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High-Electron-Density C_6H_6 Units: Stable Ten-π-Electron Benzene Complexes

Martin Diefenbach*[a, b] **and Helmut Schwarz**[a]

Dedicated, with admiration, to Professor Paul von Ragué Schleyer

Abstract: The first stable benzene molecule with ten π electrons is predicted. Stability is achieved through barium atoms acting as an electron-donating "matrix" to C_6H_6 in the inverted sandwich complex $[Ba_2(C_6H_6)]$. The bis(barium)benzene complex has been computed at the density functional level of theory by using the hybrid functional *m*PW1PW91. Ab initio calculations were performed by using the coupled-cluster expansion, CCSD(T). Nucleus independent chemical shift (NICS) indices imply distinct aromatic character in the benzene ring of bis(barium)benzene. The D_{6h}-symmetric structure with a $^1A_{1g}$ electronic ground state represents a thermochemically stable, aromatic benzene molecule with four excess π electrons, stabilised by two barium ions. A possible molecular wire, built up from Ba end-capped thorium–benzene "sandwiches", is discussed.

Keywords: ab initio calculations · aromaticity · barium · benzene · molecular wires

Introduction

An "electron-rich" form of benzene with ten π electrons obeys the famous Hückel $(4n+2)$ rule for aromaticity. In this state, interesting properties resulting from the special electronic structure may arise. In a π–π stack arrangement, for example, one could think of new forms of organic conductors due to the high π-electron density; aligned in linear stacks, molecular wires with axial conductance may result. In its sole molecular state as a tetraionic species $C_6H_6^{4-}$, however, the four additional electrons suffer from Coulomb repulsion[1] and must reside in the two antibonding δ-type π* orbitals, thus turning the tetraanionic form of benzene into an unstable molecule. To transform benzene into a ten-π-electron species, an electron source is needed that not only supplies the four additional electrons, but also electronically and thermochemically stabilises the resulting supermolecule.

In a density functional study, Straka has shown that the nitrogen analogue N_6^{4-} can be transformed into a metastable species by using thorium as a stabilising agent to give the C_{6v}-symmetric $[ThN_6]$ complex with a planar ten-π-electron N_6 ligand.[2] Similarly, N_7^{3-} may be "trapped" in $[ScN_7]$[3] or $[CsN_7Ba]$.[4] According to theory, all these systems are stable singlet species representing local minima on the potential-energy surface, separated by sizeable barriers from the global minima, that is, decomposition into N_2. Higher spin multiplicities are energetically unfavourable. For $C_6H_6^{4-}$complexes, the stability trend is opposite to that of the N_6^{4-} complexes, for example, high-spin quintet and triplet $[Ti(C_6H_6)]$ are both favoured over the singlet electromer,[5] whereas singlet $[Ti(N_6)]$ is the overall minimum among the different spin states.[2] Thus, finding a stable singlet molecule incorporating a ten-π-electron benzene moiety constitutes a particular challenge.

This article presents theoretical evidence of such a stable singlet ten-π-electron species, supported by barium atoms as electron-donating and stabilising agents. Further, a possible way to conceptually construct a molecular wire with axial alignment of high-electron-density C_6H_6 units is suggested.

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[a] Dr. M. Diefenbach, Prof. Dr. H. Schwarz
Institute of Chemistry, Technical University Berlin
Strasse des 17. Juni 135, 10623 Berlin (Germany)
Fax:(+49) 30-314-21102
E-mail: martin.diefenbach@mail.chem.tu-berlin.de
helmut.schwarz@mail.chem.tu-berlin.de

[b] Dr. M. Diefenbach
Current address:
Center for Superfunctional Materials, Department of Chemistry
Pohang University of Science and Technology
San 31, Hyojadong, Namgu, Pohang 790-784 (Korea)
E-mail: mad@postech.ac.kr

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Results and Discussion

To generate a stable benzene molecule with ten π electrons, a transition-metal centre can be employed. In such a transition-metal–benzene complex, the metal centre must fulfill three requirements: 1) the metal centre must supply four valence electrons; 2) the ionisation energies (IE) of the metal must be low so that the metal centre may act as facile electron source and 3) the metal centre must supply d or f orbitals of appropriate size, symmetry, and energy that match the π* orbitals of benzene so as to stabilise the excess π electrons. Furthermore, the complete molecule must have a singlet ground state with a planar, C_6-symmetric benzene subunit, such that it is a formal ten-π-electron benzene moiety.

