

Structures, Stabilities, and Bonding in CBe_2 , C_2Be , and C_2Be_2

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Abstract: The structures and energies of the binary beryllium compounds CBe_2 , C_2Be , and C_2Be_2 in their energetically lowest singlet and triplet states have been investigated by means of ab initio quantum chemical methods, employing second order Møller-Plesset (MP2) perturbation theory and, for the triatomic molecules, CASSCF techniques. Nonlinear geometries are predicted to be the global minima for CBe_2 (1A_1) and C_2Be (1A_1) by both methods, MP2/6-31G**//6-31G* and CASSCF using a DZ+P basis set and an active space of eight electrons in nine orbitals. For C_2Be_2 , the MP2/6-31G**//6-31G* results favor a linear triplet isomer ($^3\Sigma_u^+$) by more than 80 kcal/mol relative to the next low-lying structure (a cyclic form, 1A_1). The results of one electron density analysis indicate that charge transfer from Be to C is responsible for the stabilities of the nonlinear isomers and that there is little covalent CBe bonding in the singlet nonlinear minima of CBe_2 and of C_2Be .

I. Introduction

The structures of organic molecules containing electropositive elements often are influenced crucially by coulomb forces; as a consequence bridged or nonclassical structures occur frequently. This is exemplified by the unusual geometries of organolithium compounds, which seldom favor the typical structures of covalent compounds.¹ Moreover, boron compounds, although usually considered to be covalent, also frequently prefer bridged structures and sometimes very unusual geometries.² Less is known about beryllium compounds, but available results indicate that bridged structures also are common.³ A recent theoretical investigation of CBe_2 in the crystal state⁴ indicated a high degree of ionicity but also an important contribution of covalent bonding. Analysis of the computed wave function may reveal the nature of the bonding. Since Mulliken population analysis has been shown to be unreliable for compounds with electropositive elements,⁵ we prefer to employ an analysis of the one electron density which has been demonstrated to be highly useful for the interpretation of the nature of bonding in molecules.⁶ This paper reports results of an ab initio investigation of the structures, stabilities, and bonding of CBe_2 , C_2Be , and C_2Be_2 .

II. Computational Details

Theoretical investigations have been performed by using a modified Gaussian 76 program,⁷ which includes the Davidson-Fletcher-Powell multiparameter search⁸ with analytically evaluated forces⁹ for the 3-21G basis set.¹⁰ Stationary points on the potential energy hypersurface at 3-21G have been checked by diagonalization of the force-constant matrix, and the optimized geometries reported here have only positive eigenvalues in the Hessian matrix. Further geometry optimization has been carried out with the polarized 6-31G* basis with parabolic search. Correlation energy has been estimated for the single-point calculations by Møller-Plesset perturbation theory terminated at second order¹¹ in the frozen-core approximation. This level of theory is denoted MP2/6-31G**//6-31G*. For the calculation of the triplet states we used the unrestricted Hartree-Fock (UHF) method.¹² The optimizations of the linear triatomic triplets have frequently been marked by technical problems such as jumping among several states and high spin contamination. The results presented here have been obtained by using damping for the initial SCF iterations and choosing the lowest energy isomer irrespective of the degree of spin contamination.

CASSCF calculations¹³ have been performed for all triatomic singlets and triplets by using analytical gradients for the geometry optimizations.¹⁴ For carbon, the (10s6p1d) basis set contracted to (5s4p1d) developed by Huzinaga¹⁵ and Dunning¹⁶ and for beryllium, a (12s5p1d) basis set contracted to (7s3p1d) were employed,¹⁷ both are of double- ζ plus polarization (DZ + P) quality. For the active space, eight electrons in nine valence orbitals have been chosen, with the three lowest lying

doubly occupied MOs for CBe_2 (four in case of C_2Be) taken as frozen core.

III. Results and Discussion

Our computed total and relative energies of the optimized geometries are listed in Table I, and the geometrical details are shown in Table II. Properties of the one-electron density distribution $\zeta(r)$ ^{6,18} of some selected CBe compounds are summarized in Table III.

CBe_2 . Only one singlet form, the nonlinear species 1S, has been found to be a minimum on the CBe_2 potential energy hypersurface. However, the energies of the three triplets, 1T, 2T, and 3T, relative to 1S, vary considerably with the level of theory employed. As is generally the case, (UHF) SCF data artificially favor triplets over singlets. Due to the high spin contamination, the SCF results show an unrealistic preference for the linear triplet isomers. The inclusion of correlation energy at the MP2 level leads to drastic

