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AMPAC (Semichem Inc.) AM1 semiempirical calculations on stacked benzenes delocalized ring systems suggest that very large third order polarizabilities (Y) can be obtained. Systems of +2 charge consisting of benzene rings separated by 3A, display finite-field zero frequency Y(0;0;0;0)s that are many orders of magnitude larger than any thus far encountered or previously predicted for organics. The ratio of Y to A is an increasing function with system size, suggesting that the nonlinear optical process susceptibility may be able to be increased sufficiently to overcome linear optical losses. Up to 14 rings, the largest systems currently calculated, there is not yet a clear indication of leveling-off or saturation of Y or Y/A. The feasibility of such material systems is discussed, as well as limitations to the calculations that need to be further investigated.

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FINAL TECHNICAL REPORT ON AFOSR CONTRACT F49620-94-1-0231
"A MECHANISTIC APPROACH TO LARGER MOLECULAR THIRD ORDER OPTICAL POLARIZABILITIES"

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THE UNIVERSITY OF TEXAS AT EL PASO

What follows is a technical summation of the most significant result of the work that was funded, in part, by way of this grant.. This represents a manuscript to be submitted shortly to The Journal of Physical Chemistry. This technical presentation represents essentially the same final report submitted at the formal end of the contract in Spring 1997, prior to the formal six moth no-cost contract extension.

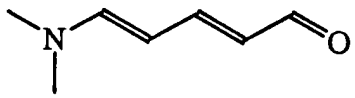
ABSTRACT

AMPAC (Semichem Inc.) AM1 semiempirical calculations on stacked benzenes delocalized ring systems suggest that very large third order polarizabilities (γ) can be obtained. Systems of +2 charge consisting of benzene rings separated by 3 Å, display finite-field zero frequency $\gamma(0;0,0;0)$s that are many orders of magnitude larger than any thus far encountered or previously predicted for organics. The ratio of γ to α is an increasing function with system size, suggesting that the nonlinear optical process susceptibility may be able to be increased sufficiently to overcome linear optical losses. Up to 14 rings, the largest systems currently calculated, there is not yet a clear indication of leveling-off or saturation of γ or γ/α. The feasibility of such material systems is discussed, as well as limitations to the calculations that need to be further investigated.

The pursuit of large third order optical polarizabilities ($\gamma(\omega_4, \omega_3, \omega_2, \omega_1)$ for microscopic systems, and $\chi^{(3)}$ $(\omega_4, \omega_3, \omega_2, \omega_1)$ for macroscopic systems) in organic materials has been fraught with considerable frustration. Third order polarizabilities that have been achieved are relatively small or are small relative to linear optical losses so that the ideal materials appear unattainable, and good-enough materials with either sufficient γ (or bulk $\chi^{(3)}$) with low enough linear losses are often on a borderline of real utility. Indeed, based on extensive work on conjugated hydrocarbons, the prediction has been that larger third order susceptibilities are unattainable, and that the loss problem cannot be overcome.[1]

The most recent intriguing work that appears to go beyond the neutral hydrocarbons - at least in apparent magnitude of γ or $\chi^{(3)}$ – is the investigation into bipolaronic systems broadly investigated by Spangler and co-workers.[2-12] Bipolaronic systems experience enhanced delocalization by removing two electrons chemically or electrochemically. The difference in filled and empty orbitals relative to the neutral leads to an apparent significant enhancement in third order (nonlinear) optical polarizabilities. The question of optical loss has not been fully resolved, since electronic transitions are shifted to lower in energy, which normally reduces the useful window in the visible and near IR. However, it is unresolved whether potentially useful windows of transparency may broaden in the visible or there may be other useful optical regions further into the near IR. Photonic switching devices based on third order processes are relatively primitive in practical concept such that the preferred frequency regions of operation are still not clearly defined.

Largely, investigation into nonlinear optical materials based on organics has followed the lines of either readily available materials or traditionally well known simple dye chemistry variants. These systems, when viewed in terms of their electronic and optical dimensionality are either approximately one or two dimensional. Approximate one dimensional systems are for instance,

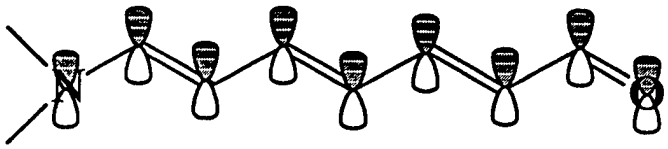


while two dimensional systems might be thought of in terms of phthalocyanines[13-17] as a model. There are of course few real truly one dimensional systems. Even p-nitroaniline, while extremely polar in its optical response, will display a non-zero response orthogonal to the polar axis, so that it may be considered one dimensional in one concept of approximation and somewhat two-dimensional in another. However, electronic delocalization and optical response dimensionality higher than two-dimensional is not commonly thought to be a significant contributor to these most commonly investigated systems. The main reason has likely been synthetic accessibility. Making molecules with interacting planes of conjugated atoms is not necessarily straightforward, though examples exist. In the solid state, molecular metals and conductive polymers display this higher dimensionality of interaction, though the interaction may be too long range usually leading to absorptions extending into the IR. In principle, very one-dimensional neutral polydiacetylenes could as well display inter-chain delocalizations, though chains are likely too far away, and their filled shells do not promote band formation. Cyclophanes are examples of discrete molecular systems that can offer higher dimensionality delocalization.

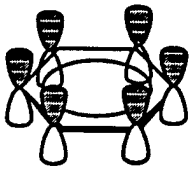
Donor/acceptor cyclophane type systems show clear low energy transitions that suggest enhanced delocalization between the rings. [18,19]

An approach taken by us is to consider higher dimensional delocalized systems such as cyclophanes. Oxidative enhancement of delocalization such as in bipolarons is an obvious step. This report covers our preliminary work on investigating the calculational results of a model higher dimensional bipolaronic system.

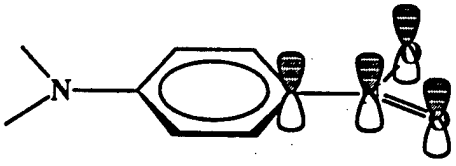
The investigation of organic molecules for nonlinear optics has been fairly isolated to traditional conjugated structures, and the traditional modes of delocalization inherent to dye chemistry developed in the late 19th Century. These common modes of delocalization are:



1D - Linear - commonly used in organic NLO molecules

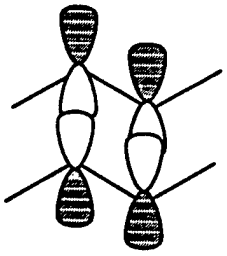


2D - Circular - commonly used in organic NLO molecules

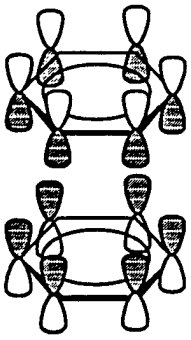


2D - Branched - commonly used in organic NLO molecules

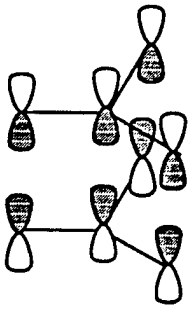
The labeling as 1D or 2D is an approximate assertion, and is primarily for descriptive purposes. Less commonly investigated systems, especially in terms of organic nonlinear optics are as follows:



