The evaluation of moments for benzenoid hydrocarbons

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Summary. A systematic derivation of moments for polyhexes is presented, covering the tenth and twelfth members for the first time. The total Hückel π-electron energy is computed in terms of moments with desired precision. Equations governing various molecular fragments are useful for enumerating embeddings of acyclic chains (rooted trees) in polyhexes.

1 Introduction

Presumably it was Hall [1] who first introduced moments into chemistry for the approximate derivation of the total π-electron energy of conjugated molecules. Since then, chemists have become interested in the moment method as a tool to deal with a wide range of problems [2–17] which include the total π-electron energies [6, 12], densities of states [8], HOMO–LUMO gaps [9], reactivity indices [11], characteristic polynomials [7, 13], etc. All of these problems could be solved if moments of the system have been evaluated.

   One of us reported the results for the evaluation of the lth order moment $\mu_l(l \leqslant 14)$ for acyclic hydrocarbons and generalized to bipartite cyclic species with $l \leqslant 12$ [4, 11]. Meanwhile, Hall [6] developed formulae for up to sixth moments of benzenoid hydrocarbons. Markovic [16] extended the results to eighth moment in terms of seven parameters. A slightly different formula for μ_8 of polyhexes with one less parameter than Markovic is also available [17]. Here we can find the continuous interest in benzenoid hydrocarbons, and it can be ascribed to the great significance of benzenoids in both experimental and theoretical chemistry [18].

   In this paper, a larger set of graphical parameters are introduced for properly formulating higher moments of polyhexes based on the previous results in Ref. [11] which have been transformed into a new appearance. Amongst, the results for μ_l ($l \leqslant 8$) are consistent with the published results by Hall [6, 17] and Markovic [16], while formulae for the 10th and 12th moments of benzenoids are given for the first time. The validity of the novel results has been tested for a few huge polyhexes with numerical values exactly coincident with that calculated from the definition of moments as power sum of the energy sequence.

As one of the applications of moments, the total π-electron energy of benzenoids has been formulated additively in terms of a set of peripheral fragments as parameters in various order of approximations. Besides, equations governing various molecular fragments are tabulated in Appendix 2 which are useful for enumerating embeddings of acyclic chains [19] in polyhexes.

2 Graphical parameters

Very often a conjugated system is represented by its molecular graph characterized by the adjacency matrix A made up of zero diagonal entries and unit off-diagonal elements corresponding to each pair of neighboring vertices. The lth moment of the molecular system is defined as

$$\mu_l = \sum_{i=1}^{N} x_i^l = \mathrm{TR}(A^l) = \sum_{i=1}^{N} (A^l)_{ii} \tag{1}$$

in which N is the number of vertices, and x_i ($i = 1, 2, \ldots, N$) are the eigenvalues of A, i.e., the Hückel MO energies of the conjugated system.

As is well known, $(A^l)_{ij}$ represents the count of the random walks of length l from vertex i to vertex j. Thus, it is possible to formulate moments in terms of molecular fragments as parameters. For benzenoid hydrocarbons, parameters used by Hall [6, 17] and Markovic [16] are reproduced in Fig. 1, which include vertices, edges, three peripheral paths and four distinct types of hexagons. In specifying fragments at the periphery, it is instructive to shadow the neighboring internal regions as done for the diagrams of bay, cove and fjord in Fig. 1.

The hexagons in Fig. 1 are discriminated by their degree-sequences of vertices, however, one can find two more such species involving four vertices of degree 3 in distinguishable arrangements (see Fig. 2). And these hexagons can be further divided into twelve categories in accordance with their neighboring features shown in Fig. 2 where shadows indicate adjacent hexagons [18].

By inspection, one can write the following relations between these two sets of ring parameters,

$$H_1 = L_1, \qquad H_2 = P_2,$$
$$H_5 = P_4 + P_3, \qquad H_6 = L_6 + L_5 + L_4 + A_4 + A_3 \tag{2}$$

and the total number of hexagons is

$$H = L_1 + P_2 + L_2 + H_4 + H_5 + H_6. \tag{3}$$

The species listed in Figs. 1 and 2 are not sufficient to formulate the higher moments ($l \geqslant 8$) of polyhexes, so that it is necessary to choose some fragments in addition as parameters, where the peripheral paths are preferred candidates because they can be easily counted. The chosen fragments are displayed in Fig. 3.

