communications in mathematical
match
and in computer chemistry

33 (1996), 47 - 56

Supplementary Notes on Indacenoids with Applications to Semibuckminsterfullerene

S. J. Cyvin, J. Brunvoll, and B. N. Cyvin

Department of Physical Chemistry, The University of Trondheim,
Trondheim–NTH, Norway

Indacenoids are polygonal systems which consist of exactly two pentagons each and arbitrary numbers of hexagons. They represent a certain class of polycyclic conjugated hydrocarbons. General formulations of relevance to extremal systems are reported for the C_nH_s chemical formulas. Finally, a "spectrum" of formulas is defined, which relates a given C_nH_s formula of a polygonal system to the benzenoid formulas.

Introduction

The recent synthesis of $C_{30}H_{12}$ semibuckminsterfullerene [1] (see Figure 1) prompted Dias [2] to continue his studies of indacenoids [3]. An indacenoid is a polygonal system [4] consisting of two pentagons alone (pentalene) or exactly two pentagons in addition to an arbitrary number of hexagons. These chemical graphs [5] represent a class of polycyclic conjugated hydrocarbons, where indacene is a prototype. More completely, the three $C_{12}H_8$ isomers of indacenoids represent *s*–indacene, *as*–indacene and benzopentalene, of which the structural formulas are found elsewhere [4].

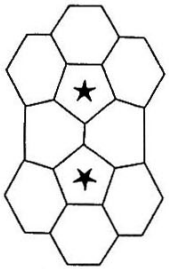

Figure 1. Semibuckminsterfullerene or circumfulvalene, $C_{30}H_{12}$. The two pentagons are marked by asterisks.

In the present notes, we wish to give some general formulations for the chemical formulas of indacenoids. This work is supposed to be a significant supplement to the works of Dias [2,3,6], and it demonstrates the wide applicability of an approach which was first applied to benzenoids [7–11]. The same approach has most recently been applied to single coronoids [12], a monograph which includes references to numerous further applications.

Invariants

Consider the chemical formula $C_nH_s \equiv (n;\ s)$ for an indacenoid. Then

$$(n;\ s) = (4r - n_i\ ;\ 2r - n_i + 2) \tag{1}$$

and conversely:

$$r = \frac{1}{2}(n - s) + 1 \quad , \quad n_i = n - 2s + 4 \tag{2}$$

where $r = 2, 3, 4, \ldots$ is the number of polygons (or rings), and $n_i = 0, 1, 2, \ldots$ is the number of internal vertices. The degenerate case C_5H_5 ("phantom formula" [6]) is a natural extension of "indacenoids" to $r = 1$. As such, C_5H_5 acquires $n_i = -1$, which of course does not reflect the number of internal vertices. From (1) it is clear that the condition of parity is fulfilled: either n and s are both even, or both of them are odd. Specifically, the even–carbon formulas (n and s even) occur when n_i is even, while the odd–carbon formulas (n and s odd) occur when n_i is odd. Furthermore, one finds in general for indacenoids: $n = 5, 8, 11, 12$ or $n \geq 14$ (where the degenerate case is included), while $s \geq 5$. The possible combinations of n and s in an indacenoid (or benzenoid) formula are treated in a subsequent paragraph.

Circumscribing

Circum–C_nH_s for indacenoids, when referring to circumscribing by hexagons, has the formula [2]

$$(n_1; s_1) = (n + 2s + 4\,;\ s + 4) \tag{3}$$

Semibuckminsterfullerene is circum–$C_{10}H_8$, where $C_{10}H_8$ is the formula for fulvalene; cf. Figure 1. If $(n;\ s) = C_{10}H_8$, then $(n_1;\ s_1) = C_{30}H_{12}$, the formula for semibuckminsterfullerene, is correctly obtained from eqn. (3).

