents a naphthylene radical, this radical may be attached by fusion at the 1,2- or 2,3-position.

Surprisingly, it has been that the novel compounds of formula (I) show *inter alia* a marked effect on micro-organisms. This effect can be seen both *in vitro* and in the infected organism (following parenteral or oral administration of the substances). For example, the DC_{50} (that dose following administration of which 50% of the test animals are cured of the infection) when orally administered to mice infected with *Echerichia coli* is approximately 0.5 mg/20 g. of mouse for the substances of general formula (I) in which Z represents an *o*-phenylene radical and R^1 a phenyl or thienyl-(2)-radical, and approximately 0.6 mg/20 g. of mouse for the substance of formula (I) in which Z represents an *o*-phenylene radical and R^1 a *p*-tolyl radical.

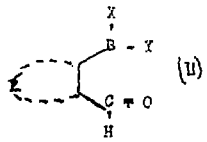
In addition to their destructive effect on Gram-negative bacteria, many of the compounds of formula I are also highly effective against protozoa, trypanosomes and plasmodia in particular. For example, groups each comprising 10 mice, were infected with *Plasmodium berghei*. All the animals from an untreated control group died within a period of 11 to 30 days after infection. By contrast, all the animals which, for five days, had been given a daily dose, administered orally, of 2.5 mg/20 g. of mouse of 1 - hydroxy - 2 - (*p*-tolylsulphonyl) - benzo - 2,3,1 - diazaborine (product of Example 2) were still alive on the 40th day after infection. In their case, it was impossible to detect any plasmodia, even in blood smears.

In addition, mice were infected with *Trypanosoma brucei*. Whereas all the animals from the untreated control group died on the 5th day after infection, 60% and 70%, respectively, of the animals which for four days had been given a daily orally-administered dose of 5 mg/20 g. of mouse of 1 - hydroxy-2 - (*p*-tolylsulphonyl) - benzo - 2,3,1 - diazaborine and 1 - hydroxy - 2 - (*p* - methoxyphenylsulphonyl) - benzo - 2,3,1 - diazaborine, respectively, were still alive on the 14th day after the beginning of the test.

Some of the compounds of general formula (I), in particular those in which R^1 represents an optionally substituted hetero-cyclic radical, also show cytostatic properties.

In addition, several of the compounds are pharmacologically active and, in particular, antiphlogistacally active.

The valuable new compounds are prepared by reacting a compound corresponding to the general formula



(II)

wherein Z has the meaning given above, whilst X and Y are the same or different and represent hydroxyl groups, etherified hydroxyl groups or halogen atoms, with a sulphonic acid hydrazine corresponding to the formula

$$H_2N—NH—SO_2—R^1 \qquad (III)$$

in which R^1 has the meaning given above, and, if X and Y do not represent OH groups, hydrolysing the residual group X or Y in the product into OH, and optionally converting the OH group into one of the other groups of the formula — OR^2. Suitable methods for carrying out this last optional step are described in "Progress in Boron Chemistry" Vol. 1 (1964) page 255; *J. Org. Chem.29* (1964), pages 2168-2172; and in *J.Amer. Chem.Soc.86* (1964), pages 433-436, by the conversion of the radical OH into the group —OR^2.

The compound of general formula (II) is preferably reacted with the sulphonic acid hydrazide of general formula (III) in the presence of a solvent or suspending agent, for example, an alcohol, dioxan or benzene, at elevated temperatures. The water formed during the reaction, or the resulting compound corresponding to the formula Y—H may be removed from the reaction mixture by azeotropic distillation with a suitable solvent, for example, benzene, and the reaction may thus be favourably displaced.

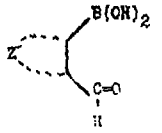
If, in the compound of general formula (I), the radical —OR^2, but not X, represents a hydroxyl group, the substituent X may readily be converted into a hydroxyl group, for

example, by treatment with alkalis or water, optionally accompanied by heating.

