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NOVEL BERYLLIUM DERIVATIVES OF $(CH)_n$ CARBOCYCLES: AN MNDO STUDY

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Summary

Structures have been investigated, using MNDO, of beryllium derivatives of the carbocycles $(CH)_n$ for n in the range 3—8. When $n = 3$, no minima are found corresponding to η^3 derivatives, but the beryllium atom always undergoes insertion into the ring: when $n = 4$, stable minima are found corresponding to $(\eta^4\text{-}C_4H_4)Be$ of C_{4v} symmetry, $(\eta^4\text{-}C_4H_4)_2Be$ (D_{2h}) and $(\eta^2\text{-}C_4H_4)_2Be$ (C_{2h}), the latter of which contains planar four-coordinate beryllium. When $n = 6$, the minima correspond to $(\eta^2\text{-}C_6H_6)Be$ of C_{2v} symmetry, $(\eta^2\text{-}C_6H_6)_2Be$ (D_{2d}), $(\eta^1\text{-}C_6H_6)(\eta^2\text{-}C_6H_6)Be$ (C_s) and $(\eta^2,\eta^2\text{-}C_6H_6)Be_2$ (C_s). C_7H_7 forms an η^3 derivative, $(\eta^3\text{-}C_7H_7)BeH$ of C_s symmetry, and C_8H_8 forms $(\eta^2\text{-}C_8H_8)Be$ of C_s symmetry and $(\eta^2,\eta^2\text{-}C_8H_8)Be_2$ (C_{2h}). The beryllaheterocycles C_nBeH_n (for $n = 4, 6, 8$) and $C_{n+1}BeH_{n+2}$ (for $n = 2, 4, 6$) were also investigated, together with the *spiro* compounds $(C_nH_n)_2Be$ for $n = 3, 4$: the species C_nBeH_n are all planar with C_{2v} symmetry, but of the species $C_{n+1}BeH_{n+2}$ only the 2π-electron species C_3BeH_4 is planar: the 4π C_5BeH_6 and the 6π C_7BeH_8 are non planar. $(C_3H_3)_2Be$ adopts a D_{2d} geometry, but $(C_4H_4)_2Be$ undergoes ring opening to yield a non-planar isomer of $(C_8H_8)Be$. High symmetry species, constrained to D_{nh}, D_{nd} or C_{nv}, are also discussed.

Introduction

Beryllium forms a number of *pentahapto* cyclopentadienyl derivatives, including $(C_5H_5)_2Be$ and the series $(C_5H_5)BeX$, where X = H, Cl, Br, CCH, and CH_3. It is therefore of interest to investigate the structures of compounds formed between beryllium and other monocyclic C_nH_n hydrocarbons: although this is a difficult and hazardous undertaking experimentally, it is readily feasible when undertaken computationally. Here we report the results of a theoretical

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exploration of the main structural features of derivatives of beryllium containing one or two ligands C_nH_n where n ranges from 3 up to 8.

Method

Calculations were made using the MNDO method [1]: initially, completely free optimisations, with no geometrical constraints were undertaken for each system starting from several different input geometries. Subsequently, optimisations were made subject to the constraints of particular point groups: within these point groups, all independent geometric variables were optimised. The resulting molecular energies are summarised for both free and constrained optimisations in Table 1, and the corresponding molecular geometries are recorded in Tables 2 and 3.

Molecular structures

Two types of molecules were investigated, those containing *polyhapto* ligands, and those which are beryllaheterocycles. Free optimisations were undertaken in both classes for derivatives of the carbocycles C_nH_n for values of n ranging up to 8. These will be discussed in groups, in order of increasing n: finally constrained systems of high symmetry will be discussed.

Species containing polyhapto ligands

C_3H_3 *derivatives.* Free optimisation of species containing one or two η^3-C_3H_3 rings, and these species are discussed under the heading Beryllaheterocycles, below.

C_4H_4 *derivatives.* We have previously [2] recorded that the free optimisation of $(C_4H_4)Be$ starting from approximately C_{4v} yields a singlet of exact C_{4v} symmetry in which the carbocycle is exactly planar, or a triplet of C_{2v} symmetry in which the carbocycle is puckered.

Two minima were found for $(C_4H_4)_2Be$ when inputs analogous to beryllocene were employed: when the optimisation was started from an input geometry of approximately D_{4h} symmetry, i.e. with the two C_4H_4 rings eclipsed, the structure optimised to exact D_{2h} symmetry with the rings still planar and parallel, but rectangular rather than square. The bonded distances in the rings are 1.436 Å and 1.535 Å, rather similar to the bonded distances calculated for singlet cyclobutadiene, 1.357 Å and 1.534 Å: the structure is shown in Fig. 1a. The interaction between the beryllium atom and the two rings is almost exclusively in terms of the p orbitals on the carbon atoms which are of π symmetry with respect to the rings. These eight orbitals in D_{2h} span the symmetry classes $A_g + B_{1g} + B_{2g} + B_{3g} + A_u + B_{1u} + B_{2u} + B_{3u}$, while the atomic orbitals of the beryllium atom span the classes $A_g(2s) + B_{1u} + B_{2u} + B_{3u}$ $(2p_{x,y,z})$. There are therefore four bonding orbitals, which are in fact in the order $A_g, B_{1u}, B_{2u}, B_{3u}$; four non-bonding orbitals, $B_{3g}, B_{2g}, B_{1g}, A_u$; and four antibonding orbitals A_g, B_{2u}, B_{1u} and B_{3u}. There are ten electrons in all in this metal-ligand system, eight in the four bonding orbitals and one non-bonding pair in B_{3g}. In a similar way, the interaction between the beryllium atom in $(C_4H_4)Be$ and the carbocycle is largely via the π system of the ring; the carbon $p\pi$ orbitals span the symmetry

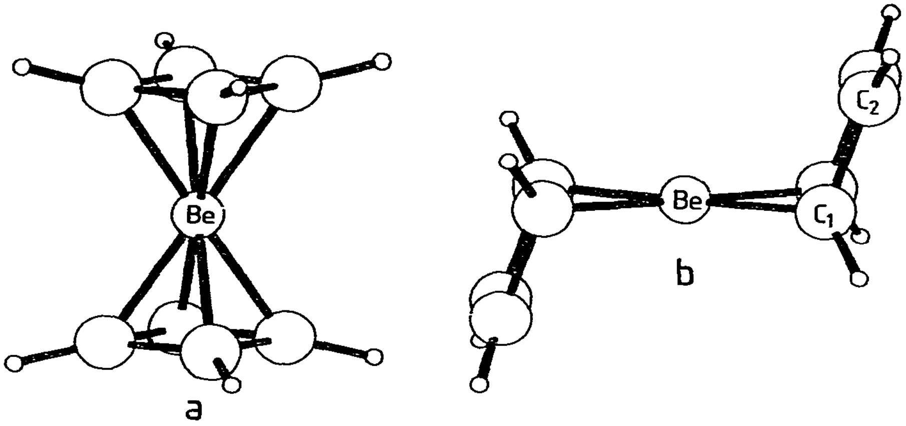

Fig. 1. a, The structure of (η^4-C_4H_4)$_2$Be; b, the structure of (η^2-C_4H_4)$_2$Be.

classes in C_{4v}: $A_1 + B_1 + E$, while the beryllium atomic orbitals span the classes $2A_1 + E$. There are consequently three bonding orbitals ($A_1 + E$), two non-bonding ($A_1 + B_1$) and three antibonding ($E + A_1$): the six available electrons occupy the three bonding orbitals.

