Bond lengths and reorganization energies in fullerenes and their ions

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Abstract. A very simple tight binding method with bond-length-dependent couplings, similar to the Su-Schrieffer-Heeger model, is described and applied to fullerenes in different charge states. The bond lengths, calculated from the π bond orders, are in good agreement with results obtained by ab initio methods which include correlation, where comparisons can be made. The Jahn-Teller distortions are found to be small for the examples C_{20}, C_{28}-T_d, and C_{60}-I_h. Often many possible distortions are found, for example two different D_{5d} distortions for the C_{20} spin triplet state. Bond reorganization energies (λ_b) for reduction and oxidation, which are measures for trapping efficiency and vibronic coupling, are obtained using a parabolic approximation of the energy surface.

Key words: Reorganization energy – Fullerene – Jahn – Teller

1 Introduction

In studies of electron transport in fullerenes it is important to know the nature of the relaxation process that occurs when electrons or holes are moved between the molecules. A large trapping efficiency is connected to a large barrier for electron transfer between molecules. For example in alkali fullerides the trapping may depend on (1) motion of the alkali ions in their cavities and (2) changes of bond lengths in the fullerenes as electrons are accepted or donated. A measure of the trapping efficiency is the reorganization energy λ [1–3]. We have found contributions to λ from bond length changes in alkali doped linear polyenes of about (2·)0.25 eV (multiplication by two for the simultaneous process of oxidation and reduction) and even larger contributions

from the motion of the alkalis. We also found that Hartree-Fock methods tend to overestimate λ by about a factor of 2 compared to methods which include electronic correlation. Unfortunately ab initio wave functions which account for electronic correlation are hard to apply for most fullerenes and we therefore turn to parametrized, simple methods.

Bond lengths may be obtained quite accurately in π systems [1, 3] using the Hückel – self-consistent field (SCF) method of Longuet – Higgins and Salem [4] where the resonance integral β is allowed to depend on the bond length in an iterative manner [1–4]. The calculated increase or decrease in bond length as the number of electrons is changed, and hence the bond length reorganization energy λ_b, is as good as with the best ab initio methods. The reason why a very simple method works so well may be that in a conjugated π system electrons are added to and removed from π orbitals without affecting the σ structure very much. The bond length distortions depend primarily on the change in π bond orders when electrons are added or removed. Here we calculate the bond reorganization energy in fullerenes directly from the bond length changes.

A different way of calculating λ was designed by Mikkelsen et al. [5], who used the Hessian matrix in ab initio SCF methods. In this way a much smaller value for λ than the directly calculated Hartree-Fock value, which tends to be too large, is obtained. The agreement with our directly calculated MP2 value is good [5] in spite of the fact that Hartree-Fock tends to overestimate bond length changes compared to methods which include correlation. An important question is whether the method of Mikkelsen et al. [5] would give an even smaller value had they used methods which include correlation effects. In that case the MP2 value of λ_b, which tends to be smaller than by other methods, would still be an overestimation. However, from the consistency between different methods, all better than Hartree-Fock, regarding bond lengths, we conclude that our general procedure is indeed reasonable and gives good results.

The simple Hückel model [6] with constant β has been used quite extensively to predict properties of fullerenes

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[7–16] and also in connection with the superconductivity in A_3C_{60} [17, 18]. The iterative method [4], here simply called Hückel-SCF, is similar to the method of Su, Schrieffer and Heeger (SSH) which has been used to describe the motion of solitons in polymers [19]. Versions of the latter method have been employed by Harigaya [20], Friedman [21] and Stafström and Fagerström [22] for C_{60}. We believe that Hückel-SCF bond lengths may at least serve as a good point of departure for the much more demanding accurate ab initio methods.

2 Method

The Hückel molecular orbitals (HMO) are linear combinations of the C2p atomic orbitals χ_μ perpendicular to the molecular plane or surface:

$$\phi_i = \sum_{\mu=1}^{N} \chi_\mu C_{\mu i} \tag{1}$$

The hamiltonian matrix has the same diagonal matrix element α for all carbon atoms. In the traditional Hückel method the off-diagonal matrix element is the same (β_0) for neighboring carbon atoms, otherwise zero. The off-diagonal overlap matrix elements are zero.

The π bond order, measuring the strength of the $C_\mu - C_\nu$ bond, are obtained from the coefficients (n_i is the occupation number of HMO ϕ_i):

$$P_{\mu\nu} = \sum_{i=1}^{N} n_i C_{\mu i} C_{\nu i} \tag{2}$$

Longuet-Higgins and Salem derived the following distance dependence for the coupling matrix element $\beta_{\mu\nu}$ between χ_μ and χ_ν [4]:

$$\beta_{\mu\nu} = \beta_0 \exp[-(R_{\mu\nu} - 1.4)/a] \tag{3}$$

where a equal to 0.3106 Å is obtained from vibration spectra [4] and this value will also be used here. By dividing the Hamiltonian matrix by β_0 a dimensionless problem is obtained.

