

## SCF and CASSCF Studies of Geometrical Rearrangements in LiBO

Alexandr V. Nemukhin\*, Jan E. Almlöf and Anders Heiberg

Department of Chemistry, University of Oslo, Blindern, Oslo 3, P.O. Box 1033, Norway

The minimum energy path for the rearrangement  $\text{LiOB} \rightarrow \text{OBLi}$  was calculated with the SCF approximation using a double-zeta plus polarization basis set. Stationary points on the potential surface were studied with the help of the CASSCF method using different choices of active space. The results indicate that LiBO may be regarded as a polytopic type molecule. The relative energies of different geometrical configurations changed considerably when the CASSCF method was used, compared to those obtained at the SCF level, demonstrating the importance of correlation effects for this system.

**Key words:** Geometrical rearrangements in LiBO – Multi-configuration SCF.

### 1. Introduction

**Ab initio** studies of potential energy surfaces (PES) present an important field of quantum chemistry applications. In particular, calculations of the rearrangement process  $\text{ABC} \rightarrow \text{BCA}$  are of interest for polytopic molecules which are characterized by close energies of very different geometries, separated by low barriers [1, 2]. These studies are related to the more general problem of the structure of non-rigid molecules [3, 4].

It is generally hoped that the self-consistent field (SCF) approximation provides an accurate description of potential energy surfaces for rearrangement processes, especially for systems with primarily ionic bonding [2, 5, 6]. Clementi et al. [2] estimated the correlation energy contributions for LiNC and LiCN semi-empirically and found them nearly equal in value. The detailed study of the  $\text{HNC} \rightarrow \text{HCN}$  PES by means of SCF and configuration interaction (CI) methods

\* *Permanent address:* Department of Chemistry, Moscow State University, Moscow 117234, USSR

[5] revealed that the results of both approaches were qualitatively the same, the most important discrepancy being the 5 kcal/mol exothermicity difference.

We present here the results of PES calculations for the LiBO system carried out with the SCF and the complete active space SCF (CASSCF) [7, 8] methods. Our experience on the importance of correlation effects when studying isomerization is opposite to previous findings. The results of the CASSCF calculations were contradictory to those obtained with the SCF method.

Neither theoretical nor experimental work on LiBO seems to have been reported. The compound LiBO<sub>2</sub> has been the subject of a number of studies (see Ref. [9]). SCF calculations on LiBO<sub>2</sub> [9] indicate that the molecule is a polytopic type species.

Recently the PES for the rearrangement BOH → HBO was calculated within the SCF approach [6]. The energy difference between the two linear isomers H—B—O and B—O—H was found to be 44 kcal/mol with a separating barrier of 46 kcal/mol counted from the species with the higher energy (B—O—H).

## 2. Computational Aspects

The parameters which determine the relative orientation of the atoms are shown in Fig. 1. The origin of the coordinate system is placed at the O—B center of mass. As the rearrangement proceeds from Li—O—B to Li—B—O the angle  $\vartheta$  varies from 0° to 180°.

One of the possible ways to obtain a minimum energy path (MEP) for the reaction Li—O—B → [LiBO] → O—B—Li (where [LiBO] stands for a non-linear configuration on the top of the barrier if it occurs) is to optimize  $R_{OB}$  and  $R_{Li}$  for each  $\vartheta$  value, thereby deriving a function  $E(\vartheta)$ . However, when describing the orbiting of one atom (Li) around the remainder of a molecule (BO), a reasonable approximation is to keep  $R_{OB}$  fixed for the majority of configurations.