Examples of suitable compounds of formula (II) include, in particular, *o*-formylphenyl boric acid, 2-formylthienyl-3-boric ocid, 3-formylthienyl-4-boric acid, 1-formylnaphthalene-2-boric acid, 2-formylnaphthalene-1- or -3-boric acid, and their substitution products.

As already mentioned, compounds of general formula (I) in which Z and/or R^1 are substituted by one or more nitro groups, may be prepared using compounds of formula (II) and/or (III) containing nitro groups. However, it is also possible, for example, initially to prepare the corresponding compound without any nitro groups and then to nitrate it. The nitro groups present in the products obtained in this way may be reduced to amino groups in the usual way (for example, with nascent or catalytically active hydrogen). The compounds of general formula (I) in which Z and/or R^1 are substituted by one or more amino groups, may also be prepared by initially producing the corresponding compound in which Z and/or R^1 are substituted by an acylamino group or groups, and subsequently splitting off the acyl radical in a manner as known *per se*. Other substituents of Z and/or R^1 may also be similarly converted.

In one preferred embodiment of the process according to the invention, the sulphonic acid hydrazide of the formula (III) is reacted at elevated temperature with a boric acid derivative having the formula



(IV)

in which Z has the meaning given in connection with formula (I), and in the presence of a solvent or suspending agent.

In another preferred embodiment, the sulphonic acid hydrazide of formula (III) is the hydrazide of an aromatic sulphonic acid, optionally substituted in the ortho and/or para-position to the SO_2-group by alkyl radicals or by etherified hydroxy or mercapto groups, or of thienyl-2-sulphonic acid.

The invention is illustrated by the following Examples in which no importance was attached to obtaining optimum yields. All temperatures are uncorrected.

Example 1

A solution of 3.44 g. of benzene sulphonic acid hydrazide in 20 ml. of hot ethyl alcohol is mixed with a solution of 3.0 g. of *o*-formylphenyl boric acid in 15 ml. of hot ethyl alcohol. The reaction mixture is boiled under reflux for a few minutes. The crystals formed on cooling are filtered off and recrystallised from alcohol. 1 - hydroxy - 2 - benzenesulphonyl - benzo - 2,3,1 - diazaborine, melting at 163—165°C. is obtained in a yield of 4.2 g. (73% of the theoretical).

Example 2

The procedure is as in Example 1, except that 15 g. of *o*-formylphenyl boric acid, dissolved in 50 ml. hot ethyl alcohol, and 18.6 g. of *p*-toluene sulphonic acid hydrazide dissolved in 200 ml. of hot ethyl alcohol are used. 1 - hydroxy - 2 - (*p* - tolylsulphonyl)-benzo - 2,3,1 - diazaborine is thus obtained in a yield of 28.5 (95% of the theoretical), melting at 155—157°C. following recrystallisation from ethyl alcohol/toluene.

Example 3

Following the procedure described in Example 2, the following 1 - hydroxybenzo-2,3,1 - diazaborines substituted in the 2-position by the groups mentioned in the following Table, are obtained from *o*-formylphenyl boric acid and the corresponding sulphonic acid hydrazides:

TABLE

Substituent at position-2	Melting Point (°C.)	Yield in % of theoretical	Recrystallised from
2-(*p*-fluorophenylsulphonyl	173	85	ethanol/benzene
2-(*p*-chlorophenylsulphonyl)-	171—173	92	ethanol/benzene
2-(2',4',6'-trimethylphenylsulphonyl)-	153—155	82	ethanol
2-(thienyl-2'-sulphonyl)-	203—206	49	toluene
2-(*p*-ethylphenylsulphonyl)	97— 99	56	ethanol
2-(*m*-nitrophenylsulphonyl)	201—204	66	toluene
2-(2',4'-dimethylphenylsulphonyl)-	152—154	79	toluene
2-(*p*-ethylmercaptophenylsulphonyl)	129—131	71	ethanol/benzene
2-(*o*-tolylsulphonyl)-	136—138	65	ethanol/toluene
2-(2',5'-dimethylthienyl-3'-sulphonyl)	142—143 °C	74	ethanol/benzene
2-(pyridyl-3'-sulphonyl)	185—188	35	ethanol/dimethyl formamide
2-(2',5'-dimethylfuryl-3'-sulphonyl)-	128—129	55	ethanol/benzene
2-(1'-methyl-5'-chloroimidazolyl-4'-sulphonyl)-	220—225 (decomp)	76	dimethyl form amide/water
2-(pyridyl-4'-sulphonyl)-	181—182 (decomp.)	48	ethanol/dimethyl formamide
2-(3'-methylisothiazolyl-4'-sulphonyl)-	181—183	71	toluene