The bond length $R_{\mu\nu}$ is obtained from the bond order $P_{\mu\nu}$ in a slightly different way from Ref. [4]. We use the double bond length 1.334 Å (ethene [23]) and the single bond length 1.534 Å (ethane [23]) and obtain the following bond-length bond-order relation:

$$R_{\mu\nu} = -0.2P_{\mu\nu} + 1.534 \tag{4}$$

The HMO eigenvalue problem may be solved iteratively for each oxidation state of the polyene. The bond lengths of Eq.(4) calculated in the first iteration are used to obtain $\beta_{\mu\nu}$ in Eq.(3) for the second iteration, and so on. This iterative procedure converges slowly in some cases but ensures that β for a given bond is consistent with the length of this bond, as must hold for the final solution.

The reorganization energy due to CC bond-length changes (λ_b) may be calculated [24] from the equation:

$$\lambda_b = \sum_{bonds} \frac{1}{2} k \, \delta R_{\mu\nu^2}, \tag{5}$$

where the force constant k corresponding to CC stretch vibrations is taken to be k = 750 N/m (0.4817 a.u.) [24].

Special care has been taken to compare the smallest possible calculated bond-length differences, to avoid long and short bonds just changing carbon atoms in the iterations, without any actual change in structure.

Using Eqs.(4, 5) we obtain the same λ_b for oxidation $C_n^k \rightarrow C_n^{k+1}$ as for reduction $C_n^{k+1} \rightarrow C_n^{k+}$. In reality this is only approximately true since the force constants may be different in the two states.

In the case where the Highest Occupied Molecules Orbital (HOMO) is degenerate in ordinary Hückel the bond orders do not generally have the symmetry of the molecule. Adjusting the bond lengths according to these bond orders leads to a lower symmetry where the degeneracy has been lifted and the Jahn-Teller effect accounted for. For cyclobutadiene we obtain, for example, two long and two short bonds.

It should be stressed that Eqs.(1–4) include the vibronic interactions in the same way as the SSH equations. The only difference is that we have not emphasized the motion of the nuclei and that the choice of parameters may be slightly different. The method used here should not be considered as conventional Hückel with more parameters. Conventional Hückel trivially leads to bond-length changes which converge to zero with the number of carbon atoms in polyenes, which is physically incorrect [3]. Hückel-SCF solves this problem in an acceptable way from the point of view of physics.

The Hückel-SCF model also takes the second-order Jahn-Teller (SOJT) into account. For example, in benzene C_6H_6 and cyclic polyenes of the type C_{2n+4} there is an excited state of symmetry L_b [25]. The transition density expressed in π bond orders $P_{\mu\nu}$ between this state and the ground A_g state is alternatingly positive and negative. This means that if mixture with the excited state bond order is allowed in one step in the iterative procedure, the bonds *may* distort to alternating long and short. Using the parameters given above, C_6H_6 and $C_{10}H_{10}$ remain with equal bond lengths whereas $C_{14}H_{14}$ and larger cyclic $C_{2n+4}H_{2n+4}$ systems become alternating. This holds in general and stability may be restated as a principle of maximum hardness. Molecules arrange themselves to be as hard as possible [26]. For polyenes this is consistent with the Peierls distortion into alternating long and short bonds [27].

3 Results

3.1 C_{20}

In a free-electron model where the electrons are restricted to moving on the surface or within a shell of a certain width, the orbitals may be assigned ℓ quantum numbers. This quantization is well obeyed for small values of ℓ. Hence filling of the $s + p + d$ subshells gives 18 as a magic number, corresponding to C_{20}^{2+}. In a Hückel treatment where the icosahedral point group (I_h) applies, the $s, p,$ and d orbitals remain degenerate while the f orbital is split into a lower quartet and an upper triplet.

Since both are above the d orbital in energy, C_{20}^{2+} has closed shells and consequently all bonds have the same length (Table 1). In C_{20}^{+} the new electron enters one of the four-fold degenerate g_u orbitals. The symmetry descends to D_{3d} and no further lowering is necessary to satisfy the Jahn-Teller theorem.

In neutral C_{20}, the ground state may be one of the following multiplets: ^1A_g, ^1G_g, ^1H_g, $^3T_{1g}$, or $^3T_{2g}$ in I_h. However, different Jahn-Teller distortions occur depending on occupancy. In the case of a doubly occupied HOMO we find D_{3d} as for C_{20}^+ whereas in the high spin Hund's rule case, when the top occupied MO have one electron each, we find D_{5d}. The degeneracy of HOMO and the Singly Occupied Molecules Orbital (SOMO) is split in both cases. For simplicity we call the two cases LS (low spin) and HS (high spin).

