

A Theoretical Study of Bi(cyclobutadienyl) and Higher Homologues. Polycyclobutadiene as a Novel Organic Metal?

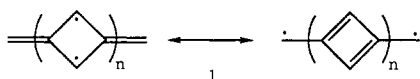
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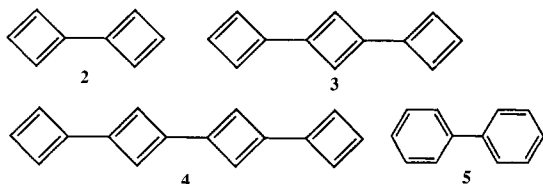
Abstract: Bi(cyclobutadienyl) (**2**), the cyclobutadiene analogue of biphenyl, and its homologues tri- (**3**) and tetra(cyclobutadienyl) (**4**) have been studied by electronic structure theory methods. Ab initio calculations on **2** reveal that the central bond is a true double bond and that the structure is best thought of as two allyl radicals plus an ethylene. The singlet and triplet states are essentially degenerate. Trimer **3** is two allyls plus a dimethylenecyclobutanediyl, while **4** is two coplanar bi(cyclobutadienyl) units connected by a single bond with a small amount of double-bond character. For both **3** and **4**, the quintet, triplet, and singlet states are essentially degenerate, indicating that they are tetraradicals. The infinite polymer, polycyclobutadiene, has been studied by ECHO and VEK methods. Several geometries based on the structures of **2–4** have been studied, and the band structures are quite intriguing. A novel valence band–conduction band crossing produces a small band gap and a high density of states at the Fermi level.

In our recent theoretical study of the non-Kekulé acenes (**1**), we also considered the infinite polymer (**1**, $n = \infty$).¹ In such a



structure the effect of the methylene end groups must become negligible, and one is left with polycyclobutadiene. The Hückel band structure of this polymer displays a remarkable crossing between the valence and conduction bands. A Peierls distortion toward rectangular cyclobutadiene units results in avoidance of this crossing, producing a narrow band gap.¹

We have now undertaken a more detailed theoretical study of the smaller, finite structures related to polycyclobutadiene, specifically bi-, tri-, and tetra(cyclobutadienyl) (**2–4**). The first



member of this homologous series, cyclobutadiene, has been extensively studied as the prototype of antiaromaticity. Structure **2** is related to cyclobutadiene as biphenyl (**5**) is related to benzene, yet, surprisingly, only a few studies have appeared that mention **2**.² We could find no reference to **3** or **4** in the literature.

We have also extended our studies of polycyclobutadiene by using more realistic geometries derived from our studies of **2–4** and by applying more sophisticated theoretical methods. We find that, depending on geometry, polycyclobutadiene has either a very small band gap or none at all. Thus, it could represent a novel design for an organic metal.

Structures **2–4** (and all higher homologues) are alternant hydrocarbons, which means their atoms can be divided into two sets, termed “starred” and “unstarred”, such that no two atoms of the same set are nearest neighbors. Furthermore, unlike the non-Kekulé acenes, all members of this series have an equal number of starred and unstarred atoms. Qualitative models for such

structures predict a singlet ground state.^{2c,3} However, Hückel theory predicts the existence of nonbonding molecular orbitals (NBMOs) for these structures (two for **2**, four for **3** and **4**; the same number as for the analogous non-Kekulé acenes). Thus, we can expect the presence of low-lying excited states of higher spin multiplicities to be characteristic of this series of molecules. Producing quantitatively reliable results for structures with many NBMOs presents a substantial theoretical challenge⁴ and is not the goal of the present work. Rather, we seek a qualitative understanding of the molecular and electronic structures of these molecules. However, a fairly high level of theory is required even to achieve this more modest goal.

Bi(cyclobutadienyl)

Bi(cyclobutadienyl) (**2**) was studied using ab initio molecular orbital theory.⁵ The molecule is fairly large by current standards (for biradicals), and we limited ourselves to the STO-3G basis set⁶ for geometry optimizations and the 4-31G basis set⁷ for more refined energy calculations. Although probably inadequate for quantitatively accurate results, we believe these calculations predict the qualitative trends correctly.

