Theoretical Study of Polymerization Mechanism of p-xylylene Based Polymers

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Theoretical study of polymerization mechanism of *p*-xylylene based polymers

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ABSTRACT

The mechanism of polymerization of p-xylylene and its derivatives is analyzed at the theoretical level. The polymerization reaction takes place in vacuo without any catalyst. The first step is a pyrolytic decomposition of starting material for polymerization, paracyclophane, a cyclic dimer of p-xylylene, into biradical linear dimer and finally into two quinonoid monomeric molecules of p-xylylene. The quinonoid monomer is diamagnetic, i.e., it has a singlet ground state. The monomers after pyrolysis, when temperature is lowered, do not form back cyclic dimers but instead polymerize into long chain molecules. The initiation of polymerization requires dimerization of two monomers leading to formation of a genuine non-coupled biradical dimer. The chain molecules grow through the propagation reaction only one unit at a time, by the attachment of a monomer to a radical chain end. In this work the pyrolysis

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reaction, the initiation reaction and the first propagation steps of parylene polymerization (up to pentamer) are studied in details using different quantum chemical methods: AM1 and PM6 semiempirical methods and density functional theory (DFT) approach using B3LYP functional with two basis sets of different size (SVP and TZVP).

KEYWORDS parylene, poly-p-xylylene, chemical vapor deposition, radical polymerization, density functional theory, semiempirical methods.

INTRODUCTION

Members of poly(p-xylylene) family of polymers, also known as parylenes, are polymers that can be deposited in thin film form at room temperature by chemical vapor deposition.[1] The discovery of the poly(p-xylylene) was first reported by Szwarc in 1947 when he found a polymer as one of the products formed in the vacuum thermal decomposition (pyrolysis) of *p*-xylene.[2] However, the yields of polymer film were only a few percent even at very high pyrolysis temperature. It was not until 1966 when Gorham found a much more effective process starting with the vacuum pyrolysis of di-*p*-xylylene ([2.2]paracyclophane).[3] Parylenes become technically important materials for use in electronics, medical applications, and optical devices. Today the parylene polymer is widely used for the coating of printed circuits, for barrier coatings, in corrosion control and as a dry lubricant.[4, 5] Parylene based polymers are hydrophobic and offer an attractive low dielectric permittivity. These polymers exhibit excellent thermal and mechanical properties, good solvent resistance, bulk barrier properties that are among the best of organic coatings. The chemical vapor deposition is able to produce the desired film thickness and uniformity over the coating area, which is essential in many applications in the biotechnology and microelectronics industries. Three commercially most popular members of parylene family are shown on Figure 1.

Figure 1.

Parylene N, is poly-p-xylylene, a completely linear, highly crystalline material. Parylene C, the second commercially available member of the series, is produced from similar monomer modified only by the substitution of a chlorine atom for one of the aromatic hydrogen atom. Parylene D is produced from the monomer modified by the substitution of the chlorine atoms for two of the aromatic hydrogen atoms. Recent introduction of novel substituents into parylene broaden its applications. Variable degrees of substitution and functionalities including hydroxy, methoxy, amino, triflate, or trifluoroacetyl groups are used to prepare thin films of poly(p-xylylenes) with distinct chemical and optical properties.[6, 7] Parylene

based chemically functionalized polymer coatings have potential biomedical applications. [8] Various acetylenic [2.2]paracyclophanes such as 4-ethynyl-[2.2]paracyclophane were subjected to gas phase vacuum pyrolysis and the resulting polymer was then treated with biotinazide to covalently attach biotin molecule to the polymer surface.[9] Biotin is known to for a noncovalent complex with streptavidin protein thus allowing preparation of bioactive surfaces that could be employed as novel biosensors and microarrays. Chemical vapor deposition of the germanium derivative of [2.2]paracyclophane and subsequent annealing produces germanium grains embedded in the parylene matrix.[10] Traditional metal-polymer systems can be obtained by the treatment of parylene coating with metal vapors or by the reduction of metal salts in solution in the presence of polymers.[5]

In spite of wide industrial application of the polymerization of p-xylylene and its substituents leading to parylene family of polymers, the polymerization reaction has not been studied by computational methods extensively. The fact that no solvents or catalysts take part in polymerization of p-xylylene makes this process very interesting from a theoretical point of view. Over the several decades only a few articles regarding the mechanism of formation of poly(p-xylylene) from the vapor phase have been published since Errede and Szwarc prepared their review article in 1958.[11] Their qualitative picture of the polymerization mechanism still seems valid. Parylene polymerization is of the chain growth type except that the chains are not terminated during growth.[12] In the chain growth polymerization polymer chain grows only one unit at a time, by the attachment of a monomer to the chain end. In general the chain ends could be a radical, cation or anion, and in case of parylene the chain ends are radical. Chain growth polymerization takes place in three common steps: initiation, propagation and termination. In case of parylene polymerization there is no termination step and unreacted chain ends are buried in the film as it grows. Subsequent termination of the radical chain ends can occur post-deposition via reactions with atmospheric oxygen that has diffused into the polymer film [13].

Beach worked on quantitative understanding of p-xylylene vapor deposition polymerization.[14] He compared results from his kinetic model with the activation energy for the propagation, 8.7 kcal/mol, as measured by Errede in solution.[15] At the time of Beach publication no measure of the activation energy

for initiation reaction existed, but Errede[15] suggested earlier that it should be considerably larger than the activation energy for the propagation. A simple estimation of the heat of formation from bond and resonance energies carried out by Kubo's[16] gives 16.1 kcal/mole difference between the heat of formation for the biradical dimer and the heat of formation of two starting monomers and -2.3 kcal/mol difference between the heat of formation for the biradical trimer and the heat of formation of three starting monomers. From this it can be roughly estimated that the activation energy for initiation (according to Beach[14] this is the highest potential energy during the reaction forming the trimer, assuming that the activation energy for reaction between two monomers is smaller than the activation for reaction between monomer and biradical dimer) is 16.1+8.7 = 24.8 kcal/mol. In his review Szwarc[12] defined initiation reaction not as the formation of the trimer but of the dimer. He criticized earlier kinetic experiment in solution performed by Errede[15]. In his opinion the measured propagation activation energy of 8.7 kcal/mol may have substantial error. The measured value depends on the concentration of monomer in the swollen polymer particles (where polymerization in solution takes place), which may be different from its bulk concentration.[12] Most of the recent studies of polymerization of p-xylylene were focused on modeling physical process of deposition of polymer [17-20], together with chain growth, but not the chemical reactions during polymerization. Recently an analytical kinetic model for the chemical vapor deposition of poly(p-xylylene) was modeled as multistep process that includes both physisorption of monomer on the surface and subsequent chemisorption.[21] The best fit parameters from this kinetic model to experimental data gives 9.41 kcal/mol as the difference between the activation energy for desorption and the activation energy for chemisorption. Monte Carlo simulation of vapor deposition polymerization using a simple two-dimensional model shows that the polymer chain length, the polymer film thickness and density, and polymer structure depends on the ration of diffusion coefficient to deposition rate.[22]

The thermolysis of the [2.2]-paracyclophane has been studied experimentally by kinetic measurements in the presence of NO or O_2.[23] The enthalpy and entropy of transition state for the reaction of the ring opening was determined from the temperature dependence of trapping rates of the intermediate

biradicals by NO or O_2.[23] These values were compared with the heats of formation for reactants, products and transition state calculated with the empirical forcefield making use of the EVBH method,[23] which allows to calculate radical stabilization energies with high accuracy. The experimental activation barrier for the opening of [2.2]-p-cyclophane ring was measured as 37.7±0.5 kcal/mol, and the barrier for the reverse reaction was 11.8±1.0 kcal/mol. Together with experimental heat of formation of [2.2]-p-cyclophane equal 58.5±0.5 kcal/mol[24] or more commonly known value 59.9±1.9 kcal/mol[25] this allows estimation of the heat of formation of the biradical dimer as 84.4 or 85.8 kcal/mol. Experimental heat of formation for p-xylylene is 50±4 kcal/mol,[26] so the heat of formation for two monomers is around 15 kcal/mol higher than the heat of formation the biradical dimer. The initiation reaction of formation of the biradical dimer is an exothermic process. This is in disagreement with simple estimation of the heat of formation from bond and resonance energies carried out by Kubo's[16] and later used by Beach.[14]

Thermal isomerization of disubstituted [2.2]-p-cyclophane was also studied experimentally and only the diradical mechanism of the ring opening is consistent with the measured equilibrium and the rate constants.[27] The quantative conversion of dimer to monomer as a function of the pyrolysis furnace temperature was studied by mass spectroscopy. [28] Cracking of the dimer begins at 385°C and by 565°C one hundred percent of dimer flowing through the pyrolysis zone is cracked into monomer. The experiment was performed in non equilibrium conditions, the residence time of the dimer in the pyrolysis zone effected the conversion, and therefore authors did not try to estimate the activation energy for the pyrolysis reaction. [28]

Alexandrova and Salcedo studied the chemical reaction of decomposition of the unsubstituted [2.2]-p-cyclophane, chloro-p-cyclophane and cyano-p-cyclophane in the pyrolytic zone into the intermediate quinoid monomer molecules using AM1 semiempirical method [29]. They calculated the total energies, ionization potentials and analyzed frontier orbitals for both [2.2]-p-cyclophane and p-quidodimethane with and without substitutions and discussed the influence of the substituents on the polymerization reactions on the basis of the Taft and Topson rules for aromatic compounds. Authors did not studied polymerization reaction in details but concluded that the intermediate molecule p-quinodimethane is

very important in starting polymerization process and can exist in two forms: a closed shell tetraolefin and an aromatic biradical which has the higher energy but is accessible in the environment of reaction. Alexandrova and Salcedo postulated that during the polymerization the monomer must take a polar form in order to join with another monomer or continue in propagation but they did not present any results supporting this statement. In opposition to the mechanism presented by Alexandrova and Salcedo the generally accepted mechanism of polymerization of para-xylylene based polymers is radical not ionic. [11] In this work the pyrolysis reaction, the initiation and the first propagation steps of parylene polymerization are studied in details using different quantum chemistry methods: AM1 and PM6 semiempirical methods and density functional theory (DFT) approach using B3LYP functional with two basis sets of different size.

METHODS.

