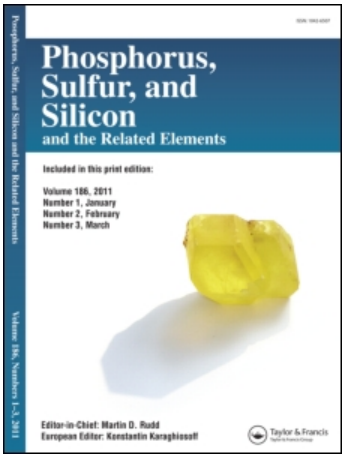

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An Ab Initio Molecular Orbital Study of Isophosphinines

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AN AB INITIO MOLECULAR ORBITAL STUDY OF ISOPHOSPHININES

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Ab initio molecular orbital calculation at HF/6-31G, HF/6-31G**, HF/6-311G**, HF/6-311++G**, RMP2-FC/6-31G*, and B3LYP/6-31G* levels of theory for geometry optimization and MP4(SDQ)/6-31G* for a single-point total energy calculation are reported for phosphinine and 13 isophosphinines* ***7–19****. Isomers* ***7–11*** *with an allenic system are calculated to be 8–18 kcal mol*$^{-1}$ *more stable than structures* ***12–17*** *with an acetylenic moiety. The calculated energy difference (66.19 kcal mol*$^{-1}$*) between phosphinine and the most stable isophosphinine (1-phospha-1,2,4-cyclohexatriene,* ***10****) is smaller than the difference (78.96 kcal mol*$^{-1}$*) between benzene and the most stable isobenzene (cyclohexa-1,2,4-triene,* ***2****). The isophosphinines* ***18*** *and* ***19****, with a butatriene moiety, are calculated to be the least stable isomers.*

Keywords: Ab initio calculations; cyclic acetylenes; cyclic allenes; isophosphinines; strained molecules

INTRODUCTION

Since their discovery, phosphinines have been the subject of a number of theoretical studies.[1–5] These studies were motivated by the need for phosphorus chemists to have a good understanding of the electronic factors that render phosphinines so different from their nitrogen counterparts (pyridines) with regard to their chemical reactivity[6] and their coordination properties.[7] A second important point is that this heterocycle and its derivatives constitute an ideal model for studying the ability of the —P═C double-bond system to participate in

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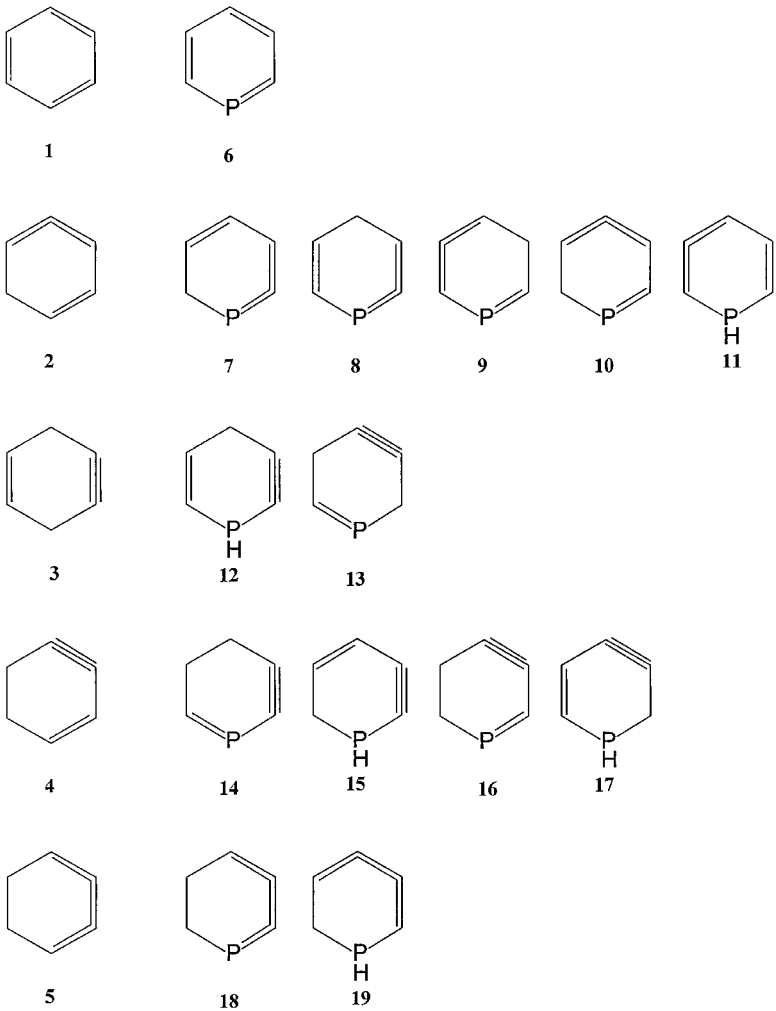
conjugative interactions.[8] While the structure and properties of isobenzenes **2–5** and isopyridines have been studied by experimental[9–11] and theoretical[12,13] methods, the extent of our present understanding regarding the geometries and stabilities of isophosphinines is meager. The number of different positions that a nitrogen atom can occupy in various isobenzenes to yield isophosphinines is 13 (see Scheme 1). We report the results of ab initio calculations for structural optimization of strained isobenzenes **2–5**, phosphinine (6), and isophosphinines