In the neutral C_{20}LS-D_{3d} case there is a bond alternation (1.479–1.395 Å) in a girdle (bonds 3, 4 in Fig. 1) of 12 bonds around the molecule (Table 1). The 3 + 3 bonds from the two apex atoms (bond 1) are 1.434 Å and the remaining 6 + 6 bonds 1.437 Å (bond 2). The 12 atoms in the girdle have the same charge: 1.059. The two apex atoms and the three atoms connected to it are electron deficient: 0.921 and 0.908 electrons, respectively. This is explained by the splitting of the four-fold degeneracy of C_{20}^{2+}-LUMO. In both C_{20}^+ and C_{20}-LS the lowest energy MO of the four is one where only the

coefficients for equatorial girdle atoms are different from zero and alternating as $-1/\sqrt{12}, -1/\sqrt{12}, +1/\sqrt{12}, +1/\sqrt{12}$, etc., i.e. alternatingly bonding and antibonding contributions to the bond order.

In the C_{20}-HS case two different Jahn-Teller minima are obtained, both with geometry D_{5d}. The situation parallels the singly charged benzene molecule where elongated and compressed geometries have been obtained. One of the states agrees well with the elongated geometry obtained by Parasuk and Almlöf in an ab initio Hartree-Fock calculation [28] (ours: 1.425, 1.458, 1.424 Å; P-A: 1.425, 1.474, 1.416 Å). The other is compressed (Table 1).

The bond reorganization energy λ_b [Eq.(5)] for both $C_{20}^+ \to C_{20}$ and $C_{20}^{2+} \to C_{20}^+$ is small (0.123 and 0.125 eV, respectively, Table 2). λ_b for $C_{20} \to C_{20}^{2+}$-LS is about four times as large since the bond-length changes are twice as large when two electrons are subtracted as when one electron is subtracted. For C_{20}-HS the distortions from C_{20}^{2+} are smaller than for C_{20}-LS.

In C_{20} ϕ_{11} and ϕ_{12} are degenerate and hence if one electron is added there is a Jahn-Teller distortion. C_{20}^- acquires C_{2h} symmetry where ϕ_{11} is nondegenerate. In C_{20}^{2-} the symmetry is D_{5d} where ϕ_{10} and ϕ_{11} are degenerate. The D_{5d} symmetry is not possible for C_{20}^- since removing an electron from C_{20}^{2-} has to be connected to a Jahn-Teller distortion which splits the degeneracy.

Although only one or two electron reductions are permitted in a single step we have also listed reorganization energies for many-electron reductions in Table 2. λ_b is large for both LS $C_{20} \to C_{20}^-$ and $C_{20}^- \to C_{20}^{2-}$. One reason is the difference in point group for the different oxidation states. For two-electron reductions λ_b is usually larger than for one-electron reductions. However, in some cases many electrons can be added or removed without a great change of structure. For example HS C_{20}^{2-}, corresponding to the ^5A_g state, is predicted to have the same bond length as C_{20}^{+2}, with a single bond length equal to 1.436 Å. The sum of bond-order contributions is equal to zero for the four degenerate MOs which are singly occupied.

3.2 C_{28}

In the free-electron model mentioned above, filled $s + p + d + f$ gives 32 as a magic number of valence

Table 1. Calculated point groups (P.G) and bond lengths for C_{20} and its ions in their ground states. The bond lengths are given in the order indicated in Fig. 1 for D_{5d} (a), D_{3d} (b) and C_{2h} (c)

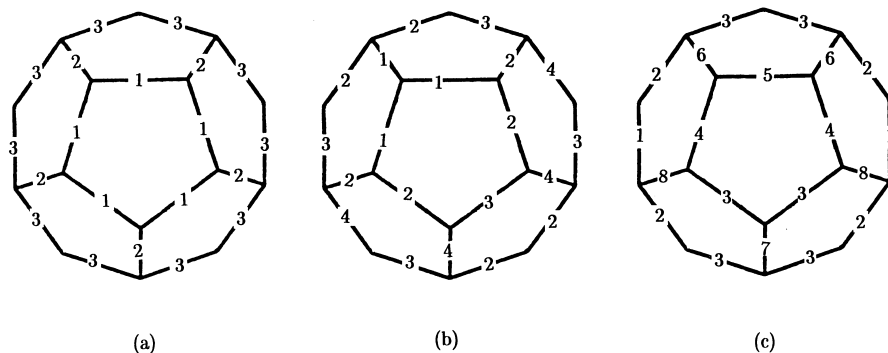| Charge	P.G.	Bond lengths			
+2	I_h	1.436			
+1	D_{3d}	6 × 1.435	12 × 1.436	6 × 1.458	6 × 1.415
High spin:					
0	D_{5d}	10 × 1.447	10 × 1.413	10 × 1.448	
	D_{5d}	10 × 1.425	10 × 1.458	10 × 1.424	
−1	D_{3d}	6 × 1.436	12 × 1.436	6 × 1.415	6 × 1.457
−2	I_h	1.436			
Low spin:					
0	D_{3d}	6 × 1.434	12 × 1.437	6 × 1.479	6 × 1.395
−1	C_{2h}	2 × 1.478	4 × 1.399	8 × 1.462	4 × 1.415
		2 × 1.441	4 × 1.448	2 × 1.386	4 × 1.433
−2	D_{5d}	10 × 1.460	10 × 1.389	10 × 1.460	

| (a) | (b) | (c) |

Fig. 1a–c. Numbering of bonds for C_{20}; **a** D_{5d}; **b** D_{3d}; **c** C_{2h}

