

Exploration of C₆H₆ Potential Energy Surface: A Computational Effort to Unravel the Relative Stabilities and Synthetic Feasibility of New Benzene Isomers[†]

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Ab initio (MP2, CCSD(T)) and hybrid density functional theory (B3LYP) calculations with up to triple- ζ basis set were done to locate all possible minima, where each carbon in the molecule is tetracoordinate, on the C₆H₆ potential energy surface. The search was initiated with a total of 218 structures, and in few cases, geometrical and stereoisomers were considered. The exhaustive study on all these topological structures resulted in a total of 263 stationary points on the C₆H₆ potential energy surface. The B3LYP level characterizes 209 as minima, 31 as transition states, 8 as second-order, 7 as third-order, and 1 as fourth-order saddle points. The remaining 7 structures could be located as stationary points only at the MP2 level. The molecules were classified into acyclic, monocyclic, bicyclic, tricyclic, and tetracyclic. The acyclic isomers fall within a range of 60–80 kcal/mol higher in energy compared to benzene. Among the cyclic structures, the range of relative stabilities of minima is larger, viz., monocyclic (31–146 kcal/mol), bicyclic (72–159 kcal/mol), tricyclic (72–300 kcal/mol), and tetracyclic (102–156 kcal/mol). Strain due to small three and four membered rings and constrained double and triple bonds control the relative stabilities of these isomers. The computed isomers exhibit various novel bonding modes for carbon, namely, planar tetracoordinate, hypervalent, pyramidal, bent/twisted double bonds, vicinal dicarbenes, nonlinear triple bonds, and so forth. Absolute chemical hardness values have no correlation with the relative stabilities, and about 45 molecules have higher hardness values than that of benzene.

Introduction

Benzene, discovered by Faraday in 1825, may be regarded as an icon for the structural concept in chemistry and triggered intensive interplay between theory and experiment for over a century in laying fundamental foundations.^{1–3} The structure of benzene was established by Kekule 40 years after its discovery.⁴ Many compounds, which include drugs, dyes, and polymers, contain benzene as a fundamental structural unit. In principle, about 330 isomers for the molecular formula C₆H₆ can be written with tetravalent arrangement around all carbons, considering the geometrical and stereoisomers. Excluding the diastereomers and enantiomers, there are 217 possible C₆H₆ isomeric structures, and some of them are well-known.³ Six valence isomers, consisting of (CH)₆ units, attracted considerable attention as the prime isomeric forms of benzene.^{5–19} Dewar benzene was synthesized in 1963 by van Tamelen and Pappas.^{6a} Wilzbach et al.⁷ isolated benzvalene in 1967, and it was eventually synthesized by Katz et al. in 1971.^{8a} Prismane was prepared from benzvalene by Katz and Acton in 1973.⁹ Derivatives of bicycloprop-2-enyl have been prepared by Breslow and Davis et al.,^{20,21} while the synthesis of the parent isomer was achieved in 1989 by Billups and Haley.¹⁰

In addition to the valence isomers of benzene, several other isomers, both cyclic and acyclic, exist and are interesting in their own right.^{22–48} Exploration of the structural limitations in

organic chemistry is an inspiring and challenging arena, which warrants a judicious combination of experiment and theory. Several experimental studies have been reported on the rearrangements of acyclic isomers of C₆H₆ in generating other acyclic and cyclic isomeric structures.^{28–40} Prominently, the rearrangement of 1,5-hexadiyne to other isomeric forms of C₆H₆ has been the interest for more than three decades.^{31–35,49–53} Huntsman and Wristers have synthesized 3,4-dimethylenecyclobutene, a monocyclic isomer, in high yield from 1,5-hexadiyne by thermal cyclization at 350 °C, which was reported to occur via 1,2,4,5-hexatetraene.³³ The study of heteroskeletally substituted benzene isomers is also interesting in its own right.⁵⁴ Rearrangement reactions among mono- and disilabenzene isomers show the rich diversity in the structures of this class of compounds.⁵⁵ Hopf has reported the synthesis of 2-ethynyl-1,3-butadiene from the thermal isomerization of 1,2-hexadien-5-yne.^{35–37} Houk and co-workers have studied the thermal rearrangement reactions of 1,5-hexadiyne and 1,2-hexadien-5-yne.⁴⁹ Rearrangements of diverse nature have been observed among the C₆H₆ isomers.^{18,28–38,49–53} Some of the cyclic isomers obtained through electrocyclization reactions show intriguing reactivities.^{24–29} 1,3-Hexadien-5-yne converts to benzene upon thermal cyclization.³⁴ The cyclic aromatization reactions of 1,3-hexadien-5-yne gained momentum in the early 1990s; several planar, bowl shaped polycyclic aromatic hydrocarbons and other novel aromatic compounds have been synthesized by cycloaromatization of the structures incorporating 1,3-hexadien-5-yne as a fragment at different thermal conditions.^{29,56–58} A quantum chemical study on the reaction pathways for intramolecular

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isomerization of 1,2,4-cyclohexatriene, which is a cyclic isomer of C_6H_6 , to benzene has been carried out recently.⁵⁹

Synthesis of highly strained organic compounds, particularly cyclic allenes and cumulenes, was considered to be impossible a few decades ago. Unusual ring strained isomers of benzene have generated considerable interest for experimentalists for the past few years.^{23–28} Numerous six membered strained cyclic allenes have been trapped in addition or cycloaddition reactions.^{23–28,60} In 1992, Christl and co-workers generated 1,2,4-cyclohexatriene and then subjected it to trapping reactions.²⁶ Another route, electrocyclization of 1,3-hexadien-5-yne, has been used for successful synthesis of the same compound in recent years.^{28,29} Shakespeare and Johnson have reported an elegant synthesis of two highly strained benzene isomers, cyclohexan-1,2,3-triene and cyclohexan-1-en-3-yne.²³ The synthetic success of these isomers redefines some of the limitations of strain in that homologous series of organic compounds and has gained the momentum of theoreticians to study the structures, energetics, and reactivities of these types of strained compounds.^{15,61} The simplest member of the radialene family, trimethylenecyclopropane, is another interesting benzene isomer and has attracted experimental and theoretical studies.^{45,62}

The range and variety of C_6H_6 isomers provide an ideal platform to understand and focus on the unique structural and bonding patterns in organic chemistry. One important aim of undertaking the task of thoroughly exploring the potential energy surface of C_6H_6 is that understanding the relationship of energetics among the diverse structural types enables one to draw principles of general applicability. The study is also focused to address the following questions. What factors control the relative stability orderings? What are the relative stabilities of compounds with novel structural features, such as bent cumulenic bonds, planar tetracoordinate carbon, bent double bonds, and so forth? While many structural connectivities are possible, how many actually turn out to be minima on the potential energy surface?

The aim of this study is to identify the stabilities of hitherto unknown structures with the C_6H_6 structural formula. The highly strained systems which are minima on the potential energy surface provide good leads for high energy materials.⁶³ Therefore, exploration of strained polycyclic structures may provide valuable information to generate high energy materials based on hydrocarbons. Such molecules are important for both their fundamental chemistry as well as possible technological applications. A high energy material typically has a very strained geometry and can be decomposed into simpler gases upon releasing considerable energy through an exothermic process.

Previous studies reported the possibility of 217 isomers with tetravalency to each carbon,^{1–3} but we found one more isomer in tetracyclic form (**217**) in this study. Thus, initially, a total of 218 structural arrangements were considered in this study (Scheme 1). To our knowledge, all the isomers with the molecular formula C_6H_6 have been considered taking into account the tetravalency for carbon. In other words, all six carbon atoms in the 218 structures have tetravalency; structures with carbenes were not considered. However, as some of the structures have led to carbene types upon optimization, we did consider them in the study. The nature of the stationary points obtained in this study is discussed first, followed by a discussion on the equilibrium geometries, the various bonding modes, and the relative energies of the isomers. The results and discussion section is arranged in the following order: (a) acyclic, (b) monocyclic, (c) bicyclic, (d) tricyclic, and (e) tetracyclic. Hybrid density functional theory (B3LYP) and ab initio (MP2 and

CCSD(T)) calculations with up to valence triple- ζ basis set were employed in this study.

Computational Details

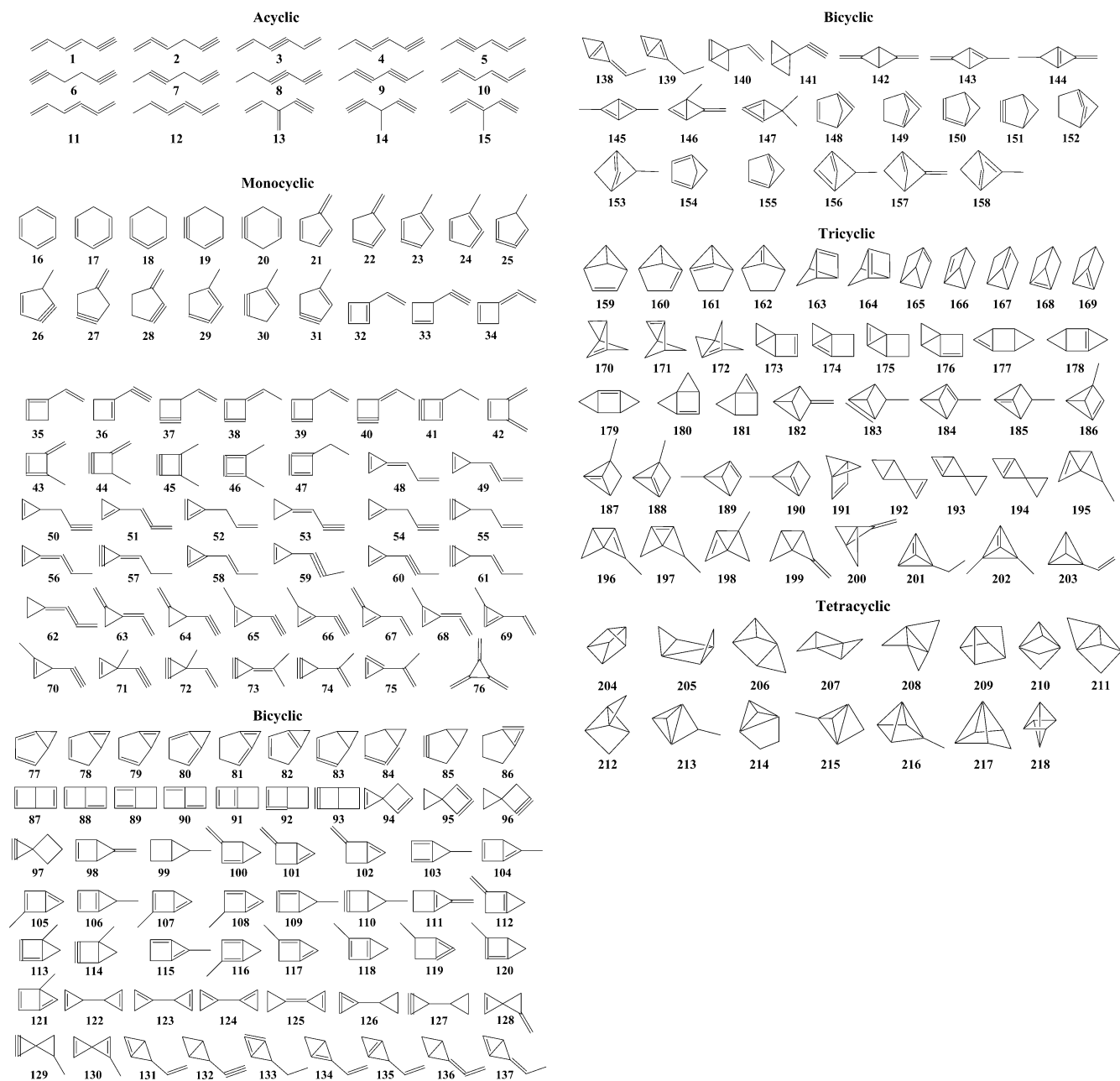
All the structures considered in the study were initially optimized within the symmetry constraints at the B3LYP/6-31G* and MP2/6-31G** levels of theory using the default gradients implemented in the Gaussian 98 program.⁶⁴ Frequency calculations were done at the B3LYP level in order to characterize the stationary points obtained. Geometries obtained using the MP2 method were taken for further calculations at higher levels of theory. MP2 single point energy calculations with the 6-311+G** basis set were performed to assess the effect of improving the quality of the basis set on the relative energies. 6-311+G** is a valence triple- ζ type basis set, which includes polarization functions on all the atoms and a set of diffuse functions on the carbon atoms. We have adopted a correction scheme (eq 1) to account for the inadequate 6-31G* basis set employed at the CCSD(T) level. This scheme, which includes the effect of improving the basis set from 6-31G** to 6-311+G** estimated at the MP2 level, provides relative energies which are similar to the CCSD(T)/6-311+G** level. The relative enthalpies for the valence isomers of benzene obtained using this equation are in very good agreement with those computed using the G2 and G3 methodologies (Table 1).^{14,15}