Because it has two NBMOs, **2** can be thought of as a biradical. For such structures one needs at least a two-configuration self-consistent-field (TCSCF) wave function, or an equivalent generalized valence-bond wave function (GVB(1/2)),⁸ to describe the singlet state properly.⁹ As restricted Hartree–Fock (RHF) calculation¹⁰ is often adequate for the triplet. However, **2** is a

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(5) (a) SCF calculations (RHF, UHF, TCSCF) were performed using the GAUSSIAN 86 program package: Frisch, M. J.; Binkley, J. S.; Schlegel, H. B.; Raghavachari, K.; Melius, C. F.; Martin, R. L.; Stewart, J. J. P.; Bobrowicz, F. W.; Rohlfing, C. M.; Kahn, L. R.; Defrees, D. J.; Seeger, R.; Whiteside, R. A.; Fox, D. J.; Fleuder, E. M.; Pople, J. A. *Gaussian 86*; Carnegie-Mellon Quantum Chemistry Publishing Unit: Pittsburgh, PA, 1984. (b) CI calculations were performed using the MQM:CI2P5 program: Bobrowicz, F. W.; Goodgame, M. M.; Bain, R. A.; Walch, S. P.; Goddard, W. A., III, unpublished work. Bobrowicz, F. W. Ph.D. Thesis, California Institute of Technology, 1974. The CI calculations allow all possible occupations of the 8π orbitals of a conceptual minimum basis set.

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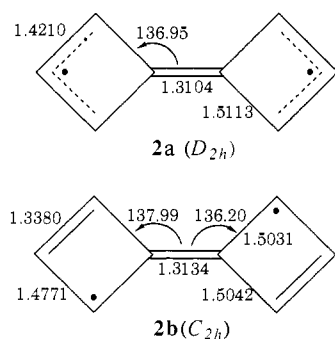


Figure 1. UHF-optimized (**2a**) and RHF-optimized (**2b**) geometries (bond lengths in angstroms, angles in degrees) for triplet bi(cyclobutadienyl). Structure **2a** was fully optimized within D_{2h} symmetry, following a partial optimization within C_{2h} symmetry, which led to a D_{2h} structure. Frequency calculations show **2a** to be a true minimum. Structure **2b** was partially optimized (hydrogen positions not optimized) within C_{2h} symmetry.

Table I. Energies of Structures **2a** and **2b** (au)

	2a ^a	2b
triplet		
RHF/STO-3G	-302.427 453	-302.433 348
RHF/4-31G	-305.734 695	-305.738 786
π -CI/4-31G	-305.831 344	-305.821 868
singlet		
TCSCF/STO-3G	-302.427 467	-302.444 206
TCSCF/4-31G	-305.734 887	-305.739 949
π -CI/4-31G	-305.833 126	-305.824 634

^a UHF/STO-3G energy = -302.505 710 au.

conjugated biradical. Borden and co-workers have demonstrated that for such structures, the RHF/TCSCF calculations can be inadequate.¹¹ The reason is related to the "doublet instability problem", such as found in RHF calculations for allyl radical.¹² For this radical, RHF calculations provide inadequate correlation between the unpaired electron in the NBMO and the electron with opposite spin in the next lower MO. This problem also manifests itself in conjugated biradicals. It can be avoided by doing a configuration interaction (CI) calculated over the MOs of π symmetry. Alternatively, an unrestricted Hartree-Fock (UHF) calculation¹³ can be performed for the triplet. The problem with the UHF method is that it does not result in a pure spin eigenfunction. Furthermore, an analogous calculation that can be directly compared to the triplet cannot be performed for the singlet, making predictions about singlet-triplet gaps impossible.

Given the above considerations, we have used the UHF method on the triplet state for geometry optimizations of **2** using the STO-3G basis set.^{5a} The geometry calculated in this manner is a reasonable approximation of the geometry obtained by π -CI calculations.¹¹ Energies of the singlet and triplet states were then calculated at this optimized geometry, with π -CI calculations^{5b} on RHF-optimized (for the triplet) or TCSCF-optimized (for the singlet) molecular orbitals, using the 4-31G basis set. We also investigated the inadequacy of the RHF method by performing geometry optimizations using this method.

