

π -Electron Charge Density on Boron in the Borate Structures

S. E. SVANSON

Department of Physical Chemistry, Chalmers University of Technology and University of Gothenburg, S-402 20 Gothenburg 5, Sweden

Using the Coulson, Longuet-Higgins integral formula for the calculation of charge densities of conjugated systems, it is shown that the size of the π -electron charge on boron varies very little between boron atoms of different borate structures. The variations occurring are dependent upon whether the oxygen atoms surrounding the boron atom considered are singly or doubly connected to the conjugated system. It is in a similar way shown that the bond orders of the boron-oxygen bonds are dependent upon the coordination of the oxygen atom to the conjugated system.

A very large constancy of the quadrupole coupling constant of three-coordinated boron in the borate structures has been observed.^{1,2} As the quadrupole coupling constant is dependent upon the electron charge density in the environment of the boron nuclei, this condition should be regarded as showing a great similarity of the bonding between three-coordinated boron and surrounding oxygen atoms. A significant difference exists only between compounds containing BO_3 -groups of three-fold symmetry on the one side and compounds of groups which are not quite in perfect symmetry on the other. The 10 % lower value of the quadrupole coupling constant (eqQ) of the second group of compounds should probably be attributed to changes of the electron charges of the boron valence orbitals which accompany the distortion. Both groups contain namely compounds with greatly varying numbers of cations and BO_4 -groups, for which reason it could be concluded that these surrounding atom groups do not influence the value of eqQ appreciably.

It could possibly be assumed that the boron oxygen bonds of the second group of borates are less ideal than those of the first group. In the compounds of the second group large variations of the OBO and BOB valence angles are observed, and occurring conjugated groups are appreciably distorted from planarity. Whereas the effects of such distortions upon the σ -electrons are not so easily predicted, it could be concluded that the main effect upon

the π -electron charge distribution should be traced back to a reduction of the π -electron resonance integrals. The σ -electrons are responsible for the major contribution to the quadrupole coupling constant and the π -electrons make a negative contribution to this constant. It could then be concluded that the observed variation in eqQ between the two groups could not be assigned to changes of the π -electron charges caused by the reduction of the π -electron resonance integrals. It could for this reason be assumed that the observed effect is due to changes of the σ -electron densities, and that the variations of the π -electron charges only slightly counteract the observed effect. It has, however, also to be ascertained that the π -electron charge on boron does not vary appreciably between idealized planar conjugated borate groups. That this must be the case follows from the arguments given below, and it is due to the fact that all conjugated systems under consideration here are alternant, in a first order treatment, having all bonding orbitals occupied and all non-bonding orbitals empty.

π -ELECTRON CHARGE DENSITY ON BORON

A very convenient method for the treatment of large conjugated systems has been set out by Coulson and Longuet-Higgins.³ Total π -electronic energy, charge densities and bond orders could here be calculated in one single step without solving the secular determinant for the individual molecular orbitals. The contributions from the different orbitals to the total charge density on the r -th nucleus could, for example, be summed up in the form of an integral of the type

$$q_r = 1 - \frac{1}{\pi i} \int_{-i\infty}^{+i\infty} \frac{\Delta_{rr}(\varepsilon)}{\Delta(\varepsilon)} d\varepsilon \quad (1)$$

$\Delta(\varepsilon)$ is here the secular determinant expressed as a function of an argument ε representing the π -electronic orbital energy. Δ_{rr} is similarly the cofactor of the r -th row and r -th column of the secular determinant. The zero of the energy scale has here to be chosen in such a way that all occupied orbitals obtain negative energies and the unoccupied orbitals positive energies.

We will make use of eqn. (1) to calculate the charge density on boron in conjugated borate systems being built up of BO_3 -triangles sharing oxygen atoms in the corners. The systems studied are then assumed to contain boron atoms which all form π -orbital overlap to three nearest oxygen atoms, and oxygen atoms either forming overlap to two nearest boron atoms or to only one boron atom, when placed at the boundary of the conjugated system. To determine the appropriate value of the zero of the energy scale for this general conjugated system we develop the secular determinant according to cofactors. The secular determinant could be expressed as a sum of determinants of lower order, when developed according to a row associated with a boron atom at the boundary of the system. This boron atom is bonded to at least one oxygen atom, which is not further connected to the conjugated system, and the secular determinant could therefore be written as