The second minimum for (C_4H_4)$_2$Be was found by starting the optimisation at approximately D_{4d} symmetry. The resulting structure, which is shown in Fig. 1b, has overall C_{2h} symmetry and contains *dihapto*-cyclobutenyl ligands compared with *tetrahapto*-cyclobutadiene ligands in the D_{2h} isomer. The beryllium atom forms four bonds to four individual carbon atoms, and these bonds are strictly coplanar: this is a very unusual stereochemistry for beryllium, and has generally been observed only when forced upon the beryllium atoms, as for example in beryllium phthalocyanine [3].

C_5H_5 derivatives. The question of η^1,η^5 isomerism in C_5H_5BeX compounds has been discussed by Dewar and Rzepa [4]: we have also discussed the question of the location of the beryllium atom in the isolated molecule of (C_5H_5)$_2$Be [2], and no further investigation of these species has been undertaken during the present work.

C_6H_6 derivatives. In (η^4-C_4H_4)Be the beryllium atom may be considered to be a six-electron atom, while in (η^5-C_5H_5)BeX where X = H, Cl, Br, CH_3 or C≡CH, the beryllium atom may be considered to be an eight-electron atom. Similarly in the solid state where (C_5H_5)$_2$Be is η^1,η^5 at 120 K [5] and η^3,η^3 at room temperature [6], the beryllium atom here is always an eight electron atom: in the gas phase the asymmetric placing of the beryllium atom in (C_5H_5)$_2$Be [7], suggesting a major contribution from the form $[(\eta^5\text{-}C_5H_5)\text{Be}]^+(C_5H_5)^-$ is here indicative of a six-electron beryllium atom.

It is therefore of considerable interest to investigate the structures of species containing one or more C_6H_6 rings and one or two beryllium atoms. (C_6H_6)Be would, if the ring were η^6, contain an eight electron beryllium atom: (C_6H_6)$_2$Be on the other hand seems unlikely to adopt a symmetric η^6,η^6 structure, as this would involve a fourteen electron beryllium atom in either D_{6h} or D_{6d} symmetry.

Optimisation of the geometry of (C_6H_6)Be from an input of approximate C_{6v}

TABLE 1

MOLECULAR ENERGIES AND POINT GROUPS

Molecule	Point group	Figure	$\Delta H_f^\ominus$ (kJ mol^{-1})
(a) Polyhapto species			
$(\eta^4\text{-}C_4H_4)Be$	C_{4v}		453.8
$(\eta^4\text{-}C_4H_4)_2Be$	D_{2h}	1a	634.3
$(\eta^2\text{-}C_4H_4)_2Be$	C_{2h}	1b	562.6
$(\eta^5\text{-}C_5H_5)BeH$	C_{5v}		53.7
$(\eta^5\text{-}C_5H_5)_2Be$	D_{5d}		199.4
$(\eta^2\text{-}C_6H_6)Be$	C_{2v}	2a	218.6
$(\eta^2\text{-}C_6H_6)_2Be$	D_{2d}	2b	454.4
$(\eta^1\text{-}C_6H_6)(\eta^2\text{-}C_6H_6)Be$	C_s	2c	227.9
$(\eta^2,\eta^2\text{-}C_6H_6)Be_2$	C_s	2d	358.3
$(\eta^3\text{-}C_7H_7)BeH$	C_s	3	113.8
$(\eta^2\text{-}C_8H_8)Be$	C_s	4a	192.9
$(\eta^2,\eta^2\text{-}C_8H_8)Be_2$	C_{2h}	4b	174.3
(b) Beryllaheterocycles			
C_3BeH_4	C_{2v}	5a	157.7
$C_3BeH_3(C_3H_3)$	C_s	5b	382.2
$(H_3C_3)_2Be$	D_{2d}	5c	299.3
C_4BeH_4	C_{2v}	6a	130.9
C_5BeH_6	C_s	6b	133.0 [a]
C_6BeH_6	C_{2v}	6c	64.2
C_7BeH_8	C_s	6d	194.0 [b]
C_8BeH_8	C_{2v}	6e	199.6
C_8BeH_8	C_2	6f	126.7
(c) D_{nh}, D_{nd}, and C_{nv} species			
$(\eta^3\text{-}C_3H_3)BeH$	C_{3v}		461.9
$(\eta^3\text{-}C_3H_3)_2Be$	D_{3h}		777.4
$(\eta^3\text{-}C_3H_3)_2Be$	D_{3d}		812.0
$(H_3C_3)_2Be$	D_{2h}		479.7
$(\eta^4\text{-}C_4H_4)_2Be$	D_{4h}		698.5
$(\eta^4\text{-}C_4H_4)_2Be$	D_{4d}		680.4
$(\eta^6\text{-}C_6H_6)Be$	C_{6v}		431.0
$(\eta^6\text{-}C_6H_6)_2Be$	D_{6h}		507.2
$(\eta^6\text{-}C_6H_6)_2Be$	D_{6d}		511.6
$(\eta^6,\eta^6\text{-}C_6H_6)Be_2$	D_{6h}		752.5
$(\eta^7\text{-}C_7H_7)BeH$	C_{7v}		229.7
$(\eta^8\text{-}C_8H_8)Be$	C_{8v}		465.1
$(\eta^8,\eta^8\text{-}C_8H_8)Be_2$	D_{8h}		940.5

[a] $\Delta H_f^\ominus$ is 144.0 kJ mol^{-1} when planar. [b] $\Delta H_f^\ominus$ is 222.3 kJ mol^{-1} when planar.

symmetry yields a structure of exact C_{2v} symmetry, as shown in Fig. 2a: this structure contains a dihapto ligand which is very similar to the newly discovered valence isomer of C_6H_6 recently described in reference [8] as isomer V, although with extensive bond fixation (see Table 2). In this dihapto complex, the beryllium atom can be regarded as a four-electron atom; however the eight electron η^6 isomer of C_{6v} symmetry is some 212 kJ mol^{-1} higher in energy (see Table 1).