Geometries. The geometries obtained using the UHF (**2a**) and RHF (**2b**) methods are shown in Figure 1, and energies of these structures at various levels of theory are shown in Table I. These geometries clearly indicate that **2** is best represented as two allyl radicals plus an ethylene. In other words, there is a double bond between the two four-membered rings. The same conclusion was reached earlier by Iwamura and Hoffmann from PPP-SCF-CI calculations.^{2b} In contrast, the central bond in biphenyl (**5**) is clearly a single bond; in the gas phase two rings are twisted 42°

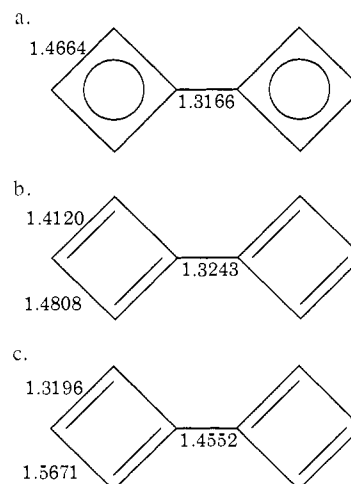


Figure 2. Other structures (bond lengths in angstroms) considered for bi(cyclobutadienyl). The rings are constrained to be rectangular and only CC bond lengths were optimized. (a) Optimized as a UHF triplet ($E = -302.492 089$ au; $E(\text{RHF triplet}) = -302.405 178$ au; $E(\text{TCSCF singlet}) = -302.405 207$ au). (b) Optimized as an RHF triplet. $E(\text{RHF triplet}) = -302.415 978$ au; $E(\text{TCSCF singlet}) = -302.417 891$ au. (c) Optimized as an RHF singlet ($E = -302.379 478$); $E(\text{RHF triplet}) = -302.344 666$ au; $E(\text{TCSCF singlet}) = -302.408 227$ au (all with STO-3G basis set).

around this bond, and the bond length is 1.489 Å.¹⁴

We have also attempted to locate geometries corresponding to "classical" structures, i.e. those containing rectangular or square cyclobutadiene rings connected by a single bond. However, as shown in Figure 2, the inter-ring bond is still very short for these structures and must be essentially a double bond. As such, these structures represent simple ring-breathing distortions of **2a**, and they all lie fairly close in energy to it. The only exception is the geometry obtained by optimization as an RHF singlet (Figure 2c), which forces all the electrons to be paired. In this case the central bond is longer, though still short for a single bond. The singlet at this geometry is only ca. 12 kcal/mol above singlet **2a**, but the triplet, as expected, is much higher in energy.

The inadequacy of the RHF method for geometry optimization is reflected in the energies shown in Table I: at the highest level of theory (i.e. π -CI), the more symmetrical, UHF-optimized geometry is preferred. The gap, however, is only ca. 6 kcal/mol. At the UHF geometry the two allyl fragments have equal CC bond lengths (as expected for a free allyl radical), whereas the RHF-optimized geometry predicts unequal bond lengths (the same problem experienced by RHF for a free allyl radical). In spite of the incorrect geometry, the RHF/TCSCF method does predict the same ordering of the singlet and triplet states as the π -CI calculations. All levels of theory predict the singlet to be the ground state, with the triplet being a low-lying excited state. However, the difference is quite small, and given the uncertainties of the calculations, perhaps it is best to say that the singlet and triplet states are essentially degenerate.

Rotation Barriers. The existence of a double bond between the two rings indicates that **2** strongly prefers a planar structure. This was further confirmed when we performed calculations to estimate the rotation barrier around this bond. Two structures were considered. In **2c**, we simply rotate the rings until they are



perpendicular to each other, keeping the geometry of the rings at the UHF-optimized values (those of **2a**). As this would obviously break the exocyclic π bond, the bond length was increased to 1.48 Å. Structure **2c** is a tetraradical, formed by a spirofusion of two biradicals. Our earlier studies have shown that an adequate

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(14) Bastiansen, O.; Traetteberg, M. *Tetrahedron* **1962**, *17*, 147-154.

