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Approximate Self-consistent Field Molecular Orbital Calculation on Trithiadiborolane, Dichlorotrithiadiborolane, Dimethyltrithiadiborolane, Trioxadiborolane, Dichlorotrioxadiborolane, and Dimethyltrioxadiborolane

ODD GROPEN* and PER VASSBOTN

Department of Chemistry, University of Oslo, Blindern, Oslo 3, Norway

The electronic structure of trithiadiborolane, dichlorotrithiadiborolane, dimethyltrithiadiborolane, trioxadiborolane, dichlorotrioxadiborolane and dimethyltrioxadiborolane have been investigated using the CNDO/2 method. The calculations indicate a nearly similar degree of multiplicity in the ring bonds for the two types of compounds.

The molecules H_2S_2 and H_2O_2 have been shown [1–3] to have dihedral angles of 90 and 60 – 90 degrees from *trans*, respectively. Later the *cis* barriers for these molecules were calculated by *ab initio* methods [4,5] to 9.33 and 8.35 kcal/mol. The origin of these barriers are widely discussed and it is claimed that the repulsion between the lone pairs in the planar state is mainly responsible for the twisted form.[6]

In ring compounds where S – S and O – O bonds are present one should for the same reason expect a none-planar skeleton, except when conjugation is present in the system. In the case of conjugation one obtains a very favorable delocalization of the π-electrons, and at the same time the lone pair repulsions are reduced.

In the ring compound trioxadiborolane the boron atom is contributing to the π-system with a formally vacant $2p_z$-orbital. One should expect this vacant orbital to be especially well suited for conjugation with the $2p_z$ lone pairs on the oxygen atoms. This also seems to be the situation as trioxadiborolane has been established to have planar equilibrium.[7] Semiempirical calculations have suggested considerable π-bond orders in this ring.[8,9]

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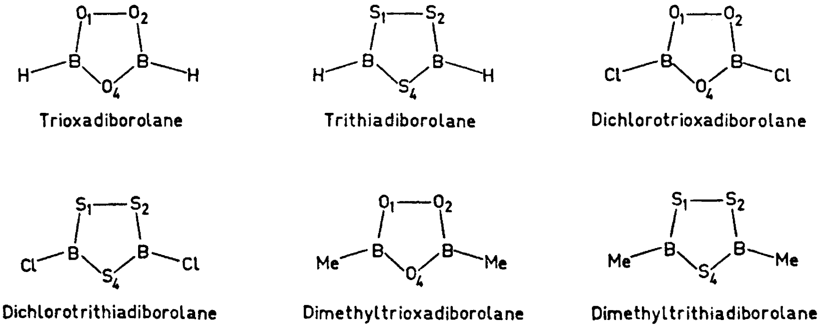
* Present address: Institute of Medical Biology, University of Tromsø, Box 977, N-9001 Tromsø, Norway.



Trioxadiborolane Trithiadiborolane Dichlorotrioxadiborolane

Dichlorotrithiadiborolane Dimethyltrioxadiborolane Dimethyltrithiadiborolane

Fig. 1. Labelling of the atoms.

Lately the dichloro-1,2,4-trithia-3,5-diborolane[10] and the dimethyl-1,2,4-trithia-3,5-diborolane[11] were investigated by electron diffraction, and these compounds were also found to have at least nearly planar rings.

To study the electronic structure of these rings, and compare the degree of multiplicity in the ring bonds were either oxygen or sulfur is engaged we have performed semi-empirical calculations on the molecules $(BH)_2O_3$, $(BCl)_2O_3$, $(BCH_3)_2O_3$, $(BH)_2S_3$, $(BCl)_2S_3$ and $(BCH_3)S_3$.

METHOD AND STRUCTURE PARAMETERS

For only three of the compounds the experimental structure is etablished.[7,10,11] For these compounds the experimental structures are used. For the other three we have made estimates of the necessary geometry parameters. Calculations with different geometries have shown the results not to be sensitive with respect to these variations.