2D - p-pi / p-sigma

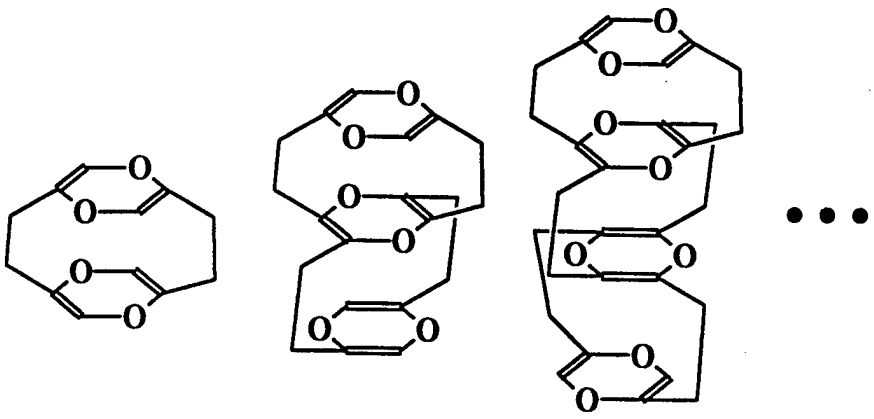


3D - Circular p-pi / p-sigma

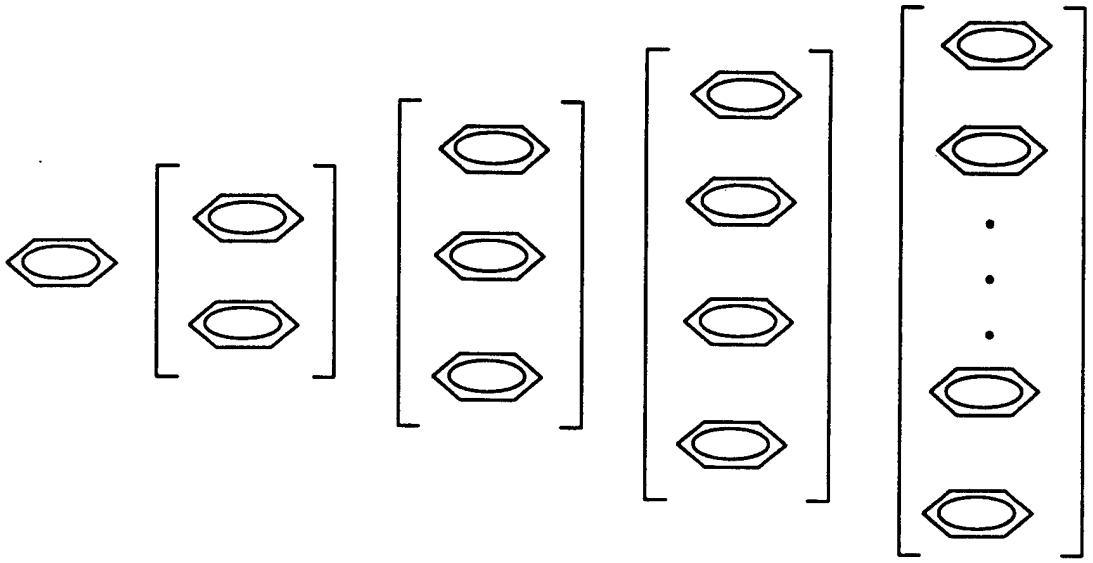


3D - Branched p-pi / p-sigma

Again, labeling is for descriptive purposes. The model system in which we are interested would fall into class 3D Circular p-pi/p-sigma. Our earlier work[20] in this area was on a series of dioxodiene cyclophanes,



where calculation in the +2 state resulted in systems displaying large negative second hyperpolarizabilities, γ. The dioxodiene system is antiaromatic as neutral, and aromatic as +2, thus implying the delocalization of aromaticity between rings in these +2 dioxodiene cyclophane systems. In the present work, the model system representing this higher dimensionality delocalization is merely a series of benzene rings stacked over each other and separated by 3 Å. This would be a system of aromatic rings which upon oxidation to +2 would be delocalizing anti-aromaticity. This system is also different from our earlier work on dixodienes in that we are not covalently linking the rings through ethylenic bridges, but are fixing an interplanar distance between non-covalently linked rings.



This different type of constraint was used to avoid what appeared to be Jahn-Teller or Peirls type instabilities observed in the dioxodiene cyclophanes, which were allowed to fully optimize including their ethylenic bridges. By eliminating the bridge, and enforcing a fixed spacing, we can completely inhibit a Peirls type distortion, at least for the purposes of clarifying the behavior of undistorted systems.

Calculations on the model system have been done either as neutral or dications (bipolaronic) using AMPAC 5.0 licensed from Semichem. Inc., on SGI INDIGO2 workstations (either a R4400 with 48MB memory or a R4600 with 32MB memory). In all calculations the inter-ring distance of 3 Å was fixed, though all other coordinates were free to optimize. A distance of 3 Å is not unreasonable since real cyclophane distances are in some cases significantly less than this. The AM1 approximation was used, and all structures were fully SCF optimized, except for the fixed inter-planar spacing. Results are reported for the E4 Energy expansion in the finite field and the DIP dipole expansion in the finite field. Calculations reported here were quite time consuming, and sometimes

required up to 600-700 hours of CPU time to achieve refinement of the structure. Refined structures were then subject to AMPAC zero-frequency Finite Field analysis of polarizability properties up the 3rd order tensor γ.

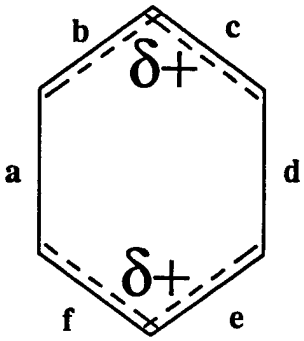
RESULTS:

Numerical results are summarized in Tables 1 & 2. The discussion which follows focuses primarily on graphical presentation of these results.

Structural results fall into two main categories of consideration: the symmetry of the collection of rings, and the structural variation in rings across the system.

Even though rings are permitted complete optimization freedom within the plane, final optimized structures do not differ significantly from starting structures in that the rings remain effectively eclipsed, albeit with some very slight angle of variation. The very slight angle of variation (less than 0.2 degrees) depends on what atoms are being compared, and is a consequence of the distortion within all rings to an antiquinoidal bisallyl structure, the extent of which depends on the position of the ring within the stack.

Within the rings, the neutral systems largely remain aromatic as evidenced by their bond-length alternation. The dication systems however, clearly show a antiquinoidal bisallyl cation character.



$$BLA = (a+d)/2 - (b+c+e+f)/4$$

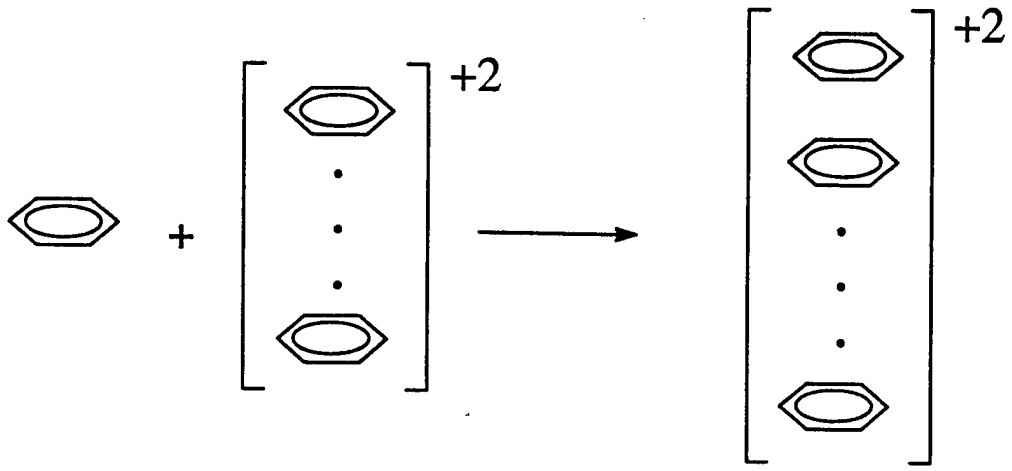
Defining a bond-length alternation parameter of (a+d)/2-(b+c+e+f)/4 , and plotting (Figures 1 & 2) this parameter as a function of ring position within a given dicationic stack of benzenes shows that the BLA peaks at the penultimate - from either terminal end - benzene. Two figures are shown, one with all systems from one ring to 14 (Figure 1), the other (Figure 2) showing systems only larger than 4 rings to clearly show the effect in the larger systems. The positive charges are most localized on these penultimate from either end rings, with terminal rings serving as a domain cap on either side. The implication is that while there is some localization, the variation in BLA of antiquinoidal bisallylic structures suggests delocalization across these structures. This really is not an unexpected or startling conclusion since partial charge delocalization across many adjacent rings is commonly accepted for electrically conductive organic solids. The relative localization near the domain wall is perhaps a new detail not earlier identified in such systems.

The average BLA per system size decreases smoothly with increasing system size (Figure 3), apparently just beginning to approach an asymptote at 14 rings for the +2 charged systems. It is clear that as we progress from smaller to larger dicationic stacks of benzenes, the BLA is reduced on all rings, again suggesting improved delocalization by

way of the availability of more sites. The more the delocalization the less charge that will exist on any given ring.

A plot (Figure 4) of ionization potential (IP) versus system size (number of stacked benzenes) shows that for the dicationic and neutral systems, there is a systematic monotonic reduction in IP with increase in the number of available benzenes. The implication is again that clear through-space delocalization occurs, even for the neutral systems. In these plots, and as implied by the trends for BLA versus number of rings or system size, it is clear that a size of system of maximum effect has not been reached. Thus, and in other words, the delocalization effect is clearly not saturated at 13-14 rings. A saturation effect is anticipated, based on the observation of similar effects in delocalizing excitons in conductive polyenes, and polyeneyne polymers. The barest hint of the onset of saturation may be observable in the BLA plot of the 14 ring dication. Once can note that charge localization doesn't as clearly peak at the penultimate to the terminal rings as much as it does for smaller systems. This may be a first hint of a split to form relatively discrete electronic domains. If so, we might very roughly estimate that saturation will be observed in the range of 25-40 rings.

An analysis of the calculated heat of formations shows that the neutral system increase fairly linearly (Table 1) in ΔH_f, while the dication systems decrease then increases perhaps along an asymptote (Figure 5). If we calculate a hypothetical reaction between a dicationic system of a given size and a neutral benzene,



we can see in Figure 6 that such a reaction is favored to self assemble up to five rings. This is not unexpected, since molecular metals must self assemble based on a favored thermodynamic situation. The results are of course gas-phase, but at least in the gas phase, oligomeric +2 systems should form spontaneously, upon +2 oxidation of a single ring. Whether solution effects would be favorable or unfavorable is unknown. However, benzene, being so purely 4n+2 aromatic, is not a best case system for self assembly of dicationic stacks of antiaromatic character, but still appears to be favored. Thus, a systematic way to construct such systems is to effect some sort of clever control of the self assembly to promote such, but limit the system size to maintain bandgaps or transparent windows in the visible or near-IR. This will be a challenge for synthetic chemists to consider.