In this context, thorium appears to be the ultimate candidate, which already in Straka's studies[2] turned out to stabilise N_6 best. Thorium has four valence electrons with particularly low ionisation energies.[6] Furthermore, thorium can provide d and f orbitals for δ-donor interactions from benzene to Th. In a simplistic ionic picture, a formal $[Th^{4+}-C_6H_6{}^{4-}]$ complex with singlet multiplicity is thus conceivable. Natural population analysis[7] extracted from density functional calculations of a C_{6v}-symmetric singlet thorium–benzene complex reveals quite a high partial charge of $+2.4\,e$ indicating strong electron transfer and a d-orbital occupation ($6d^{1.2}$) indicating Th–benzene δ interaction. The data in Table 1 show, however, that the singlet $[Th(C_6H_6)]$ species is the least stable among the three spin multiplicites considered. Furthermore, the singlet minimum is of C_{2v} symmetry, and the C_{6v}-symmetric structure with a planar benzene subunit represents a higher order saddle point that is higher in energy.

Evidently, electron transfer of all four valence electrons of a single thorium atom to benzene is unfavourable. Instead of employing only one electron donor, two atoms with two valence electrons each, for example, alkaline earth metals, could perhaps serve better. In an "inverted sandwich" complex with one atom at each face of benzene, the sixfold symmetry can be retained. Cummins and co-workers found strong δ back-bonding interactions in inverted arene sandwich complexes incorporating uranium(II) centres, that is, $[L_2U-arene-UL_2]$ (L = amide);[8] while in the limit of U^{IV} centres this would result in a ten-π-arene complex, these systems are viewed as divalent uranium synthons with a neutral arene bridge. Gagliardi and Pyykkö suggested that barium can be regarded as "honorary" d element.[4] This notion implies that barium should be a useful "ligand" to benzene: barium can supply d orbitals to stabilise the occupied π* orbitals of benzene. Further, two barium atoms may supply four electrons to benzene to give a formal $[Ba^{2+}-C_6H_6{}^{4-}-Ba^{2+}]$ complex with D_{6h} symmetry. In comparison to thorium, for which ionisation into the quadruply ionised species costs $\sum_{n=0}^{3} IE(Th^{n+}) = 64.9$ eV,[6] the energy demand for generation of two barium dications is substantially lower, that is, $2\times\sum_{n=0}^{1} IE(Ba^{n+}) = 30.4$ eV.[9] Thus, barium is one of the most promising benzene "layers" for this purpose.

According to *m*PW1PW91 computations, a singlet bis(barium)benzene molecule with D_{6h} symmetry indeed represents the lowest energy structure among the different spin and symmetry species considered (see Figure 1 and Table 2).

Table 1. Absolute and relative energies including zero-point vibrational energy (ZPE) contributions [given in Hartree and kJ mol1^{-1}, respectively] for $[Th(C_6H_6)]$ complexes calculated at the *m*PW1PW91 density functional level of theory. Thorium–benzene distances are given in pm.

Species	occ.	E_{abs}	E_{rel}	$d_{Th-C_6H_6}$[a]
$^1A_1$ (C_{6v})	$7s^06d^05f^0/\pi^{*4}$	−267.952972	0.0	197.8
$^1A_1$ (C_{2v})	$7s^06d^05f^0/\pi^{*4}$	−267.964102	−29.2	235.8
$^3E_2$ (C_{6v})	$7s^16d^05f^0/\pi^{*3}$	−267.970194	−45.2	217.9
$^3A_2$ (C_{2v})	$7s^16d^05f^0/\pi^{*3}$	−267.974898	−57.6	219.2
$^5B_1$ (C_{6v})	$7s^16d^05f^1/\pi^{*2}$	−267.966461	−35.4	233.4

[a] Distance between the thorium atom and the centroid of the benzene ring.