$$\Delta H = \Delta E_{\text{CCSD(T)}} + (\Delta E_{\text{MP2/6-311+G**}} - \Delta E_{\text{MP2/6-31G**}}) + \Delta H^{\text{corr}} \quad (1)$$

where ΔH^{corr} is the relative enthalpy correction values obtained at the B3LYP/6-31G* level.

The best estimates were calculated using eq 1 for all the structures considered in the study.⁶⁵ The comparison of the relative energies computed at the B3LYP and MP2 levels of theory with those obtained at the CCSD(T) level and the best estimates indicates the better performance of the MP2 method compared to B3LYP (see the Supporting Information). Benchmark calculations on the six valence isomers of benzene and comparison with the values reported at G2 and G3 theories also pointed out the better performance of the MP2 level to model this class of compounds.^{13,14}

Considering the enormous diversity of prevalent C_6H_6 isomers, identifying the uniform level of theory for the relative stability of all the isomers is an impossible task. While a majority (more than 90%) of the structures involved can be adequately treated by a single reference wave function, a few of them cannot. For example, in structure **58a**, the open shell singlet state 1A_2 appears to be more stable than the closed shell 1A_1 state. Obviously, such structures warrant application of multiconfiguration methods. Estimation of relative stabilities among the structures computed with single and multireference wave functions is a daunting task. Therefore, in the present study, we would like to restrict the use of computations employing single reference wave functions. More detailed computational treatment of selected molecules will be useful although it is not under the purview of the current study. Such detailed studies are necessary and will be taken up later in the group. All the calculations were done using the Gaussian 98 suite of programs,⁶⁴ and a graphical interface program, Moplot,⁶⁶ was used to examine the equilibrium geometries and the nature of the normal modes. Chemical hardness values were calculated at the MP2/6-31G** level. Within Koopmans' approximation, the chemical hardness $\eta = (E_{\text{LUMO}} - E_{\text{HOMO}})/2$.

SCHEME 1^a

^a The triple bond and the allenic part outside the ring and in acyclic isomers are shown bent for convenience in drawing.

Results and Discussion

The optimization and the frequency calculations on the initial 218 structures considered led to a few transition state structures and higher order saddle points in addition to several minima at the B3LYP/6-31G* level of theory. Out of the 218 structures considered, 11 structures collapsed to already existing isomers (Scheme 2) and three other isomers underwent ring opening upon optimization at both B3LYP and MP2 levels of theory, which resulted in drastic skeletal distortion (Scheme 3). Considering the geometrical isomers in some cases, a total of 256 stationary points were located of which 209 are minima.⁶⁷ Thirty-one structures were computed to be transition states; the normal mode corresponding to the imaginary frequency was followed in each case to obtain the minimum energy structures. The remaining isomers were characterized as higher order saddle points (8 second-order, 7 third-order, and 1 fourth-order saddle points). The structural arrangements of **37**, **40**, **44**, **96**, **148**, **161**,

and **186** could be located only at the MP2 level; the frequency calculations indicate that structure **186** is a transition state and the rest are minima. These seven isomers however do not correspond to stationary points collapsed to other isomers at the B3LYP level. Later, the new stationary points were also located at the MP2 level (**37a**, **40a**, **44a**, **96a**, **148a**, and **186a**). The relative energies obtained for the structures considered at various levels and the correlation of the relative energies as a figure are given in the Supporting Information. The discussion on the relative energies will be based on those obtained using eq 1 unless otherwise specified. The geometric features and the relative energies and reactivities assessed based on hardness values of all the isomers will be discussed in the following order: acyclic; monocyclic; bicyclic; tricyclic; tetracyclic. The optimized geometries for minima and higher order saddle points along with the imaginary frequencies, the best estimate relative energies, and the absolute hardness values are depicted in

TABLE 1: Comparison of the Relative Enthalpies Calculated Using Best Estimate (Equation 1) with the Values at G2 and G3 Levels of Theory for the Valence Isomers^a

structure	G2		G3		ΔH (best estimate) this work
	H^b	ΔH	H^c	ΔH	
benzene (16)	-231.77508	0.0	-232.04675	0.0	0.0
benzvalene (159)	-231.66147	71.3	-231.93024	73.1	72.3
Dewar benzene (87a)	-231.65465	75.6	-231.92336	77.4	74.8
prismane (204)	-231.59673	111.9	-231.86381	114.8	114.9
bicyclopentenyl (122)	-231.58545	119.0	-231.85451	120.6	118.2

^a The total enthalpies are in hartrees and the relative energy values are in kcal/mol. ^b The values are taken from ref 14a. ^c The values are taken from ref 14b.

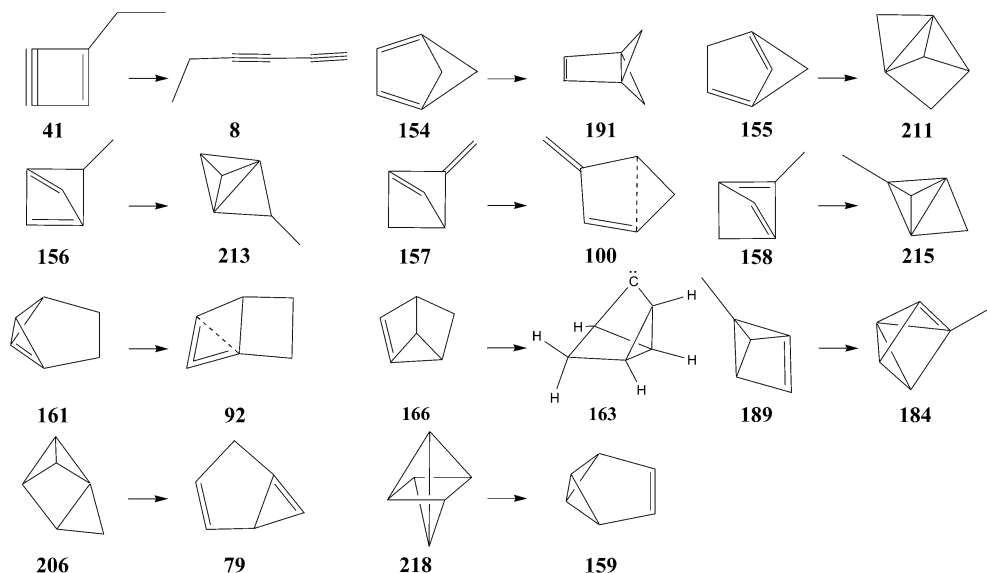
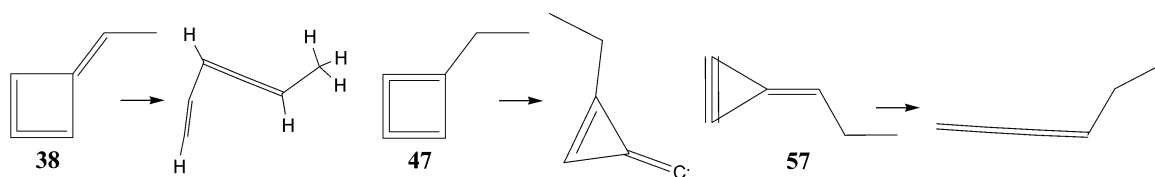
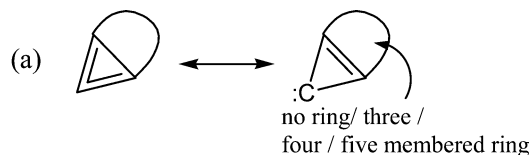
Figures 1–5 for these five classes of isomers; the compounds with novel structural features are highlighted with boxes. The transition state structures obtained for all five classes are depicted in Figure 6.

Some of the structures considered undergo reorganization in the bonding upon optimization; for example, the structure considered with an allene bond in the three-membered ring on optimization leads to a geometry with carbene which is more properly called cyclopropenylidene. Any single valence bond structure is not possible in such cases; the resultant geometry is a nearly equivalent mix of at least two valence bond structures. Scheme 4 depicts a general picture of the valence bond structures for a three-membered ring containing an allene bond and also depicts the valence bond structures for a four-membered ring involving an allene bond that leads to carbene in some cases. In some structures, a three-membered ring consisting of a triple bond and a four-membered ring incorporating a triple bond or cumulenic bond may lead to structures with vicinal dicarbenes; the valence bond structures in these cases are depicted in Scheme 5.

