

## Electronic structure of $X_2Y_3$ molecules ( $X = B, Al, Ga$ ; $Y = O, S$ ): A theoretical study

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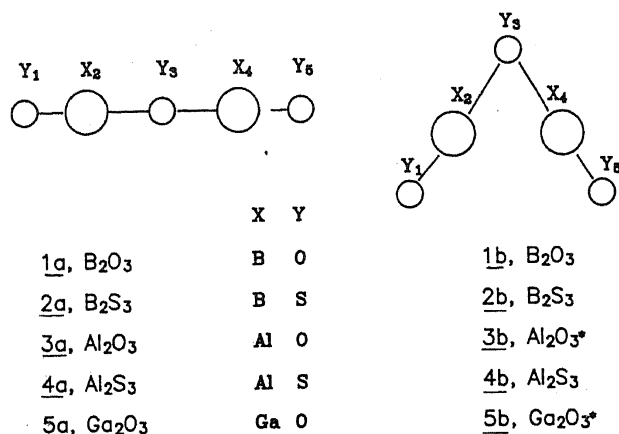
**Abstract.** *Ab initio* molecular orbital and density functional theory calculations on  $X_2Y_3$  ( $X = B, Al, Ga$ ;  $Y = O, S$ ) indicate a bent structure with  $C_{2v}$  symmetry to be the preferred arrangement for  $B_2O_3$ ,  $B_2S_3$  and  $Al_2S_3$ . In contrast, the linear isomer is favoured for  $Al_2O_3$  and  $Ga_2O_3$ . These are in agreement with the experimentally observed structures. The electronegativity difference between X and Y, the MO patterns and the ionic nature of the bonding explain variations in the molecular structure. The results from the two theoretical approaches (MP2/6–31G\* and Becke3LYP/6–311 + G\* level) are comparable.

**Keywords.** *Ab initio* MO theory; density functional theory;  $X_2Y_3$  molecules.

### 1. Introduction

Metallorganic chemical vapour deposition (MOCVD) has become an increasingly important technique in the production of thin films of reactive materials (Sherman 1987; Pierson 1992). This method also helps in generating highly reactive molecules in extremely low pressure conditions so that molecules, otherwise inaccessible, can be generated (Andrews 1971; Hallam 1973; Craddock and Hinchliffe 1975). The matrix isolation technique combined with the power of MOCVD enables the isolation and characterization of such reactive molecules trapped in inert matrices.  $X_2Y_3$  ( $X = B, Al, Ga$ ;  $Y = O, S$ ) forms one such class of compounds. While the inorganic solids were known for several years (Scholze 1956; Schäfer 1963; Prewitt 1968; Donohue 1970; Shannon *et al* 1970; Range 1973; Diercks and Krebs 1977; Ishizawa *et al* 1980), stoichiometric compositions of these molecules have been reported only recently. Except for  $Ga_2O_3$  and  $Ga_2S_3$ , all of them were generated in the gas phase and trapped in argon matrices using the MOCVD technique. IR spectral investigations on these molecules identified  $B_2O_3$  (Sommer *et al* 1963; Burkholder and Andrews 1991),  $B_2S_3$  (Beattie *et al* 1987) and  $Al_2S_3$  (Ault 1994) as bent (V-shaped;  $C_{2v}$  symmetry) and  $Al_2O_3$  (Andrews *et al* 1992) as linear ( $D_{\infty h}$  symmetry). Further support for the experimentally observed species like  $B_2O_3$ ,  $Al_2O_3$  and  $Al_2S_3$  has been provided by theoretical studies using *ab initio* molecular orbital (Nguyen *et al* 1983; Nemukhin and Weinhold 1992, 1993) and density functional (Ault 1994) studies. Though the deviation of the structure of  $Al_2O_3$  from the rest of the molecules has been pointed out, the reasons underlying these have not been addressed in detail (Nemukhin and Weinhold

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\* Does not correspond to a stationary point

1993; Ault 1994). We present here the electronic structure of B<sub>2</sub>O<sub>3</sub>, B<sub>2</sub>S<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>S<sub>3</sub> and Ga<sub>2</sub>O<sub>3</sub> (1–5) using the *ab initio* molecular orbital (MO) as well as the density functional theories with a view to compare the reliability and computational economy of the two methods. A qualitative explanation for the difference in the structure of Al<sub>2</sub>O<sub>3</sub> and Ga<sub>2</sub>O<sub>3</sub> from the other molecules considered is provided. The good level of agreement of the calculated structures with experiments gives confidence in the results on Ga<sub>2</sub>O<sub>3</sub> which is yet to be synthesized.