Table II. Energies of Structures **2c** and **2d** (au)

	2c	2d
quintet		
RHF/4-31G	-305.674 696	
π -CI/4-31G	-305.729 835	-305.653 887
triplet		
NBMO-CI/4-31G	-305.671 228	
π -CI/4-31G	-305.742 839	-305.698 498
singlet		
RHF/4-31G		-305.657 494
NBMO-CI/4-31G	-305.669 715	
π -CI/4-31G	-305.753 839	-305.739 129

description of such structures may be obtained by optimization of the molecular orbitals for a quintet state using RHF, followed by a CI calculation within the full NBMO space to obtain energies of the singlet and triplet states.¹⁵ For **2c**, we also performed a larger CI calculation within all the orbitals that formerly had π symmetry in the planar structure. Although some σ - π mixing occurs in the perpendicular structure, it turns out that the " π "-type orbitals are quite easy to identify. This type of CI calculation would allow meaningful energy comparisons to the planar structure. The energies of structure **2c**, at the various levels of theory for the various states, are shown in Table II.

The other structure we considered is **2d**, which is simply two mutually perpendicular, rectangular cyclobutadienes. The cyclobutadiene geometry used was one obtained by Borden and co-workers at the π -CI level using a minimum basis set ($r_{C-C} = 1.539 \text{ \AA}$, $r_{C=C} = 1.369 \text{ \AA}$).¹⁶ The central bond was again assumed to be 1.48 \AA . There is some uncertainty as to what level of theory would be adequate for **2d**. TCSCF calculations on singlet cyclobutadiene at this geometry result in CI coefficients of 0.9543 and -0.2990 for the two configurations. Clearly, one configuration is dominant, and so at this geometry cyclobutadiene can be approximated by a closed-shell singlet, which is adequately described by an RHF wave function. Since the two rings are perpendicular in **2d**, there is essentially no interaction (other than weak spiro-conjugation) between the frontier orbitals of the two cyclobutadiene fragments. We conclude that RHF is an adequate method to obtain the orbitals of **2d**. To obtain energies comparable to the other structures, " π "-CI calculations are of course necessary. The same type of " π "-CI calculation as performed for **2c** was thus performed for **2d** also. The state energies are shown in Table II. There is, of course, some uncertainty as to the accuracy of these energies, given that they are not calculated for optimized structures. However, they are quite significantly (ca. 50 kcal/mol) above the energies of the planar structure. We conclude that **2** strongly prefers the planar geometry. It is remarkable that, at least computationally, tetraradical **2c** is more stable than "closed shell" **2d**, a real testimony to the destabilization of a cyclobutadiene ring.

Excited-State Energies and Transition Wavelengths. We have also calculated the energies of the higher lying singlet and triplet states of **2** (at the geometry of **2a**). These were obtained by CI calculations from the orbitals optimized for the ground state (RHF for triplets, TCSCF for singlets). These are still relatively crude calculations for excited states but should provide useful guidelines. The results are shown in Table III.

Unfortunately, the calculations indicate that *both* the triplet and singlet states have absorptions at about 410 nm. Thus, UV-vis spectroscopy is not expected to be able to distinguish between these two spin states, an observation of considerable importance to experimental efforts to prepare **2** that are under way in our (and perhaps other) laboratories.