The generalization to k–fold circumscribing reads:

$$(n_k; s_k) = (n + 2ks + 4k^2\,;\ s + 4k) \tag{4}$$

Extremal Indacenoids and Some of Their Subclasses

An *extremal* indacenoid has by definition $n_i = (n_i)_{max}$ for a given r. This definition conforms with the "extremal animals" [13,14] or extremal benzenoids in particular [7–11,15]. It was found for indacenoids:

$$(n_i)_{max} = 2r - \lceil (8r)^{1/2} \rceil \tag{5}$$

Circular indacenoids form a subclass of the extremal indacenoids. A *circular* indacenoid has by definition $r = r_{max}$ for a given s. It was found:

$$r_{max} = \left\lfloor \tfrac{1}{8}(s-2)^2 \right\rfloor \tag{6}$$

A general expression for the formulas $(n^0; s^0)$ of circular indacenoids reads

$$(n^0; s^0) = (s - 2 + 2\left\lfloor \tfrac{1}{8}(s-2)^2 \right\rfloor ;\ s) \tag{7}$$

for $s = 5, 6, 7, \ldots$.

Constant–isomer series [16–18] have been detected for indacenoids by Dias [3–6]. These series contain exactly the formulas for extremal indacenoids. The first formula in each of these series, referred to as the "base (first generation) formula" [6], represents the *ground form(s)* [18,19]. All the other formulas of the constant–isomer series represent *higher members* [18,19], which are circumextremal systems. A *circumextremal* indacenoid is defined as a circumscribed extremal indacenoid. There is one degenerate circumextremal indacenoid, which has the formula $C_{19}H_9$. It is cyclopentadienyl (C_5H_5) circumscribed by one pentagon and four hexagons. Notice that this "degenerate circumscribing" $C_5H_5 \rightarrow C_{19}H_9$ is compatible with Eq. (3). For benzenoids, the

one–isomer series [9,11,16,18,20] represent exactly the circular systems. The situation for indacenoids is different; the circular indacenoids are associated with the three one–isomer series, which start with C_5H_5, C_8H_6 and $C_{11}H_7$ [3], in addition to the unique three–isomer series starting with $C_{14}H_8$ [3].

In summary, the ground form indacenoids are the extremal indacenoids which are not circumextremal. They have the formulas C_5H_5, C_8H_6, $C_{11}H_7$, $C_{14}H_8$, $C_{17}H_9$, $C_{22}H_{10}$, ... , listed by Dias [6] up to $C_{145}H_{25}$. All these $(n^g;\ s^g)$ formulas are reproduced by

$$(n^g;\ s^g) = \left(s + 2\left\lfloor \tfrac{1}{8}(s-3)^2 \right\rfloor\ ;\ s\right) \tag{8}$$

for $s = 5, 6, 7, \ldots$. This general formulation belongs to what has been called the *Harary–Harborth picture* [11] because it emerged from a continuation of the pioneering analysis of Harary and Harborth [13]. The "floating function" [6] for the same chemical formulas belongs to the *Balaban picture* [11] because of its relevance to a general formulation by Balaban [21] for a certain class of annulenes. A *new picture* has been proposed, introducing the original idea to reproduce series of chemical formulas by generating functions [4]. For the ground forms of indacenoids it was found:

$$n^g(x) = \sum_{s=5}^{\infty} n^g\, x^s = \frac{x^5(5-2x-5x^4+4x^5)}{(1-x)^2(1-x^4)}$$

$$= 5x^5 + 8x^6 + 11x^7 + 14x^8 + 17x^9 + 22x^{10} + \ldots \tag{9}$$

Formula Index

Some theorems on benzenoids [14,15,23,24] are immediately transferable to

indacenoids; in the following it is referred to circumscribing by hexagons. (i) Any extremal indacenoid can be circumscribed, whereby another (larger) extremal indacenoid emerges; hence any extremal indacenoid can be circumscribed arbitrarily many times. (ii) A non–extremal indacenoid becomes extremal when circumscribed sufficiently many times, if this is possible. (iii) Among the indacenoid isomers with a given formula C_nH_s, at least one system can always be found which can be circumscribed arbitrarily many times.