The polymerization of parylene was modeled using semiempirical AM1 and PM6 methods as implemented in Mopac 2007,[30] and the density functional theory (DFT) with B3LYP functional using single zeta basis set with polarization (def2-SVP) and triple zeta basis set with polarization (def2-TZVP) as implemented in Turbomole.[31] Two selected semiempirical methods represent evolution of this class of computational methods over last 30 years. The classical AM1 method was parameterized in 1985 to reproduce molecular properties of around 200 compounds.[32] Experimental and ab initio data from over 9000 compounds were used to develop the new PM6 method.[33] In the case of semiempirical calculations for molecules with biradical character the lowest singlet energy state, resulting from the mixing of four microstates using configuration interaction (CI) method, was optimized. These microstates included the microstate arising from a one electron excitation from the HOMO to the LUMO; the microstate resulting from the time-reversal operator acting on the parent microstate; the microstate resulting from de-excitation from the formal LUMO to the HOMO; and the microstate resulting from the single electron in the formal HOMO being excited into the LUMO. The lowest singlet energy state in configuration interaction model describes correctly both closed shell and open shell biradical molecules. This allows

the use of standard methods for a search of the transitions state of each reaction. Energy profiles for breaking of the bond in the paracyclophane molecule and in the linear biradical di-para-xylylene dimer molecule calculated using semiempirical PM6 method with RHF and CI (singlet and triplet state) wavefunctions are compared in Figure 2.

Figure 2.

Both closed shell systems: paracyclophane molecule (a minimum for short distance in Fig. 2a) and two monomer xylylene molecules (a minimum for large distance in Fig. 2b) have almost the same heat of formation calculated using RHF and singlet CI model. Open shell biradical di-para-xylylene dimer (a minimum for large distances in Fig 2a and a minimum for short distances in Fig 2b) has the same heat of formation in singlet and triplet state calculated using CI method. Equal energy of singlet and triplet state can be explained by large distance between atomic centers where the single electrons are located in this molecule. RHF model can describe only closed shell paracyclophane and two monomer xylylene molecules. Triplet CI model can describe only the ground state of open shell di-para-xylylene dimer. Transition state points for both reactions estimated from maxima on singlet CI profiles are close to the crossing points between RHF and triplet CI profiles. For the first reaction of breaking of the bond in paracyclophane the crossing point between RHF and triplet CI profiles is 8 kcal/mol higher than the maximum on singlet CI profile but appears at the same distance of around 2.5 Å. For the second reaction of breaking bond in biradical di-para-xylylene dimer the crossing point between RHF and triplet CI profiles is 3 kcal/mol lower than the maximum on singlet CI profile and appears at the distance shorter by 0.1 Å.

DFT method was selected for this work because it includes dynamic correlation energy without the additional computational overhead as in post-Hartree–Fock methods. B3LYP is the commonly used hybrid density functional which offers a good compromise between computational cost, coverage, and accuracy of results. It has become a standard method used to study organic chemistry in the gas phase.[34]

In the DFT calculations biradical molecules were treated as triplets with UHF method. In the case of reactants and products of different multiplicity, the chemical reaction was modeled using both standard restricted density functional theory (RDFT) and unrestricted density functional theory (UDFT). The transition state energy was estimated from the crossing between two calculated potential energy profiles as shown on Figure 3.

Figure 3.

Unrestricted density functional theory can be used for the description of open-shell biradicals[35] especially when overlap between the open-shell orbitals is small and the single electrons are located at different atomic centers as in the case of all molecules studied in this work.

RESULTS AND DISSCUSSION.

The first modeled reaction was the pyrolysis reaction of cracking the cyclo-di-para-xylylene dimer ([2.2]paracyclophane) into monomers as shown on Figure 4.

Figure 4.

In this process the system changes multiplicity twice, both a reactant, a cyclic dimer cyclo-di-para-xylylene, and the final product, two monomer para-xylylene molecules, are a close shell molecules. The intermediate product, linear dimer, di-para-xylylene, has biradical character. The results of both semiempirical AM1 and PM6 methods and DFT B3LYP/SVP and B3LYP/TZVP calculations are gathered in Table 1 as energies in kcal/mol relative to the reactant. The absolute values of the heat of formation in kcal/mol and total energies in hartree as calculated for the reactant using semiempirical and DFT methods, respectively, are also show in Table 1. Calculations using DFT method give lower values of both the differences between reactant and product energies and the transition state energies.

Table 1

The results of calculations are in a good agreement with the experimental data available for thermolysis reaction of the unsubstituted [2.2]-p-cyclophane (parylene N).[23] As shown in Table1 cyclic dimer (cyclo-di-para-xylylene or [2.2]paracyclophane, DI) is the most stable compound but in high enough temperature can be decomposed into monomers of p-xylylene (M). The highest energy barrier for pyrolysis, necessary to break the first bond in cyclic dimer, is about 50 kcal/mol using both AM1 and PM6 methods and about 43 kcal/mol using DFT B3LYP method with smaller SVP basis set and 40 kcal/mol with larger TZVP basis set. The last value is with a good agreement with the experimental value of 37.7±0.5 kcal/mol. Breaking the second bond in biradical linear dimer (MM) is easier, with energetic barrier of about 42 kcal/mol from AM1, 38 kcal/mol from PM6 methods and about 29 and 28 kcal/mol from DFT calculations with SVP and TZVP basis sets, respectively. The experimental barrier for this reaction is not available. The total enthalpy of the pyrolysis reaction is overestimated by both semiempirical methods, 60 kcal/mol from AM1 and 56 kcal/mol from PM6, and underestimated by DFT B3LYP method using larger TZVP basis set which gives value of 31 kcal/mol. The results from DFT B3LYP method using smaller SVP basis set give perfect agreement with the experimental value of 41.5 kcal/mol. Experimental data are available only for parylene N, and our calculations show only small differences for parylene C and parylene D caused by the substitution of the chlorine atom for one or two of the aromatic hydrogen atoms. The activation energy barriers, the energies of intermediate biradical dimer and the total energy changes during the reaction are on average slightly higher for parylene C and slightly lower for parylene D in comparison to parylene N for both semiempirical and DFT methods. The pyrolysis reaction is also driven by entropy factor (higher entropy of two monomer molecules compared to one dimer molecule), which we did not consider in our modeling.

The monomers after pyrolysis, when temperature is lowered, do not form back cyclic dimer (DI) but instead polymerize into long chain molecules.[11] The schematic reaction is show on Figure 5 and results

of semiempirical AM1 and PM6 and DFT B3LYP/SVP and B3LYP/TZVP calculations are presented in Tables 2-5.

Figure 5, Table 2

The barrier for reaction between two monomers (Table 2) is around 16 kcal/mol using AM1, and around 20 kcal/mol using PM6 methods. DFT B3LYP calculations give smaller barrier, around 10 kcal/mol using smaller SVP basis set and around 15 kcal/mol using larger TZVP basis set. All computational methods show that this is an exothermic reaction, with biradical dimer having lower energy compared to two monomers. There is no experimental measurement for the activation barrier of this reaction. The experimental energetic effect of the biradical dimer formation starting from two monomers is around 14 kcal/mol, but this value has a substantial uncertainty. Both semiempirical methods and the DFT calculations with smaller SVP basis set overestimate this value, while the DFT calculations with larger TZVP basis set underestimate it. Results obtained for this reaction are similar for all types of parylene.

Table 3

The data for next reaction, between monomer (M) and biradical linear dimer (MM) forming biradical trimer (MMM), are presented in Table 3. The barrier in this reaction is around 7 kcal/mol using AM1 and 9 kcal/mol using PM6 methods, and only around 1-3 kcal/mol from DFT calculations depending on the basis set. This is a much lower barrier then the barrier of forming cyclic dimer (DI), which is around 15 kcal/mol using DFT method with larger basis set or AM1 semiempirical method, around 10 kcal/mol using DFT with smaller basis set, and around 20 kcal/mol using PM6 semiempirical method (a reaction reverse to this is shown in Table 1). The difference between energy barrier of the reaction of two monomers and monomer with biradical dimer explains why existing chain molecules are growing faster in comparison to forming of a new chain, which must be initiated by creating the new linear biradical

dimer. We have also modeled reactions between a monomer and tri- and tetramer to form tetramer and pentamer, respectively. As shown in Tables 4 and 5 barriers and energetic effects for these reactions are similar to reaction between a monomer and biradical dimer.

Table 4, Table 5

Both semiempirical methods, AM1 and PM6, give worse agreement with available experimental data compared to DFT B3LYP calculations. Correct description of biradical molecules is very important for current study, however parameterization of AM1 and PM6 methods is focused on close shell molecules. The DFT method gives better agreement but surprisingly in some cases larger basis set, TZVP, gives worse agreement with experiment than smaller basis set SVP. The possible explanation of this result is an error cancellation for smaller basis set. An approximation of height of barrier of reactions calculated by DFT method from the crossing between two calculated potential energy profiles can produce large errors.

CONCLUSION

The three reactions modeled: pyrolytic decomposition of paracyclophane (a cyclic dimer of p-xylylene); the initiation reaction between two p-xylylene monomers; and the first propagation step of parylene polymerization, formation of the trimer are summarized on Fig.6.

Figure 6

The pyrolytic decomposition of paracyclophane into two monomers is an endothermic reaction with the total calculated barrier around 45 kcal/mol. The calculated values are in moderate agreement with available experimental data. The initiation reaction of formation of biradical linear dimer from two monomers is an exothermic reaction with the activation barrier around 15 kcal/mol. There are no direct

experimental data to compare with this value. The reaction of propagation of parylene polymerization is also exothermic with much smaller calculated activation barrier of around 3 kcal/mol. The experimental value of the activation energy for propagation, 8.7 kcal/mol, comes from measurement in solution not in vacuo, and there is no standard deviation available and this value.[15] The results of our calculations confirm the generally accepted mechanism of polymerization of para-xylylene based polymers: a high activation barrier for paracyclophane decomposition, a moderate activation barrier for initiation reaction between two monomer p-xylylene molecules, and a low activation barrier for propagation reaction between a monomer p-xylylene molecule and a biradical chain molecule.

The details of calculated energy profiles provide a new physical insight into reaction mechanism of polymerization of p-xylylene based polymers. To date, there are no experimental data for all details of both profiles, but a good agreement between our theoretical values and available experimental data can prove the reliability of our modeling. Our calculations show that a high activation barrier for paracyclophane decomposition is not a result of the high energy of intermediate product, biradical dimer, and that the highest potential energy during the [2.2]paracyclophane decomposition into two monomers is the transition state for breaking the second bond between two monomers in the biradical dimer. Theoretical modeling proves that the initiation reaction for polymerization of para-xylylene is the reaction between two monomers. The reaction for forming the biradical trimer has the same energy profile as any reaction between biradical oligomer and monomer (we calculated formations of oligomers up to pentamer). This result support the model of polymerization mechanism proposed by Szwarc[12] but is in disagreement with many proposed mechanisms assuming that initiation reaction is the formation of the trimer and not the dimer. Our results show that the low activation barrier for propagation reaction is due to reactivity of biradical chain molecule. Biradical chain molecule is more reactive than closed shell monomer. This is a good starting point for modeling of mechanism of copolymerization or reactions of parylene with suitable substrate during the CVD polymerization leading to modified layer of parylene over the reactive substrate.[36] This research is in progress in our laboratory.

