

# Fixation of Nitrogen and Carbon Monoxide by Beryllium Oxide: Theoretical Investigation of the Structures and Stabilities of NNBeO, OCBEO, and COBeO

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*Ab initio* calculations at the MP4(SDTQ)/6-311G(2df,2pd)//MP2/6-31G(d,p) level of theory, corrected by zero-point energies, predict that the linear NNBeO structure is stable with respect to dissociation into N<sub>2</sub> and BeO by 30.0 kcal mol<sup>-1</sup>, whereas a cyclic isomer is 19.7 kcal mol<sup>-1</sup> higher in energy; the linear molecule OCBEO is calculated to have a dissociation energy *D*<sub>0</sub> of 40.8 kcal mol<sup>-1</sup>, with the linear isomer COBeO being 22.4 kcal mol<sup>-1</sup> less stable.

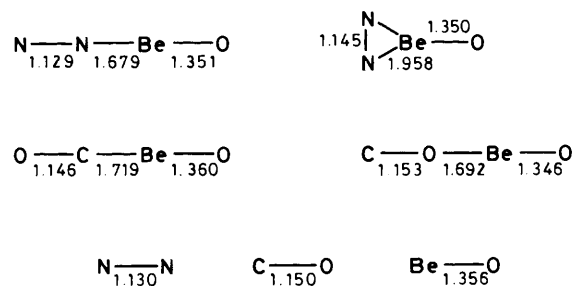
We have recently shown<sup>1</sup> that beryllium oxide is capable of forming a stable species HeBeO with a dissociation energy *D*<sub>0</sub> of ca. 3 kcal mol<sup>-1</sup> (for loss of He). The unusually strong acceptor ability of BeO has been attributed<sup>2</sup> to the combination of (i) a strong dipole moment, (ii) a positive partial charge at Be which is greater than +1, and (iii) a rather low-lying empty orbital. The remarkable Lewis acid strength of BeO, sufficient to attract the very poor Lewis base He, suggests that other poor donor species might also form stable adducts with BeO. It has been suggested<sup>3</sup> that CO and N<sub>2</sub> should form the tetra-atomic species OCBEO and NNBeO. Here we report a theoretical study of the structures and stabilities of these two molecules.

Standard *ab initio* calculations were carried out using the programs GAUSSIAN 82<sup>4</sup> and GAUSSIAN 86.<sup>5</sup> Geometries and zero-point vibrational energies were obtained at MP2/6-31G(d,p) level and total energy calculations were performed at MP4(SDTQ)/6-311G(2df,2pd) level. Table 1 shows the calculated energies for the linear structure NNBeO (1), the cyclic analogue (2), the linear structures OCBEO (3) and COBeO (4), and their dissociation fragments. Structures (1)–(4) are confirmed to be minima on the potential energy hypersurfaces by having only positive eigenvalues of the diagonalized force constant matrix. A cyclic COBeO species has not been found as a minimum. The geometries of the calculated molecules are shown in Scheme 1.

Dinitrogen forms a linear (σ) donor–acceptor compound (1) with BeO which is 19.7 kcal mol<sup>-1</sup> lower in energy than the cyclic (π) complex (2) (Table 1). The dissociation energy of (1) into N<sub>2</sub> and BeO is calculated to be 30.0 kcal mol<sup>-1</sup> (Table 2) and that for (2) is 10.3 kcal mol<sup>-1</sup>. The higher stability of the linear molecule (1) relative to (2) can be explained by the fact that N<sub>2</sub> is a better σ-donor than a π-donor. Similarly, the carbon atom is a better donor than the oxygen atom in CO because the highest occupied molecular orbital (HOMO) is a σ M.O. located mainly at C. Consequently, the OCBEO isomer (3) is 22.4 kcal mol<sup>-1</sup> lower in energy than the COBeO structure (4). Carbon monoxide is a better donor than

dinitrogen, and the dissociation energy *D*<sub>0</sub> of (3) is higher (40.8 kcal mol<sup>-1</sup>; Table 2) than for (1). The isomer COBeO (4) has a dissociation energy of 18.4 kcal mol<sup>-1</sup>.

The formation of the donor–acceptor compounds (1)–(4) is accompanied by only small variations in the bond lengths of N<sub>2</sub>, CO, and BeO as compared with the isolated species. The largest change is found for the N–N distance in the cyclic compound (4). Figure 1 shows schematically the valence molecular orbitals of the donor molecules N<sub>2</sub> and CO and the acceptor molecule BeO. In the linear structures (1), (3), and (4) electronic charge is donated from the (σ) HOMO of N<sub>2</sub> or CO, *i.e.* the 3σ<sub>g</sub> M.O. to the 3σ<sub>g</sub> LUMO of BeO. Since the 3σ<sub>g</sub> orbital has a positive overlap in the interatomic region, HOMO–LUMO interactions should yield a shorter Be–O distance and longer N–N and C–O bonds, respectively. However, the character of the 3σ<sub>g</sub> M.O. is essentially non-bonding because the 2σ<sub>g</sub> and 3σ<sub>g</sub> orbitals can mix, which enhances the bonding nature of the 2σ<sub>g</sub> M.O. and greatly reduces the overlap in the bonding region of the 3σ<sub>g</sub> M.O.<sup>6</sup> Thus, only small changes in the interatomic distances of N<sub>2</sub>, CO, and BeO can be expected as a result of the dominant frontier orbital interaction in (1), (3), and (4); other forces such as π–π\* interaction and coulombic forces will influence



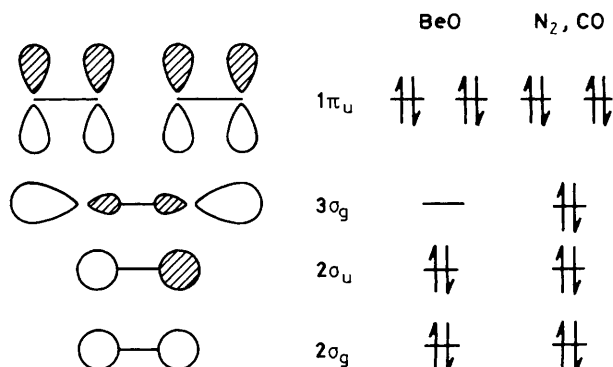
**Scheme 1.** Calculated interatomic distances (in Å) at MP2/6-31G(d,p) level.