Fig. 2. Numbering of bonds for T_d, D_{2d}, and C_{2v} point groups of C_{28}-T_d

electrons. The only cubic fullerene of roughly this size is tetrahedral C_{28}, one of two possible C_{28} fullerene isomers. In C_{28}-T_d there are four apices with three pentagons in each. HOMO is four-fold (partly accidentally) degenerate. C_{28}^{4+} and C_{28}^{4-} have closed shells whereas a lower symmetry is always obtained for ions with charge $-3 \le q \le 3$ (Table 3). The negative ion C_{28}^{4-} has strict T_d geometry and a large HOMO-LUMO (Lowest Unoccupied Molecules Orbital) gap. Tetrahedral C_{28} can form endohedral complexes and this molecule and its ions have therefore attracted considerable attention from experimentalists and quantum chemists [29–33].

We find that the four apex atoms for C_{28}^{4-} carry a large negative charge (0.27 e^-). The 12 atoms adjacent to it have the much lower charge of 0.08 e^- each and the 12 atoms connecting apex tripentagons 0.16 e^- each. If the apex atom is saturated by hydrogen the three bonds to this atom become single bonds with zero π bond order, which should be 0.10 Å longer than in C_{28}^{4-}, in good agreement with Ref. [30].

The ground state of tetrahedral C_{28} has been calculated to be a pentet state using ab initio Hartree-Fock [30]. However, as exchange integrals are small and internal correlation large in fullerenes [18], the spin symmetry of the ground state is still an open question. In any case there is a ^5A_g state at low energy with a strictly tetrahedral equilibrium geometry [30]. Our results for the three distinct bonds are 1.467, 1.444, and 1.423 Å while the Hartree-Fock treatment results for the same bonds are 1.581, 1.460, and 1.435 Å [30]. The order is the same but the magnitudes are at variance. Accurate calculations are needed to determine the bond lengths in the lowest pentet state of C_{28}. As a comparison Hartree-Fock predicts exaggerated bond-length alternation also in polyenes whereas Hückel-SCF agrees well with MP2

Table 2. Calculated reorganization energies (eV) for adding electrons to C_{20} and its ions. Values in parentheses pertain to the second high spin structure for C_{20} (see text)

Original fullerene ion	Number of added electrons			
	1	2	3	4
High spin:				
C_{20}^{2+}	0.125	0.188 (0.173)	0.126	0.000
C_{20}^{+}	0.176 (0.167)			
C_{20}	0.176 (0.167)	0.188 (0.173)		
C_{20}^{-}	0.126			
Low spin:				
C_{20}^{2+}	0.125	0.498		
C_{20}^{+}	0.123	0.271		
C_{20}	0.282	0.719		
C_{20}^{-}	0.187			

Table 3. Calculated point groups and bond lengths for tetrahedral C_{28} and its ions in their ground states. The bond lengths are given in the order indicated in Fig. 2 for the T_d, D_{2d}, and C_{2v} point groups

Charge	P.G.	Bond lengths						
+4	T_d	2 × 1.497	8 × 1.418	8 × 1.454	4 × 1.454	8 × 1.418	8 × 1.418	4 × 1.497
+3	D_{2d}	2 × 1.456	8 × 1.431	8 × 1.455	4 × 1.455	8 × 1.407	8 × 1.422	4 × 1.504
−3	D_{2d}	2 × 1.470	8 × 1.419	8 × 1.441	4 × 1.423	8 × 1.432	8 × 1.435	4 × 1.430
−4	T_d	2 × 1.437	8 × 1.429	8 × 1.433	4 × 1.433	8 × 1.429	8 × 1.429	4 × 1.497
High spin:								
+2	C_2	2 × 1.504.....2 × 1.408						
+1	C_{2v}	1.503, 1.470	4 × 1.413, 4 × 1.423		4 × 1.455, 4 × 1.441		2 × 1.439, 2 × 1.450	
		4 × 1.423, 4 × 1.426	4 × 1.425, 4 × 1.421		4 × 1.468			
0	T_d	2 × 1.467	8 × 1.423	8 × 1.444	4 × 1.444	8 × 1.423	8 × 1.423	4 × 1.467
−1	C_{2v}	1.426, 1.439	4 × 1.437, 4 × 1.431		4 × 1.436, 4 × 1.441		2 × 1.450, 2 × 1.444	
		4 × 1.419, 4 × 1.418	4 × 1.421, 4 × 1.423		4 × 1.472			
−2	C_2	2 × 1.473.....2 × 1.414						
Low spin:								
+2	C_{2v}	1.387,1.456		4 × 1.463, 4 × 1.426		4 × 1.435, 4 × 1.466		2 × 1.468, 2 × 1.417
		4 × 1.400, 4 × 1.404		4 × 1.414, 4 × 1.436		4 × 1.501		
+1	C_1	1.503.....1.387						
	D_{2d}	2 × 1.402	8 × 1.453	8 × 1.450	4 × 1.429	8 × 1.396	8 × 1.431	4 × 1.497
0	C_1	1.501.....1.385						
−1	C_2	2 × 1.501.....2 × 1.395						
−2	D_{2d}	2 × 1.500	8 × 1.410	8 × 1.449	4 × 1.412	8 × 1.434	8 × 1.440	4 × 1.423

