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# SUBSTITUTED BENZENEBORONIC ACIDS FOR THE GAS CHROMATOGRAPHIC DETERMINATION OF BIFUNCTIONAL COMPOUNDS WITH ELECTRON-CAPTURE DETECTION*

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## SUMMARY

Seven aromatic boronic acids have been prepared and evaluated as selective analytical reagents for the gas chromatographic analysis of bifunctional compounds. The introduction of halogen atoms into the aromatic ring provides volatile derivatives which can be determined with an electron-capture detector at the picogram level.

## INTRODUCTION

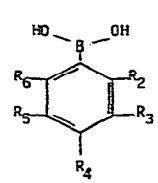
Most polyfunctional compounds are unsuitable for gas chromatography (GC) unless first modified by chemical derivatization to provide a less polar and more thermally stable form. Among this class of polyfunctional molecules can be recognized a much smaller sub-group of bifunctional molecules which are characterized by having one or more functional groups in close proximity to each other. Previous attempts at chromatographic analysis have tended to ignore the special features of bifunctional molecules and to treat them in an identical manner to other polyfunctional components. By this approach, all potential analytical selectivity is lost and the eventual analysis is made more complex than it need otherwise be.

One of the principle problems in the selective analysis of bifunctional compounds by GC is the lack of suitable volatile reagents for their formation. Reagents are limited almost entirely to the cyclic volatile derivatives formed with ketones, phenylenediamines, diacetoxydimethylsilanes, chloromethyldimethylchlorosilanes, and boronic acids[1,2]. When a wide-range of functional group types are considered, only the alkyl and aromatic boronic acids introduced by Brooks and co-workers could be described as generally applicable[3,4]. The boronic acids form stable volatile derivatives with good mass spectral properties of compounds containing hydroxyl, phenolic, amino, keto, thiol and carboxylic acid groups on adjacent, 1,3- or 1,4-carbon atom systems. Among the biologically important bifunctional compounds determined by GC as their cyclic boronic esters can be mentioned lipids[5], steroids[3,6–8], catecholamines[3,9,10], prostaglandins[11–14], sphingosines and ceramides[15,16], $\alpha$-hydroxyamines[4], $\alpha$- and $\beta$-keto acids[4] and carbohydrates[17–19].

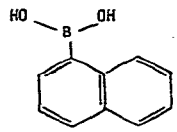
* Determination of Bifunctional Compounds Part II; for part I see ref. 23.

The mechanism of the boronic acid reaction provides chemical selectivity to distinguish the bifunctional compounds from the general pool of functionalized molecules. The specificity and sensitivity could be improved further if use was made of a selective detector rather than the universal flame ionization detector (FID) for the final determination. Selective detectors for boron include the alkali flame ionization detector[20,21] and a specific boron detector working on the flame photometric principle[22]. However, only a limited amount of data has been presented to indicate the specificity of the detectors to boron and the increase in sensitivity for boron containing compounds compared to the FID was about fifty-fold.

In a preliminary communication we have shown that boronic acids containing electron-capturing groups can be determined at trace levels with an electron-capture detector (ECD)[23]. An increase in sensitivity of approximately four thousand-fold compared to the FID was found. In this report we will describe the properties of seven substituted aromatic boronic acids for the selective analysis of bifunctional compounds at trace levels with an ECD. The structural formulas, names and suggested abbreviations for the boronic acids under consideration are presented in Fig. 1.




(I) → (VI)




(VII)

(I) $R_2 = R_3 = R_4 = R_5 = R_6 = H$; benzeneboronic acid (BB)

(II) $R_2 = R_3 = R_4 = R_5 = R_6 = F$; pentafluorobenzeneboronic acid

(III) $R_2 = R_4 = R_5 = R_6 = H$, $R_3 = NO_2$; 3-nitrobenzeneboronic acid (3-NBB)

(IV) $R_2 = R_3 = R_5 = R_6 = H$, $R_4 = Br$; 4-bromobenzeneboronic acid (4-BrBB)

(V) $R_3 = R_5 = R_6 = H$, $R_2 = R_4 = Cl$; 2,4-dichlorobenzeneboronic acid (2,4-DCBB)

(VI) $R_2 = R_4 = R_6 = H$, $R_3 = R_5 = Cl$; 3,5-dichlorobenzeneboronic acid (3,5-DCBB)

(VII) 1-naphthaleneboronic acid (1NAPBB)

Fig. 1. Structure, nomenclature and abbreviations for the substituted benzeneboronic acids.