$$\begin{aligned} \Delta(\varepsilon) = & [(\alpha_B - \varepsilon)(\alpha_O - \varepsilon) - \beta^2] \Delta(\bar{O}_0^1 \cdot \bar{B}_0) + \beta(\alpha_O - \varepsilon) \Delta(\bar{O}_0^1 \cdot B_0 O_0^2) + \\ & + \beta(\alpha_O - \varepsilon) \Delta(\bar{O}_0^1 \cdot B_0 O_0^3) \end{aligned} \quad (2)$$

when denoting the boron atom considered by B_0 , the singly connected oxygen atom by O_0^1 , and the two other oxygen atoms connected to the boron atom by O_0^2 and O_0^3 . The determinant $\Delta(r \cdot st)$ is here obtained from Δ by calculating in a first step the cofactor associated with the row and column r , and by calculating from this latter determinant the cofactor associated with the row s and the column t . The further assignment of indices to the atoms of the conjugated group follows from Fig. 1. All oxygen and three-coordinated

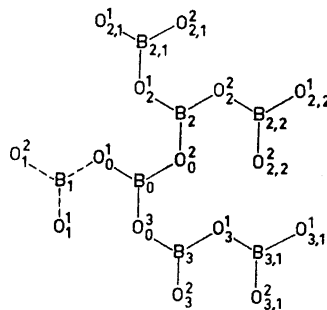


Fig. 1. Assignment of indices to the atoms of a representative non-ring forming conjugated borate system.

boron atoms are here treated as equivalent and values α_O and α_B are assigned to the Coulomb integrals of the oxygen and boron atoms, respectively. The resonance integrals β between adjacent boron and oxygen atoms are further assumed to be equal which means that all second order effects are here neglected. The determinants of eqn. (2) could all be reduced to diagonal determinants of a part of the conjugated system. $\Delta(\bar{O}_0^1 \cdot \bar{B}_0)$ simply represents a system from which the atoms O_0^1 and B_0 have been struck out. The non-diagonal determinants $\Delta(\bar{O}_0^1 \cdot B_0 O_0^2)$ could be developed into diagonal form by a further development according to cofactors.⁴ $\Delta(\bar{O}_0^1 \cdot B_0 O_0^2)$ is, for example, obtained as a sum of terms each containing one diagonal determinant obtained by striking out from the total conjugated system atoms B_0 , O_0^1 , O_0^2 and all atoms being placed along a continuous non-crossing chain connecting atoms B_0 and O_0^2 . For the alternant conjugated borate groups this is expressed as

$$\Delta(\bar{O}_0^1 \cdot B_0 O_0^2) = (-1)^{r+s} \sum_l \beta^l (-1)^l \Delta_1 \left[N - \frac{l-1}{2} - 1, M - \frac{l-1}{2} - 2 \right] \quad (3)$$

where the summation has to be taken over all such non-crossing lines. l here gives the number of bonds of each line and r and s the numbers associated with atoms B_0 and O_0^2 , $\Delta[I, J]$ stands for a diagonal determinant, in which I boron and J oxygen atoms remain, the total conjugated system being assumed to contain N boron and M oxygen atoms.

It is easily shown for small conjugated systems of this type that the secular determinant could be factorized to give one factor $(\alpha_O - \varepsilon)^{M-N}$ and one other factor which is a power expression in the determinant

$$A = \begin{vmatrix} \alpha_B - \varepsilon & \beta \\ \beta & \alpha_O - \varepsilon \end{vmatrix} \text{ and } \beta$$

of an order equal to N . Making use of eqns. (2) and (3) it then follows from similar arguments that the secular determinant could be factorized in a similar way for all conjugated systems considered here. The factor $(\alpha_O - \varepsilon)^{M-N}$ gives rise to $M-N$ degenerate orbitals of energy α_O . These orbitals are all non-bonding with nodal planes through the sites of the boron atoms and the whole electron charge concentrated on the oxygen atoms. The polynomial expression has N negative roots, which is why the corresponding energy levels occur in pairs evenly distributed around $(\alpha_O + \alpha_B)/2$. The set of N orbitals of energy lower than $(\alpha_O + \alpha_B)/2$ are bonding and the other anti-bonding. As the number of π -electron pairs is equal to the number of oxygen atoms in the system, all bonding and non-bonding orbitals are occupied, and we can, consequently, choose the zero of the energy scale equal to $(\alpha_O + \alpha_B)/2$ in order that the integral expression of eqn. (1) should sum up the charge densities of the occupied orbitals. For the convenient calculation of the charge densities we express the integral of eqn. (1) in the quotient $(\alpha_O - \alpha_B)/2\beta = a$, the size of which quantity could be estimated from the electronegativity difference of boron and oxygen to about 0.75. This substitution and the proper choice of zero energy level is introduced by replacing α_O/β by a , α_B/β by $-a$, and ε by $z = \varepsilon/\beta$ in eqn. (1).