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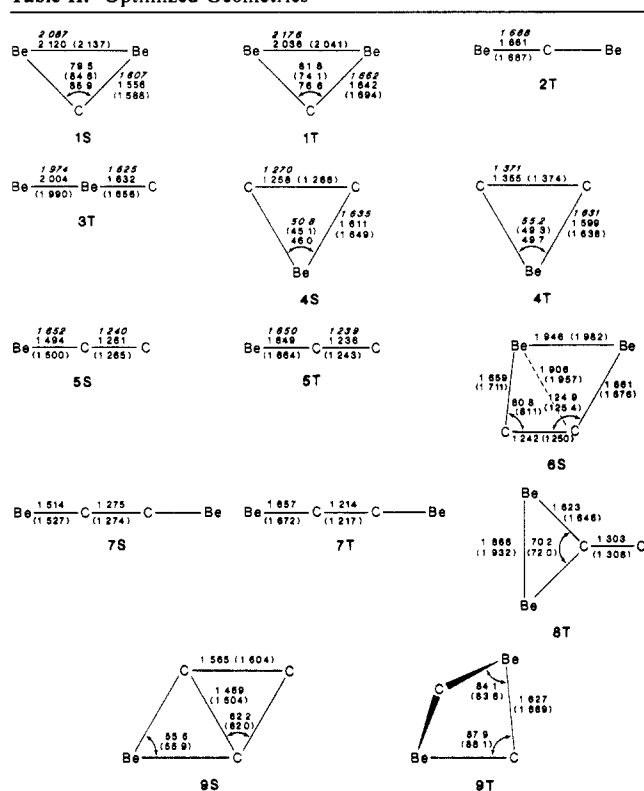
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Table I.

molec.	symm.	state	3-21G/3-21G			6-31G*/6-31G*			MP2/6-31G*// 6-31G*		CASSCF	
			E_{tot}	$\langle S^2 \rangle$	E_{rel}	E_{tot}	$\langle S^2 \rangle$	E_{rel}	E_{tot}	E_{rel}	E_{tot}	E_{rel}
(a) Calculated Total (au) and Relative (kcal/mol) Energies of CBe_2 Forms												
1S	C_{2v}	1A_1	-66.5083		68.3	-66.8843		65.6	-67.1113	0.0	-67.0454	0.0
1T	C_{2v}	3B_1	-66.5413	2.13	47.6	-66.9171	2.21	45.0	-67.1793	20.1	-67.0176	17.4
2T	$D_{\infty h}$	$^3\Sigma_u^+$	-66.6172	3.01	0.0	-66.9888	3.01	0.0	-67.1000	7.1	-67.0126	20.6
3T	$C_{\infty v}$	$^3\Pi$	-66.5363	3.07	50.8	-66.9024	3.12	54.2	-67.0057	66.3	-66.9578	54.9
(b) Calculated Total (au) and Relative (kcal/mol) Energies of C_2Be Forms												
4S	C_{2v}	1A_1	-89.6522		25.9	-90.1770		9.2	-90.4666	0.0	-90.3329	0.0
4T	C_{2v}	3B_2	-89.5979	2.01	60.0	-90.1129	2.01	49.4	-90.3574	68.5	-90.2109	76.5
5S	$C_{\infty v}$	$^1\Sigma^+$	-89.6374		35.2	-90.1392		32.9	-90.4094	35.9	-90.3249	5.0
5T	$C_{\infty v}$	$^3\Sigma^+$	-89.6935	2.55	0.0	-90.1917	2.50	0.0	-90.3919	46.9	-90.3219	6.9
(c) Calculated Total (au) and Relative (kcal/mol) Energies of C_2Be_2 Forms												
6S	C_s	1A_1	-104.2249		55.2	-104.8272		42.4	-105.0345	83.8		
7S	$D_{\infty h}$	$^1\Sigma_g^+$	-104.0797		146.3	-104.6590		148.0	-104.8587	194.1		
7T	$D_{\infty h}$	$^3\Sigma_u^+$	-104.3129	2.01	0.0	-104.8948	2.00	0.0	-105.1680	0.0		
8T	C_{2v}	3B_1	-104.1531	2.11	100.3	-104.7471	2.11	92.7	-104.9014	167.3		
9S	D_{2h}	1A_g	-104.1797		83.6	-104.7913		64.9	-104.9956	108.2		
9T	C_{2v}	3A_2	-104.1252	2.22	117.8	-104.7066	2.17	118.1	-104.9789	118.7		

Table II. Optimized Geometries^a

^aCASSCF data are given in italics, 3-21G data in parentheses; all other values are at 6-31G* level. Distances are given in Å, angles in degrees.

changes in relative stabilities which further demonstrate the unreliability of the SCF results. However, CASSCF and MP2/6-31G* energy values agree that the nonlinear singlet isomer 1S is the global CBe_2 minimum. This contrasts sharply with A_2B molecules with 10–16 valence electrons, where linear forms are expected to be the most stable isomers by Walsh's rules.¹⁹

The theoretical interatomic distances for 1S (Table II), 1.556 (6-31G*) and 1.607 Å (CASSCF) for C–Be, are substantially less than the standard value for a carbon–beryllium single bond (1.69 Å).^{3a} The computed Be–Be distances correspond closely