## EXPERIMENTAL

Benzeneboronic acid, 4-bromobenzeneboronic acid, 1-bromonaphthalene, 3,5-dichloroiodobenzene and trimethylborate were obtained from Aldrich (Milwaukee, Wisc., U.S.A.), 3-nitrobenzeneboronic acid from K & K Labs (Plainview, N.Y., U.S.A.) and 2-4-dichloroiodobenzene from Fairfield (Blythewood, S.C., U.S.A.). Pentafluorobenzeneboronic acid was available from a previous study[24]. 1-Naphthaleneboronic acid was prepared by published procedures[25]. The dichlorobenzeneboronic acids (V*, VI) were prepared for the first time by the general procedure detailed below.

* 2,4-Dichlorobenzeneboronic acid (V) is commercially available from Lancaster Synthesis, St. Leonards Gate, Lancaster, Great Britain.

Using the general experimental arrangement for a Grignard reaction, a solution of the dichloroiodobenzene (0.1 mole) in anhydrous ether (80 ml) was added dropwise to magnesium turnings (0.1 mole) in ether (20 ml) at a rate sufficient to maintain a gentle reflux. After the addition of all the dichloroiodobenzene, the reflux was maintained for a further 0.5 h or until all the magnesium was consumed and then transferred to a nitrogen-equalized dropping funnel.

For the preparation of the boronic acids, the reaction was carried out under nitrogen in a 1-l three-necked flask surrounded by an acetone-dry ice slush bath. In the flask, ether (100 ml) was pre-cooled and the reagents added via two nitrogen-equalized dropping funnels with their tips bent inwards towards the shaft of an efficient mechanical paddle stirrer. The solution of the Grignard reagent and trimethylborate (0.1 mole in 100 ml ether) were added periodically and in equal portions over a period of 0.5 h and the dense white precipitate vigorously stirred for a further 0.5 h. The coolant bath was then lowered until the bottom of the flask just touched the coolant surface and the mixture was stirred overnight. The Grignard complex was decomposed with hydrochloric acid (15%, v/v; 50 ml), the ether layer collected, extracted with aqueous sodium hydroxide and the aqueous phase acidified with ice and hydrochloric acid. Extraction with ether and recrystallization of the residue from toluene (2,4-DCBB, m.p. 242–245°C, yield 55%) or heating to boiling point twice in toluene followed by filtration (3,5-DCBB, m.p. 310–315°C, yield 30%) gave chromatographically pure boronic acids.

The pinacol derivatives were prepared on a gram scale by the dissolution of equal molar quantities of boronic acid and pinacol in tetrahydrofuran containing a small quantity of molecular sieves. The solution was warmed to promote dissolution if required and allowed to stand at room temperature for 15 min. The tetrahydrofuran solution was decanted from the molecular sieves, evaporated *in vacuo* and the residue recrystallized. Physical constants are indicated in Table I.

TABLE I

PHYSICAL CONSTANTS FOR THE BORONIC ACID DERIVATIVES OF PINACOL

| *Number* | *Boronic acid* | *M.p. (°C) of pinacol derivative* | *Solvent of recrystallization* |
|---|---|---|---|
| I | Benzeneboronic acid | 29 –30 | * |
| III | 3-Nitrobenzeneboronic acid | 73 –74 | Acetonitrile–water |
| IV | 4-Bromobenzeneboronic acid | 65 –67 | Ethanol–water |
| V | 2,4-Dichlorobenzeneboronic acid | 29.5–30.5 | Ethanol–water |
| VI | 3,5-Dichlorobenzeneboronic acid | 47 –49 | Acetonitrile–water |
| VII | 1-Naphthaleneboronic acid | 55 –56 | Ethanol–water |

* Distilled *in vacuo*[23].