For the calculation of the charge density the secular determinant is developed in cofactors according to the row associated with the boron atom considered. The quotient Δ_{BB}/A is the obtained as

$$\frac{\Delta_{BB}}{A} = \frac{a-z}{(a+z)(a-z) - \sum_{i=1}^3 \frac{\Delta(\text{B}_0\text{O}_0^i)}{\Delta(\text{B}_0)} (a-z)} \quad (4)$$

and we could further develop

$$\Delta(\text{B}_0\text{O}_0^i) = -\Delta(\bar{\text{B}}_0 \cdot \bar{\text{O}}_0^i) \quad (5)$$

when restricting the treatment in a first step to systems not containing rings but only linear and branched conjugated groups for which $\Delta(\text{B}_0\text{O}_0^i \cdot \bar{\text{O}}_0^i \text{B}_i) = 0$.⁴ We could also write

$$\Delta(\bar{\text{B}}_0) = (a-z)\Delta(\bar{\text{B}}_0 \cdot \bar{\text{O}}_0^i) - \Delta(\bar{\text{B}}_0 \cdot \bar{\text{O}}_0^i \cdot \bar{\text{B}}_i) \quad i = 1, 2, 3 \quad (6)$$

which holds for any borate system, since here $\Delta(\text{B}_0\text{B}_0 \cdot \text{O}_0^i \text{B}_i) = -\Delta(\bar{\text{B}}_0 \cdot \bar{\text{O}}_0^i \cdot \bar{\text{B}}_i)$. Δ_{BB}/A is then obtained as

$$\frac{\Delta_{BB}}{A} = \frac{1}{(a+z)(a-z) + \sum_{i=1}^3 \frac{1}{1 - \frac{\Delta(\bar{\text{B}}_0 \cdot \bar{\text{O}}_0^i \cdot \bar{\text{B}}_i)}{\Delta(\bar{\text{B}}_0 \cdot \bar{\text{O}}_0^i)(a-z)}}} \quad (7)$$

All determinants in the quotients of this equation represent conjugated systems, which could be derived from the system studied by striking out a number of atoms. One more boron atom is here eliminated from the determinant in the numerator than from the determinant in the denominator. These expressions thus resemble $\Delta_{\text{BB}}/\Delta$ and the development according to cofactors could then be repeated in successive steps. For an infinite conjugated system not containing rings $\Delta_{\text{BB}}/\Delta$ could then be expressed as a continued fraction from which charge densities could easily be calculated with quite sufficient accuracy after a suitable truncation of the development. The ratio of determinants of eqn. (6), for example, by developing in one further step is obtained as

$$\frac{\Delta(\bar{\text{B}}_0 \cdot \bar{\text{O}}_0^i \cdot \bar{\text{B}}_i)}{\Delta(\bar{\text{B}}_0 \cdot \bar{\text{O}}_0^i)(a-z)} = - \frac{1}{(a+z)(a-z) + \sum_{j=1}^2 \frac{1}{1 - \frac{\Delta(\bar{\text{B}}_0 \cdot \bar{\text{O}}_0^i \cdot \bar{\text{B}}_i \cdot \bar{\text{O}}_i^j \cdot \bar{\text{B}}_{ij})}{\Delta(\bar{\text{B}}_0 \cdot \bar{\text{O}}_0^i \cdot \bar{\text{B}}_i \cdot \bar{\text{O}}_i^j)(a-z)}}} \quad (8)$$