## 2. Method of calculation

The molecular orbital and the density functional theories were used in this study. Structures 1–5 were optimized at the MP2(full)/6-31G\* level (Moller and Plesset 1934; Hehre *et al* 1986). For Ga the (4333/433/4\*) basis set was employed (Huzinaga *et al* 1984). The optimizations were repeated with density functional theory (Becke3LYP) involving Becke's 3-parameter functional (Becke 1988, 1993) and the nonlocal correlation functionals provided by Lee *et al* (1988). For these calculations the standard 6-311 + G\* basis set was used (Hehre *et al* 1986). All calculations were carried out using the Gaussian 92 (Frisch *et al* 1992) and Gaussian 92/DFT (Frisch *et al* 1993) program package. The nature of the stationary point was ascertained by harmonic vibrational frequency computations. Thus, minima were characterized as those structures with no imaginary frequency. The total, relative and zero point energies along with the number of imaginary frequencies (NIM) are given in table 1. The relative energies in table 1 include zero point energy correction scaled by a factor of 0.95 for the known deficiencies of the MP2 level of calculations (Hehre *et al* 1986). The relative energies obtained from DFT calculations include unscaled zero point energy (Schleyer *et al* 1994). Table 2 includes some of the important geometric parameters obtained at both the levels of theory.

## Results and discussion

The relative energies in table 1 clearly indicate that B<sub>2</sub>O<sub>3</sub>, B<sub>2</sub>S<sub>3</sub> and Al<sub>2</sub>S<sub>3</sub> prefer a bent V-shaped structure. However, similar structures for Al<sub>2</sub>O<sub>3</sub> and Ga<sub>2</sub>O<sub>3</sub> do not

**Table 1.** Total (Hartree), relative (kcal/mol) and zero point energies (ZPE – kcal/mol) of  $X_2Y_3$  (X = B, Al; Y = O, S). A: MP2/6-31G\*; B: Becke3LYP

No.	X	Y	Total energy		Relative energy <sup>a</sup>		ZPE (NIM) <sup>b</sup>	
			A	B <sup>c</sup>	A	B <sup>c</sup>	A	B <sup>c</sup>
<u>1a</u>	B	O	–247·82877	–275·62682	1·2	0·7	11·7(2)	11·6(2)
<u>1b</u>	B	O	–274·83058	–275·62838	0·0	0·0	11·8(0)	11·9(0)
<u>2a</u>	B	S	–1242·50233	–1244·40206	37·2	33·0	6·9(2)	6·7(2)
<u>2b</u>	B	S	–1242·56247	–1244·45559	0·0	0·0	7·5(0)	7·3(2)
<u>3a<sup>d</sup></u>	Al	O	–709·14746	–710·73322			6·7(0)	7·0(0)
<u>4a</u>	Al	S	–1676·97815	–1679·67544	13·9	11·4	4·0(2)	3·7(2)
<u>4b</u>	Al	S	–1677·00062	–1679·69413	0·0	0·0	4·2(0)	4·0(0)
<u>5a<sup>d</sup></u>	Ga	O	–4067·57377				6·0(0)	

<sup>a</sup>Includes ZPE correction scaled by a factor 0·95 for the MP2/6-31G\* level. The Becke3LYP relative energies do not include ZPE correction (Schleyer *et al* 1994); <sup>b</sup>NIM – number of imaginary frequencies in parentheses; <sup>c</sup>Calculation at Becke 3LYP/6-311 + G\* level; <sup>d</sup>3b and 5b do not correspond to stationary points.

**Table 2.** Bond distances (Å) and bond angles (deg) for 1–5 calculated at the MP2/6-31G\* and Becke3LYP/6-311 + G\* levels.

No.	X	Y	MP2/6-31G*			Becke3LYP/6-311 + G*		
			Y <sub>1</sub> –X <sub>2</sub>	X <sub>2</sub> –Y <sub>3</sub>	X <sub>2</sub> –Y <sub>3</sub> –X <sub>4</sub>	Y <sub>1</sub> –X <sub>2</sub>	X <sub>2</sub> –Y <sub>3</sub>	X <sub>2</sub> –Y <sub>3</sub> –X <sub>4</sub>
<u>1a</u>	B	O	1·221	1·316	180·0	1·208	1·313	180·0
<u>1b</u>	B	O	1·221	1·335	135·6	1·206	1·326	141·7
<u>2a</u>	B	S	1·611	1·717	180·0	1·614	1·720	180·0
<u>2b</u>	B	S	1·609	1·771	91·9	1·611	1·779	95·6
<u>3a</u>	Al	O	1·626	1·691	180·0	1·610	1·688	180·0
<u>4a</u>	Al	S	2·004	2·117	180·0	2·012	2·131	180·0
<u>4b</u>	Al	S	2·005	2·162	95·9	2·011	2·179	101·7
<u>5a</u>	Ga	O	1·656	1·734	180·0			

