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A THEORETICAL STUDY OF CYCLOOCTATETRAENEBERYLLIUM *

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Summary

An ab initio STO-3G SCF study of beryllium cyclooctatetraenide (BeCOT) shows that a Saturn-like structure is less stable than alternative non-planar and polymeric structures. In the Saturn structure the Be lies in a number of nodal planes and bonding is largely ionic. Moving the Be out of the ring plane permits covalent bonding interactions as well.

Cyclooctatetraene (COT) forms organometallic derivatives in an impressive variety of ways. The alkali metals form salts of cyclooctatetraene dianion in which the 10-π-electron C_8H_8 rings are planar [1,2]. The planar aromatic character of this ring system has been further demonstrated by recent X-ray crystal structures of the dipotassium salts of COT dianion [3] and of 1,3,5,7-tetramethylcyclooctatetraene dianion [4]. These salts undoubtedly represent ionic bonding.

The alkaline earth derivatives, however, provide some interesting contrasts. Cyclooctatetraenecalcium appears to be an ionic salt whose infrared spectrum is characteristic of a planar COT dianion [5]. Cyclooctatetraenemagnesium has been reported [6] and shows the additional strong IR absorptions [7] characteristic of the reduced symmetry of nonplanar COT rings. Cyclooctatetraeneberyllium presents the potential of a further novel feature. The ionic radius of Be^{2+}, 0.3—0.4 Å [8], is the smallest of any known metal cation crystal radius. This small ionic radius is undoubtedly responsible for the reduced symmetry structure of di-π-cyclopentadienylberyllium, in which the metal has a different structural relationship to the two rings **. This ionic radius is sufficiently small to fit completely inside the "hole" in a planar COT dianion ring and suggests the possible existence of a Saturn-like D_{8h} structure I, for monomeric C_8H_8Be. Such a structure, however, is expected to be most likely only if ionic bonding dominates

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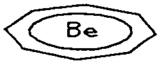
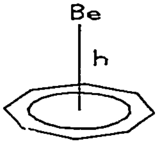
* This paper is dedicated to Professor H.C. Brown on the occasion of his 66th birthday. We note for this purpose that beryllium lies next to his beloved boron in the Periodic Table.

** For a complete historical introduction and a theoretical discussion see ref. 9.



(I)



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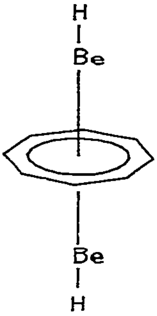

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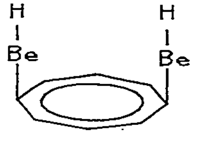

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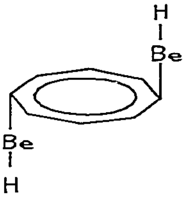

(VI)

with the metal cation. In particular, such a structure is not well suited for π-bonding to the ring.

This intriguing structural possibility was tested by ab initio SCF calculations at the STO-3G level using standard molecular exponents [10]. The Gaussian 70 program [11] was adapted for use at Berkeley in part by Dr. J.M. McKelvey in our group. Structure II, in which the beryllium ion is situated on the C_8 axis, taken as the z-axis, of the COT dianion, was optimized with respect to h, the distance between the Be ion and the ring plane. The optimum h of 1.0 Å is 26 kcal mol^{-1} lower in energy than the planar D_{8h} structure I, and alone suggests that the unique structure I does not obtain. These results are summarized in Table 1.

Examination of charge distribution and overlap populations offers a rationale for the greater stability of II (h = 1.0 Å) compared with I. With h = 0 Å, only the $Be_{2p\pi}$ orbital can interact with the π-system and then only with the most stable π-MO, a_1. Correspondingly, the total Mulliken overlap population for

TABLE 1

STO-3G RESULTS

Structure[a]	Total energy (a.u.)
I (h = 0)	−317.9216
II (h = 1.0 Å)	−317.9628
III (h = 1.37 Å)	−333.6188
V (h = 1.37 Å)	−333.6192
VI (h = 1.37 Å)	−333.6227

[a] The COT ring is taken as a planar octagon with r(C—C) 1.40 Å and r(C—H) 1.08 Å.