For the numerical integration the substitution $z=iy$ is introduced. It then follows that the expressions

$$- \frac{\Delta(\bar{\text{B}} \cdot \bar{\text{O}} \cdot \bar{\text{B}} \cdot \bar{\text{O}} \cdot \bar{\text{B}})}{\Delta(\bar{\text{B}} \cdot \bar{\text{O}} \cdot \bar{\text{B}} \cdot \bar{\text{O}})(a-z)}$$

do not exceed 1 within the whole interval of y , and that the largest value appears for $y=0$. It is a reasonable approximation to neglect these quotients compared to 1 at an earlier or later stage of the development according to cofactors. Charge densities have been calculated for some small representative systems (Fig. 2), which values could be used to approximate the densities on boron in similar positions of larger systems. For the smallest values of y ($y < 2$) the ratio of the determinants of eqn. (7) does make some contribution to the integrand. As a considerable contribution to the integral arises from larger values of y the effect is, however, not very drastic on the charge density (Fig. 3). From the development of the integrand into a continued fraction it could be seen that the charge density of these types of conjugated systems could be estimated from a schedule that very much resembles the effect of a near neighbour interaction. For a first estimate of the charge density of three-coordinated boron in any conjugated system we can use the simple integrand

$$\frac{\Delta_{\text{BB}}}{\Delta} = - \frac{a-z}{(a+z)(a-z) + 3} \quad (9)$$

which expression gives the exact solution for the isolated BO_3 - group. When employing this approximation we thus consider the effects of the π -orbital overlap to the three nearest oxygen atoms but neglect the effects of more remote nuclei of the conjugated system.

The π -electron charge density on boron is reduced to some degree by the enlargement of the conjugated system, the reduction being mainly

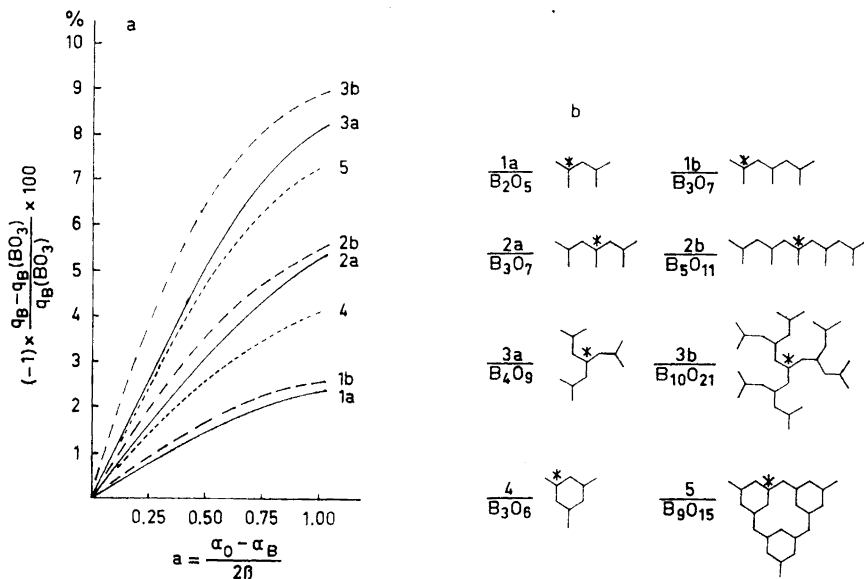


Fig. 2. π -Electron charge density (q_B) at boron compared with the density of the isolated BO_3 -group ($q_B(\text{BO}_3)$) for some representative conjugated borate systems as listed in Fig. 2 b. * marks the boron atom considered in the different groups.

dependent upon how many of the nearest oxygen neighbours are further connected to the conjugated system. The size of these changes is reproduced in Fig. 2 where the reduction of the charge density from the value found for the isolated BO_3 -group is given for some conjugated systems. Whereas the charge density is reduced by 2 to 3 % by enlargement of the group in such a way that one more oxygen atom becomes doubly connected to the system, it will change only by 0.2 to 1.0 % by an enlargement of the group under conditions where the π -electron coordination of the three near neighbour oxygens is not altered.