The CNDO-method used here[12,13] is based on a minimal Slater basis for the first and second period, and including 3*d*-polarization functions for the third period. Santry and Segal pointed out that calculations including 3*d*-orbitals predict experimental results slightly better than without.[14] This is not surprising as several *ab initio* calculations have shown the importance of including 3*d*-orbitals on third period atoms.[15]

Recent calculations with the CNDO-method have, however, shown some difficulties in predicting reasonable charge distribution when *d*-orbitals are included on the third period atoms.[16] We performed calculations both with 3*d*-orbitals included and excluded. From these calculations we concluded that the results were not much influenced of the *d*-orbitals except from the charge distribution. Where *d*-orbitals were included a total charge transfer from sulfur to boron was predicted. This result is so unexpected that we decided to concentrate on the results obtained without *d*-orbitals on sulfur and chlorine.

RESULTS AND DISCUSSION

a. Orbital energies. The calculated orbital energies are presented in Tables 1 and 2. We have given a tentative assignment of the molecular orbitals in terms of π-orbitals and more or less localized σ-orbitals. The proposed assignments are presented in the tables.

Disregarding the chlorine lone-pairs we found the highest filled orbital in all the oxygen rings to be a oxygen lone pair, whereas the highest filled orbital

Table 1. Orbital energies for the oxygen compounds. All values in a.u.

Sym.	(ClB)$_2$O$_3$ Energy	Int.pr.	Sym.	(HB)$_2$O$_3$ Energy	Int.pr.	Sym.	(CH$_3$B)$_2$O$_3$ Energy	Int.pr.
$1a_1$	−1.981	B−O$_2$	$1a_1$	−1.951	B−O$_2$	$1a_1$	−1.929	B−O$_2$
$2a_1$	−1.629	B−O$_4$	$2a_1$	−1.388	B−O$_4$	$2a_1$	−1.569	B−O$_4$
$1b_1$	−1.374	B−O$_2$	$1b_1$	−1.331	B−O$_2$	$1b_1$	−1.435	B−C
$3a_1$	−1.173	B−Cl	$2b_1$	−0.948	B−O$_4$	$3a_1$	−1.364	B−C
$2b_1$	−1.160	B−Cl	$3a_1$	−0.929	O−O	$2b_1$	−1.249	B−O$_2$
$4a_1$	−0.957	O−O	$4a_1$	−0.923	B−H	$1b_2$	−0.932	π
$1b_2$	−0.949	π	$1b_2$	−0.898	π	$4a_1$	−0.907	O−O
$3b_1$	−0.853	B−O$_4$	$3b_1$	−0.689	B−H	$3b_1$	−0.867	B−O$_4$
$5a_1$	−0.820	l*p* Cl	$5a_1$	−0.643	l*p* O	$5a_1$	−0.810	C−H
$4b_1$	−0.707	l*p* Cl	$2b_2$	−0.633	π	$1a_2$	−0.778	π C−H
$2b_2$	−0.675	π	$1a_2$	−0.615	π	$4b_1$	−0.741	C−H
$1a_2$	−0.673	π	$6a_1$	−0.614	l*p* O	$6a_1$	−0.718	C−H
$6a_1$	−0.658	l*p* O	$4b_1$	−0.597	l*p* O	$2b_2$	−0.700	π C−H
$7a_1$	−0.608	l*p* O				$5b_1$	−0.607	C−H
$5b_1$	−0.581	l*p* O				$3b_2$	−0.598	π
$2a_2$	−0.558	π Cl				$7a_1$	−0.584	l*p* O
$3b_1$	−0.557	π Cl				$8a_1$	−0.578	l*p* O
$8a_1$	−0.557	l*p* Cl				$2a_2$	−0.567	π
$6b_1$	−0.552	l*p* Cl				$6b_1$	−0.558	l*p* O

Table 2. Orbital energies for the sulfur compounds. All values in a.u.