SCHEME 1

7–19 by comparing the geometries (HF/6-311++G**) and energies [MP4(SDQ)/6-31G*//RMP2-FC/6-31G*]. The results from these calculations are used in the energies discussions below.

Even though isophosphinines **7–19** are not presently available for more studies, it is possible to learn something about them by using theoretical methods that have been reliable in other applications.

RESULTS AND DISCUSSION

Benzene and Isobenzens 2–5

The results of ab initio calculations for benzene and isobenzenes **2–5** are shown in Table I. All of the basis sets employed in these calculations, except B3LYP/6-31G*, give the same order of stabilities for compounds **1–5** (Table I). According to these calculations, the most stable isobenzene is cyclohexa-1,2,5-triene (**2**), which is 78.96 kcal mol^{-1} less stable than benzene. The calculated strain energies for isobenzenes **3** and **4**, containing acetylenic moieties are 86.65 and 93.83 kcal mol^{-1} above that of benzene. The butatrienic isomer **5** is calculated to be the least stable isobenzene (see Table I).

Phosphinine and Isophosphinines 7–19

The results of ab initio calculations for structure optimization and energies of phosphinine and isophosphinines **7–19** are shown in Tables II and III, and Figures 1 and 2. The isophosphinines **7–19** can be divided into three series: (1) enallenic **7–11**; (2) enynic **12–17**; and (3) butatrienic **18** and **19**. All of isophosphinines have strained grouping in small-ring structures. This strain implies some deviations from an ideal bonding geometry in small-cyclic structures of isophosphinines, engender substantial strain energy, and resultant reactivity. These features are apparent from total energy and representative structural parameters for the most stable geometries of isophosphinines (see Figures 1 and 2, and Tables II and III). Isomers **7–11** have dissymmetric enallenic structures. Ring constraints bend the allene moiety and exert torsion toward a planar arrangement of ligands. Thus, for enallenic isophosphinines **7–11**, two forms are possible: (1) chiral (C_1 symmetry) and (2) achiral (C_s symmetry) geometries with singlet (S) and triplet (T) electron configuration. The equilibrium geometries of enallenic structures **7–11** with singlet electron configuration are chiral (C_1 symmetry). The calculated strain energy for the achiral geometry is 30–50 kcal mol^{-1}. These isomers can be racemized by rotation around allene-like

TABLE I Total Energies (Hartree) and Relative Energies (in Parenthesis, kcal mol^{-1})[a] of Benzene and Isobenzenes **2–5**

Structure	 **1**	 **2**	 **3**	 **4**	 **5**
HF/6-31G*// HF/6-31G*	−230.703137 (0.0)	−230.555602 (90.83)	−230.545215 (97.51)	−230.533068 (104.89)	−230.507186 (120.72)
HF/6-31G**// HF/6-31G**	−230.713858 (0.0)	−230.566018 (91.02)	−230.555098 (98.04)	−230.542860 (105.47)	−230.516979 (121.31)
HF/6-311G**// HF/6-311G**	−230.754097 (0.0)	−230.608597 (89.55)	−230.599780 (95.25)	−230.586787 (103.16)	−230.560035 (119.54)
HF/6-311++G**// HF/6−311 ++G**	−230.756847 (0.0)	−230.611943 (89.18)	−230.602967 (94.97)	−230.589944 (102.90)	−230.563256 (119.24)
RMP2-FC/6-31G*// RMP2-FC/ 6-31G*	−231.457733 (0.0)	−231.319989 (84.69)	−231.313431 (88.96)	−231.300750 (96.68)	−231.279530 (109.59)
MP4(SDQ)/6-31G*// RMP2-FC/ 6-31G*	−231.493431 (0.0)	−231.364815 (78.96)	−231.352815 (86.65)	−231.340977 (93.83)	−231.322077 (105.29)
B3LYP/6-31G*// B3LYP/6-31G*	−232.248661 (0.0)	−232.091099 (97.12)	−232.100263 (91.53)	−232.115499 (81.73)	−232.078198 (104.73)

