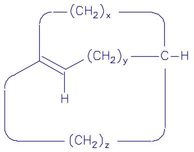
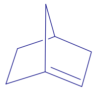
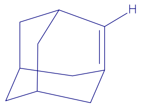
SOME POSSIBLE PROBLEMS FOR INVESTIGATION WITH MOLECULAR MECHANICS

These are mostly problems dealing with strained hydrocarbons. Choose one (or suggest one of your own) and sign up for it. [First come, first served; no duplications will be permitted between members of the class.] You should set up and calculate all of the molecules stated in a given problem; also do any related compounds which your own imagination suggests. Be creative! You'll find that as you get preliminary answers, new "experiments" (i.e. new MM calculations) will be suggested. Get printouts of the structure (SDUMP) with pertinent energies, bond lengths, bond angles, dihedral angles, etc. displayed; to avoid cluttering a given page, you may want to use several sheets to print all of this out. You should also save your structures on the 3.5-inch diskettes (WRITF) and turn these in. Finally, you should examine the data (energies, bond lengths, bond angles, dihedral angles, etc.) and write up a discussion (three or more pages, whatever it takes) of your calculations, comparing them with literature results where appropriate. Be sure to include numerical values from the calculations to support any claims made in your discussion. Pay special attention to major sources of strain energy (where appropriate) and to unusual or interesting structural features.

1. Bredt's rule violations. For various values of x, y, and z in the generalized structure shown, calculate the strain energy. How does the double bond's geometry differ from that of an unstrained alkene? The [2.2.1] (shown), [2.2.2], [3.2.2], and [3.3.1] cases are of interest. Adamantene (shown) is a special case; there are a few recent reports of its transient existence. Do calculations on these (and other of your choosing).
   [Warner, P. M. *Chem. Rev.* **1989,** *89,* 1067 and references therein; see also Luef, W.; Keese, R. Top. Stereochem. **1991,** *20,* 231.]

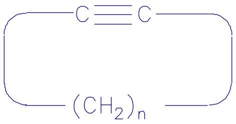



[2·2·1]

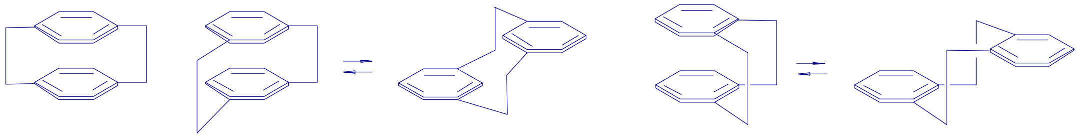


Adamantene

2. Cycloalkynes. The smallest one prepared and isolated (although very reactive) is cycloheptyne. How strained are the C_4 through C_{11} cycloalkynes? Is the crossover in stability from the C_6 to the C_7 compound reasonable, based on your calculations? [For the larger rings, there is a fair degree of conformational flexibility around the various C-C bonds; try to be sure that you have found the global, rather than a local, minimum.]



3. Cyclophanes. These consist of benzene rings held face-to-face (in some cases) by short bridges. Shown here are the various [2,2] cyclophanes; note that the ortho and meta forms have the possibility of existing in two different conformations. What are the relative energies of the five forms shown? How bent are the benzene rings?
   [Tsuzuki, S.; Tanabe, K. *J. Chem. Soc., Perkin Trans. 2* **1990,** 1687.]

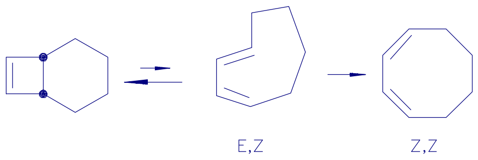


4. Steric bulk. How strained are the alkanes $(t\text{-}Bu)_3C\text{-}R$, ranging from R = H to R = t-Bu? How about the same series for the 1,2-disubstituted alkenes cis-t-Bu-CH=CH-R?

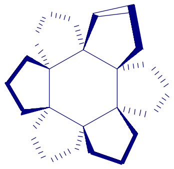
5. Equatorial vs. axial substituents in cyclohexane. For G-cyclohexane, where G = -Me, -F, -OH, $-NH_2$, $-BH_2$, what are the relative energies of the two conformations? How do these compare with the experimentally determined A-values? What is the steric effect of lone-pairs on the

heteroatoms?