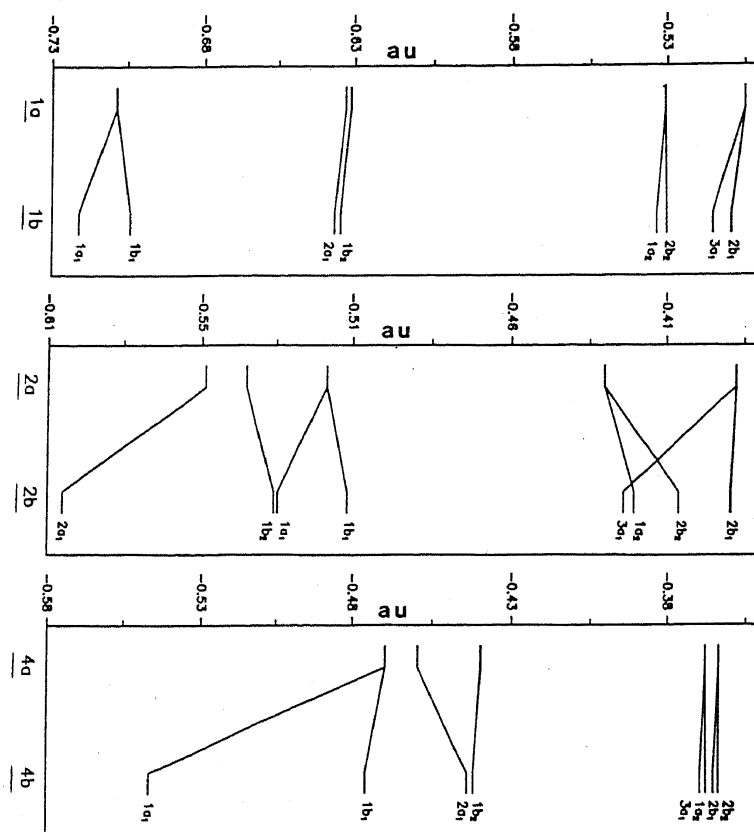
correspond to stationary points. These results calculated at the correlated MP2 level and the Becke3LYP-DFT level are in agreement with experimental observations. The structure of the molecules were identified spectroscopically and hence detailed information regarding the bonding features has not been provided for comparison. The Y<sub>1</sub>–X<sub>2</sub> distances in 1–5 are calculated to be shorter than the X<sub>2</sub>–Y<sub>3</sub> distances (table 2). Further, the Y<sub>1</sub>–X<sub>2</sub> distance does not change appreciably as the structure goes from the linear (1a–5a) to the bent geometry (1b–5b). However, there is an elongation of the X<sub>2</sub>–Y<sub>3</sub> distance for the same process. The X<sub>2</sub>–Y<sub>3</sub>–X<sub>4</sub> angle in the bent structures 1b–5b (table 2) shows a systematic variation and correlates well with the electronegativity difference ( $\Delta EN$ ) between X and Y in the molecule (Pauling 1960). The larger the  $\Delta EN$ , the smaller the X<sub>2</sub>–Y<sub>3</sub>–X<sub>4</sub> bending, and thus, Al<sub>2</sub>O<sub>3</sub> and Ga<sub>2</sub>O<sub>3</sub> which have the largest  $\Delta EN$  (2·0; 1·9 – Pauling scale) among the molecules considered are calculated to be linear (table 1). The  $\Delta EN$  between B and O in B<sub>2</sub>O<sub>3</sub> is 1·5 which has the next largest

$X_2-Y_3-X_4$  angle (table 2).  $B_2S_3$  with a  $\Delta EN$  of 0.5 has the maximum  $X_2-Y_3-X_4$  bending (table 2). This shows that increasing  $\Delta EN$  lead to structure with linear arrangement while structures with smaller  $\Delta EN$  between X and Y prefer a bent geometry. Other electronegativity scales essentially parallel the same results (Huheey *et al* 1993).