[a] 1 kcal mol^{-1} = 4.184 kJ mol^{-1}.

TABLE II Total Energies (Hartree) of Isophosphinines **7–11**. Values in Parenthesis are Relative Energies (kcal mol^{-1}) with Respect to Phosphinine: HF/6-31G*//HF/6-31G* (−532.954812); HF/6-31G**//HF/6-31G** (−532.963732); HF/6-311G**//HF/6-311G** (−533.017735); HF/6-311++G**//HF/6-311++G** (−533.020678); RMP2-FC/6-31G*//RMP2-FC/6-31G* (−533.695405); MP4(SDQ)/6-31G*//RMP2-FC/6-31G* (−533.731773); B3LYP/6-31G*//B3LYP/6-31G* (−534.877989); Open Shell UHF/6-311++G**//UHF/6-311++G** (−532.927445)

Structure	7		8		9		10		11	
	C_1	C_s	C_1	C_s	C_1	C_s	C_1	C_s	C_1	C_s
HF/6-31G*// HF/6-31G*	−532.829976 (76.81)	−532.797550 (95.82)	−532.829069 (77.58)	−532.794349 (98.08)	−532.829159 (77.28)	−532.774218 (109.64)	−532.826821 (78.69)	−532.761180 (117.24)	−532.835774 (71.81)	−532.795628 (96.44)
HF/6-31G**// HF/6-31G**	−532.838673 (76.95)	−532.806199 (95.99)	−532.837623 (77.81)	−532.802904 (98.31)	−532.837908 (77.39)	−532.783586 (109.36)	−532.835566 (78.80)	−532.770456 (117.02)	−532.845286 (71.44)	−532.805212 (96.02)
HF/6-311G**// HF/6-311G**	−532.894369 (75.88)	−532.863654 (93.82)	−532.893525 (76.62)	−532.861109 (95.68)	−532.894230 (75.94)	−532.840623 (107.46)	−532.891833 (77.38)	−532.825661 (116.26)	−532.901637 (69.97)	−532.864543 (92.68)
HF/6-311++G**// HF/6-311++G**	−532.897569 (75.72)	−532.868122 (92.86)	−532.896929 (76.33)	−532.866003 (94.45)	−532.897710 (75.60)	−532.844930 (106.60)	−532.895182 (77.13)	−532.829288 (115.83)	−532.905116 (69.63)	−532.870433 (90.83)
RMP2-FC/6-31G*// RMP2-FC/6-31G*	−533.577739 (72.31)	−533.531972 (99.69)	−533.577370 (72.74)	−533.527675 (102.64)	−533.576724 (72.91)	−533.520911 (105.81)	−533.577318 (72.48)	−533.495506 (121.17)	−533.571755 (74.71)	−533.537716 (95.50)
MP4(SDQ)/6-31G*// RMP2-FC/6-31G*(S)	−533.623856 (66.19)	−533.573966 (96.16)	−533.623309 (66.74)	−533.570642 (98.50)	−533.621935 (67.36)	−533.561005 (103.48)	−533.621774 (67.40)	−533.539234 (116.56)	−533.617562 (67.88)	−533.572452 (96.52)
MP4(SDQ)/6-31G*// RMP2-FC/6-31G*(T)	−533.598517 (82.09)	−533.598538 (80.85)	−533.606393 (77.35)	−533.606424 (76.27)	−533.582384 (92.18)	−533.582379 (90.06)	−533.596246 (83.42)	−533.596215 (82.09)	−533.586552 (88.24)	−533.557283 (101.23)
B3LYP/6-31G*// B3LYP/6-31G*	−534.765153 (69.28)	−534.726265 (92.34)	−534.763500 (70.52)	−534.721437 (95.63)	−534.763877 (70.04)	−534.715809 (98.36)	−534.765052 (69.25)	−534.695695 (110.13)	−534.767147 (66.67)	−534.729165 (89.93)
Open shell UHF/6-311++ G**//UHF/6-311++G**	−532.897569 (75.72)	−532.868122 (92.86)	−532.896929 (76.33)	−532.866003 (94.45)	−532.897711 (75.60)	−532.844931 (106.60)	−532.895182 (77.13)	−532.829289 (115.83)	−532.905116 (69.63)	−532.870433 (90.83)