The above property (ii) is quantified through the *formula index* [12,14,23]:

$$x = \lfloor \tfrac{1}{8}(s-3)^2 - \tfrac{1}{2}(n-s) \rfloor \qquad (10)$$

If a non–extremal indacenoid with a formula $(n; s)$ can be circumscribed x times, then the x–fold indacenoid is extremal; it possesses the formula $(n_x ; s_x)$, which is obtainable from (4) and pertains to ground form(s). For any ground form indacenoid, $x = 0$. A circumextremal indacenoid has $x < 0$ and is an $|x|$–fold circumscribed ground form, for which the formula is again obtainable from (4) by inserting $k = x$ (now a negative number).

For $C_{30}H_{12}$, eqn. (10) gives $x = 1$. Therefore, circumsemibuckminsterfullerene, which acquires the formula $C_{58}H_{16}$, is an extremal system. It is in fact one of the ground forms of a constant–isomer series, in consistency with the findings of Dias [2,3,6]. For $C_{58}H_{16}$, eqn. (10) gives correctly $x = 0$.

Which Chemical Formulas are Possible for Indacenoids?

Dias [3] has published extensive listings of chemical formulas which are compatible with indacenoids, but has not given an explicit general formulation to this effect. Here it was found, in the style of the analogous relations for benzenoids [10,18,25]:

$$2\left\lceil \tfrac{1}{2}n + (n+1)^{1/2} \right\rceil - n \leq s \leq n + 2 - 2\lceil n/4 \rceil \quad (n > 5) \tag{11}$$

$$s - 4 + 2\lceil s/2 \rceil \leq n \leq s - 2 + 2\left\lfloor \tfrac{1}{8}(s-2)^2 \right\rfloor \quad (s > 5) \tag{12}$$

By using these relations, the condition of parity (see above) should be observed. Here the upper and lower bounds are always realized.

Examples with relevance to semibuckminsterfullerene, $C_{30}H_{12}$: (a) for $n = 30$, $12 \leq s \leq 16$; the possible indacenoid formulas with $n = 30$ are $C_{30}H_{12}$, $C_{30}H_{14}$, $C_{30}H_{16}$; (b) for $s = 12$, $20 \leq s \leq 34$; the possible indacenoid formulas with $s = 12$ are $C_{20}H_{12}$, $C_{22}H_{12}$, $C_{24}H_{12}$, $C_{26}H_{12}$, $C_{28}H_{12}$, $C_{30}H_{12}$, $C_{32}H_{12}$, $C_{34}H_{12}$.

A Spectrum of Formulas

Dias [3] has pointed out that an indacenoid may be or may be not isomeric to a benzenoid. It is also implied in his work that the indacenoid formulas surpass the benzenoid formulas at their relatively hydrogen–poor regions. A detailed explanation is furnished in the following.

In general, two polygonal systems with the same formula C_nH_s possess necessarily the same number of polygons. For a given number of polygons, any such formula can be related to the corresponding benzenoid formulas, which span from the formula for catacondensed benzenoid(s) to the formula for extremal benzenoid(s). A non–benzenoid formula may be found outside these limits. On this basis we define a *spectrum* of the C_nH_s formulas for polygonal systems in the following precise terms.

$s > \frac{1}{2}n + 3$; *infrabenzenoid* formula (f.)
$s = \frac{1}{2}n + 3$; *catabenzenoid* f.
$3 + \lceil (6n - 6s + 9)^{1/2} \rceil \leq s \leq \frac{1}{2}n + 3$; *benzenoid* f.

$s = 3 + \lceil (6n - 6s + 9)^{1/2} \rceil$; *extremalbenzenoid* f.

$s < 3 + \lceil (6n - 6s + 9)^{1/2} \rceil$; *ultrabenzenoid* f.

In this terminology, an indacenoid formula may be benzenoid (including extremalbenzenoid) or ultrabenzenoid, but never catabenzenoid or infrabenzenoid. An illustrative example is given below for systems with five polygons.