Sym.	(ClB)$_2$S$_3$ Energy	Int.pr.	Sym.	(HB)$_2$S$_3$ Energy	Int.pr.	Sym.	(CH$_3$B)$_2$S$_3$ Energy	Int.pr.
$1a_1$	−1.345	B−S$_2$	$1a_1$	−1.309	B−S$_2$	$1a_1$	−1.411	B−C
$1b_1$	−1.195	B−Cl	$2a_1$	−1.034	B−S$_4$	$1b_1$	−1.394	B−C
$2a_1$	−1.145	B−Cl	$1b_1$	−0.988	B−S$_2$	$2a_1$	−1.245	B−S$_2$
$3a_1$	−1.059	B−S$_4$	$3a_1$	−0.835	B−H	$3a_1$	−1.038	B−S$_4$
$2b_1$	−0.913	B−S$_2$	$2b_1$	−0.807	B−S$_4$	$2b_1$	−0.924	B−S$_2$
$3b_1$	−0.752	B−S$_4$	$4a_1$	−0.706	S−S	$3b_1$	−0.811	B−S$_4$
$4a_1$	−0.747	S−S	$1b_2$	−0.634	π	$1b_2$	−0.804	$\pi_{\text{C-H}}$
$1b_2$	−0.699	π	$3b_1$	−0.548	B−H	$4a_1$	−0.781	S−S
$5a_1$	−0.691	l*p* Cl	$5a_1$	−0.533	l*p* S	$1a_2$	−0.772	$\pi_{\text{C-H}}$
$4b_1$	−0.614	l*p* Cl	$4b_1$	−0.482	l*p* S	$5a_1$	−0.695	C−H
$1a_2$	−0.597	π Cl	$2b_2$	−0.476	π	$4b_1$	−0.687	C−H
$6a_1$	−0.595	l*p* Cl	$6a_1$	−0.460	l*p* S	$6a_1$	−0.664	C−H
$2b_2$	−0.539	π_{Cl}	$1a_2$	−0.443	π	$2b_2$	−0.569	π
$7a_1$	−0.500	l*p* S				$5b_1$	−0.494	C−H
$5b_1$	−0.495	l*p* Cl				$7a_1$	−0.491	l*p* S
$3b_2$	−0.489	π				$3b_2$	−0.456	π
$8a_1$	−0.474	l*p* S				$6b_1$	−0.455	l*p* S
$6b_1$	−0.474	l*p* S				$8a_1$	−0.432	l*p* S
$2a_2$	−0.441	π				$2a_2$	−0.414	π

in all the sulfur compounds is a π-orbital. Also the energy of the totally symmetric π-orbital we found to be relatively lower in the oxygen compounds than in the sulfur compounds.

This tendency of the π-orbitals to have a lower energy in the oxygen compounds may indicate a slightly better delocalization in these compounds compared to the sulfur compounds.

b. Charge distribution. The gross atomic populations are presented in Table 3. In all rings we found a charge transfer from boron to oxygen or sulfur in the σ-skeleton, and a smaller backbond effect in the π-system.

Table 3. Gross atomic population.

Atom	$(ClB)_2O_3$			$(HB)_2O_3$			$(CH_3B)_2O_3$			$(ClB)_2S_3$			$(HB)_2S_3$			$(CH_3B)_2S_3$		
	σ	π	tot.	σ	π	tot.	σ	π	tot.	σ	π	tot.	σ	π	tot.	σ	π	tot.
O4/S_4	4.65	1.61	6.26	4.67	1.57	6.24	4.67	1.61	6.28	4.42	1.70	6.12	4.44	1.65	6.09	4.46	1.70	6.17
B	2.07	0.47	2.54	2.23	0.43	2.65	2.19	0.46	2.66	2.30	0.44	2.74	2.46	0.38	2.83	2.40	0.42	2.82
O2/S_2	4.34	1.81	6.15	4.36	1.79	6.14	4.36	1.81	6.17	4.23	1.83	6.05	4.25	1.80	6.05	4.26	1.83	6.09
Cl/H/CH_3	5.26	1.91	7.17	1.08		1.08			7.05	5.27	1.88	7.15	1.07		1.07			7.00

As has been expected the π-charge transfer into the vacant $2p_z$-orbital on boron is significant. But though the inductive effect in the σ-skeleton is different in the two types of compounds the back-bonding is almost constant.