Derivatives for GC were prepared by adding equal volumes of 0.05 *M* tetrahydrofuran solutions of boronic acid and analyte to each other and diluting further with tetrahydrofuran if required. All reactions were complete within 15 min at room temperature.

For FID analysis, a Perkin-Elmer 3920 gas chromatograph was used with a 90 × 0.2 cm I.D. nickel column packed with 1% OV-17 on Gas-Chrom Q (100–120 mesh) and a nitrogen flow-rate of 60 ml/min. The temperature for analysis and re-

tention time data of the compounds studied is summarized in Table II. For electron-capture studies, a Victoreen 4000 gas chromatograph fitted with a custom-designed ECD was used[26]. The ECD contained a 30 mCi Ni-63 source and was operated in the pulse mode with a pulse width of 4 $\mu$sec and pulse period of 2000 $\mu$sec.

TABLE II

RETENTION TIME DATA FOR THE BENZENEBORONATE DERIVATIVES OF SOME REPRESENTATIVE BIFUNCTIONAL COMPOUNDS

| *Compound* | *Derivative* | | | | | | *Column temperature (°C)* |
|---|---|---|---|---|---|---|---|
| | *BB* | *3-NBB* | *4-BrBB* | *2,4-DCBB* | *3,5-DCBB* | *NAPBB* | |
| Ethylene glycol | 0.14 | 1.74 | 0.58 | 1.00 | 0.76 | 4.47 | 120* |
| Lactic acid | 0.25 | 4.20 | 1.24 | 2.00 | 1.51 | 6.10 | 120 |
| Pinacol | 0.15 | 0.82 | 0.34 | 0.47 | 0.46 | 1.66 | 140** |
| 1,3-Propanediol | 0.17 | 1.47 | 0.55 | 0.84 | 0.74 | 2.82 | 140 |
| 1,4-Butanediol | 0.24 | 2.80 | 1.00 | 1.43 | 1.35 | 5.67 | 140 |
| 3-Amino-1-propanol | 0.20 | 2.81 | 0.95 | 0.79 | 1.3 | 4.00 | 140 |
| 1,3-Propanediamine | 0.21 | 2.78 | 1.00 | 0.93 | 1.38 | 3.08 | 140 |
| 2-Amino-1-butanol | 0.18 | 2.57 | 0.77 | 0.71 | 1.01 | 4.17 | 140 |
| Catechol | 0.37 | 4.60 | 1.54 | 2.38 | 1.77 | 7.56 | 140 |
| *o*-Phenylenediamine | 0.81 | 6.76 | 2.91 | 2.89 | 3.46 | 6.99 | 140 |
| Mandelic acid | 0.62 | — | 1.80 | 2.55 | 2.15 | 6.06 | 200*** |
| Salicylic acid | 0.61 | — | 2.28 | 2.10 | 2.66 | 7.67 | 200 |
| Anthranilic acid | 3.20 | — | — | 6.78 | — | — | 200 |

* Internal standard, $C_{18}$; $t_R$ = 3.6 min.
** Internal standard, $C_{20}$; $t_R$ = 3.8 min.
*** Internal standard, $C_{24}$; $t_R$ = 1.5 min.

## RESULTS AND DISCUSSION

In designing a new derivative for GC, there are several interrelated criteria which have to be considered. In this study, an electrophore had to be selected and attached to boron to provide the selectivity and sensitivity towards the ECD. It is important that this group be volatile as well as thermally and hydrolytically stable to the conditions employed for the formation and separation of the derivatives. There is therefore a limitation on the selection of suitable electrophores due to the chemical properties of boron. Having selected and prepared suitable electron-capturing boronic acids it is then necessary to evaluate these in terms of conditions for formation, the range of application, hydrolytic stability, GC properties and sensitivity to the ECD.