For the system of neutral benzenes, the FF γ is seen in Figure 7 to increase linearly. The magnitude is not large, and is what might be expected. The DIP expansion results show some significant deviation from linearity at the large system sizes which could be due to accuracy of the convergence in the field-applied SCF solution. The energy expansion results, typically more stable, are still fairly linear up to systems of 13 rings. A plot of γ/α

in Figure 8 shows a decreasing value for this ratio with increased system size. This is not beneficial from device considerations because this implies that α (and potentially, linear loss) increase faster than γ. These are zero frequency quantities, and of course are then real values for both α and γ, while the imaginary value for α is responsible for linear optical loss. However, far off resonance, the real and imaginary quantities will track-with and be proportional to one another, so that it is reasonable to presume that the ratio $Re\{\gamma\}/Re\{\alpha\}$ implies the nature of the variation in the ratio $Re\{\gamma\}/Im\{\alpha\}$, at least as a function of system size.

The dicationic system displays a vastly different response when looking at γ versus system size. As the system becomes larger, γ is seen in Figure 9 to rapidly turn negative achieving huge magnitude values. These magnitudes dwarf typical known experimental systems that might be calculated under the AM1 model. The negative sign clearly suggests that two-photon effects are minimized relative to one-photon effects, which should in principle yield the largest possible magnitude of γ in the extreme of no two-photon influence. This would be a best case scenario for minimizing two-photon absorption while maximizing $Re\{\gamma\}$ device effects. The magnitudes are startling, and just as startling is the apparent lack of saturation even up to 14 rings. A plot of γ/α shows in Figure 10 an increasing function with system size, which basically implies that $Re\{\gamma\}$ should increase faster than linear loss with increase in size of the system. Again, saturation effects are not seen up to 14 rings. The significance of this result is that huge γs are available with perhaps relatively minimal linear and nonlinear loss. This is the best case scenario for an all-optical material. Shown in Figure 11 is the ratio of Figure 10 to Figure 9. The

improvement in figure of merit (γ/α) upon oxidizing from neutral to +2 is as large as nearly 10000 up to the 13 ring system.

Conclusions:

The significant result reported here is the prediction of extremely large, gigantic, third order optical susceptibilities, γ, in through-space three-dimensionally delocalized systems. A companion significant result is the implication of ratios of $Re\{\gamma\}$ to $Im\{\alpha\}$ that may be increasing with system size. The combination of the two results suggest this general materials class as a concept is potentially of great significance, and should be investigated as candidate all-optical molecules/materials.

Some significant caveats are warranted.

- Calculations reported here on charged systems have been performed in the absence of counter-ions. Obviously the counter-ion field will have some effect, and likely deleterious since it will promote localization. However, it is unclear what crystal field arrangements might be optimal, and might effectively mute the localization effect.
- Calculations have been performed at the SCF level without CI, primarily because of limits on our available computational equipment. For SOS calculations it is clear that significant mutlipley excited configurations of CI are necessary to properly characterize the γ tensor, particularly when two-photon effects must be calculated correctly. In fact, the apparent less significance of two-photon effects in these calculations implies either they really aren't there to the extent implied by the calculation, or the calculation was insufficient to adequately account for them. The

major contributions to γ fall into three different types in terms of their sign. This is clearly seen in the three-level model we have defined[21-26] in earlier work.

$$\gamma \approx -(\mu_{01})^4 D_{11} + (\mu_{01})^2(\Delta\mu_{01})^2 D_{111} + (\mu_{01})^2(\mu_{12})^2 D_{121} + \ldots$$

$$\text{or,} \quad \gamma \approx \gamma_c + \gamma_n + \gamma_{tp} + \ldots$$

where μ_{rs} are transition moments between state r and s, $\Delta\mu_{01} = \mu_{11}-\mu_{00}$, and D_{lm} and D_{lmn} are perturbation type dispersion terms. In this equation, γ_c is negative, γ_n is positive, and γ_{tp} is positive. γ_n , proportional to dipole moments, is small due to the high degree of symmetry. γ_{tp} depends on the magnitude of the overlap between the one-photon and two-photon excited states. Negative perturbation contributions to γ (e.g. γ_c type components of the form $-(\mu_{0n})^4 D_{nn}$, where the notation is defined earlier[21-23]) that are large in magnitude can dominate inappropriately as a result of an inadequate calculation of two-photon contributions. This would lead to γ's that are too large in the negative direction, which would be consistent with our unusual results. However, the same methods have been applied to squarylium dyes with success at predicting both their negative γ as well as the relative differences between dyes. Also, it is unclear how much electronic correlation matters for zero frequency FF relative to standard frequency-dependent SOS results, at least in terms of characterizing two-photon effects.

- We did not allow the systems to fully optimize. Inter-ring distances were fixed at 3 Å. This may not be realistic as might be anticipated in a self assembly sense. However, known cyclophanes possess distances smaller than this, so such distances can be imposed if necessary to render a real analogous system.

- Earlier calculations[20] that we performed on potentially real systems such as dioxodiene cyclophanes showed problems in structure optimization when all degrees of freedom were allowed to optimize, which we interpreted as a Jahn-Teller or Peirls instability. Real laboratory systems, either cyclophanic or self-assembled rings may display similar instabilities, complicating a practical demonstration of the optical effects.

These caveats outline further investigations that must be done. Our present computational resource capability precludes resolving these issues without considerable further computation time.

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system size, number of rings	symmetry	IP (ev)	ΔHf	α (E4)	α (DIP)	γ (E4)	γ (DIP)
1	D2H	21.6	589.6	15.11	15.11	1.14E+00	1.15E+00
2	D2H	18.2	570.9	50.34	50.34	-4.09E+01	-4.11E+01
3	D2H	15.89	579.6	110.75	110.75	-4.44E+02	-4.46E+02
4	D2H	14.52	597.9	119.22	119.21	-1.96E+03	-1.99E+03
5	D2H	13.6	620.9	317.55	317.57	-6.00E+03	-6.13E+03
6	C2H	12.93	646.6	468.01	468.1	-1.50E+04	-1.54E+04
7	D2H	12.43	674.1	653.88	654.18	-3.47E+04	-3.46E+04
8	C2H	12.03	702.8	876.28	875.11	-6.52E+04	-6.32E+04
9	D2H	11.71	732.4	1137.85	1138.66	-1.12E+05	-1.15E+05
10	D2H	11.45	762.7	1440.58	1420.38	-1.81E+05	-1.58E+05
11	C2H	11.22	793.5	1782.5	1732.3	-2.72E+05	-2.20E+05
12	C2H	11.03	824.7	2192.76	2200.33	-4.81E+05	-5.05E+05
13	C2H	10.87	856.3	2643.88	2654.89	-7.36E+05	-7.63E+05
14	C2H	10.72	888.2	3149.28	3160	-1.09E+06	-1.09E+06

TABLE 1: AM1 results for Charge = +2 stacked benzene systems. Heats of formation are in kcal/mole. Polarizabilities (10^{-24} esu) and second hyperpolarizabilities (10^{-36} esu) are reported for the energy (E4) and dipole (DIP) expansions of the finite field.

system size, number of rings	symmetry	IP (ev)	ΔHf	α (E4)	α (DIP)	γ (E4)	γ (DIP)
1	D6H	9.65	22	14.45	14.45	7.48E-01	7.49E-01
2	D6H	9.01	56	25.7	25.7	1.05E+00	1.05E+00
3	D6H	8.71	90.1	36.68	36.69	1.39E+00	1.39E+00
4	D6H	8.55	124.2	47.57	47.57	1.71E+00	1.73E+00
5	D6H	8.46	158.3	58.41	58.4	2.07E+00	2.04E+00
6	D6H	8.4	192.5	69.22	69.21	2.37E+00	2.39E+00
7	D6H	8.36	226.6	80.01	80	2.75E+00	2.71E+00
8	D6H	8.33	260.7	90.79	90.79	3.06E+00	3.05E+00
9	D6H	8.31	294.9	101.57	101.56	3.32E+00	3.40E+00
10	D6H	8.295	328.98	112.33	112.33	3.84E+00	3.78E+00
11	D6H	8.283	363.11	123.1	123.09	4.04E+00	3.94E+00
12	D6H	8.27	397.2	133.86	133.85	4.37E+00	4.55E+00
13	D6H	8.266	431.37	144.62	144.61	4.71E+00	5.47E+00

TABLE 2: AM1 results for Charge = 0 (neutral) stacked benzene systems. Heats of formation are in kcal/mole. Polarizabilities (10^{-24} esu) and second hyperpolarizabilities (10^{-36} esu) are reported for the energy (E4) and dipole (DIP) expansions of the finite field.

FIGURE CAPTIONS

Figure 1: Plot of bond length alternation (BLA; as defined in the text) versus ring position in any given charge=+2 stacked benzene system. The +2 benzene 'monomer is represented by a single point, while all other groups of data are connected by lines.