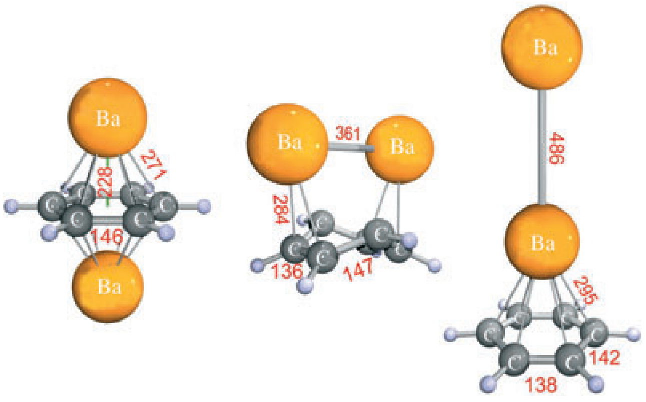

Figure 1. Geometries of bis(barium)benzene complexes, calculated at the *m*PW1PW91 level of theory. Left: $^1A_{1g}$ (D_{6h}). Middle: $^1A_1$ (D_{2v}). Right: $^3A_{1g}$ (C_{2v}). Selected distances are given in pm.

Table 2. Absolute and relative energies [given in Hartree and kJ mol^{-1}, respectively] for $[Ba_2(C_6H_6)]$ complexes. *m*PW1PW91 data include ZPE contributions.

	*m*PW1PW91		CCSD(T)//*m*PW1PW91		CCSD(T)	
Species	E_{abs}	E_{rel}	E_{abs}	E_{rel}	E_{abs}	E_{rel}
bis(η^6)Ba–C_6H_6–Ba						
$^1A_{1g}$ (D_{6h})	−283.110553	0.0	−282.367118	0.0	−282.367641	0.0
$^3A_2$ (C_{2v})	−283.109196	3.6	−282.363943	8.3		
$^3E_{2u}$ (D_{6h})	−283.109022	4.0	−282.361809	13.9	−282.362370	13.8
$^5A_{2u}$ (D_{6h})	−283.104439	16.1	−282.359850	19.1	−282.360820	17.9
bis(η^2)Ba–Ba–C_6H_6						
$^1A_1$ (C_{2v})	−283.084463	68.5	−282.344317	59.9		
mono(η^6)Ba–Ba–C_6H_6						
$^3A_1$ (C_{2v})	−283.072331	100.4	−282.315839	134.6		

Next to such a D_{6h} symmetric benzene molecule layered by two barium atoms, there are two other structural isomers with Ba–Ba contacts that are to be accounted for. They play, however, only a very minor role. At the CCSD(T)//*m*PW1PW91 level, a complex with η^2-coordinated barium atoms lies 60 kJ mol^{-1} higher in energy with respect to the overall D_{6h} minimum; the isomer with a quasi-linear Ba–Ba–benzene alignment in which only one barium atom coordinates to benzene is another 75 kJ mol^{-1} less favourable. The discussion therefore focuses on the different spin states of the low-energy isomer.

In this context, the *m*PW1PW91 functional predicts the singlet molecule to be the most stable bis(barium)benzene species, while a triplet C_{2v} configuration lies within quite close proximity (Table 2); the D_{6h}-symmetric $^3E_{2u}$ state corresponds to a higher order saddle point with two imaginary frequencies. Based on CCSD(T)//*m*PW1PW91 data, the energetic order of spin states is $^1A_{1g}$ (E_{rel}=0.0 kJ mol^{-1}) followed by $^3A_2$ (E_{rel}=8.3 kJ mol^{-1}) and $^5A_{2u}$ (E_{rel}=19.1 kJ mol^{-1}). If the zero-point vibrational energy contributions of the *m*PW1PW91 results are included, the separation is even more definite: 0.0 ($^1A_{1g}$) versus 11.3 ($^3A_2$) versus 30.9 kJ mol^{-1} ($^5A_{2u}$).

