Extremal Mono-q-polyhexes†

Bojan Mohar‡

Department of Mathematics, University of Ljubljana, Jadranska 19, 61111 Ljubljana, Slovenia

Received January 7, 1993®

A conjecture of Cyvin (Cyvin, S. J. *J. Math. Chem.* **1992**, *9*, 389) concerning mono-q-polyhex graphs is proved for $q \le 6$ and disproved for $q > 6$. The correct result for $q > 6$ is then established.

1. INTRODUCTION

A *polyhex* can be defined as a graph H which is obtained from the hexagonal lattice L_6 of the plane by taking a cycle C in the graph of L_6 and defining H to be the part of L_6 in the disk bounded by C, including C. Similarly, a *mono-q-polyhex*, q an integer greater than 3, is obtained from the mono-q-hexagonal lattice (all faces are hexagons except one which is a q-gon, and three faces meet at each vertex) by specifying a cycle C such that the q-gon is included in the disk bounded by C.

A simple description of the mono-q-hexagonal lattice is as follows. Let L_1 be one-sixth of the hexagonal lattice obtained by taking one of its hexagons Q, the middle point x of Q, and the six rays from x through each vertex of Q toward infinity (see Figure 1). Then L_1 is one of the wedges of the plane between the two consecutive rays. The mono-q-hexagonal lattice is then obtained by taking q copies of L_1 and identifying their sides in circular order. Note that L_3, L_4, L_5, and L_6 can be realized in 3-space so that all the hexagons remain congruent (as an unbounded cone with its apex in the middle of the q-gon), while L_7, L_8, ... cannot be modeled with congruent hexagons due to their hyperbolic nature. The above description of L_q also helps us to represent the mono-q-polyhexes by specifying the q wedges in the copies of L_1 (see Figure 2).

Let H by a mono-q-polyhex, and let n_{int} and h denote the number of internal vertices of H and the number of hexagons (if $q = 6$, let h be the number of hexagons minus 1, so that the q-face is not counted by h), respectively. A useful relation was derived by Gutman[2] in case of $q = 6$:

$$n_{\text{int}} \le 2h + 3 - \lceil (12h + 9)^{1/2} \rceil \qquad (1)$$

and it was conjectured by Cyvin[1] that (1) can be generalized to

$$n_{\text{int}} \le 2h - \lceil (4rh + r^2)^{1/2} - r \rceil \qquad (2)$$

where $r = q/2$, and $\lceil x \rceil$ denotes the ceiling of x.

In this paper we prove (2) for $q \le 6$ (theorem 2.1) and also show that this bound is the best possible (theorem 2.2). On the other hand, for every $q \ge 7$ we construct infinitely many counterexamples for (2). The correct result for $q > 6$ is then provided as theorem 3.1.

The mono-q-polyhexes have some chemical significance as interesting molecular graphs. Take, for example, the (q)-circulenes. The corannulene $C_{20}H_{10}$ is a (5)circulene;[3] the coronene $C_{24}H_{12}$ corresponds to a (6)circulene. A (7)circulene,

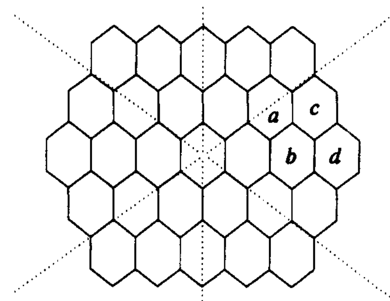

Figure 1. The hexagonal lattice.

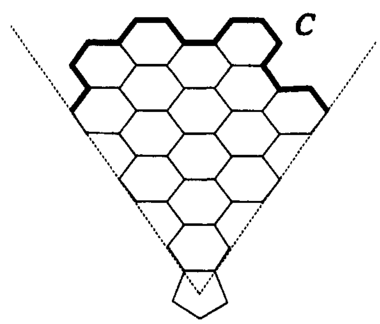

Figure 2. A wedge of a mono-5-polyhex.

$C_{28}H_{14}$, has also been synthesized,[4] and a synthesis of (8)-circulene $O_{32}H_{16}$ has been attempted.[5]

2. CASE $q \le 6$

In this section we will prove the following two theorems.