Tri(cyclobutadienyl) and Tetra(cyclobutadienyl)

Due to their size, ab initio calculations comparable to those for **2** are infeasible for **3** and **4**. We studied these structures using

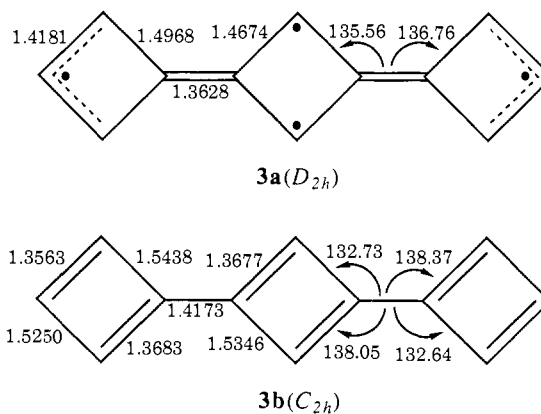


Figure 3. MNDO-optimized structures (bond lengths in angstroms; angles in degrees) for tri(cyclobutadienyl). **3a** was fully optimized as an UHF quintet within D_{2h} symmetry, after a partial optimization with C_{2h} symmetry, which led to a D_{2h} structure. **3b** was fully optimized as an RHF singlet within C_{2h} symmetry.

Table III. Electronic States and Transitions in **2**

state symmetry	excitation energy, eV	wavelength, nm
triplet		
B_{1u}	0	
B_{3g} (allowed)	2.9064	410.6
A_g (allowed)	3.0887	401.4
A_g (allowed)	3.0899	401.3
B_{2u} (forbidden)	3.0926	400.9
singlet		
A_g	0	
B_{3g} (forbidden)	2.9064	426.6
B_{2u} (allowed)	3.0078	411.2
A_g (forbidden)	3.3088	374.7
B_{3g} (forbidden)	5.2428	236.5

the semiempirical MNDO method.^{17,18} In order to test the validity of this method, we performed MNDO calculations at the SCF level on triplet **2** for comparison with the ab initio results. Qualitatively, the results are the same as the results obtained from ab initio calculations: RHF incorrectly predicts unsymmetric allyl fragments, whereas UHF predicts symmetric allyls. At both geometries, the singlet and triplet states are essentially degenerate.¹⁹

HMO calculations on **3** and **4** predict the existence of four NBMOs for each structure.¹ Thus, a UHF quintet calculation is necessary to obtain the correct geometry. Relative energies among the singlet, triplet, and quintet states can then be obtained from CI calculations within the NBMO space.¹⁵ Our results for **2** indicate that a full π -CI calculation is not necessary, once the correct geometry is obtained by UHF. The UHF-optimized geometry **3a** is shown in Figure 3. At this geometry, CI calculations within the NBMO space, using RHF-optimized quintet orbitals, give the following relative energies for the various spin states: 0 kcal/mol (quintet); 0.026 kcal/mol (triplet); 0.060 kcal/mol (singlet).²⁰ Given the uncertainties of calculations, the three spin states are essentially degenerate, and clearly the molecule is best thought of as a tetraradical.¹⁵ It is worthwhile to note that **3** does *not* undergo a distortion toward rectangular

(17) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899-4907.

(18) MNDO-UHF calculations were performed using GAUSSIAN 86.^{5a} THF and CI calculations were performed using the AMPAC program. Dewar, M. J. S.; Stewart, J. J. P. *QCPE Bull.* **1986**, *6*, 24a-24b.

(19) UHF-optimized geometry: allyl bond lengths 1.4245 Å, internal single bonds 1.4952 Å, external double bond 1.3309 Å; ΔH_f (UHF triplet) = 141.333 kcal/mol, ΔH_f (RHF triplet) = 158.841 kcal/mol, ΔH_f (singlet) = 158.840 kcal/mol. RHF-optimized geometry: allyl bond lengths 1.4118 and 1.4116 Å, internal single bonds 1.4932 and 1.4939 Å, external double bond 1.3323 Å; ΔH_f (RHF triplet) = 158.416 kcal/mol, ΔH_f (singlet) = 158.412 kcal/mol. Since AMPAC does not allow TCSCF calculations, the singlet energies were obtained by specifying two NBMOs and performing CI calculations within the NBMOs.

(20) ΔH_f (quintet) = 239.318 kcal/mol.