[3]. Density functional results have also been obtained: 1.510, 1.446, 1.428 [30], 1.505, 1.451, 1.430 in Ref. [31], and 1.519, 1.459, 1.431 [32]. These results are closer to ours than to the Hartree-Fock results, but the disagreement in the long bond is still so large that one may suspect that σ-effects may be involved. The latter cannot be accounted for in the Hückel-SCF method, of course.

Reorganization energies are given in Table 4. Generally much larger λ_b's are obtained for LS than for HS.

Table 4. Calculated reorganization energies (eV) for adding electrons to tetrahedral C_{28} and its ions

Original fullerene ion	Number of electrons added			
	1	2	3	4
High spin:				
C_{28}^{4+}	0.148	0.165	0.146	0.175
C_{28}^{3+}	0.165	0.174	0.218	
C_{28}^{2+}	0.110	0.154		
C_{28}^{+}	0.057	0.139	0.200	0.264
C_{28}	0.095	0.160	0.211	
C_{28}^{-}	0.109	0.150	0.179	
C_{28}^{2-}	0.070	0.152		
C_{28}^{3-}	0.103			
Low spin:				
C_{28}^{4+}	0.148	0.722	0.842	1.280
C_{28}^{3+}	0.350	0.301	1.089	
C_{28}^{2+}	0.223[a]	0.967		
C_{28}^{+}	0.307[b]	0.478	0.642	0.599
C_{28}	0.311	0.729	0.752	
C_{28}^{-}	0.186	0.233		
C_{28}^{2-}	0.091	0.387		
C_{28}^{3-}	0.103			

[a] 0.312 eV for C_{2v}-HS geometry of C_{28}^{+}
[b] 1.158 eV for C_{2v}-HS geometry of C_{28}^{+}

3.3 C_{60}

For neutral C_{60} we obtain lengths (Table 5) which are close to the values obtained earlier using other Hückel methods, for example ordinary Hückel with some consideration of the effects of σ-electrons [12], a different Hückel-SCF method than the one used here [13], and ordinary Hückel with vibrational analysis [14]. Remarkably enough and consistent with the results for other π systems [1, 3] the agreement is good with the extensive ab initio MP2 calculations of Häser et al. [34] (1.406 and 1.446 Å compared to our values of 1.404 and 1.444 Å). If correlation effects are not included, there is a larger difference between the long and short bond [35–37]. A larger difference is also obtained using the local density [38] and local spin density [39] method, whereas other density functional methods give values close to ours [40, 41]. The experimental results are in between the latter and the MP2 results. NMR [42, 43] gives 1.40 ± 0.015 Å and 1.45 ± 0.015 Å. Neutron diffraction gives 1.391 and 1.455 [44, 45], X-ray diffraction 1.388(5) and 1.432(9) [46] and gas-phase electron diffraction 1.401 and 1.458 Å [47].

The systems $C_{60}^{2+}, C_{60}^{+}, C_{60}^{-}$, and C_{60}^{2-} all have the geometry D_{5d}. This is consistent with the ab initio and other results of Refs. [48–52]. The greatest bond-length changes occur in the equatorial girdle (the periphery in Fig. 3). The changes are such that the bond-length alternation decreases from the C_{60} alternation of 1.40–1.44 Å as we go to higher (positive or negative) charge (Table 5 and [20–22]). In C_{60}^{2+} and C_{60}^{2-} the bonds in the girdle are almost of equal length (1.423 and 1.425 for C_{60}^{2-} D_{5d}; 1.421 and 1.425 for C_{60}^{2+} D_{5d}). A comparison to the results of Bendale et al. [53] for C_{60} and C_{60}^{+} is given in Table 6. The same trends are seen but the bond-length alternation is slightly larger in Ref. [53].