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to the standard value for a single bond (2.10 Å).^{3a} Assuming that three-membered rings have bent bonds (like cyclopropane), the internuclear distances should be smaller than in the corresponding acyclic reference compounds. On this basis, the geometry of CBe_2 (1S) points to enhanced C–Be bonding but decreased Be–Be bonding. This suggestion is supported by an analysis of the one-electron density distribution $\zeta(r)$ of 1S. As shown in Figure 1a, there are two paths of maximum electron density (bond paths)^{6,18} which connect C with the Be atoms. The shift in the position of the bond critical points²⁰ (dots in Figure 1) toward the Be nuclei indicates the large polarity of the CBe bonds.²¹ There is no Be,Be bond path, although the Laplace concentration $\nabla^2\zeta(r)$ ²² depicted in the form of contour line diagrams in Figure 1 clearly reveals that there is an attractive Be,Be interaction leading to some electron concentration in the Be,Be internuclear region (dashed contour lines in Figure 1a). This, however, is far less pronounced than the charge concentration in the CBe region; the attractive Be,Be interactions evidently are not sufficient for covalent bonding. 1S possesses an acyclic structure²³ contrary to expectations resulting from geometrical data.

Characteristically, all the calculated $\nabla^2\zeta(r)$ distributions in Figure 1 show large areas of electron charge depletion surrounding the Be nuclei and the innermost shell with $\nabla^2\zeta(r) < 0$ (not shown in Figure 1). Comparison with the $\nabla^2\zeta(r)$ distribution of an isolated Be atom reveals that large parts of its valence sphere have been lost to the C atoms in the molecules investigated. Hence, a considerable amount of charge seems to be transferred from Be to C in all those compounds. The local energy density $H(r_p)$

(20) The bond critical point P corresponds to the minimum of $\zeta(r)$ along the path of maximum electron density connecting two atomic nuclei A and B. (Point P is a saddle point of $\zeta(r)$ in three dimensions). According to Cremer and Kraka¹⁸ a covalent bond between two atoms exists if (i) a bond critical point is found between A and B (necessary condition) and (ii) the local energy density $H(r_p)$ is lower than zero (sufficient condition). Utilizing calculated values ρ_p , a bond order n can be defined according to $n(A,B) = \exp(a[\zeta_p(A,B) - b])$. At the HF/6-31G* level, the following constants have been used: $a(CC) = 0.94$, $b(CC) = 1.52 (e/\text{Å}^3)^{18b}$, $a(CBe) = 5.63$; $b(CBe) = 0.69 (e/\text{Å}^3)$. The latter have been evaluated by using CH_3BeH and CH_2Be as reference compounds.

(21) The position of the point P is determined by the parameter Δ_p , which is zero for P at the midpoint of the bond and larger than zero for a shift of P in the direction of the electropositive atom. The value of Δ_p is the larger the larger the charge transfer and the more polar the bond is. If bonds between atoms of different rows of the periodic system are considered, the different number of inner shells has to be taken into account.

(22) In general, the Laplacian of any scalar field is negative, where the scalar field concentrates while it is positive, where the scalar fields expands. For more information, see: Bader, R. F. W.; Essen, H. *J. Chem. Phys.* **1984**, *80*, 1943 and ref 18b and 18c.

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Table III. Properties of One-Electron Density $\zeta(r)$ and Energy Density $H(r)$ at the Critical Points P (HF/6-31G*)

molecule	bond	$\zeta_p(e/\text{\AA}^3)$	n^a	$\nabla^2\zeta_p^b(e/\text{\AA}^5)$	H_p^c [hartree/ \AA^3]	Δ_p^d [%]
CBe ₂ , 1S	CBe	0.666	0.9	15.2	-0.15	31
C ₂ Be, 4S	CC	2.806	2.9	-34.8	-3.98	0
	(C) ₂ Be	0.745		17.7	-0.13	36
C ₂ Be ₂ , 6S	CC	2.804	2.9	-30.6	-5.06	27
	CBe ^e	0.593	0.6	10.2	-0.13	32
	BeBe	0.354		-0.4	-0.13	2
C ₂ Be ₂ , 9S	CC	1.872	1.2	-12.8	-1.82	0
	CBe	0.732	1.3	17.2	-0.13	32

^a Calculated from $n(\text{CC}) = \exp\{0.94(\zeta_p - 1.52)\}$ and $n(\text{CBe}) = \exp\{5.63(\zeta_p - 0.69)\}$. See ref 18 and 20. ^b See ref 22. ^c See ref 20. ^d See ref 21. ^e Averaged values.