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FIGURE CAPTIONS

Fig 1. The structures of three commercially most popular p-xylylene based polymers.

Fig 2. Energy profiles for breaking of the bond in paracyclophane molecule **(a)** and in a linear biradical di-para-xylylene dimer molecule **(b)** calculated using semiempirical PM6 method. Changes in heat of formation calculated using closed shell model (RHF, solid line) are compared with those calculated using configuration interaction (CI) method and singlet (dashed line) or triplet (dotted line) state. Singlet CI model describes correctly both closed shell systems: paracyclophane for short distance in (a) and two monomer xylylene molecules for larger distance in (b), and an open shell biradical di-para-xylylene dimer for the larger distances in (a) and shorter distances in (b). For the mixing of four microstates triplet CI model gives the same energy as singlet CI for the biradical linear di-para-xylylene dimer. Transition state energies for both reactions estimated from maxima on singlet CI profiles are compared to the crossing points between RHF and triplet CI profiles.

Fig 3. (a) Energy profiles for breaking of the bond in paracyclophane molecule calculated using closed shell model (RHF) and open shell model (UHF) with B3LYP/SVP and B3LYP/TZVP method. Energies of closed shell dimer were used as zero energy baselines for both methods. The cyclic dimer, paracyclophane molecule, is a closed shell molecule (RHF, solid line, gives the lowest energy for the ground state with short distance and the intact bond) but the first step of decomposition reaction produces open shell biradical product, the linear dimer (UHF, dashed line, gives lower energies for larger distances with the broken bond). **(b)** Energy profiles for breaking of the bond in a linear biradical di-para-xylylene dimer molecule calculated using closed shell model (RHF) and open shell model (UHF) with B3LYP/SVP and B3LYP/TZVP method. As in Fig 2a, energies of closed shell paracyclophane dimer were used as zero energy baselines for both methods. The linear di-para-xylylene dimer is an open shell molecule (UHF, dashed line, gives the lowest energy for the ground state with short distance and the intact bond) but the second step of decomposition reaction produces close shell

products, two monomeric para-xylylene molecules (RHF, solid line, gives lower energies for larger distances with the broken bond). Transition state energies for both reactions were estimated from crossing between RHF and UHF profiles. In case of larger basis set B3LYP/TZVP method only points around the transition state and for stable reactants and products were calculated.

Fig 4. Scheme of cracking of the cyclo-di-para-xylylene dimer into monomers in the pyrolysis reaction.

Fig 5. Schemes of the initiation reaction of polymerization of parylene and the first propagation step of the biradical di-para-xylylene dimer reaction with the monomer forming the biradical trimer.

Fig.6. Energy profiles from the DFT B3LYP/TZVP calculations for the pyrolysis reaction of cracking the cyclo-di-para-xylylene dimer ([2.2]paracyclophane) into monomers (top); and the initiation reaction and the first propagation step of parylene polymerization (bottom). The energy scale on the left uses the energy of cyclo-di-para-xylylene as zero, the available experimental values are shown in parenthesis for comparison.

Table 1. Relative to the reactant energies (kcal/mol) for various species in the reaction of cracking of the cyclic dimer (DI[a]) into two monomers (M[e]) calculated at different levels of theory for parylene N, C and D. For the reactants (DI) the absolute values of calculated energies are shown. Experimental reference data are available only for parylene N.

	DI [a]	DI/MM [b]	MM [c]	MM/M+M [d]	M+M [e]
parylene N					
AM1	59.839 [f]	51.887	34.621	76.581	59.955
PM6	50.963 [f]	50.657	39.663	77.302	56.584
B3LYP SVP//SVP	-618.4482598990 [g]	43.062	23.364	52.207	41.595
B3LYP SVP//TZVP	-619.1065393245 [g]	39.565	18.493	46.606	31.304
B3LYP TZVP//TZVP	-619.1083035010 [g]	39.821	18.434	46.481	31.133
Exp.[23, 24, 26]	58.5±0.5 [f]	37.7±0.5	25.7±1.5	n/a	41.5±4.5
Parylene C					
AM1	47.035 [f]	51.808	35.193	76.768	56.424
PM6	29.214 [f]	51.172	41.228	78.442	56.348
B3LYP SVP//SVP	-1537.260995702 [g]	43.588	25.060	54.302	44.822
B3LYP SVP//TZVP	-1538.235887620 [g]	40.059	20.471	46.095	33.609
B3LYP TZVP//TZVP	-1538.237685220 [g]	39.941	20.424	48.375	33.482
Parylene D					
AM1	36.000 [f]	51.268	34.829	75.930	55.901
PM6	12.936 [f]	50.824	38.981	75.744	53.907
B3LYP SVP//SVP	-2456.061840702 [g]	43.114	21.215	50.523	40.858
B3LYP SVP//TZVP	-2457.353619613 [g]	39.621	16.446	44.444	29.932
B3LYP TZVP//TZVP	-2457.354993232 [g]	38.639	16.169	44.071	29.451

[a] reactant, paracyclophane molecule; [b] transition state for the reaction of breaking the first bond in paracyclophane; [c] biradical dimer; [d] transition state for the reaction of breaking the second bond, [e] product, two p-xylylene monomer molecules; [f] heat of formation of the reactant in kcal/mol; [g] absolute total energy in Hartree for the reactant

Table 2. Relative to the reactant energies (kcal/mol) for transition state and product for the reaction of two monomers forming biradical dimer calculated at different levels of theory for parylene N, C and D. For the reactants (M+M) the absolute values of calculated energies are shown. Experimental reference data are available only for parylene N.

	M+M[a]	M+M/MM[b]	MM[c]
parylene N			
AM1	119.794 [d]	16.625	-25.335
PM6	107.548 [d]	20.718	-16.921
B3LYP SVP//SVP	-618.3819744756 [e]	10.613	-18.230
B3LYP SVP//TZVP	-619.0566527226 [e]	15.302	-12.811
B3LYP TZVP//TZVP	-619.0586905636 [e]	15.348	-12.698
Exp.[23, 26]	100±8 [d]	n/a	-14.2±5.0
parylene C			
AM1	103.459 [d]	20.350	-21.231
PM6	85.562 [d]	22.095	-15.120
B3LYP SVP//SVP	-1537.189567172 [e]	9.481	-19.762
B3LYP SVP//TZVP	-1538.182327324 [e]	12.486	-13.138
B3LYP TZVP//TZVP	-1538.184327261 [e]	14.892	-13.058
parylene D			
AM1	91.901 [d]	20.032	-21.072
PM6	66.844 [d]	21.836	-14.926
B3LYP SVP//SVP	-2455.996728480 [e]	9.664	-19.643
B3LYP SVP//TZVP	-2457.305919033 [e]	14.511	-13.486
B3LYP TZVP//TZVP	-2457.308059982 [e]	14.620	-13.282

[a] reactants, two p-xylylene molecules; [b] transition state for the initiation reaction of forming the biradical dimer; [c] biradical dimer; [d] heat of formation of the reactants in kcal/mol; [e] absolute total energy in Hartree for the reactants

Table 3. Relative to the reactants energies (kcal/mol) for transition state and products for the first step of propagation reaction of a monomer with biradical dimer forming biradical trimer calculated at different levels of theory for parylene N, C and D. For the reactants (MM+M) the absolute values of calculated energies are shown.

	MM+M[a]	MM+M/MMM[b]	MMM[c]
parylene N			
AM1	154.268 [d]	7.467	-47.165
PM6	143.265 [d]	9.710	-40.483
B3LYP SVP//SVP	-928.6083741428 [e]	1.760	-40.183
B3LYP SVP//TZVP	-928.6054064264 [e]	3.137	-35.438
B3LYP TZVP/TZVP	-928.6083741428 [e]	3.374	-35.213
parylene C			
AM1	135.813 [d]	7.251	-46.983
PM6	113.362 [d]	8.593	-41.262
B3LYP SVP//SVP	-2305.815947413 [e]	1.145	-41.065
B3LYP SVP//TZVP	-2307.294556202 [e]	2.862	-35.808
B3LYP TZVP/TZVP	-2307.297341500 [e]	2.896	-35.814
parylene D			
AM1	118.426 [d]	7.267	-46.603
PM6	84.757 [d]	9.124	-40.588
B3LYP SVP//SVP	-3684.027265700 [e]	1.317	-40.871
B3LYP SVP//TZVP	-3685.980417783 [e]	2.456	-36.236
B3LYP TZVP/TZVP	-3685.983376906 [e]	2.461	-36.027

[a] reactants, biradical dimer and a p-xylylene molecule; [b] transition state for the propagation reaction of forming the biradical trimer; [c] biradical trimer; [d] heat of formation of the reactants in kcal/mol; [e] absolute total energy in Hartree for the reactants

Table 4. Relative to the reactants energies (kcal/mol) for transition state and products for the second step of propagation reaction of a monomer with biradical trimer forming biradical tetramer calculated at different levels of theory for parylene N, C and D. For the reactants (MMM+M) the absolute values of calculated energies are shown.