Theorem 2.1. *Let H be a mono-q-polyhex where $q \le 6$. Then (2) holds.*

Theorem 2.2. *Let $q \ge 3$ and $r = q/2$. There are infinitely many mono-q-polyhexes for which*

$$n_{\text{int}} = 2h + r - (4rh + r^2)^{1/2} \qquad (3)$$

Let us first describe the special extremal mono-q-polyhexes of theorem 2.2. Note that the square root will be an integer or a half-integer (if q is odd) in this case. It is worth mentioning that it also follows from our proofs that the constructed examples are the only ones for which (3) holds if $q \le 6$ (while in (2) we may have equality for many other mono-q-polyhexes).

Let $k \ge 0$ be an integer, and let $H(q,k)$ be the mono-q-polyhex that contains the q-gon Q plus all the hexagons that are at a distance (measured by the number of hexagons) of at most k from Q. One easily verifies that the number of hexagons in $H(q,k)$ (not counting Q if $q = 6$) is equal to

$$h = q(1 + 2 + 3 + ... + k) = qk(k + 1)/2 \qquad (4)$$

† Supported in part by the Ministry of Research and Technology of Slovenia under Grant P1-0206-101-92.

‡ E-mail: bojan.mohar@uni-lj.si.

® Abstract published in *Advance ACS Abstracts*, June 15, 1994.

0095-2338/94/1634-1127$04.50/0

Similarly,

$$n_{\text{int}} = q(1 + 3 + 5 + \ldots + 2k - 1) = qk^2 \quad (5)$$

Using (4) and (5), it is easy to verify that eq 3 is satisfied. We thus have proved theorem 2.2.

Let H be a mono-q-polyhex. Denote by n_2 and n_3 the number of vertices on the boundary of H that are of degree 2 or 3 in H, respectively. By summing the degrees of vertices in H we get

$$2e = 3n_{\text{int}} + 3n_3 + 2n_2 \quad (6)$$

where e is the number of edges. By counting the number of incident vertex–face pairs in two ways we obtain the following relation:

$$6h + q = 3n_{\text{int}} + 2n_3 + n_2 \quad (7)$$

Note that H has $n_{\text{int}} + n_3 + n_2$ vertices and $h + 2$ faces (counting the unbounded face as well). Therefore we get by using Euler's formula and (6) and (7)

$$3n_{\text{int}} + 2n_3 + n_2 - q = 6h = -6(n_{\text{int}} + n_3 + n_2) + 6e = 3n_{\text{int}} + 3n_3$$

It follows that

$$2h = n_{\text{int}} + n_3 \quad (8)$$

and

$$n_2 = n_3 + q \quad (9)$$

The rest of this section is devoted to the proof of theorem 2.1. We suppose that H is a mono-q-polyhex for which (2) does not hold, i.e.,

$$n_{\text{int}} > 2h + r - (4rh + r^2)^{1/2} \quad (10)$$

We will first show that H gives rise to another mono-q-polyhex H' violating (2) such that H' has no two consecutive boundary vertices of degree 3. This will be achieved by a sequence of additions of hexagons to H, as it is described below. After that, we will show that (2) is satisfied for mono-q-polyhexes having the above property of H', thus obtaining a contradiction.

Consider the operation on H shown schematically in Figure 3. The drawing has to be understood as a part of the mono-q-hexagonal lattice, and the bold path is a part of C, the boundary of H. It is assumed that H is "below" C at this part of C. Suppose that the boundary cycle C of H has a local pit as shown on the left in Figure 3. Suppose, moreover, that the two vertices a and b above the pit are not vertices of H. Then we may change C to another cycle C' as shown on the right-hand side of Figure 3 (we add a hexagon). Then C' determines another mono-q-polyhex H'. We claim that H' also violates (2). Let n'_{int} and h' be the parameters of H'. Then $n'_{\text{int}} = n_{\text{int}} + 2$ and $h' = h + 1$. By (10), it follows that

$$n'_{\text{int}} > 2h' + r - (4rh + r^2)^{1/2} > 2h' + r - (4rh' + r^2)^{1/2}$$

which we were to show.