Figure 2: An expansion of Figure 1, more clearly showing the variation of BLA versus ring position in any given charge=+2 stacked benzene system.

Figure 3: Bar graph illustrating the BLA alternation averaged over all rings for any given system.

Figure 4: The AM1 calculated ionization potential (IP) for both charge=0 (neutral) and charge=+2 (dication) stacked benzene systems.

Figure 5: The AM1 calculated heat of formation (ΔH_f) for both charge=0 (neutral) and charge=+2 (dication) stacked benzene systems.

Figure 6: The heat of formation for reaction of a (n-1) size dication system with a neutral benzene to make a n size dication system, based on the AM1 calculated results presented here.

Figure 7: The AM1 finite field $\gamma(0)$ calculated using the DIP (dipole expansion; squares) and E4 (energy expansion; circles), as a function of the size of the system, for neutral systems. The esu untis are cm^7esu^{-2}.

Figure 8: The ratio γ/α as a function of the size of the system for neutral systems. The DIP (dipole expansion) is the dotted line while the solid line is the E4 (energy expansion). The units are 10^{-12} cm^4esu^{-2}.

Figure 9: The AM1 finite field $\gamma(0)$ calculated using the DIP (dipole expansion; squares) and E4 (energy expansion; circles), as a function of the size of the system, for charge =+2 systems. The esu untis are cm^7esu^{-2}.

Figure 10: The ratio γ/α as a function of the size of the system for neutral systems. The DIP (dipole expansion) is the dotted line while the solid line is the E4 (energy expansion). The units are 10^{-12} cm^4esu^{-2}.

Figure 11: The improvement of figure of merit (γ/α) for the charge=+2 systems relative to neutral systems as a function of system size.

Figure 1

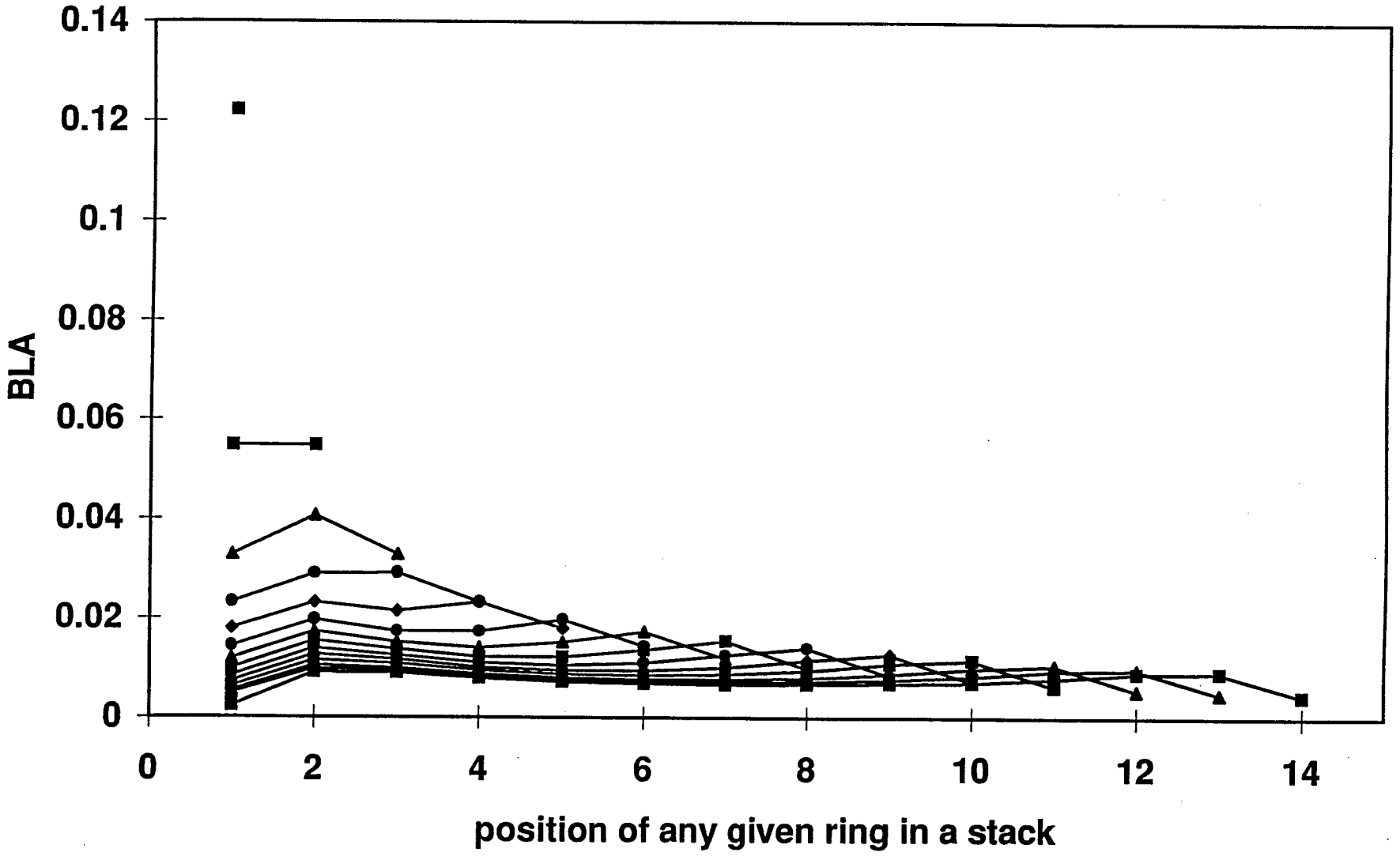

0.14
0.12
0.1
0.08
0.06
0.04
0.02
0
BLA
0
2
4
6
8
10
12
14
position of any given ring in a stack

Figure 2

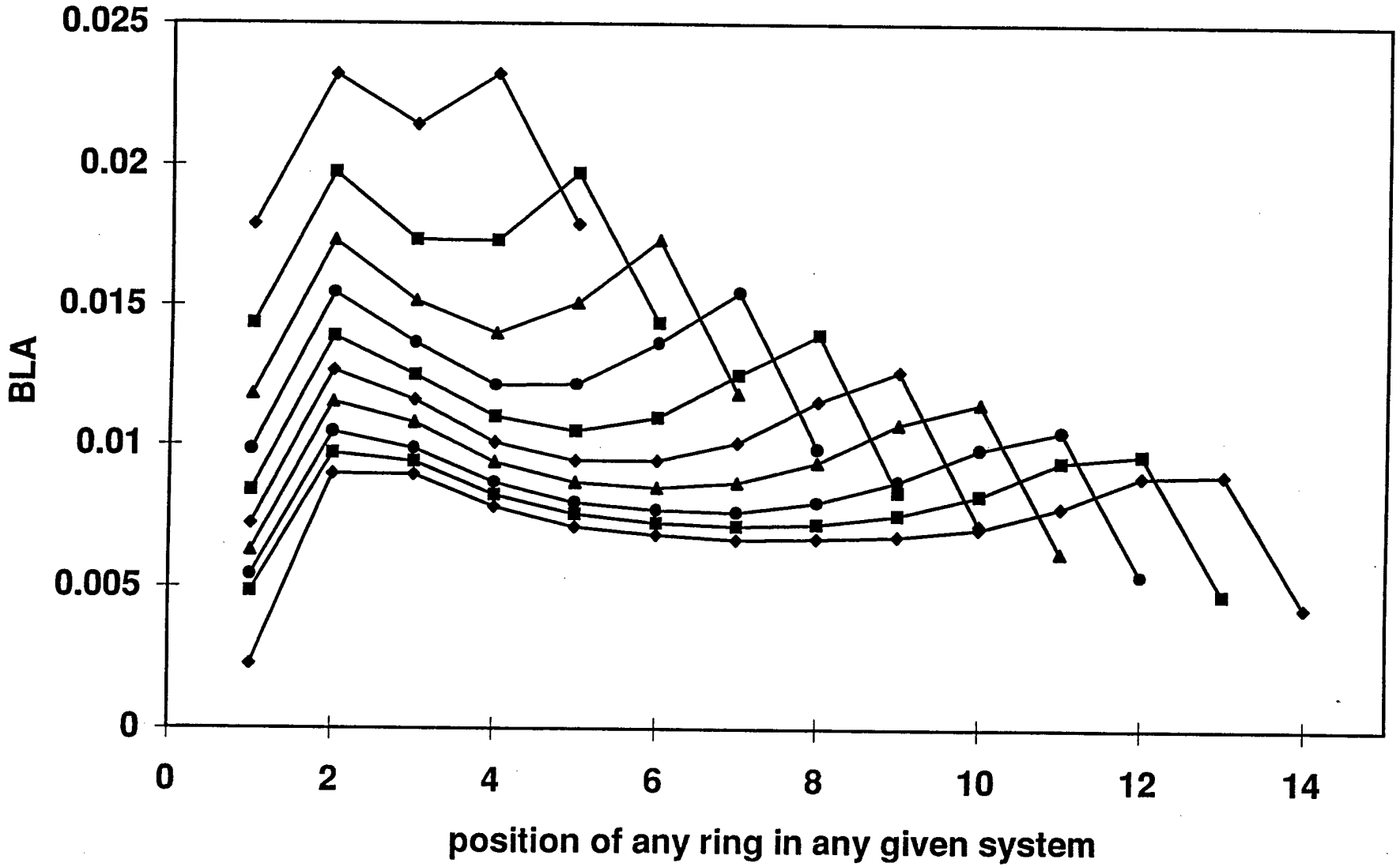

0.025
0.02
0.015
0.01
0.005
0
BLA
0
2
4
6
8
10
12
14
position of any ring in any given system

