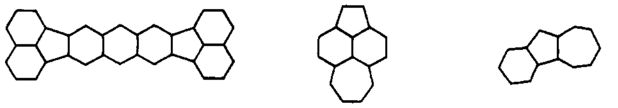
Chart I



-0.381	-0.503	-0.668
-0.371	-0.445	-0.388
0.298 (6.74)	0.445 (7.17)	0.323 (7.05)
0.618 (7.53)	0.669 (7.87)	0.842 (8.20)

seen from Figure 7 where the observed band positions for Clar's hydrocarbon are compared with those calculated by eq 2–4. Conversely, among hydrocarbons with the same p band position,[38] the nonalternant ones have always higher IP_1 values.

At the most naive level, this seemingly paradox behavior is due to the fact that in alternant hydrocarbons (for which the pairing theorem holds) the partial bond orders between AO's of the same—starred or unstarred—set are positive for HOMO and LUMO, while they are negative for the second highest occupied and second lowest unoccupied orbitals. Introduction of a new bond to give a five-membered ring will thus lower the HOMO and LUMO energies, while the second highest occupied and second lowest unoccupied levels are raised. This results in a decrease of the HOMO–LUMO gap, as shown in the Hückel correlation diagram (Figure 11) for the simplest case of interest, namely, 3,4-benzophenanthrene and 2,13-benzofluoranthene. Although the latter has the higher IP_1 value (7.90 vs. 7.61 eV), it absorbs at longer wavelengths.

Hückel calculations for a large number of known as well as unknown nonalternant hydrocarbons show that the lowering of the HOMO and LUMO energies is a quite general result. Among the known compounds, for which PE spectra are available, only three exceptions were found; their eigenvalue coefficients for the two lowest unoccupied and highest occupied levels, with measured IP's in brackets, are shown in Chart I. Yet their absorption bands are at longer wavelengths than expected on the basis of eq 2–4. This applied also to acepleiadylene which, judging from its level scheme, might be considered as quasi-alternant. Its p band in benzene as solvent is expected at 385 nm, while it is found at about 570 nm.

A forthcoming paper in this series will describe application of our scheme to some long-standing structural problems, for instance, the hydrocarbon obtained from naphthalene and fumaryl chloride[39] and the compounds formed in the attempted syntheses of terrylene and quaterrylene.[40]

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(38) The p band corresponds in a good approximation (see eq 3) to the HOMO–LUMO transition.

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A Molecular Orbital Study of Hydrogen, Methyl, and Phenyl Bridging in Beryllium Compounds

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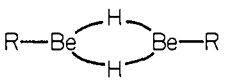
Abstract: A detailed molecular orbital study of molecules of the type $\mathrm{R^tBeR^b{}_2BeR^t}$ and the corresponding monomers $\mathrm{R^tBeR^b}$ is presented for $\mathrm{R^t}$ = H, CH_3, F, BH_4, C_5H_5, and phenyl and $\mathrm{R^b}$ = H, CH_3, or phenyl. The effect of a substituent in the $\mathrm{R^t}$ position is measured by calculating ΔE's for dimerization and comparing them to that for $\mathrm{R^t}$ = H. Cyclopentadiene groups are shown to *strongly* disfavor dimerization, while CH_3 or F substituents in the $\mathrm{R^t}$ position slightly destabilize the dimers. BH_4 substituents provide a small dimer stabilization. Phenyl bridging is shown to be highly favored relative to methyl bridging. These effects are rationalized by examining orbital interactions, particularly π-bonding effects involving formally vacant orbitals on beryllium.

Introduction

While the phenomenon of hydrogen bridging has been well studied in the boron hydrides, carboranes, and related molecules,[1] significantly less is known about bridge formation in molecules containing beryllium. Of particular interest is the fact that unlike boron, beryllium-containing molecules are known to form bridges with methyl[2] and phenyl[3] groups, in addition to hydrogen bridges.

The simplest system in which a Be–H–Be bond occurs is the beryllium hydride dimer. Although I has not been observed experimentally, it has been thoroughly studied by accurate SCF-CI calculations,[4] which have placed the dimerization energy at ~30 kcal/mol. This value is comparable to the borane dimerization energy, which is thought to be ~35 kcal/mol.[5] Other examples of bridge hydrogens involving beryllium include solid BeH_2, $EtBeH_2BeEt_2{}^{2-}$, beryllium borohydride, and methylberyllium borohydride,[6-9] the latter two examples having Be–H–B bridges.



$$\mathrm{R{-}Be(\mu\text{-}H)_2Be{-}R}$$

I

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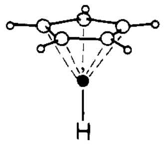
While it is generally true that molecules containing Be–H terminal bonds tend to dimerize via the formation of double hydrogen bridges, a notable exception is cyclopentadienylberyllium hydride (II), which exists as a monomer in the gas phase.[10]



II

The known structural chemistry of methylberyllium compounds closely parallels that of the beryllium hydrides. In the solid phase, dimethylberyllium exists as an infinite polymer with double methyl bridges.[11] The gas-phase energy of dimerization of dimethylberyllium is not accurately known; however, observations of some monomer and dimer are consistent with a ΔH in the range of −10 to −15 kcal/mol.[12,13] Derivatives of methylberyllium compounds include methylberyllium borohydride, which exist only as dimers (via double methyl bridges) in the gas phase.[9] However, as in the corresponding case of hydrogen, the compound methylcyclopentadienylberyllium exists only as gas-phase monomers.[14] Both cyclopentadienylberyllium hydride and methylcyclopentadienylberyllium have structures in which the beryllium is symmetrically π-bonded to the cyclopentadienyl ring.

