Monatshefte für Chemie 133, 987–990 (2002)

Monatshefte für Chemie
Chemical Monthly

Classical Valence Similarity in Fullerene Derivatives

Susumu Narita[1,*], **Takeshi Hamakawa**[1], **Tetsuo Morikawa**[2], and **Tai-ichi Shibuya**[1]

[1] Faculty of Textile Science and Technology, Shinshu University, Ueda, Japan
[2] Department of Chemistry, Joetsu University of Education, Joetsu, Japan

Summary. The generalized *Pauling* bond order was enumerated in the C_{60} fullerene cage molecule (truncated icosahedral symmetry). This index measures chemical similarity in fullerene derivatives such as dihydrofullerene ($C_{60}H_2$), anionized monohydrofullerene ($C_{60}H^-$), N-substituted monohydrofullerene ($C_{59}NH$), the fullerene dimer ($(C_{60})_2$), and the dianionic fullerene dimer ($(C_{60})_2^{2-}$). It is also useful in judging the chemical stability of isomers.

Keywords. Chemical similarity; Unconjugated carbon site; C_{60} Fullerene derivative; *Pauling* bond order; *Kekulé* structure counting.

Introduction

Much has been discussed about the chemistry of the C_{60} fullerene molecule (carbon cage, truncated icosahedral symmetry) [1–3]. A conjugated carbon atom $\rangle C=$ of the cage can be chemically modified into an unconjugated site such as $\rangle CH-$ (hydrogen attached), $\rangle C^{\bullet -}$ (anionic), $\rangle N-$ (nitrogen exchanged), and $\rangle \overset{|}{C}-$ (bonding between fullerene dimers). Such unconjugated sites can be found in dihydrofullerene ($C_{60}H_2$), anionic monohydrofullerene ($C_{60}H^-$), N-substituted monohydrofullerene ($C_{59}NH$), the fullerene dimer ($(C_{60})_2$), and the dianionic fullerene dimer ($(C_{60})_2^{2-}$).

It is known that the number of conjugated sites in stable fullerene derivatives is even. This may be understood in terms of classical valence theory, just as for benzenoid hydrocarbons (*Clar* postulate) [4, 5]: A π-electron conjugated system is chemically/thermodynamically unstable if it has no *Kekulé* structure. Clearly, if the number of chemically modified sites in a fullerene derivative is odd, then the number of conjugated sites also becomes odd, and there is no *Kekulé* structure. Hence, there might be arrangements of a pair of unconjugated sites (*i.e.* chemically modified sites) on each fullerene derivative cage; such a fullerene derivative has geometrical isomers.

* Corresponding author. E-mail: snarita@giptc.shinshu-u.ac.jp

It seems that in the $C_{60}H_2$ isomers the chemical surroundings of the hydrogenated carbons (unconjugated sites) are similar, and that the conjugation frame of carbon sites (conjugated sites) other than reaction sites remain unchanged after the addition of hydrogen atoms. Hence, chemical stability/instability of the $C_{60}H_2$ isomers can be determined by the degree of conjugation in the conjugation frame [6, 7]. This view of chemical similarity among carbon sites in C_{60} should render some simple theory such as classical valence theory [8] useful to judge which isomer of a given C_{60} derivative is chemically stable.

Results and Discussion

The generalized *Pauling* bond order $P_{i,j}(M)$ measures the degree of conjugation in a given conjugated molecule M with two unconjugated sites i and j [7]. This graph-theoretical index is defined as the ratio of $K(M_{i,j})$ to $K(M)$. The denominator $K(M)$ is equal to the total number of *Kekulé* structures in M, and the numerator $K(M_{i,j})$ is the number of *Kekulé* structures in a molecular subgraph $M_{i,j}$ of M where the vertices i and j ($i \neq j$) as well as all edges that meet with i and j are removed from M. $P_{i,j}(C_{60})$ is reduced to the *Pauling* bond order of bond $i-j$ if the vertices i and j are adjacent. The choice of $i = 1$ is possible with no loss of generality. The second column of Table 1 shows the calculated $P_{1,j}(C_{60})$ for j in decreasing order. The site numbering j is shown in Fig. 1 ($K(C_{60}) = 12500$ [10]).