Therefore, the “reference” MEP was obtained as follows. A series of SCF calculations were carried out for the  $^1\Sigma^+$  ( $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma^2 6\sigma^2 1\pi^4$ ) state of

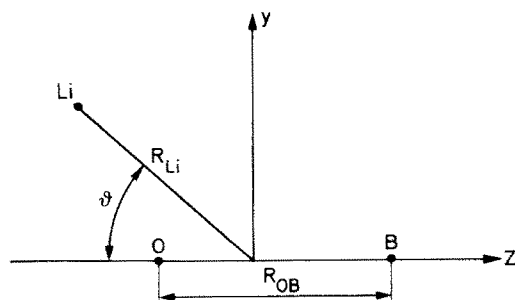


Fig. 1. Geometry parameters for the LiBO system

both linear isomers Li—O—B and O—B—Li resulting in two sets of optimal  $R_{OB}$  and  $R_{Li}$  values. The energy of Li—O—B was found lower than that of Li—B—O, and the value for  $R_{OB}$  optimized for Li—O—B was used in the subsequent calculations for the non-linear configurations. For each of 6 values of  $\vartheta$  between  $0^\circ$  and  $180^\circ$  only  $R_{Li}$  was optimized with the exception of the point  $\vartheta = 120^\circ$ , which was found to be the transition state. At this point the parameters  $R_{OB}$  and  $R_{Li}$  were both reoptimized.

The basis set used in these calculations consisted of double-zeta sets on boron and oxygen [10, 11], polarization 3d-functions with exponents  $\zeta_B = 0.7$ ,  $\zeta_O = 0.85$  [12] (including the symmetric  $x^2 + y^2 + z^2$  combinations), and the set of  $s$ - and  $p$ -functions for Li quoted in Ref. [13]. This basis set, which contains 42 contracted Gaussian functions, will be referred to below as “basis B”.

A reduced basis of 32 functions obtained from the basis B by exclusion of the 3d-functions is denoted as “basis A”. This basis was used for some of the geometries studied with the basis B in order to clarify basis set effects.

In order to employ the MOLECULE program system [14] the  $C_{2v}$  subgroup of the full  $C_{\infty v}$  point group was used in calculations of linear species.

Three points on the PES, namely those with  $\vartheta = 0^\circ$ ,  $120^\circ$  and  $180^\circ$  and the corresponding optimal values of  $R_{OB}$  and  $R_{Li}$  were also studied with the CASSCF method. Preliminary calculations using this technique gave results contradictory to those obtained with the SCF approach, and several ways of choosing the active space were tried therefore.

Initially, the inactive space (i.e. the set of orbitals kept doubly occupied in all configuration state functions) included not only MO's corresponding to the 1s-AO's of the constituent atoms, but also the  $4\sigma$  ( $4a'$ ) MO, correlating with  $2s$  on oxygen. This character of the  $4\sigma$  orbital remained in the final wavefunction for Li—B—O. However, in the converged CASSCF solution for the Li—O—B isomer this MO was interchanged with  $2s$  on B. Therefore, in the subsequent calculations  $4\sigma$  was also included among the active orbitals, and the inactive space was reduced to the three 1s-orbitals.

The number of orbitals in the active space was varied from 6 to 9 resulting in different lengths of the CI expansions. The different wavefunctions used in this work are described in Table 1. In this table the notation CASSCF-7/10, for example, is used to indicate a wavefunction resulting from the distribution of 10 electrons among 7 active orbitals. This gives rise to 106 configuration state functions of  $C_s$  symmetry.

It sometimes turned out difficult to obtain convergence in the CASSCF calculations, especially for the Li—O—B case. With the CASSCF-6/8 approach, 27 iterations were required to obtain a converged solution ( $10^{-6}$  a.u. in total energy and  $10^{-4}$  a.u. in Brillouin matrix elements), starting with converged SCF orbitals. 23 additional iterations were required in a subsequent CASSCF-9/10 calculation taking these CASSCF-6/8 MO's as initial orbitals.