Other bridging groups in which carbon is the bridging atom are known. Diethylberyllium, diisopropylberyllium, and several other similar species are all though to be dimeric.[2,3] Phenyl bridging is also thought to occur in diphenylberyllium[3] and in $(LiBePh_3)_2$.[15] However, little structural data are available. Finally, many electron-rich atoms or groups such as ethers, substituted amines, and halogens are thought to participate in bridge formation to beryllium;[2] however, when more than one electron pair is available for bonding, these bonding arrangements are probably more accurately described as coordinate bonds rather than two-electron, three-center bonds.

In this paper, we present a molecular orbital study of a large number of monomers and dimers of compounds containing beryllium. Our discussion will be limited to dimerization through hydrogen, methyl, or phenyl groups. Of particular interest to us is the substituent effect on the dimerization energy due to a group R^t when dimerization is through some other (possibly different) group R^b. Such effects will be quantitatively measured by calculating *relative* ΔE's for the series of reactions

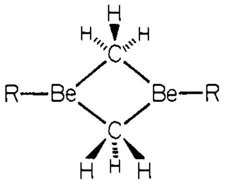
$$2R^t\text{–Be–}R^b \xrightarrow{\Delta E} R^t\text{–}R^b{}_2\text{Be–}R^t$$

where we denote the bridging group as R^b and the terminal group as R^t. Our study includes all possible combinations of R^b and R^t, where R^b = H, CH_3, or Ph and R^t = H, CH_3, Ph, BH_4, or F. We will show that the degree of R^t–Be π bonding plays an important role in understanding the substituent effects on the dimerization energy. Some of the important conclusions we will arrive at include the following: (1) cyclopentadienylberyllium derivatives (hydride, methyl, phenyl, and fluoro) should be monomers in the gas phase, (2) phenyl bridging is energetically favored relative to methyl bridging, and (3) BH_4 in the R^t position tends to favor dimerization, while CH_3 and F destabilize the dimers.

Calculations

Most calculations were done within the approximation of partial retention of diatomic differential overlap (PRDDO).[16] This method, which closely simulates ab initio minimum basis set calculations, is particularly suited to this study because the basic n^3 dependence inherent in PRDDO results in enormous savings in computer time for the large (up to 150 minimum basis set orbitals) systems studied here. Standard exponents given by Hehre et al.[17] were used throughout.

To avoid lengthy geometry optimizations, we adopted a set of standard bond lengths for most calculations reported here. Terminal Be–H (1.30 Å) and Be–CH_3 (1.68 Å) were taken from optimized values for BeH_2 and H–Be–CH_3, respectively. Terminal methyl groups were assumed to be tetrahedral. For hydrogen bridging, the optimized parameters of $HBeH_2BeH$ (Be–H_b = 1.46 Å, Be–Be = 1.90 Å) were used. Methyl-bridged parameters were taken from partially optimized H–Be $(CH_3)_2$Be–H (III) constrained to C_{2h} symmetry. The Be–H and C–H distances were held constant at 1.30 and 1.09 Å, respectively. Optimized bond lengths and angles are as follows: Be–C = 1.811 Å; Be–Be = 1.852 Å; H_1–C–H_1' = 100.8°; H_1–C–H_2 = 105.3°. $BeBH_4$ parameters were taken from previous optimizations of beryllium borohydride.[18] Be–B = 1.918 Å; Be–H_b = 1.487 Å, B–H_b = 1.323 Å. Beryllium–carbon distances for phenyl rings were taken as 1.68 Å (terminal) and 1.81 Å (bridging). For π-bound cyclopentadiene rings, the Be–ring distance was 1.47 Å, optimum for cyclopentadienylberyllium borohydride. Carbon–carbon distances were 1.40 Å in all cyclopentadienyl and phenyl rings.



III

The above choice of geometrical parameters makes this study computationally practical; however, they should also be usefully accurate. As a partial check of their reliability we have calculated ΔE's for the dimerization of $HBeCH_3$, BH_4BeH, and PhBeH via hydrogen-bridge formation with optimization of the Be–Be, Be–H, and Be–R^t distances in the monomer and the dimer. Relative ΔE's were not affected significantly (see below). We note also that the use of standard geometries greatly facilitates the analysis of the relative importance of effects such as π bonding in stabilizing a particular structure. This will be shown to be important in the methyl and phenyl derivatives studied here. With C–Be distances held constant at 1.81 Å for Be–R^b and 1.68 Å for Be–R^t, the π-bonding effects manifest in the population analysis will be due solely to electronic effects and not to geometry differences.