Surely the  $X_2-Y_3-X_4$  angle in these molecules also reflects the inherent bond angles in the simple derivatives of Y. The correlation of the H-Y-H angle in  $H_2Y$  (O, S, Se) with the electronegativity of Y has been noted previously (Albright *et al* 1985). In addition, the variation in the barrier for the linear inversion structure over the linear arrangement in  $H_2O$ ,  $H_2S$  and  $H_2Se$  has also been explained from the Walsh diagrams. A linear H-O-H arrangement for  $H_2O$  reveals two filled  $p$ -orbitals perpendicular to each other on oxygen. On bending, the in-plane  $p$ -orbital lowers in energy by mixing with a higher lying  $\sigma^*$  orbital (of the same symmetry) leading to a hybridized lone pair orbital. The extent of this stabilization depends on the energy difference between the in-plane  $p$ -orbital and the  $\sigma^*$  level. This difference decreases as one goes from  $H_2O$  to  $H_2S$  and lower elements in the group. Obviously the non-bonding H...H repulsions also become dominant as the angle decreases leading to the observed structure. Substitution of the hydrogens in  $H_2O$  by the isoelectronic lithium atoms leads to  $Li_2O$ . Calculations (Rehm *et al* 1992; Azavant and Lichanot 1993) and experiments (Buchler *et al* 1963; Seshadri *et al* 1966; Tolmachev *et al* 1969; Spiker and Andrews 1973) indicate  $Li_2O$  to be linear. The ionic character (due to the large electronegativity difference) of the Li-O bond and consequent electrostatic repulsions between the lithium atoms keep the molecule linear. Theoretical studies on  $X_2O$  ( $X = B, Al, Ga$ ) also gave similar results (Leszczynski and Kwiatkowski 1992).

The structures of  $X_2Y_3$  molecules can also be analysed following this pattern. Scheme 1 shows the correlation diagram for the linear and bent geometries of 1, 2 and 4. The linear (1a) and bent (1b) geometries of  $B_2O_3$  are taken as models to explain the nature of the interactions responsible for the bent geometries in  $X_2Y_3$  molecules. The energy levels are labelled according to the  $C_{2v}$  point group. Apart from the four  $\sigma$  bonding MO's in 1a (not shown in scheme 1) there are three degenerate sets of MO's corresponding to the in-plane and out-of-plane  $\pi$ -orbitals. This enhances the  $\pi$ -delocalization in the linear arrangement. In addition, the  $\sigma$  lone pair orbitals (2a<sub>1</sub> and 1b<sub>2</sub>) on  $Y_1$  and  $Y_5$  are also occupied. On bending, the in-plane  $\pi$ -MO's (1a<sub>1</sub>, 1a<sub>2</sub> and 3a<sub>1</sub>) of the degenerate sets (linear) decrease in energy substantially while the perpendicular  $\pi$ -MO's (1b<sub>1</sub>, 2b<sub>2</sub> and 2b<sub>1</sub>) are slightly perturbed (scheme 1). As a result, the delocalization of the  $\pi$ -electrons in the linear framework (1a) is disturbed in the bent structure, 1b. Again, the in-plane  $p$ -orbital on  $Y_3$ , which was involved in the  $\pi$ -delocalization (1a<sub>1</sub>) rehybridizes by mixing with the higher lying orbitals (of the same symmetry) to the sigma type lone pair orbital on  $Y_3$ . This loss in  $\pi$ -delocalization is clearly reflected in the lengthening of the  $X_2-Y_3$  distance on going from 1a to 1b (table 2). On the other hand, the  $\pi$ -MO's between  $Y_1-X_2$  and  $X_4-Y_5$  are not affected by the same process. As a result, there is no change in the  $Y_1-X_2$  and  $X_4-Y_5$  distances upon bending (table 2).

Further, the antibonding interaction between ( $X_2, Y_3$ ) and ( $Y_3, X_4$ ) bonds present in the HOMO of the linear arrangement (2b<sub>1</sub>, 3a<sub>1</sub>) is reduced to a large extent by the rehybridization of the in-plane  $p$ -orbitals on  $Y_3$  (3a<sub>1</sub>) during the process of bending (scheme 1). As a result, a slight bonding interaction is developed between  $X_2-Y_3$  and  $Y_3-X_4$  in the bent geometry. Thus, the loss in the  $\pi$ -delocalization during the process of



**Scheme 1.** Correlation diagram for linear (1a, 2a, 4a) and bent (1b, 2b, 4b) structures. All molecular orbitals are occupied. Energy in atomic units (au).