TABLE 2

MULLIKEN POPULATIONS

	Structure I ($h = 0$)	Structure II ($h = 1.0$ Å)
Orbital populations		
Be(2s)	0.223	0.421
Be($2p_z \equiv 2p_\pi$)	0.332	0.086
Be($2p_{x,y} \equiv 2p_\sigma$)	0.288	0.367
C(2s)	1.106	1.124
C($2p_\pi$)	1.209	1.142
C($2p_\sigma$)	1.890	1.901
Overlap populations		
Be—C (π)	0.023	0.001
Be—C (Total)	0.096	0.073
C—C (π)	0.085	0.074
C—C (Total)	0.435	0.450
Net atomic charges		
Be	+0.884	+0.772
C	—0.197	—0.160
H	+0.086	+0.063

C—Be is only 0.096, of which 0.023 is the π(C—Be) contribution. For comparison, the overlap population between adjacent carbons in the ring is 0.435 of which 0.085 is π(C—C). Table 2 summarizes the results of moving Be out of the plane of the ring. The total C—Be overlap population drops by the amount of the decrease in C—Be π-overlap (that is, overlap with $2p_z$ of Be) which is now vanishingly small. However, C—Be overlap is not an important bonding term in any event. Far more important is charge transfer from the π-system of cyclooctatetraene dianion to Be^{2+}, principally to Be($2p_z$). Note, for example, that the C($2p_\pi$) population is significantly lower than that for cyclooctatetraene anion itself, 1.125. For Be out of the ring plane the Be-s, $2p_{x,y}$ orbitals can now interact with the ring π-system; accordingly, the populations of the Be(2s) and Be($2p_{x,y} \equiv 2p_\sigma$) orbitals increase whereas that of Be($2p_z$) decreases. The net charges show that charge transfer to Be^{2+} is more efficient for the non-planar structure; that is, the 26 kcal mol^{-1} of stabilization in moving Be from the center of the ring to a distance of 1.0 Å from the ring plane is apparently the result of increased charge transfer which stabilizes this two-component system. The above analysis was based on Mulliken populations which are known to be basis set dependent and hence unreliable. That is, the absolute values have little significance but relative values for closely related systems such as I and II with the same basis set should have significance.

Structure III may be viewed as arising from the addition of BeH_2 to structure II. The product of this hypothetical reaction, structure III, is energetically favored over the reactants by 60 kcal mol^{-1}; i.e., this value is the calculated energy change for the isodesmic [12] reaction:

$$\underset{\text{(II)}}{C_8H_8Be} + BeH_2 \rightarrow \underset{\text{(III)}}{HBe \cdot C_8H_8 \cdot BeH}$$

Structure III represents a primitive polymer model in that the ring is associated with two berylliums in such a fashion that could be logically extended to a linear polymer, as indicated by IV, $(\mathrm{Be} \cdot \mathrm{C_8H_8})_n$. For structure III, h was optimized at 1.37 Å. Be—H bond lengths of 1.34 Å from Sutton [13] were used. Note that in structure III the presence of the newly introduced Be—H bond should have little effect on the 60 kcal mol^{-1} driving force for the reaction II + $\mathrm{BeH_2}$ = III since the same number of Be—H bonds exist in the reactants as in the products. This point is corroborated by the fact that the Be—H overlap population in III (0.406) is virtually identical to that of $\mathrm{BeH_2}$ (0.405).

Structures V and VI represent modifications of III in which each beryllium is localized on one carbon of the ring. Both structures are slightly more stable than III, the *syn* form, V, by a miniscule 0.25 kcal mol^{-1}, and the *anti* form, VI, by a still relatively small 2.4 kcal mol^{-1}.

The two significant predictions resulting from this theoretical study are that structure I is unfavorable and does not even represent a relative minimum of potential energy, and secondly, that some degree of aggregation may be expected in the ring—metal interactions.

Acknowledgements

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