The accuracy of our calculations must be discussed from two perspectives: how accurate are minimum basis set calculations for quantities such as dimerization energies and how successful is the PRDDO approximation in reproducing ab initio results?

Ab initio minimum basis set calculations tend to underestimate *absolute* dimerization energies when bridge bond formation is involved. For instance, minimum basis set calculations on the dimerization of borane yield[19] a calculated ΔE of −7.3 kcal/mol, compared to the most probable experimental value[20] of −35 kcal/mol. This error is due partly to the lack of polarization functions (~12 kcal/mol) and partly to neglect of electron correlation (~16 kcal/mol). Similar trends are evident in the BeH_2 dimerization, where the most probable dimerization energy[4] is

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Table I. Comparison of PRDDO and ab Initio Results[a]

reaction	$\Delta E_{\mathrm{PRDDO}}$	ΔE_{c}[b]	ΔE_{4G}
$2BeH_2 \rightarrow HBeH_2BeH$	−40.4	−17.9	−18.3
$CH_3BeH + BeH_2 \rightarrow CH_3BeH_2BeH$	−32.4	−15.2	−15.8
$2CH_3BeH \rightarrow CH_3BeH_2BeCH_3$	−25.0	−13.0	−13.1
$2FBeH \rightarrow FBeH_2BeF$	−10.0	−2.0	−1.8
$2BH_4BeH \rightarrow BH_4BeH_2BeBH_4$	−38.7	−23.4	−28.0
$CH_3BeH + (CH_3)_2Be \rightarrow CH_3Be(CH_3)_2BeH$	+0.3	+6.2	+4.9
$2CH_3BeH \rightarrow HBe(CH_3)_2BeH$	−7.2	+0.5	+0.7
$FBeCH_3 + CH_3BeH \rightarrow FBe(CH_3)_2BeH$	+0.4	+6.3	+7.2
$FBeH \rightarrow HBeF_2BeH$	−126.3	−90.0	−84.4

[a] kcal/mol, standard geometries. [b] Corrected ΔE, see text.

~30 kcal/mol, but the minimum basis set value is ~−18 kcal/mol (Table I). Our primary interest, however, is not the *absolute* values of the dimerization energies but rather the *relative* values as the R^b or R^t group is varied. Minimum basis sets should be substantially more reliable at predicting such trends. Furthermore, we will show that our results are qualitatively consistent with available experimental data.

The accuracy of PRDDO compared to ab initio minimum basis set calculations can be tested directly. First, we note that approximate molecular orbital methods less sophisticated than PRDDO (e.g., extended Hückel, CNDO, or INDO) are not likely to give usefully accurate results for a study of bridge bond formation. For instance, in a comparative study of the ΔE's for nine reactions involving boron hydrides with CNDO, INDO, PRDDO, and ab initio SCF calculations,[21] Halgren et al. find root-mean-square errors (relative to the ab initio calculations) of over 200 kcal/mol for CNDO and INDO, compared to only 7 kcal/mol for PRDDO. In Table I, we show a comparison of PRDDO and STO-4G calculated ΔE's for nine association reactions involving formation of bridging hydrogens, methyls, or fluorines. One systematic error is obvious: for reactions involving BeH_2, PRDDO predicts ΔE's which are too low. This problem is related to the fact that BeH_2 was included in the original PRDDO parameterization[16] and, therefore, PRDDO reproduces the ab initio energy quite accurately. Since PRDDO in general tends to yield energies which are too low, this leads to relatively lower energies for the dimers and, therefore, dimerization energies which are too low. This effect, and most other sources of error, can be eliminated by assuming a least-squares relationship between ΔE_{4G} and $\Delta E_{\mathrm{PRDDO}}$ to yield corrected PRDDO energies

$$\Delta E_{\mathrm{c}} = 0.76\Delta E_{\mathrm{PRDDO}} + 6.0 - 3.4n$$

where n is the number of BeH_2 monomers in the reaction. This equation amounts to an additive correction to ΔE of 3.4 kcal/mol for each BeH_2, coupled with an assumed linear relationship between E_{PRDDO} and E_{4G}. The standard deviation for the nine values in Table I is 2.9 kcal/mol, while the dimerization energies themselves vary from +7.2 to −84.4 kcal/mol. We have used this correction without change for all dimerizations studied here; however, we wish to emphasize that with the exception of the additive correction for BeH_2, the *qualitative conclusions derived from these calculations are independent of this correction* and can also be obtained directly from the PRDDO energetics. In Table II, we present the PRDDO total energies, and Table III gives the calculated dimerization energies.

