

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

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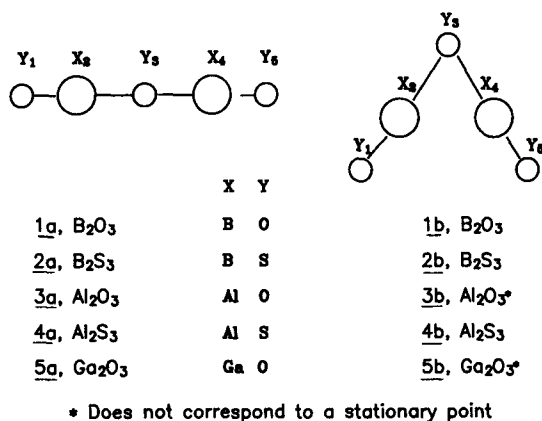
Abstract. *Ab initio* molecular orbital and density functional theory calculations on X_2Y_3 ($X = B, Al, Ga; Y = O, S$) indicate a bent structure with C_{2v} symmetry to be the preferred arrangement for B_2O_3 , B_2S_3 and Al_2S_3 . In contrast, the linear isomer is favoured for Al_2O_3 and Ga_2O_3 . 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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1993; Ault 1994). We present here the electronic structure of B₂O₃, B₂S₃, Al₂O₃, Al₂S₃ and Ga₂O₃ (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 Al₂O₃ and Ga₂O₃ from the other molecules considered is provided. The good level of agreement of the calculated structures with experiments gives confidence in the results on Ga₂O₃ 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.

3. Results and discussion

The relative energies in table 1 clearly indicate that B₂O₃, B₂S₃ and Al₂S₃ prefer a bent (V-shaped) structure. However, similar structures for Al₂O₃ and Ga₂O₃ 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 ^a		ZPE (NIM) ^b	
			A	B ^c	A	B ^c	A	B ^c
<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</u> ^d	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</u> ^d	Ga	O	-4067.57377				6.0(0)	

^aIncludes 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); ^bNIM – number of imaginary frequencies in parentheses; ^cCalculation at Becke 3LYP/6-311 + G* level; ^d3b 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_1-X_2	X_2-Y_3	$X_2-Y_3-X_4$	Y_1-X_2	X_2-Y_3	$X_2-Y_3-X_4$
<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			

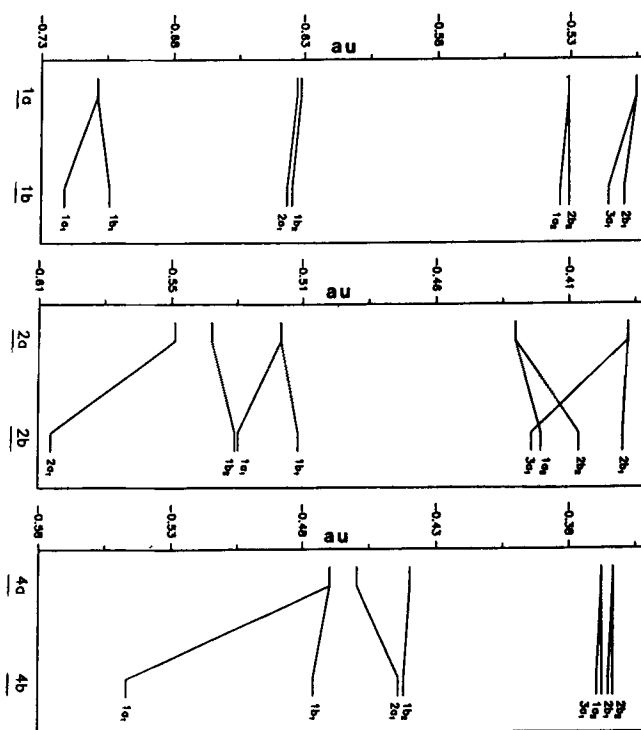
correspond to stationary points. These results calculated at the correlated MP2 level and the Becke3LYP-DFT level are in agreement with experimental observations. The structure of the molecules were identified spectroscopically and hence detailed information regarding the bonding features has not been provided for comparison. The Y_1-X_2 distances in 1–5 are calculated to be shorter than the X_2-Y_3 distances (table 2). Further, the Y_1-X_2 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_2-Y_3 distance for the same process. The $X_2-Y_3-X_4$ angle in the bent structures 1b–5b (table 2) shows a systematic variation and correlates well with the electronegativity difference (ΔEN) between X and Y in the molecule (Pauling 1960). The larger the ΔEN , the smaller the $X_2-Y_3-X_4$ bending, and thus, Al_2O_3 and Ga_2O_3 which have the largest ΔEN (2.0; 1.9 – Pauling scale) among the molecules considered are calculated to be linear (table 1). The ΔEN between B and O in B_2O_3 is 1.5 which has the next largest

X_2 - Y_3 - X_4 angle (table 2). B_2S_3 with a ΔEN of 0.5 has the maximum X_2 - Y_3 - X_4 bending (table 2). This shows that increasing ΔEN lead to structure with linear arrangement while structures with smaller ΔEN 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 σ^* 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 σ^* 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 σ 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 π -orbitals. This enhances the π -delocalization in the linear arrangement. In addition, the σ lone pair orbitals (2a₁ and 1b₂) on Y_1 and Y_3 are also occupied. On bending, the in-plane π -MO's (1a₁, 1a₂ and 3a₁) of the degenerate sets (linear) decrease in energy substantially while the perpendicular π -MO's (1b₁, 2b₂ and 2b₁) are slightly perturbed (scheme 1). As a result, the delocalization of the π -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 π -delocalization (1a₁) 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 π -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 π -MO's between Y_1 - X_2 and X_4 - Y_3 are not affected by the same process. As a result, there is no change in the Y_1 - X_2 and X_4 - Y_3 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 (2b₁, 3a₁) is reduced to a large extent by the rehybridization of the in-plane p -orbitals on Y_3 (3a₁) 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 π -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 σ -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 2a₁ and 3a₁ orbitals in 2 and 1a₁ 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

^aDifference in the NPA charges between X₂ and Y₃.

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 X₂Y₃ (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 π -orbitals in the bent geometry compared to the linear geometry. The bonding in Al₂O₃ and Ga₂O₃ is calculated to be ionic and hence the dominant electrostatic interactions force the linear arrangement. On the other hand, the bonding in B₂S₃ is described to be more covalent. Al₂S₃ and B₂O₃ are intermediate between Al₂O₃ and B₂S₃. 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.

Acknowledgement

The authors thank the Computer Centre, University of Hyderabad and the Jackson State University, Mississippi for computational facilities. GS thanks the Council of Scientific and Industrial Research, New Delhi for a fellowship.

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