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MO-SCF Calculations for B_2O_3*

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The results of *ab-initio* molecular self-consistent field calculations with atomic optimized Gaussian bases are reported for the B_2O_3 molecule. These distinguish between several plausible structures and yield a *V*-shaped structure as the minimum energy geometry.

Ab-initio self-consistent-field calculations have been carried out for the B_2O_3 molecule in order to determine its minimum-energy geometry. These calculations were prompted by an interesting controversy over the structure of this molecule. Infrared spectra [1] and electron diffraction [2] studies have provided evidence for a *V*-shaped molecule with C_{2V} symmetry. However, another analysis [3] of the IR spectra pointed out inconsistencies in this assignment of structure, and a bipyramidal geometry was suggested. Subsequent molecular beam deflection studies [4] eliminated any non-polar structure such as a bipyramidal one, but did not resolve the ambiguities of the original IR analysis. The present calculations were undertaken to examine plausible structures for the B_2O_3 molecule.

The basis used consisted of atomic-optimized Gaussian-type-functions of the form:

$$X = N r^{A+l} \exp(-\alpha r^2)\, Y_l^m(\theta, \phi)$$

where the $Y_l^m(\theta, \phi)$ are normalized spherical harmonics, A is an integer which is zero in this case, and α is the orbital exponent. The basis consisted of a total of thirty functions, with a $(3s\,1p)$ set centered at each boron and oxygen nucleus, with atomic-optimized exponents as listed in Table 1. A modified IBMOL program [6] was used for these calculations. Keeping in mind the molecular beam work of Kaiser, Muenter and Klemperer which shows that B_2O_3 is a polar molecule, only models capable of permanent dipole moments were examined. The four structures considered are listed in Table 2, along with the bond lengths and angles used in the calculations. In cases of ambiguity of configurations the calculations were performed without utilizing orbital symmetries. Thus the minimum-energy orbital configuration is also a consequence of the calculations rather than an assumption.

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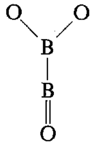
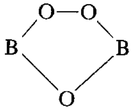
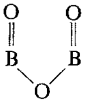
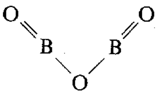
Table 1. *Optimized atomic orbital exponents of* (3*s* 1*p*) *gaussian bases for boron and oxygen*[a]

Atom	Orbital exponents		Total energy
	s	*p*	(h)
B	31.4700		−23.7136
	4.5090		
	0.1960		
		0.1990	
O	84.9300		−71.2526
	12.4200		
	0.6212		
		0.7440	

[a] Ref. [5].

Table 2. *Geometric parameters, orbital configurations and total energies of plausible* B_2O_3 *structures*

	Bond lengths (Å)		Bond angles (°)		Orbital configuration	Total energy (h)
	O–B	1.36	∢OBO	120°	$13A_1 1A_2 1B_1 2B_2$	−255.0055
	B–B	1.74				
	B=O	1.20				
	O–O	1.47	∢OOB	105	$9A_1 1A_2 5B_1 2B_2$	−261.8703
	O–B	1.36	∢OBO	113		
	B–O	1.38	∢BOB	104		
	O=B	1.20	∢OBO	160	$8A_1 1A_2 6B_1 2B_2$	−261.9236
	B–O	1.36	∢BOB	150		
	O=B	1.20	∢BOB	95	$8A_1 1A_2 6B_1 2B_2$	−261.9721
	B–O	1.36		105		−261.9745
				115		−261.9685
				130		−261.9522

The total energies of the four forms show that the previously-proposed *V*-shape structure with linear O=B–O arms is the minimum energy one. The energy has been calculated at four different angles, and a simple parabolic fit yields a minimum energy of −261.9747 h at an angle of 103°. This is to be compared with the sum of the atomic energies calculated with the same bases −261.1850 h. The ring and bent-*V* structures also yield energies lower than that of the isolated atoms, but significantly higher than that of the straight-*V* form.

The *Y*-form on the other hand exhibits a much higher energy, probably due to the drastically-different electron configuration required to accommodate a direct boron-boron bond. Increase of basis size will result in lower calculated energies for each structure, but this is unlikely to change the ordering of the energies.

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