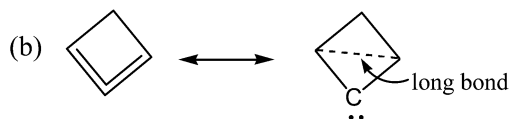
Acyclic. The principal geometric parameters of the acyclic isomers (**1**–**15**) obtained at the B3LYP/6-31G* level and the MP2/6-31G** level are given in Figure 1. Also depicted are the best estimates of the relative energies and the absolute chemical hardness of the isomers along with the nature of the stationary points. Initially, 15 isomers were characterized as minima and 3 (**2TS**, **13aTS**, and **15TS**) were computed to be transition states (Figure 6). The normal mode of the imaginary frequencies in these three cases corresponds to the C–C bond rotations; they were followed to obtain the true minima (**2**, **13a**, and **15**). Thus, about 18 acyclic isomers of C₆H₆ were characterized as minima. The energy difference between the transition state and the corresponding minimum energy structure is very little (0.5–1.1 kcal/mol), indicating facile interconversions. The geometric parameters obtained using the B3LYP and MP2 methods are in good agreement with each other in most of the cases; a few exceptions are seen in structures **11** and **12**, where the maximum difference between the bond lengths computed by the two methods is 0.046 Å. The planar form of **13a** was characterized as a transition state (**13aTS**) (Figure 6). The corresponding trans isomer (**13b**) is the minimum on the potential energy surface in its planar form. All the acyclic isomers lie within a narrow range of relative enthalpies from 60 to 79 kcal/mol with respect to the global minima, benzene (**16**). This may be attributed to the fact that all the acyclic isomers are devoid of strain due to smaller rings and structural constraints, which is possible in the cyclic isomers. Hence the relative energies of these isomers may be decided mainly by the subtle electronic factors due to the number and positioning

of sp, sp², and sp³ carbons and various types of bonds in the hydrocarbon chain. While the isomers with two double bonds and a triple bond (**1a**, **1b**, **3**, **13a**, and **13b**) have a relative energy around 60 kcal/mol, the isomers having high energy are the ones possessing acetylenic, allenic, and cumulenic bonds. All the acyclic isomers are experimentally known; experimental studies on the rearrangement reactions of some of the acyclic isomers to yield other acyclic and cyclic isomers have been reported.^{28–43} No correlation was obtained between the hardness values and relative stabilities, and interestingly, four isomers have higher hardness values compared to benzene.

Monocyclic. In this category, a total of 83 structures were located, which are depicted in Figures 2 and 6. Twelve structures were characterized as transition states, 11 isomers are higher order saddle points (5 second-order, 5 third-order, and 1 fourth-order saddle points), and the rest are minima. Benzene (**16**), the global minimum on the C₆H₆ potential energy surface, falls in the class of monocyclics. In addition to benzene, four more minima and three transition states possess six-membered rings. Of the remaining 75 structures, 15, 23, and 37 fall under the subclasses of five-, four-, and three-membered ring isomers, respectively. Only benzene (**16**) and **20** are planar among the isomers containing six-membered rings; the planar forms of the other three isomers (**17TS**, **18TS**, and **19TS**) were computed to be transition states, while the minima are **17**, **18**, and **19**. The stabilization arising from puckering the skeletons is only about 1–2 kcal/mol in the case of Shakespeare benzenes, **18** and **19**. In contrast, the energy difference between **17TS** and **17** is computed to be more than 40 kcal/mol at all the levels of theory employed. This may be traced to the fact that the substituents at the two ends of the allenic moiety are constrained in the same plane in the planar form of **17**. In general, allenes prefer a perpendicular arrangement to achieve maximum overlap, which is possible only in the puckered structures. The minimum energy structure **17** is found to be the more stable molecule among the isomers possessing six-membered rings next to benzene. The structural arrangement of **17** is interesting due to the presence of a chiral-allene type structure, which has been studied previously, similar to 1,2-cyclohexadiene.^{15,24,62} Several experimental studies have been reported on **17** and its derivatives.^{26–28} All the six-membered monocyclic isomers are experimentally known except **20**.^{23,26} Both **19** and **20** are strained enynes; **19** in which the two multiple bonds are delocalized is less stable by about 5 kcal/mol than **20**, where a double bond and a triple bond are separated by a methylene unit. The strain in the skeleton seems to primarily control the relative energies of these isomers. Out of 15 structures with five-membered rings, 8 are minima and 4 structures were characterized as transition states, and 4 as third-order saddle points. Similar to the situation in **17**, the planar form of **22** is a transition state and is traced to the constrained allenic moiety. The energy difference between the planar (**22TS**) and puckered (**22**) structures is about 43 kcal/mol. The planar forms of the isomers **23**, **24**, and **25**, which possess two or three consecutive double bonds, were characterized as third-order saddle points. Fulvene (**21**), which is one of the products in the photolysis of benzene and benzvalene,^{5c,6,7} is computed to be less stable by about 31 kcal/mol than benzene (**16**), and this is the next lowest energy isomer in the benzene potential energy surface. Fulvene (**21**) has been reported as one of the products in the thermal isomerization of 1,5-hexadiyne.³⁵ Except **21** and **22**, the computed relative energies for all other isomers with five-membered rings lie more than 100 kcal/mol above that of benzene owing to the strain in the skeleton due to bent acetylenic, allenic, or cumulenic bonds present in the

SCHEME 2: Structural Arrangements Initially Considered Which Collapsed to Already Existing Isomers upon Optimization at Both B3LYP and MP2 Levels of Theory

SCHEME 3: Structural Arrangements Initially Considered Which Yielded Significantly Different Skeletal Arrangements

SCHEME 4


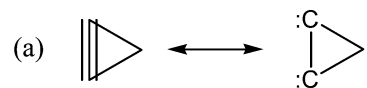
Structures: 52, 58a, 58b, 69a, 69b, 75a, 75b, 86, 126a, 126b



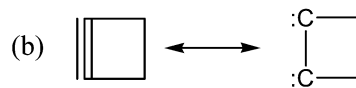
Structures: 35a, 35b, 92, 95, 152, 153

rings. In structure **26**, one of the C–C single bond distances is longer by about 0.3 Å than the normal single bond length and the longer triple bond length, indicating a structure possessing the vicinal dicarbene.

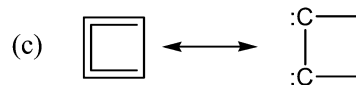
Among the four-membered monocyclic isomers, **42** is found to be the most stable isomer which has been known experimentally.^{33–35,42} In the monocyclic isomers of four-membered ring skeletons, three structures (**35aTS**, **35bTS**, and **39TS**) were characterized as transition states, three of the isomers (**38**, **43**, and **46**) as second-order saddle points, and one (**45**) as a fourth-order saddle point. The minimum energy structure **39** possesses a chiral-allene type geometry. In contrast to the situation in six- and five-membered ring structures, the energy difference between the structure with the planar four-membered ring, which is a transition state (**39TS**), and its corresponding minimum (**39**) is only about 4 kcal/mol. The structural arrangement of the isomers **37**, **40**, and **44** possessing a triple bond could be located

SCHEME 5


Structures: 55, 61, 72, 73, 74, 127, 129



Structures: 37, 40, 44, 45



Structure: 46

only at the MP2 level, where the triple bond distances are longer than the normal C–C triple bond lengths. These structures upon optimization at the B3LYP level lead to new stationary points (**37a**, **40a**, and **44a**), which seem to be the skeleton with a three-membered ring and an alkylidene carbene; the new bond forming the three-membered ring is longer by about 0.05–0.1 Å. The molecules **35a** and **35b** that contain an allenic bond upon optimization yielded bicyclic arrangements where the bridging bond of the two three-membered rings has elongated. The longer bond length of the allenic bond and the bridging bond in these two molecules seem to be the structures with a cyclopropenylidene skeleton. In contrast, for other isomers containing allenic bonds, **38** underwent ring opening and a stationary point corresponding to the connectivity in **43** could be obtained. The bond lengths of the two consecutive double

