ing new structural information about DNA and its interaction with binding agents. It highlights the close correlation between structure and force and points out the particular role of force as a parameter controlling biological function, for example, in preventing mechanical strand separation in DNA.

Experimental Section

λ-BstE II digested DNA and cisplatin (*cis*-diammine(dichloro)platinum(II)) were purchased from Sigma (Deisenhofen, Germany). All other DNA molecules were purchased from Pharmacia (Freiburg, Germany). For the reaction, a saturated cisplatin stock solution (50 μL) was added to a DNA-containing solution (150 μL; 100 μg mL^{-1}, 130 mM NaCl, 10 mM Tris, 1 mM EDTA, pH 8.0) and allowed to react for 24 h at 37 °C in darkness to give an excess of cisplatin per base pair. The sample preparation and the details of the force experiments are described elsewhere.[6, 7] All experiments were carried out in Tris buffer (10 mM, pH 8.0) containing NaCl (150 mM) and EDTA (1 mM). The spring constants of all cantilevers (Microlevers, Park Scientific Instruments, Sunnyvale, CA) were determined using the thermal noise method.[12] All force curves shown consist of 4096 points and were smoothed using an 11-point box integrator.

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Spherical Aromaticity in I_h Symmetrical Fullerenes: The $2(N+1)^2$ Rule**

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Dedicated to Professor Fred Wudl
on the occasion of his 60th birthday

Aromatic compounds exhibit a significantly raised diamagnetic susceptibility.[1] The aromaticity of annulenes follows the Hückel rule. Due to their closed-shell structures, annulenes with $4N+2$ π electrons are not distorted (D_{nh} symmetry) and show strong diamagnetic ring currents, while $4N$ π annulenes are often distorted and have paratropic character. Although there is no such comparable rule for hetero- and polycyclic π systems, substructures with $4N+2$ π electrons frequently possess pronounced diamagnetic ring currents. Spherical fullerenes represent a special group of polycyclic π systems. In neutral C_{60}, an encapsulated ^{3}He nucleus is only subject to weak diamagnetic shielding.[2] The 20 six-membered rings in C_{60} show diamagnetic ring currents,[3] as indicated by the negative nucleus-independent chemical shifts (NICS)[4] in the center[5] as well as above and under the six-membered rings,[6] but this effect is roughly compensated by the 12 paratropic five-membered rings[3] (positive NICS values),[5] therefore the ^{3}He chemical shift of He@C_{60} is only $\delta = -6.3$.[2] Other neutral fullerenes,[7] such as He@C_{70}, He@C_{76}, He@C_{78}, He@C_{82}, and He@C_{84}, behave similarly[5] and the highest diamagnetic endohedral chemical shift of $\delta = -28.8$ is observed for He@C_{70}.[2] For the other cases, the chemical shifts are in the range between these two values.[5] Dramatic effects are found upon reduction to hexaanions.[8] While adding six electrons to C_{60} leads to an extreme shielding effect (δ(He@C_{60}^{6-}) $= -48.7$), the opposite effect is observed for C_{70} (δ(He@C_{70}^{6-}) $= 8.3$). Significantly, the five-membered rings in both cases become diatropic but the diatropy of the six-membered rings in C_{60} increases, whereas, to a large extent, it decreases in C_{70}. The experimentally determined ^{3}He NMR chemical shifts of fullerenes can be well reproduced computationally.[3, 5, 7, 9–13] No correlation between magnetism and cluster size or charge of fullerenes has been found as yet. Herein, we demonstrate that the total diatropy of icosahedral fullerenes such as C_{20},[14] C_{60}, and C_{80},[15] (Figure 1) and their cluster distortion depend on the degree of the electron occupation in the valence shell. The resulting $2(N+1)^2$ rule represents the spherical analog to the $4N+2$ rule for the cyclic annulenes.