With a prescription, a path having all of its constituent edges at the periphery is well characterized by its degree-sequence of vertices arranged in a round bracket, $(a_1 a_2 \ldots a_i \ldots)$ where a_i is the degree of ith vertex. In this way, bays, coves and fjords in Fig. 1 can be denoted by symbols (2 3 3 2), (2 3 3 3 2) and (2 3 3 3 3 2), respectively. In the case that the path has inner edges, say one between the second and the third vertices, then a dash is added between a_2 and a_3 for designation, namely $(a_1 a_2' a_3 \ldots a_i \ldots)$. Sometimes, it is necessary to discriminate between cis and transforms for a path with given degree-sequence, one uses c, t as corner indices for
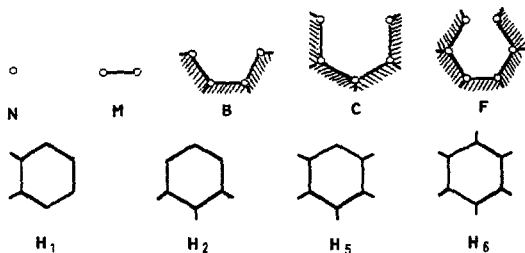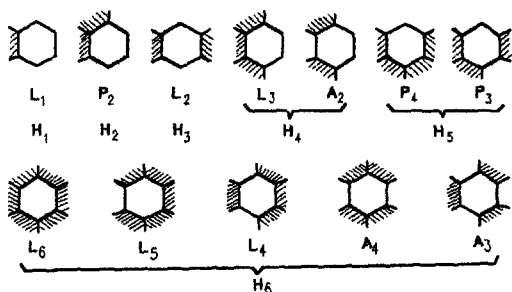
Fig. 1. Parameters used by Hall and Markovic.

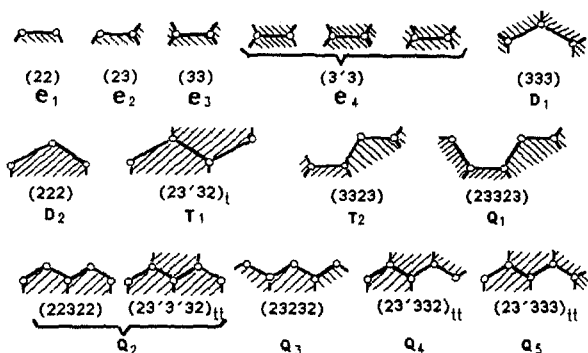Fig. 2. Classification of hexagons in benzenoid graphs.

Fig. 3. Paths used as parameters.

paths of length 3 and cc, ct, tt for longer paths of length 4. In addition, Latin letters are also given below each diagram in order to simplify our later formulation.

Besides, one more parameter represented by Q_6 is chosen for the evaluation of the twelfth-order moment. It involves seven vertices with one peripheral (3 3)-type edge incident to the hexagon, the vertex para to this edge is of degree 3 whereas the remaining vertices (with question marks) are of degree 2 or 3. Actually it represents a set of 12 possibilities collected in Fig. 4.

3 Transformations

In Ref. [11], moments up to $l = 12$ for benzenoid hydrocarbons were given in terms of another set of parameters which were distinguished into acyclic (trees) and cyclic
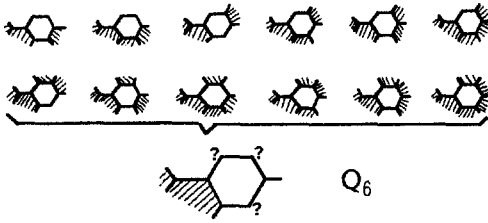
Fig. 4. Fragments and its sub-ones representing parameter Q_6.

categories. Due to the troublesomeness in counting the acyclic fragments embedding in polyhexes, the central theme now is to transform them to a new set of parameters enumerable with facility, i.e., which have already been introduced in this paper. For clarifying the discussion, formulae of μ_4 to μ_{12} in company with parameters used in Ref. [11] are reproduced in Appendix 1 where symbols $\{a\}$, $\{ab\}$, $\{\bar{a}\}$, $\{\bar{a}b\}$ with a, b being positive integers are put below each diagram for identification.