The operation of Figure 3 is called the *flattening of a pit*. We use the same name for the operation in Figure 4. It is clear that the claim of the previous paragraph also holds in this case. The same is true if we have a pit corresponding to four consecutive vertices on C that are of degree 3 in H.

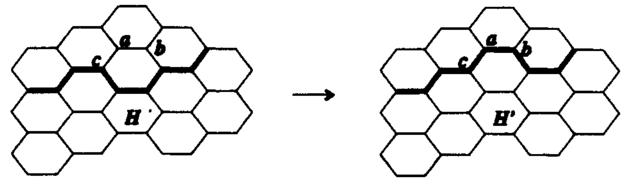

Figure 3. Flatten a pit.

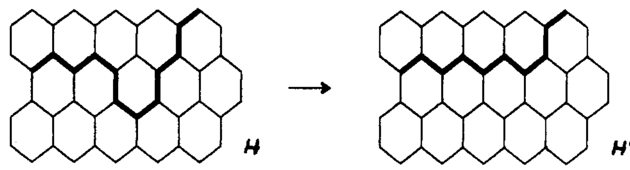

Figure 4. Flatten a deep pit.

Suppose that we have a pit (as in Figure 3) whose vertex a belongs to H. In this case, the addition of the hexagon to flatten the pit can result in a non-simply connected complex. We will show that in this case one can find another pit on C which can be flattened. Clearly, we have a $\in V(C)$. Let c be the vertex on C at the pit that is adjacent to a, and let S_1 and S_2 be the two segments of C from a to c. Then exactly one of S_1 and S_2, say S_1, together with the edge ac bounds a disk D whose interior is disjoint from H. Since D is isomorphic to a polyhex, it is easy to see that there are other pits on the segment S_1. We may try to flatten those pits. If the operation is not possible, we get a smaller disk, etc. Sooner or later we end up with a pit which can be flattened. As a consequence we have the following important fact: *If there are two consecutive vertices on C whose degree in H is equal to 3, then there is a pit that can be flattened.*

When a pit is flattened, the length of C does not increase but the number of hexagons bounded by C increases by 1. Therefore, after a finite number of steps we get a mono-q-polyhex H' for which no further flattening is possible. Hence the boundary C' of H' has the property that no two consecutive vertices on C' are of degree 3 in H'. Moreover, by (9), there are exactly q edges on C' with both endpoints of degree 2 in H'.

We will prove by induction on h that H' satisfies (2). By using (8) and (9), it is easy to show that (2) is equivalent to

$$n_2 n_3 \geq 2qh \quad (11)$$

where n_2 and n_3 are the number of vertices of degree 2 and 3, respectively, on the boundary of H'.

Let Q be the q-face of H'. Suppose first that Q does not lie on the boundary of H'. Let H'' be obtained from H' by deleting all hexagons that lie on the boundary of H'. We claim that H'' is connected (and thus it is a mono-q-polyhex). Suppose that this is not true. Then there are connected components H_1 and H_2 of H'' having faces Q_1 and Q_2, respectively, which are "at a distance of at most two" from each other. (Note that either Q_1 or Q_2 can be the q-gon.) More precisely, Q_1 and Q_2 are related as the central hexagon in Figure 1 with one of the hexagons denoted by a, b, c, d, and the hexagons between them belong to the removed boundary part of H'. It can be shown that in each of the four possibilities (a smart order for the analysis of the four cases where we exclude the previous ones is a, b, c, d), we get two consecutive vertices of degree 3 on the boundary of H'. A contradiction. The same conclusion holds also in cases when one of Q_1 and Q_2 is the q-gon. Despite being a mono-q-polyhex, H'' also satisfies the property that no two consecutive vertices on its boundary are of degree 3 in H''. If this were not the case, then

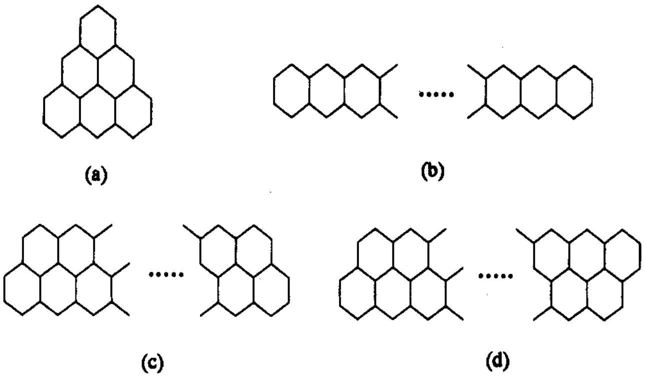

Figure 5. All hexagons on the boundary.