TABLE III Total Energies (Hartree) of Isophosphinines **12–19**. Values in Parenthesis are Relative Energies (kcal mol^{-1}) with Respect to Phosphinine: HF/6-31G*//HF/6-31G* (−532.954812); HF/6-31G**//HF/6-31G** (−532.963732); HF/6-311G**//HF/6-311G** (−533.017735); HF/6-311++G**//HF/6-311++G** (−533.020678); RMP2-FC/6-31G*//RMP2-FC/6-31G* (−533.695405); MP4(SDQ)/6-31G*//RMP2-FC/6-31G* (−533.731773); B3LYP/6-31G*//B3LYP/6-31G* (−534.877989); Open Shell UHF/6-311++G**//UHF/6-311++G** (−532.927445)

Structure	 **12**, C_1	 **13**, C_s	 **14**, C_1	 **15**, C_1	 **16**, C_s	 **17**, C_1	 **18**, C_1	 **19**, C_1
HF/6-31G*// HF/6-31G*	−532.830986 (75.29)	−532.816863 (85.08)	−532.818742 (84.12)	−532.820681 (81.17)	−532.803143 (93.49)	−532.811180 (87.23)	−532.801678 (94.54)	−532.790313 (99.85)
HF/6-31G**// HF/6-31G**	−532.839903 (75.29)	−532.825202 (85.45)	−532.826857 (84.62)	−532.829733 (81.09)	−532.811374 (93.93)	−532.820182 (87.18)	−532.809877 (95.00)	−532.799344 (99.78)
HF/6-311G**// HF/6-311G**	−532.897993 (72.73)	−532.883480 (82.77)	−532.885076 (81.98)	−532.888007 (78.41)	−532.068826 (91.76)	−532.878277 (84.61)	−532.866205 (93.54)	−532.856876 (97.57)
HF/6-311++G**// HF/6-311++G**	−532.901320 (72.49)	−532.886775 (82.54)	−532.888396 (81.74)	−532.891153 (78.28)	−532.871957 (91.64)	−532.881762 (84.27)	−532.869218 (93.49)	−532.860460 (97.16)
RMP2-FC/6-31G*// RMP2-FC/6-31G*	−533.562394 (81.05)	−533.566931 (79.14)	−533.563840 (81.29)	−533.553837 (85.84)	−533.556507 (85.48)	−533.550741 (87.87)	−533.551918 (88.49)	−533.534922 (97.33)
MP4(SDQ)/6-31G*// RMP2-FC/6-31G*	−533.607972 (75.27)	−533.608369 (75.96)	−533.607064 (76.99)	−533.598782 (80.46)	−533.596947 (82.92)	−533.593903 (83.61)	−533.595594 (83.90)	−533.578675 (92.70)
B3LYP/6-31G*// B3LYP/6-31G*	−534.751923 (76.70)	−534.749530 (79.13)	−534.748075 (80.26)	−534.745951 (79.86)	−534.740561 (84.56)	−534.740329 (83.48)	−534.744759 (82.05)	−534.731355 (88.64)
Open shell UHF/6-311++G**//UHF/6-311++G**	−532.901319 (72.49)	−532.886776 (82.54)	−532.888395 (81.74)	−532.891153 (78.28)	−532.871957 (91.64)	−532.881763 (84.27)	−532.869218 (93.49)	−532.860460 (97.16)