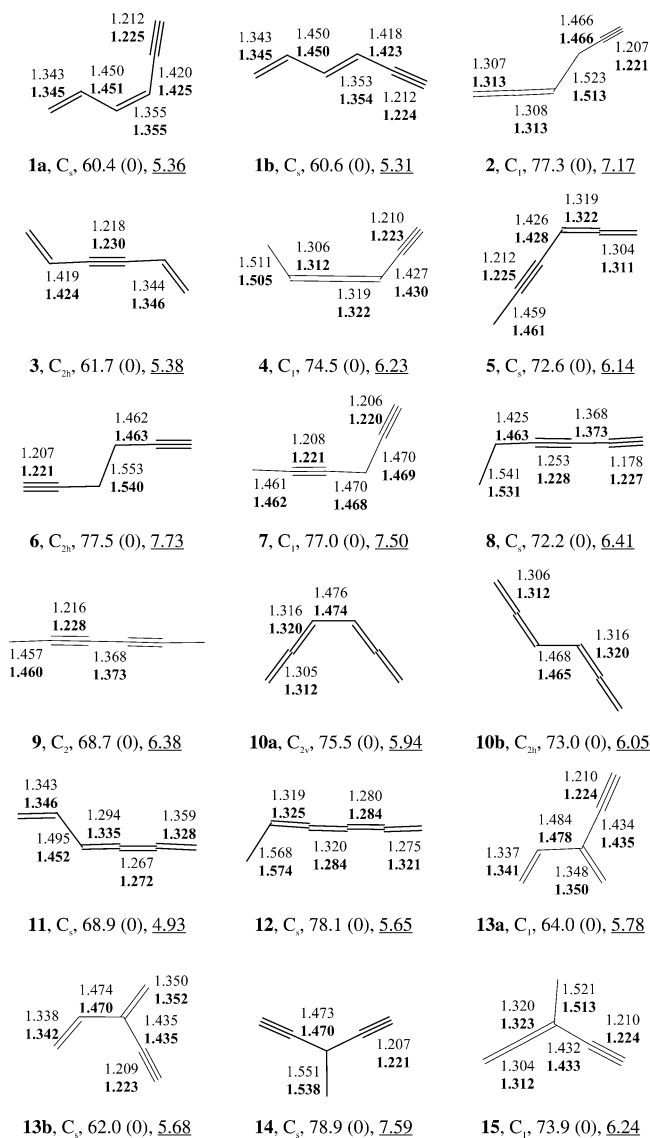


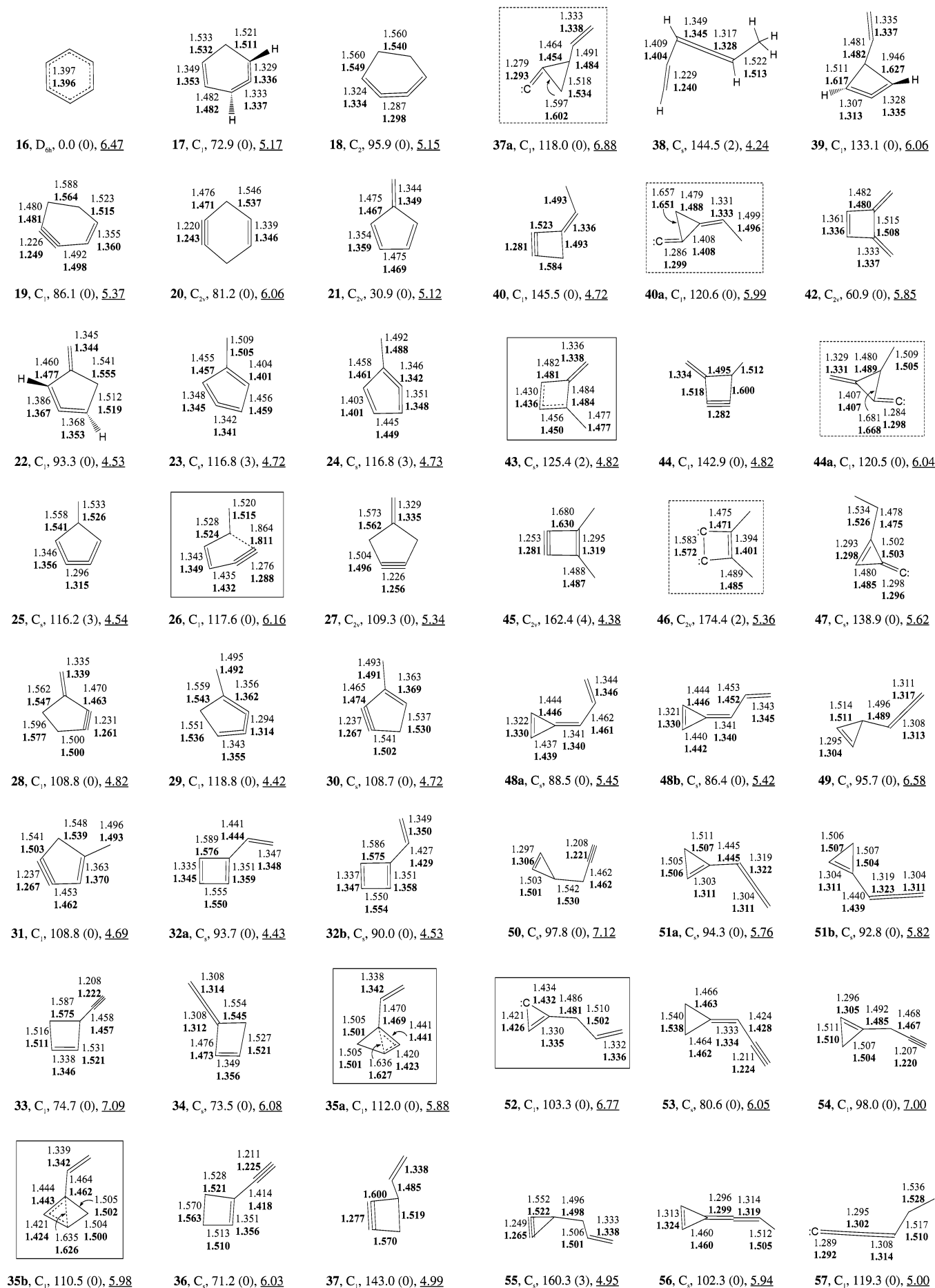
Figure 1. Optimized geometric parameters (in Å) of all the acyclic isomers obtained at B3LYP (normal) and MP2 (bold) levels of theory. The relative enthalpies (in kcal/mol) are obtained using the best estimate (eq 1), and the number of imaginary frequencies is given in parentheses. The underlined number corresponds to the absolute hardness values (in eV) obtained at the MP2 level.

bonds in the latter structure are longer than the normal bond lengths in allene type. The structures with acetylenic bonds in the four-membered ring collapse to a three-membered ring isomer at the B3LYP level; however, at the MP2 level, the structures with four-membered rings are located as stationary points. The geometries of **45** and **46** indicate that the structures seem to possess vicinal dicarbenes. Similar to the situation in the five-membered ring isomers, acetylenic, allenic, and cumulenic bonds cause the strain in the four-membered rings, which is reflected in the relative stabilities. The initial structure of **38** collapsed to the ring opened structure; similarly, the original structure of **47** collapsed to a three-membered ring with a carbene (Scheme 3). The collapsed structure of **47** is a minimum and lies about 139 kcal/mol above the global minima (**16**). Among the four-membered ring isomers, the relative energies of those rings which are devoid of acetylenic, allenic, or cumulenic bonds (**32a**, **32b**, **33**, **34**, **36**, and **42**) are within 100 kcal/mol of benzene energy. The high relative energy for the

rest of the molecules is traced to the strained multiple bonds present in their skeletons.

The relative energy of monocyclic isomers with three-membered rings ranges from 80 to 160 kcal/mol. Out of 31 minima in this category, 27 isomers have relative energies of less than 100 kcal/mol. [3]-Radialene, **76**, which has been studied both experimentally and theoretically,^{45,62} is about 84 kcal/mol less stable than benzene. Figure 2 clearly shows that the isomers possessing the triple bond in the three-membered ring were characterized as higher order saddle points except **73**, which is a minimum and has higher relative energy compared to other isomers, indicating the high strain induced by the acetylenic bond. The longer triple bond length (by about 0.1 Å) compared to the normal C–C single bond distance in structure **73** may be traced to the presence of vicinal dicarbene. The initial structure of **57**, which possesses a triple bond in the three-membered ring, upon optimization yielded a ring opened structure that consists of carbene carbon (Scheme 3). Of the three-membered rings, isomers **53**, **62**, and **64** have two sp³ carbon centers. The lower stability of **62** may be attributed to the exocyclic three contiguous double bonds. The isomer **53**, which is the lowest energy structure in the class of monocyclic three-membered ring isomers, is about 80 kcal/mol less stable than the global minima (**16**). The optimized geometries indicate that three-membered rings with allenic bonds afford more cyclopropenylidene structure to the resonance hybrid (**52**, **58a**, **58b**, **69a**, **69b**, **75a**, and **75b**). Cyclopropenylidene structures have attracted much experimental and theoretical interest.^{68,69} All the isomers with a cyclopropenylidene moiety in the monocyclic category lie within a narrow range of relative enthalpies from 95 to 103 kcal/mol. While the isomers **69a** and **69b** possessing substituents at two carbon centers of the cyclopropenylidene ring and also possessing the conjugated double bonds have the relative energy of about 95 kcal/mol, the isomer **52**, where the double bond of cyclopropenylidene and the other double bond are separated by a methylene unit, has the relative energy of 103 kcal/mol. The relative energies of these isomers indicate that expectedly, conjugated systems are more stable than nonconjugated ones. The isomers with bent acetylenic bonds are the ones that are highly unstable compared to the other isomers. Among the structures containing acetylenic bonds in the rings, all except **73** are characterized as higher order saddle points precluding the possibility of observing these compounds. Ten of the isomers (**33**, **37a**, **49**, **50**, **52**, **54**, **59**, **64**, **65**, and **71**) in the class of monocyclic isomers are computed to have higher hardness values than that of benzene. Furthermore, the molecules except the first two belong to three-membered rings.

Bicyclic. Among the 94 structures in this class, 79 are minima followed by 10 transition states and 2 second-order (**127** and **142**) and 1 third-order (**97**) saddle points (Figures 3 and 6). The remaining two structures (**96** and **148**) could be located only at the MP2 level, and both of them are minima. The bicyclic isomers represent the maximum number of C₆H₆ isomers. Three of the valence isomers, Dewar benzene (**87a**), trans-Dewar benzene (**87b**), and bicyclopropenyl (**122**), belong to this category. The two rings in the bicyclic isomers of C₆H₆ can have the following modes of arrangement: (a) the two rings can share one or more bonds, where the skeletons possess two bridgehead positions that are connected by three arms; (b) two rings can be separated by a bond; (c) two rings can have a common atom (spiro compounds). The diverse structural modes and energetics of the huge number of bicyclic isomers may be better understood when they are classified and discussed according to the skeleton



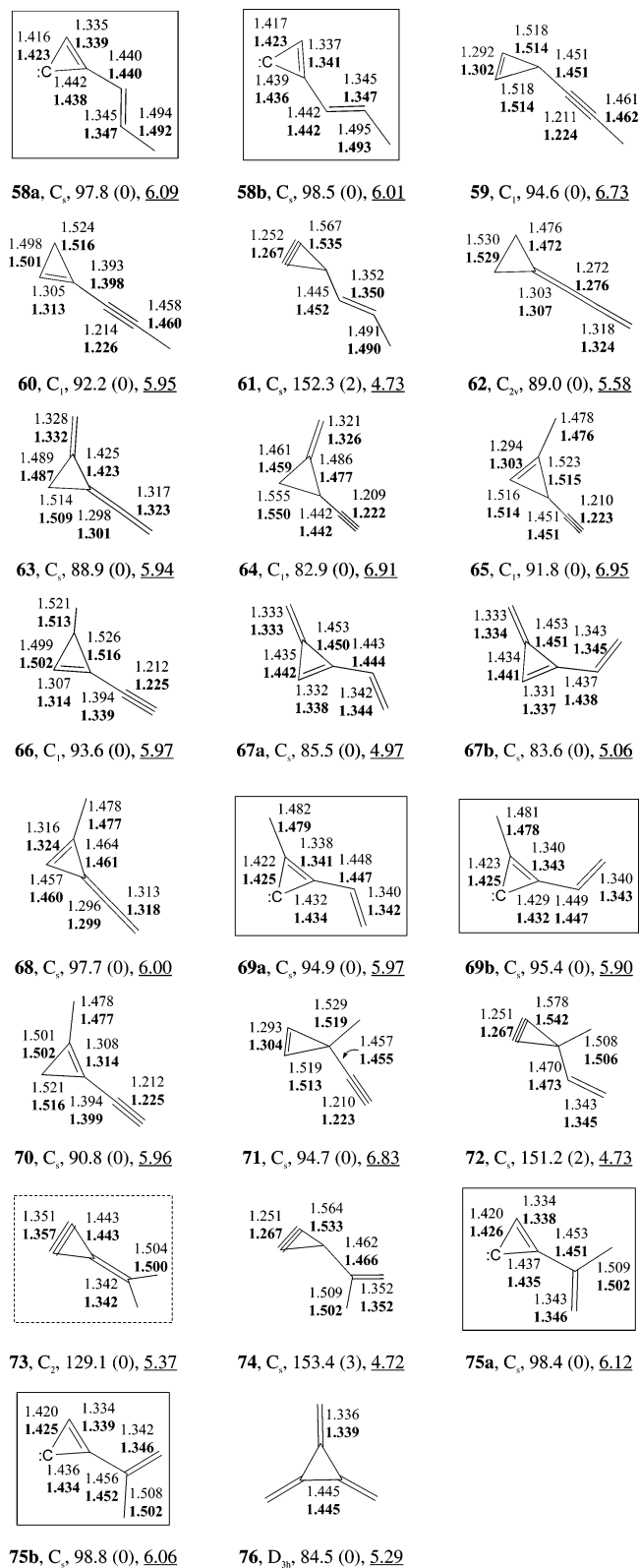


Figure 2. Optimized geometric parameters (in Å) of all the monocyclic isomers obtained at B3LYP (normal) and MP2 (bold) levels of theory. The relative enthalpies (in kcal/mol) are obtained using the best estimate (eq 1), and the number of imaginary frequencies is given in parentheses. Absolute hardness values (in eV) obtained at the MP2 level are given as underlined numbers. The compounds with novel structural features are highlighted with boxes.