H' would violate the same condition. By the induction hypothesis for H'', we have $n''_2 n''_3 \geq 2qh''$. But $n''_2 = n_3 = n_2 - q$, $n''_3 = n_3 - q$, and $h'' = h - n_3$. Therefore,

$$n''_2 n''_3 = n_2 n_3 - q(n_3 + n_2 - q) \geq 2qh'' = 2qh - 2qn_3$$

By using (9) we derive (11).

The other case is when Q is on the boundary of H'. Let us first consider the case $q = 6$. In this case we may use any hexagon to be Q. Therefore we may assume that every hexagon is on the boundary. In this case, H' is one of the polyhexes shown in Figure 5. For them, (11) is easy to prove.

We are left with the case $q < 6$ and Q on the boundary. By adding $6 - q$ vertices of degree 2 on an edge of Q on the boundary of H', we get a mono-6-polyhex for which we have the inequality (11). It can be written as

$$(n_2 + 6 - q)n_3 \geq 12h \tag{12}$$

It follows that $n_2 n_3 \geq 12h - (6 - q)n_3 = 2qh + (6 - q)(2h - n_3)$. By (8) we have $2h - n_3 \geq 0$, and (11) follows.

3. CASE $q > 6$

Suppose now that $q > 6$. Take the polyhex $H(6,k)$ introduced in the proof of theorem 2.2 and subdivide an edge on the boundary by inserting $q - 6$ vertices of degree 2. We get a mono-q-polyhex satisfying (2) for $q = 6$ and not for the real value $q > 6$. These examples thus disprove Cyvin's conjecture given in ref 1. We claim that the bound

$$n_{\text{int}} \leq 2h + 3 - (12h + 9)^{1/2} \tag{13}$$

is the best possible. (Note that $2h + 3 - (12h + 9)^{1/2} \geq 2h + r - (4rh + r^2)^{1/2}$ with the equality only in the case when $h = 0$.) Also in this case we may use the flattening of pits in order to get a mono-q-polyhex H' with no two adjacent vertices on the boundary having degree 3 in H'. Now, (13) is equivalent to the condition

$$n_3(n_3 + 6) \geq 12h \tag{14}$$

Now we use induction. If the q-gon Q is not on the boundary of H', we delete all hexagons on $\partial H'$ to get H''. By the induction hypothesis we have $n''_3(n''_3 + 6) \geq 12h$. As $n''_3 = n''_2 - q = n_3 - q$ and $h'' = h - n_3$, we easily derive (14). The remaining case is when Q is on the boundary of H'. Since H' has no two adjacent vertices of degree 3 on its boundary, two consecutive edges of Q lie on $\partial H'$. Then we may replace these two edges by a single one and obtain a mono-$(q - 1)$-polyhex satisfying (13) (by induction on q). Since h and n_{int} have not been changed by this, (13) holds for H' as well. We proved the following:

Theorem 3.1. *If $q \geq 6$ then (13) holds. For every fixed value of q, there are infinitely many mono-q-polyhexes for which the equality holds in (13).*

REFERENCES AND NOTES

(1) Cyvin, S. J. *J. Math. Chem.* **1992**, *9*, 389.
(2) Gutman, I. *Bull. Soc. Chim. Beograd* **1982**, *47*, 453.
(3) Barth, W. E.; Lawton, R. G. *J. Am. Chem. Soc.* **1971**, *93*, 1730.
(4) Yamamoto, K.; Harada, T.; Nakazaki, M.; Naka, T.; Kai, Y.; Harada, S.; Kasai, N. *J. Am. Chem. Soc.* **1983**, *105*, 7171.
(5) Thulin, B.; Wennerström, O. *Acta Chem. Scand. B* **1976**, *30*, 369.