### *Criteria for selection of an electrophore*

Very few organic molecules can be described as having a significant response to the ECD (the origin of the selectivity of this detector). Among those compounds that do, a range in sensitivity of over a million-fold is observed. Generally speaking, the most strongly electron-capturing molecules contain halogens, nitro groups, organometallics, sulfides or contain two or more unsaturated groups in conjugation[27–29]. Most of the reagents in use today make use of reactive compounds containing either halogen atoms or nitro groups to provide the necessary high response to the ECD. The order of response for the halogens is I > Br > Cl > F which is of course the

reverse order of the volatility of their compounds towards GC. The introduction of fluorine is attractive from the volatility point of view due to the fact that closely bound fluorine atoms in alkyl or aryl compounds increase the boiling point of the compounds very little over that of the equivalent hydrocarbon of the same carbon number, in spite of the significant increase in molecular weight[30]. Although multiple substitution favors an increase in ECD response, with the exception of fluorine compounds, this leads to a considerable decrease in volatility. In the specific case of fluorine compounds, multiple substitution does not provide a useful ECD response unless it forms part of a conjugated electrophore. This can be seen from the very high response of the heptafluorobutyryl esters compared to the insignificant response of the heptafluoropentyldimethylsilyl ethers[28,30]. The pentafluorophenyldimethylsilyl ethers (flophemesyl derivatives) are volatile derivatives with a significant ECD response, indicating the usefulness of the pentafluorophenyl group as a volatile electrophore[31,32]. Reagents containing the pentafluorophenyl group as part of the electrophore are becoming increasingly popular[28]. The dichlorobenzene group is reasonably volatile with a good ECD response, the absolute magnitude of which is influenced by the relative position of the chlorine atoms[33,34].

*Criteria for the selection of an electrophore based on the chemistry of boron*

The above discussion indicates that for the preparation of a boronic acid with a significant ECD response, the introduction of a heptafluorobutyryl, pentafluorophenyl, nitro group, alkylbromide or iodide or dichlorobenzene group would provide the best compromise between ECD response and derivative volatility. From the chemical view-point, the boron–acyl bond is too labile and reactive to form stable derivatives[35]. Alkylboronic acids with halogen atoms on $\alpha$-, $\beta$- or $\gamma$-carbon atoms lack the necessary thermal and hydrolytic stability to be useful[36,37]. Alkylboronic acids with halogen atoms attached to the $\Delta$-carbon atom were thought to be unattractive from the volatility point of view for initial study. By comparison, the aromatic boronic acids with electronegative groups are stable to the hydrolytic conditions likely to be encountered during chromatographic analysis[38]. The dichlorobenzeneboronic acids were synthesized for the first time for this study on the expectation that they would have favorable analytical properties.

*Range of application and GC*

The boronic acids (I–VII) were reacted with a representative series of bifunctional compounds containing a wide variety of functional group types (Table II). Their reactivity, stability and GC properties were compared with those of the benzeneboronic acid derivatives. Initially, it was observed that several derivatives were decomposed on stainless-steel columns and the use of glass or nickel is recommended[39].

None of the boronic acids (I–VII) formed chromatographically stable derivatives with propane-1,3-dithiol, 3-hydroxypropionic acid, methylguanidine, pentane-1,5-diol, ethylenediamine and 3-aminophenol. The aromatic carboxylic acids, salicylic and anthranilic acid formed derivatives which degraded rapidly on standing at room temperature and were also readily exchanged on the GC column by any previous build-up of an excess of another boronic acid. The boronic acids are not good derivatives for the determination of these carboxylic acids at low levels. The derivatives formed with ethanolamine produced broad tailing peaks on chromato-

graphy. With the exception of benzeneboronic acid (I), the sugars arabinose and xylose did not produce any peaks on GC. The 3-nitrobenzeneboronate derivatives show some slight tailing on the OV-17 column but can be chromatographed as symmetrical peaks on OV-225[23].