For $(C_6H_6)_2Be$, two optimisations were performed starting from both approximately D_{6h} and approximately D_{6d} inputs. The optimisation starting from approximately D_{6d} rapidly converged to a geometry of D_{2d} symmetry in which each of the rings is puckered in the same way as in $(\eta^2\text{-}C_6H_6)_2Be$ and in which the four bonds from beryllium are quasi-tetrahedral with CBeC angles of 88.1°

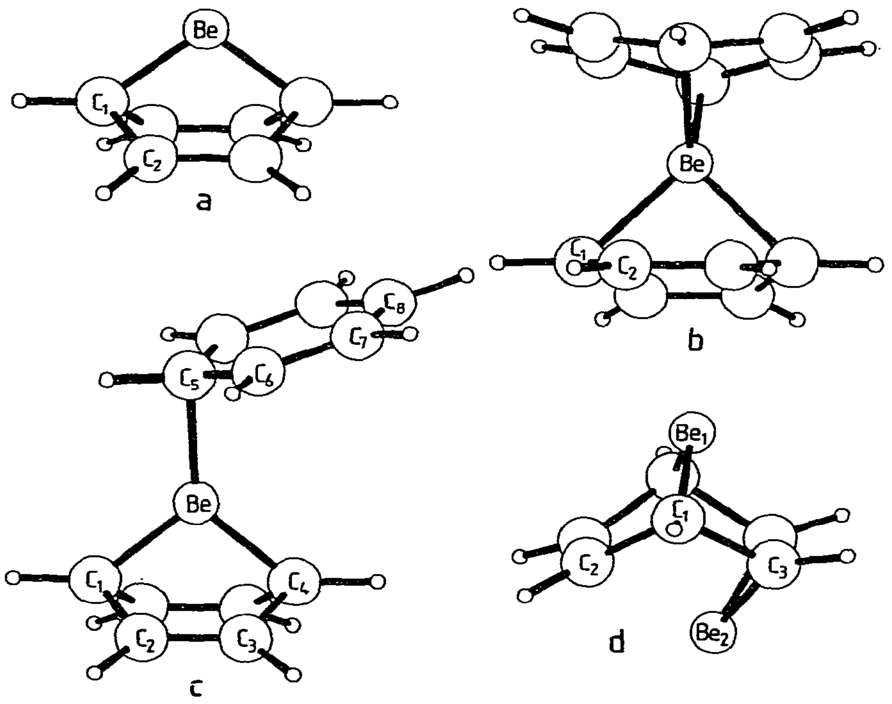

Fig. 2. a, The structure of $(\eta^2\text{-}C_6H_6)Be$; b, the structure of $(\eta^2\text{-}C_6H_6)_2Be$; c, the structure of $(\eta^1\text{-}C_6H_6)$-$(\eta^2\text{-}C_6H_6)Be$; d, the structure of $(\eta^2,\eta^2\text{-}C_6H_6)Be_2$.

(× 2) and 121.2° (× 4). Again, extensive bond fixation occurs in the ligands: the beryllium atom can here be regarded as a six-electron atom; the structure of this bis-*dihapto* complex is shown in Fig. 2b. The D_{6d} isomer containing two η^6 rings is only 57.2 kJ mol^{-1} higher in energy. The optimisation starting from a D_{6h} input was extremely lengthy, requiring some 22 hours of CPU time on the VAX 11/780 computer: during the course of the optimisation, the structure passed through a number of well defined geometries, none of which proved to represent a minimum on the potential energy surface. From the bis-*hexahapto* start of D_{6h} symmetry, the structure first approached a bis-*dihapto* configuration of D_{2h} symmetry, analogous to the structure in Fig. 2b with puckered rings, but with the four Be—C bonds coplanar: at this point the $\Delta H_f^{\ominus}$ is around 395 kJ mol^{-1}, which should be compared with a value of 507.2 kJ mol^{-1} in the fully constrained D_{6h} structure. Proceeding with the optimisation, one C_6H_6 ring remained in the puckered η^2 configuration throughout, but the other then became planar again and symmetrically bound to the beryllium atom to give a η^2,η^6 configuration: at this point $\Delta H_f^{\ominus}$ was around 290 kJ mol^{-1}. Beyond this point, the η^2 ring remained essentially unchanged but the other changed from η^6 to η^1, yielding finally the structure shown in Fig. 2c.

In this η^1,η^2 molecule, the total electron population calculated for the beryllium atom is 3.762 *e*, whereas in the isomeric η^2,η^2 species it is 3.502 *e*: similarly in $(\eta^2\text{-}C_6H_6)Be$, the beryllium population is 3.596 *e*. The much higher population in the η^1, η^2 isomer, together with the planarity of the η^1 ring, suggests that it should be regarded as a charge transfer complex between C_6H_6 and

TABLE 2

MOLECULAR GEOMETRIES FOR FREE OPTIMISATIONS

Distances X, Y in Å; bond angles X, Y, Z and torsional angles W, X, Y, Z in degrees