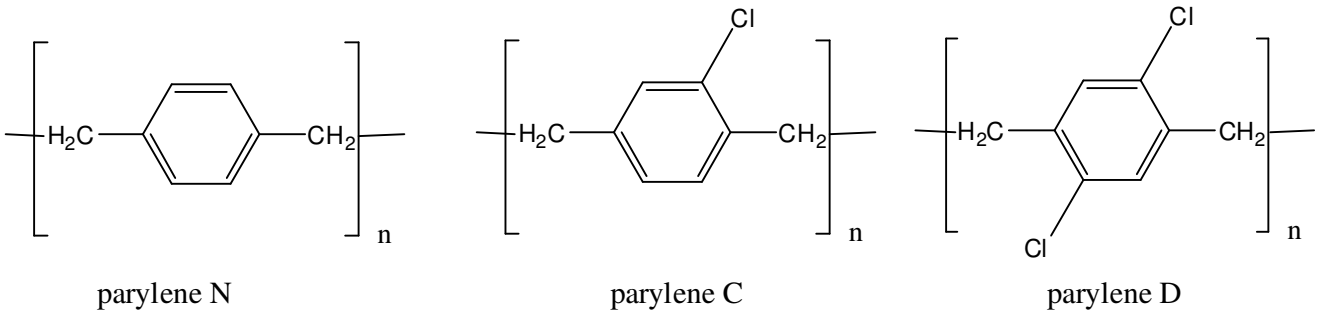
	MMM+M[a]	MMM+M/MMMM[b]	MMMM[c]
parylene N			
AM1	166.356 [d]	7.953	-46.713
PM6	155.209 [d]	9.891	-40.384
B3LYP SVP//SVP	-1236.921990671 [e]	2.117	-39.812
B3LYP SVP//TZVP	-1238.190328402 [e]	3.230	-35.327
B3LYP TZVP/TZVP	-1238.194063441 [e]	3.228	-35.429
parylene C			
AM1	142.377 [d]	7.161	-47.034
PM6	114.572 [d]	8.960	-40.928
B3LYP SVP//SVP	-3074.478126195 [e]	2.205	-39.806
B3LYP SVP//TZVP	-3076.442992874 [e]	2.967	-35.625
B3LYP TZVP/TZVP	-3076.446859126 [e]	3.024	-35.564
parylene D			
AM1	119.379 [d]	7.183	-46.763
PM6	77.002 [d]	9.054	-40.691
B3LYP SVP//SVP	-4912.090459006 [e]	0.760	-41.591
B3LYP SVP//TZVP	-4914.691215035 [e]	2.586	-36.059
B3LYP TZVP/TZVP	-4914.694916713 [e]	2.656	-35.956

[a] reactants, biradical trimer and a p-xylylene molecule; [b] transition state for the propagation reaction of forming the biradical tetramer; [c] biradical tetramer; [d] heat of formation of the reactants in kcal/mol; [e] absolute total energy in Hartree for the reactants

Table 5. Relative to the reactants energies (kcal/mol) for transition state and products for the third step of propagation reaction of a monomer with biradical tetramer forming biradical pentamer calculated at different levels of theory for parylene N, C and D. For the reactants (MMMM+M) the absolute values of calculated energies are shown.

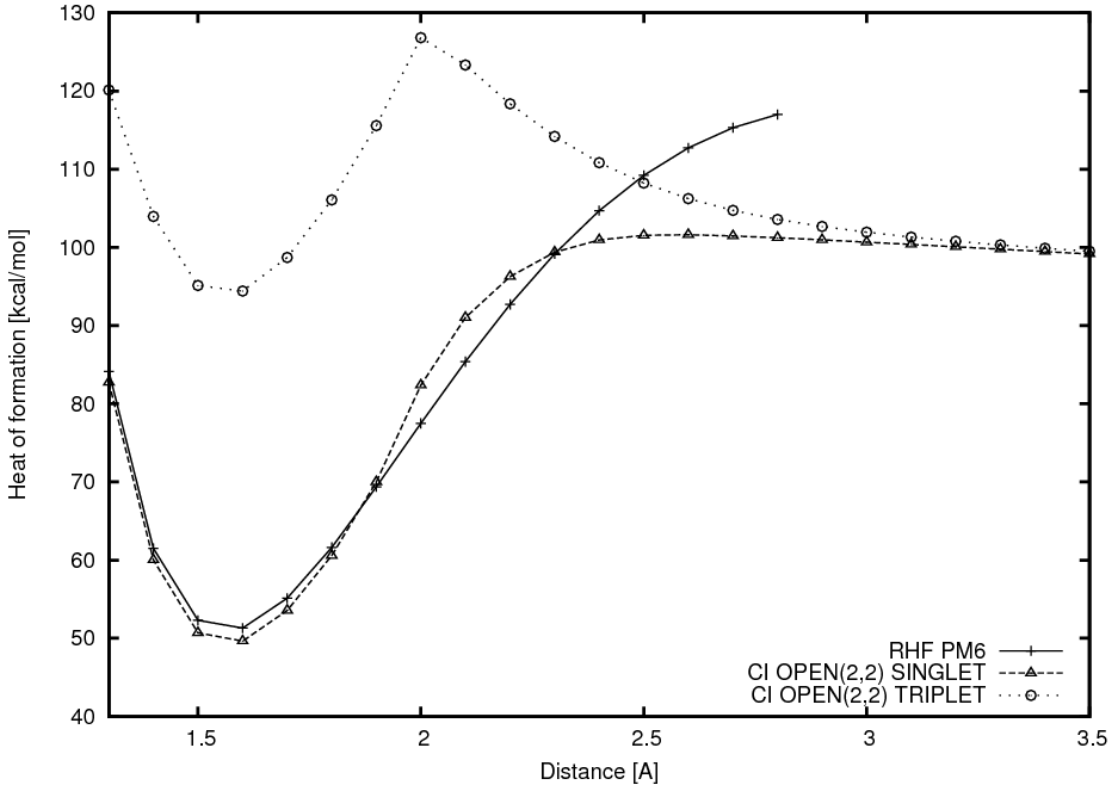
	MMMM+M[a]	MMMM+M/MMMMM[b]	MMMMM[c]
parylene N			
AM1	179.450 [d]	7.402	-47.264
PM6	167.455 [d]	9.658	-40.575
B3LYP SVP//SVP	-1546.113187153 [e]	1.829	-40.143
B3LYP SVP//TZVP	-1547.775140025 [e]	3.205	-35.434
B3LYP TZVP/TZVP	-1547.779530559 [e]	3.402	-35.218
parylene C			
AM1	148.594 [d]	7.382	-46.756
PM6	116.210 [d]	8.865	-41.005
B3LYP SVP//SVP	-3843.136479708 [e]	1.024	-41.063
B3LYP SVP//TZVP	-3845.590988954 [e]	2.818	-35.850
B3LYP TZVP/TZVP	-3845.595564644 [e]	2.826	-35.854
parylene D			
AM1	120.139 [d]	7.248	-46.615
PM6	69.210 [d]	8.988	-40.760
B3LYP SVP//SVP	-6140.154488006 [e]	0.581	-41.643
B3LYP SVP//TZVP	-6143.401762053 [e]	2.591	-36.008
B3LYP TZVP/TZVP	-6143.406218852 [e]	2.462	-35.976

[a] reactants, biradical tetramer and a p-xylylene molecule; [b] transition state for the propagation reaction of forming the biradical pentamer; [c] biradical pentamer; [d] heat of formation of the reactants in kcal/mol; [e] absolute total energy in Hartree for the reactants



parylene N parylene C parylene D

Figure 1.


Heat of formation [kcal/mol]
Distance [A]
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CI OPEN(2,2) TRIPLET
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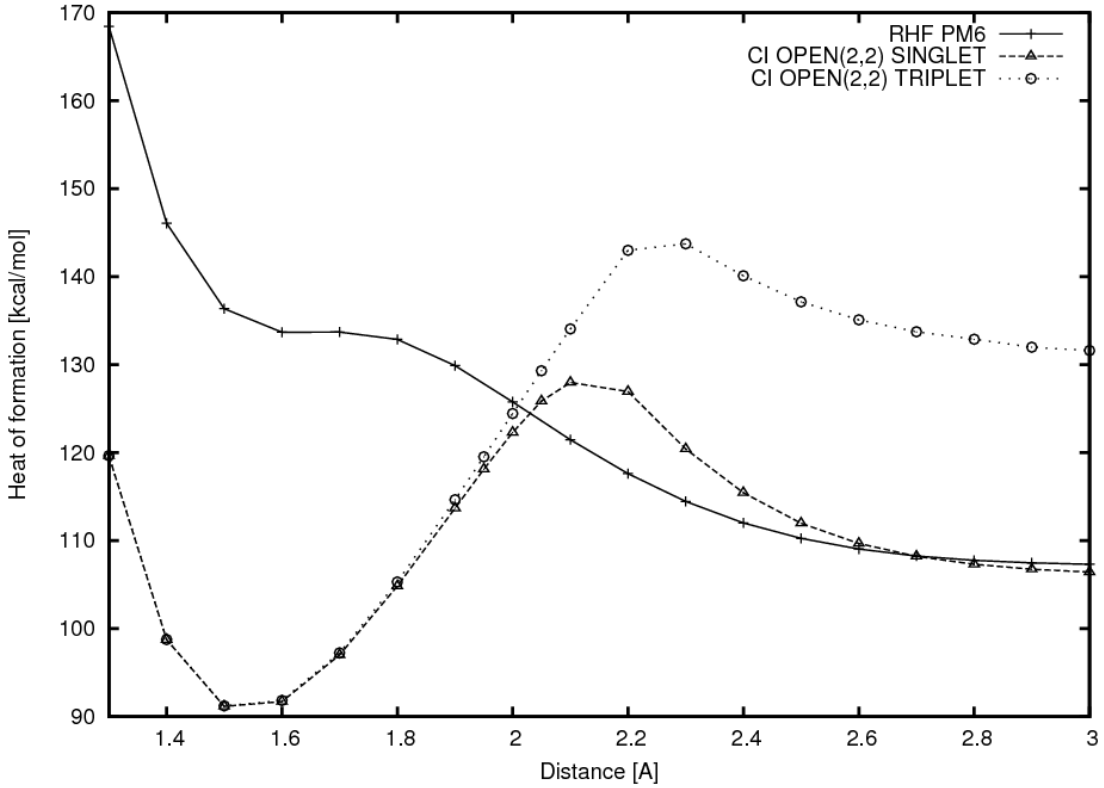
110
100
90
80
70
60
50
40
1.5
2
2.5
3
3.5

Figure 2a.