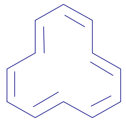
6. In the orbital symmetry course (Chem. 651) a stepwise mechanism has been suggested for the thermal conversion of cis-bicyclo[4.2.0]oct-7-ene into Z,Z-1,3-cyclooctadiene. What does molecular mechanics indicate about the feasibility of this? What about the analogous transformation of the [3.2.0] system? How well does molecular mechanics (a non-orbital calculation) mimic the orbital symmetry calculation?

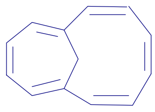


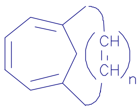
7. In the second issue of *Angew. Chem., Int. Ed. Engl.* in 1987, the synthesis of this compound is reported. How strained is it? What about the corresponding compound with a central four-membered ring? What about a central eight-membered ring? Compare these to the permethylated cyclohexane, cyclobutane, and cyclooctane.



8. The syntheses of the [12], [18], [20], [22], and [24] 1,6-methanobridged annulenes have been reported [*J. Chem. Soc., Chem. Commun.* **1987**, 199]. These are reported to be appropriately homoaromatic or homoantiaromatic; unlike 1,6-methano[10]annulene, these compounds appear to be conformationally flexible. Calculate the even-numbered [10] through [24] annulenes and 1,6-bridged methanoannulenes; how flexible or planar do these compounds seem to be?

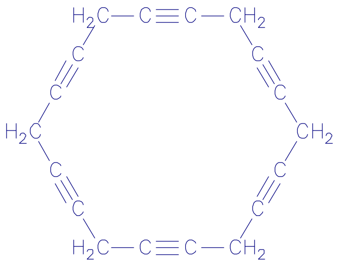

[12]annulene


methano[12]annulene

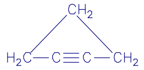


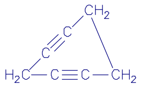
n = 3 [12]
n = 4 [14]
etc.

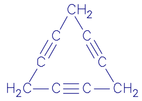
9. An acetylenic linkage (C≡C) is linear, and can be inserted between a pair of CH_2 groups with no change in geometry except for increasing the distance between the sp^3 carbons. Consider the effect of inserting six such C≡C units between adjacent pairs of CH_2 groups in cyclohexane. Is the resulting cyclooctadeca-1,4,7,10,13,16-hexayne still a chair, compared to cyclohexane? Similarly: what about inserting four C≡C units into a four-membered ring or five into a five-membered ring? What are the energies of an axial vs. equatorial t-butyl group in the eighteen-membered ring (shown)?



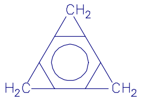
10. Here is a problem related to number 9 (above). Start with cyclopropane and insert one, two, or three C≡C units between pairs of CH_2 groups. Calculate the energies of the molecules. For the compound with three acetylenic units, is the molecule better represented by the non-aromatic or the aromatic structure? [The current version of the MM program does not have the proper parameters for a cyclopropene ring; don't do MM calculations on the aromatic structure.]



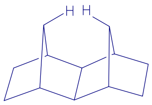


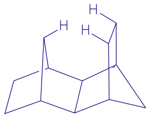


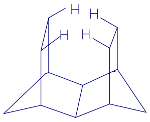
or



11. Exo-fused norbornyl derivatives are know to undergo transannular hydride transfers in the carbocations. How close are the hydrogens in the hydrocarbons shown? What are the relative strain energies vs. the non-fused analogs?

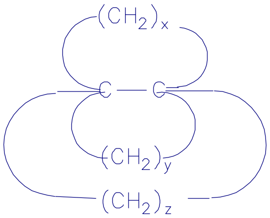


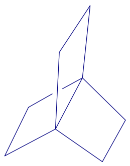




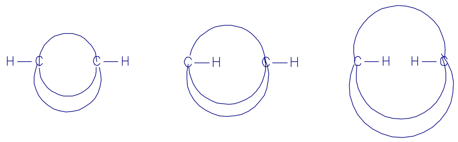
12. Trans-cycloalkenes. Most cycloalkenes are cis. Trans cycloalkenes as small as the trans-cyclooctene are isolable; smaller rings have been detected but not isolated. How strained are the C_6 through C_{11} trans cycloalkenes? For comparison to the analogous cis-cycloalkenes, you may use experimentally-derived heats of formation.
[see the literature citation from Problem 1, and references therein.]