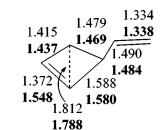
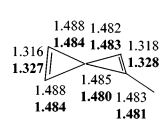
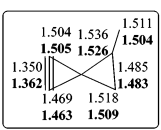
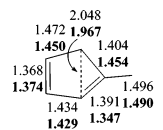
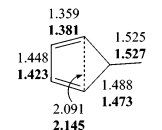
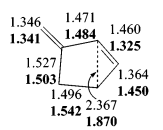
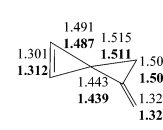
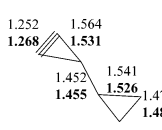
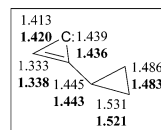
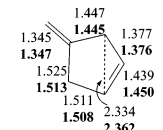
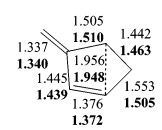
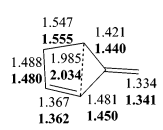
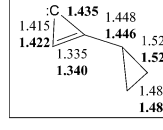
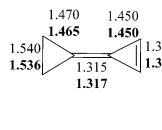
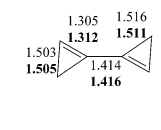
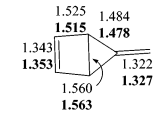
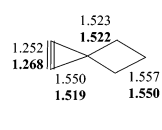
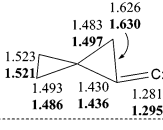
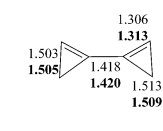
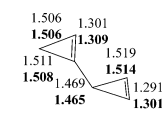
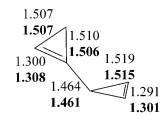
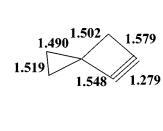
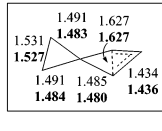
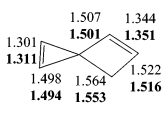
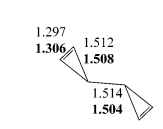
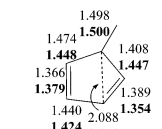
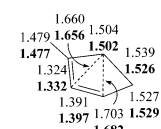
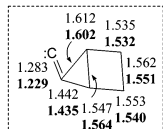
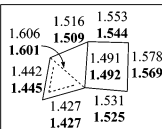
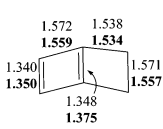
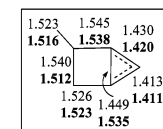
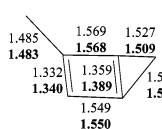
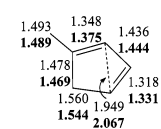
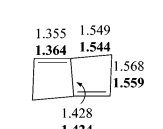
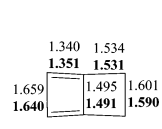
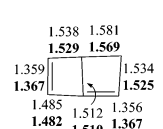
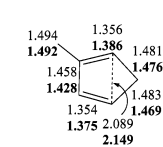
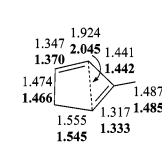
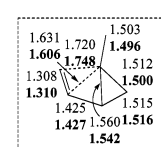
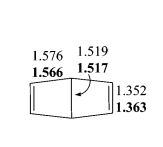
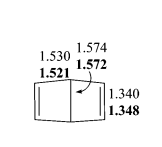
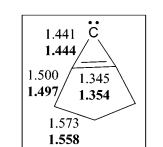
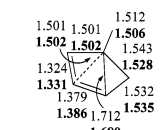
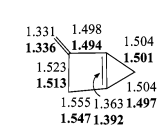
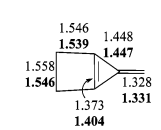
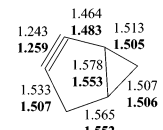
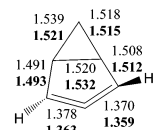
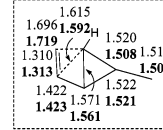
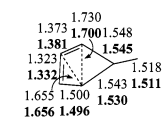
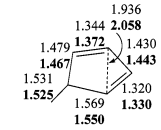
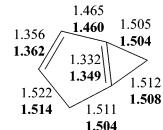
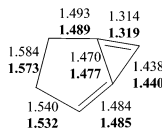
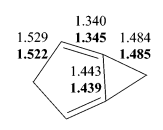
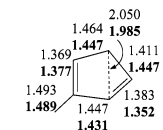
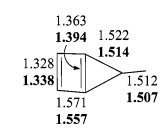
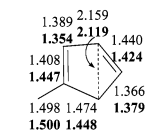
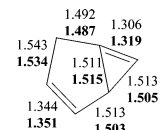
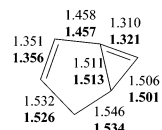
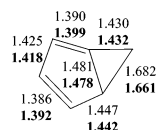
represents the isomers possessing 5- and 3-membered rings) and the isomers containing bridge carbons.

Five and three (5/3) membered rings share a bond and furnish 12 bicyclic structures, of which 10 are minima on the potential energy surface and their energies range from 72 to 121 kcal/mol. The other two structures were characterized as transition states (**83TS** and **86TS**), which lie about 7.8 and 0.2 kcal/mol higher than the corresponding minimum energy structures, respectively. Out of the 10 local minima, **80** and **81** are planar and the bonds connected to the bridgehead carbon atoms lie within a semicircle. The minimum energy structures of other isomers are nonplanar; interestingly, many have pyramidal sp² carbons except **85**. Isomer **77**, which is 72 kcal/mol above the global minimum (**16**), is the most stable among the bicyclic isomers, and this is followed by the valence isomer, Dewar benzene (**87a**), which belongs to the 4/4-membered ring category. Minimum energy structure **83** possesses chiral-allene type arrangement. The geometric parameters of **86** indicate that the three-membered ring is the cyclopropenylidene but the initial structure possesses an allenic bond in the three-membered ring (Scheme 1). Structure **86** is about 10–17 kcal/mol less stable than the monocyclic isomers with a cyclopropenylidene ring, and it is the only structure that has a higher hardness value than that of benzene in the 5/3-membered category.

Ten structures are possible with bicyclic arrangement containing two four-membered rings (4/4), of which two were characterized as transition states (**91TS** and **93TS**) and the others as minima. Isomers **89** and **91** have a cyclobutadiene moiety, and their planar forms are the least stable among this class of compounds next to **87b** where the destabilization is due to the trans ring junction. While **89** is a minimum, its automer **91** is a transition state in the planar form. The corresponding minimum, the nonplanar structure (**91**), has a puckered double bond and is about 12 kcal/mol more stable than **89**. The experimentally and theoretically well studied valence isomer Dewar benzene (**87a**) is about 75 kcal/mol more stable than trans-Dewar benzene (**87b**), which is in agreement with the previous results.¹³ Johnson and Daoust have reported extensive calculations on the electrocyclic ring openings of Dewar benzene to yield benzene, Moebius benzene, and trans-Dewar benzene.¹⁸ The isomers **88**, **89**, **90**, and **91** which possess conjugated double bonds are less stable than **87a**, which is attributed to the presence of one or two sp² carbon atoms in the bridgehead. The thermal isomerization of 1,2-hexadien-5-yne to 2-ethynyl-1,3-butadiene has been reported to occur via the intermediate formation of **88**.³⁵ Isomers **89** and **90** are planar, and the central C–C bond, which is shared by both the four-membered rings, is shorter than the typical C–C single bond length. In the case of the former, the outer C–C single bond lengths are much longer (up to 0.10 Å) than the normal C–C single bond length, which may be due to the strain caused by two double bonds present in the same ring. Isomer **92** seems to be tricyclic since a new bond is formed in one of the four-membered rings containing an allenic bond. The new bond formation and the longer allenic bond indicate that the structure seems to have a cyclopropenylidene moiety. **93** with C_s point group is computed to be a transition state, and the corresponding minimum energy structure has four- and three-membered rings with carbene, which is formed by collapsing of the four-membered ring containing a triple bond. Seven of the structures (**87a**, **92**, **93**, **94**, **95**, **96a**, and **98**) in this category have higher hardness values than that of the global minimum (**16**).

Four and three (4/3) membered rings share either a bond or an atom to form bicyclic skeletons of C₆H₆ isomers. Thirty-

containing different sizes of the rings, and the classification is as follows: 5/3-, 4/4-, 4/3-, and 3/3-membered rings (e.g., 5/3



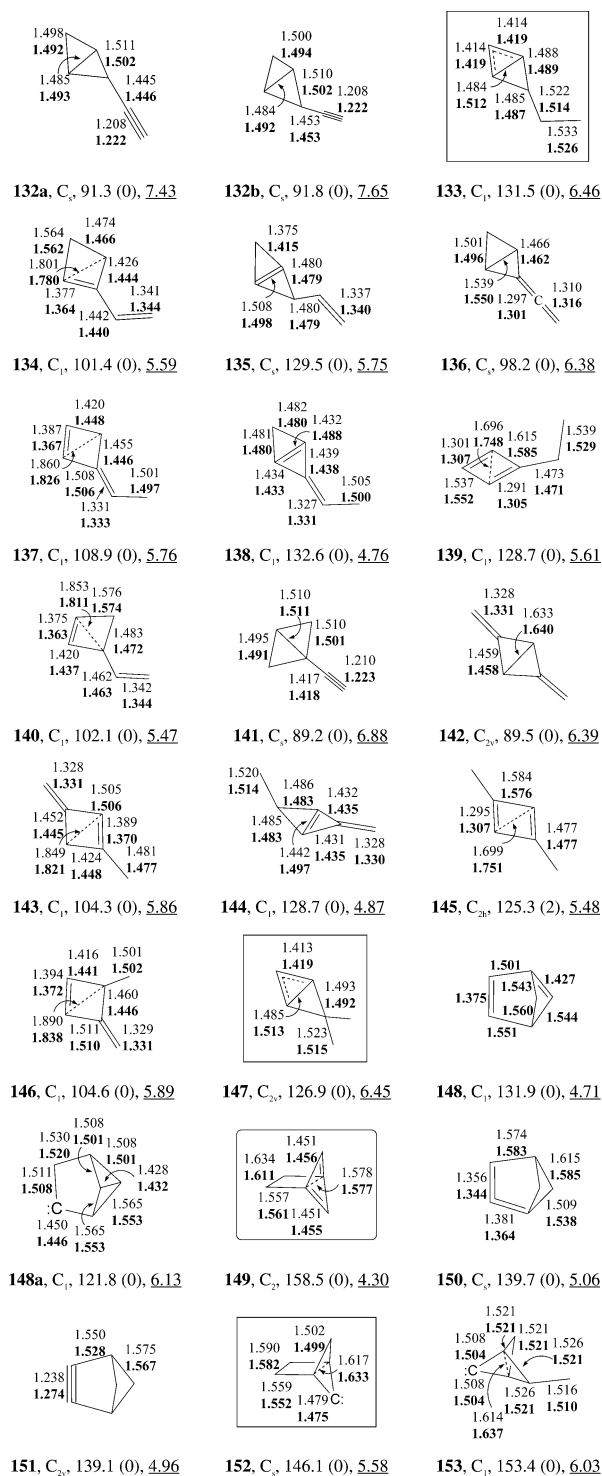


Figure 3. Optimized geometric parameters (in Å) of all the bicyclic isomers obtained at B3LYP (normal) and MP2 (bold) levels of theory. The relative enthalpies (in kcal/mol) are obtained using the best estimate (eq 1), and the number of imaginary frequencies is given in parentheses. Absolute hardness values (in eV) obtained at the MP2 level are given as underlined numbers. The compounds with novel structural features are highlighted with boxes.