This simple way of calculating charge densities of large conjugated systems, where the continued fraction of the integrand is truncated to represent a smaller conjugated group containing only the nearest neighbours of the studied atom, could be used only for systems having all bonding orbitals occupied and the non-bonding empty. The proper choice of zero of the energy scale implies that all expressions

$$\frac{A(\bar{B}_0 \cdot \bar{O}_0^i \cdot \bar{B}_i)}{A(\bar{B}_0 \cdot \bar{O}_0^i)(a-z)}$$

in this case could be given as quantities between polynomials in $a^2 + y^2$ of only positive coefficients, the order of the numerator being one unit smaller than that of the denominator. It is then easily ensured that these ratios of determinants are not large compared to 1. If, on the other hand, the zero

of the energy scale is chosen in such a way that some of the bonding orbitals are not included, or if some of the anti-bonding orbitals are included in the summation of the charge densities of eqn. (1), the ratios of the determinants are obtained as polynomials in a^2 , y^2 , and y . These expressions are then generally not small compared to 1, and it is for this reason not possible to truncate the continued fraction at any stage of the development in order to obtain a simple approximation. The size of the charge density is in this case dependent upon the extension of the conjugated system, and this quantity will change appreciably between different conjugated systems even for atoms with a similar environment of near neighbours.

For the treatment of general conjugated systems the non-diagonal determinants $\Delta(\text{B}_0\text{O}_0^i \cdot \text{O}_0^i\text{B}_i)$ has also to be considered. The terms of the denominator of eqn. (4) are then obtained as

$$-\frac{\Delta(\text{B}_0\text{O}_0^i)}{\Delta(\overline{\text{B}}_0)}(a-z) = \frac{1 - \frac{\Delta(\text{B}_0\text{O}_0^i \cdot \text{O}_0^i\text{B}_i)}{\Delta(\overline{\text{B}}_0 \cdot \overline{\text{O}}_0^i)}}{1 - \frac{\Delta(\overline{\text{B}}_0 \cdot \overline{\text{O}}_0^i \cdot \overline{\text{B}}_i)}{\Delta(\overline{\text{B}}_0 \cdot \overline{\text{O}}_0^i)}} \quad (10)$$

The second term of the numerator of this eqn. is obtained by making use of a development in accordance with eqn. (3). It then follows that this term is obtained as a quotient between a polynomial in $a^2 - z^2$ of an order equal to $N - [(l-1)/2] - 1$ and a similar polynomial of order $N - 1$, where l gives the number of bonds in the shortest non-crossing line connecting B_0 and B_i . This term is consequently not large compared to 1, and it decreases rapidly with enlargement of the conjugated ring. In the borate systems we do not meet smaller than six membered rings which is why the order of the numerator is always at least two units smaller than that of the denominator. Specific calculations have been performed for two ring-forming systems as shown in Fig. 2. It follows from these examples that the effect of these terms are not quite negligible, but that they do not completely invalidate the correlation schedule between charge density and structure appropriate for non-ring forming groups.

BOND ORDER AND SECOND ORDER EFFECTS

Expressions of similar type could be derived for the bond order, from which a simple correlation between the size of this quantity and the structure of the conjugated system follows. The bond order for a bond r-s is given by

$$\rho_{rs} = \frac{(-1)}{\pi i} \int_{-i\infty}^{i\infty} \frac{A_{rs}(\varepsilon)}{A(\varepsilon)} d\varepsilon \quad (11)$$

and the integrand Δ_{rs}/Δ is for a non-ring forming group obtained as

$$\frac{\Delta(\overline{B}_0\overline{O}_0^1)}{\Delta} = \frac{1}{1 + (a+z)(a-z) - (a+z)(a-z) \frac{\Delta(\overline{B}_0\overline{O}_0^1\overline{B}_1)}{\Delta(\overline{B}_0\overline{O}_0^1)(a-z)} + \frac{\Delta(\overline{B}_0\overline{O}_0^2)}{\Delta(\overline{B}_0\overline{O}_0^1)} + \frac{\Delta(\overline{B}_0\overline{O}_0^3)}{\Delta(\overline{B}_0\overline{O}_0^1)}} \quad (12)$$

by developing Δ according to cofactors making use of eqns. (4), (5), and (6). $\Delta(\overline{B}_0\overline{O}_0^2)/\Delta(\overline{B}_0\overline{O}_0^1)$ is by a further development according to cofactors obtained as

$$\frac{\Delta(\overline{B}_0\overline{O}_0^2)}{\Delta(\overline{B}_0\overline{O}_0^1)} = \frac{1 - \frac{\Delta(\overline{B}_0\overline{O}_0^1\overline{O}_0^2\overline{B}_1)}{\Delta(\overline{B}_0\overline{O}_0^1\overline{O}_0^2)(a-z)}}{1 - \frac{\Delta(\overline{B}_0\overline{O}_0^1\overline{O}_0^2\overline{B}_2)}{\Delta(\overline{B}_0\overline{O}_0^1\overline{O}_0^2)(a-z)}} \quad (13)$$