It is believed that every carbon site of C_{60} is sp^2 hybridized with a small admixture of sp^3 character [1]. The C_{60} molecule has only two symmetry-independent bonds: a shorter one (1−2) with $P_{1,2} = 0.440$ and a longer one (1−6) with $P_{1,6} = 0.280$. The *Pauling* bond order ranges from 0 (single bond) to 1 (double bond). Hence, one can state that the longer bond lying in the pentagons of C_{60} has partly 'double bond' character and therefore participates in the delocalization of the π-electrons. Therefore, hydrogen addition occurs easily and yields the $C_{60}H_2$ isomers. As can be seen from the second column of Table 1, the largest value of $P_{1,j}(C_{60})$ is 0.440 for $P_{1,2}(C_{60})$. This is consistent with the experimental fact that the reaction of C_{60} with BH_3 affords the 1,2-isomer rather than the 1,4- and 1,6-isomers [11, 12]. This favourable addition of hydrogen has been clearly explained by the degree of $P_{i,j}(C_{60})$ [7].

As a second example we discuss $C_{59}NH$, where the hydrogenated (unconjugated) carbon is $i = 1$ and the substituted nitrogen atom j of the fullerene cage is

Table 1. Calculated results of $P_{1,j}(C_{60})$, AM1 optimized heat of formation for $C_{60}H_2$ and $C_{59}NH$, and population analysis for $C_{60}H^-$ and $(C_{60})_2^{2-}$

Site j [1]	$P_{1,j}$	$C_{60}H_2$ [2]	$C_{59}NH$ [3]	$C_{60}H^-$ [4]	$(C_{60})_2^{2-}$ [5]
2	0.440	0.0	0.0	−0.298	−0.251
4	0.300	18.4	24.2	−0.140	−0.108
6	0.280	78.6	68.6	−0.070	−0.030
16	0.238	67.7	68.6	−0.085	−0.084
13	0.224	104.9	84.9	−0.042	−0.042

[1] Numbering as in Fig. 1; [2,3] AM1 MacSpartan Pro, relative heat of formation in kJ/mol; [4] AM1, *Mulliken* population analysis; [5] AM1 Gaussian 98, *Mulliken* population analysis

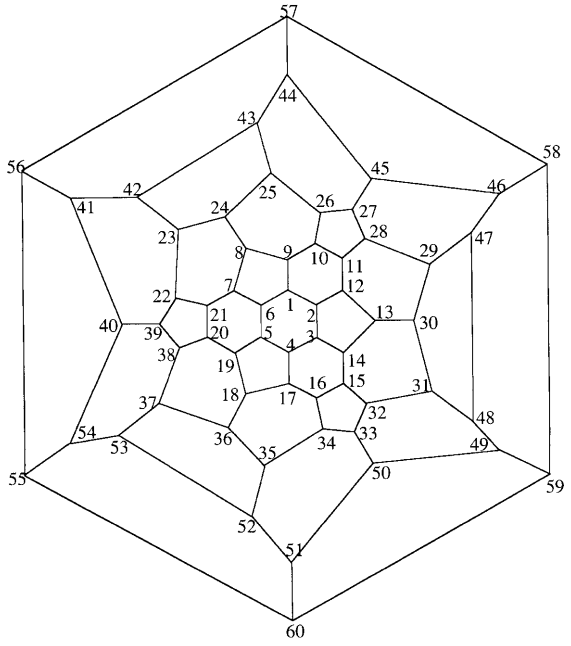

Fig. 1. The numbering of carbon sites in a *Schlegel* diagram of the C_{60} molecule (truncated icosahedral symmetry; top view, projected on a plane [9])

also an unconjugated site. Note that $P_{1,j}(C_{59}NH) = P_{1,j}(C_{60})$. The AM1 optimized energy (relative heat of formation) for each isomer is given in the fourth column of Table 1. The calculated results suggest that the most stable isomer for $C_{59}NH$ is 1,2-$C_{59}NH$.

As a third example of the application of the generalized *Pauling* bond order $P_{1,j}(C_{60})$ we discuss the hydride anion $C_{60}H^-$. The number of symmetry-independent isomers of $C_{60}H^-$ is 23 [12]. In each of the isomers there are two unconjugated sites, hydrogenated $i = 1$ and anionic carbon j. Note that $P_{1,j}(C_{60}H^-) = P_{1,j}(C_{60})$. Population analysis with AM1 optimization by use of MacSpartan Pro (Wavefunction, Ltd.) gives a charge distribution as shown in the fifth column of Table 1. The order of the first two largest values agrees with that for $P_{1,j}(C_{60})$. The chemical background is as follows: After fixing of one hydrogen-attached site as $i = 1$, one anionic carbon site j, *i.e.* $\diagdown C^{\bullet-}\!\!-$, is chemically similar to another in the conjugated isomers, and hence the degree of conjugation determines the electronic population of the conjugated isomers.