**Table 1.** Calculated total energies (*E*<sub>tot</sub>) (in hartrees), relative energies (*E*<sub>rel</sub>), and zero-point vibrational energies (ZPE) (in kcal mol<sup>-1</sup>).

Structure	Symmetry	No.	MP2/6-31G(d,p)		MP4/6-311G(2df,2pd)		
			<i>E</i> <sub>tot</sub>	ZPE	<i>E</i> <sub>tot</sub>	<i>E</i> <sub>rel</sub>	
NNBeO	linear	1Σ <sup>+</sup>	(1)	-198.9614	7.4	-199.1724	0.0
NNBeO	cyclic	1A <sub>1</sub>	(2)	-198.9325	6.0	-199.1406	19.9
OCBeO	linear	1Σ <sup>+</sup>	(3)	-202.7514	7.5	-202.9748	0.0
COBeO	linear	1Σ <sup>+</sup>	(4)	-202.7173	7.0	-202.9383	22.9
BeO		1Σ <sup>+</sup>		-89.6547	2.0	-89.7529	
CO		1Σ <sup>+</sup>		-113.0282	3.0	-113.1528	
N <sub>2</sub>		1Σ <sup>+</sup> <sub>g</sub>		-109.2616	3.1	-109.3698	

**Table 2.** Calculated dissociation energies  $D_e$  and  $D_o$  (in kcal mol<sup>-1</sup>) at MP4/6-311G(2df,2pd)/MP2/6-31G(d,p) levels.

Reaction			$D_e$	$D_o$
NNBeO (1)	→	NN $^1\Sigma_g^+$ + BeO $^1\Sigma^+$	32.3	30.0
NNBeO (2)	→	NN $^1\Sigma_g^+$ + BeO $^1\Sigma^+$	11.2	10.3
OCBeO (3)	→	CO $^1\Sigma^+$ + BeO $^1\Sigma^+$	43.3	40.8
COBeO (4)	→	CO $^1\Sigma^+$ + BeO $^1\Sigma^+$	20.4	18.4



**Figure 1.** Schematic representation of the low-lying valence orbitals of BeO, N<sub>2</sub>, and CO.

the geometry changes. Consequently, the C–O distance in (3) is shorter and the Be–O bond is longer than in the isolated entities, while the opposite is found for (4). Both distances N–N and Be–O are slightly shorter in linear NNBeO (1) than in N<sub>2</sub> and BeO. In case of the cyclic compound (2), electronic charge is donated from the 1π<sub>u</sub> HOMO (Figure 1). Since this orbital has a bonding character, there is a much greater change in the N–N distance when (2) is formed than with the linear

isomer (1), although the interaction energy is much higher for the latter (30.0 kcal mol<sup>-1</sup>) than for the former (10.3 kcal mol<sup>-1</sup>).

The rather strong donor–acceptor interactions theoretically predicted between BeO and N<sub>2</sub> (30.0 kcal mol<sup>-1</sup>) and BeO and CO (40.8 kcal mol<sup>-1</sup>) should be sufficient for the observation of (1) and (3), and perhaps also the isomers (2) and (4) under appropriate experimental conditions, for example in the gas phase. It seems doubtful whether the calculated stabilization energies are sufficient to allow the isolation of these molecules in a condensed phase because BeO has a strong tendency to polymerize. Nevertheless, we suggest experimental investigation of the theoretically predicted compounds (1)–(4) in order to characterize these as yet unknown structures.

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## References

- (a) W. Koch, G. Frenking, J. Gauss, D. Cremer, and J. R. Collins, *J. Am. Chem. Soc.*, 1987, **109**, 5917; (b) W. Koch, J. R. Collins, and G. Frenking, *Chem. Phys. Lett.*, 1986, **132**, 330.
- G. Frenking, W. Koch, J. Gauss, and D. Cremer, *J. Am. Chem. Soc.*, in the press.
- N. Bartlett, *Nature*, 1988, **331**, 487.
- J. S. Binkley, M. J. Frisch, D. J. DeFrees, K. Raghavachari, R. A. Whiteside, H. B. Schlegel, E. M. Fluder, and J. A. Pople, 'GAUSSIAN 82,' Carnegie-Mellon University, Pittsburgh, PA.
- M. J. Frisch, J. S. Binkley, H. B. Schlegel, K. Raghavachari, C. F. Melius, R. L. Martin, J. J. P. Stewart, F. W. Bobrowicz, C. M. Rohlfing, L. R. Kahn, D. J. DeFrees, R. Seeger, R. A. Whiteside, D. J. Fox, E. M. Fluder, and J. A. Pople, 'GAUSSIAN 86,' Carnegie-Mellon Quantum Chemistry Publication Unit, Pittsburgh, PA 1984.
- N. D. Epiotis, 'Unified Valence Bond Theory of Electronic Structure—Applications,' Lecture Notes in Chemistry, vol. 34, Springer Verlag, Berlin, 1983.