one structures come under this category, out of which two structures (**95TS** and **110TS**) were characterized as transition states and one as a third-order saddle point (**97**). Among the four spiro compounds formed by 4/3-membered rings, **97** which possesses a triple bond in the three-membered ring is a third-order saddle point. The spiro compound with a four-membered ring containing a triple bond (**96**) was obtained only at the MP2

level and is a minimum; the same is not a stationary point at the B3LYP level and it collapses to a distorted structure (**96a**) since the four-membered framework is opened and the isomer possesses carbene. Isomer **94**, the spiro arrangement of four- and three-membered rings each having a double bond, has a relative enthalpy of about 94 kcal/mol, while the other spiro compounds have relative enthalpies of more than 128 kcal/mol. Molecule **95** has an allenic bond, and if the four-membered ring is planar the structure is characterized as a transition state (**95TS**). In the minimum energy structure **95**, the four-membered ring skeleton seems to be bicyclic since the allenic moiety collapsed to a three-membered ring with one carbene. Twenty-five bicyclic isomers belong to a 3/4-membered ring arrangement shared by a bond. In this category, isomers **109**, **113**, and **120**, which have two contiguous double bonds in the four-membered framework considered, seem to be tricyclic with hypervalent carbon atoms. The geometries of the isomers **110** and **114** indicate that the four-membered ring with a triple bond in each case considered collapsed to a three-membered ring and carbene. Twenty-four compounds are minima, and one (**110TS**) was characterized as a transition state on the potential energy surface; the isomers **98**, **101**, **105**, and **121** have relative enthalpies of less than 100 kcal/mol, and 10 of the isomers lie in the energy range of 100–120 kcal/mol. Some of the C–C single bond lengths are significantly shorter than the normal C–C single bond length in most of the 4/3 bicyclic systems shared by a bond. The length of the sharing C–C single bond is longer (by about 0.2–0.8 Å) than the normal C–C single bond length in 15 of the isomers, which possess the double bond in a four-membered ring or in a three-membered ring or in both, and one of the carbons of the double bond is the bridgehead position. In isomers **106**, **111**, **112**, and **118**, the sharing C=C bond is bent and the sp² carbons are pyramidal. Structures **106** and **118** having two double bonds in the four-membered ring are more than 142 kcal/mol less stable than the global minima (**16**). In addition to these two isomers, the isomers containing two consecutive double bonds in the four-membered ring (**109**, **113**, and **120**) and in the three-membered ring (**119**) have relative enthalpies of more than 140 kcal/mol, indicating more strain induced in these isomers. The structure considered for **119** consists of an allene bond in the three-membered ring, and the bond lengths indicate that the three-membered ring appears to be a cyclopropenylidene moiety. It is interesting to note that both three- and four-membered rings of isomer **119** are in the same plane, whereas a similar arrangement involving a 5/3-membered ring is not coplanar (**86**). However, in isomer **119**, the sharing bond length is less than or closer to the normal C–C single bond length. The bicyclic ring skeleton is planar for the isomers **103**, **108**, **115**, **116**, **117**, and **119**, and as many as 14 structures have pyramidal sp² carbons.

Among the bicyclic isomers, 33 structures contain two three-membered rings (3/3-membered ring bicyclic isomers); three structures (**130TS**, **139TS**, and **144TS**) were characterized as transition states, two isomers (**127** and **145**) as second-order saddle points, and the rest of them are minima. These 33 isomers can further be classified based on the structural arrangement of two three-membered rings: (a) separated by a bond (9 isomers); (b) spiro, shared by a common atom (4 isomers); (c) bicyclo[2.2.0] moiety, shared by a bond (20 isomers). Similar to 4/3-membered bicyclic isomers, here also most of the C–C single bond lengths in almost all the isomers are shorter than the normal C–C single bond distance. Except the isomer **127**, which has a C–C triple bond in one of the three-membered rings and was characterized as a second-order saddle point, other

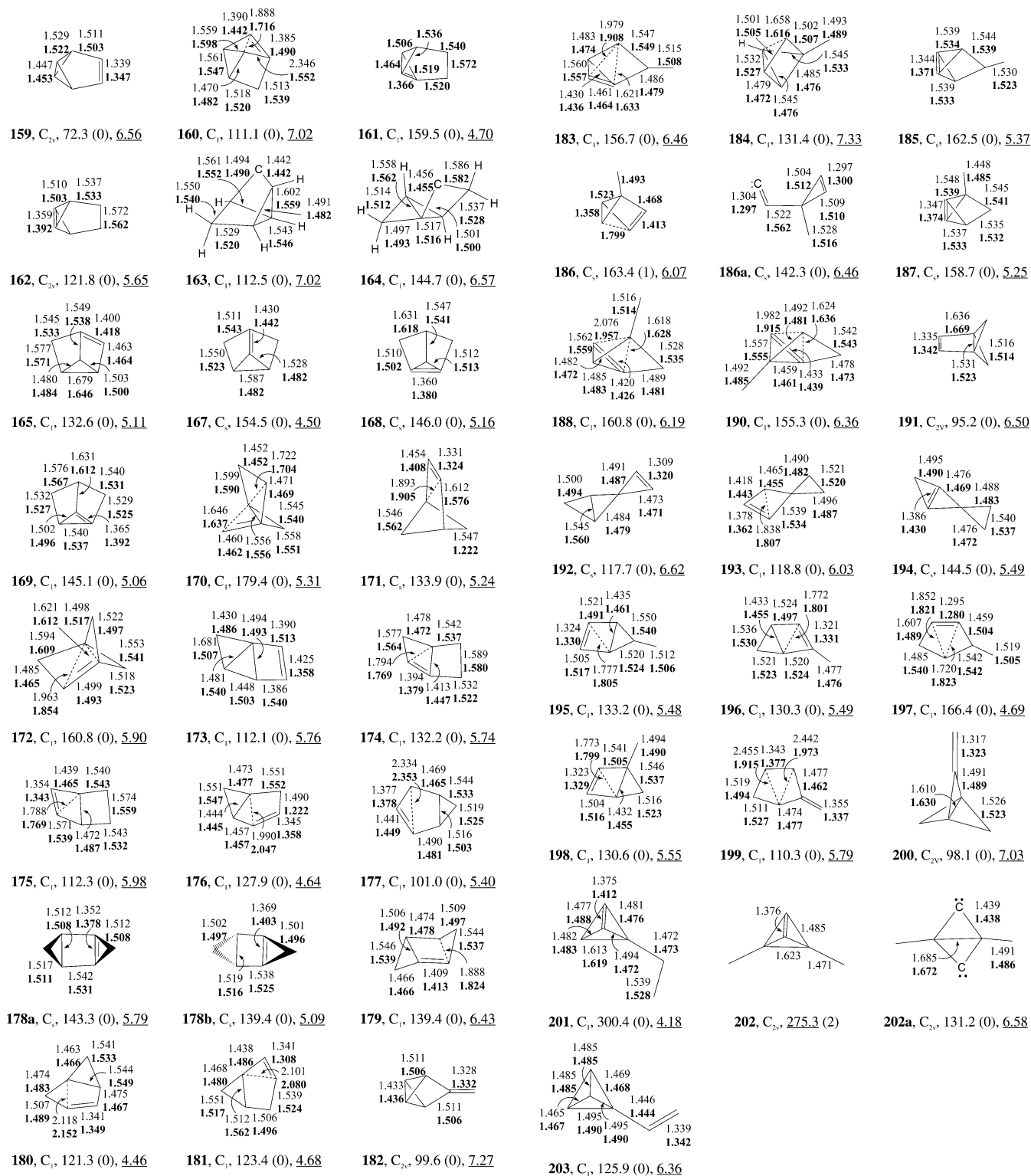


Figure 4. Optimized geometric parameters (in Å) of all the tricyclic isomers obtained at B3LYP (normal) and MP2 (bold) levels of theory. The relative enthalpies (in kcal/mol) are obtained using the best estimate (eq 1), and the number of imaginary frequencies is given in parentheses. Absolute hardness values (in eV) obtained at the MP2 level are given as underlined numbers. For structure **202** only, the relative energy is given at the CCSD(T) level.

bicyclic 3/3-membered ring isomers separated by a bond (**123a**, **123b**, **124a**, **124b**, **125**, **126a**, and **126b**) are lower in energy compared to that of the well-known valence isomer bicyclopropenyl (**122**) that has a similar type of skeletal arrangement. Geometries of the isomers **126a** and **126b** indicate the isopropylidene moiety in the skeleton, and these structures are more stable by about 10–11 kcal/mol than the valence isomer **122**.

The isomers **123a/b**, **124a/b**, and **125** have been synthesized.^{10,11} Out of the three spiro bicyclo 3/3-membered ring isomers, **129** is found to have a nontraditional bonding mode with a planar tetracoordinate central carbon and has an energy about 150 kcal/mol above that of benzene. Attempts to locate a stationary point where the carbon atom has a traditional tetrahedral arrangement were futile; all the initial putative structures collapse to the planar

form upon optimization at both levels. Some interesting planar tetracoordinate carbon (ptC) containing neutral compounds analogous to this have been reported in our group recently.⁷⁰ The geometrical parameters indicate the presence of vicinal dicarbene, and the delocalization can take place in the three-membered ring possessing vicinal dicarbene since the occupied p-orbital at the central ptC is perpendicular to the molecular plane. The other two spiro type isomers (**128** and **130**) prefer a tetrahedral arrangement for the central carbon and are found to be local minima.