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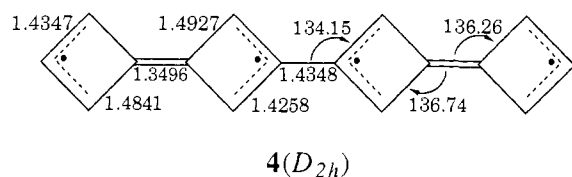


Figure 4. MNDO-optimized structure (bond lengths in angstroms; angles in degrees) for tetra(cyclobutadienyl) (**4**). The structure was optimized as a UHF quintet within D_{2h} symmetry.

cyclobutadiene structures, which we earlier expected to take place in the polymer.¹ Optimization of **3** as an RHF *singlet* does lead to such a structure (**3b**, Figure 3). However, the energy obtained for this structure is much higher (about 70 kcal/mol) than the energy for **3a**.²¹

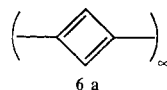
For **4**, the optimized (UHF quintet) geometry is shown in Figure 4. Relative energies of the spin states are 0 kcal/mol (singlet), 0.000 kcal/mol (triplet), and 0.007 kcal/mol (quintet).²² Once again, the three spin states are essentially degenerate, and the molecule is a tetraradical.

A feature of **4** not seen in **2** or **3** is an exocyclic *single* bond between the middle rings. Although the bond length indicates some partial double-bond character, it is still substantially longer than the exocyclic bonds in **2** and **3** and the other two exocyclic bonds in **4** itself. We performed further calculations on **4**, assuming a perpendicular orientation of the two fragments around this bond. The results indicate that the rotation barrier is only about 2 kcal/mol, much smaller than the rotation barrier in **2**, but the planar structure is still preferred.²³

Polycyclobutadiene

Our calculations predict a near degeneracy of the various spin states in **2–4**. If this trend continues, the infinite homologue, polycyclobutadiene (**6**), would be a very interesting material. Relatively little work has been done on polymers derived from open-shell monomers, and it has not been established what level of theory would be required to produce quantitatively meaningful results. However, as before, our goal is a qualitative description of the electronic structure of these materials, and we have performed several band structure calculations on **6**, using the extended Hückel crystal orbital (EHCO)²⁵ and valence effective Hamiltonian (VEH) methods.^{26,27} We emphasize that these methods were developed for "ordinary", closed-shell polymers, so their results for **6** must be regarded as tentative at best.

Three geometries were considered. In **6a**, we have assumed that the unit cell is a rectangular cyclobutadiene. We have used the middle ring of structure **3b** to approximate the structural parameters of the polymer. This is the "intuitive" structure of



6: rectangular rings would be expected if one considers the monomer. Also, as we described earlier¹ distortion toward rec-

(21) $\Delta H_f(\text{singlet}) = 312.468$ kcal/mol. This was obtained using an RHF calculation followed by CI within the two highest occupied and two lowest unoccupied molecular orbitals.

(22) $\Delta H_f(\text{singlet}) = 310.373$ kcal/mol.

(23) In general, MNDO tends to underestimate the extent to which conjugated π systems prefer planarity, including polymer systems.²⁴ As such, the rotation barrier in **4** may be a lower limit.

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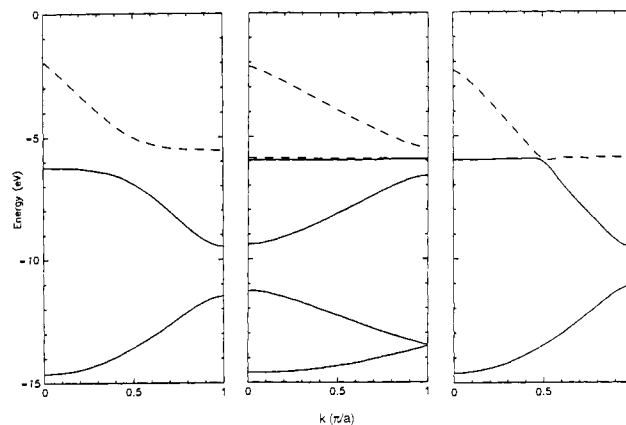


Figure 5. VEH band structures for **6a** (left), **6b** (middle), and **6c** (right). Unoccupied bands are shown as dashes. **6b** has a greater number of bands due to its larger unit cell.