RHF PM6
CI OPEN(2,2) SINGLET
CI OPEN(2,2) TRIPLET
Heat of formation [kcal/mol]
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150
140
130
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100
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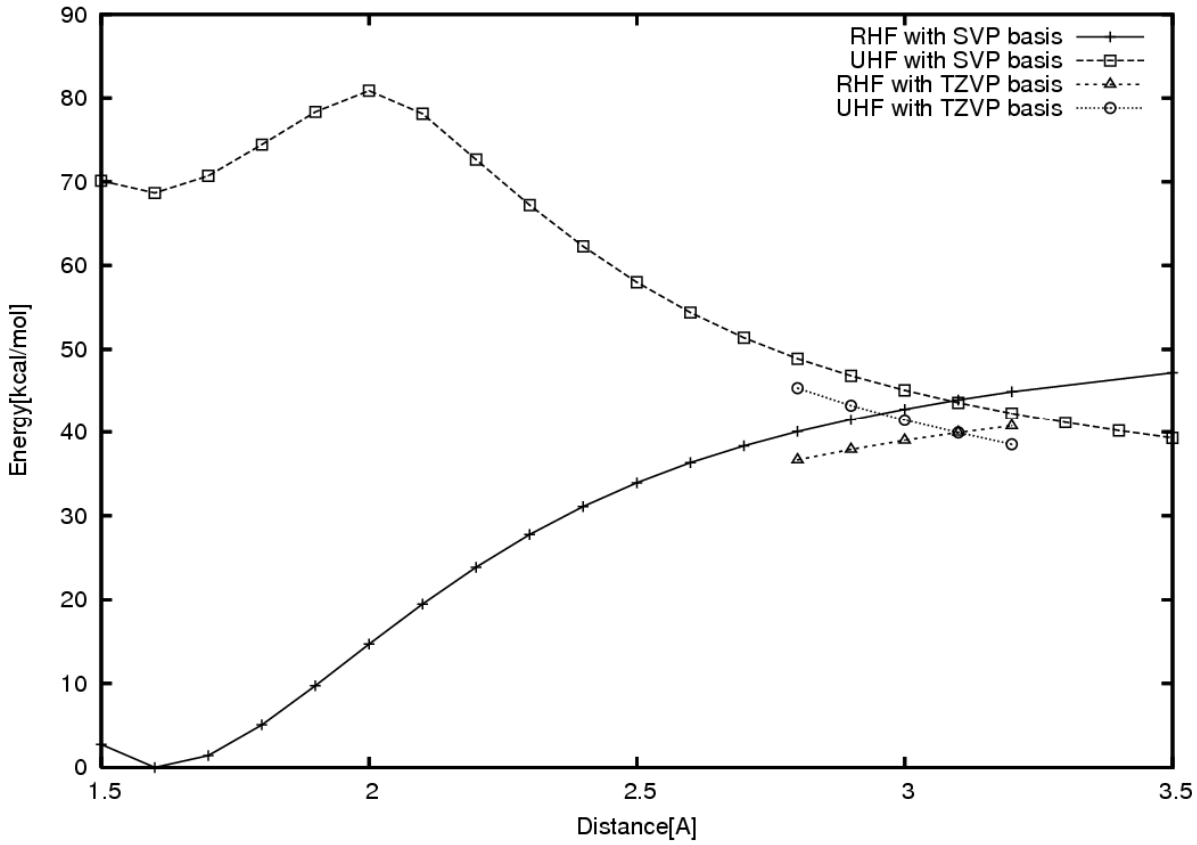
1.6
1.8
2
2.2
2.4
2.6
2.8
3

Figure 2b.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UHF with SVP basis
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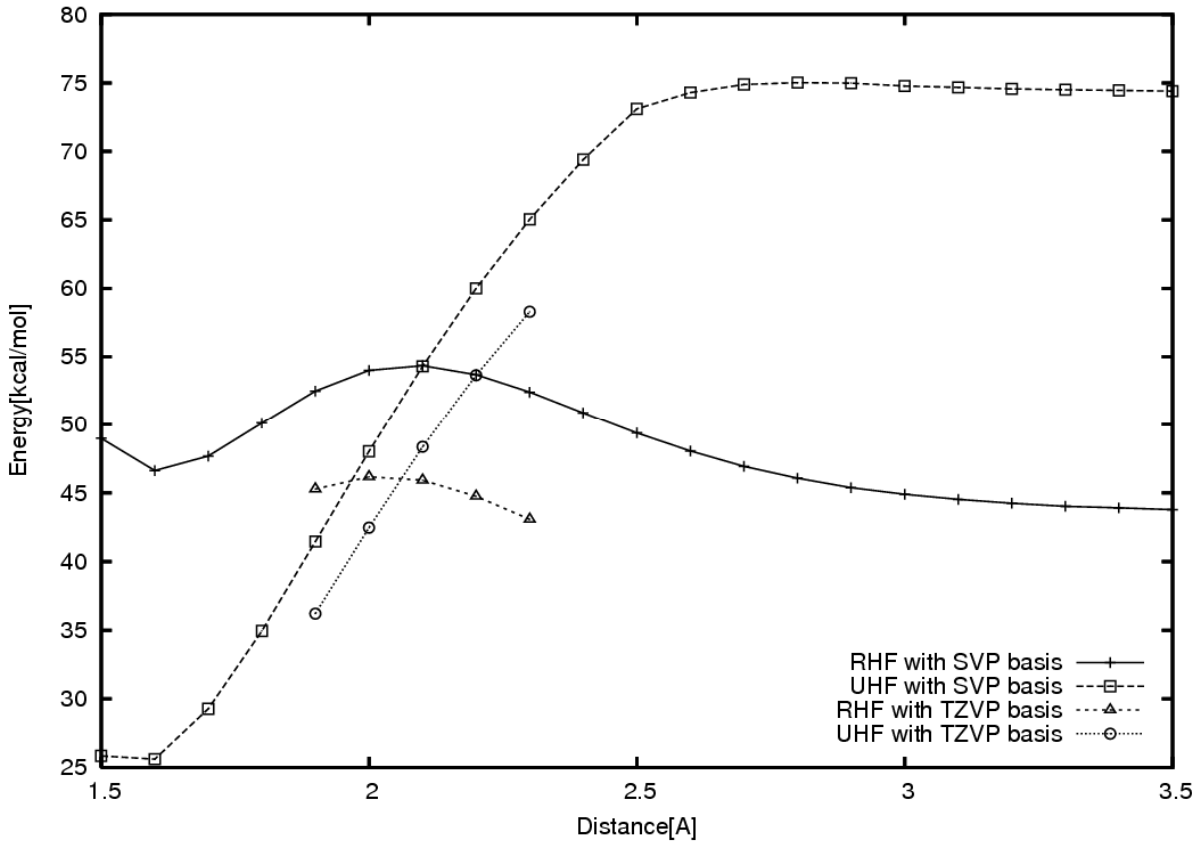
3
3.5

Figure 3a.


Energy[kcal/mol]
Distance[A]
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UHF with TZVP basis
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35
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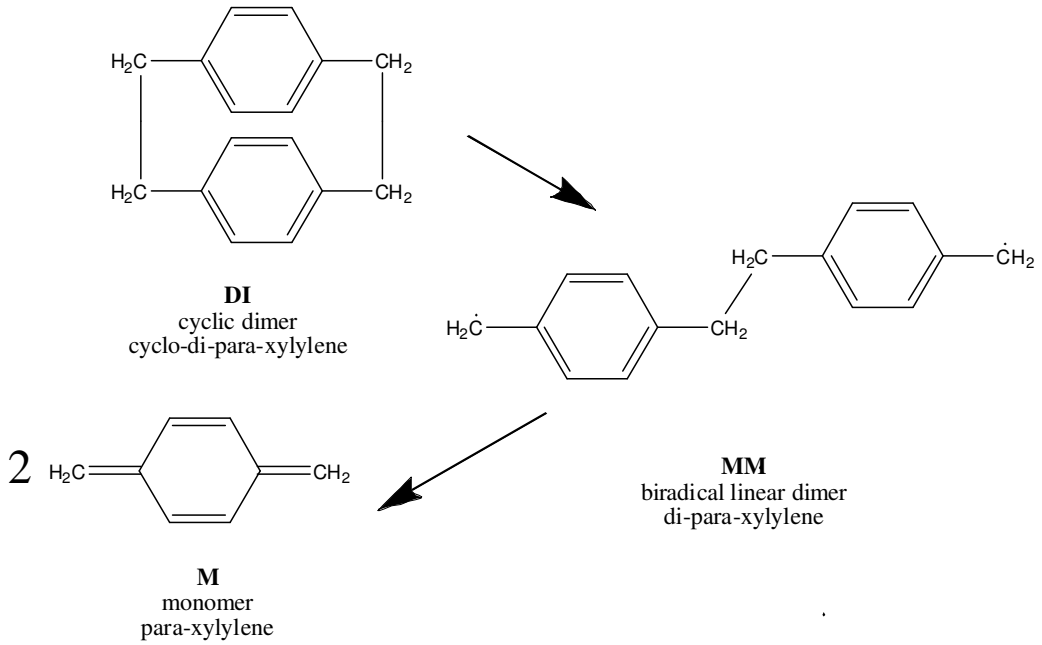
25
1.5
2
2.5
3
3.5

Figure 3b.


H2C
CH2
H2C
CH2
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cyclic dimer
cyclo-di-para-xylylene
H2C
CH2
H2Ċ
CH2
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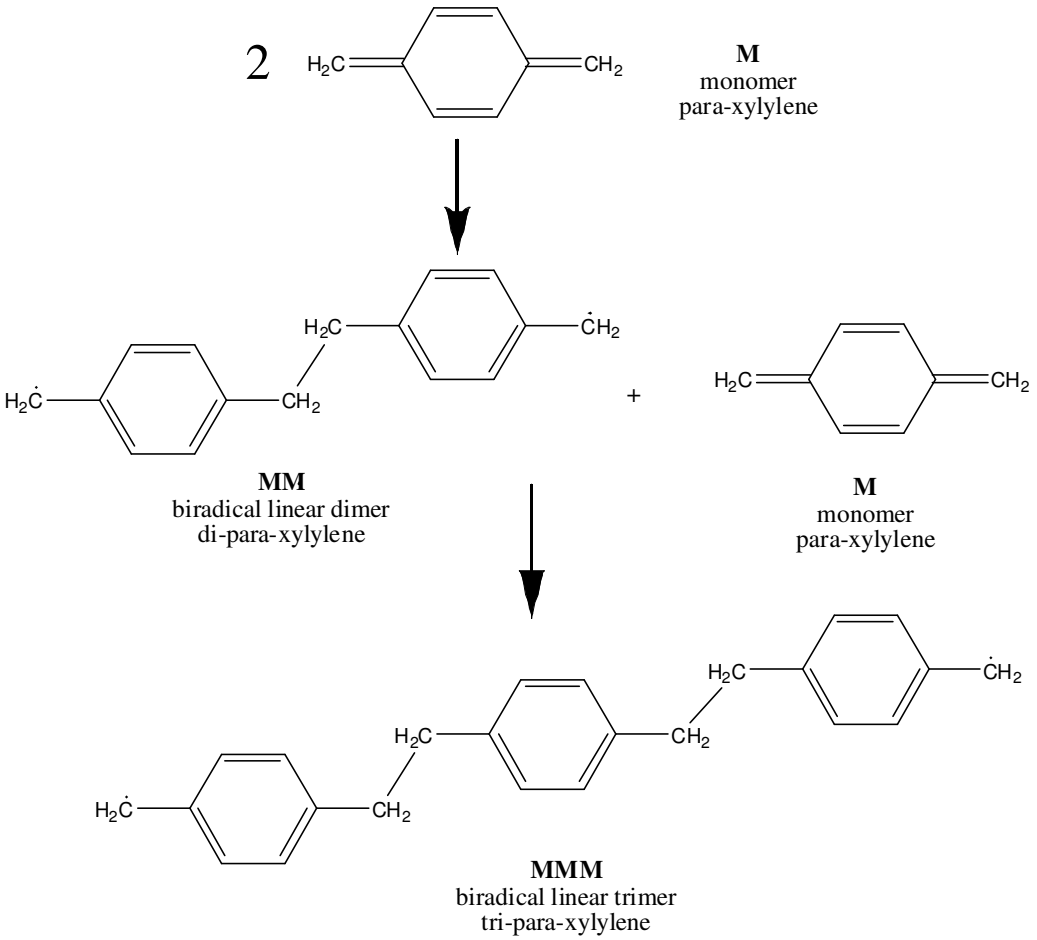
H2C
CH2
M
monomer
para-xylylene