13. Propellanes are tricyclo[x.y.z.0] molecules. How strained are the [2.2.2.0] and related [2.y.z.0] compounds?
[For some recent calculations on propellanes having at least one four-membered ring, see Wiberg, K. B.; Caringi, J. J.; Matturo, M. G. J. Am. Chem. Soc. **1990**, 112, 5854.]

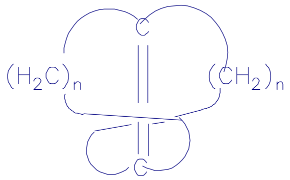




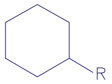
14. Small bicyclic molecules normally have the bridgehead hydrogens (or other substituents) pointing out from the center of the molecule, but for sufficiently large rings the in-out and even the in-in structures are possible. Calculate the energies of the out-out, in-out, and in-in isomers of the bicyclo[5.5.5] and bicyclo[4.4.4] alkanes. What are the relative stabilities of the various isomers?
[For a recent discussion, see Alder, R. Tetrahedron **1990,** 46, 683.]



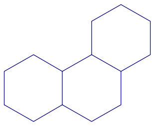
15. Betweenanenes are bis-trans-cycloalkenes fused at the double bond. That is, they are two fused cycloalkenes which share a common double bond, but in which that double bond is trans in both rings. What factors control the stability of the [n,n] compounds ranging from n = 8 to n = 11? [If someone else does Problem 12, a comparison of those answers with these would be informative; see the literature citation from Problem 1, and references therein.]



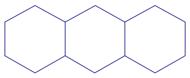
16. Do a complete conformational analysis of monoalkylcyclohexanes with R = Me, Et, iPr, tBu. Calculate relative energies of axial vs. equatorial conformations; be sure to include both of the completely staggered conformations for Et and iPr, in both axial and equatorial conformations. Do the axial/equatorial energy differences calculated for the series methyl, ethyl, isopropyl agree with expectations? Discuss fully.
[Booth, H.; Everett, J. R. *J. Chem. Soc., Perkin Trans 2* **1980**, 255; Squillacote, M. E. *J. Chem. Soc., Chem. Commun.* **1986***,* 1406.]



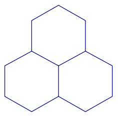
17. Do the complete conformational analysis of the perhydrophenanthrenes (six isomers).
[Hönig, H.; Allinger, N. L. *J. Org. Chem.* **1985,** *50,* 4630.]



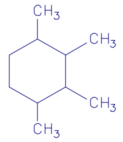
18. Do the complete conformational analysis of the perhydroanthracenes (five isomers).
[Allinger, N. L.; Wuesthoff, M. T. *J. Org. Chem.* **1971,** *36,* 2051.]



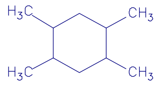
19. Do the complete conformational analysis of the perhydrophenalenes (four isomers).
[Dillen, J. L. M. *J. Org. Chem.* **1984,** *49,* 3800.]



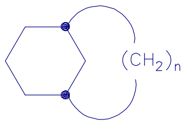
20. Do the complete conformational analysis of the 1,2,3,4-tetramethylcyclohexanes (six isomers) plus an estimation of the 1,3-diaxial CH_3/CH_3 interaction.
[Mann, G.; Werner, H.; Miethe, D.; Mühlstädt, M. *Tetrahedron* **1972,** *28,* 1839.]



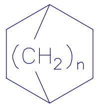
21. Do the complete conformational analysis of the 1,2,4,5-tetramethylcyclohexanes (five isomers) plus an estimation of the 1,3-diaxial CH_3/CH_3 interaction.
[Allinger, N. L.; Pamphilis, N. A. *J. Org. Chem.* **1971,** *36,* 3437.]



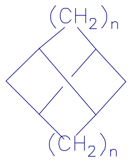
22. Do the complete conformational analysis of the various bicyclo[3.n.1]alkanes. For n = 3, calculate the energies of the three reasonable conformations: chair-chair, chair-twist, and twist-twist; comment on the strain factors which affect the relative energies. Similarly, calculate the energies of the chair and twist conformations for the molecule with n = 1 and the one with n = 2.
[Camps, P.; Castane, J.; Feliz, M.; Jaime, C.; Minguillon, C. *Chem. Ber.* **1989,** *122,* 1313.]