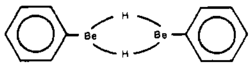
Results and Discussion

Monomer Conformations. All calculations refer to the lowest energy conformation of the monomer. For all cyclopentadienylberyllium derivatives (H, CH_3, and phenyl) there is a strong preference for η^5 bonding (Table II). The double-bridged forms of BH_4BeH and BH_4BeCH_3 are calculated to be 0.1 and 0.4 kcal/mol more stable than the triple-bridged forms (full-geometry optimization). Ahlrich[4] finds HBH_3BeH to be ~7 kcal/mol more stable than H_2BH_2BeH. The structure of methylberyllium borohydride is not known experimentally, but the dimer is known[9] to have double hydrogen bridges. Diphenylberyllium is calculated to have perpendicular phenyl rings, the planar structure being 0.4 kcal/mol less stable. Finally, phenylberyllium borohydride shows a preference for a double-bridged structure with the bridge hydrogens in the plane of the phenyl ring. The structure obtained by rotating the phenyl ring 90° is 3.0 kcal/mol less stable, while the triple-bridged structure is 1.9 kcal/mol less stable.

Bridging Hydrogen Dimers. For hydrogen-bridged dimers, we have checked the appropriateness of our standard bond lengths and angles by performing partial optimizations of the monomers and dimers of BH_4BeH, CH_3BeH, and PhBeH as discussed above. We find that geometry optimization results in the following changes in the calculated $\Delta E_{\mathrm{PRDDO}}$ values relative to those reported in Table III: BH_4BeH (−2.2 kcal/mol), CH_3BeH (0.0 kcal/mol), and PhBeH (−1.3 kcal/mol). The use of standard bond lengths is clearly justifiable for these molecules.

The effects of substituents in the R^t position will be discussed relative to $R^t = H$. For $R^t = CH_3$, ΔE is raised by 4.9 kcal/mol (here and in the remainder of the discussion we refer to corrected ΔE values, column 2 of Table III). This effect is most probably due to a stabilization of the monomer rather than destabilization of the dimer. The monomer is stabilized by methyl–beryllium π donation, which is manifest in the population analysis by a total Be π-orbital population of 0.16 e. In the dimer, π donation is substantially reduced, since the dimer possesses only half the number of formally unoccupied orbitals on beryllium capable of acting as π acceptors. Implicit in this argument is the reasonable assumption that upon bridge bond formation, the monomer π orbital which participates in bonding to the bridging group will be substantially less receptive to R^t–Be π bonding, since it is formally occupied in the dimer. The same explanation holds for $R^t = F$. Here, the π-orbital population on Be is 0.48 e in the monomer, and this stabilizing effect increases ΔE by 15.9 kcal/mol (relative to $R^t = H$).

The phenyl substituent effects depend on the conformation of the dimer. The planar dimer IV is 13.4 kcal/mol more stable than the conformation with the BeH_2Be plane perpendicular to the phenyl rings. Again, this is clearly related to π-donation effects. In the planar configuration, the π system of the planar rings delocalize to the extent of 0.14 e in the vacant Be π orbital. In the perpendicular conformer, the phenyl π system is orthogonal to the vacant Be p orbital, and delocalization is negligible. Since π donation is operative in the monomer, phenyl substitution destabilizes the dimer in the perpendicular configuration. This effect is calculated to be 6.3 kcal/mol relative to $R^t = H$. In the more stable planar configuration, however, phenyl substitution favors dimerization by 3.8 kcal/mol. This effect can be rationalized by comparing the relative amounts of π donation in PhBeH monomer and planar dimers. The π-electron populations on Be are 0.11 e (monomer) and 0.14 e (dimer). Note that the reduction in the number of formally occupied orbitals in the dimer is not important when considering the relative amount of π donation in the phenyl-substituted molecules, since effectively all of the phenyl π donation originates from only one perpendicular p component (the phenyl π system) as opposed to both perpendicular π components in the case of methyl substitution. The increase of π donation in the dimer is probably associated with direct Be–Be interaction, as indicated by the increase in the Be–Be overlap population from 0.361 (perpendicular conformer) to 0.374 (planar conformer).



IV

The case of $R^t = C_5H_5^-$ is particularly interesting. With use of the standard geometry, the calculated ΔE of dimerization is +50 kcal/mol, a full 68 kcal/mol higher than the case $R^t = H$. This result is in complete accord with experiment, since cyclopentadienylberyllium hydride exists only as monomers in the gas phase.[10] The explanation for this dramatic substituent effect may

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Table II. Total Energies[a]