In the last section, we have emphasized the role of peripheral paths. In general, paths are designated [4] by the degree-sequence in square bracket $[a_1 a_2 \ldots a_i \ldots]$, disregarding whether the constituting edges are peripheral or not. Various substructure counts are mutually interrelated. For example, the edges of types $[2\,2]$, $[2\,3]$ and $[3\,3]$ sum to the total number of edges,

$$[22] + [23] + [33] = M \tag{4}$$

and it can be seen that

$$[22] = e_1, \qquad [23] = e_2, \qquad [33] = e_3 + e_4 \tag{5}$$

One can also inspect that the vertex types satisfy

$$[2] = [22] + [23]/2, \qquad [3] = [23]/3 + 2[33]/3. \tag{6}$$

Moreover, it is imaginable that peripheral edges are related to bay regions and hexagons, which are as follows

$$e_1 = (B + 2C + 3F) + 6, \quad e_2 = 2N - 4H - 2(B + 2C + 3F) - 8, \quad e_3 = B + 2C + 3F. \tag{7}$$

Besides, the inner edges e_4 can be written out as

$$e_4 = 6H - M \tag{8}$$

and Euler's equation deserves to be mentioned, i.e.

$$M = H + N - 1. \tag{9}$$

With these equations, it will be an easy job to carry out the transformations for acyclic fragments $\{2\}$, $\{3\}$, $\{4\}$, $\{31\}$ in terms of new parameters. That is

$$\{2\} = M,$$

$$\{3\} = [2] + 3[3] = 4M - 3N, \tag{10}$$

$$\{4\} = [22] + 2[23] + 4[33] = 12M - 12N + e_1,$$

$$\{31\} = [3] = 2M - 2N.$$

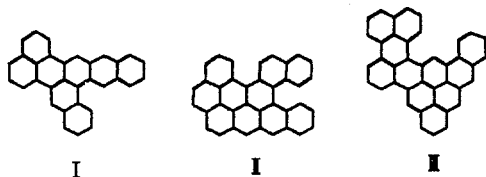I   II   III

Fig. 5. Benzoid molecules for illustration of moments μ_8, μ_{10} and μ_{12}.

The cyclic parameter $\{\bar{6}\}$ is obviously identical to the number of hexagons, H. Therefore, moment expressions listed in Appendix 1 with $l \leqslant 6$ are readily converted to those given by Hall, i.e.

$$\mu_4 = 2\{2\} + 4\{3\} = 18M - 12N, \tag{11a}$$

$$\mu_6 = 2\{2\} + 12\{3\} + 6\{4\} + 12\{31\} + 12\{\bar{6}\}$$

$$= 158M - 144N + 48 + 6e_3. \tag{11b}$$

This procedure can be carried on for the remaining acyclic and cyclic parameters. For example, two peripheral paths of length 2, D_1, D_2 can be written out as

$$D_1 = C + 2F, \qquad D_2 = 2L_1 + P_2. \tag{12}$$

The results for all the acyclic and cyclic fragments are collected in Appendix 2. In consequence, higher moments of polyhexes up to $l = 12$ are derived as follows

$$\mu_8 = 1362M - 1404N + 720 + 80B + 168C + 256F + 16L_1 + 8P_2$$

$$\equiv 1362M - 1404N + 720 + 80e_3 + 8D_1 + 8D_2, \tag{13a}$$

$$\mu_{10} = 11702M - 12900N + 8280 + 830B + 1820C + 2820F$$

$$+ 320L_1 + 140P_2 + 40L_2 + 10T_1 + 10T_2, \tag{13b}$$

$$\mu_{12} = 100710M - 115896N + 86688 + 7878B + 17928C + 28218F$$

$$+ 4560L_1 + 1824P_2 + 1248L_2 + 240T_1 + 240T_2 + 240A_2 + 120P_3$$

$$- 12Q_1 + 12Q_2 + 12Q_3 - 12Q_4 - 24Q_5 + 48Q_6. \tag{13c}$$

Here μ_8 is consistent with that obtained by Markovic and Hall but the present expression has fewer parameters than either of these earlier expressions. Further, here μ_{10} and μ_{12} appear for the first time. Also the formulae listed in Appendix 2 can be used to enumerate both acyclic and cyclic fragments embeddable in polyhexes analytically instead of a computer approach for searching [19].

In the following, three molecules of polyhexes numbering I, II, III are displayed in Fig. 5 to illustrate how to evaluate the higher moments by using the above results. The parameters involved are evaluated by counting the related fragments in the molecule, then μ_8, μ_{10} and μ_{12} are calculated from Eq. (13). They are tabulated in Table 1. On the other hand, one can also evaluate moments directly from their definition as in Eq. (1) with the aid of a computer. As expected, both values are found to be in exact coincidence.