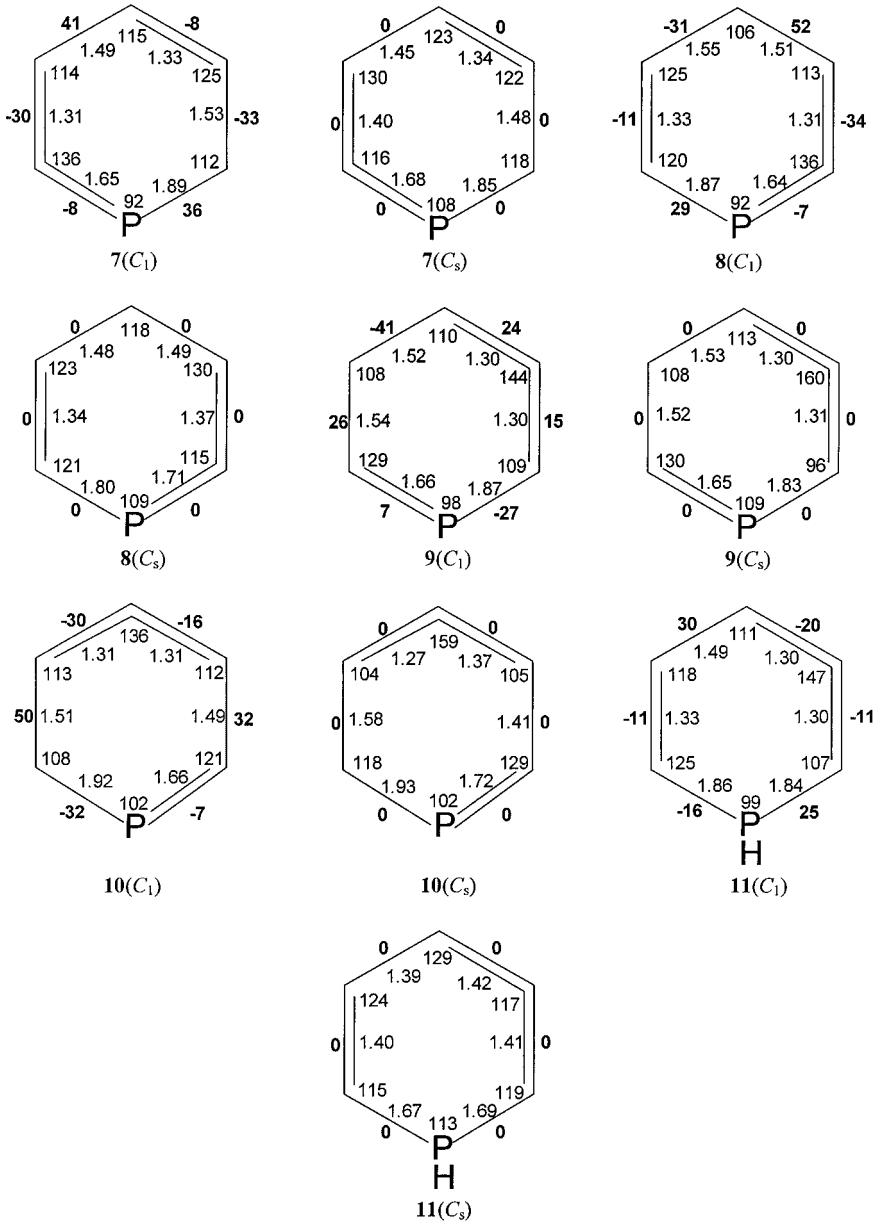


FIGURE 1 HF/6-311++G** calculated structural parameters (bond lengths in Å, bond angles, and dihedral angles in degrees) for isophosphinines **7–11**.