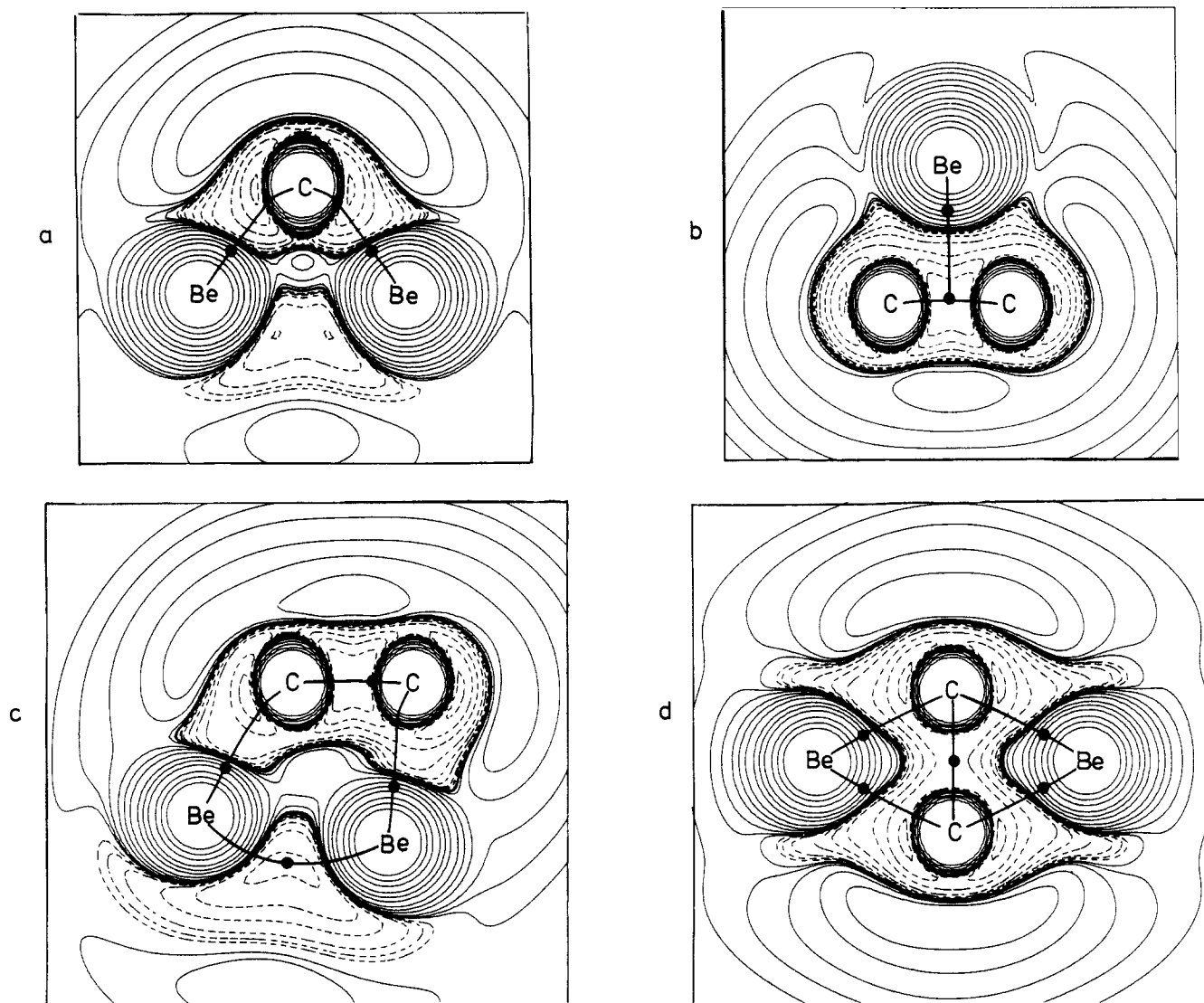


Figure 1. Contourline diagrams of $\nabla^2\zeta(r)$. Dashed contour lines indicate molecular regions with charge concentration ($\nabla^2\zeta(r) < 0$). Bond paths are denoted by heavy solid lines, bond critical points by dots: (a) 1S; (b) 4S; (c) 6S; (d) 9S. Inner shell regions with $\nabla^2\zeta(r) < 0$ are not shown.

is always close to zero for all CBe bonds considered. This indicates that they are only weakly covalent^{18b,23} ($H(r_p) < 0$) and do possess partial ionic character.

Charge concentration typical of an electron lone pair is found at carbon above and below the molecular plane of 1S. As is shown in Figure 2, the 1S HOMO is made up essentially of the $p\pi$ orbital of C, with very little contribution from the $p\pi(\text{Be})$ orbitals. Accordingly, we find only moderate π character to be present in the C-Be bonds of 1S.

MP2/6-31G* and CASSCF lead to different predictions for the geometry of the lowest lying triplet state (Table I). In view of the high spin contamination of the UHF triplet state, the MP2 relative energies (favoring linear 2T) probably are less reliable than the CASSCF result (which prefers nonlinear 1T). On the

other hand, the CASSCF energy difference between 1T and 2T may be too small to be conclusive. The linear Be-Be-C arrangement (3T) is the least stable form at all levels.