Molecules	Structural data
(a) Polyhapto species	
$(\eta^4\text{-}C_4H_4)_2Be$	BeC, 1.946; CC, 1.535(X4), 1.436(X4); CH, 1.076; HCC, 131.5; HCCC, 159.8
$(\eta^2\text{-}C_4H_4)_2Be$	BeC(1), 1.781(X4); C(1)C(2), 1.532(X4); C(1)C(1′), 1.515(X2); C(2)C(2′), 1.362(X2); C(1)H, 1.087; C(2)H, 1.074; HC(1)C(2), 124.4; HC(1)C(1′), 129.1; HC(2)C(1), 130.4; HC(2)C(2′), 136.7; CBeC, 50.3(X2), 129.7(X2); dihedral 106.7
$(\eta^2\text{-}C_6H_6)Be$	BeC(1), 1.717(X2); BeC_2, 2.195(X4); C(1)C(2), 1.535(X4); C(2)C(2′), 1.376(X2), 2.492(X2), 2.847(X2); C(1)C(1′), 2.694; HC(1), 1.094(X2); HC(2), 1.086(X4); HC(1)C(2), 115.5; HC(2)C(1), 119.7; HC(1)C(2)C(2′), 179.8; HC(2)C(2′)C(1), 179.8; dihedral in ring, 137.3
$(\eta^2\text{-}C_6H_6)_2Be$	BeC(1), 2.002(X4); BeC(2), 2.235(X8); C(1)C(2), 1.463(X8); C(2)C(2′), 1.402(X4), 2.522(X4), 2.886(X4); C(1)C(1′), 2.783(X2); HC(1), 1.092(X4); HC(2), 1.089(X8); HC(1)C(2), 117.9; HC(2)C(1), 119.7; HC(1)C(2)C(2′), 181.3; HC(2)C(2′)C(1), 180.9; dihedral in ring, 158.5
$(\eta^1\text{-}C_6H_6)(\eta^2\text{-}C_6H_6)Be$	C(1)C(2), 1.527(X2); C(2)C(3), 1.370(X2); C(3)C(4), 1.527(X2); C(2)C(2′), 2.492(X1); C(3)C(3′), 2.492(X1); C(1)C(4), 2.636(X1); C(1)H, 1.097(X1); C(2)H, 1.086(X2); C(3)H, 1.086(X2); C(4)H, 1.097(X1); C(1)Be, 1.758(X1); C(4)Be, 1.757(X1); BeC(5), 1.926(X1); C(5)C(6), 1.437(X2); C(6)C(7), 1.407(X2); C(7)C(8), 1.409(X2); C(6)C(6′), 2.466(X1); C(7)C(7′), 2.446(X1), C(5)C(8), 2.843(X1); C(5)H, 1.111(X1); C(6)H, 1.093(X2); C(7)H, 1.091(X2); C(8)H, 1.091(X1)
$(\eta^2,\eta^2\text{-}C_6H_6)Be_2$	Be(1)C(1), 1.690(X2); Be(1)C(2), 2.325(X2); Be(1)C(3), 2.222(X2); Be(2)C(1), 2.473(X2); Be(2)C(2), 2.194(X2); Be(2)C(3), 1.656(X2); C(1)C(2), 1.556(X2); C(1)C(3), 1.585(X2); C(1)C(1′), 2.751(X1); C(2)C(2′), 1.403(X1); C(3)C(3′), 1.728(X1); C(1)C(2′), 2.506(X2); C(1)C(3′), 2.697(X2); C(2)C(3), 2.447(X2); C(2)C(3′), 2.901(X2); C(1)H, 1.095(X2); C(2)H, 1.090(X2); C(3)H, 1.093(X2).
$(\eta^3\text{-}C_7H_7)BeH$	BeC(1), 1.744(X1); BeC(2), 2.438(X2); BeC(3), 2.581(X2); BeC(4), 2.221(X2); C(1)C(2), 1.510(X2); C(2)C(3), 1.363(X2); C(3)C(4), 1.479(X2); C(4)C(4′), 1.385(X1); C(3)C(3′), 3.146(X1); C(2)C(2′), 2.511(X1); HBe, 1.292; HC(1), 1.105; HC(2), 1.091; HC(3), 1.091; HC(4), 1.099; HC(1)C(2), 112.2; HC(2)C(3), 121.7; HC(3)C(4), 115.8; HC(4)C(4′), 118.2.
$(\eta^2\text{-}C_8H_8)Be$	BeC(1), 2.175(X2); BeC(2), 1.681(X2); BeC(3), 2.546(X2); BeC(4), 2.969(X2); C(1)C(2), 1.546; C(2)C(3), 1.508; C(3)C(4), 1.357; C(4)C(4′), 1.467; C(3)C(3′), 3.301; C(2)C(2′), 2.898; C(1)C(1′), 1.368; HC(1), 1.089; HC(2), 1.106; HC(3), 1.097; HC(4), 1.100; HC(1)C(2), 117.9; HC(2)C(3), 110.6; HC(3)C(4), 117.2; HC(4)C(4′), 111.7.
$(\eta^2,\eta^2\text{-}C_8H_8)Be_2$	BeC(1), 2.445(X4); BeC(2), 1.744(X4); C(1)C(2), 1.543(X4); C(2)C(2′), 1.392(X2), 2.840(X2), 3.261(X2); C(1)C(1′), 1.601(X2), 3.598(X2), 3.858(X2); HC(1), 1.092(X4); HC(2), 1.098(X4); BeBe′, 2.566; HC(1)C(2), 122.4; HC(2)C(1), 113.2; ring dihedral, 99.9.
(b) Beryllaheterocycles	
C_3BeH_4	BeC, 1.753(X2); CC, 1.416(X2); BeH, 1.295; CH, 1.087(X2), 1.086(X1); CBeC, 80.3; CCC, 105.9; HCBe, 150.4.
$C_3BeH_3(C_3H_3)$	BeC(1), 1.753(X2); C(1)C(2), 1.415(X); BeC(3), 1.678(X1); C(3)C(4), 1.525(X2); C(4)C(4′), 1.323(X1); C(1)H, 1.087; C(2)H, 1.086; C(3)H, 1.119; C(4)H, 1.062; C(1)BeC(1′), 80.2; BeC(1)C(2), 87.0; C(1)C(2)C(1′), 105.8; BeC(3)C(4), 129.1; C(1)BeC(3), 139.8; HC(1)Be, 150.3; HC(3)Be, 108.3; HC(4)C(3), 144.3; dihedral, 134.3.

TABLE 2 (continued)

Molecules	Structural data
$(H_3C_3)_2Be$	BeC(1), 1.773(X4); C(1)C(2), 1.412(X4); C(1)H, 1.088(X4); C(2)H, 1.085(X2); CBeC, 78.6(X2), 126.8(X4); CCC, 105.4(X2); HCBe, 149.8 (X4).
C_4BeH_4	BeC(1), 1.649(X2); C(1)C(2), 1.371(X2); C(2)C(2'), 1.535(X1); C(1)H, 1.084(X2); C(2)H, 1.089(X2); BeC(1)C(2), 90.5; C(1)C(2)C(2'), 119.2; C(1)BeC(1'), 120.6; HC(1)C(2), 123.3; HC(2)C(1), 124.6.
C_5BeH_6	BeC(1), 1.719(X2); C(1)C(2), 1.395(X2), C(2)C(3), 1.422(X2); BeC(2), 2.574(X2); BeC(3), 2.847(X1); C(1)C(3), 2.474(X2); C(1)C(1'), 2.860 (X1); C(2)C(2'), 2.546(X1); C(1)C(2'), 3.037(X2); BeH, 1.317; C(1)H, 1.097(X2); C(2)H, 1.094(X2); C(3)H, 1.094(X1); HC(1)C(2), 117.6(X2); HC(2)C(3), 116.7(X2); HC(3)C(2), 116.4; HBeC(1), 120.0.
C_6BeH_6	BeC(1), 1.618(X2); C(1)C(2), 1.367(X2); C(2)C(3), 1.460(X2); C(3)C(3'), 1.365(X1); BeC(1)C(2), 111.1(X2); C(1)C(2)C(3), 130.2(X2); C(2)C(3)C(3'), 134.0(X2); C(1)BeC(1'), 149.3; HC(1), 1.095(X2); HC(2), 1.100(X2); HC(3), 1.101(X2); HC(1)C(2), 118.0(X2); HC(2)C(3), 112.1(X2); HC(3)C(3'), 114.6(X1).
C_7BeH_8	BeC(1), 1.703(X2); C(1)C(2), 1.385(X2); C(2)C(3), 1.415(X2); C(3)C(4), 1.400(X2); BeC(1)C(2), 128.1(X2); C(1)C(2)C(3), 130.7(X2); C(2)C(3)C(4), 136.4(X2); C(3)C(4)C(4'), 137.4(X1); C(1)BeC(1'), 113.2; BeH, 1.315(X1); C(1)H, 1.106(X2); C(2)H, 1.102(X2); C(3)H, 1.106(X2); C_4H, 1.105(X1); HC(1)C(2), 114.8(X2); HC(2)C(3), 112.7(X2); HC(3)C(4), 111.7(X2); HC(4)C(3), 111.4(X1); HBeC(1), 122.8.
C_8BeH_8 (C_{2v})	BeC(1), 1.621(X2); C(1)C(2), 1.350(X2); C(2)C(3), 1.464(X2); C(3)C(4), 1.353(X2); C(4)C(4'), 1.461(X1); BeC(1)C(2), 124.3(X2); C(1)C(2)C(3), 133.0(X2); C(2)C(3)C(4), 142.0(X2); C(3)C(4)C(4'), 145.4(X2); C(1)BeC(1'), 170.1; HC(1), 1.104(X2); HC(2), 1.103(X2); HC(3), 1.109(X2); HC(4), 1.112(X2); HC(1)C(2), 116.3(X2); HC(2)C(3), 110.3(X2); HC(3)C(4), 110.9(X2); HC(4)C(4'), 105.4(X2).
C_8BeH_8 (C_2)	BeC(1), 1.677(X2); C(1)C(2), 1.361(X2), C(2)C(3), 1.481(X2); C(3)C(4), 1.368(X2); C(4)C(4'), 1.494; BeC(1)C(2), 102.8(X2); C(1)C(2)C(3), 117.8(X2); C(2)C(3)C(4), 125.8(X2); C(3)C(4)C(4'), 79.9(X2); C(1)BeC(1'), 203.5(X1); HC(1), 1.090(X2); HC(2), 1.090 (X2); HC(3), 1.096(X2); HC(4), 1.099(X2); HC(1)C(2), 121.4(X2); HC(2)C(3), 117.0(X2); HC(3)C(4), 115.3(X2); HC(4)C(4'), 118.1(X2).