molecule	energy	molecule	energy	molecule	energy
BeH_2	−15.7219	$HBe(CH_3)_2BeH$	−109.4727	$CH_3BePh_2BeCH_3$	−568.1165
Be_2H_4	−31.5082	$HBe(CH_3)_2BeCH_3$	−148.4674	BH_4BePh[i]	−271.4216
CH_3BeH	−54.7306	$(CH_3BeCH_3)_2$	−187.4589	BH_4BePh[j]	−271.4168
CH_3BeH_2BeH	−70.5042	BH_4BeCH_3	−81.1188	$(BH_4BePh)_2$	−542.9273
$CH_3BeH_2BeCH_3$	−109.5011	$(BH_4BeCH_3)_2$	−162.2580	FBEPh	−343.5085
BH_4BeH	−42.1187	$FBeCH_3$	−153.2103	$FBePh_2BeF$	−687.0659
$(BH_4BeH)_2$	−84.2991	$FBe(CH_3)_2BeF$	−306.4085	PhBePh[k]	−474.3369
FBeH	−114.2098	$PhBeCH_3$	−284.0354	PhBePh[l]	−474.3362
$FBeH_2BeF$	−228.4364	$PhBe(CH_3)_2BePh$[b]	−568.0710	$(PhBePh)_2$[b]	−948.7493
PhBeH	−245.0283	$PhBe(CH_3)_2BePh$[c]	−568.0623	$(PhBePh)_2$[c]	−948.7349
$PhBeH_2BePh$[b]	−490.1147	$CpBeCH_3$[d]	−246.2340	CpBePh[d]	−436.5371
$PhBeH_2BePh$[c]	−490.0934	$CpBeCH_3$[f]	−246.1639	CpBePh[f]	−436.4646
CpBeH, C_{5v}	−207.2493	$CpBe(CH_3)_2BeCp$[d]	−492.1299	$CpBePh_2BeCp$[d]	−872.8572
CpBeH, C_s	−207.1547	$CpBe(CH_3)_2BeCp$[e]	−492.2222	$CpBePh_2BeCp$[e]	−872.9211
$CpBeH_2BeCp$[d]	−414.4055	$CpBe(CH_3)_2BeCp$[f]	−492.3127	$CpBePh_2BeCp$[f]	−872.9863
$CpBeH_2BeCp$[e]	−414.3962	$FBe(CH_3)_2BeH$	−207.9402	$HBeF_2BeH$	−228.6209
$CpBeH_2BeCp$[f]	−414.3616	$HBePh_2BeH$[g]	−490.1323		
CH_3BeCH_3	−93.7363	$HBePh_2BeH$[h]	−489.9631		

[a] Atomic units. [b] Planar conformation for R^t. [c] Perpendicular conformation for R^t. [d] π-bound Cp rings. [e] 1 σ- and 1 π-bound Cp ring. [f] σ-bound Cp rings. [g] Perpendicular configuration for Ph. [h] Planar configuration for Ph. [i] Plane defined by Be and bridge hydrogens coplanar to phenyl ring. [j] Plane defined by Be and bridge hydrogens perpendicular to phenyl ring. [k] Phenyl rings are perpendicular. [l] Phenyl rings are coplanar.

Table III. Calculated ΔE's and Substituent Effects

	ΔE[a]	ΔE_c[b]	$\Delta\Delta E$[c]
Bridge Hydrogen Formation			
$2BeH_2 \rightarrow Be_2H_4$	−40.4	−17.9	0
$2CH_3BeH \rightarrow CH_3BeH_2BeCH_3$	−25.0	−13.0	+4.9
$2BH_4BeH \rightarrow (BH_4BeH)_2$	−38.7	−23.4	−5.5
$2FBeH \rightarrow FBeH_2BeF$	−10.5	−2.0	+15.9
$2PhBeH \rightarrow PhBeH_2BePh$[d]	−36.4	−21.7	−3.8
$2PhBeH \rightarrow PhBeH_2BePh$[e]	−23.1	−11.6	+6.3
$2CpBeH \rightarrow (CpBeH)_2$[f]	+58.4	+50.4	+68.3
$2CpBeH \rightarrow (CpBeH)_2$[g]	+64.3	+54.9	+72.8
$2CpBeH \rightarrow (CpBeH)_2$[h]	+86.0	+71.4	+89.3
Bridge Methyl Formation			
$2CH_3BeH \rightarrow HBe(CH_3)_2BeH$	−7.2	+0.5	0
$2CH_3BeCH_3 \rightarrow (CH_3BeCH_3)_2$	+8.6	+12.5	+12.0
$2BH_4BeCH_3 \rightarrow (BH_4BeCH_3)_2$	−12.8	−3.8	−4.3
$2FBeCH_3 \rightarrow FBe(CH_3)_2BeF$	+7.7	+11.9	+11.4
$2PhBeCH_3 \rightarrow PhBe(CH_3)_2BePh$[d]	−0.1	+5.9	+5.4
$2PhBeCH_3 \rightarrow PhBe(CH_3)_2BePh$[e]	+5.3	+10.0	+9.5
$2CpBeCH_3 \rightarrow CpBe(CH_3)_2BeCp$[f]	+212.2	+167.3	+166.8
$2CpBeCH_3 \rightarrow CpBe(CH_3)_2BeCp$[g]	+154.2	+123.2	+122.7
$2CpBeCH_3 \rightarrow CpBe(CH_3)_2BeCp$[h]	+97.5	+80.1	+79.6
Bridge Phenyl Formation			
$2HBePh \rightarrow HBePh_2BeH$	−47.5	−30.1	0
$2CH_3BePh \rightarrow CH_3BePh_2BeCH_3$	−28.7	−15.8	+14.3
$2BH_4BePh \rightarrow (BH_4BePh)_2$	−52.8	−34.1	−4.0
$2FBePh \rightarrow FBePh_2BeF$	−30.7	−17.3	+12.8
$2PhBePh \rightarrow PhBePh_2BePh$[d]	−47.4	−30.0	+0.1
$2PhBePh \rightarrow PhBePh_2BePh$[e]	−39.2	−23.8	+6.3
$2CpBePh \rightarrow CpBePh_2BeCp$[f]	+136.2	+109.5	+139.6
$2CpBePh \rightarrow CpBePh_2BeCp$[g]	+96.1	+79.0	+109.1
$2CpBePh \rightarrow CpBePh_2BeCp$[h]	+55.2	+48.0	+78.1