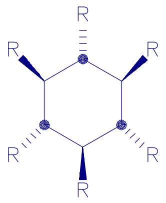
23. Do the conformational analysis of the bicyclo[2.2.n]alkanes. Calculate the geometries and energies for n = 1, 2, 3, etc. How large does n have to be for the six-membered ring to exist in an unstrained chair conformation?



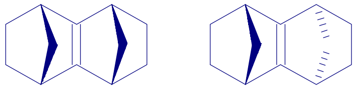
24. Do the conformational analysis of the doubly 1,4-bridged cyclohexanes. Calculate the geometries and energies for n = 1, 2, 3, etc. When n = 2, the molecule is called twistane - how large must n be before the central ring can exist in an unstrained chair conformation?



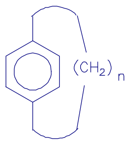
25. Do the conformational analysis of all-trans-1,2,3,4,5,6-hexaalkylcyclohexanes. For R = CH_3, it is alleged that the all equatorial conformation is more stable than the all axial, but that R = $CH(CH_3)_2$ exists preferentially as the all axial structure. Calculate the geometries and energies of the all equatorial and all axial conformations of R = methyl, ethyl, and isopropyl.
[Goren, Z.; Biali, S. E. *J. Am. Chem. Soc.* **1990**, *112,* 893; Golan, O; Goren, Z.; Biali, S. E. *Ibid.* **1990**. *112.* 9300.]



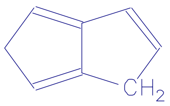
26. Calculate the strain energy of pyramidalized alkenes, such as those shown to the right.
[Borden, W. T. *Chem. Rev.* **1989,** *89,* 1095; Ermer, O.; Bell, P.; Mason, S. A. *Angew. Chem., Int. Ed. Engl.* **1989,** *28,* 1239; Irngartinger, H.; Deuter, J.; Charumilind, P.; Paquette, L. A. *J. Am. Chem. Soc.* **1989,** *111,* 9236; see also Luef, W.; Keese, R. *Top. Stereochem.* **1991**, *20*, 231.]



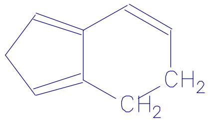
27 Calculate the strain energy and geometry of the various [n]-paracyclophanes (related to the cyclophanes in Problem 3, but with only one benzene ring).
[Tobe, Y.; Takahashi, T.; Ishikawa, T.; Yoshimura, M.; Suwa, M.; Kobiro, K.; Kakiuchi, K.; Gleiter, R. *J. Am. Chem. Soc.* **1990**, *112,* 8889; Tobe, T.; Takahashi, T.; Kobiro, K.; Kakiuchi, K. *Chem. Lett.* **1990**, 1587; see also the reference from Problem 3.]



28. There are five possible isomers for the bicyclo[3.3.0]octatrienes, of which **A** is one. Do an MM analysis (including π calculations) for **A** and its four isomers; move the pair of double bonds around the left-hand five-membered ring in order to generate the other structures. Similarly, do the complete analysis for the homologous **B** and its four positional isomers. Comment on the importance of π-conjugation in stabilizing the various [3.3.0] and [4.3.0] systems.
[Griesbeck, A. G.; Peters, K.; Peters, E.-M.; von Schnering, H. G. *Angew. Chem., Int. Ed. Engl.* **1990,** *29*, 803.]



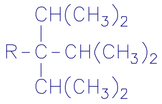
A



B

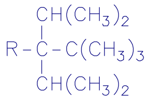
29. Do a complete MM analysis of compound **A** when R = H and when R = CH_3. Do the same for R = H and R = CH_3 for system **B**. Compare your answers with the calculated and experimental quantities in the literature citation; be sure to see the article for which conformations are to be calculated - do the relatively stable conformations <u>only</u>.
[Anderson, J. E.; Bettels, B. R. *Tetrahedron* **1990,** *46,* 5353.]