$(\eta^2\text{-}C_6H_6)Be$: the process

$$(\eta^2\text{-}C_6H_6)Be + C_6H_6 \rightarrow (\eta^1\text{-}C_6H_6)(\eta^2\text{-}C_6H_6)Be$$

is exothermic by 79.4 kJ mol^{-1}, whereas the analogous process

$$(\eta^2\text{-}C_6H_6)Be + C_6H_6 \rightarrow (\eta^6\text{-}C_6H_6)(\eta^2\text{-}C_6H_6)Be$$

would be exothermic by no more than 15—20 kJ mol^{-1}.

Optimisation of the geometry of $(C_6H_6)Be_2$ from a starting point of approximately D_{6h} symmetry, with one beryllium atom on each side of the ring, gave the structure shown in Fig. 2d. In this the two beryllium atoms are no longer equivalent, but the ring is puckered as in the previous C_6H_6 derivatives. One beryllium atom, Be(1), is bonded to a pair of *para* carbon atoms, C(1), with a bonded Be(1)C(1) distance of 1.690° and distances Be(1)C(2) and Be(1)C(3) of 2.324 Å and 2.222 Å, respectively. The other beryllium atom, Be(2), on the

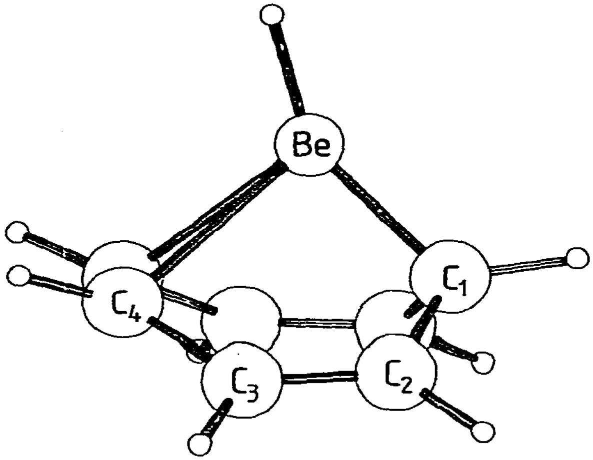

Fig. 3. The structure of (η^3-C_7H_7)BeH.

other hand, is bonded to a pair of *ortho* carbon atoms, C(3), with a bonded Be(2)C(3) distance of 1.656 Å: this beryllium atom lies below the central plane C(2)C(2')C(3)C(3') of the ring, but is much closer to C(3) and C(3') (2.194 Å) than to C(2) and C(2') (2.473 Å). The ring is essentially a puckered form of cyclohexenetetrayl, and each of the beryllium atoms may be regarded as a four-electron atom.

C_7H_7 derivatives. A symmetric η^7 ring in (C_7H_7)BeH implies a ten-electron beryllium atom and is therefore unlikely to be found: when the geometry of (C_7H_7)BeH was optimised starting from a C_{7v} input, the resulting structure contained an η^3 ring and had overall C_s symmetry as shown in Fig. 3; in this species the beryllium is formally a six-electron atom. There is a strong π-bond fixation in the ring: although the beryllium atom is four coordinate, the bond angles at this atom are very far from tetrahedral: CBeC, 36.3° (× 1), 93.5° (× 2); CBeH, 150.7° (× 1), 114.3° (× 2).

C_8H_8 derivatives. Optimisation of (C_8H_8)Be from a starting point of approximately C_{8v} symmetry leads to the C_s structure shown in Fig. 4a, in which the

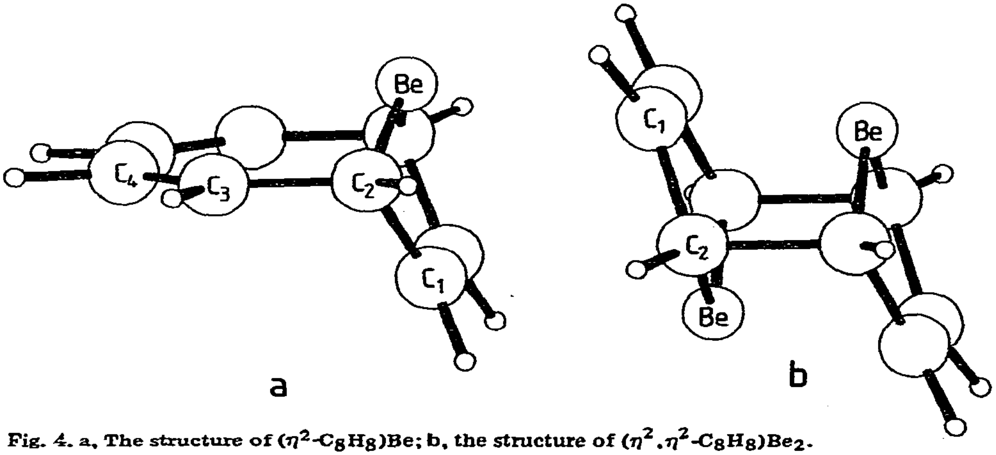

Fig. 4. a, The structure of (η^2-C_8H_8)Be; b, the structure of (η^2,η^2-C_8H_8)Be_2.

TABLE 3

GEOMETRIES IN CONSTRAINED POINT GROUPS

Distances in Å, angle in degrees

Molecule	Point group	CBe	CC	CH	BeH	CCH	h_1 [a]	h_2 [b]
$(\eta^3\text{-}C_3H_3)BeH$	C_{3v}	1.851	1.495	1.075	1.282	139.2	1.638	0.522
$(\eta^3\text{-}C_3H_3)_2Be$	D_{3h}	1.800	1.494	1.073	—	139.6	1.580	0.511
	D_{3d}	1.816	1.490	1.073	—	140.1	1.599	0.497
$(\eta^4\text{-}C_4H_4)Be$ [c]	C_{4v}	1.785	1.514	1.076	—	131.6	1.402	0.384
$(\eta^4\text{-}C_4H_4)_2Be$	D_{4h}	1.944	1.484	1.076	—	133.1	1.637	0.277
	D_{4d}	1.945	1.484	1.076	—	133.1	1.637	0.277
$(\eta^5\text{-}C_5H_5)BeH$ [c]	C_{5v}	1.990	1.458	1.084	1.284	125.6	1.489	0.079
$(\eta^5\text{-}C_5H_5)_2Be$ [c]	D_{5d}	2.071	1.449	1.084	—	125.6	1.663	0.147
$(\eta^6\text{-}C_6H_6)Be$	C_{6v}	2.191	1.430	1.091	—	119.9	1.660	0.066
$(\eta^6\text{-}C_6H_6)_2Be$	D_{6h}	2.153	1.437	1.090	—	119.8	1.602	0.116
	D_{6d}	2.155	1.437	1.090	—	119.8	1.606	0.116
$(\eta^6,\eta^6\text{-}C_6H_6)Be_2$	D_{6h}	2.019	1.502	1.088	—	120.0	1.349	0.000
$(\eta^7\text{-}C_7H_7)BeH$	C_{7v}	2.120	1.431	1.095	1.289	115.6	1.332	0.051
$(\eta^8\text{-}C_8H_8)Be$	C_{8v}	1.992	1.436	1.097	—	112.5	0.670	0.0097
$(\eta^8,\eta^8\text{-}C_8H_8)Be_2$	D_{8h}	2.279	1.429	1.100	—	112.5	1.307	0.000