bending is partly compensated for by a stabilizing interaction in the  $\sigma$ -framework (scheme 1). These features in the MO pattern of the linear and bent geometries in  $B_2O_3$  is quite similar to that of  $H_2Y$  discussed earlier. Further, a similar pattern is also observed for 2 and 4 (scheme 1). In addition to the above mentioned factors, the preference of 2b and 4b (in comparison to 2a and 4a) also arises from the 2a<sub>1</sub> and 3a<sub>1</sub> orbitals in 2 and 1a<sub>1</sub> orbital in 4 (scheme 1). The extent of the stabilizing interactions which vary for 1, 2 and 4 is reflected in the energy difference between the linear and bent structures (table 1).

The linearity of  $Al_2O_3$  (3a) and  $Ga_2O_3$  (5a) arises due to the large electronegativity difference between Al and O (2.0) and Ga and O (1.9). The bonding in  $Al_2O_3$  has been described earlier as ionic (Nemukhin and Weinhold 1992, 1993). This is supported by the charges ( $Y_1 = -1.257$ ;  $X_2 = 2.023$ ;  $Y_3 = -1.533$  for  $Al_2O_3$ ;  $Y_1 = -0.849$ ;  $X_2 = 1.433$ ;  $Y_3 = -1.167$  for  $Ga_2O_3$  – table 3) derived from the natural population analysis – NPA (Reed *et al* 1985; Reed and Schleyer 1990). This can be compared to  $B_2S_3$  (2a) where the bonding between B–S ( $\Delta EN = 0.5$ ) is more covalent in nature. The charges on  $Y_1 = -0.195$ ,  $X_2 = 0.311$  and  $Y_3 = -0.233$  (table 3) also support this.  $B_2O_3$  and  $Al_2S_3$  fall between these two extremes. The NPA charges derived for these two molecules are also given in table 3. Thus, repulsive electrostatic interactions rather than orbital interactions, dominate in  $Al_2O_3$  and  $Ga_2O_3$ . We hesitate to extend the qualitative argument beyond a stage where predictions become less certain. Quantitative results which can be obtained with less computer time are needed in such cases (especially for the larger molecules).

**Table 3.** Natural population analysis (NPA) derived charges calculated for 1–5 at the MP2/6-31G\* level.

No.	$Y_1$	$X_2$	$Y_3$	$ X_2 - Y_3 ^a$
<u>1a</u>	–0.911	1.441	–1.061	2.502
<u>1b</u>	–0.906	1.423	–1.033	2.456
<u>2a</u>	–0.195	0.311	–0.233	0.544
<u>2b</u>	–0.199	0.235	–0.072	0.307
<u>3a</u>	–1.257	2.023	–1.533	3.556
<u>4a</u>	–0.922	1.526	–1.207	2.733
<u>4b</u>	–0.907	1.386	–0.960	2.346
<u>5a</u>	–0.849	1.433	–1.167	2.600

<sup>a</sup>Difference in the NPA charges between  $X_2$  and  $Y_3$ .

This study also provides a comparison between the results obtained from the computationally expensive MP2/6-31G\* and the cost effective Becke3LYP/6-311 + G\* methods. First of all, we note that the results obtained from both the levels are qualitatively similar (tables 1 and 2). The local minima are correctly reproduced by both the methods. The relative energies (table 1) are surprisingly close, the largest difference being 3.8 kcal/mol (2). The geometrical trends are also reproduced by both the methods (table 2). There is a computational advantage in using DFT because DFT calculations using extended and flexible basis sets are seen to have taken less time than MP2/6-31G\* calculations.

#### 4. Conclusions

The electronic structure of  $X_2Y_3$  ( $X = B, Al, Ga$ ;  $Y = O, S$ ) molecules using *ab initio* MO and density functional theories clearly explain the extra stability of the bent structures (1b, 2b, 4b) over the linear ones (1a, 2a, 4a). This has been attributed to the stabilization of the in-plane  $\pi$ -orbitals in the bent geometry compared to the linear geometry. The bonding in  $Al_2O_3$  and  $Ga_2O_3$  is calculated to be ionic and hence the dominant electrostatic interactions force the linear arrangement. On the other hand, the bonding in  $B_2S_3$  is described to be more covalent.  $Al_2S_3$  and  $B_2O_3$  are intermediate between  $Al_2O_3$  and  $B_2S_3$ . The reliability of the DFT method is shown to be comparable to *ab initio* MO methods with electron correlation in predicting the structure and stabilities of these molecules.

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