Figure 4.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para-xylylene
MM
biradical linear dimer
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+
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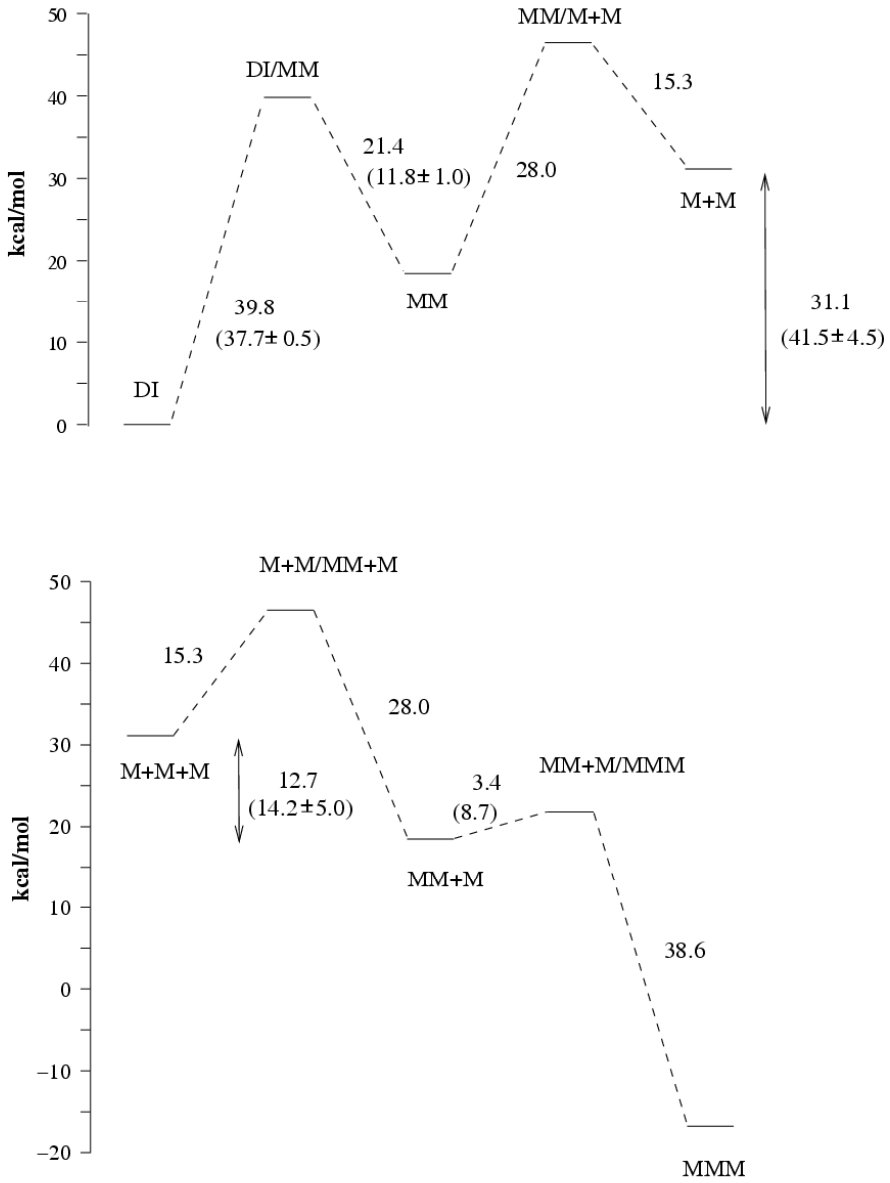
monomer
para-xylylene
MMM
biradical linear trimer
tri-para-xylylene

Figure 5.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DI/MM
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21.4
(11.8± 1.0)
28.0
15.3
31.1
(41.5±4.5)
kcal/mol
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40
30
20
10
0
−10
−20
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M+M/MM+M
MM+M
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MMM
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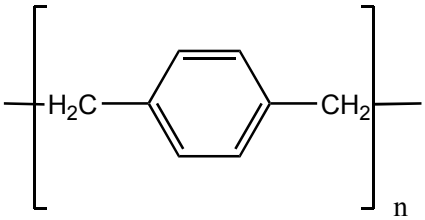
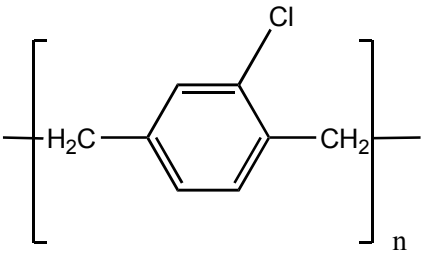
28.0
3.4
(8.7)
38.6

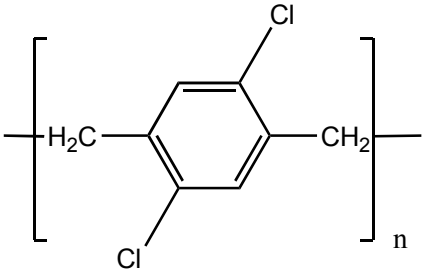
Figure 6.