The "inverted sandwich" structures have also been optimised in D_{6h} symmetry at the CCSD(T) level of theory. As is evident from the data in Tables 2 and 3, the density functional approach agrees very well with the CCSD(T) results, both with respect to geometrical parameters and relative energies. Although the triplet species is a C_{2v}-symmetric ground-state molecule, it is reasonable to assume that a CCSD(T)-optimised C_{2v} structure is close in geometry to the *m*PW1PW91 structure (see Table 3) and thus will be higher in energy by about 8 kJ mol^{-1} with respect to the singlet D_{6h} species. Formation of singlet bis(barium)benzene is exothermic with respect to the reactants 2 Ba + C_6H_6, that is, from CCSD(T)//*m*PW1PW91 calculations, bond energies are D_e[Ba–(C_6H_6)Ba] = 162.0 kJ mol^{-1} and D_e[Ba–(C_6H_6)] = 54.9 kJ mol^{-1}. We note that structures involving fragmentation of the C–C framework are unlikely to be thermochemically favourable. Expulsion of ethyne from ground-state bis(barium)benzene, for example, to form $^3A_{2u}$ (D_{4h}) [$Ba_2(C_4H_4)$] is endothermic by 464 kJ mol^{-1} according to CCSD(T)//*m*PW1PW91 computations. Therefore, it can be concluded that $^1A_{1g}$ (D_{6h}) bis(barium)benzene represents the lowest energy minimum on the $Ba_2C_6H_6$ potential-energy surface.

Table 3. Geometries for D_{6h}-symmetric [$Ba_2(C_6H_6)$] complexes, calculated at the *m*PW1PW91 and CCSD(T) levels of theory. Bond distances are given in pm.

	*m*PW1PW91			CCSD(T)		
Species	$d_{\mathrm{Ba-C_6H_6}}$[a]	$d_{\mathrm{C-C}}$	$d_{\mathrm{C-H}}$	$d_{\mathrm{Ba-C_6H_6}}$[a]	$d_{\mathrm{C-C}}$	$d_{\mathrm{C-H}}$
$^1A_{1g}$ (D_{6h})	227.9	145.8	108.3	226.6	146.6	108.9
$^3E_{2u}$ (D_{6h})	240.1	144.3	108.2	238.2	145.1	108.8
$^5A_{2u}$ (D_{6h})	257.0	142.6	108.2	253.6	143.6	108.8

[a] Distance between the barium atom and the centroid of the benzene ring.

In the singlet molecule, the 5d occupation of 0.43 *e* per barium atom from the natural population analysis (NPA) of the *m*PW1PW91 density is remarkably high and implies considerable Ba–benzene δ interaction to stabilise the complex. The NPA partial charge of +1.54 *e* per barium atom on the other hand indicates substantial charge transfer to benzene, thus pointing towards an electron-transfer limit of 4 e^-. The five highest occupied molecular orbitals (HOMO) in Figure 2 support this notion. The triplet configuration comprises a singly occupied 6s(Ba) type orbital and three electrons in the π*(benzene) type orbitals. In the quintet species, both 6s(Ba)-type orbitals ($(a_{1g})^1$ and $(a_{2u})^1$) are singly occupied, the other two unpaired electrons reside in the antibonding π^*-type orbital of e_{2u} symmetry.

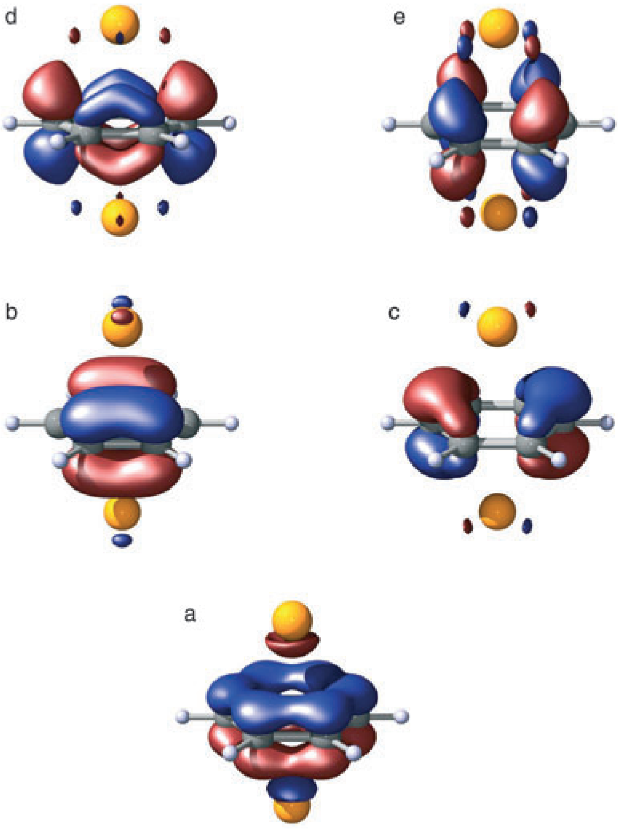

Figure 2. Illustration of the five highest occupied molecular orbitals in $^1A_{1g}$ (D_{6h}) [$Ba_2(C_6H_6)$].