**Table 1.** Description of the CASSCF wavefunctions and dimensions of the corresponding secular equations

Designation	Group	Electron distribution	Total number of CSF's
CASSCF-7/10	$C_s$	$(1a'^2 2a'^2 3a'^2)(4a'5a'6a'7a'8a'1a''2a'')^{10}$	106
CASSCF-8/10	$C_{2v}$	$(1\sigma^2 2\sigma^2 3\sigma^2)(4\sigma 5\sigma 6\sigma 7\sigma 1\pi_x 2\pi_x 1\pi_y 2\pi_y)^{10}$	328
	$C_s$	$(1a'^2 2a'^2 3a'^2)(4a'5a'6a'7a'8a'9a'1a''2a'')^{10}$	616
CASSCF-9/10	$C_{2v}$	$(1\sigma^2 2\sigma^2 3\sigma^2)(4\sigma 5\sigma 6\sigma 7\sigma 8\sigma 1\pi_x 2\pi_x 1\pi_y 2\pi_y)^{10}$	1436
CASSCF-6/8	$C_{2v}$	$(1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2)(5\sigma 6\sigma 7\sigma 8\sigma 1\pi_x 1\pi_y)^8$	41
	$C_s$	$(1a'^2 2a'^2 3a'^2 4a'^2)(5a'6a'7a'8a'9a'1a'')^8$	65
CASSCF-9/8	$C_{2v}$	$(1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2)(5\sigma 6\sigma 7\sigma 8\sigma 9\sigma 1\pi_x 2\pi_x 1\pi_y 2\pi_y)^8$	1436
	$C_s$	$(1a'^2 2a'^2 3a'^2 4a'^2)(5a'6a'7a'8a'9a'10a'11a'1a''2a'')^8$	2744

### 3. Results and Discussion

The energies on the MEP calculated with the SCF and the CASSCF-7/10 approaches are listed in Table 2. Results obtained for the three important points with  $\vartheta = 0^\circ$ ,  $120^\circ$  and  $180^\circ$  are also shown in Table 3.

Clearly, LiBO is a polytopic type molecule: the energy difference between the two linear isomers Li—O—B and O—B—Li found with the basis  $B$  does not exceed 9 kcal/mol in any approach. The same quantity for LiNC calculated with the SCF approximation is 8.85 kcal/mol [1].

Comparison of the SCF energies obtained without (basis  $A$ ) and with (basis  $B$ ) polarization functions shows that the results are qualitatively the same, but exclusion of polarization functions leads to an overestimation of both the energy difference between the linear isomers and the barrier height.

**Table 2.** Minimum energy path for the rearrangement Li—O—B  $\rightarrow$  O—B—Li

$\vartheta$ (deg)	Energy (a.u.) relative to Li—O—B				
	$R_{OB}$ (a.u.)	$R_{Li}$ (a.u.)	SCF, basis $B$	SCF, basis $A$	CASSCF-7/10, basis $A$
0	2.39	4.14	0.	0.	0.
10	2.39 <sup>a</sup>	4.14	0.000033		0.000253
25	2.39 <sup>a</sup>	4.06	0.000245		
45	2.39 <sup>a</sup>	3.87	0.001101	0.007287	0.004608
90	2.39 <sup>a</sup>	3.62	0.012530	0.026951	0.014972
120	2.30	4.47	0.021516	0.036360	0.018355
120	2.39 <sup>a</sup>	4.40	0.025727		0.021073
150	2.39 <sup>a</sup>	5.27	0.016760		
180	2.30	5.47	0.004111	0.015550	-0.002724

<sup>a</sup> Non-optimized value.

**Table 3.** Energies for the selected geometries of LiBO

Approximation	Total energy (a.u.)			O—B—Li ( $\vartheta = 180^\circ$ )	Energy of O—B—Li relative to Li—O—B (kcal/mol)	Energy of [LiBO] relative to Li—O—B (kcal/mol)
	Li—O—B ( $\vartheta = 0^\circ$ )	[LiBO] ( $\vartheta = 120^\circ$ )	O—B—Li ( $\vartheta = 180^\circ$ )			
SCF, basis A	-107.027551	-106.991191	-107.012001	9.758	22.816	
SCF, basis B	-107.060225	-107.038709	-107.056114	2.580	13.501	
CASSCF-7/10, basis A	-107.085215	-107.066860	-107.087939	-1.709	11.518	
CASSCF-8/10, basis A	-107.128889	-107.111403	-107.133236	-2.728	10.973	
CASSCF-8/10, basis B	-107.158961	-107.153255	-107.171769	-8.037	3.581	
CASSCF-9/10, basis B	-107.194397	<sup>a</sup>	-107.202302	-4.960	—	
CASSCF-6/8, basis B	-107.089866	-107.093431	-107.079856	6.281	-2.237	
CASSCF-9/8, basis B	-107.199487	<sup>a</sup>	-107.185674	8.668	—	