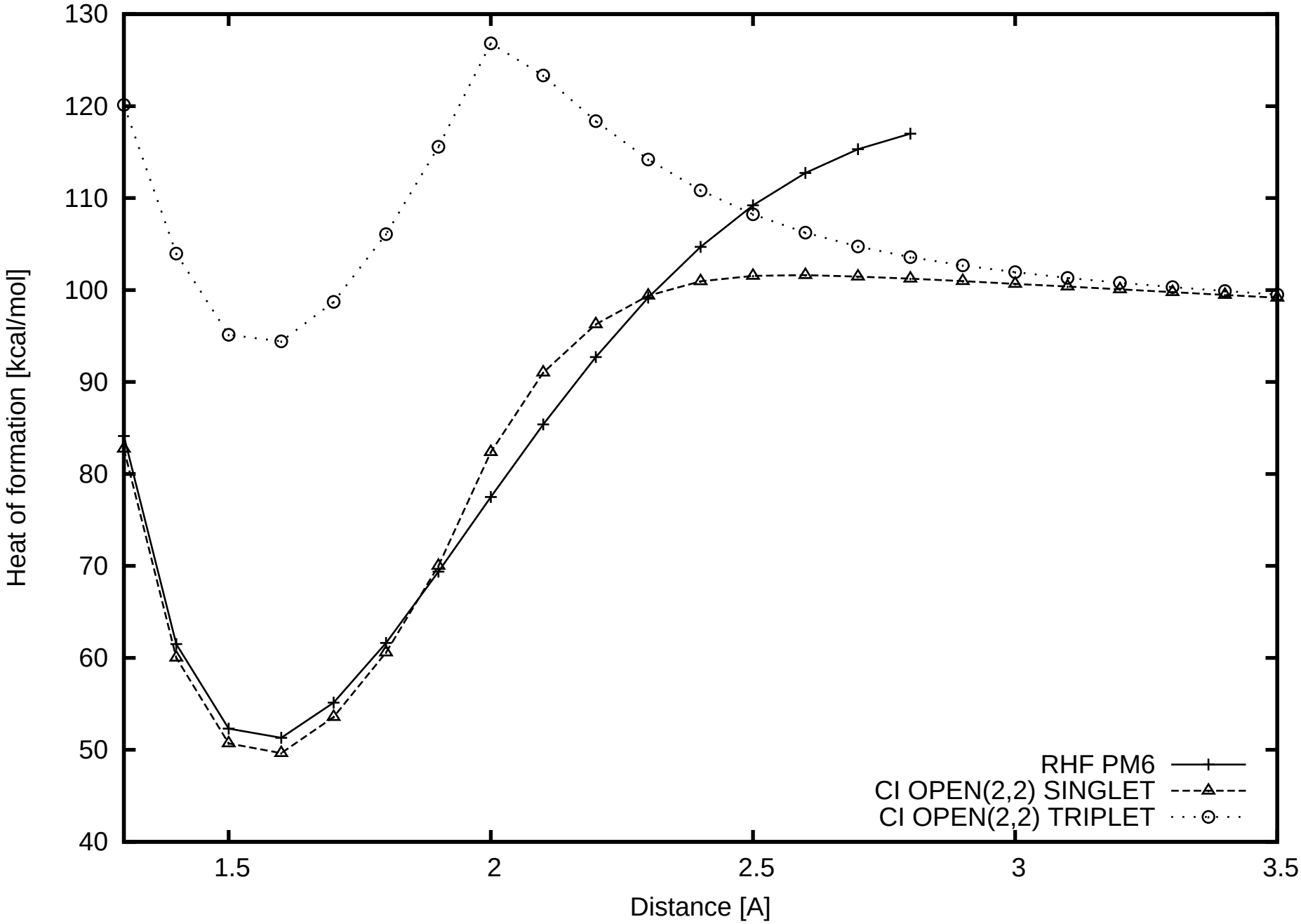
parylene N

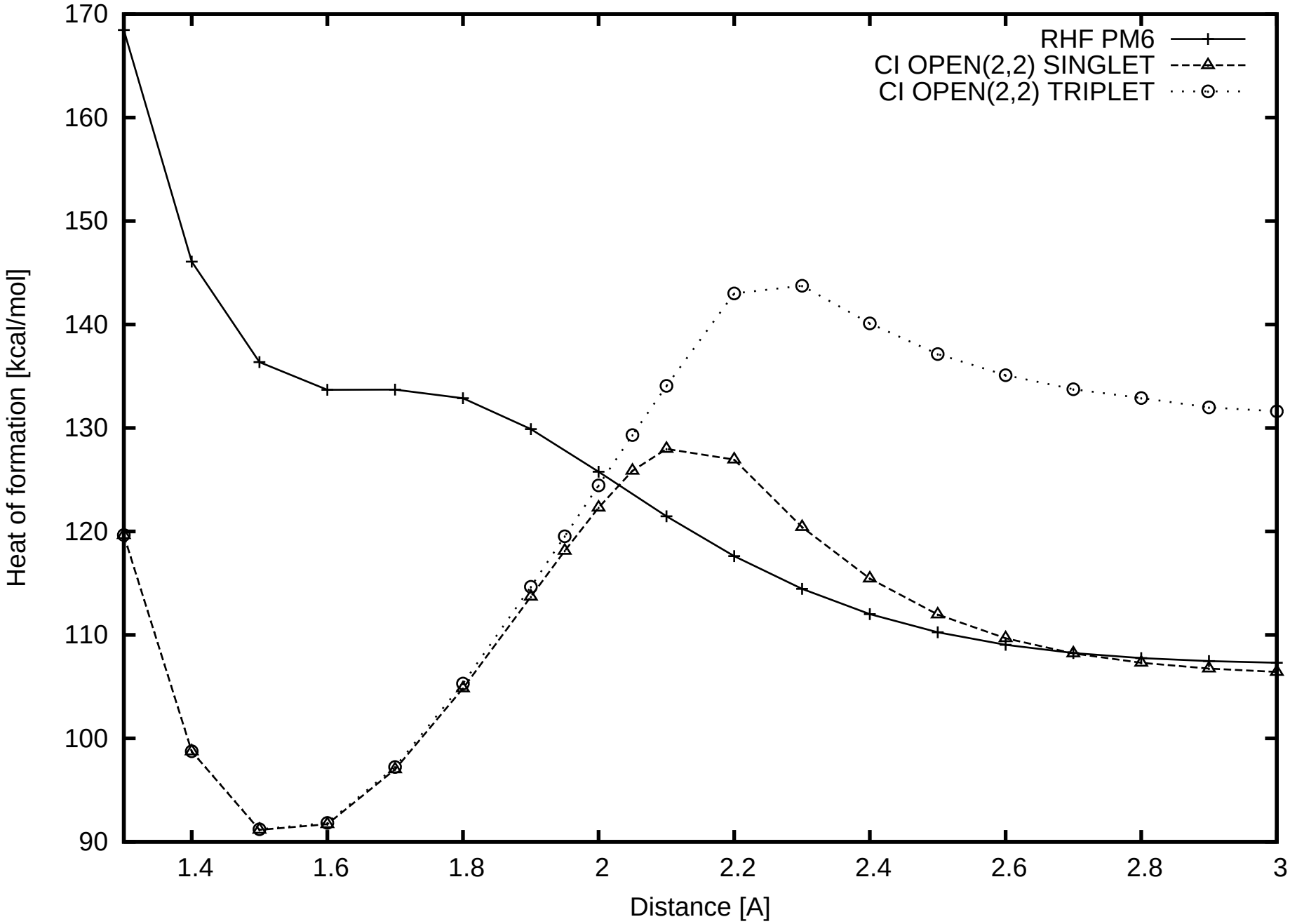


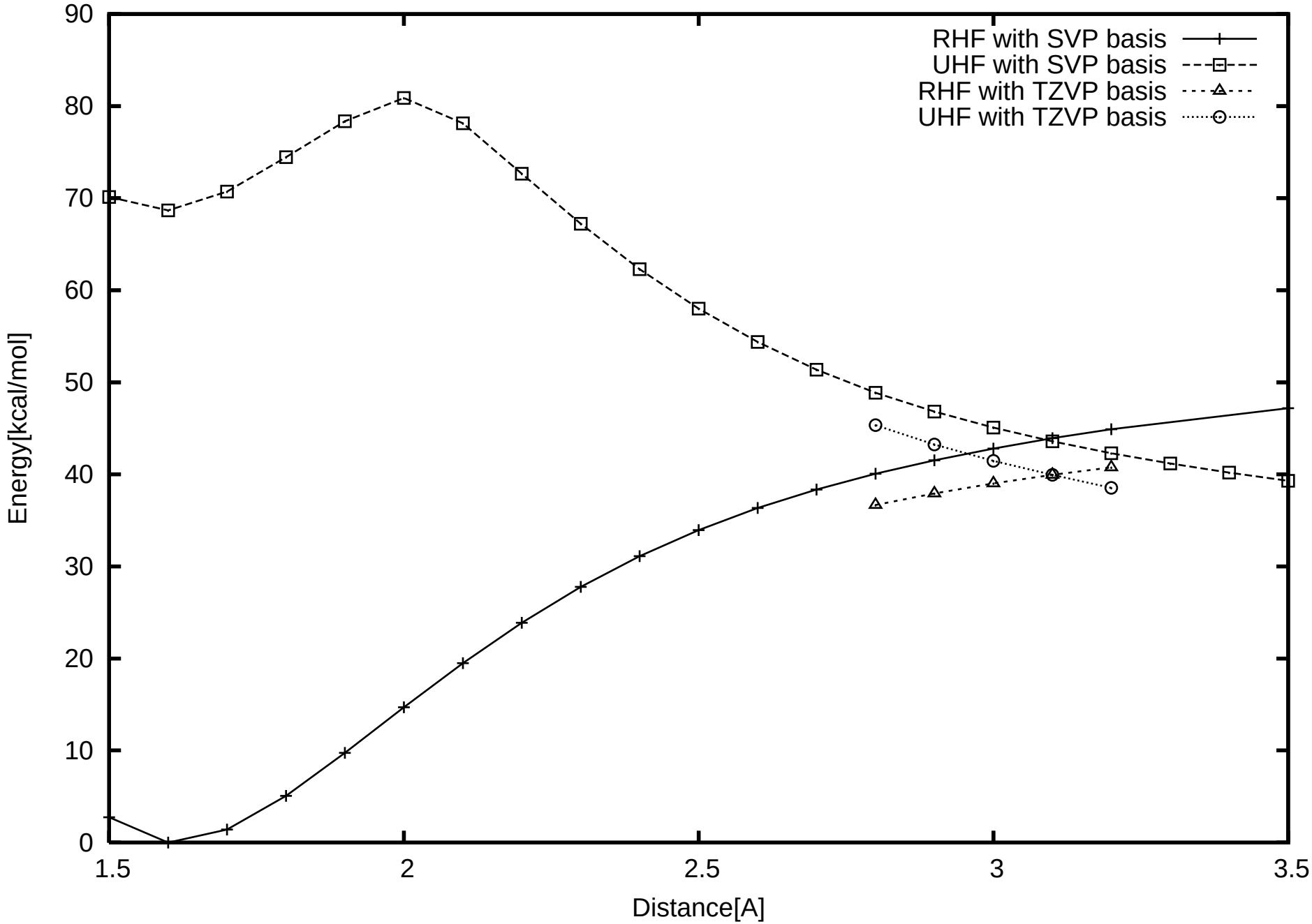
parylene C



parylene D



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RHF with TZVP basis
UHF with TZVP basis
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Distance[A]
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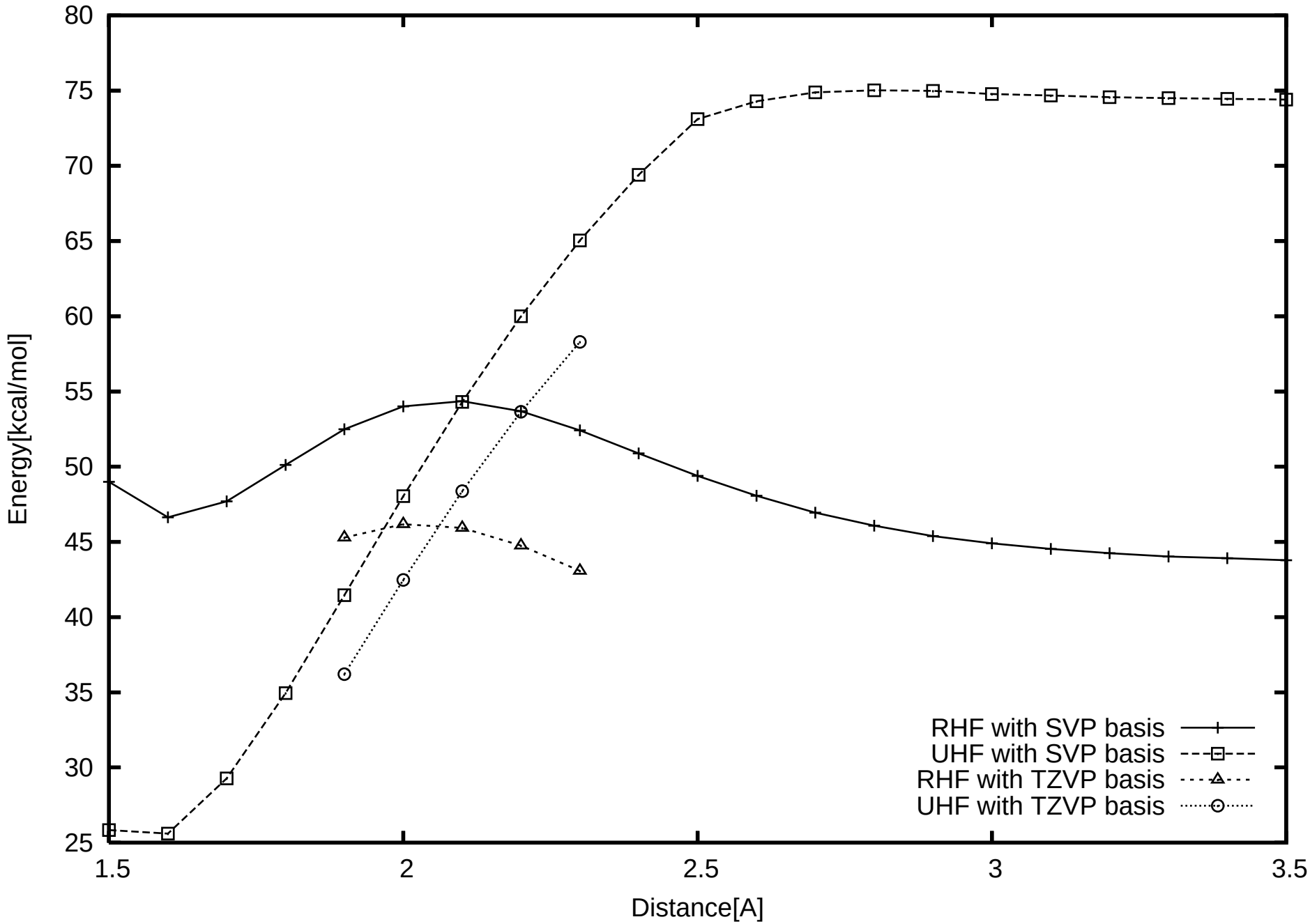
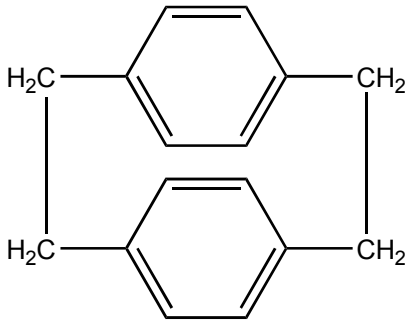
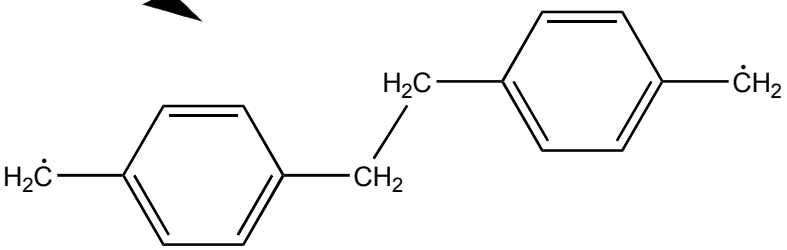
2.5
3
3.5