Pentafluorobenzeneboronic acid (II) was too susceptible to nucleophilic attack, resulting in the elimination of pentafluorobenzene, to be a useful reagent. This displacement was complete when only a slight molar excess of water was present and could be inhibited by the addition of acid. However, conditions could not be found for the formation of stable derivatives and no further studies were undertaken.

With the exceptions discussed above, the boronic acid derivatives listed in Table II were easy to prepare, stable and had good GC properties. The introduction of substituents onto the benzene ring leads to a decrease in volatility when chromatographed on the OV-17 column. Compared to the benzeneboronate derivatives, the approximate increase in retention time was found to be:

| BB | < | 4-BrBB | < | 2,4-DCBB | < | 3,5-DCBB | < | 3-NBB | < | NAPBB |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | | 4–5 | | 4–7 | | 5–7 | | 10–14 | | 15–22 |

The introduction of substituents onto the benzene ring of benzeneboronic acid is known to have a marked effect on the acidity of the boronic acid[41]. We therefore suspected that a similar effect would be operating with the derivatives and the introduction of the strongly directing groups used here could have a considerable influence on the hydrolytic stability of the derivatives. A study of the hydrolysis by moist air of a series of benzeneboronate derivatives has shown that ring size (6- > 5- > 7-membered) and the size of the organic substituent at the point of attachment of the bifunctional derivative (*e.g.*, pinacol > ethylene glycol) are important in judging stability[40]. We tried some model hydrolysis experiments using either water, acetic acid or 9 *M* hydrochloric acid in tetrahydrofuran as the reagent. Although some qualitative differences in hydrolytic stability could be discerned, there were no gross differences between the boronic acid derivatives. The overall stability was excellent and the derivatives of such compounds as pinacol, ethylene glycol and catechol were hardly changed over several days of keeping in the above reagents. Lactic acid, mandelic acid and butane-1,4-diol were very slowly hydrolyzed with water (large excess) overnight. In many cases the addition of the hydrolysis reagent would cause a small change to occur rapidly and then a steady state would be reached and any subsequent reaction was extremely slow.

*ECD response and mechanism*

A notable feature of the ECD response is its marked temperature dependence[42]. This dependence arises as a consequence of the electron-capture mechanism and can be conveniently evaluated by plotting the data graphically in the form of $\ln AT^{3/2}$ *vs.* $1/T$, where $A$ is the peak area for a fixed mass of derivative and $T$ the detector temperature in °K[43]. A plot of this type provides three pieces of information of direct interest to the analyst: (a) it indicates the optimum temperature for maximum detector response; (b) it provides a qualitative assessment of the magnitude of detector response as a function of detector temperature (the slope of the line); (c) it provides some insight into the electron-capture mechanism. The pinacol derivatives of the boronic