In the D_{5d} geometry ϕ_{32} and ϕ_{33} are degenerate. Thus in C_{60}^{3-}-LS, C_{60}^{4-}-LS, and C_{60}^{-5} the geometry cannot

Table 5. Geometry of the C_{60} football isomer and its ions. For D_{5d} the order of distances is as indicated in Fig. 3 and for D_{3d} as in Fig. 4.

| Charge	P.G.	Bond lengths				
+2	D_{5d}	10×1.444	10×1.403	20×1.445	10×1.398	20×1.454
		10×1.421	10×1.425			
+1	D_{5d}	10×1.444	10×1.404	20×1.444	10×1.401	20×1.449
		10×1.432	10×1.415			
0	I_h	60×1.444	30×1.404			
−1	D_{5d}	10×1.442	10×1.407	20×1.443	10×1.405	20×1.445
		10×1.433	10×1.415			
	D_{3d}	6×1.403	6×1.444	12×1.445	12×1.438	12×1.409
		6×1.437	6×1.416	12×1.447	12×1.438	6×1.407
−2-LS	D_{5d}	10×1.441	10×1.410	20×1.441	10×1.405	20×1.446
		10×1.423	10×1.425			
	D_{3d}	6×1.403	6×1.444	12×1.446	12×1.432	12×1.414
		6×1.430	6×1.428	12×1.449	12×1.433	6×1.410
−3-LS	C_{2h}	$4 \times 1.4454......2 \times 1.4051$				
−3-HS	I_h	60×1.437	30×1.418			
−4	D_{3d}	6×1.434	6×1.432	12×1.428	12×1.442	12×1.423
		6×1.445	6×1.408	12×1.425	12×1.442	6×1.427
−5	D_{3d}	6×1.433	6×1.432	12×1.430	12×1.437	12×1.428
		6×1.438	6×1.420	12×1.428	12×1.436	6×1.430
−6	I_h	30×1.432	60×1.431			
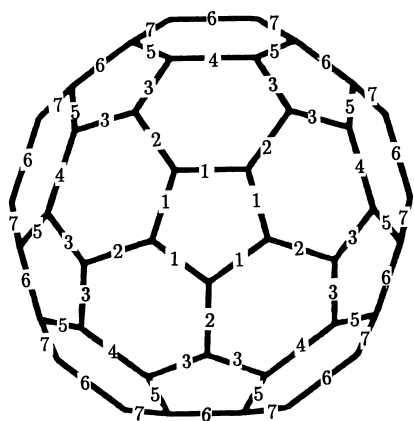
Fig. 3. Numbering of bonds for D_{5d} point group of C_{60} football isomer
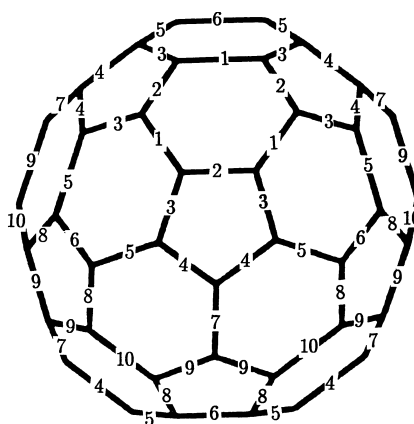
Fig. 4. Numbering of bonds for D_{3d} point group of C_{60} football isomer

Table 6. Comparison with the bond distances calculated for C_{60} and C_{60}^+ by Bendale et al. [53] using the INDO model

Bond	C_{60} Hückel-SCF	INDO	C_{60}^+ Hückel-SCF	INDO
A[a] (4)[b]	1.404	1.398	1.401	1.394
B (2)			1.404	1.398
C (7)			1.415	1.408
D (6)	1.444	1.451	1.432	1.436
E (3)			1.444	1.450
F (1)			1.444	1.451
G (5)			1.449	1.454

[a] Notation used in Ref. [53]
[b] Our notation

Table 7. Calculated bond distance changes (pm) at reduction of the C_{60} football isomer for D_{5d} and D_{3d} geometries of C_{60}^{-1}, compared to the results obtained by Koga and Morokuma (KM) using ab initio Hartree-Fock [48]

D_{5d} this paper	KM	D_{3d} this paper	KM
−0.2	−0.2	−0.1	−0.1
0.3	0.5	0.0	0.1
−0.1	−0.1	0.1	0.3
0.1	0.1	−0.6	−1.0
0.1	0.2	0.5	0.7
−1.1	−1.8	−0.7	−0.9
1.1	1.7	1.2	2.0
		0.3	0.5
		−0.6	−0.9
		0.3	0.6

be D_{5d}. We have found C_{2h} and D_{3d}, respectively. In C_{60}^{4-} and C_{60}^{5-} D_{3d} geometry was found. There is again a smooth change of the bond lengths as the number of electrons is increased. In C_{60}^{6-} the geometry is I_h with a very small difference between the pentagon bonds and the bond between two hexagons. The changes in bond length from C_{60} to C_{60}^{6-} correspond to $\lambda_b = 0.8$ eV. The bond-length changes from C_{60} to C_{60}^{3-}-HS are about half as large, since the change in bond order is half. Consequently λ_b for C_{60} to C_{60}^{3-}-HS is about one quarter (0.2 eV) of λ_b for C_{60} to C_{60}^{6-}.