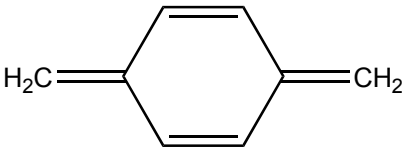




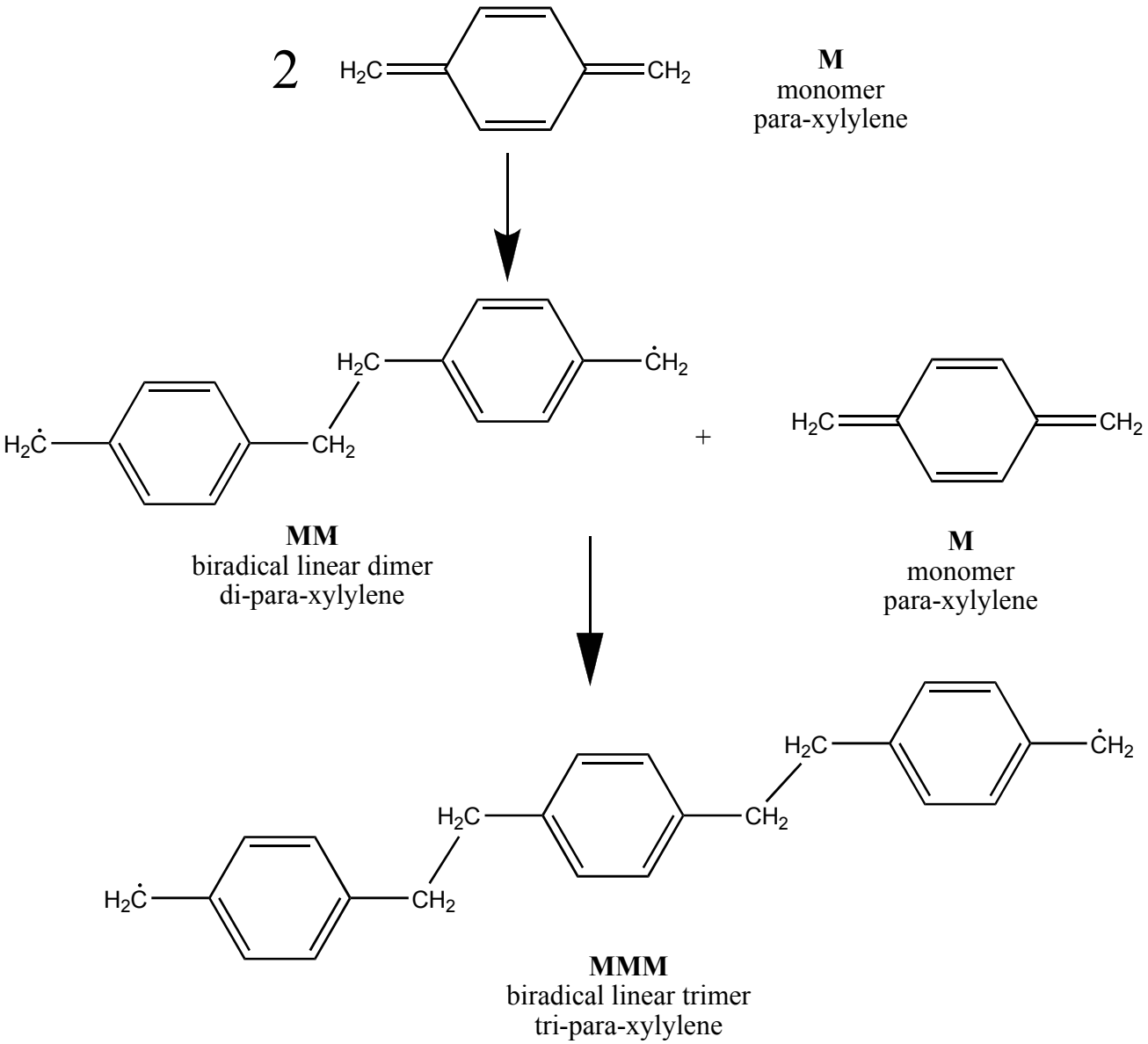
DI
cyclic dimer
cyclo-di-para-xylylene



MM
biradical linear dimer
di-para-xylylene

2 

M
monomer
para-xylylene


2
H2C
CH2
M
monomer
para-xylylene
H2C
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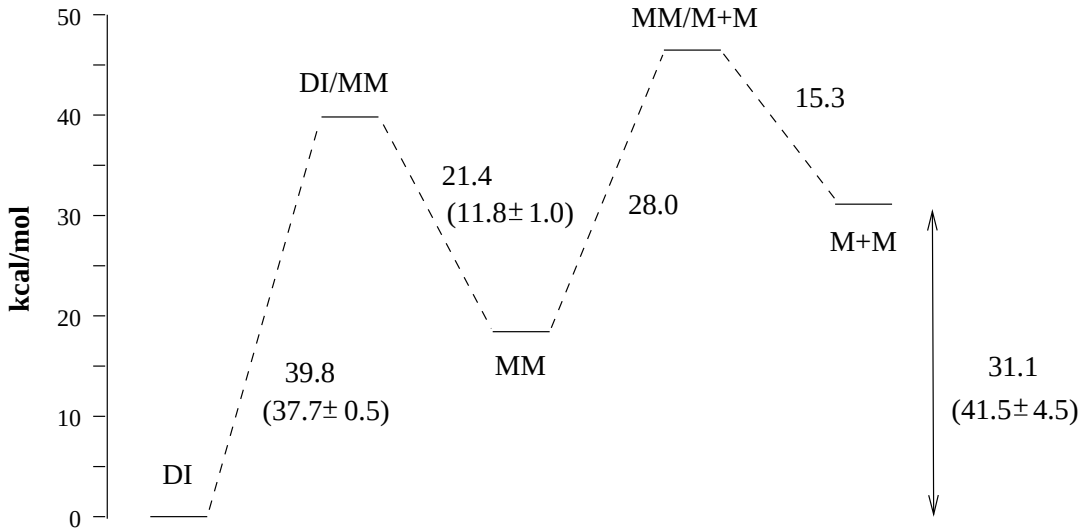
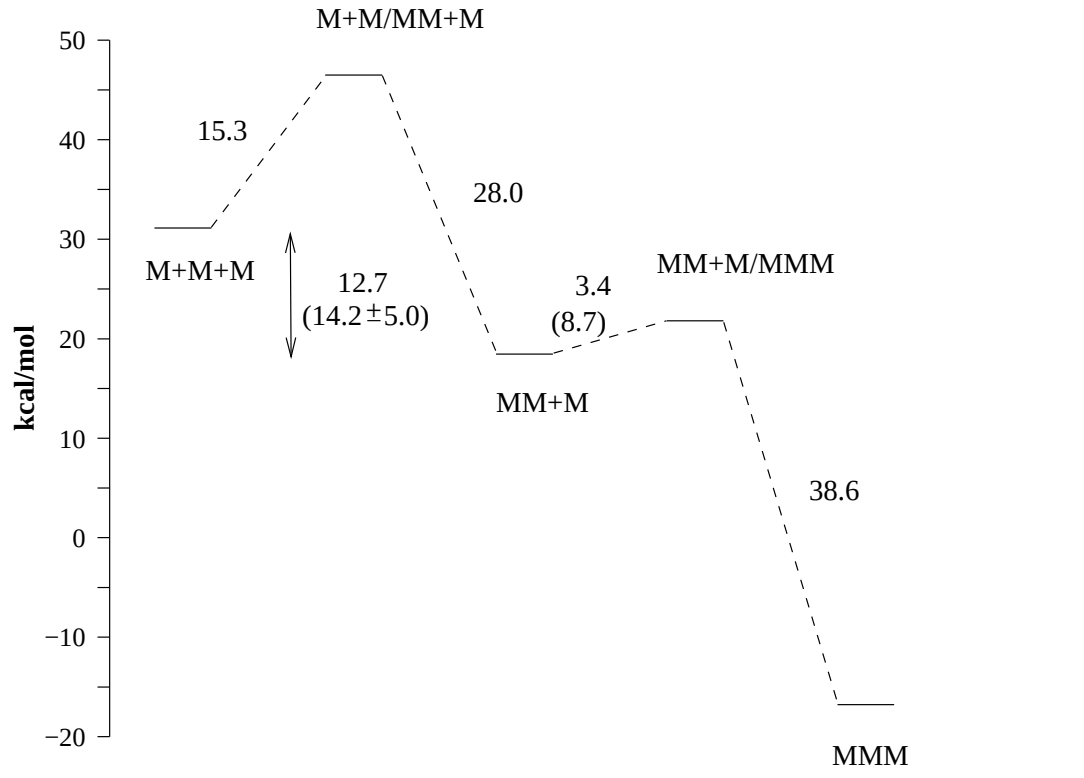
H2Ċ
CH2
+
H2C
CH2
MM
biradical linear dimer
di-para-xylylene
M
monomer
para-xylylene
H2C
CH2
H2C
CH2
H2Ċ
CH2
MMM
biradical linear trimer
tri-para-xylylene


kcal/mol
50
40
30
20
10
0
DI
DI/MM
MM
MM/M+M
M+M
39.8
(37.7± 0.5)
21.4
(11.8± 1.0)
28.0
15.3
31.1
(41.5± 4.5)


kcal/mol
50
40
30
20
10
0
−10
−20
M+M+M
M+M/MM+M
MM+M
MM+M/MMM
MMM
15.3
12.7
(14.2 ±5.0)
28.0
3.4
(8.7)
38.6