EXAMPLE 4

16.5 g. of *o*-formylphenyl boric acid are dissolved in 70 ml. of hot ethyl alcohol. A hot solution of 24.7 g. of *p*-acetaminobenzenesulphonic acid hydrazide in 400 ml. of 50% by weight ethyl alcohol is added to the resulting solution and the mixture is boiled and left to cool. The crystals obtained are recrystallised from ethyl alcohol/dimethyl formamide. 28 g. (62% of the theoretical) of 1 - hydroxy-2 - (*p* - acetaminophenylsulphonyl) - benzo-2,3,1 - diazaborine melting at 234—236°C. (with decomposition) are obtained.

EXAMPLE 5

A hot solution of 3 g. of *o*-formylphenyl boric acid and 10 ml. of ethyl alcohol is added with stirring to a hot suspension of 3.4 g. of p-methoxybenzene sulphonic acid hydrazide in 20 ml. of ethyl alcohol. Brief boiling of the reaction mixture results in the formation of a clear solution from which 1 - hydroxy-2 - (*p* - methoxyphenylsulphonyl) - benzo-2,3,1 - diazaborine crystallises out on cooling. Following recrystallisation from ethyl alcohol/toluene, this compound melts at 140—141°C. Yield = 4.2 g. (67% of the theoretical).

EXAMPLE 6

A mixture of 11.7 g. of *o*-formylphenyl boric acid, 18 g. of benzothiazole-2-sulphonic acid hydrazide and 150 ml. of ethyl alcohol is boiled under reflux, resulting initially in the formation of a clear solution. Continued heating results in the precipitation of 1 - hydroxy-2 - (benzothiazolyl - 2' - sulphonyl) - benzo-2,3,1 - diazaborine which is recrystallised from benzene/ethyl alcohol. Yield 21 g. (78% of the theoretical). Melting point 161—162°C.

EXAMPLE 7

The procedure is as in Example 6, except that 10.2 g. of 2 - formyl - thienyl - 3 - boric acid, 12.1 g. of *p* - toluene sulphonic acid

hydrazide and 100 ml. of ethyl alcohol are used. 1 - hydroxy - 2 - (*p* - tolylsulphonyl)-thieno - [2,3 - e] - 2,3,1 - diazaborine is obtained in a yield of 17 g. (86% of the theoretical) and melts at 175—177°C.

EXAMPLE 8

21.8 g. of *p*-methylmercapto-benzene sulphonic acid hydrazide and 15 g. of *o*-formyl phenyl boric acid are mixed together and then dissolved in 150 ml. of hot ethyl alcohol. Brief boiling of the clear solution results in the precipitation of crystals which, after the mixture has been cooled, are suction-filtered and recrystallised from ethyl alcohol/benzene. 1-hydroxy - 2 - (*p* - methylmercaptophenylsulphonyl) - benzo - 2,3,1 - diazaborine, melting at 128—130°C., is obtained in a yield of 27 g. (81% of the theoretical).

EXAMPLE 9

The procedure is as described in Example 8, except that 9.9 g. of 2 - formyl - thienyl-3 - boric acid, 13.8 g of *p*-methylmercapto-benzene sulphonic acid hydrazide and 70 ml. of ethyl alcohol are used. Following recrystallisation from ethyl alcohol benzene, 1-hydroxy - 2 - (*p* - methylmercaptophenylsulphonyl) - thieno - [2,3 - e] - 2,3,1 - diazaborine is obtained, melting at 163—165°C. Yield 14.4 g. (67% of the theoretical).