The π-electron system of an icosahedral fullerene can be approximately considered as a spherical electron gas, which surrounds the surface of a sphere. The wave functions of this electron gas can be characterized by the angular momentum quantum numbers ($l = 0, 1, 2, 3, \ldots$). The s shell ($l = 0$) is

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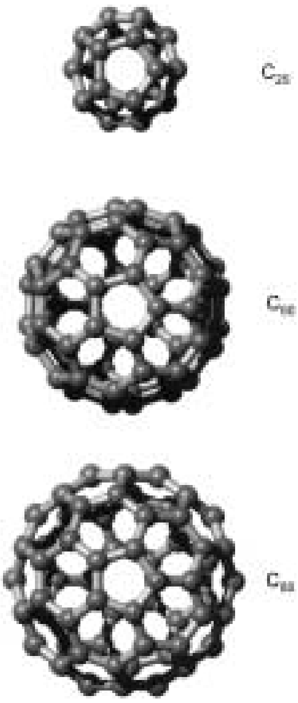

Figure 1. Models of the fullerenes C_{20}, C_{60}, and C_{80}.

comparable to an atomic s orbital. The major difference is that the surface of the sphere represents a nodal plane and the electron density in the center should approach zero (Figure 2).[16] The wave functions characterized by $l = 1, 2, 3, \ldots$ are analogous to the atomic p, d, and f orbitals, and so forth (Figure 1). The irreducible representations of the icosahedral symmetry can be deduced by lowering the symmetry using group theory (Table 1).[17] Considering the Pauli principle, all π shells are fully filled with $2(N+1)^2$ electrons and show therefore a spherical charge distribution (Figure 2).

For example, the charged fullerene $C_{60}{}^{10+}$ represents a closed-shell system, in which all π orbitals, including $l = 4$ (the g shell), are fully filled. The analogous shape of the calculated molecular s, p, d, f, and g orbitals of the π electron systems of $C_{60}{}^{10+}$ and the hydrogen atomic orbitals is obvious (Figure 2). The B3LYP/6-31G*[18] computed lengths of the [6,6] and [5,6] bonds of $C_{60}{}^{10+}$ are 1.43 and 1.46 Å, while their alternation (0.03 Å) is smaller than that of C_{60} (0.06 Å) but comparable with that of the T_h-symmetrical hexakis adducts with benzenoid substructures such as $C_{66}(COOEt)_{12}$.[19] We have shown recently that the characteristic bond length alternation in C_{60} is due to the incomplete filling of the h shell ($l = 5$).[20] No distortion of the π electron system is expected for fully filled shells, since the angular momenta are symmetrically distributed. In C_{60}, only the h_u orbitals of the h shell are filled. The h_u orbitals display bonding interactions within the [6,6] bonds and antibonding interactions within the [5,6] bonds.[20] Therefore, the molecule stabilizes itself by shortening the [6,6] bonds relative to the [5,6] bonds. In $C_{60}{}^{6-}$ and $C_{60}{}^{12-}$, this effect is suppressed,[21] since the next higher t_{1g} and t_{1u} orbitals[22] are filled and display bonding interactions within the [5,6] bonds and antibonding interactions within the [6,6] bonds.

The correlation of aromatic character with the electronic level filling of C_{60} is shown in Table 2. The computed He chemical shift for the closed-shell $He@C_{60}{}^{10+}$ molecule is $\delta = -81.4$ and this is the largest theoretically estimated diamagnetic shielding up to now. The same behavior is found for the next smaller and larger icosahedral fullerenes C_{20} and C_{80}. The wave functions for $l = 0, 1, 2, \ldots$ also show a formal analogy to the atomic s, p, and d orbitals, and so forth. The diatropic character of C_{20} is smaller than that of $C_{20}{}^{2+}$, which has a closed-shell system fully filled with $n_c = 18$ electrons ($N = 2$) (Table 1). As expected, the incomplete filling of the $l = 3$ shell in C_{20} leads to an asymmetrical distribution of the angular momenta. Therefore, C_{20} is distorted (C_2 symmetry), while $C_{20}{}^{2+}$ has I_h symmetry (Table 3). With the cluster size of 80, the octacation $C_{80}{}^{8+}$ ($n_c = 72$) forms a closed-shell structure of I_h symmetry (Table 3). With increasing energetic order, the t_{1u}, t_{2u}, and h_u orbitals of the $l = 5$ shell are completely filled. Therefore, the octacation exhibits the largest diamagnetic ring currents (in both the five- and six-membered rings) within this series. The stepwise filling up of the $l = 6$ shell leads first to the decrease of the diamagnetic behavior and then, especially within $C_{80}{}^{2-}$, to the highly antiaromatic character. In $C_{80}{}^{6-}$, diamagnetic shielding appears again in the cluster center. Apart from the closed-shell $C_{80}{}^{8+}$ with I_h symmetry, all other systems with partially filled shells are distorted to D_{5d} symmetry, most pronounced within paratropic $C_{80}{}^{2-}$.