Benzenoid	Indacenoid
$^{c}C_{22}H_{14}$	
$C_{21}H_{13}$	
$C_{20}H_{12}$	$^{c}C_{20}H_{12}$
$^{e}C_{19}H_{11}$	$C_{19}H_{11}$
	$C_{18}H_{10}$
	$^{e}C_{17}H_{9}$

^{c} catacondensed; ^{e} extremal

For $C_{30}H_{12}$,

$$s < 3 + \lceil (6n - 6s + 9)^{1/2} \rceil = 14.$$

Therefore, the semibuckminsterfullerene formula is ultrabenzenoid.

Conclusion

The present work demonstrates the virtues of an approach which has been applied previously to benzenoids and other polygonal systems representing polycyclic conjugated hydrocarbons. This approach is applied to indacenoids, which have attracted new interest quite recently.

References

[1] P. W. Rabideau, A. H. Abdourazak, H. E. Folsom, Z. Marcinow, A. Sygula, and R. Sygula, J. Am. Chem. Soc. **116**, 7891 (1994).

[2] J. R. Dias, J. Chem. Inf. Comput. Sci. **35**, 148 (1995).

[3] J. R. Dias, J. Chem. Inf. Comput. Sci **32**, 203 (1992).

[4] J. Brunvoll, B. N. Cyvin, and S. J. Cyvin, Z. Naturforsch. **48a**, 1017 (1993).

[5] N. Trinajstić, Chemical Graph Theory, Second Edition, CRC Press, Boca Raton 1992.

[6] J. R. Dias, J. Chem. Inf. Comput. Sci. **33**, 117 (1993).

[7] S. J. Cyvin and J. Brunvoll, Chem. Phys. Letters **176**, 413 (1991).

[8] S. J. Cyvin, J. Chem. Inf. Comput. Sci. **31**, 340 (1991).

[9] S. J. Cyvin, Theor. Chim. Acta **81**, 269 (1992).

[10] J. Brunvoll, B. N. Cyvin, and S. J. Cyvin, Topics Current Chem. **162**, 181 (1992).

[11] S. J. Cyvin, B. N. Cyvin, and J. Brunvoll, Topics Current Chem. **166**, 65 (1993).

[12] S. J. Cyvin, J. Brunvoll, R. S. Chen, B. N. Cyvin, and F. J. Zhang, Lecture Notes in Chemistry **62** (1994).

[13] F. Harary and H. Harborth, J. Combin. Inf. Syst. Sci. **1**, 1 (1976).

[14] J. Brunvoll, B. N. Cyvin, and S. J. Cyvin, J. Math. Chem. **12**, 109 (1993).

[15] S. J. Cyvin, B. N. Cyvin, and J. Brunvoll, Monatsh. Chem. **124**, 477 (1993).

[16] J. R. Dias, J. Chem. Inf. Comput. Sci. **30**, 61 (1990).

[17] J. R. Dias, J. Chem. Inf. Comput. Sci. **30**, 251 (1990).

[18] J. Brunvoll and S. J. Cyvin, Z. Naturforsch. **45a**, 69 (1990).

[19] S. J. Cyvin, J. Brunvoll, and B. N. Cyvin, Commun. Math. Chem. **26**, 27 (1991).

[20] J. R. Dias, J. Chem. Inf. Comput. Sci. **22**, 15 (1982).

[21] A. T. Balaban, Tetrahedron **27**, 6115 (1971).

[22] B. N. Cyvin, S. J. Cyvin, and J. Brunvoll, J. Chem. Inf. Comput. Sci. **33**, 745 (1993).

[23] S. J. Cyvin, J. Brunvoll, and B. N. Cyvin, J. Serb. Chem. Soc. **56**, 369 (1991).

[24] S. J. Cyvin, B. N. Cyvin, J. Brunvoll, I. Gutman, and P. E. John, J. Serb. Chem. Soc. **58**, 1 (1993).

[25] S. J. Cyvin and B. N. Cyvin, Struct. Chem. **4**, 303 (1993).