To assess the aromatic character of the benzene fragment in bis(barium)benzene, nucleus independent chemical shift (NICS) indices[10] have been calculated. A NICS(d) value is defined as the (sign-reversed) NMR shielding contribution at a given point in the molecule, *d*, above the centroid of the cyclic fragment. A negative NICS value serves as an indicator for cyclic electron delocalisation (CED), thereby implying aromatic character. At the *m*PW1PW91 level, benzene has a NICS(0) value of −7.9 ppm, the "naked" tetraanion $C_6H_6^{4-}$ has one of −26.3 ppm. Taking these numbers as reference for CED, the NICS(0) value of −42.8 ppm in $Ba_2(C_6H_6)$, which relates to that of the 1,3-dehydro-5,7-adamantanediyl dication (NICS[HF/6-31+G*//MP2/6-31G*] = −50.1 ppm),[10] clearly indicates aromatic character in the singlet ground-state molecule. In comparison, the NICS(0) index for the triplet complex, (D_{6h}) $^3E_{2u,}$ amounts to +150.3 ppm, that is, exhibiting distinct antiaromatic character, which suggests that the aromaticity in the singlet complex is not simply an artefact caused by the high electron density of the benzene ring in these complexes. Likewise, a free trianionic benzene fragment, $^2E_{lu}$ (D_{6h}) $C_6H_6^{3-}$, exhibits a slightly positive NICS(0) index of +0.5 ppm; this further demonstrates that the NPA partial charge of 2×+1.54 *e* from Ba to benzene in $^1A_{1g}$ $[Ba_2(C_6H_6)]$ reflects a formal transfer of four electrons rather than only three. If the latter were to be assumed and $^1A_{1g}$ bis(barium)benzene were a nine-π-electron system, a negative NICS(0) value would as well be expected for $C_6H_6^{3-}$.

NICS is also affected by the local effects of σ bonds and lone pairs. To dissect the total NICS into paratropic components arising mainly from C–C σ bonds and diatropic components that are due to C–C π multiple bonds, the NICS values can be determined at increasing distances from the ring centroid.[11] Thereby, the paratropic C-C(σ) effects are faded out and the diatropic ring current is isolated, typically at a distance of around 100 pm. From the calculated NICS profile in the region between zero and 100 pm no decrease of NMR shielding contribution is observed, thereby confirming a diatropic ring current. The aromatic character in the benzene fragment of bis(benzene)barium is thus corroborated. For distances beyond 150 pm, the NICS index of $Ba_2(C_6H_6)$ even suggests an increase in aromatic character. This is, however, due to shielding by the barium atom and accordingly decreases after $d_{Ba-C_6H_6} = 228$ pm (see Figure 3). To some extent, there may also be three-dimensional aromatic character involved. However, comparison of the trends in the "naked" two-dimensional systems, $C_6H_6^{4-}$ and C_6H_6, with those in the $^1A_{1g}$ and $^3E_{2u}$ bis(barium)benzene complexes implies that this is not predominant. The planar two-dimensional aromatic systems and the three-dimensional $^1A_{1g}$ complex all have negative NICS values, whereas the three-dimensional $^3E_{2u}$ complex has a highly positive one. Further, according to the $2(n+1)^2$ rule of three-dimensional aromaticity,[12,13] ten π electrons are unfavourable.

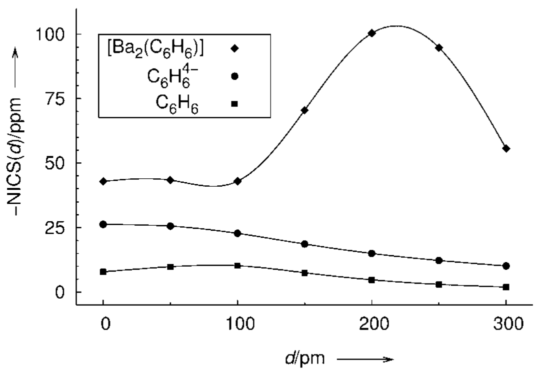

Figure 3. NICS(d) indices in the centre of the benzene rings and at a distance d above the centroid for benzene, $C_6H_6^{4-}$ and $[Ba_2(C_6H_6)]$.