EXAMPLE 10

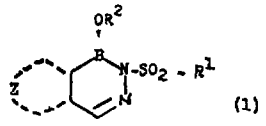
A mixture of 4.5 g. of 2 - formyl - 5-methylphenylboric acid and 5.1 g. of *p*-toluene sulphonic acid hydrazide is mixed with 70 ml. of hot ethanol and the resulting mixture is boiled under reflux for 10 minutes. Crystals are precipitated during heating from the initially obtained clear solution. To complete their precipitation, the solution is cooled. After filtration and recrystallisation from benzene/ethanol, 1 - hydroxy - 2 - (*p* - tolylsulphonyl) - 7 - methylbenzo - 2,3,1 - diazaborine is obtained in a yield of 6.8 g. (79. of the theoretical). M.p. 163—165°C.

EXAMPLE 11

28 g. of the product of Example 4 are heated with stirring on a water bath in 300 ml. of concentrated hydrochloric acid. After a time, a clear solution is obtained which is diluted with 300 ml. of water and adjusted to pH 3—4 with 30% by weight aqueous sodium hydroxide. After the mixture has been cooled, it is filtered and the residue is recrystallised from dimethyl formamide/ethyl alcohol. The hydrochloride of 1 - hydroxy - 2 - (*p* - aminophenylsulphonyl) - benzo - 2,3,1 - diazaborine is obtained in a yield of 21 g. (75% of the theoretical). M.p. 179°C.

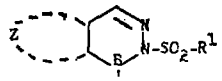
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(1)

wherein Z represents a fused *o*-phenylene, naphthylene or thienylene ring which may optionally be substituted by one or more alkyl radicals, halogen atoms, etherified hydroxy or mercapto groups, alkyl, aralkyl or aryl sulphonyl groups, amino or acylamino groups, or nitro groups, R^1 represents a mono- or polynuclear aromatic or heterocyclic radical, optionally substituted by one or more alkyl radicals, etherified hydroxy or mercapto groups, halogen atoms, amino or acylamino groups or nitro groups, and R^2 represents a hydrogen atom, a monovalent cation or the radical



wherein R^1 and Z have the meanings given above.

2. Boron-containing heterocyclic compounds as claimed in claim 1 wherein R^1 represents a thienyl - 2 - radical or an aromatic radical optionally substituted in the *ortho*- and/or *para*-position to the SO_2-group by alkyl radicals or etherified hydroxy or mercapto groups.

3. 1 - hydroxy - 2 - benzenesulphonyl-benzo - 2,3,1 - diazaborine.

4. 1 - hydroxy - 2 - (*p* - tolylsulphonyl-benzo - 2,3,1 - diazaborine.

5. 1 - hydroxy - 2 - (*p* - fluorophenyl-sulphonyl) - benzo - 2,3,1 - diazaborine.

6. 1 - hydroxy - 2 - (*p* - chlorophenyl-sulphonyl) - benzo - 2,3,1 - diazaborine.

7. 1 - hydroxy - 2 - (2',4',6' - trimethyl-phenylsulphonyl) - benzo - 2,3,1 - diazaborine.

8. 1 - hydroxy - 2 - (thienyl - 2' - sulphonyl) - benzo - 2,3,1 - diazaborine.

9. 1 - hydroxy - 2 - (*p* - ethylphenyl-sulphonyl) - benzo - 2,3,1 - diazaborine.

10. 1 - hydroxy - 2 - (*m* - nitrophenyl-sulphonyl) - benzo - 2,3,1 - diazaborine.

11. 1 - hydroxy - 2 - (2',4' - dimethyl-phenylsulphonyl) - benzo - 2,3,1 - diazaborine.

12. 1 - hydroxy - 2 - (*p* - ethylmercapto-phenylsulphonyl) - benzo - 2,3,1 - diazaborine.

13. 1 - hydroxy - 2 - (*o* - tolylsulphonyl)-benzo - 2,3,1 - diazaborine.

14. 1 - hydroxy - 2 - (2',5' - dimethyl-thienyl - 3' - sulphonyl) - benzo - 2,3,1-diazaborine.