C_{60}^- was earlier analyzed in detail by Koga and Morokuma on the basis of ab initio calculations of Hartree-Fock type [48]. In this case as in other applications of Hartree-Fock to fullerenes or polyenes, the bond-length alternation is larger than in MP2 and Hückel-SCF. For C_{60}^- Koga and Morokuma found D_{5d}, D_{2h} and D_{3d} structures close in ground state energy. We find that a D_{3d} structure is stable for more than 100 iterations. The bond-length changes when an electron is added are larger in Hartree-Fock than in our results for both D_{3d} and D_{5d}, which is consistent with the results for polyenes [2, 3]. However, as shown in Table 7, the bond-length changes when C_{60} is reduced go in the same direction as ours, bond for bond, and are about 0.02 Å in D_{5d} for the

20 bonds in the girdle. The resulting λ_b for reduction of C_{60} to $C_{60}^{-1} - D_{5d}$ is 0.056 eV in our calculation (and slightly smaller for D_{3d}), primarily due to the bond equalizations in the girdle. The ab initio Hartree–Fock results calculated using Eq.(5) are 2–3 times larger, reminescent of the situation for polyenes [2, 3], benzene, naphthalene, and anthracene [1].

If the I_h point group is assumed for C_{60}^{2-}, there are three multiplets: ^1A_g, ^1H_g, and $^3T_{1g}$ [18, 49]. The highest, incompletely occupied MO is t_{1u}, which means that the multiplet splitting is the same as in the carbon atom, with the triplet as the ground state. However, since the exchange integrals are much smaller for C_{60} than for C while the internal correlation is much larger [18], the order is changed between the states for C_{60} when correlation is introduced, with ^1A_g as the lowest state.

In icosahedral symmetry for C_{60}^{2-} we should get bond-length changes which are 2/3 of the changes to C_{60}^{3-}-HS. Hence λ_b for $C_{60} \rightarrow C_{60}^{2-}$ with symmetry restriction to I_h would be $(2/3)^2$ times λ_b for $C_{60} \rightarrow C_{60}^{-3}$-HS (0.206 eV), which is equal to 0.09 eV. λ_b with symmetry restriction is then 0.09 eV. We have calculated $\lambda_b = 0.23$ eV for $C_{60} \rightarrow C_{60}^{2-}$ if D_{5d} distortions are allowed (Table 8). Hence relaxation to D_{5d} leads to an energy gain of 0.23–0.09 = 0.14 eV, which is a measure of the Jahn-Teller stabilization for C_{60}^{2-}. The multiplet splitting and internal correlation discussed previously [18, 49] exist even in the

Table 8. Calculated reorganization energies (eV) for adding electrons to the C_{60} football isomer and its ions in low spin states

Original fullerene ion	Number of added electrons					
	1	2	3	4	5	6
C_{60}^{2+}	0.074	0.291	0.125	0.066		
C_{60}^{+}	0.071	0.017	0.076			
C_{60}	0.056	0.232	0.308[a]	0.496		0.792
C_{60}^{-}	0.060	0.125	0.309			
C_{60}^{2-}	0.057	0.240	0.307	0.482		
C_{60}^{3-}	0.088	0.136	0.292[a]			
C_{60}^{4-}	0.055	0.218				
C_{60}^{5-}	0.055					

[a] Value for C_{60}^{3-}-HS is $\lambda_b (0,-3) = 0.206$ eV and $\lambda_b(-3,-6) = 0.190$

presence of the Jahn-Teller distortion and contribute to the stabilization of the low spin state. Hence it is theoretically very likely that the ground state is low spin for C_{60}^{-2}, which is consistent with the latest experimental results [53, 54].

The calculated λ_b is considerably smaller than for benzene. For benzene it has been found that the vibronic ground state is in fact symmetric in spite of the fact that the energy surface has two different minima due to a large Jahn-Teller effect [55]. It is very likely that the situation is the same for C_{60} negative ions, particularly since there are six different D_{5d} and ten different D_{3d} local minima. The vibronic ground states of the negative (and positive) ions of C_{60} are therefore very likely symmetric (I_h). This means in turn that λ_b should be calculated in the I_h symmetry for all ions. If this is done there is a smooth equalization of the two different bond lengths from C_{60} to C_{60}^{6-} [16, 56]. Since the bond-length change when one electron is added is one third of the distance change when three electrons are added, we calculate in the same way as in the previous paragraph that λ_b for one electron reduction is $(1/3)^2 \, 0.206$ eV = 0.023 eV, i.e. very small. On the other hand, in condensed phase environmental effects may easily distort the I_h symmetry [57].

The electron pairing that is connected to the superconducting properties of A_3C_{60} is generally considered to be an electronic "effect" [17, 18]. This electronic effect is connected to different minima in the energy surface. If the pair trapping is large a "negative U" state may occur, preventing superconductivity [18, 59]. This is particularly the case if the "coupling" is small. In A_3C_{60} one may suspect that the coupling between the molecules is small and the small reorganization energy for the C_{60} ions is then a prerequisite for the occurrence of superconductivity in the model of Refs [18, 59].