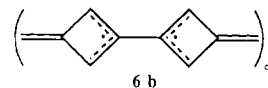
Table IV. Results of Band Structure Calculations (eV)

structure	energy/unit cell ^a	ionization potential ^{b,c}	band gap ^b	band-widths ^{b,d}
6a	-317.843	4.33	0.68	3.24, 3.59
6b	-635.217 (-317.609) ^e	4.03	0.00	2.77, 0.03, 0.05, 3.29
6c	-317.646	4.06 ^f	0.00	0.08, 7.21

^aFrom EHCO calculations. ^bFrom VEH calculations. ^c1.9 eV subtracted from calculated values.²³ ^dFor the highest occupied and lowest unoccupied bands of **6a**, the two half-occupied bands in **6c**, and the two highest occupied and two lowest unoccupied bands of **6b**. ^eSince the unit cell in **6b** is twice that in **6a** and **6c**, the energy per unit cell has to be divided by two (giving the value in parentheses) for comparison to the other structures. ^fTaken to be the crossing point of the two half-occupied bands.

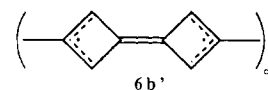
tangular rings opens up a band gap, which generally stabilizes closed-shell structures.

However, *none* of the smaller oligomers we investigated show any tendency toward this type of structure. Thus, other structures must be considered, and **6b** is a sensible choice. The structure

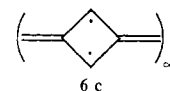


is obtained from the two middle rings of **4** and essentially consists of allyl radicals and ethylenes. It appears to be the structure that maximizes bonding without forming antiaromatic cyclobutadiene units.

In the infinite polymer there is an equivalent structure **6b'**. This situation is reminiscent of the two degenerate but distinct structures seen in polyacetylene. This suggests an additional form, which



would be best represented by **6c** and which is analogous to polyacetylene with all equal bond lengths. The geometry of **6c** may be approximated by the middle ring of **3a**.



The results of band structure calculations on **6a–6c** are shown in Table IV and Figure 5. EHCO is used to obtain the energies, and VEH, to obtain the other parameters, including the band structures of Figure 5. EHCO band structures are similar.

The calculations indicate no clear preference for any of the three structures we considered. Although **6a** is calculated to be slightly lower in energy, this is to be expected since **6a** is the best representation of a closed-shell structure, and the calculations are biased in favor of such structures. Thus, structures **6b** or **6c**, which have zero band gaps, cannot be ruled out as the ground-state

structure of polycyclobutadiene.

The most intriguing feature of these band structures is the existence of a crossing (avoided in **6a**, but allowed in the higher symmetry **6c**) between the valence and conduction bands. Such crossings are rare^{25b,29} and, when seen, typically occur very near the zone edge. We are unaware of any system with a crossing at $\pi/2a$, as in **6c**, or even nearly as far back toward the center of the Brillouin zone. In the present system this produces a very high density of states at the Fermi level. Formally, **6b** and **6c** are true metals, while **6a** has a small band gap and a low ionization potential compared to other conducting polymers. While one might expect that the parent polycyclobutadiene would be a very reactive substance, suitably substituted derivatives could have truly remarkable properties.

(29) Kivelson, S.; Chapman, O. L. *Phys. Rev. B* **1983**, *28*, 7236–7243.

Conclusions

Unlike the analogous polyphenyls, which are essentially a chain of benzene rings, the homologous structures based on cyclobutadiene exhibit structural and electronic properties quite unlike the monomer. Bi(cyclobutadienyl) is best considered as two allyls plus ethylene, tri(cyclobutadienyl) as two allyls plus dimethylenecyclobutadienyl,²⁸ and tetra(cyclobutadienyl) as two bi(cyclobutadienyl) units. The band structure of the infinite polymer is quite intriguing, suggesting a very small (or zero) band gap and a high density of states near the Fermi level.