C₂Be. Two minima each have been found on the singlet and on the triplet C₂Be potential energy hypersurfaces. Again, the relative energies of the triplets are too low compared to the singlets at the (UHF) SCF level due to the reductions in electron correlation. Both correlated methods agree that the singlet structure 4S is the C₂Be global minimum. However, the CASSCF energy differences among 4S, 5S, and 5T are not very large and are much smaller than the MP2 differences. Furthermore, optimization of 5S leads to very different CBe distances with both methods. The 6-31G* value of 1.494 Å corresponds to a CBe double bond, while the 1.652 Å obtained at the CASSCF level indicates a single bond.

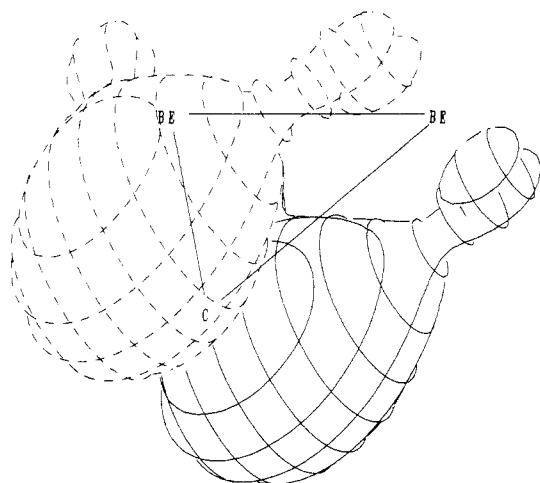


Figure 2. HOMO of CBe_2 1S, plotted with a contour of 0.1 au.

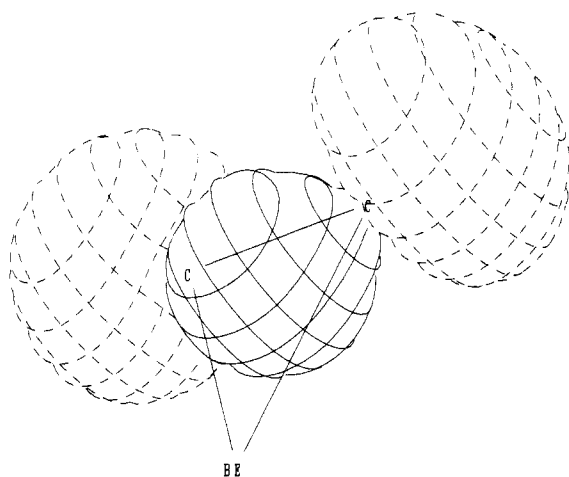


Figure 3. HOMO of C_2Be 4S, plotted with a contour of 0.1 au.

The coefficients of the leading configurations in the CASSCF optimizations provide an explanation for this discrepancy. The SCF ground-state configuration has a coefficient of 0.74, but the next important configuration has comparable weight with a coefficient of 0.59. Both configurations differ in the nature of the highest occupied σ -type orbital, being the plus and minus combination of the terminal σ -type lone-pair orbitals



Clearly, reoptimization of the orbitals is very important. Note that the energies and bond distances for the singlet and triplet forms 5S and 5T predicted by CASSCF are nearly the same.

One of us considered 4S as a candidate for a three-membered cyclic structure which might possess a CC triplet bond.²⁴ Since that time, two more molecules have been found theoretically with a CC triplet bond in a three-membered ring, i.e., SiC_2 ^{25a} and MgC_2 .^{25b} There is experimental evidence for a nonlinear geometry of SiC_2 .²⁶ However, the results for MgC_2 already are indicative of an ionic rather than a covalent complex.^{25b} Although covalent bonding is generally stronger for first row than that for second row elements, our analysis of the electron density of 4S does not reveal any differences for these systems: there are no C,Be bond paths corresponding to covalent bonding between these atoms. Instead, we find a path of maximum electron density connecting

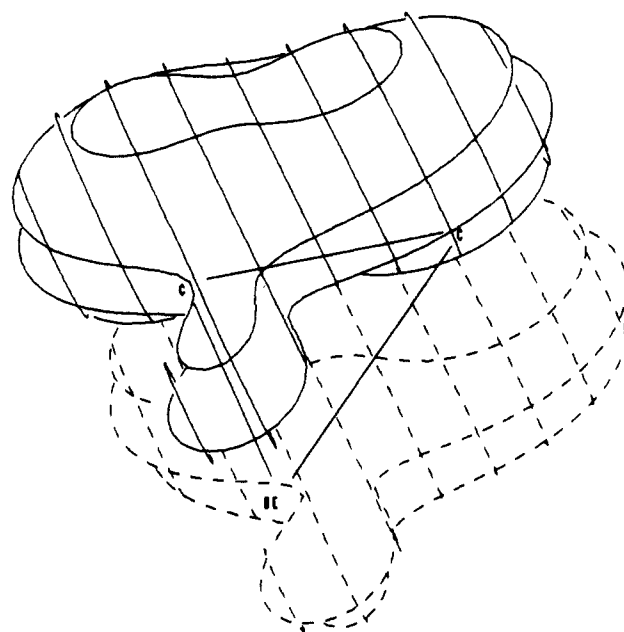


Figure 4. Second highest occupied MO of C_2Be 4S, plotted with a contour of 0.1 au.