4 Discussion

Fortunately and much due to the efforts of Jan Almlöf and his collaborators [28, 29, 34, 36], ab initio results are available for comparison with our semi-empirical results. In this comparison we see the same pattern as for the smaller polyenes [1–3]. In the Hartree-Fock approxima-

tion the bond-length alternation and the bond-length changes at reduction or oxidation are exaggerated. The Hückel-SCF method agrees well with the correlated ab initio results [28, 34]. In particular the bond-length changes at oxidation or reduction are very close and this implies, as we have seen in earlier papers [1], that the reorganization energies should be well reproduced with the Hückel-SCF model, whereas too large reorganization energies are predicted by the Hartree-Fock method. This shows that bond lengths essentially depend on structural properties via the bond orders of the π orbitals. In uniform systems where the σ system does not change from one carbon atom to the next the Hückel-SCF method may be expected to do well. In one of the bonds in C_{28} we found quite a large disagreement with the density functional and Hartree-Fock results and this may be explained as due to non-uniform contributions from the σ bonds. In the calculation of reorganization energy the effect of the σ bonds may be expected to be the same in the different redox states.

The resulting λ_b's for the structural change when electrons are added or removed are in most cases small. In the literature there have been many discussions on the formation of solitons and polarons. The bond-length changes are confirmed in the present study. However, the resulting λ_b's are smaller than for linear polyenes. This means that electrons are not easily trapped by fullerenes and capable of floating through a lattice of C_{60} without much resistance. Contrary to the case in polyenes there is no formation of solitons in fullerenes. This is expected since the Peierls theorem [27] only applies to one-dimensional systems as has been pointed out before [60]. If electrons are added or removed they remain spread over the surface leading to very small bond-length changes, implying small bond reorganization energies.

It should be noted that reorganization energies are not additive at repeated reduction or oxidation. Bond-length changes, however, are additive in the sense that if two electrons instead of one are removed from or added to the same MO, twice as large a change in the bond order takes place with four times as large reorganization energy. Hence if the two electrons are added one at a time the sum of reorganization energies is only half of the value obtained when they are added at the same time.

In the Hückel-SCF model the degeneracies are broken and a Jahn-Teller minimum attained. The agreement with ab initio methods is quite remarkable in view of the fact that Coulomb interactions are not explicitly included. However, the important thing is that the π electrons are rather uniformly distributed on the carbon atoms. If this is the case the Coulomb energy is formally included in the parameter α (whose value is immaterial anyway).

In trapping problems it is important that the ratio between the intermolecular coupling t and λ_b is large [18, 59, 61]. Since the coupling t between two fullerenes is probably small it is important that λ_b is small. We see (Table 8) that λ_b is small for the negative ions of C_{60}. If we assume, consistent with the situation for the benzene ions [57], that these ions are in fact icosahedral in spite of

Jahn-Teller distortions, λ_b is even smaller, as has been remarked above. However, λ associated with the motion of the alkali ions is still unknown at this stage.

Other theories for superconductivity have been presented where the vibrational coupling also plays a role [17, 20–22, 60, 62]. We believe that λ is the only reasonable measure for such interactions. In the theory of Ref. [18] these interactions are decisive and the chance for superconductivity in our opinion is greater the smaller λ.

The calculated reorganization energies have a potential usefulness in the calculation of rates for electron transfer between fullerenes. Fullerenes may have a great future as storage of charge in electron transfer reactions since many electrons can be trapped, each (usually) with a small λ_b. Perhaps in the future fullerenes with "tailor-made" redox potential and λ can be made to perform a particular oxidation or reduction at a suitable speed.

5 Conclusion

An expedient bond-order-based method which simulates ab initio MP2 and density functional calculations on π systems has been applied to fullerenes. We have made a comparison with the most accurate theoretical results, particularly the work of Almlöf and his collaborators, and find a surprisingly good agreement. We suggest that the method presented here is used in connection with ab initio calculations to obtain a good starting point in geometry optimizations. We also want to point out the importance of good reorganization energies in electron transfer and conductivity problems. Our results may be taken as an indication that the problem is not trivial and must be approached by very accurate ab initio methods. We refer to Ref. [5] for additional discussion.

Since the method presented here does not include the σ bond energies at all, it cannot be used to order isomers of a given fullerene in order of energy. For less spherical fullerenes (possibly C_{28}-T_d in the present case) this may prevent a good prediction of some bond lengths. However, our main purpose for using the method has been to be able to predict changes of bond lengths as the fullerenes undergo redox reactions and in that case we believe that errors due to σ strains tend to cancel each other out.

The calculated bond-length changes as the number of electrons on the fullerene is changed are usually small (below 0.02 Å). The resulting reorganization energies are therefore also small in most cases and suggest that fullerenes may be used in electron transfer reactions as electron storage to provide optimum conditions. In the case of superconductivity we believe that the small reorganization energies in C_{60} compensate for the small coupling between sites, as compared to other superconductors.

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