[a] ΔE_{PRDDO}, kcal/mol. [b] Corrected ΔE_{PRDDO}, kcal/mol. [c] Change in ΔE as the R^t group is varied, kcal/mol. [d] Planar conformation for R^t. [e] Perpendicular conformation for R^t. [f] π-bound Cp rings. [g] 1 σ- and 1 π-bound Cp ring. [h] σ-bound Cp rings.

be seen by examining the orbital interaction diagram for two C_5H_5BeH fragments (Figure 1) and the nature of the highest occupied molecular orbital in the dimer (Figure 2). The lowest a_1 symmetry orbital (omitting orbitals exclusively on the cyclopentadiene ring) is associated with ring–Be interactions in the monomer. These orbitals interact upon dimerization to produce plus and minus combinations which have relatively little effect on the overall energetics. The second lowest a_1 orbitals, well localized on beryllium and hydrogen, combine to produce two lower energy orbitals in the dimer, corresponding to the bridge hydrogen orbitals. The e type orbitals in the monomer, which

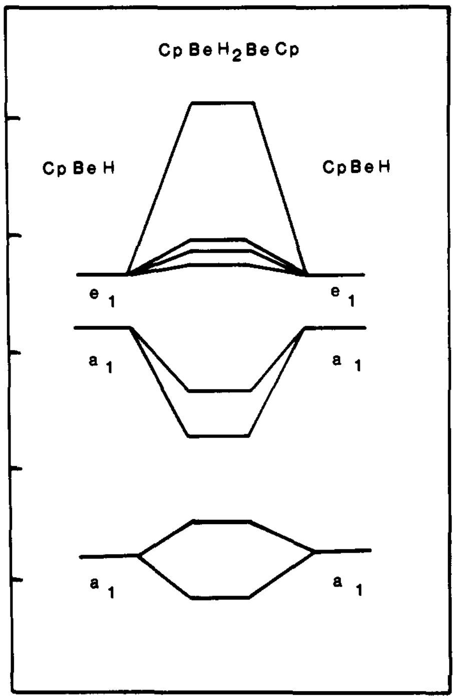


Figure 1. Interaction diagram of two cyclopentadienylberyllium hydride monomers (C_{5v} symmetry) forming the double hydrogen-bridged dimer.

consist primarily of carbon p_z–beryllium p_x,p_y, produce three orbitals which are relatively unchanged and one (the highest occupied molecular orbital in the dimer) which is greatly elevated in energy. This pattern is characteristic of all dimers of $C_5H_5Be–R$ (R^b = H, CH_3, or Ph). The shape of the highest occupied molecular orbital (Figure 2) shows at once why this orbital adversely affects dimerization. The ring contributions to this orbital are similar in shape to one of the two degenerate orbitals in $C_5H_5^-$ and are bonding. Likewise, the beryllium-bridge hydrogen interaction is bonding (although there is very little electron population on Be); however, the interactions between the rings and the BeH_2Be fragment is antibonding, or if one neglects the small population on Be, it may be considered nonbonding. The reason for this ring–Be weakening is clear. For effective ring–Be bonding in C_5H_5BeH, the beryllium uses both p_x and p_y orbitals to overlap with the ring π orbitals, forming a degenerate set. The remaining orbitals on beryllium are used for ring–Be and Be–H orbitals of a_1 symmetry. Dimerization forces one of the beryllium p orbitals perpendicular to the pseudo-fivefold axis to be used for bridge

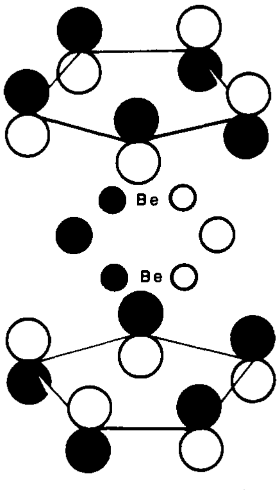
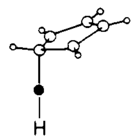


Figure 2. Shape of the highest occupied molecular orbital of cyclopentadienylberyllium hydride dimer. The orbitals shown are the bridge hydrogen 1s, one component of the beryllium 2p's, and the cyclopentadiene π orbitals.

hydrogen formation and weakens the ring–Be interaction. The situation is very similar to previous interpretations of the relative instability of D_{5d} dicyclopentadienylberyllium.[22,23] One might think that this problem could be alleviated by making one or both of the cyclopentadiene rings σ bound to the beryllium as in V,



V

but the calculated energy difference between V and II is so large (59 kcal/mol)[24] that dimers with one or two Be σ bonds to the cyclopentadiene ring have substantially higher energy (Table II).