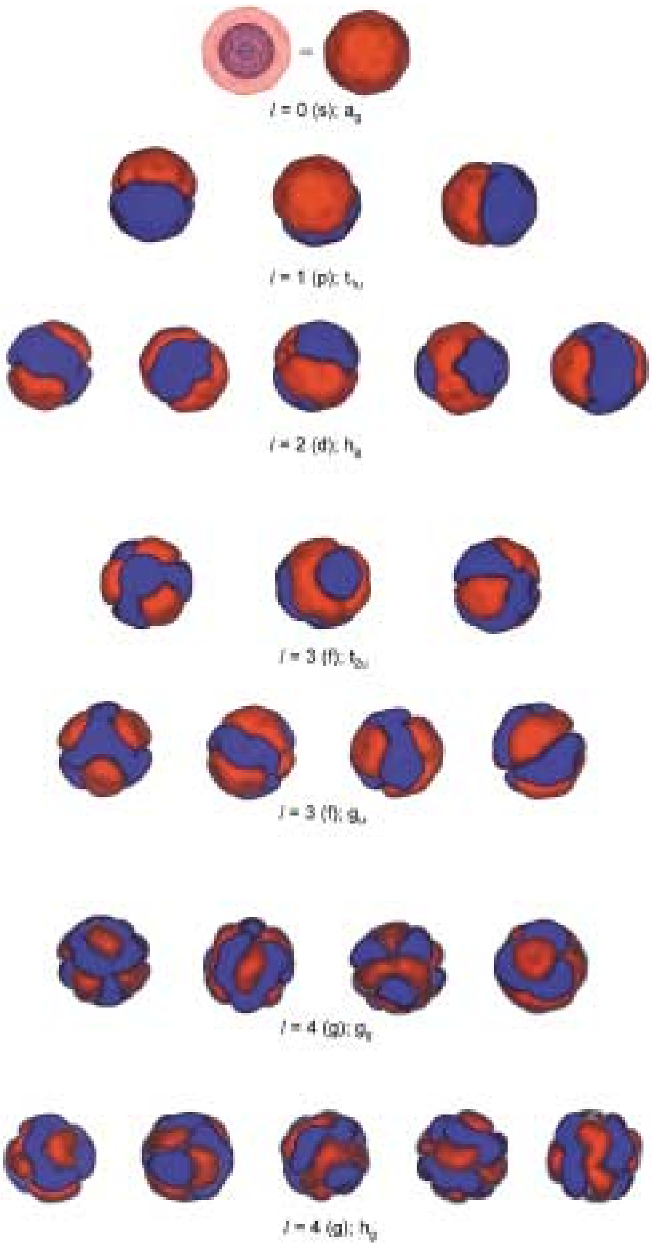

Figure 2. The π orbitals of $C_{60}{}^{10+}$ calculated at the PM3//MNDO level.[16] The position of the C_{60} skeleton is the same in all orbital presentations. The "s" orbital is also shown in a wire mesh presentation to make the nodal plane visible, which is otherwise hidden in the other representations.