Figure 3

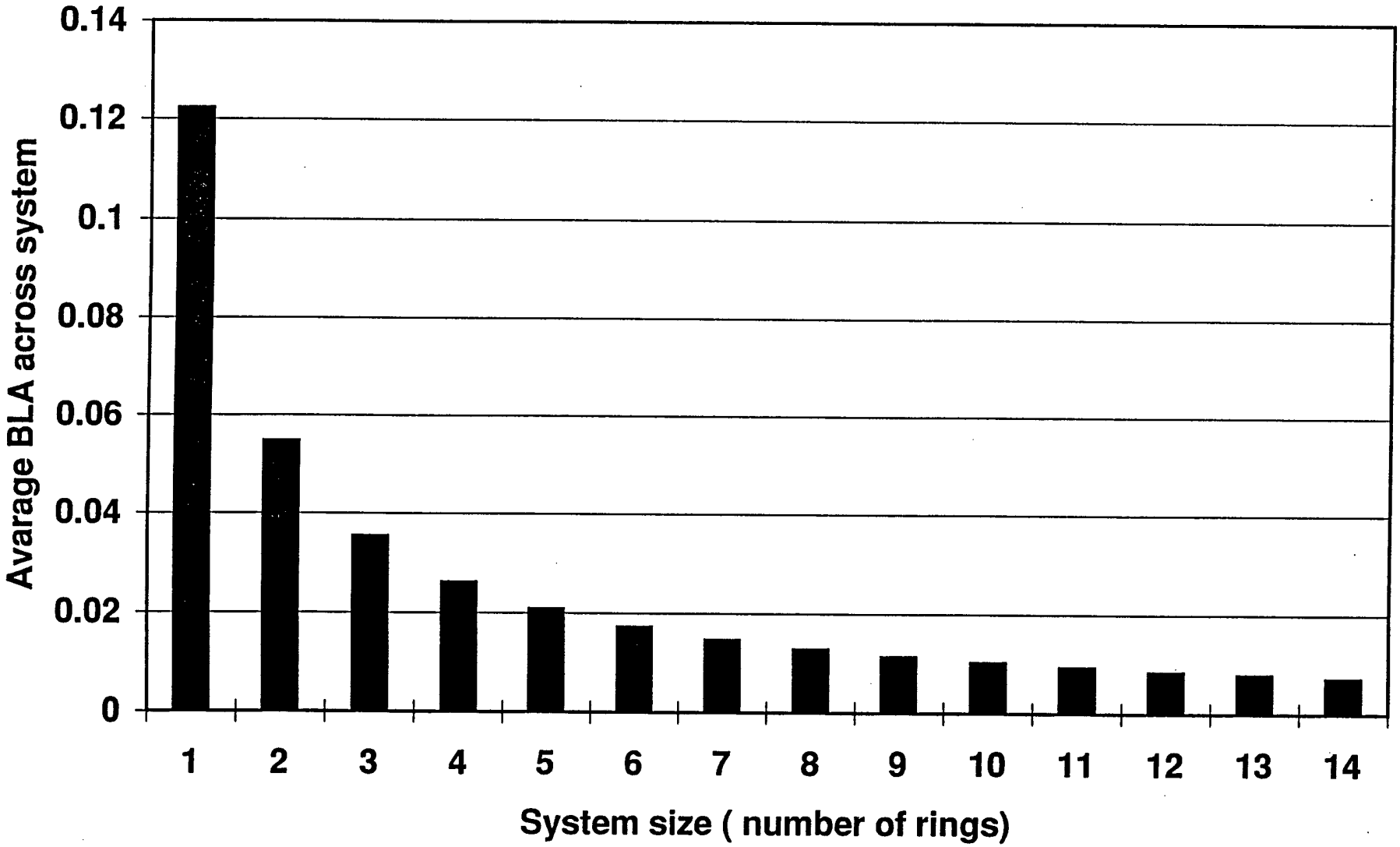

0.14
0.12
0.1
0.08
0.06
0.04
0.02
0
Avarage BLA across system
1
2
3
4
5
6
7
8
9
10
11
12
13
14
System size (number of rings)

Figure 4

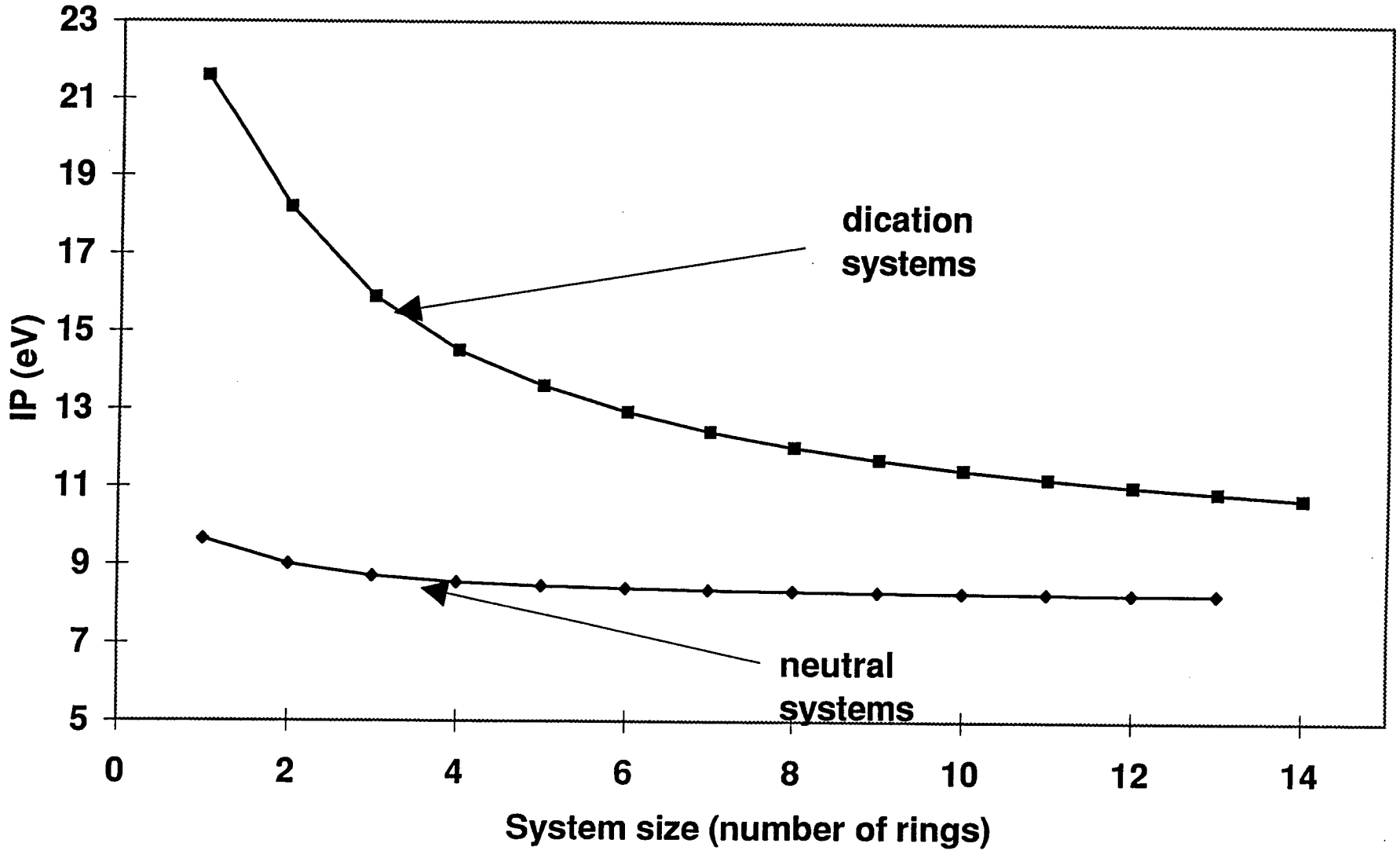

23
21
19
17
15
13
11
9
7
5
IP (eV)
0
2
4
6
8
10
12
14
System size (number of rings)
dication
systems
neutral
systems