[a] h_1 is perpendicular distance of Be from plane C_n. [b] h_2 is perpendicular distance of plane C_n from plane H_n. [c] Free optimisation.

beryllium atom spans 1,4 positions in an η^2 ligand: there is strong π-bond fixation in the ring which contains three double bonds, C(1)C(1′), C(3)C(4), and C(3′)C(4′). This complex contains a four-electron beryllium atom. When the optimisation of $(C_8H_8)_2Be_2$ is begun from an approximately D_{8h} input, the

TABLE 4

SYMMETRIES AND ENERGIES (eV) OF π MOLECULAR ORBITALS IN C_4 AND C_3Be RINGS

(a) Monocyclic molecules

C_3BeH_4, $C_{2v}(^1A_1)$		$C_3BeH_3(C_3H_3)$, $C_s(^1A')$		C_4H_4, $D_{2h}(^1A_g)$		C_4H_4, $D_{4h}(^3A_{2g})$	
B_1	3.364	A'	3.292	A_u	2.047	B_{2u}	1.919
B_1	0.399	A'	0.477	B_{2g}	0.124	- - - -	- - - -
				- - - -	- - - -	E_g	−4.141
A_2	−1.469	A''	−1.387	B_{1g}	−8.443		
- - - -	- - - -	- - - -	- - - -				
B_2	−11.564	A'	−11.397	B_{3u}	−11.880	A_{2u}	−11.747

(b) Bicyclic molecules

spiro-$Be(C_3H_3)_2$, $D_{2h}(^1A_1)$		*spiro*-$Be(C_3H_3)_2$, $D_{2h}(^1A_g)$	
		B_{3u}	4.137
E	1.582	B_{2g}	1.979
A_2	−0.531	B_{3u}	1.079
B_1	−0.628	A_u	−0.307
		B_{1g}	−0.376
- - - -	- - - -	- - - -	- - - -
E	−9.775	B_{2g}	−10.208
		B_{3u}	−10.915

structure converges to C_{2h} symmetry, as shown in Fig. (4b), with beryllium atoms spanning the 1,4 and 5,8 positions of a bis-*dihapto* ligand, in which again strong π-bond fixation occurs (see Table 2).

Beryllaheterocycles

C_3H_3 derivatives. When the free optimisation of $(C_3H_3)BeH$ was started from an input point of approximately C_{3v} symmetry, the resulting structure was one in which the beryllium atom was inserted into the C_3 ring to yield a completely planar C_3BeH_4 beryllacyclobutadiene of overall C_{2v} symmetry. This is a system in which four π molecular orbitals, normal to the molecular plane, are occupied by only two electrons: the energies and symmetries of these orbitals are listed in Table 4 where they may be compared with those for the singlet and triplet states of the prototype cyclobutadiene. This molecule is shown in Fig. 5a: it is impossible to draw a single classical valence structure.

Completely free optimisation of $(C_3H_3)_2Be$ from either a D_{3h} or a D_{3d} input gave a structure in which the beryllium atom was inserted into one of the C_3 rings to yield a C_3Be heterocycle exactly as for $(C_3H_3)BeH$ but the substituent on beryllium was now not hydrogen but a Δ^2-cyclopropenyl group. The molecule has C_s symmetry overall, and is shown in Fig. 5b: again the heterocycle is completely planar with two π electrons, and the π molecular energy levels are very similar to those in C_3BeH_4 (see Table 4), being only weakly perturbed by the orbitals of the cyclopropenyl ring. The principal perturbation results from the two single C—C bonds of the C_3 ring.

Although optimisations starting from D_{3h} or D_{3d} inputs lead to insertion of the beryllium atom in one ring only, it is quite plausible for the beryllium to be at the ring junction of a *spiro* compound. Optimisations from a *spiro* input of either approximately D_{2h} or D_{2d} symmetry both yielded a structure of exact D_{2d} symmetry which is shown in Fig. 5c; when the optimisation was constrained

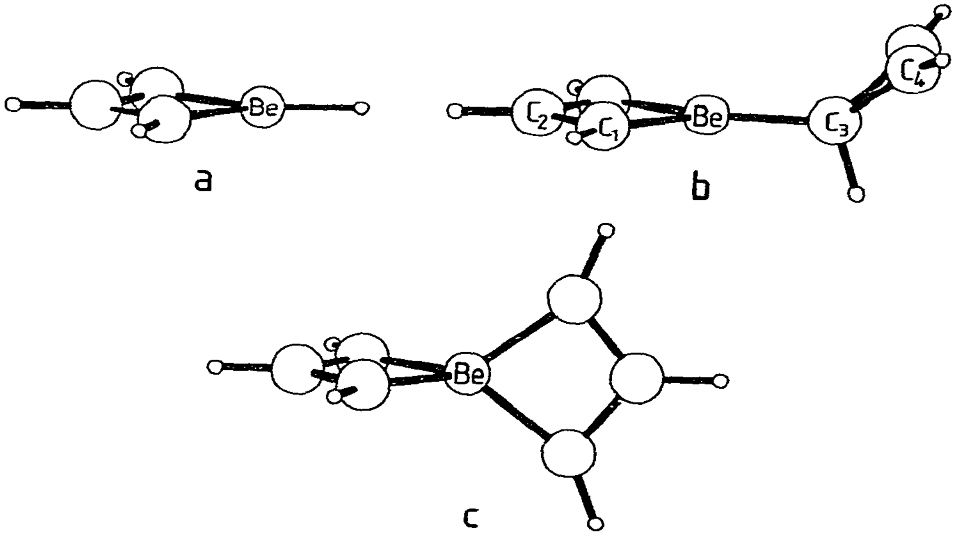

Fig. 5. a, The structure of C_3BeH_4; b, the structure of $C_3BeH_3(C_3H_3)$; c, the structure of $(H_3C_3)_2Be$.