15. 1 - hydroxy - 2 - (pyridyl - 3' - sulphonyl) - benzo - 2,3,1 - diazaborine.

16. 1 - hydroxy - 2 - (2',5' - dimethyl-

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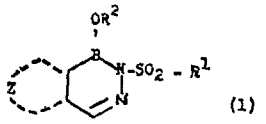
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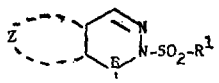
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furyl - 3' - sulphonyl) - benzo - 2,3,1 - diazaborine.

17. 1 - hydroxy - 2 - (1' - methyl - 5' - chloroimidazolyl - 4' - sulphonyl) - benzo - 2,3,1 - diazaborine.

18. 1 - hydroxy - 2 - (pyridyl - 4' - sulphonyl) - benzo - 2,3,1 diazoborine.

19. 1 - hydroxy - 2 - (3' - methylisothiazolyl - 4' - sulphonyl) - benzo - 2,3,1 - diazaborine.

20. 1 - hydroxy - 2 - (*p* - acetaminophenylsulphonyl) - benzo - 2,3,1 - diazaborine.

21. 1 - hydroxy - 2 - (*p* - methoxyphenylsulphonyl) - benzo - 2,3,1 - diazaborine.

22. 1 - hydroxy - 2 - (benzothiazolyl - 2' - sulphonyl) - benzo - 2,3,1 - diazaborine.

23. 1 - hydroxy - 2 - (*p* - tolylsulphonylthieno - [2,3 - e] - 2,3,1 - diazaborine.

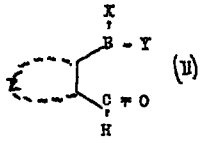
24. 1 - hydroxy - 2 - (*p* - methylmercaptophenylsulphonyl) - benzo - 2,3,1 - diazaborine.

25. 1 - hydroxy - 2 - (*p* - methylmercaptophenylsulphonyl) - thieno - [2,3 - e] - 2,3,1-diazaborine.

26. 1 - hydroxy - 2 - (*p* - tolylsulphonyl)-7 - methylbenzo - 2,3,1 - diazaborine.

27. 1 - hydroxy - 2 - (*p* - aminophenylsulphonyl) - benzo - 2,3,1 - diazaborine.

28. A process for the preparation of a boron-containing heterocyclic compound as claimed in claim 1 which comprises reacting a compound having the general formula (II)



(II)

wherein Z has the meaning given in claim 1 and X and Y are the same or different and represent hydroxyl groups, etherified hydroxyl groups or halogen atoms with a sulphonic acid hydrozide having the formula (III)

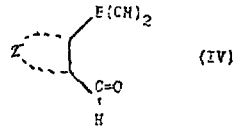
$$H_2N—NH—SO_2—R^1 \quad (III)$$

wherein R^1 has the meaning given in claim 1, and, if X and Y do not represent OH groups, hydrolysing the residual group X or Y in the product into OH, and optionally converting the OH group into one of the other groups of the formula $—OR^2$.

29. A process as claimed in claim 28 wherein the reaction between the compounds of formulae (II) and (III) is carried out at elevated temperature.

30. A process as claimed in claim 28 wherein the reaction between the compounds of formula (II) and (III) is carried out in the presence of a solvent or suspending agent.

31. A process as claimed in claim 28 wherein the sulphonic acid hydrazide of formula (III) is reacted at elevated temperature with a boric acid derivative having the formula



(IV)

in which Z has the meaning given in formula I, and the presence of a solvent or suspending agent.

32. A process as claimed in any of claims 28 to 31 wherein the sulphonic acid hydrazide of formula (III) is the hydrazide of an aromatic sulphonic acid, optionally substituted in the *ortho-* and/or *para*-position to the SO_2-group by alkyl radicals, or by etherified hydroxy or mercapto groups, or of thienyl-2-sulphonic acid.

33. A process as claimed in claim 28 substantially as described with reference to any of the Examples.

34. Boron-containing heterocyclic compounds when prepared by a process as claimed in any of claims 28 to 33.

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