Table 1. Parameters and moments μ_8, μ_{10} and μ_{12} for the benzenoid molecules in Fig. 5

Molecule	N	M	B	C	F	L_1	P_2	L_2	T_1	T_2	A_2	P_3
I	32	39	2	1	0	2	2	1	4	3	0	2
II	37	46	0	1	1	2	1	0	2	0	1	1
III	40	50	3	1	0	1	4	0	1	3	0	1

Molecule	Q_1	Q_2	Q_3	Q_4	Q_5	Q_6	μ_8	μ_{10}	μ_{12}
I	2	3	1	0	2	3	9286	56368	355446
II	0	3	2	0	3	5	11888	74712	489354
III	2	5	2	1	0	5	13116	82610	541134

4 Total π-electron energy

One traditional application of moments is to evaluate the total π-electron energy of conjugated molecules via the expansions truncated at finite order L [12]. This gives

$$E_\pi(L) = \sum_{n=0}^{L} \alpha_{2n}\mu_{2n} - \alpha_0\sigma, \tag{14}$$

where σ is the number of zero eigenvalues (absent for Kekuleans) and

$$\alpha_0 = \frac{1}{\pi}\frac{6}{2L+1},$$

$$\alpha_{2n} = (-1)^{n+1}\frac{1}{\pi}\frac{2^{2n+1}}{3^{2n-1}}\frac{(L+n)!}{(2L+1)(2n-1)(2n)!(L-n)!} \tag{14a}$$

On substituting Eqs. (11) and (13) into Eq. (14), one obtains the total π-electron energy of polyhexes expressed additively in terms of molecular fragments in various approximations given below

$$E_\pi(1) = 0.56588M + 0.63662N - 0.63662\sigma, \tag{15a}$$

$$E_\pi(2) = 0.56588M + 0.68378N - 0.38197\sigma, \tag{15b}$$

$$E_\pi(3) = 0.59523M + 0.66087N + 0.22995 + 0.02874B$$
$$+ 0.05749C + 0.08623F - 0.27284\,\sigma, \tag{15c}$$

$$E_\pi(4) = 0.62361M + 0.63218N + 0.40027 + 0.06186B$$
$$+ 0.11426C + 0.16666F - 0.01892L_1 - 0.00946P_2 - 0.21221\,\sigma, \tag{15d}$$

$$E_\pi(5) = 0.65121M + 0.59674N + 0.59598 + 0.09302B$$
$$+ 0.16988C + 0.25009F - 0.03231L_1 - 0.02284P_2$$
$$+ 0.01338L_2 + 0.00334T_1 + 0.00334T_2 - 0.17362\sigma, \tag{15e}$$

$$E_\pi(6) = 0.67067M + 0.56991N + 0.72754 + 0.1260B$$
$$+ 0.23102C + 0.34289F - 0.06257L_1 - 0.04662P_2$$
$$- 0.00391L_2 + 0.00643T_1 + 0.00643T_2 - 0.02470A_2$$
$$- 0.01235P_3 + 0.00124(Q_1 - Q_2 - Q_3 + Q_4 + 2Q_5 - 4Q_6) - 0.14691\sigma. \tag{15.f}$$

Table 2. Relative errors of E_π calculated by Eq. (15)

Molecule	$L = 1$	$L = 2$	$L = 3$	$L = 4$	$L = 5$	$L = 6$	E_π(exact)
I	− 6.5	− 3.2	− 1.5	− 0.6	− 0.04	− 0.00	45.390
II	− 7.4	− 3.6	− 1.7	− 0.7	− 0.14	− 0.00	52.869
III	− 7.9	− 3.8	− 1.7	− 0.6	0.00	0.10	57.012

These formulae have been applied to calculate the total π-electron energy for dozens of molecules. The three in Fig. 5 are extremely interesting because they contain zero, one and two zero-eigenvalues, respectively. Results are listed in Table 2 in terms of relative errors defined by

$$\frac{E_\pi(L) - E_\pi(\text{exact})}{E_\pi(\text{exact})} \times 100\%. \tag{16}$$

and errors turn out to be no higher than 0.3% when L equals 5 or 6, which implies that it is a fairly good approximation when the role of higher moments such as μ_{10} and μ_{12} are taken into consideration.

As one knows, there are many other applications of moments. And now they are under our careful investigation and the results will be published elsewhere.