All the isomers with two three-membered rings shared by a bond (**131–147**) are minima except **145**, which is a second-order saddle point. The bridging C–C single bond distance is longer (0.25–0.35 Å) compared to the typical C–C single bond length in the isomers where either one or both of the three-membered rings contain a C=C double bond. The bicyclic framework of isomers **133** and **147** is in the plane and the lengths of the sharing C–C bonds are shorter than the normal C–C single bond, indicating the presence of a double bond in the bridging position and a carbene. The sp² carbons are pyramidal in isomers **135**, **138**, and **144** due to the presence of bent C=C double bonds which are common for both the three-membered rings. The sharing C=C double bond lengths are longer by about 0.1–0.15 Å in these cases. These three isomers lie about 129–133 kcal/mol above the global minima (**16**). Isomers **132a**, **132b**, **136**, **141**, and **142**, which have no double bonds inside any of the three-membered rings, are computed to be competitive in energy, where the relative enthalpies are in the range 89–98 kcal/mol and all other 3/3-membered bicyclic isomers have relative enthalpies of more than 100 kcal/mol. This indicates that the bicyclic isomers with two three-membered rings which possess multiple bonds are not favorable compared to the saturated ring systems. Interestingly, the bond lengths of structures **86**, **119**, **133**, and **147**, where the three-membered ring contains an allenic bond in the initial structures considered, indicate that the contribution from the cyclopropenylidene structure to the resonance hybrid was smaller when the size of the other fused ring decreased, i.e., decreased while going from 5/3 (**86**) to 4/3 (**119**) then to 3/3 (**133** and **147**) membered ring bicyclic systems. Among these four structures, **119** and **86** are the least and most stable compounds, respectively. Isomer **118** has the highest relative energy among the isomers where two rings are shared by a bent double bond in the bicyclic category. Among the 3/3-membered bicyclic isomers, eight structures (**122**, **126a**, **126b**, **128**, **129**, **132a**, **132b**, and **141**) have higher hardness values compared to that of benzene (**16**).

The rest of the bicyclic isomers **148–153** possess two bridgehead carbon atoms. The initial structures considered for **149**, **152**, and **153** are bicyclic, but the optimized geometries seem to be tricyclic since C–C bonds, which have slightly longer bond length (1.58–1.63 Å) compared to the typical C–C single bond length, appear between the bridgehead atoms in each of these isomers. The relative enthalpies for these three isomers lie in the range from 146 to 158 kcal/mol. The isomers **152** and **153** appear to have a cyclopropenylidene moiety in the skeleton. Structure **148** is a stationary point only at the MP2 level; all our attempts for this structure at the B3LYP level lead to a new isomer **148a**, which is a tricyclic arrangement with carbene and the length of the shared single bond of the bicyclobutane moiety is about 1.4 Å. **148a** is a minimum and is about 122 kcal/mol less stable than the global minima (**16**). The structure obtained initially for **153** is a transition state, and its normal mode corresponds to C–C single bond rotation. In

fact, **153** has been located by following the normal mode of the imaginary frequency of **153TS**. The double bond at the bridgehead position and the presence of a triple bond in the ring lead to destabilization causing high relative energies (more than 130 kcal/mol) for isomers **148–153**. Here, isomers **154–158** upon optimization collapsed to the already existing isomers at both the B3LYP and MP2 levels (Scheme 2). The initial structures considered from **148** to **158** except **151** violate Bredt's rule which states that a double bond cannot be placed with one terminus at the bridgehead of a bridged ring system unless the rings are large enough to accommodate the double bond, and thus these structures can be termed as anti-Bredt structures. Some of the structures (**154–158**, Scheme 2) collapsed to already existing less strained structures and the rest of the molecules (**148**, **149**, **150**, **152**, and **153**) have high relative energies (133–159 kcal/mol) indicating high strain induced by the bridgehead double bonds, and these structures may be highly reactive.

Tricyclic. A total of 51 structures come under the class of tricyclic isomers, out of which 44 structures were characterized as minima and 5 isomers (**160TS**, **163TS**, **164TS**, **179TS**, and **201TS**) as transition states (Figures 4 and 6). The well-known valence isomer benzvalene (**159**), which was synthesized almost 30 years ago, belongs to tricyclic isomers, and it has been extensively studied both experimentally and theoretically.^{7,8,13–17} The B3LYP and the MP2 methods differ in locating and designating stationary points for a few structures as has been noticed before in a few cases. A stationary point corresponding to the carbon connectivity in **202** could be located only at the B3LYP level, which upon optimization at the MP2 level yields a new bicyclic isomer (**202a**). While **202** is a second-order saddle point, the bicyclic structure **202a** is at the minimum. Similarly, **161** and **186** could be located only at the MP2 level. Following the normal mode of the imaginary frequency of each of the transition state structures (**160TS**, **163TS**, **164TS**, **179TS**, and **201TS**), the minimum energy structures (**160**, **163**, **164**, **179**, and **201**) were obtained. Except in the case of **201**, for the other four isomers, the energy difference between the transition state structure and their corresponding minima is found to be more than 20 kcal/mol since the significant geometric changes were observed from transition state to minima in all four cases. The maximum energy difference of about 58 kcal/mol was observed between **163TS** and **163**, whereas the normal mode of the imaginary frequency of **201TS** corresponds to C–C single bond rotation with a very soft potential and the energy difference between the minima and the transition state is only around 3 kcal/mol at both B3LYP and MP2 levels. Tricyclic isomers can further be categorized based on the sizes of three different rings, which make the skeleton, and the classification is as follows: 5/3/3-, 4/4/4-, 4/4/3-, 4/3/3-, and 3/3/3-membered ring isomers. In general, the shared C–C single bond lengths are longer compared to the normal single bond lengths in the isomers where one of the bridgehead atoms is the sp² carbon. Only four of the tricyclic isomers have relative enthalpies of less than 100 kcal/mol, and they are **159** (73.3), **182** (99.6), **191** (95.2), and **200** (98.1). Most of the tricyclic isomers have relative enthalpies of more than 120 kcal/mol, and at least 10 of the isomers reported here possess energies of more than 150 kcal/mol. Four minima (**159–162**) and one transition state (**160TS**) structures come under the category of 5/3/3-membered ring isomers. Except **159**, the other three minima have relative energies of more than 110 kcal/mol. The isomer **161**, which is about 150 kcal/mol less stable than benzene, is a stationary point only at the MP2 level; the optimization of the same at the B3LYP level yields the

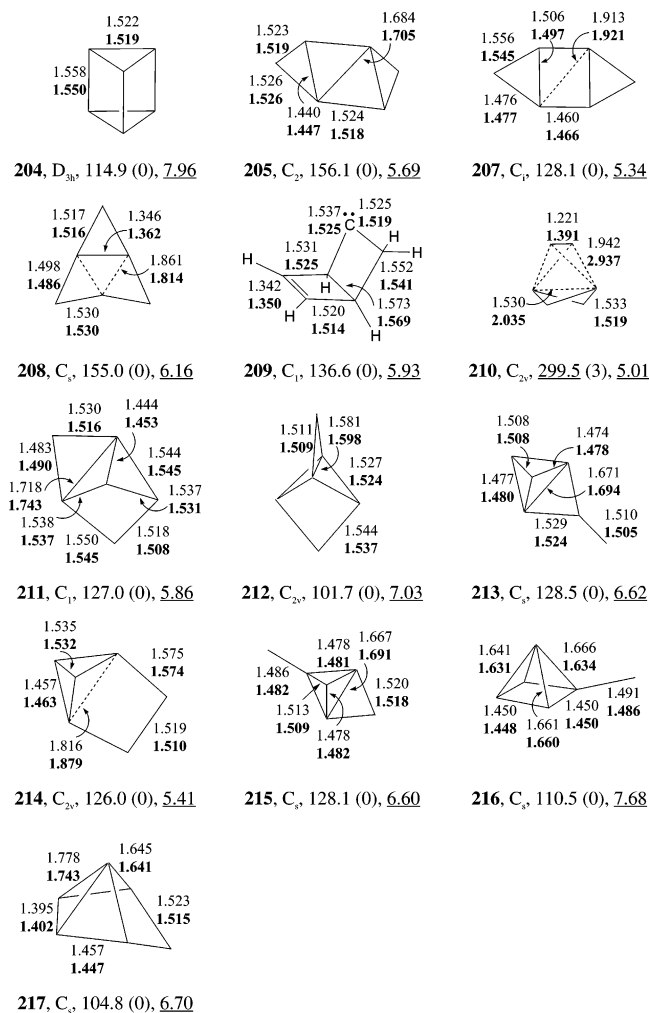


Figure 5. Optimized geometric parameters (in Å) of all the tetracyclic isomers obtained at B3LYP (normal) and MP2 (bold) levels of theory. The relative enthalpies (in kcal/mol) are obtained using the best estimate (eq 1), and the number of imaginary frequencies is given in parentheses. The underlined number corresponds to the absolute hardness values (in eV) obtained at the MP2 level. For structure **210** only, the relative energy is given at the CCSD(T) level.

already existing bicyclic isomer, **92**. Structure **160** upon optimization at the MP2 level yielded a tetracyclic isomer that has connectivity similar to that of **217**.

The initial structures of isomers **163** and **164** had the skeletal arrangement of 4/4/4-membered rings, and those were characterized as transition states (**163TS** and **164TS**). The corresponding minima of **163TS** and **164TS** are highly distorted structures possessing carbene carbon. Structures **163** and **164** are about 58 and 22 kcal/mol lower in energy compared to their corresponding transition states. Seven of the tricyclic isomers (**165**–**172**) fall in the subclass of 4/4/3-membered ring isomers, and all of them were found to be minima on the potential energy surface. All seven isomers contain pyramidal sp² carbon in their skeleton, and the relative enthalpies range from 132 to 180 kcal/mol. Two among the three rings in the tricyclic isomers of **167** and **169** share a bent double bond. In isomers **170** and **172**, a new C–C single bond joins two bridgehead atoms and is common for three three-membered rings. Significant skeletal reorganization occurs upon optimization of the initial structures of **170** and **172**. These two isomers are about 179 and 161 kcal/mol higher than the global minimum (**16**), respectively. The high relative energy for these isomers may be attributed to the

strain induced by the presence of three-membered rings fused in their skeletons.

Isomers from **173** to **191** comprise two three-membered and a four-membered ring in their skeletons considered initially. Thus, these isomers fall in the category of 4/3/3-membered ring isomers. Structure **191** is the lowest energy structure in this category, which is about 95 kcal/mol less stable than benzene (**16**). Isomer **182** has a relative enthalpy of about 100 kcal/mol, and the rest of the structures have relative enthalpies between 100 and 163 kcal/mol. Isomer **186** could be obtained only at the MP2 level, while all the putative structures upon optimization at the B3LYP level yielded the distorted skeleton of **186a** which is a minimum and contains a three-membered ring and a carbene. All of the isomers are minima except one (**179TS**), which was characterized as a transition state. The energy difference between **179TS** and its minimum energy structure is about 20 kcal/mol. The length of the sharing C–C single bond in **179** is longer than the normal C–C single bond distance. Abundantly interesting structural features are encountered among the isomers of this category. Fifteen isomers possess pyramidal sp² carbons. Several isomers possessing the bent double bonds, which are shared by two of the three rings, have relative energies in the range of 140–163 kcal/mol. One of the sharing C–C single bond lengths is much longer and is in the range of 2.0–2.3 Å in the cases of **176**, **177**, **180**, and **181**, indicating that the structures seem to be bicyclic. Remarkably, isomer **184** contains a pentacoordinate carbon, which is connected to four atoms of the four-membered ring in the plane and to the hydrogen atom, but one of the C–C single bond distances is longer (by about 0.05–0.1 Å) than the normal single bond length; it is a minimum on the potential energy surface and is about 131 kcal/mol higher in energy than the global minimum (**16**). The double bond in the initial structure of **184** (Scheme 1) becomes closer to the C–C single bond distance in the optimized geometry that appears to be tetracyclic. In the case of isomers **183**, **188**, and **190**, slightly longer new C–C single bonds are formed between the two bridgehead atoms, which are the origin for three- and four-membered rings of the skeleton. One of the three-membered rings in these three isomers contains significantly longer C=C double bonds and one of the C–C single bond lengths of the other three-membered ring is considerably longer, indicating the skeleton contains three three-membered rings rather than one four-membered and two three-membered rings. All three isomers have relative energies higher than 155 kcal/mol. A quick look at isomers **182**–**190**, which have similar skeletal frameworks but the double bonds are placed in different positions, indicates that a double bond in the three-membered ring leads to significant destabilization.