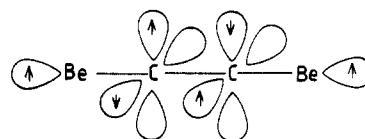


Figure 5. Schematic representation of the valence electrons in C_2Be_2 7T.

Be and the C,C, midpoint (Figure 1b). Hence, 4S possesses a "T-shaped" rather than a cyclic structure and can be regarded as an ionic complex between C_2^{2-} and Be^{2+} . The CC bond in 4S is close to a triple bond as revealed by a bond order of 2.9^{18,20} (Table III).

Figure 1b shows that charge is largely depleted from the valence sphere of the Be atom and concentrated both in the CC bonding region and in the regions represented by the back lobes of the $3\sigma_g$ orbital of C_2 . This orbital is unoccupied in the ground state of C_2 but becomes the HOMO in C_2Be (Figure 3) due to charge transfer from Be to C. The $\pi\pi$ MO shown in Figure 4 is the second highest occupied MO. Similar to the π MO of CBe_2 , it is largely made up by carbon $\pi\pi$ orbitals indicating that the 2 π electrons are confined to the C,C bond region.

C_2Be_2 . In contrast to the triatomic molecules, CBe_2 and C_2Be , the tetratomic system C_2Be_2 is clearly predicted to have a linear triplet global minimum, 7T, on the potential energy hypersurface. Although we could not perform CASSCF calculations on the C_2Be_2 isomers, the 3-21G and 6-31G* single determinant relative energies are quite unambiguous and are consistent with regard to the lowest-energy form. Inclusion of correlation energy at the MP2/6-31G* level leads to an increase in the stability difference to more than 80 kcal/mol relative to the second lowest isomer, the singlet 6S. Because of the large energy difference, it seems certain that 7T represents the most stable C_2Be_2 isomer. The high stability of 7T is due to the favorable acetylene-like structure with a strong CC triple bond and the two unpaired electrons at the beryllium atoms in the σ -orbitals pointing away from the carbon atoms, as shown in Figure 5. The electronic structure of 5T, which can be represented as $\uparrow\text{C} \equiv \text{C} - \text{Be} \uparrow$, is closely related.

The remaining C_2Be_2 forms are too high in energy to expect experimental verification. However, some of the structural features are quite interesting from a theoretical point of view, especially in comparison with other molecules. Epiotis predicted²⁷ on the basis of his MOVb model^{28,29} that the relative energy difference

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favoring the rhomboidal isomer 9S over the linear form 7S should be larger than the difference between the analogous structures of C_4 . At the same level of theory as employed here (MP2/6-31G**//6-31G*), the C_4 linear singlet is only 14.6 kcal/mol higher in energy than the rhomboidal form.³⁰ This energy difference is clearly much smaller than that of the C_2Be_2 singlets, in accord with Epiotis's conclusion.

The geometry of 6S is interesting since symmetry reduction occurs from C_{2v} to C_s symmetry due to second-order Jahn–Teller distortion. The electron density analysis for the singlet 6S shows that there is again a considerable charge transfer from Be to C. The CBe bonds are weak, while the CC bond possesses a bond order close to 3 ($n = 2.9$, Table III). For the bicyclic isomer 9S, however, the CBe bonds are relatively strong ($n = 1.3$), while the CC bond is surprisingly weak ($n = 1.2$). The 2π electrons of both 6S and 9S are largely confined to the CC bond.

IV. Discussion

The bonding in these molecules cannot be discerned adequately by conventional criteria. Geometrical parameters (distances and angles) are clearly not sufficient to distinguish between what might be termed T-shaped or cyclic bonding. Dewar and Ford³¹ differentiated in the case of nonlinear three heavy atom systems between cyclic structures and π -complexes utilizing MO theory. Clearly, a correct representation of the electronic structure is necessary to describe the BeC compounds.

In view of the structural peculiarities of the molecules investigated one may ask which model is best suited to give an understanding of CBe bonding. For example, Walsh rules¹⁹ may be used. They correctly predict a bent geometry for the eight-valence-electron system CBe_2 but fail in the case of the ten-electron system C_2Be , where a linear structure is expected rather than the nonlinear form we have found. This failure is probably due to the fact that Walsh rules have been developed on the basis of covalent bonding while CBe interactions have considerable ionic character.

The more subtle bonding features, of the nonlinear geometries in particular, can be understood by considering donor–acceptor interactions.^{18c,31} The more electropositive Be tends to donate its valence electrons to carbon. This electron donation, however, depends on the nature and the symmetry of the carbon acceptor orbitals and the degree of overlap. As shown in generalized form at the top of Figure 6, two orbitals, designated b_2 and a_1 , are present in the fragments, X and X_2 ($X = Be$ or C), which will interact in C_{2v} symmetry. These combinations, shown for C_2Be at the left bottom of Figure 6, involving charge transfer from the $a_1(Be)$ orbital to the a_1 orbital of C_2 , are responsible for the T-shaped electronic structure of 4S and for a CC bond order close to 3. A cyclic electronic structure would result if significant back-donation to Be were to occur from an occupied $b_2(CC)$ orbital or if charge transfer from Be to C were to take place via the B_2 orbital because of partial or full occupation of the bonding $a_1(C_2)$ orbital.