Finally, substitution of BH_4 for H in the R^1 position stabilizes the dimer by 5.5 kcal/mol. While it is difficult to trace the exact physical origins of this effect, we note that the Be-Be overlap population increases from 0.37 in $HBeH_2BeH$ to 0.40 in $BH_4BeH_2BeBH_4$. This increase is entirely due to 2s–2p interactions along the bond axis and may be related to the fact that in the $HBeBH_4$ monomer, the Be p_z orbital (taking z as the major axis) is relatively underpopulated (0.76 e) compared to the same orbital in BeH_2 (0.96 e) and therefore may be able to participate more fully in direct Be–Be bonding upon dimerization. The lower population of the p_z orbital in $HBeBH_4$ is a direct consequence of the lack of a strong Be–R^1 σ interaction when $R^1 = BH_4^-$.

Bridging Methyl Dimers. Substituent effects for the methyl-bridged systems closely parallel those with hydrogen bridges. While most of the calculated ΔE's for dimerization through methyl groups are positive, it must be remembered that our minimum basis set calculations neglect the effects of polarization functions and electron correlation, both of which should favor dimerization. These effects should not be seriously perturbed by substituents in the R^1 position, and our *relative* ΔE's should be reasonably reliable.

Relative to H in the R^1 position, CH_3, F, and phenyl (both conformations) all increase the dimerization energy; however, a quantitative relationship between π-orbital populations on beryllium and relative ΔE's is not found. In contrast to the hydrogen-bridged species, the phenyl groups in planar $PhBe(CH_3)_2BePh$ destabilize the dimer by 5.4 kcal/mol, relative to H, although the planar conformation is still preferred by ~5 kcal/mol. The likely explanation involves the fact that the bridging methyls themselves show appreciable π bonding to Be (0.05 e in $HBe(CH_3)_2BeH$ and 0.06 e in the perpendicular conformation of $PhBe(CH_3)_2BePh$). This has the effect of reducing the stabilizing π donation from the phenyl group, as evidenced by the Be π-orbital population of 0.15 e in planar $PhBe(CH_3)_2BePh$. If we attribute ~0.05 e to bridging methyl–Be interactions, the phenyl group donates ~0.10 e, substantially less than the 0.14-e donation found in planar $PhBeH_2BePh$. BH_4 again favors dimerization. Our calculations suggest that BH_4BeCH_3 dimerization is favored by ~16 kcal/mol over $Be(CH_3)_2$ dimerization, qualitatively consistent with the experimental observation that BH_4BeCH_3 exists only as dimers in the gas phase,[9] while $Be(CH_3)_2$ is predominately monomer.[12] With $R^1 = C_5H_5$, the calculated ΔE (Table III) is very large and positive, again in accord with the experimental observation that $C_5H_5BeCH_3$ is monomeric in the gas phase.[15] In addition to the electronic effects discussed above for the hydrogen-bridged species, steric effects between the methyl hydrogens and cyclopentadienyl rings likely contribute to the high value for this ΔE. Unlike the hydrogen-bridged system, $C_5H_5Be(CH_3)_2BeC_5H_5$ is substantially more stable if one or both rings are σ bound to the beryllium. However, even with both rings σ bound the calculated ΔE for dimerization is still very high (~80 kcal/mol).

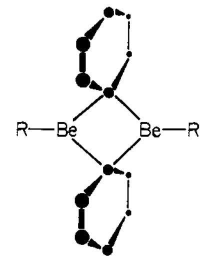


Figure 3. Structure of the most stable conformation of $RBePh_2BeR$ species.

Bridging Phenyl Dimers. Two possible conformations of phenyl-bridged dimers were considered, corresponding to the bridging phenyl rings being either perpendicular or coplanar to the plane defined by the beryllium atoms and the bridging carbons. For $HBePh_2BeH$, the planar conformation is calculated to be 106 kcal/mol less stable than the perpendicular configuration (Figure 3), due to steric interactions between phenyl hydrogens and the hydrogens bound to beryllium. For this reason, only the perpendicular configuration was considered for $R^1 = CH_3$, BH_4, F, C_5H_5, and phenyl.

Phenyl groups strongly favor dimerization. In fact, the calculated ΔE's for dimerization via phenyl bridges are negative for all groups in the R^1 position except C_5H_5 and average 29 kcal/mol lower than the corresponding methyl bridged species. This effect is due to interactions between the π electrons in the phenyl rings and the beryllium 2s and $2p_x$ orbitals (with the berylliums positioned on the z axis and bridging carbons on the x axis). The Be–C overlap population increases from 0.40 in $HBe(CH_3)_2BeH$ to 0.48 in $HBePh_2BeH$, with essentially all of the increase arising from the above two interactions. Similarly, the 2s and $2p_x$ populations on beryllium increase by 0.04 e and 0.09 e, respectively, upon going from $HBe(CH_3)_2BeH$ to $HBePh_2BeH$.