The ratios of determinants of eqn. (12) will thus all contain quotients of the type expressed by eqn. (8). They could then all be developed into continued fractions or into quotients of such expressions. It then follows that

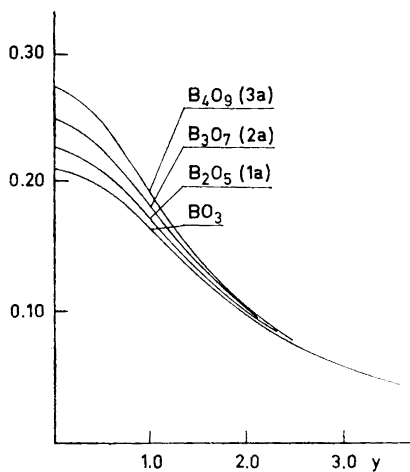


Fig. 3. The integrand of eqn. (1) for some of the borate systems of Fig. 2 for $a=0.75$.

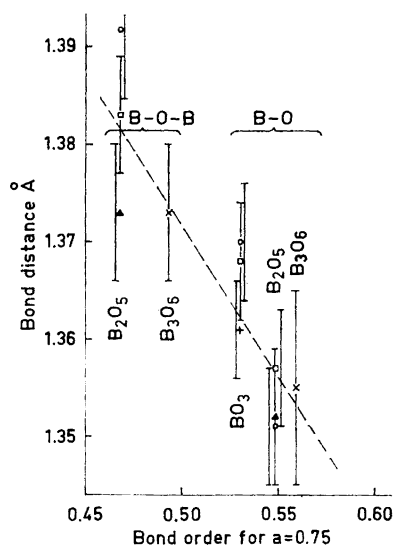


Fig. 4. Bond distance vs. bond order for boron-oxygen bonds of three-coordinated boron of some crystalline borates.

+ H_3BO_3 ; \blacktriangle $KB_5O_8 \cdot 4H_2O$; \circ $BaO \cdot 2B_2O_3$
 \times HBO_2 ; \square $Na_2O \cdot 4B_2O_3$

$$(a+z)(a-z) \frac{\Delta(\bar{B}_0 \cdot \bar{O}_0^1 \cdot \bar{B}_1)}{\Delta(\bar{B}_0 \cdot \bar{O}_0^1)(a-z)}$$

is always small compared to $1+(a+z)(a-z)$ and that

$$\frac{\Delta(\bar{B}_0 \cdot \bar{O}_0^2)}{\Delta(\bar{B}_0 \cdot \bar{O}_0^1)} \text{ and } \frac{\Delta(\bar{B}_0 \cdot \bar{O}_0^3)}{\Delta(\bar{B}_0 \cdot \bar{O}_0^1)}$$

are always close to 1. For a first estimate of the bond order between three-coordinated boron and oxygen in any conjugated system we can then use the simple integrand

$$\frac{\Delta(B_0O_0^1)}{\Delta} = \frac{1}{(a+z)(a-z) + 3} \quad (14)$$

which expression gives the exact solution for the isolated BO_3 -group. Specific calculations for some representative groups show that the bond order varies only by $\pm 10\%$ from the value appropriate for the BO_3 -group. The variations observed in the bond order are mainly dependent upon whether the oxygen atom involved in the bond considered is singly or doubly connected to the conjugated system. The term

$$-(a+z)(a-z) \frac{\Delta(\bar{B}_0 \cdot \bar{O}_0^1 \cdot \bar{B}_1)}{\Delta(\bar{B}_0 \cdot \bar{O}_0^1)(a-z)}$$