Figure 5

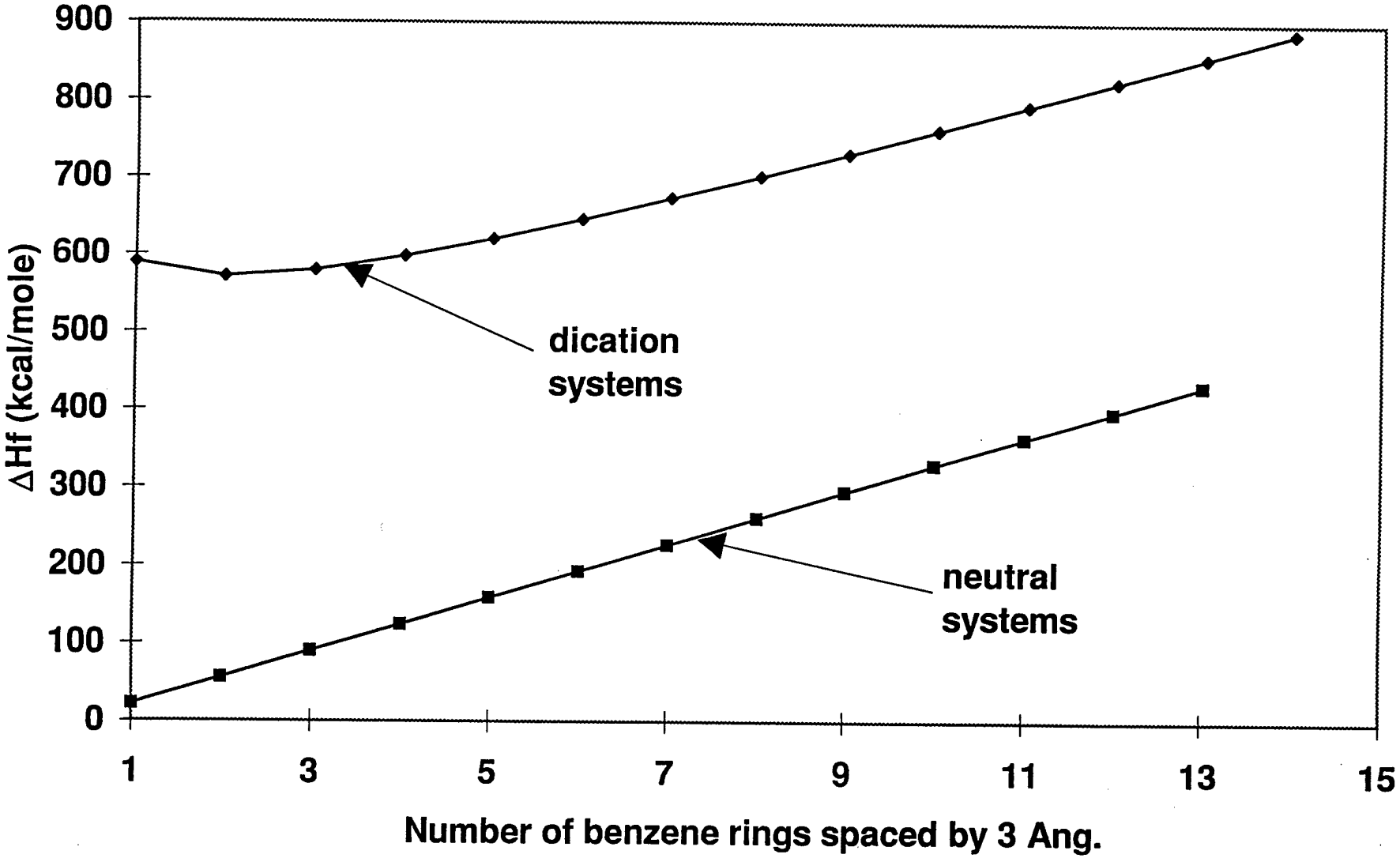

900
800
700
600
500
400
300
200
100
0
ΔHf (kcal/mole)
dication systems
neutral systems
1
3
5
7
9
11
13
15
Number of benzene rings spaced by 3 Ang.

Figure 6

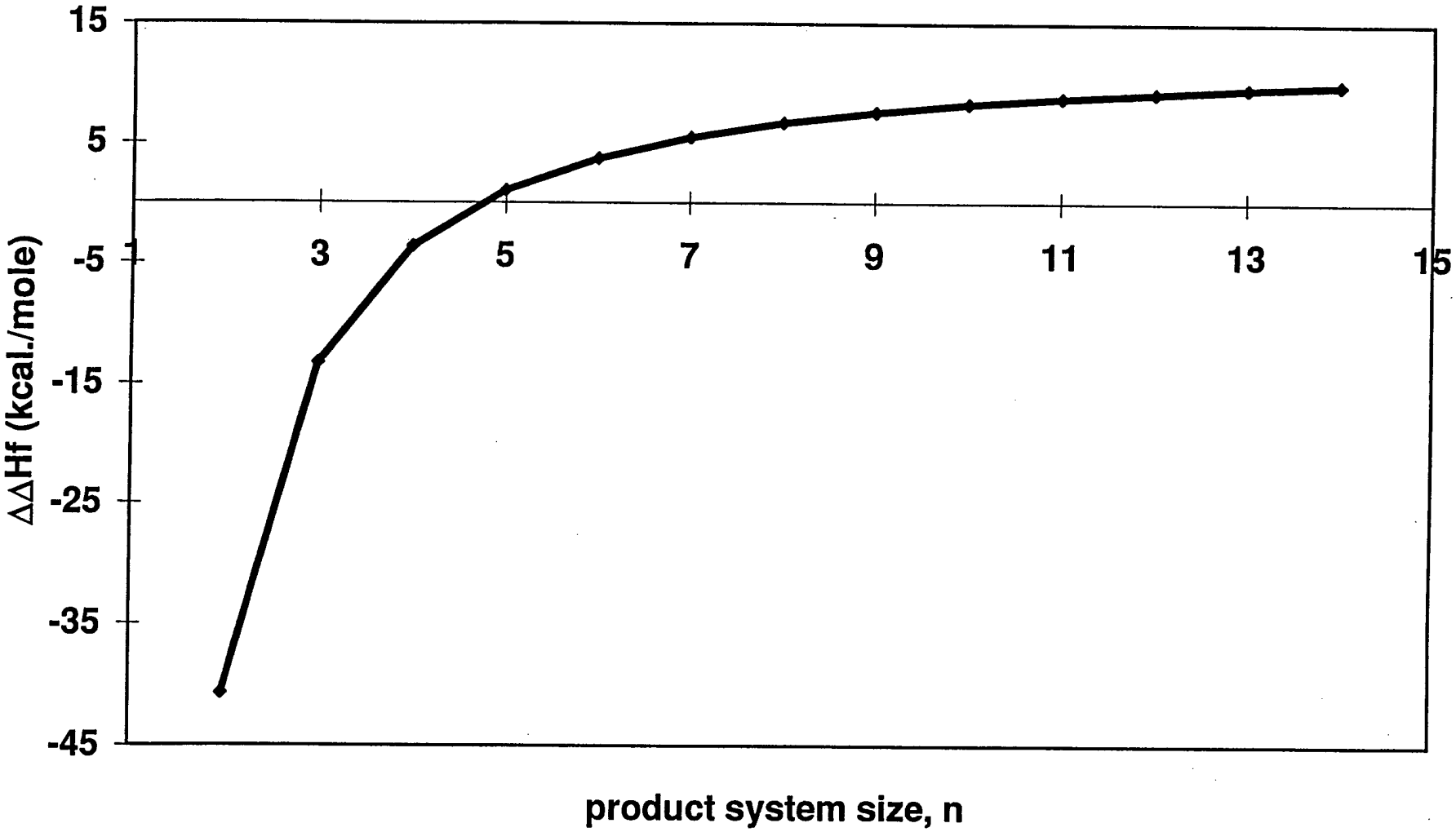

15
5
-5
-15
-25
-35
-45
3
5
7
9
11
13
15
ΔΔHf (kcal./mole)
product system size, n