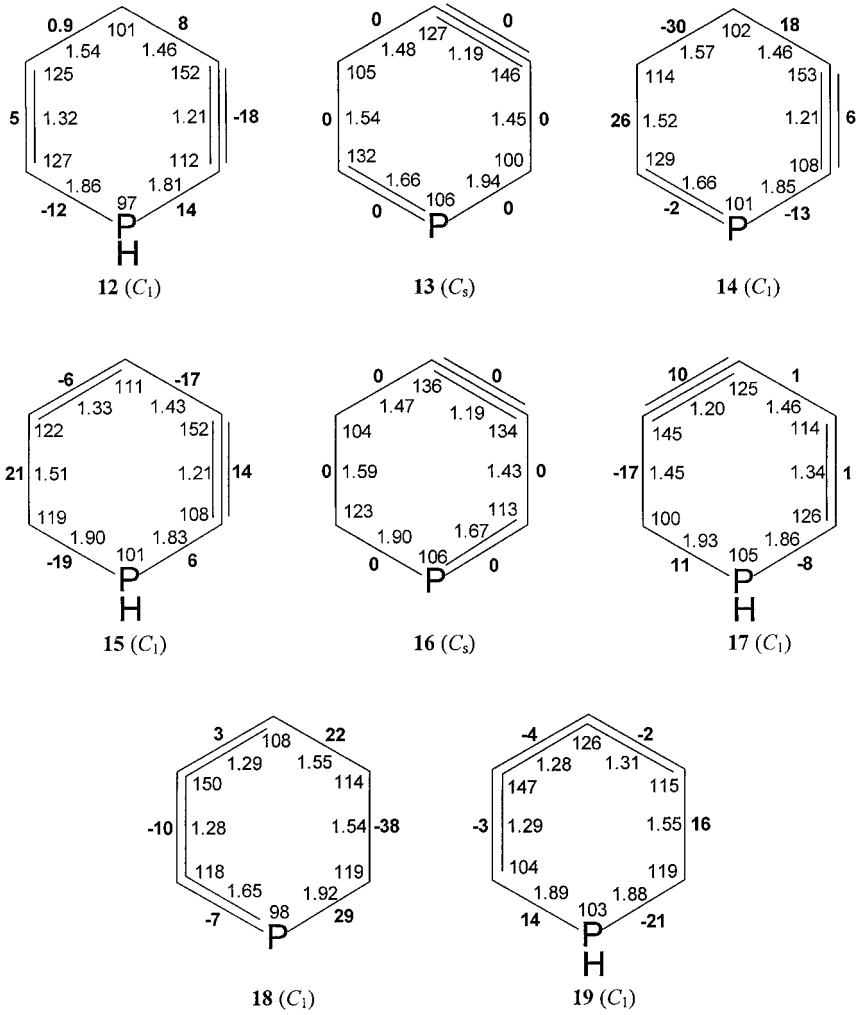


FIGURE 2 HF/6-311++G** calculated structural parameters (bond lengths in Å, bond angles, and dihedral angles in degrees) for isophosphinines **12–19**.

moieties via planar transition states. According to MP4(SDQ)/6-31G* calculations for the triplet electron configuration, the planar geometries of isophosphinines **7–10** are slightly more stable than the C_1-symmetric forms.

Isophosphinines **12–17** have enynic grouping. Stabilities of these isomers depend strongly on the extent of deviation from linear

arrangement of the acetylenic moiety. The internal angles of the acetylenic carbon atoms are strongly bent in isomers **12–17** (see Figure 2). Finally strained cyclic butatriene **19** is calculated to be the least stable isophosphinine in all the used methods.

According to these calculations, allenic isomers **7–11** are about 8–18 kcal mol^{-1} more stable than the acetylenic geometries **12–17**. The butatrienic isomers **18** and **19** are less stable than the most stable allenic structure **7** by 17.7 and 26.5 kcal mol^{-1} respectively. An energy difference of 1.7 kcal mol^{-1} arises from the occupation of different positions by phosphorus atom in enallenic geometries **7–11**, but this difference in acetylenic isomers **12–17** is 8.3 kcal mol^{-1}.

CONCLUSIONS

Ab initio SCF-MO calculations provide a fairly clear picture of the geometries of isophosphinines **7–19** from both the structural and energetic points of view. Isomers **7–11**, with an enallenic grouping, are more stable than the structures **12–17** with an acetylenic moiety. Strained cyclic butatrienic structures **18** and **19** are calculated to be the least stable isophosphinines. It would be valuable, of course, to have direct structural data on isophosphinines **7–19** for comparison with the results of the ab initio calculations.

CALCULATIONS

The ab initio molecular orbital calculations, were carried out using the GAUSSIAN 98 program.[14] Geometries for all structures were fully optimized by means of analytical energy gradients by Berny optimizer with no geometrical constraints.[15,16] Initial geometry optimizations were carried out at HF/6-31G* level, and zero point energies obtained at this level were scaled by 0.9135. In light of the fact that correction for electron correlation is often important in conformation studies, we have made use of several methods for calculating this correction. One approach involved the density functional theory at the B3LYP/6-31G* level.[17] This makes use of a three-parameter functional that is a hybride of exact (Hartree-Fock) exchange terms, similar to those first suggested by Becke.[18] Geometry optimizations also were carried out using HF/6-31G** HF/6-311G** HF/6-311++G**, and RMP2-FC/6-31G* followed by a MP4(SDQ)/6-31G* calculations using the RMP2-FC/6-31G* geometry, allowing a comparison with the B3LYP/6-31G* results.

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