The bonding feature of 4S may be compared to Dewar and Ford's (DF) concept of olefinic π -complexes vs. ring structures.³¹ In their definition, a π -complex is characterized by a π -donor bond of the CC unit to the apical atom without significant back donation. A true ring structure is found when back-coordination becomes important which is the case for less electronegative atoms or groups.³¹ 4S may serve as an example where in terms of DF only back-donation takes place resulting in an electronic structure which they may also call a π -complex.

Can true cyclic structures with C–Be bonding be formed at all? The answer is yes. For example, in the case of 9S (Figure 6,

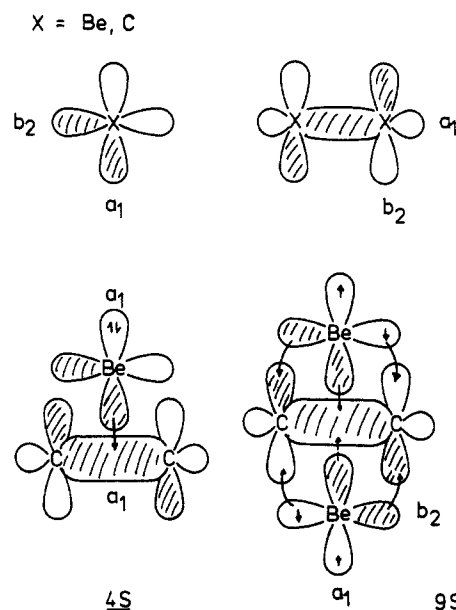


Figure 6. Donor and acceptor orbitals of C (Be) and C_2 (Be_2) with a_1 or b_2 symmetry.

bottom right) one electron can be donated from each Be to C_2 via the a_1 orbital and one each via the b_2 orbital. As a consequence, the relative high electron concentration in the region of the b_2 orbitals indicative of relatively strong CBe bonds results. This alternative mode of donation from Be gives rise to the weak CC bond in 9S (see Table III and Figure 1d).

The electronic structure of 1S contrasts with that of 4S. Consider the diagram at the bottom left of Figure 6 but with C in place of Be and Be_2 in place of C_2 . In CBe_2 (1S), charge is donated from the bonding a_1 orbital of Be_2 to a vacant carbon p-orbital (a_1). This weakens the bonding Be–Be interaction and would lead to a structure similar to a T-form.^{18c} However, back-donation from the filled carbon b_2 orbital into the Be_2 fragment orbital of the same symmetry results in C–Be bonding but in Be–Be antibonding. This participation of the $b_2(C)$ orbital in CBe bonding is seen in Figure 1a. Charge concentrates in the area of the b_2 orbital and the bond paths curve outwardly; close to the C nucleus they almost follow the direction of the b_2 orbital. The different electronic structure of C_2Be (4S, Figure 1b) is due to the extra pair of electrons involved in CC bonding and the greater electronegativity of carbon relative to beryllium.

The bonding situation in 6S is similar to that in 1S. If the interacting Be_2 and C_2 fragments are arranged in C_{2v} symmetry to allow maximum overlap between their b_2 orbitals, charge transfer from Be_2 to C_2 will significantly reduce the CC bond strength and, therefore, will be unfavorable energetically. Stabilization, however, can be achieved by a distortion of the rectangular C_{2v} arrangement to the lower C_s symmetry observed for 6S. The consequent mixing of the a_1 and b_2 MOs allows direct charge transfer from the Be_2 fragment into the " a_1 " MO of C_2 .³⁶ Thus, the CC bond order is enhanced from 2 nearly to 3. This is in line with the density (Table III) and concentration pattern of electrons found for 6S (Figure 1c).

On the basis of the simple donor–acceptor model outlined above and the characteristic charge density (concentration) patterns shown in Figure 1 it is now possible to make structural predictions with regard to other compounds. For example, $C_2(BeH)_2$ in D_{2h} symmetry should possess a double-T electronic structure rather than the bicyclic structure of 9S. Be bound to either C_2H_2 , C_2H_4 , N_2 , or O_2 in C_{2v} symmetry will lead to ring-shaped rather than T-shaped electronic structures since charge transfer has to occur via b_2 orbitals. Work is in progress to test these predictions³³ (Chart I).