<sup>a</sup> Due to slow convergence and costs of CASSCF computations with 2744 configurations and 42 basis functions, these calculations have not been completed.

**Table 4.** Dominant configuration state functions (CSF's) and population analysis for the linear isomers Li-O-B and O-B-Li. Designation of CSF's: A -  $(1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma^2 6\sigma^2 1\pi_x^2 1\pi_y^2)$ , B -  $(1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma^2 6\sigma^2 1\pi_x 2\pi_x 1\pi_y 2\pi_y)$ , C -  $(1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma^2 6\sigma^2 1\pi_x 2\pi_y)$ , D -  $(1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma^2 6\sigma^2 2\pi_x 1\pi_y^2)$ . The spin-coupling for the configuration 'B' is {1, 2, 1, 2} in the Shavitt-Paldus notation [15, 16]

SCF	Dominant CSF's		Population analysis and dipole moment (D)	
	Li-O-B	O-B-Li	Li-O-B	O-B-Li
A	A	A	$\text{Li}^{2,26}\text{O}^{8,68}\text{B}^{5,06}$ 9.83	$\text{O}^{8,39}\text{B}^{4,99}\text{Li}^{2,62}$ 9.80
CASSCF-8/10	$0.979\text{A} + 0.099\text{B} - 0.081(\text{C} + \text{D})$	$0.972\text{A} + 0.115\text{B} - 0.098(\text{C} + \text{D})$	$\text{Li}^{2,27}\text{O}^{8,59}\text{B}^{5,14}$ 10.31	$\text{O}^{8,25}\text{B}^{5,12}\text{Li}^{2,63}$ 8.95
CASSCF-9/10	$0.975\text{A} + 0.089\text{B} - 0.076(\text{C} + \text{D})$	$0.970\text{A} + 0.104\text{B} - 0.092(\text{C} + \text{D})$	$\text{Li}^{2,30}\text{O}^{8,58}\text{B}^{5,12}$ 10.05	$\text{O}^{8,25}\text{B}^{5,12}\text{Li}^{2,63}$ 9.19
CASSCF-9/8	$0.975\text{A} + 0.088\text{B} - 0.076(\text{C} + \text{D})$	$0.966\text{A} + 0.114\text{B} - 0.099(\text{C} + \text{D})$	$\text{Li}^{2,29}\text{O}^{8,59}\text{B}^{5,12}$ 10.05	$\text{O}^{8,25}\text{B}^{5,07}\text{Li}^{2,68}$ 8.75
CASSCF-6/8	0.995A	0.992A	$\text{Li}^{2,27}\text{O}^{8,68}\text{B}^{5,05}$ 9.79	$\text{O}^{8,38}\text{B}^{4,96}\text{Li}^{2,66}$ 9.56

All the completed CASSCF calculations except one, CASSCF-6/8, predict that the linear forms are separated by a barrier of about 12 kcal/mol relatively to the LiBO isomer. This is approximately 4 times less than the barrier found for  $\text{BOH} \rightarrow \text{HBO}$  [6].