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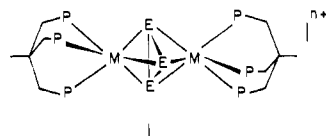
Inorganic Rings, Intact and Cleaved, between Two Metal Fragments

Wolfgang Tremel,^{†,§} Roald Hoffmann,* and Miklos Kertesz^{‡,||}

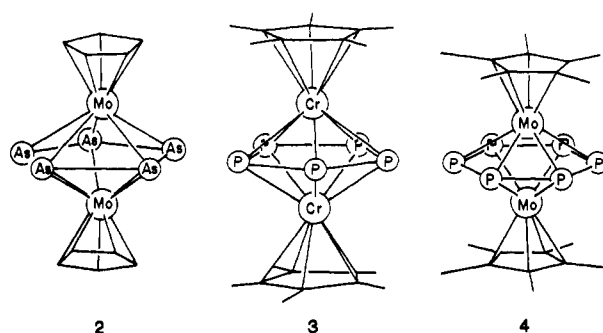
Contribution from the Anorganisch-Chemisches Institut der Universität Münster, Wilhelm-Klemm-Strasse 8, D-4400 Münster, FRG, Department of Chemistry and Materials Science Center, Cornell University, Ithaca, New York 14853-1301, and Department of Chemistry, Georgetown University, Washington, D.C. 20057. Received April 8, 1988

Abstract: The electronic structure of CpME_nMCp ($M = \text{Cr, Mo}$; $E = \text{P, As}$) triple-decker complexes is explored, where the middle deck contains a five- or six-membered ring of group 15 E atoms. From another point of view, the metal and group 15 atoms form a polynuclear cluster. All hitherto known compounds possess short metal–metal distances across the central ring, are electron deficient, and do not follow the triple-decker 30 electron or Wade–Mingos skeletal electron counting rules. In addition, the complex $\text{CpMoAs}_5\text{MoCp}$ exhibits a substantial distortion from idealized 5-fold symmetry; the middle deck shows a partitioning into As_2 and As_3 fragments. By making use of the frontier orbitals of the CpMo and E_n fragments the electronic structure of these “inorganic” triple-decker compounds is analyzed. The short metal–metal distances in these systems are responsible for their apparent electron deficiency. The distortion of the central As_5 ring in $\text{CpMoAs}_5\text{MoCp}$ is traced to the simultaneous working of first- and second-order Jahn–Teller effects.

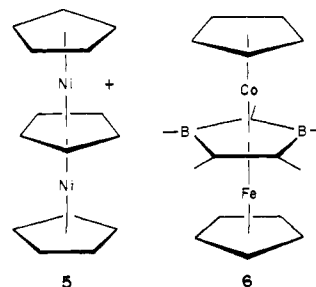
Some remarkable compounds containing homoatomic rings of main group elements stabilized by coordination to transition-metal fragments have been synthesized.¹ Sacconi and co-workers described a number of “double sandwich” compounds [(triphos)- $M'(\mu-(\eta^3\text{-E}_3)M''(\text{triphos}))^{n+}$ (**1**) containing cyclo-triphosphorus $\eta^3\text{-P}_3$ or cyclo-triarsenic $\eta^3\text{-As}_3$ groups sandwiched between two ML_3 fragments.² Rheingold, Scherer, and their co-workers added



variety to this class of compounds when they reported the synthesis and structure of $\text{CpMoAs}_5\text{MoCp}$ (**2**),³ $\text{Cp}^*\text{CrP}_5\text{CrCp}^*$ (**3**),⁴ and $\text{Cp}^*\text{MoP}_6\text{MoCp}^*$ (**4**).⁵ Although these complexes clearly look like triple-deckers,^{1c} they also differ from the classic examples such as Cp_3Ni_2^+ (**5**),^{6a} $\text{CpCo}(1,3\text{-C}_3\text{B}_2\text{H}_5)\text{FeCp}$ (**6**),^{6b} $\text{CpRuCp}^*\text{RuCp}^{+6c}$ or Sacconi compounds **1**, both structurally and electronically. First, in contrast to all known and hypothesized triple-decker sandwiches, there are relatively short metal–metal



contacts across the central ring. The metal–metal distance in **2**,



which contains a cyclo- As_5 ring, is 2.764 Å. This is intermediate

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