To build a molecular wire from ten-π-electron benzene molecules, a means to align several benzene molecules along the C_6 axis is required. If a metal–benzene unit is used as a building block such that multidecker compounds result,[14] there is a simple basic criterion that is to be fulfilled (vide supra). The metal centre (M) must be a four-electron donor. In a multidecker compound, this results in an (infinite) $[M(C_6H_6)]_n$ chain.[15] In an isolated molecule, however, defined end points must exist. The simplest molecular compound of this form is a sandwich-type bis(benzene) complex with metal end points. Thus, the central metal atom supplies two electrons to each benzene ring, the other two electrons are obtained from the end-point metal.

With Ba as the end-point metal one arrives at a doubly charged ten-π-electron ligand $Ba(C_6H_6)^{2-}$, which is closely related to the ten-π-electron ligand $C_8H_8^{2-}$, the cyclooctatetraene (COT) dianion. In analogy to [Th(cot)$_2$], thorium should be a viable candidate for the central metal. [Th(cot)$_2$] is a diamagnetic complex with 20 valence electrons. According to MRCI calculations, $[Th(C_8H_8)_2]$ is a D_{8h}-symmetric singlet molecule that may be viewed in a single-determinant picture as Th^{IV} compound, that is, a Th^{4+} closed-shell ion complexed by two aromatic $C_8H_8^{2-}$ ligands.[16] Translated to this work, the compound suggested is a thorium sandwich-type singlet complex with barium(benzene) ligands, $[Ba(C_6H_6)Th(C_6H_6)Ba]$. Table 4 shows the relative thermochemical stabilities for this complex at the different spin states, restricted to D_{6h} symmetry. For singlet, triplet and quintet spin states, these idealised geometries correspond to transition structures with low imaginary modes for ring rotation about the C_6 axis. The lowest-energy minimum was calculated for the singlet structure, and it is of D_6 symmetry. This structure is a mere 0.5 kJ mol^{-1} lower in electronic energy with respect to both D_{6h} and D_{6d} symmetries. The imaginary frequencies of the singlet D_{6h} and D_{6d} structures amount to 42i and 44i cm^{-1}. The region along this coordinate of the potential-energy surface is rather shallow for these three spin multiplicities. It is thus reasonable to confine the discussion to D_{6h} structures only. The septet species,

Table 4. Absolute and relative electronic energies calculated at the *m*PW1PW91 level for $[Th\{(C_6H_6)Ba\}_2]$ complexes [given in Hartree and kJ mol^{-1}, respectively]. Energies including zero-point vibrational energy contributions (E_0) are also given. The symmetry of the complexes is restricted to D_{6h}.

	E_{abs}		E_{rel}	
Species	E_{e1}	E_0	E_{e1}	E_0
$^1A_{lg}$ (D_{6h})	551.303865	−551.114662	0.0	0.0
$^3E_{2u}$ (D_{6h})	551.287687	−551.046484	42.5	179.0
$^5A_{2u}$ (D_{6h})	551.278807	−551.078745	65.8	94.3
$^7E_{2u}$ (D_{6h})	551.247180	−551.054409	148.8	158.2

however, features imaginary asymmetric stretching modes of Th towards one benzene ring, and it is probably therefore a C_6- or C_2-symmetric species. Nevertheless, it is assumed unlikely that relaxation from D_{6h} or D_{6d} symmetry to the septet ground-state structure will result in a relative energy close to that of the singlet species. Indications of bent structures like those found for plain bis(arene) actinide compounds[17] have not been found.