While the ΔE's for phenyl bridging are uniformly lower than those for hydrogen or methyl bridging, the relative substituent effects in the R^1 position are substantially the same. Methyl, fluoro, and cyclopendienyl groups all destabilize the dimer relative to R^1 = H, while BH_4 provides a small stabilization. Phenyl groups destabilize the dimer when the R^1 phenyls are in perpendicular configuration and have little effect when in the planar configuration. These effects may all be qualitatively accounted for by orbital interactions discussed above for hydrogen and methyl bridges.

Conclusions

Molecules of the type C_5H_5BeX, X = H, CH_3, or phenyl, should exist as monomers in the gas phase. A preliminary study[25] of

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[22] Marynick, D. S. *J. Am. Chem. Soc.* **1977**, *99*, 1436.

[23] Jemmis, E.; Alexandratos, S.; Schleyer, P. V. R.; Streitwieser, A.; Schaefer, H. F. *J. Am. Chem. Soc.* **1978**, *100*, 5695.

[24] This value is comparable to those obtained from ab initio calculations[23] and semiempirical work (Dewar, M. J. S.; Rzepa, H. S. *J. Am. Chem. Soc.* **1978**, *100*, 777).

C_5H_5BeF also shows dimerization to be disfavored by ~57 kcal/mol, even though dimerization of HBeF through fluorine is favored by ~90 kcal/mol. Both CH_3 and F in the R^t position tend to destabilize the dimers regardless of the bridging group, and BH_4 provides a uniform dimer stabilization. Phenyl bridging is calculated to be highly favorable, suggesting a rich chemistry of molecules of the type $R^tBePh_2BeR^t$.

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(25) Marynick, D., unpublished work.

Chair–Boat Equilibria in Bicyclo[3.3.1]nonane at 65 and 400 °C Studied by Electron Diffraction and Molecular Mechanics[†]

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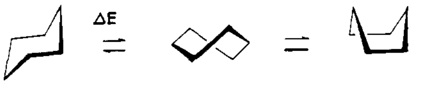
Abstract: Gaseous bicyclo[3.3.1]nonane has been studied by electron diffraction with a new high-temperature nozzle system at a temperature of 400 °C. The structural analysis revealed substantially more (ca. 25%) of the boat–chair conformer than in the previous investigation carried out at a lower temperature (ca. 5% at 65 °C). This result is in excellent agreement with molecular mechanics calculations leading to the value of 2.3 kcal/mol as the energy difference between boat–chair and twin chair conformers. The structural parameters obtained by molecular mechanics calculations are in good agreement with the experimental results, which for both conformers are (with estimated errors of 3σ): C–C = 1.536 (1) Å, C–H = 1.109 (3) Å, H–C–H = 107.6 (3.7)°, C_1–C_9–C_5 = 108.5 (4.2)°, C_2–C_3–C_4 = C_6–C_7–C_8 = 112.8 (4.5)°, θ = 123.4 (1.5)°, ϕ = 44.7 (2.3)°. The amplitudes of vibration were calculated and used in the analysis as fixed values.

Introduction

The potential conformational mobility of the bicyclo[3.3.1]nonane (henceforth BN) rings makes it an interesting system for study. Accordingly, the chemistry of BN has received much attention from both synthetic[1] and theoretical points of view. For BN three conformers CC, BC, and BB are possible by analogy with cyclohexane (C = chair, B = boat). There is, however, one important quantitative difference between BN and cyclohexane due to the serious endo 3,7 hydrogen–hydrogen transannular interaction in the former system, which leads to the relation

$$\Delta E_1 < \Delta E_2 \approx \Delta E$$

CC (C_{2v}) BC (C_s) BB (C_2)



C (D_{3d}) D_2 C_{2v}

The greater accessibility of the boat conformation in BN (ΔE_1 is calculated from 1.5 to 2.5 kcal/mol) than in cyclohexane ($\Delta E \approx$ 5–6 kcal/mol[2]) has been predicted by molecular mechanics calculations[3,4] for BN itself and verified experimentally ($\Delta E_1 \approx$ 2.1–2.7 kcal/mol[5]) for some of its derivatives.[6] This provided the hope that a detectable amount of the BC conformer might be obtained in an appropriate high-temperature experiment. Since no experimental ΔE_1 or ΔE_2 values have been previously reported for BN, we felt that even a rough measurement of this quanity would be worthwhile.[7]

Earlier we studied the geometry of the CC conformer in BN by electron diffraction.[8] It was logical, therefore, to try to use the same method for the detection of the BC conformer, because there already were many successful applications of electron diffraction to the study of conformational problems.[9-14]

It was clear from the outset that it would be a difficult task to identify the BC conformer on the background of CC conformer, since they have a similar distribution of internuclear distances. Bearing in mind the limited accuracy of electron diffraction, two

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[†] Dedicated to Professor Otto Bastiansen in honor of his sixtieth birthday.

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