in the denominator of eqn. (12) is zero for singly connected oxygen atoms but gives a positive contribution for doubly connected atoms. The bond order is consequently generally larger for boron oxygen bonds containing singly connected oxygen atoms than for bonds containing doubly connected oxygens. It has been assumed earlier that the observed differences in boron oxygen bond distances of bonds containing externally and internally bonded oxygen atoms of the conjugated B_3O_6 group met within the orthorhombic form of metaboric acid should be attributed to such a difference of bond order.^{5,6} The difference in bond distance between these two types of bonds is, in this case, quite significant and appears to be of the right order. The structure of some other crystalline borates have been determined with a high accuracy. Bond distances of these compounds are plotted in Fig. 4 as a function of bond order, calculated from eqns. (11) and (12) for a value of a equal to 0.75. The bond distance is for all these compounds somewhat longer for bonds containing an internally bonded oxygen atom than for those containing externally bonded oxygens. This fact further supports the assumption that double bonding is responsible for a considerable shortening of the bond distance of three-coordinated boron.⁷ It also provides experimental verification of the fact that there exists a correlation between bond order and structure of the conjugated system. The size of the bond order is to some degree also dependent upon the coordination to the conjugated system of the nearest oxygen neighbours. For bonds containing only singly connected oxygen atoms variations in bond orders are mainly dependent upon whether the two oxygen atoms connected to the boron atom of the bond are singly

or doubly connected to the conjugated system. For bonds containing doubly connected oxygen atoms the correlation schedule is somewhat more complicated as the bond order here is dependent upon the coordination of all four oxygen atoms forming the nearest neighbours to the bond in question. For ring-forming systems the calculation of the bond order becomes somewhat more complicated. No drastic changes do appear, however, owing to the extra terms introduced as smaller than six membered rings are not present in the borates. To account for these smaller structural effects the bond order has been calculated from the complete expressions for the conjugated groups present in the crystals reproduced in Fig. 4. As seen from the figure a better correlation between bond distance and bond order seems to be achieved when these smaller effects are also considered.

From the results obtained so far effects of second order could be predicted. In the previous calculations resonance integrals and Coulomb integrals were assumed to be equal for all bonds and for all atoms of each element, respectively. As it follows from the first order treatment that the bond order varies a little between the bonds, the size of the resonance integrals is to be adjusted proportionally. The resonance integrals are then to be chosen somewhat larger for bonds containing singly connected oxygen and somewhat smaller for bonds containing doubly connected oxygen atoms. The charge density on boron comes out as quite constant from the first order treatment. The variations, however, call for small changes of α_B for the different boron positions. The charge density on oxygen varies more drastically between the different oxygen atoms. It is easy to show by a development in accordance with eqn. (7) that the charge density is generally larger for the singly connected than for the doubly connected oxygen atoms. For $a=0.75$ the charge at the former type of oxygen atoms is about 1.80 charge units, and for the other type about 1.68. The charge variations at these two different types of oxygen atoms are less than $\pm 2\%$ for conjugated groups of different extension. α_O should thus be chosen considerably larger for the singly connected oxygen atoms than for the others. These refinements lead to a further increase of the charge density variations at boron. The correlation schedule between charge density on boron and structure of the conjugated system, however, still holds true as the variations introduced in the parameters α and β are also correlated to the structure. After introducing the proper adjustments of these parameters it could be estimated that the variations of the charge density should be in the order of 50% larger than shown in Fig. 2.

There exists no correlation, however, between the size of the quadrupole coupling constant and the structure of the conjugated group as concerns the π -electron coordination of the three oxygen atoms nearest to the boron atom considered. The size of the variations in the quadrupole coupling constant dependent upon the π -electron charge on boron could, from the above calculations, be estimated to be 0.10 Mc/s between the extreme structures. Thus this effect is not of a size that could explain the observed variations in the quadrupole coupling constant between the two groups of compounds. It is, on the other hand, somewhat too large to account only for the variations in the quadrupole coupling constants for compounds within each group.

It may then possibly be assumed that the variations of the π -electron charge densities on boron are still smaller than calculated above from the simple Hückel molecular orbital theory.

The possibility that the variation in the quadrupole coupling constants between the two groups is due to a reduction of the π -electron resonance integrals seems to be ruled out by the experimental data. As the π -electrons give a negative contribution to the quadrupole coupling constant such a reduction of the resonance integrals would imply an increase of eqQ . The reversed effect is actually observed as the quadrupole coupling constant is smaller for the group comprising compounds distorted from three-fold symmetry and perfect planarity. The bond distance bond order correlation scheme (Fig. 4) provides clear evidence of the fact that the resonance integrals of the compounds of the two groups do not differ appreciably. The bond distances of sodium tetraborate and barium tetraborate fall all in the appropriate region of the other borates although the conjugated groups here exhibit appreciable deviations from planarity. The observed differences are in all cases only a small fraction of the total shortening due to the partial double bond formation.

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