Both 1S and 4S might be considered as 2π Hückel aromatic compounds on the basis of a simple electron count. However, $\zeta(r)$ analysis clearly shows that the 2π electrons of 1S and 4S are

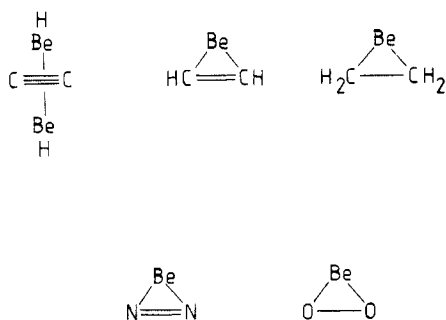
(28) Epiotis, N. D. *Unified Valence Bond Theory of Electronic Structure; Lecture Notes in Chemistry*; Springer Verlag: Berlin, 1982; Vol. 29. (b) Epiotis, N. D. "Unified Valence Bond Theory of Electronic Structure—Applications"; *Lecture Notes in Chemistry*; Springer Verlag: Berlin, 1983; Vol. 34.

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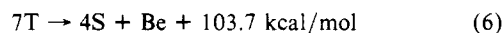
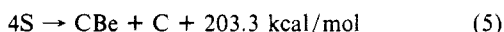
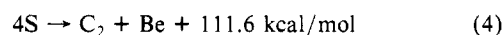
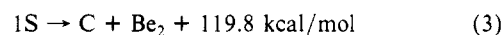
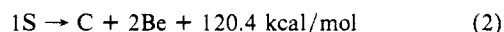
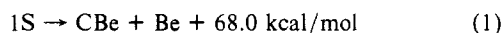
(31) Dewar, M. J. S.; Ford, G. P. *J. Am. Chem. Soc.* **1979**, *101*, 783.

Chart I



confined largely to the carbon regions. Since this also applies to 6S and 9S, carbon bonded to Be is a very weak π -donor. Thus, the basic electronic requirement for aromaticity, namely π -electron delocalization, is not fulfilled. As a consequence, we do not consider any of these compounds to be aromatic.³⁴

To assess the thermodynamic stabilities of the global minima 1S, 4S, and 7T in regard to fragmentation processes, we calculated the heats of reaction for reactions 1–6 at the MP2/6-31G*//6-31G* level³²



(32) The following total energies (au) have been taken at the MP2/6-31G//6-31G* level from ref 35: Be(¹S) -14.5933; Be₂(¹ Σ_g^+) -29.1874; C(³P) -37.7330; C₂(¹ Σ_g^+) -75.6955. For CBe(³ Σ^-) the MP2/6-31G* energy was calculated by using the 6-31G* bond distance of 1.661 Å taken from ref 35: -52.4097. Note that some of the reactions are spin forbidden, the spin allowed processes are thermodynamically even less favorable.

(33) Cremer, D.; Gauss, J.; Frenking, G.; Koch, W.; Schleyer, P. v. R., to be published.

(34) A similar conclusion has been drawn for C₂Be on the basis of semi-empirical calculations: Gropinathan, M. S.; Jug, K. *Theor. Chim. Acta* **1983**, *63*, 511.

(35) Whiteside, R. A., Frisch, M. J., Pople, J. A., Eds.; *The Carnegie-Mellon Quantum Chemistry Archive*, 3rd. ed., Carnegie-Mellon University: Pittsburgh, 1983.

The large positive values for all of the reactions 1–6 show that bonding in 1S, 4S, and 7T is quite strong and that all three compounds should be very stable in the gas phase.

V. Conclusions

(1) The global minima of the potential energy hypersurfaces of CBe₂ and C₂Be correspond to the singlet nonlinear C_{2v} geometries 1S and 4S, respectively. However, CASSCF calculations on C₂Be indicate the linear •C≡C–Be• geometries, 5S and 5T, to be quite low in energy. The most stable C₂Be₂ geometry is the linear triplet 7T, ↑Be–C≡C–Be↑. All other linear and cyclic forms are much higher in energy.

(2) Charge transfer from Be to C is the dominating force in all compounds considered. As a consequence, the CBe bonds in these molecules are only weakly covalent.

(3) Charge transfer interactions can be described by a simple donor–acceptor MO model that allows predictions with regard to CBe bonding in the nonlinear geometries. Depending on the mode of charge transfer (either via a₁ or b₂ orbitals) one can expect T-shaped (4S), bent (1S), or cyclic structures (6S and 9S) (Figure 1).

(4) Bonding and structural features are reflected by $\zeta(r)$ and $\nabla^2\zeta(r)$. Participation of b₂-orbitals in bonding leads to a concentration pattern (Figure 1d) rather different from that due to charge transfer via a₁-orbitals (Figure 1b).

(5) π -delocalization in these cyclic CBe compounds is small. None of these can be called aromatic, which is probably to be expected for other CBe compounds.

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Registry No. CBe₂, 506-66-1; C₂Be, 94740-29-1; C₂Be₂, 103619-64-3.

(36) The distribution $\zeta(r)$ in the Be₂ internuclear region of 6S is rather flat. For example, the value of $\zeta(r)$ at the saddle point between the Be atoms is only slightly large than at the ring critical point. Therefore, we cannot exclude that an acyclic structure similar to 1S is found for 6S at higher levels of theory.