CNDO-calculation[17] on aminoborane indicates a π-charge on boron (-0.394) that is very close to our result. For borazine, however, MWH-technique[18] is predicting a boron π-charge of -0.6162, which should indicate a much stronger conjugation in this compound.

The charge distribution in the rings is almost unaffected by change of substituents.

c. π-Bond order. The bond orders from a CNDO-calculation are usually not invariant under a coordinate transformation. Using only one $2p_z$-orbital for each atom in the π-representation for a planar molecule, the obtained π-bond orders may be an indication of the relative conjugation in the systems. The obtained π-bond orders are presented in Tables 4 and 5. The numbers obtained certainly predict a conjugation in the systems.

Table 4. π-Bond orders for the oxygen compounds.

Bond	$(ClB)_2O_3$	$(HB)_2O_3$	$(CH_3B)_2O_3$
O–O	0.020	0.033	0.028
B–O_4	0.514	0.548	0.516
B–O_2	0.537	0.577	0.536

Table 5. π-Bond orders for the sulfur compounds.

Bond	$(ClB)_2S_3$	$(HB)_2S_3$	$(CH_3B)_2S_3$
$S-S$	0.040	0.060	0.046
$B-S_4$	0.470	0.513	0.465
$B-S_2$	0.510	0.569	0.510

The most striking result is the very small bond orders for the $O-O$ and $S-S$ bonds. This was earlier pointed out by Coulson for the $O-O$ bond.[8] The bond orders are, however, indicating a shortening of these bonds relative to H_2S_2 and H_2O_2 as far as conjugation is concerned. They also predict a stronger shortening of the $S-S$ bond than the $O-O$ bond relative to H_2S_2 and H_2O_2, respectively.

The experimental value for the $O-O$ bond length in hydrogen peroxide is not clear as quite different values are presented in the literature (1.475 Å[2] and 1.453 Å[1]). The $O-O$ bond length in trioxa-diborolane is found to be 1.47 Å. For the $S-S$ bond the experimental results are giving a lengthening in the ring (2.067 Å) compared to hydrogen persulfide (2.055 Å).

Coulson [8] has suggested that in $(BH)_2O_3$ the repulsion between the net charges on the oxygen atoms may give just the opposite effect of conjugation. This could be the situation for the sulfur compound too. But probably the variation in the bond lengths are not deducible from our calculations.

Considering the π-bond order one should expect a shorter $B-O_2$ ($B-S_2$) bond than $B-O_4$ ($B-S_4$). This is in agreement with the experimental results for the oxygen compound, but in the two experimentally investigated sulfur compounds the electron diffraction method was not conclusive.

Compared to the CNDO-calculation on the aminoborane we have higher bond orders both for the $B-O$ and the $B-S$ bonds than for the $B-N$ bond (0.305).[17]

CONCLUSION

The results all predict a high degree of conjugation in the rings. This seems reasonable as they by experimental investigation are concluded to be planar. But what is a little unexpected is the small difference between the rings containing sulfur and oxygen. One should, however, be careful in stressing this point too far as the CNDO/2 method may give wrong conclusions. Especially the lack of 3*d*-orbitals may influence the result a great deal.

On the other side, if the conjugation alone is expected to be responsible for the planarity it is not surprising to find the same effects in the sulfur compounds as in the oxygen compounds. This because the calculated barrier to internal rotation about the $S-S$ bond is even higher in hydrogen persulfide [4] than the corresponding barrier in hydrogen peroxide.[5]

We feel that both these questions and the bond length variations may be better understood through *ab initio* calculations. We are therefore now studying the molecules $(H_2B)OH$, $H_2B(SH)$, $(H_2B)O_2(BH_2)$, and $H_2BS_2BH_2$ together with the ring compounds $(BH)_2O_3$ and $(BH)_2S_3$ by *ab initio* calculations.

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