Density functional theory predicts a singlet structure of the Ba/Th–benzene "nanowire" (Figure 4) to be clearly favoured over the other multiplicities considered so far. If zero-point vibrational energy contributions are considered, the energetically closest species has quintet multiplicity and is almost 100 kJ mol^{-1} higher in energy than the overall singlet minimum. The energetic spreading is more explicit than that of the bis(benzene)barium case, which is not too astounding regarding the analogy to the diamagnetic bis(COT)thorium complex. Preparation of such a singlet wiretype structure should thus in principle be viable. Actually, very recently, Hosoya et al. have reported the synthesis of Eu–COT nanowires by laser vaporisation techniques.[18] Extension to longer wires incorporating more Th(C_6H_6) units is also expected to result in singlet multiplicity molecules with ten-π-electron benzene fragments. A molecular wire with an adjustable length incorporating high-electron-density C_6H_6 units is therefore within reach. One crucial point will have to be addressed in future investigations, that is, the question of conductance in such molecular wires, as this is one of the most relevant properties for potential nanowires.

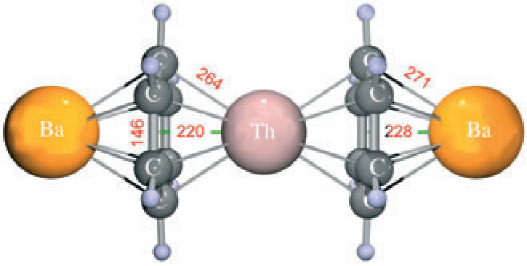

Figure 4. Geometry of bis[Ba(C_6H_6)]thorium, calculated at the *m*PW1PW91 level of theory. Selected distances are given in pm.

Computational Details

Density functional calculations[19] were performed at the unrestricted *m*PW1PW91[20] level of theory as implemented in the Gaussian 03 programme package.[21] The *m*PW1PW91 functional is specifically parametrised to adequately describe weak as well as noncovalent interactions[20] associated with metal–π complexes,[22] while, according to a theorem by Lacks and Gordon,[23] retaining accuracy for the description of covalent bonds. Carbon and hydrogen atoms were described by standard 6-311+G(2df,p) basis sets,[24,25] and for barium and thorium the Stuttgart/Köln-type relativistic pseudopotentials (ECP46MWB replacing 46 core electrons[26] and ECP78MWB replacing 78 core electrons,[27] respectively) were employed in conjunction with the corresponding (6s6p5d1f)/[4s4p2d1f] basis set[26] describing the $5s^25p^66s^2$ valence shell of Ba and the (8s8p6d5f2g)/[5s5p4d3f2g] basis set[28] for the $6s^26p^66d^27s^2$ valence space of Th. For molecules containing more than one benzene ring, the smaller 6-31+G(d,p)[29] basis sets were used for C and H for efficiency reasons. The resulting wavefunctions do not suffer from spin contamination and were found to be the energetically lowest solutions according to stability analyses.

Nucleus independent chemical shift (NICS)[10] indices were obtained from *m*PW1PW91 NMR calculations based an the GIAO formalism,[30] using the ECP/6-311+G(2df,p) basis set combination, as already mentioned above. Although the calculation of magnetic properties at nuclei described with a pseudopotential is clearly inappropriate, the employed ECP/basis set combination works quite well for the purpose at hand. The indices were calculated at the centroid of the arene ring and at distances *d* (in pm) above to give NICS(d) parameters.[11]

ROHF-based coupled cluster (CCSD(T))[31–34] calculations were carried out with the ab initio programme package Molpro 2002.[35] Here, C and H were described by Dunning's aug-cc-pVTZ and cc-pVDZ basis sets,[36] respectively. All valence electrons, that is, 1s(H), 2s2p(C) and 5s5p6s(Ba), were correlated. Geometries were optimised using the optg module. The CCSD(T) approach is expected to yield reliable results, as Lüthi has already pointed out for transition-metal sandwich compounds.[37] The T_1 diagnostic value,[38] used to measure the contribution of the singly excited configurations and to serve as an indicator for possible neardegeneracy effects, was below 0.02 for all closed-shell species and below 0.025 for all open-shell calculations. For a closed-shell CCSD calculation to be reliable, a T_1 diagnostic of <0.02 has been proposed.[38] If triplet contributions are included, as for example, in a CCSD(T) formalism, a rough estimate of recommendation is $T_1 \leq 0.04$.[39] For open-shell cases, the criterion is somewhat less stringent.[40] According to these estimates, the CCSD(T) calculations are of sufficient quality and reliability.

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