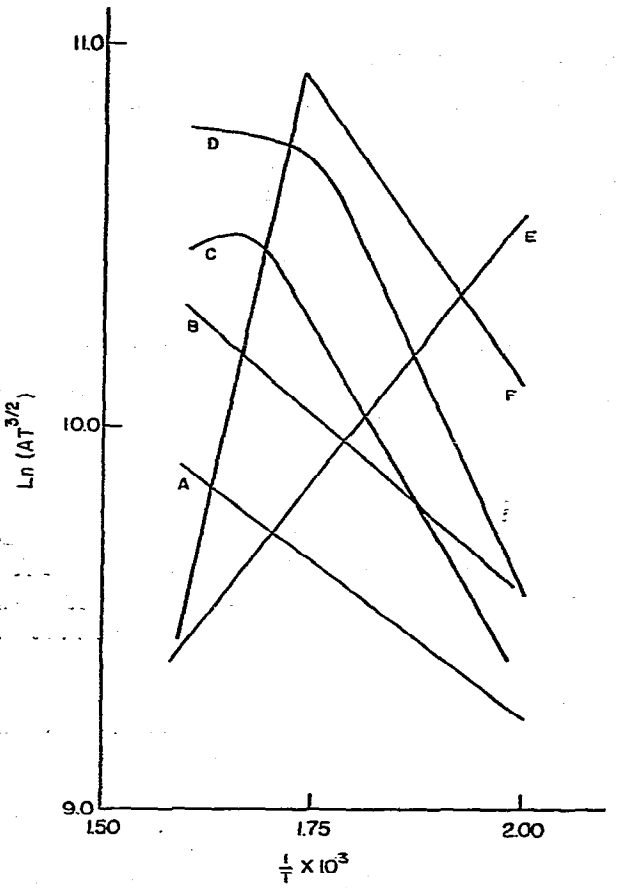



Fig. 2. A plot of ln $AT^{3/2}$ *versus* $1/T$ for 4-bromobenzeneboronate (A), naphthaleneboronate (B), 2,4-dichlorobenzeneboronate (C), 3,5-dichlorobenzeneboronate (D), benzeneboronate (E), 3-nitrobenzeneboronate (F) derivatives of pinacol.

acids (I, III–VII) studied here (Fig. 2) can be interpreted as showing either a dissociative or a non-dissociative mechanism of electron capture. These take the form indicated below for the general case of the molecule AB.

$$AB + e^- \rightleftharpoons AB^- \qquad \text{non-dissociative capture}$$
$$AB + e^- \rightarrow A + B^- \qquad \text{dissociative capture}$$

The benzeneboronate derivative of pinacol is a non-dissociative capturer and maximum detector response is obtained at low detector temperatures. The NAPBB, 4-BrBB, 2,4-DCBB and 3,5-DCBB derivatives capture by a dissociative mechanism and the bond breaking process is favored by high detector temperatures. The 3-NBB derivative shows regions of both dissociative and non-dissociative capture with a narrow detector temperature plateau for maximum response.

The maximum detector response of the pinacol boronates are compared in Table III. These new derivatives allow detection limits at the low picogram level

TABLE III

ECD RESPONSE TOWARDS THE PINACOL BORONATES

| *Boronic acid* | *Optimum detector temperature (°C)* | *Least detectable amount (pg)** |
|---|---|---|
| Benzeneboronic acid | 200** | 150 |
| 3-Nitrobenzeneboronic acid | 300 | 4 |
| 4-Bromobenzeneboronic acid | 350 | 3 |
| 2,4-Dichlorobenzeneboronic acid | 325 | 2 |
| 3,5-Dichlorobenzeneboronic acid | 325 | 9 |
| Naphthaleneboronic acid | 350 | 2550 |

* Defined as the weight of pinacol which when derivatized yielded a signal-to-noise ratio of 2 at maximum sensitivity.

** This is a practical detector temperature that might be used with biological samples. The least detectable amount would be lower if a temperature closer to the column operating temperature were used.

to be achieved. A suprising result is the greater response of the benzeneboronate derivative compared to that of the naphthaleneboronate. The response of the ECD towards pinacol benzeneboronate is approximately one hundred-fold lower than for the same compound determined using the FID. The useful response obtained with the ECD and the fact that the benzeneboronate derivatives are the most volatile of the derivatives tested indicates that this reagent could be useful for the analysis of mixtures when all but the maximum in sensitivity is required and for samples where detector contamination from less volatile components is not considered important. It also illustrates that the ECD may be used as a selective detector for the determination of benzeneboronates when discrimination against the organic background is required. However, from the practical point of view, when analyzing biological samples, there is a considerable advantage to be gained in using derivatives which have their maximum response at high detector temperatures. This enables downtime due to detector contamination to be minimized. The boronic acids (III–VI) fulfill this requirement as well as providing greater sensitivity.

## CONCLUSION

Benzeneboronic acid reagents with electronegative substituents provide a new series of reactive compounds which form stable derivatives with bifunctional compounds and have good GC properties. These derivatives can be determined at the picogram level with an ECD.

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