Table 1. Electron ground-state configurations[17] of the fully (bold) and partially filled π shells of icosahedral fullerenes.

l[a]	Shell	Electrons per shell	n_c[b]	HOMO (I_h symmetry[c])
0	s	2	**2**	$\mathbf{a_g^2}$
1	p	6	**8**	$\mathbf{t_{1u}^6}$
2	d	10	**18**	$\mathbf{h_g^{10}}$
3	f	14	24	t_{2u}^6
			26	g_u^8
			32	$\mathbf{t_{2u}^6g_u^8}$
4	g	18	40	g_g^8
			42	h_g^{10}
			50	$\mathbf{g_g^8h_g^{10}}$
5	h	22	56	t_{1u}^6 or t_{2u}^6
			60	h_u^{10}
			62	$t_{1u}^6t_{2u}^6$
			66	$t_{1u}^6h_u^{10}$ or $t_{2u}^6h_u^{10}$
			72	$\mathbf{t_{1u}^6t_{2u}^6h_u^{10}}$

[a] Angular momentum quantum number for a spherical shell of π electrons. [b] Number of π electrons for the ground state configurations with closed shell or inner shell. [c] HOMO symmetries for all levels at a given l; the superscripted digit shows the number of electrons for complete occupation of the shell.

Table 2. Calculated and experimental endohedral ^3He chemical shifts and symmetries of He@C_{60} species with different degrees of π-electron filling.

Species	Symmetry	$\delta(^3He)_{calcd}$[b]	$\delta(^3He)_{expt}$
C_{60}^{10+} (closed $l=4$ shell)	I_h[a]	–81.4	–
C_{60}	I_h[c]	–8.0	–6.3[1]
C_{60}^{6-}	I_h[a]	–55.6	–48.7[8]

[a] Weak bond length alternation between the [6,6] and [5,6] bonds of 0.03 Å for C_{60}^{10+} and 0.02 Å for C_{60}^{6-} (B3LYP/6-31G*). [b] GIAO-SCF/3-21G//B3LYP/6-31G*.[18] [c] Strong bond length alternation between [6,6] and [5,6] bonds of 0.06 Å (B3LYP/6-31G*).

Table 3. Calculated endohedral ^3He chemical shifts and symmetry of He@C_{20} and He@C_{80} species with different degrees of π-electron filling.

Species	Symmetry	$\delta(^3He)$[a]	NICS(5)[b]	NICS(6)[c]
C_{20}^{2+} (closed $l=2$ shell)	I_h	–66.2	–25.1	–
C_{20}	C_2	–31.7	–1.1, –12.7	–
C_{80}^{8+} (closed $l=5$ shell)	I_h	–82.9	–29.1	–30.3
C_{80}^{6+}	D_{5d}	–70.0	–25.1	–26.6
C_{80}^{2+}	D_{5d}	–54.5	–17.2	–20.2
C_{80} (triplet)	D_{5d}	–8.4	–17.2	–4.2
C_{80}^{2-}	D_{5d}	+78.6	–3.7	+29.8
C_{80}^{6-}	D_{5d}	–32.8	–18.9	–13.4

[a] GIAO-SCH/3-21G//HF/6-31G*.[18] [b] Nucleus-independent chemical shifts in the center of the five-membered rings. [c] Nucleus-independent chemical shifts in the center of the six-membered rings.

Compared to the cyclic annulenes, which follow the $4N+2$ rule, the spherical fullerenes show the maximum diatropy more rarely, and there are numerous intermediate situations, including molecules with both aromatic and antiaromatic regions. One key conclusion is that the entire molecule must be taken into account, in order to understand the aromatic properties of icosahedral fullerenes. The applicability of this introduced concept to less symmetrical fullerenes must be examined. It is assumed that local substructures, for example, the graphite-like equatorial belt of C_{70}, also determines the magnetic behavior. This $2(N+1)^2$ rule should be universally applicable for all conjugated π systems, including inorganic compounds, in which the nuclei are distributed symmetrically over the spherical surface.

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