Appendix I

Moment formulae and related molecular fragments for benzenoid hydrocarbons

$\mu_4 = 2\{2\} + 4\{3\}$,

$\mu_6 = 2\{2\} + 12\{3\} + 6\{4\} + 12\{31\} + 12\{\bar{6}\}$,

$\mu_8 = 2\{2\} + 28\{3\} + 32\{4\} + 72\{31\} + 8\{5\} + 16\{41\} + 96\{\bar{6}\} + 16\{\bar{6}1\}$,

$\mu_{10} = 2\{2\} + 60\{3\} + 120\{4\} + 300\{31\} + 60\{5\} + 140\{41\} + 10\{6\}$,

$\qquad + 20\{51\} + 20\{501\} + 40\{411\} + 540\{\bar{6}\} + 180\{\bar{6}1\} + 20\{\bar{6}2\}$

$\qquad + 20\{\bar{6}11\} + 20\{\bar{6}101\} + 20\{\bar{6}1001\} + 20\{\overline{10}\}$,

$\mu_{12} = 2\{2\} + 124\{3\} + 390\{4\} + 1080\{31\} + 300\{5\} + 804\{41\} + 96\{6\}$

$\qquad + 216\{51\} + 228\{501\} + 504\{411\} + 12\{7\} + 24\{61\} + 24\{601\}$

$\qquad + 48\{511\} + 48\{5101\} + 24\{502\} + 2724\{\bar{6}\} + 1344\{\bar{6}1\}$

$\qquad + 264\{\bar{6}2\} + 312\{\bar{6}11\} + 288\{\bar{6}101\} + 288\{\bar{6}1001\} + 240\{\overline{10}\}$

$\qquad + 24\{\bar{6}3^1\} + 48\{\bar{6}3^2\} + 24\{\bar{6}21\} + 24\{\bar{6}201\} + 24\{\bar{6}2001\}$

$\qquad + 24\{\bar{6}111\} + 24\{\bar{6}1101] + 24\{\bar{6}10101\} + 72\{\bar{6}|\bar{6}\} + 24\{101\}$.

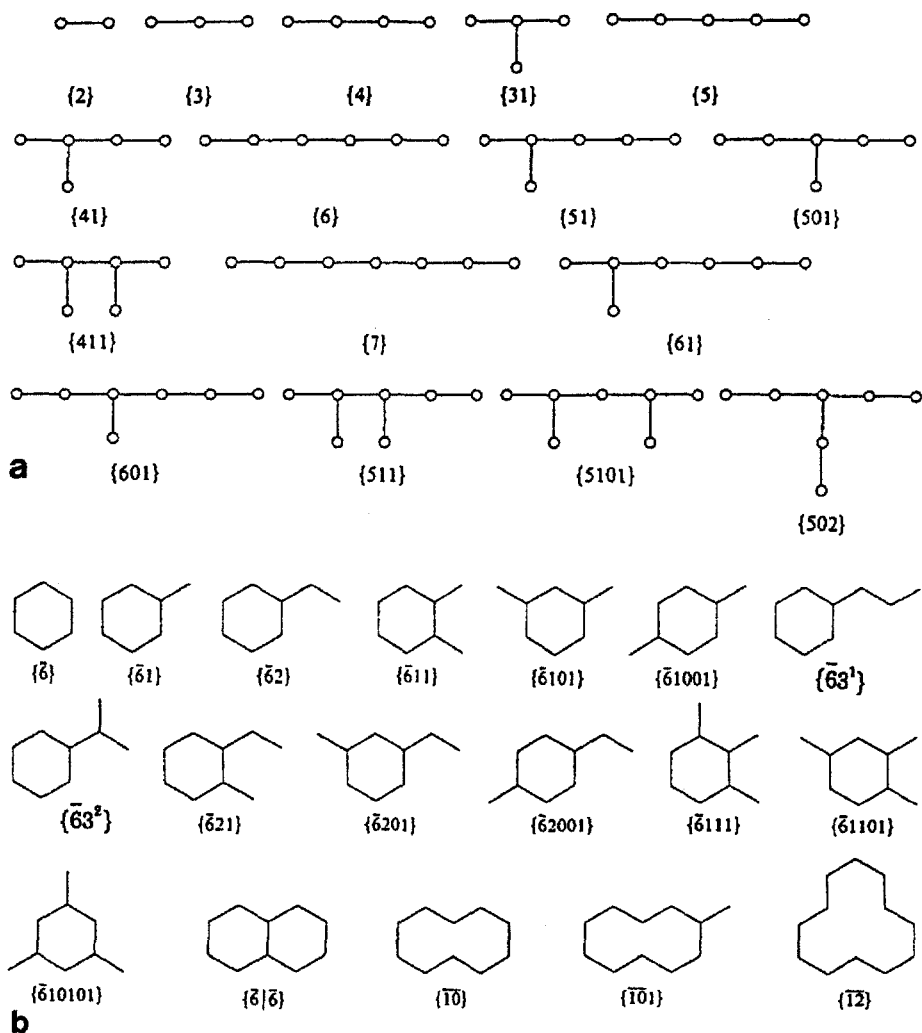Graphical parameters used in Ref. [4.11] are shown in Fig. 6.