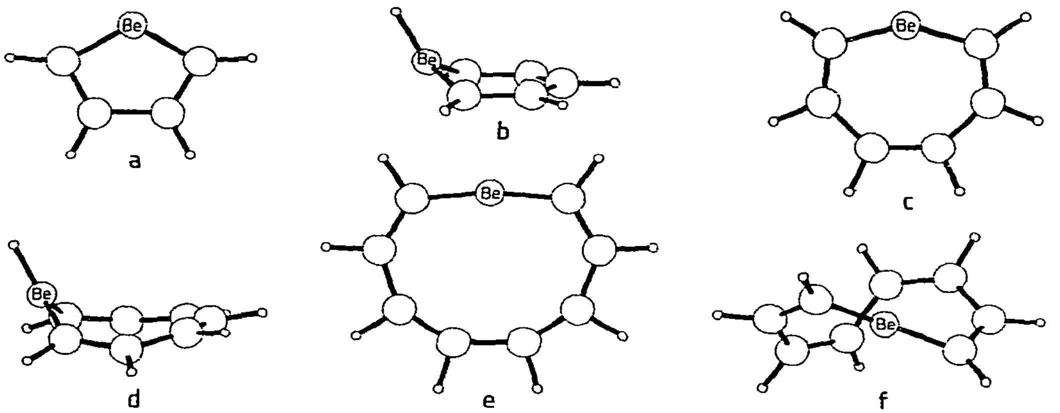

Fig. 6. a, The structure of C_4BeH_4; b, the structure of C_5BeH_6; c, the structure of C_6BeH_6; d, the structure of C_7BeH_8; e, the structure of C_8BeH_8 (C_{2v} isomer); f, the structure of C_8BeH_8 (C_2 isomer).

to D_{2h} symmetry, the energy was some 180 kJ mol^{-1} higher than for D_{2d}. The geometry of each ring in the D_{2d} *spiro* compound is very similar to those in monocyclic C_3Be rings, except that the CBe bonds are slightly (0.02 Å) longer: in the D_{2h} isomer these bonds are of length 1.841 Å, some 0.07 Å longer than for D_{2d}. For the planar D_{2h} isomer, the seven π molecular orbitals span the symmetry classes $B_{1g} + 2B_{2g} + A_u + 3B_{3u}$ of which the totally in-phase B_{3u} and one B_{2g} are occupied by the four available π electrons, equivalent to two π electrons per ring. In the D_{2d} isomer the out-of-plane $p\pi$ orbitals, of which there are now only six, span the symmetry classes $A_2 + B_1 + 2E$ of which one E pair is occupied. If the π system of each ring is regarded as an allyl fragment, for which in local C_{2v} symmetry the three π combinations have symmetries B_1 (bonding), A_2 (non-bonding) and B_1 (antibonding) then their interaction in D_{2d} gives from the two bonding B_1 orbitals, the lower E pair, from the two antibonding B_1 orbitals, the upper E pair, and from the two non-bonding A_2 orbitals, the A_2 and B_1 orbitals in D_{2d}. Again there are four electrons occupying the π bonding E orbitals, equivalent to two π electrons per ring.

C_4H_4 derivatives. Just as the beryllium atom can be inserted into a three-membered carbocycle to produce a planar C_3Be ring, as described above, so also C_4Be rings are possible. Optimisation of an input geometry corresponding to a 1-beryllacyclopentadiene yields a structure of strict C_{2v} symmetry, as shown in Fig. 6a. This planar structure is a 4π-electron cycle and unlike its 6π-electron analogue, $(C_5H_5)^-$, exhibits strong π bond fixation: the two C=C distances are 1.371 Å while the unique C—C distance is 1.525 Å. These may be compared with the corresponding values of 1.361 and 1.478 Å, respectively, calculated for the neutral C_5H_6 which also necessarily exhibits bond fixation and with 1.418 Å in $(C_5H_5)^-$. Table 5 lists the π bond energies and symmetries in C_4BeH_4, $(C_5H_5)^-$, and in the analogous $(P_3S_2)^+$ ion [9]. Inspection of the coefficients of the occupied π orbitals in C_4BeH_4 shows that the B_1 orbital is concentrated largely in the CC bonds having a rather small coefficient, 0.257, at beryllium: the A_2 orbital on the other hand is concentrated exclusively in the CC bonds, with a nodal plane perpendicular to the C_4Be plane at beryllium.

For a *spiro* derivative of C_4H_4 analogous to that shown in Fig. 5c, again two

TABLE 5

SYMMETRIES AND ENERGIES (eV) OF π MOLECULAR ORBITALS IN C_5 AND C_4Be RINGS

C_4BeH_4		$C_5H_5^-$		C_5H_6		$(P_3S_2)^+$	
B_1	3.275					A_2	−7.735
		E''_2	7.938	A_2	1.891		
A_1	1.981					B_1	−8.668
		- - - - - - - -		B_1	0.307	- - - - - - - - -	
B_1	0.134	E''_1	−2.137	- - - - - - - - -		B_1	−16.050
- - - - - - - - -				A_2	−9.046		
A_2	−8.805					A_2	−17.739
		A''_2	−6.110	B_1	−10.841		
B_1	−11.372					B_1	−20.054

optimisations were initiated from inputs of approximately D_{2d} and D_{2h} symmetry, respectively. Although in these two inputs the C_4Be rings were in one case co-planar and in the other mutually perpendicular, each optimisation converged to the same minimum, Figure 6f.

Other beryllaheterocycles. Like C_3BeH_4 and C_4BeH_4, both C_6BeH_6 and C_8BeH_8 optimise to structures of C_{2v} symmetry, shown in Figs. 6c and 6e respectively. In contrast, both C_5BeH_6 and C_7BeH_8 optimise to non-planar geometries, as shown in Figs. 6b and 6d, respectively: in each case the energy difference between the puckered structure and the planar form is modest (Table 1). C_5BeH_6 has a planar C_5 fragment, but the C_7 fragment in C_7BeH_8 forms a non-planar shallow boat.

For species in which classical valence forms can be written, i.e. those having two-coordinate beryllium of general type C_nBeH_n (n even) exhibit marked π bond fixation with alternation of CC bond distances round the ring: those for which no such classical forms can be written, which contain three coordinate beryllium, $C_{n+1}BeH_{n+2}$ (n even) show a much less marked alternation of bond distances, with the suggestion of less bond fixation and greater π electron delocalisation. In this respect it is therefore somewhat surprising that it is just these species $C_{n+1}BeH_{n+2}$ for $n = 4$ and 6, which optimise to non-planar geometries, while those species C_nBeH_n with $n = 6$ and 8, in which least π delocalisation occurs, optimise to strictly planar C_{2v} structures.