The results are not completely conclusive as to the relative stability of the linear isomers. Comparison of the energies obtained with the more accurate wavefunctions CASSCF-9/8 and CASSCF-9/10 indicates that extending the active space with the  $4\sigma$  MO strongly affects geometry predictions. This can be understood if the nature of this orbital is investigated: In LiOB the  $4\sigma$  orbital is predominantly a lone-pair on B, whereas in LiBO it is a rather pure  $2s$  on oxygen. Apparently, the amount of correlation energy recovered when the active space is augmented with the  $4\sigma$  orbital is different in these two cases. In our opinion, the results obtained with the CASSCF-8/10 (basis *B*) approach give a fairly reliable result, without leading to an excessively long CI expansion. In any case, it is obvious from the present results that correlation effects cannot be neglected when calculating the rearrangement MEP for this system and probably for other polytopic molecules as well.

The configuration state functions (CSF's) with the largest weights are presented in Table 4. The CSF's are defined in terms of natural orbitals. It should be noted that the CASSCF-6/8 wavefunction does not include configurations with occupied  $2\pi$  orbitals. Since calculations with a larger active space show such configurations to be of importance, predictions based on this approximation should be regarded as uncertain.

Table 4 also contains the results of the population analysis and calculated values of the dipole moment. Clearly, the interaction in the system is primarily ionic:  $\text{Li}^+ + \text{BO}^-$ . The results obtained with the different approximations are surprisingly similar considering the great difference in the relative energy predictions. The strongly occupied active orbitals ( $4\sigma$ ,  $5\sigma$ ,  $6\sigma$ ,  $1\pi$ ) obtained in the SCF, CASSCF-9/10 and CASSCF-9/8 calculations are also fairly similar. The relative energies seem to be the only characteristics that depend crucially on the level of approximation.

#### 4. Conclusion

The following conclusions can be formulated on the basis of the present results. First, LiBO is an example of a polytopic type molecule. By excitation of about 12 kcal/mol the lithium atom will orbit around the BO core. Second, the inclusion of correlation effects turns out to be necessary for an accurate description of LiBO, in spite of the strongly ionic character of the bonding in this system.

#### References

1. Bak, B., Clementi, E., Kortzeborn, R. N.: J. Chem. Phys. **52**, 764 (1970)
2. Clementi, E., Kistenmacher, H., Popkie, H.: J. Chem. Phys. **58**, 2460 (1973)

3. Spiridonov, V. P., Ishchenko, A. A., Zasorin, E. Z.: *Uspekhi Khimii* **47**, 101 (1978) [*Russian Chem. Rev.* **47**, 54 (1978)]
4. Bastiansen, O., Kveseth, K., Møllendal, H.: *Topics in current chemistry* **81**, 99 (1979)
5. Pearson, P. K., Schaefer, H. F., Wahlgren, U.: *J. Chem. Phys.* **62**, 350 (1975)
6. Zyubina, T. S., Charkin, O. P., Gurvich, L. V.: *Zhur. strukt. Khim.* **20**, 3 (1979)
7. Roos, B. O., Taylor, P. R., Siegbahn, P. E. M.: *Chem. Phys.* **48**, 157 (1980)
8. Siegbahn, P. E. M., Almlöf, J., Heiberg, A., Roos, B. O.: *J. Chem. Phys.*, in press
9. Dementjev, A., Kracht, D.: *Chem. Phys. Letters* **35**, 243 (1975)
10. Huzinaga, S.: *J. Chem. Phys.* **42**, 1293 (1965)
11. Dunning, T. H.: *J. Chem. Phys.* **53**, 2823 (1970)
12. Dunning, T. H., Hay, P. J., in: *Methods of electronic structure theory*, Schaefer, H. F. ed. New York: Plenum Press 1977
13. Chen, M. M. L., Schaefer, H. F.: *J. Chem. Phys.* **72**, 4376 (1980)
14. Almlöf, J.: USIP report 74-29, University of Stockholm (1974)
15. Shavitt, I.: *Intern. J. Quantum Chem.* **S11**, 131 (1977) and **S12**, 5 (1978)
16. Paldus, J.: *J. Chem. Phys.* **61**, 5321 (1974)

Received October 8, 1980/November 10, 1980