The rest of the tricyclic isomers (**192**–**203**) belong to the category of 3/3/3-membered ring isomers since the skeletal frameworks possess three three-membered rings. Some of the isomers in this category consist of longer than normal C–C single bond lengths which may be attributed to the strain induced by the fusion of three three-membered rings. Twelve isomers are minima, and the wide range of relative enthalpies from 98 to 300 kcal/mol is observed for the isomers in this category. Isomer **200**, in which the three three-membered rings are shared by a common bond with two bridgehead atoms and no double bond inside any of the rings, is the lowest energy structure in the 3/3/3-membered ring isomers. The least stable minimum energy isomer (**201**) on the C₆H₆ potential energy surface falls in this subclass of tricyclic isomers, and it is about 300 kcal/mol less stable than the lowest energy isomer benzene (**16**). Isomers **192**–**194** have three rings shared by a bond and an

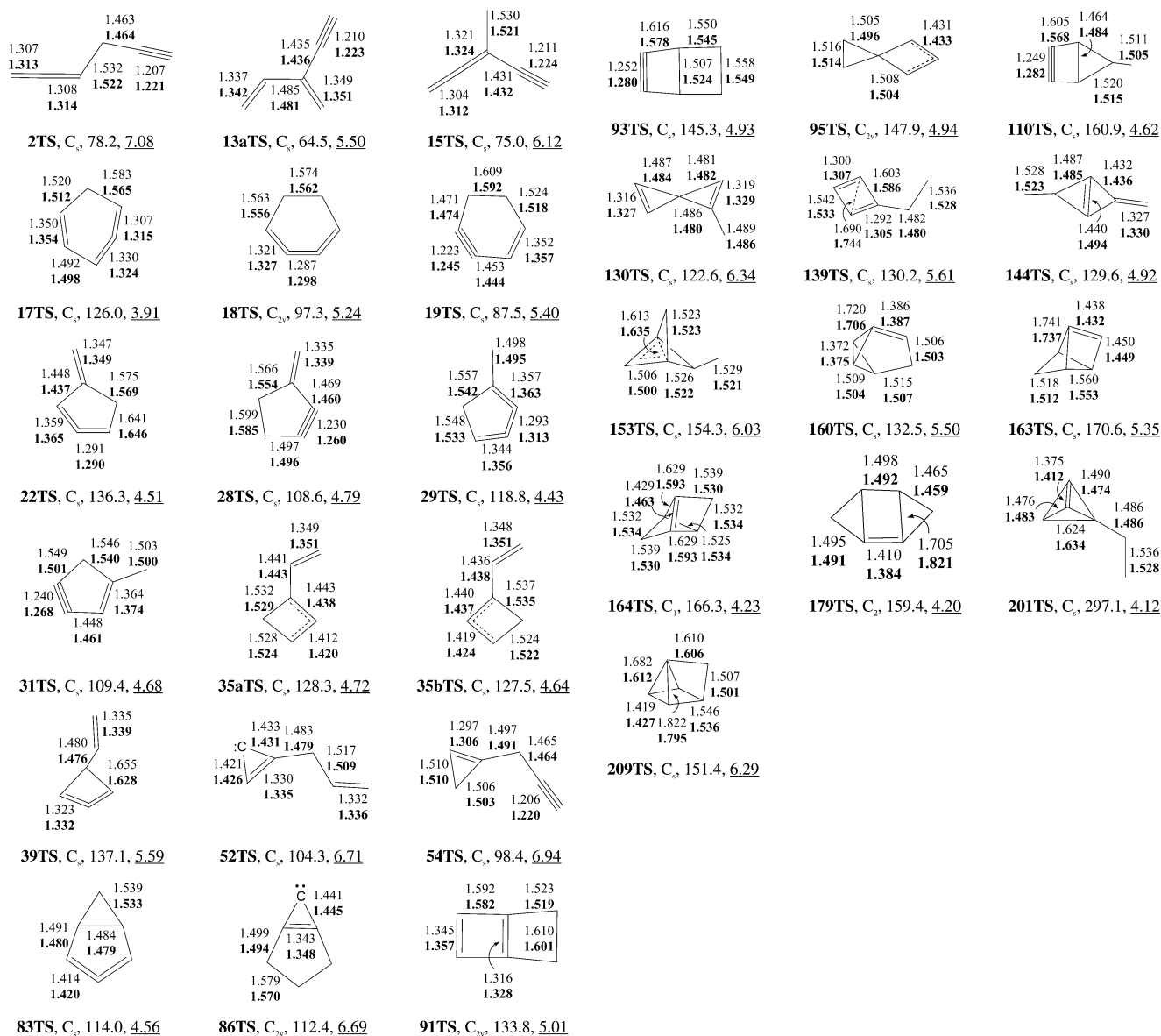


Figure 6. The principal geometric parameters (in Å) of the transition state structures obtained at B3LYP (normal) and MP2 (bold) levels of theory along with the best estimate relative enthalpies (in kcal/mol) calculated using eq 1 and absolute hardness values (in eV) obtained at the MP2 level.

atom, and these structures possess spiro arrangement. Structure **194** is predicted to be less stable by about 25 kcal/mol than **192** and **193**; this may be due to the strain caused by the bent double bond shared by two three-membered rings. The bond lengths of structure **199** indicate that the skeleton is monocyclic with carbene. Isomer **202** is a stationary point only at the B3LYP level; the optimization upon the MP2 level yielded a new isomer with two carbene carbons (**202a**) where the double bond present in the original structure **202** has broken. The stationary point corresponding to **202a** was located at the B3LYP level, and frequency calculation indicates that it is a minimum on the potential energy surface. Isomers **201–203** possess very similar skeletal arrangements. The relative energies of isomers **201** and **202** are more than 2 times that of **203**, indicating the strain due to the bent double bond which is shared by two three-membered rings. Ten structures (**159**, **160**, **163**, **164**, **182**, **184**, **191**, **192**, **200**, and **202a**) out of 44 minima in the class of tricyclic isomers possess higher hardness values than that of the global minimum (**16**).

Tetracyclic. The structures corresponding to the tetracyclic isomers of C₆H₆ and the important geometric parameters

obtained using the B3LYP and MP2 levels along with the relative best estimate energies and chemical hardness values calculated at the MP2 level are depicted in Figure 5. In this class of compounds, the strain in the skeleton is primarily due to the smaller ring systems. As in the case of mono/bi/tricyclic isomers, there is no possibility of having constrained multiple bonds in the ring systems, as all the tetracyclic structures are saturated hydrocarbons. The strain prevalent in the tetracyclic structures owing to the fused three/four-membered rings leads to high relative energies. While the relative energies of most of the isomers lie in the range of 100–156 kcal/mol, **210**, a third-order saddle point, is about 300 kcal/mol less stable than the global minima. The optimized geometry **210** indicates that two of the carbons seem to be pentacoordinated with four significantly longer C–C single bond lengths (Figure 5).⁷¹ A novel tetracyclic arrangement with a pyramidal carbon of structure **209** was characterized as a transition state (**209TS**). By following the normal mode of the imaginary frequency, the pyramidal carbon leads to carbene and the double bond is formed in the four-membered ring. Thus, the tetracyclic structure collapsed to the bicyclic form (**209**). However, the rest of the

structures were characterized as local minima. One of the sharing C–C single bond distances is much longer (more than 1.8 Å) in structures **207** and **208**. The latter structure has been studied using high level quantum mechanical calculations, and the study examined the unusual bonding pattern in the structure and the rearrangement reactions of the compound.^{61b} The geometric parameters of structure **208** indicate that the skeleton seems to have a double bond and carbene. Among the tetracyclic isomers, structures **212–217** possess one or more unusual pyramidal tetracoordinated carbon atoms, where all the bonds connected to a given carbon lie within a hemisphere. Interestingly, compounds **212**, **216**, and **217** are more stable compared to the experimentally known prismane, a valence isomer of benzene. Isomer **216**, which is a methyl derivative of pyramidane, is the global minima on the C₅H₄ potential energy surface and is found to be around 110 kcal/mol less stable than benzene.

Conclusions

The present study reports a systematic computational study on all the possible isomeric forms of benzene for the first time. The rich structural variations of C₆H₆ came to the fore in this exhaustive study. A total of 215 minimum energy structures were located on the benzene potential energy surface. In addition to these minima, several transition states and higher order saddle points were also located. The relative stabilities of these isomers are mainly controlled by the strain in the skeletal arrangements. Therefore, the present study indicates that several isomers that are minima on the potential energy surface are waiting to be explored. The study shows that benzene isomers display a wide range of bonding modes such as planar tetracoordinate carbon, pyramidal carbon, bent/twisted double bonds, vicinal dicarbenes, and nonlinear triple bonds. About six isomers (**122**, **123**, **124**, **125**, **162**, and **204**) with greater than 100 kcal/mol relative energy were experimentally available. The current study indicates that about 84 structures are within 100 kcal/mol in energy on the benzene potential energy surface. Thus, synthetic chemists have a good potential to target hitherto unknown C₆H₆ isomers and explore interesting structural and bonding patterns. The stability of planar tetracoordinate carbon over the tetrahedral arrangement in the isomeric form **129** is an interesting observation. Many of the three-membered ring monocyclic isomers are found to be more stable than four- or five-membered ring isomers. Thus, the current computational study provides the most exhaustive account of the relative stabilities of the C₆H₆ isomers and brings out that a large number of isomers are amenable for synthesis, and we feel that this study enthralls the experimentalists in synthesizing newer isomers.

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Supporting Information Available: Tables of total energies and relative energies of all the isomers considered in the study obtained at the B3LYP, MP2, and CCSD(T) levels of theory and a figure showing the correlation of relative energies at various levels of theory. This material is available free of charge via the Internet at <http://pubs.acs.org>. The frequencies and IR and Raman intensities of the minimum energy structures can be obtained from the authors.

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