One could expect the same effect of hybridization of the carbon sites as in the polymerization of C_{60} [13–15]. Now consider the stability/instability of C_{60} fullerene dimers. Suppose that only one bond connects $i = 1$ and $i' = 1'$ in the two C_{60} cages. We expect that this fullerene dimer is unstable because the number of unconjugated sites in each C_{60} cage is odd (*Clar* postulate). If two bonds between $i = 1$ and $i' = 1'$ and between $j \neq 1$ and $j' \neq 1'$ connect two C_{60} cages, then each cage has *Kekulé* structures, $P_{1,j}(C_{60})$ and $P_{1',j'}(C_{60})$ being the same. The cycle $1-1'-j'-j-1$ is a four-sided figure; the production of the dimer is called $2+2$ cycloaddition [13]. The maximum numbers of *Kekulé* structures divided by

$K(C_{60})$ are

$$P_{1,1'} \times P_{2,2'} = 0.440 \times 0.440 = 0.194$$
$$P_{1,1'} \times P_{2,6'} = 0.440 \times 0.280 = 0.123$$
$$P_{1,1'} \times P_{6,6'} = 0.280 \times 0.280 = 0.078$$

Hence, classical valence theory predicts that the $2+2$ cycloaddition reaction is favourable to two pairs ($(1,1')$ and $(2,2')$), and each of the two bonds in the $2+2$ cycloaddition is a single bond. These prediction agrees well with the experimental results.

The last example discussed here is the population analysis for $(C_{60})_2^{2-}$. The last column of Table 1 shows the calculated results by means of AM1 optimization (Gaussian 98). One C_{60} cage with an anionic $\diagdown\!\!\diagup C^{\bullet=}$— site j is connected to the other one with a single bond between 1 and $1'$; hence, $P_{j,j'}((C_{60})_2^{2-}) = P_{1,j}(C_{60}) \times P_{1',j'}(C_{60})$. The maximum value of $P_{j,j'}((C_{60})_2^{2-})$ appears at the pair of sites 2 and $2'$; this result agrees with the population analysis.

We can conclude that the generalized *Pauling* bond order $P_{i,j}(C_{60})$ is a good index for the theoretical prediction of the stability of isomers of C_{60} fullerene derivatives and that there is a chemical similarity between fullerene derivatives such as $C_{60}H_2$, $C_{60}H^-$, $C_{59}NH$, $(C_{60})_2$, and $(C_{60})_2^{2-}$ from the stand point of classical valence theory.

References

[1] Dresselhaus MS, Dresselhaus G, Eklund PC (1996) Science of Fullerens and Carbon Nanotubes. Academic Press, New York, and references cited therein
[2] Eklund PC, Rao AM (1999) Fullerene Polymers and Fullerene Polymer Composites. Springer, New York
[3] Prassides K, Polymer (2000) Dimer Phases in Doped Fullerenes. In: Andreoni W (ed) The Physics of Fullerene-Based and Fullerene-Related Materials, chapt 5. Kluwer, Dordrecht
[4] Clar E, Kemp W, Stewart DG (1958) Tetrahedron **3**: 325
[5] Trinajstić N (1992) Chemical Graph Theory, 2nd edn. CRC, Boca Raton
[6] Taylor R, Walton DRM (1993) Nature **363**: 685
[7] Narita S, Morikawa T, Shibuya T-I (2000) J Mol Struc (TheoChem) **528**: 263
[8] Pauling L, Brockway LO, Beach JY (1935) J Am Chem Soc **57**: 2075; Pauling L (1960) The Nature of the Chemical Bond, 3rd edn. Cornell University Press, pp 234–239; Pauling L (1980) Acta Cryst **B36**: 1898
[9] Taylor R (1993) J Chem Soc Perkin Trans 2, 813
[10] Schmalz TJ, Seitz WA, Klein DJ, Hite GE (1988) J Am Chem Soc **110**: 1113
[11] Henderson CC, Cahill PA (1993) Science **259**: 1885
[12] Henderson CC, Rohlfing CM, Assink RA, Cahill PA (1994) Angew Chem Int Ed Engl **33**: 786
[13] Stephenes PW, Bortel G, Faigel G, Tegze M, Janossy A, Pekker W, Oszlanyi G, Forro L (1994) Nature **370**: 636
[14] Zhu Q, Cox DE, Fisher JE (1995) Phys Rev **B51**: 3966
[15] Oszlányi G, Bortel G, Faigel G, Tegze M, Gránásy L, Pekker S, Stephenes PW, Bendele G, Dinnebier R, Mihály G, Jánossay A, Chauvet O, Forró A (1995) Phys Rev **B51**: 12228

Received October 9, 2001. Accepted November 9, 2001