Fig. 6. Graphical parameters used in Refs. [4, 11]: (a) acyclic; (b) cyclic.

Appendix II

Relations between acyclic (cyclic) fragments and parameters used in this paper

$\{2\} = M,$

$\{3\} = 4M - 3N,$

$\{4\} = 12M - 12N + 6 + B + 2C + 3F,$

$\{31\} = 2M - 2N,$

$\{5\} = 30M - 33N + 18 + 2L_1 + P_2 + 2B + 5C + 8F,$

$\{41\} = 16M - 18N + 12 + 2B + 4C + 6F,$

$$\{6\} = 72M - 84N + 60 + 5B + 14C + 24F + 6L_1 + 2P_2 + 2L_2 + T_1 + T_2,$$

$$\{51\} = 36M - 42N + 24 + 2B + 6C + 10F + 4L_1 + 2P_2,$$

$$\{501\} = 38M - 45N + 42 + 6B + 13C + 20F,$$

$$\{411\} = 5M - 6N + 6 + B + 2C + 3F,$$

$$\{7\} = 162M - 198N + 162 + 10B + 29C + 52F + 26L_1 + 9P_2 + 16L_2 + 4T_2$$
$$\qquad + 8A_2 + 4P_3 - Q_1 + Q_2 + Q_3 - Q_4 - 2Q_5 + 2Q_6,$$

$$\{61\} = 84M - 102N + 84 + 6B + 18C + 32F + 8L_1 + 2P_2 + 4L_2 + 2T_1 + 2T_2,$$

$$\{601\} = 168M - 204N + 180 + 18B + 46C + 76F + 14L_1 + 6P_2 + 4L_2 + 2T_1 + T_2,$$

$$\{511\} = 44M - 54N + 60 + 8B + 18C + 28F,$$

$$\{5101\} = 10M - 12N + 6 + C + 2F + 2L_1 + P_2,$$

$$\{502\} = 28M - 34N + 36 + 4B + 10C + 16F,$$

$$\{\bar{6}\} = M - N + 1,$$

$$\{\bar{6}1\} = 8M - 9N + 6,$$

$$\{\bar{6}2\} = 20M - 24N + 24 + 2B + 4C + 6F,$$

$$\{\bar{6}11\} = 10M - 12N + 12 + B + 2C + 3F,$$

$$\{\bar{6}101\} = 10M - 12N + 6 + 2L_1 + P_2,$$

$$\{\bar{6}1001\} = 5M - 6N + 3 + L_1 + L_2,$$

$$\{\overline{10}\} = 5M - 6N + 6,$$

$$\{\bar{6}3^1\} = 44M - 54N + 48 + 2B + 6C + 10F + 6L_1 + 2P_2 + 4L_2 + 2A_2 + P_3$$

$$\{\bar{6}3^2\} = 12M - 15N + 18 + 2B + 4C + 6F,$$

$$\{\bar{6}21\} = 44M - 54N + 60 + 4B + 10C + 16F,$$

$$\{\bar{6}201\} = 48M - 60N + 60 + 4B + 10C + 16F + 4L_1 + 2P_2 + 2T_1 + T_2,$$

$$\{\bar{6}2001\} = 24M - 30N + 24 + 6L_1 + 2P_2 + 4L_2 + 2A_2 + P_3 + Q_6,$$

$$\{\bar{6}111\} = 12M - 15N + 18 + 2B + 4C + 6F,$$

$$\{\bar{6}1101\} = 24M - 30N + 24 + 2B + 4C + 6F + 6L_1 + 2P_2 + 4L_2,$$

$$\{\bar{6}10101\} = 4M - 5N + 2 + 2L_1 + P_2,$$

$$\{\bar{6}|\bar{6}\} = 5M - 6N + 6,$$

$$\{\bar{1}01\} = 48M - 60N + 60 + 2B + 4C + 6F + 6L_1 + 2P_2 + 4L_2 + 2A_2 + P_3,$$

$$\{\overline{12}\} = 4M - 5N + 6.$$

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