In a C_{2v} species C_nBeH_n (n even), containing a total of $n + 1$ ring atoms, the π molecular orbitals of the ring comprise $\frac{1}{2}n$ of A_2 symmetry and $\frac{1}{2}n + 1$ of B_1 symmetry. In the corresponding C_{2v} species $C_{n+1}BeH_{n+2}$ with $n + 2$ ring atoms, the π molecular orbitals comprise $\frac{1}{2}n$ of A_2 symmetry and $\frac{1}{2}n + 2$ of B_1 symmetry. These correlate immediately with the π orbitals of planar carbocycles of D_{nh} symmetry, given in Table 6 for $n = 4$–9. With an even number of carbon atoms, the π orbitals of a $(CH)_n$ carbocycle consists of two singly degenerate orbitals A_{2u} and either B_{2u} or B_{2g} depending on whether $n = 4p$ or $4p + 2$ where p is a positive integer, together with $\frac{1}{2}(n - 2)$ doubly degenerate E pairs: with an odd number of carbon atoms, there is a single non-degenerate orbital A''_2 together with $\frac{1}{2}(n - 1)$ E pairs. On lowering the symmetry from D_{nh} to C_{2v}, all types of E split to $(A_2 + B_1)$; in addition A''_2 always correlates with B_1 and both B_{2g} and B_{2u} with B_1, accounting for the excess of one B_1 orbital in the C_nBeH_n examples and the excess of two B_1 orbitals in the $C_{n+1}BeH_{n+2}$: the extra B_1

TABLE 6

SYMMETRY CLASSES OF π MOLECULAR ORBITALS IN CARBOCYCLES $(CH)_n^{\pm x}$ OF D_{nh} SYMMETRY

D_{4h}	D_{5h}	D_{6h}	D_{7h}	D_{8h}	D_{9h}
				B_{2u}	E_4''
		B_{2g}	E_3''	E_{3g}	E_3''
B_{2u}	E_2''	E_{2u}	E_2''	E_{2u}	E_2''
E_g	E_1''	E_{1g}	E_1''	E_{1g}	E_1''
A_{2u}	A_2''	A_{2u}	A_2''	A_{2u}	A_2''

species arise from the singly degenerate orbitals of the D_{nh} $(CH)_n$ carbocycle, which occur at the bottom and top (for n even) of the π manifolds. The energies of the π orbitals in the beryllaheterocycles containing 5, 6, 7, or 8 carbon atoms are shown in Table 7. Always there is a B_1 orbital both at the bottom and at the top of the π manifold.

For the freely optimised structures of C_5BeH_6 and C_7BeH_8 which are no longer planar, but which have C_s symmetry, although σ—π separation is not complete, the orbitals of approximate π character can still be readily identified from the eigenvectors, and these are also listed in Table 7. In C_2 symmetry (see below), A_2 and B_1 of C_{2v} become A and B respectively: in C_s symmetry if $\sigma(zx)$ is retained, A_2 and B_1 of C_{2v} become A'' and A' respectively.

There remains the C_2 isomer of C_8BeH_8 shown in Fig. 6f: this structure results from the optimisation of *spiro*-$Be(C_4H_4)_2$, starting with either a planar D_{2h} or a D_{2d} input. It is considerably more stable, ca. 70 kJ mol^{-1}, than the planar isomer obtained by optimising a planar monocyclic input. The molecule contains a re-entrant angle at beryllium, with the consequent close approach of beryllium to two of the carbon atoms C(4) and C(4′), 2.296 Å: in view of this the ligand should not be viewed as a *dihapto* species forming a pure beryllamonocycle, but as a tetrahapto chain forming a polycycle. There is strong bond fixation and distance alternation along the chain.

D_{nh}, D_{nd} and C_{nv} species

Table 3 lists the geometrical parameters resulting from constrained optimisations in the point group D_{nh} and D_{nd}, for species $(C_nH_n)_2Be$ and C_{nv} for species $(C_nH_n)Be$ (n even) or $(C_nH_n)BeH$ (n odd): the corresponding energies are listed in Table 1. With the exceptions of $(C_4H_4)Be$, $(C_5H_5)_2Be$, and $(C_5H_5)BeH$, discussed previously [2], no carbocycle $(CH)_n$ forms an η^n derivative of stability comparable with that of the free optimised structure usually of lower symmetry and lower η number. The smallest energy difference occurs between the D_{4h} isomer of $(C_4H_4)_2Be$ and its freely optimised analogue of D_{2h} symmetry which is only some 64 kJ mol^{-1} more stable: the largest energy difference amongst monoberyllium species is that between D_{6h} $(C_6H_6)_2Be$ and the freely optimised η^1,η^2 isomer, of 279.3 kJ mol^{-1}, while amongst diberyllium compounds the D_{8h} isomer of $(C_8H_8)Be_2$ is some 766 kJ mol^{-1} less stable than the freely optimised isomer.

A number of structural features show regular variations as the value of n changes. As n increases, so does the internal CCC angle in the rings, and simulta-

TABLE 7

ENERGIES (eV) AND SYMMETRIES OF π ORBITALS IN LARGER BERYLLAHETEROCYCLES C_5Be TO C_8Be

C_5BeH_6			C_6BeH_6		C_7BeH_8			C_8BeH_8		
C_{2v} [a]		C_s	C_{2v}		C_{2v} [a]		C_s	C_{2v}		C_2 [b]
3.675	B_1	3,566	3,691	B_1	4,031	B_1	3,819	3,760	B_1	3.290
1,185	B_1	1,417	2,387	A_2	1,555	B_1	1,733	2,512	A_2	2.884
0.585	A_2	0,509	0,622	B_1	1,372	A_2	1,267	1,322	B_1	1.298
−2.240	B_1	−1,918	−0,117	A_2	−0,652	B_1	−0,231	0,943	A_2	0,050
					−2,203	A_2	−2,052	−0,727	B_1	−0,072
- - - - -		- - - - -	- - - - -		- - - - -		- - - - -	- - - - -		- - - - -
−9.895	A_2	−9,626	−8,833	B_1	−9,391	B_1	−9,010	−8,378	A_2	−9,065
−12.343	B_1	−12,167	−9,972	A_2	−11,034	A_2	−11,248	−10,029	B_1	−9,629
			−12,024	B_1	−12,852	B_1	−12,656	−10,913	A_2	−10,843
								−12,142	B_1	−11.469

[a] Constrained optimisations, [b] Optimised from *spiro*-$Be(C_4H_4)_2$, D_{2h} or D_{2d}.

neously the CH bond length increases. At the same time, the parameter h_1, the perpendicular distance of the beryllium atom from a ring decreases, although care must be taken here to compare like species with like: the value of h_1 is much greater in $(C_nH_n)Be_2$ than in $(C_nH_n)Be$ for the same value of n. Again comparing like with like, as n increases, the value of CC decreases, as also does h_2, the perpendicular distance of the plane defined by the carbon atoms of a ring to the plane defined by the hydrogen atoms. For small ring compounds h_2 is ca. 0.5 Å, so that the hydrogen atoms are strongly tilted away from the beryllium atom: as the ring size increases, this tilt decreases to less than 0.01 Å in $(\eta^8\text{-}C_8H_8)Be$; in the D_{nh} species $(C_6H_6)Be_2$ and $(C_8H_8)Be_2$, h_2 must be zero.

As in $(C_5H_5)_2Be$ [2,4] only a single minimum was calculated by MNDO for the location of the beryllium atom when the rings in $(C_6H_6)_2Be$ were constrained to be parallel, either eclipsed or staggered, and the beryllium was contrained to various sites on the six-fold axis: since the single minimum in $(C_5H_5)_2$-Be appears to be a computational artefact [7], those in the D_{6h} and D_{6d} isomers of $(C_6H_6)_2Be$ may be also.

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