Figure 7

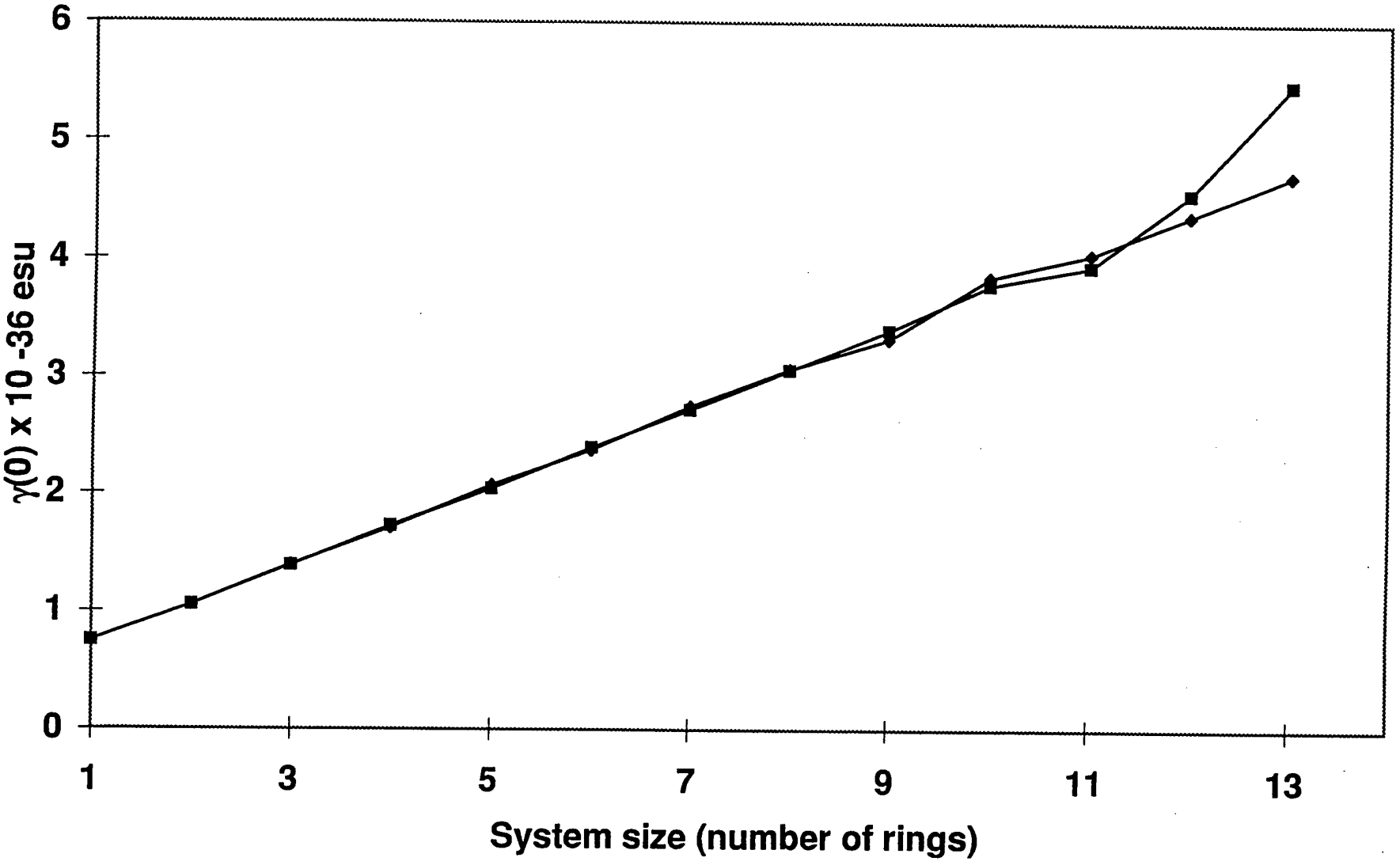


Figure 8

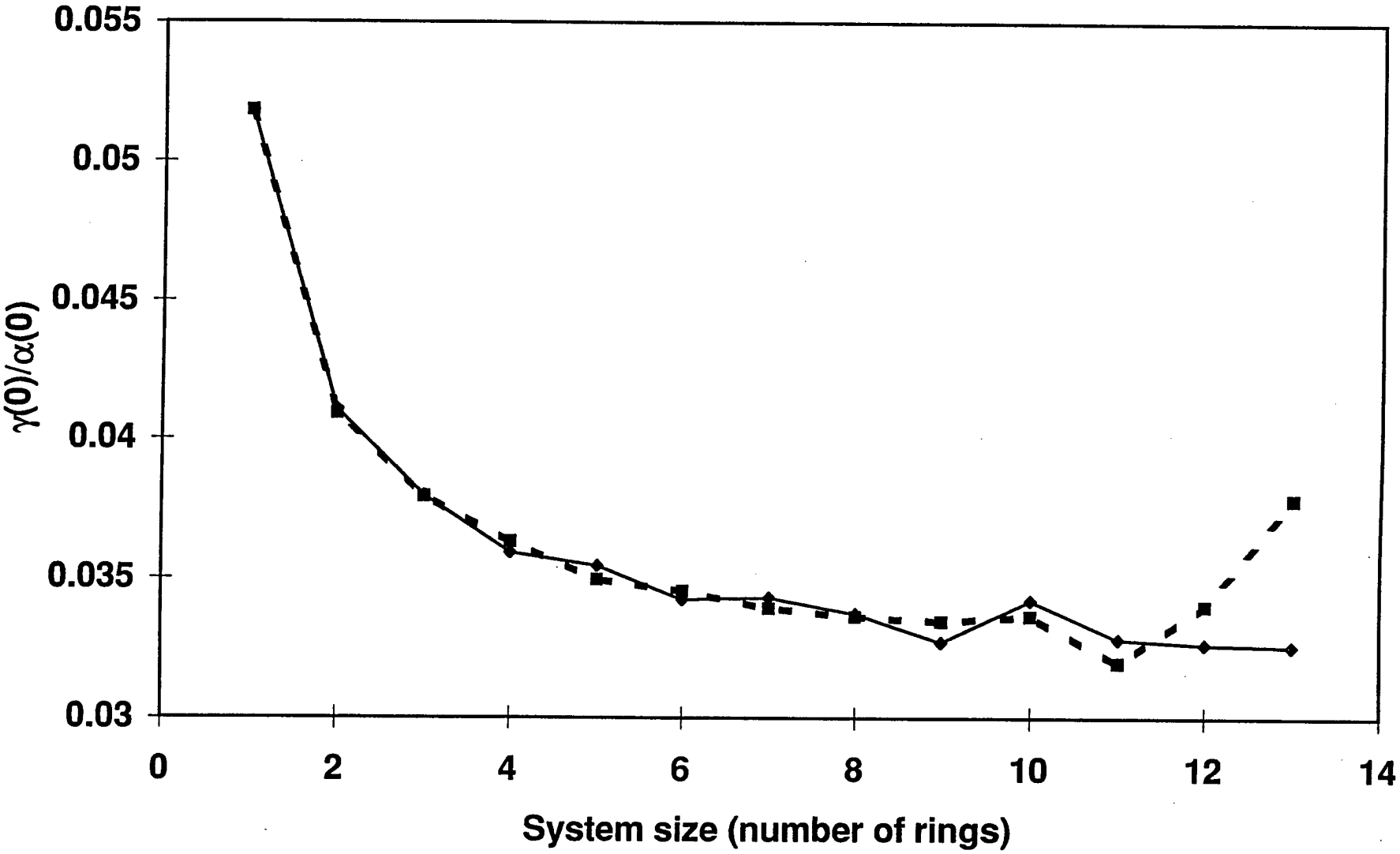

0.055
0.05
0.045
0.04
0.035
0.03
γ(0)/α(0)
0
2
4
6
8
10
12
14
System size (number of rings)

Figure 9

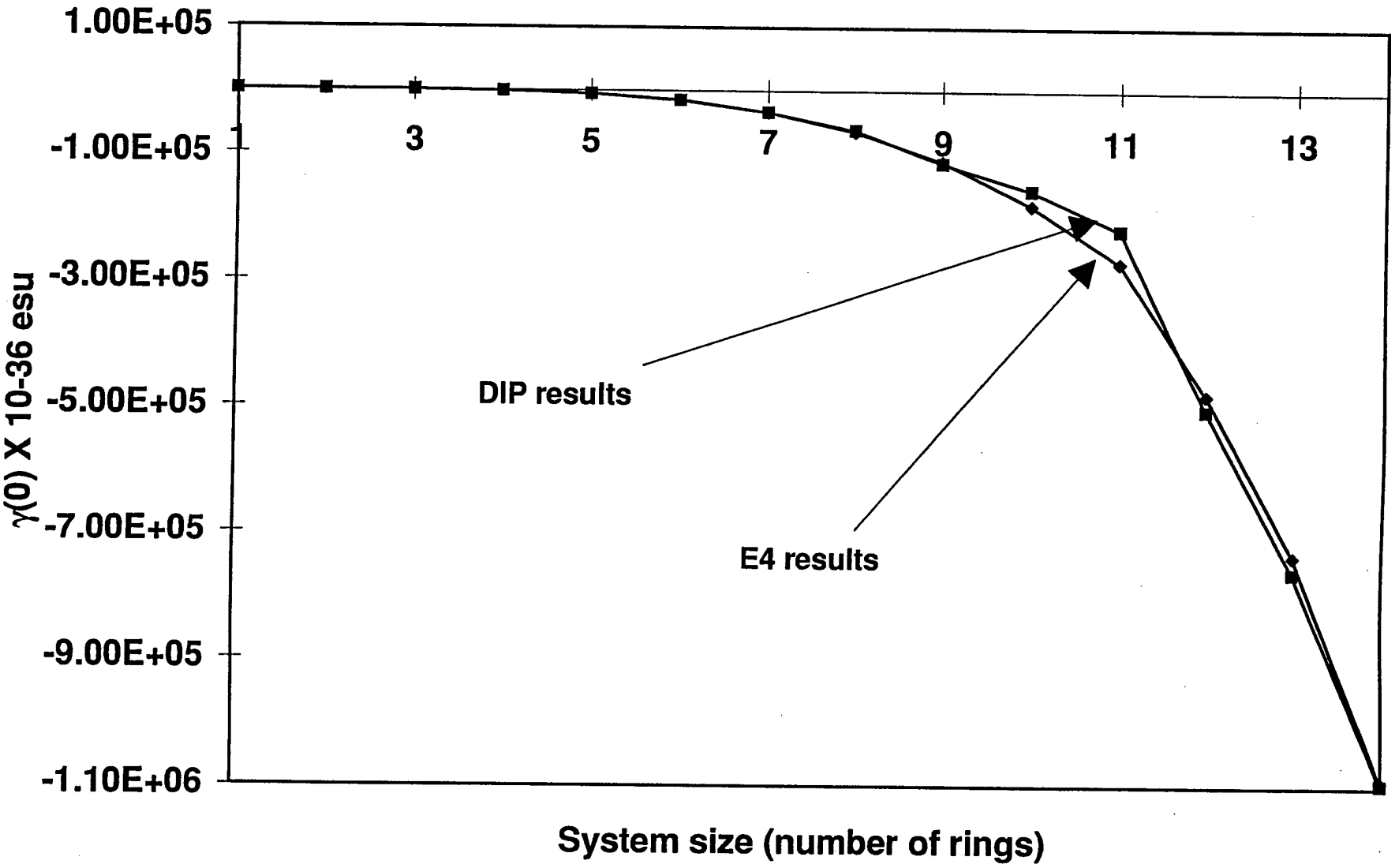

1.00E+05
-1.00E+05
-3.00E+05
-5.00E+05
-7.00E+05
-9.00E+05
-1.10E+06
γ(0) X 10-36 esu
1
3
5
7
9
11
13
DIP results
E4 results
System size (number of rings)

Figure 10

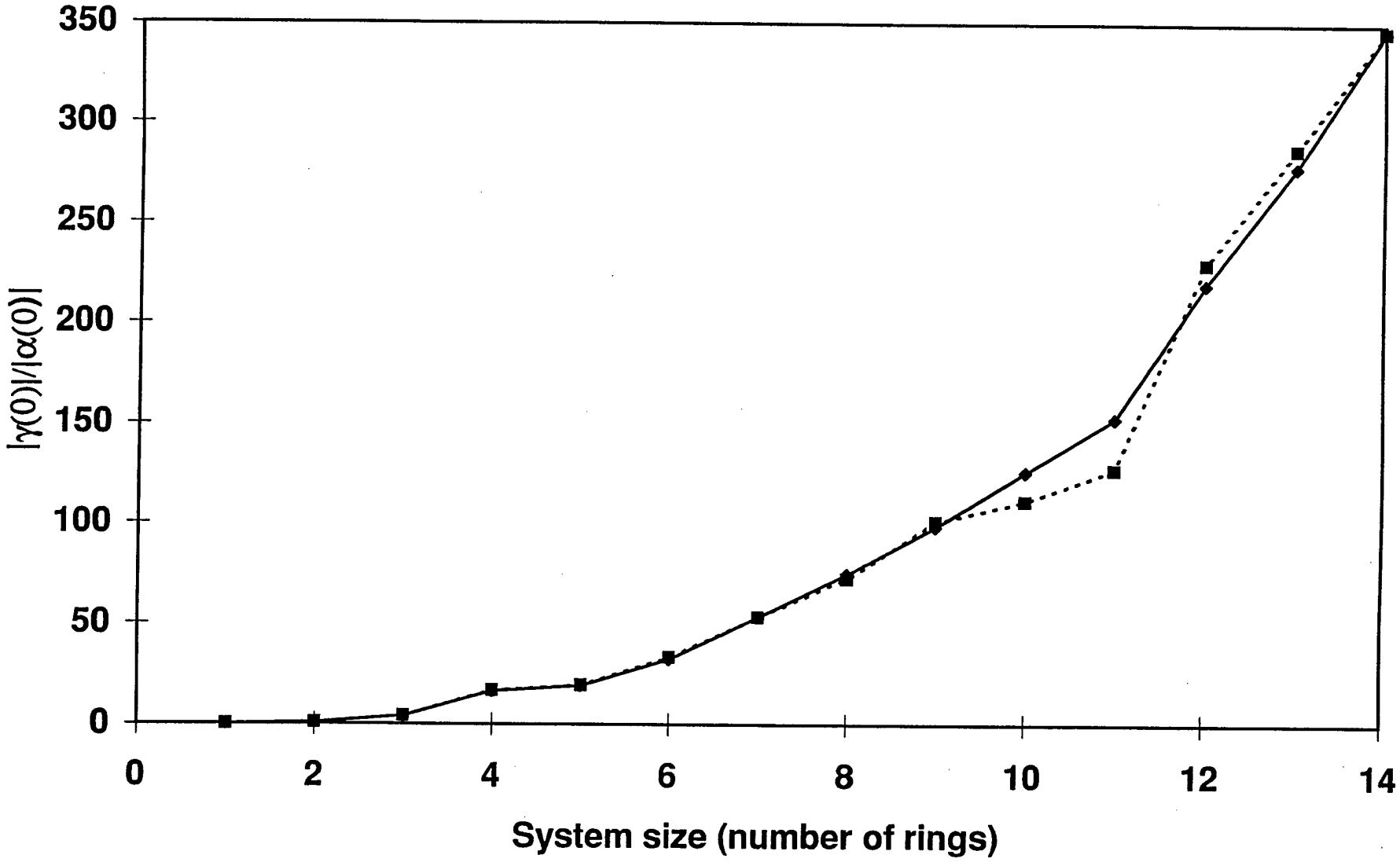
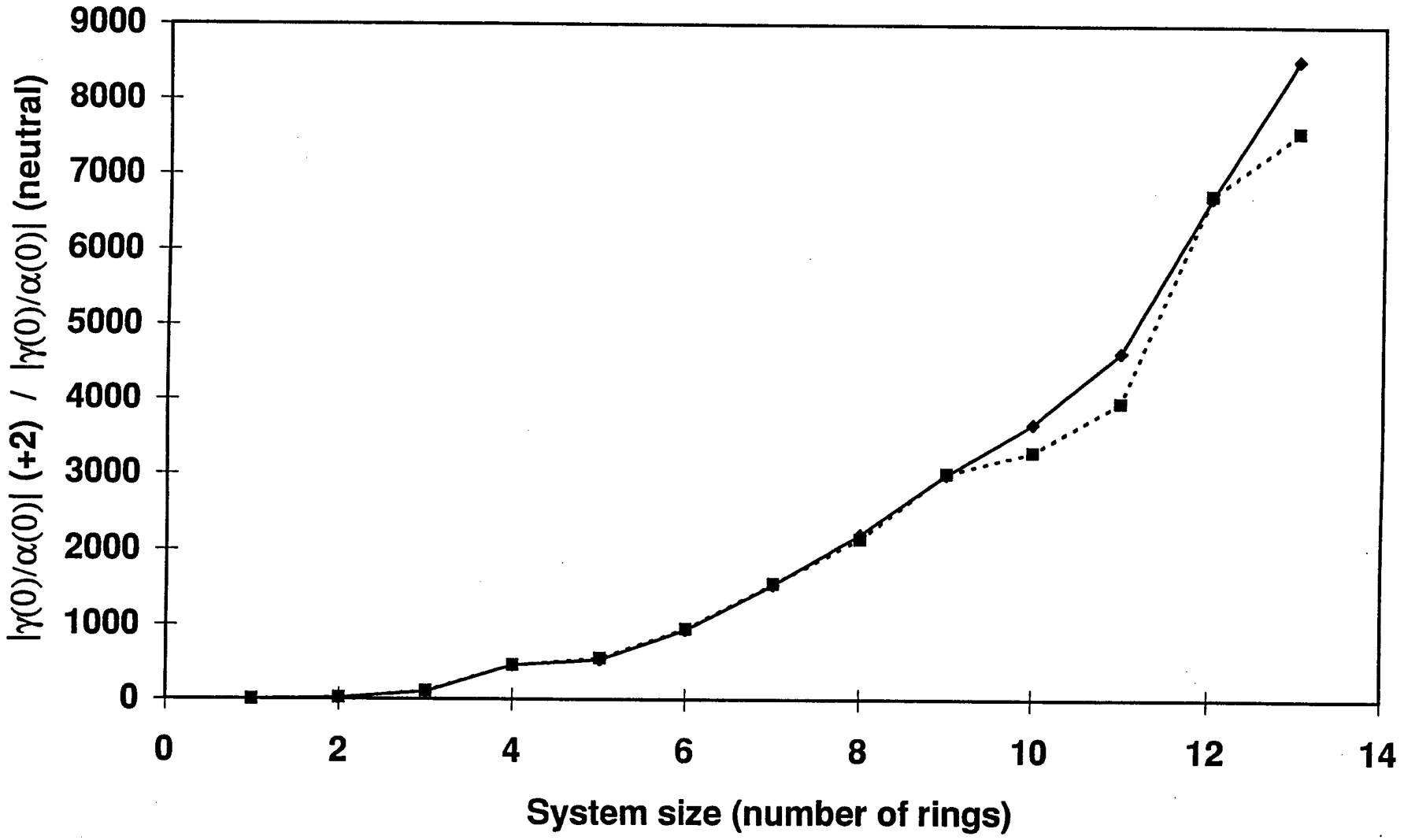

350
300
250
200
150
100
50
0
|γ(0)|/|α(0)|
0
2
4
6
8
10
12
14
System size (number of rings)

Figure 11


9000
8000
7000
6000
5000
4000
3000
2000
1000
0
|γ(0)/α(0)| (+2) / |γ(0)/α(0)| (neutral)
0
2
4
6
8
10
12
14
System size (number of rings)