A



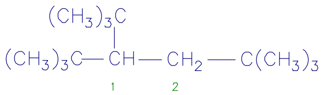
$R-\overset{CH(CH_3)_2}{\underset{CH(CH_3)_2}{C}}-CH(CH_3)_2$

B



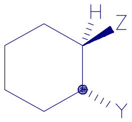
$R-\overset{CH(CH_3)_2}{\underset{CH(CH_3)_2}{C}}-C(CH_3)_3$

30. A recent article discusses the conformational analysis of the material shown to the right, incorrectly called in the article by a non-IUPAC name: 1,1,2-tri-t-butylethane. Do a complete conformational analysis of rotational possibilities about the C_1-C_2 bond and compare your results (energies, angles, bond lengths, etc.) with those in the cited article.
[Anderson, J. E. *J. Chem. Soc., Perkin Trans. 2* **1991***,* 299.]

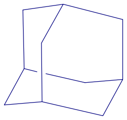


$(CH_3)_3C-\overset{(CH_3)_3C}{CH}-CH_2-C(CH_3)_3$

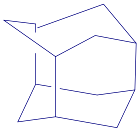
31. Do a complete MM analysis of the trans-1,2-disubstituted compounds shown to the right in which Z is SCH_3 (if you wish, you can also do Z = $SOCH_3$ or SO_2CH_3) and in which Y can be OH, OCH_3, F, Cl, Br, or **I**.
[Carreño, M. C.; Carretero, J. C.; Garcia Ruano, J. L.; Rodriguez, J. H. *Tetrahedron* **1990***, 46,* 5649.]



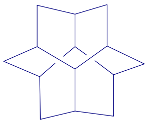
32. Carbon crystals exist in several allotropic forms. Three of these are based on repeating



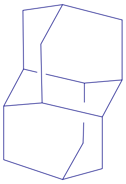
adamantane



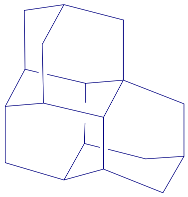
iceane



BC–8



diamantane

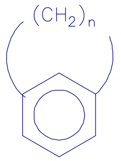


triamantane

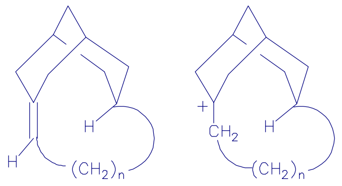
units of adamantane ($C_{10}H_{16}$), iceane ($C_{12}H_{18}$), and BC-8 ($C_{14}H_{20}$) whose structures are shown above. Calculate the strain energies of these three "monomeric" units. Then, try extending these units (e.g., from adamantane to diadamantane and triamantane) to see how the strain energy changes; do similar calculations on extensions of the iceane and BC-8 units.
[Johnston, R. L.; Hoffmann, R. *J. Am. Chem. Soc.* **1989***, 111,* 810; Laqua, G.; Musso, H.; Boland, W.; Ahlrichs, R. *ibid.* **1990***, 112,* 7391.]

33. Do a complete conformational analysis (energies, geometries, etc.) of molecules with quaternary carbons: e.g. ranging from $(CH_3CH_2)_4C$ through Et_xCMe_y to $(CH_3)_4C$; be sure to see the article for which conformations are to be calculated.
[Alder, R. W.; Maunder, C. M.; Orpen, A. G. *Tetrahedron Lett.* **1990***, 46,* 6717.]

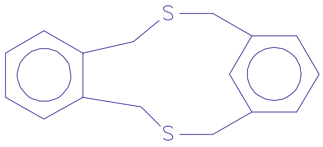
34. Use molecular mechanics to analyze the conformations of the $(CH_2)_n$ bridge in the (n)-metacyclophanes with n = 4 to n = 8. Discuss the strain, geometry, etc. as a function of n.
[Jenneskens, L. W.; de Boer, H. J. R.; de Wolf, W. H..; Bickelhaupt, F. *J. Am. Chem. Soc.* **1990***, 112,* 8941 and references cited therein.]

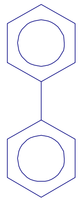


35. Use molecular mechanics to calculate the energy, geometry, strain, etc. of the bicyclic alkene (shown to the right) and of its conjugate acid after protonation; do the calculations for n = 4, 5, and 6. Determine the distance from the "inside" H to the double bond and to the cationic center to see if there is a possibility of having a hydrido-bridged structure; see the cited article for the meaning of the preceding phrase.
[Sorensen, T. S.; Whitworth, S. M. *J. Am. Chem. Soc.* **1990,** *112,* 8135.]



36. There are six reasonable conformations for the molecule shown to the right. All six are shown in the article cited below. Calculate the relative energies of these six conformations and compare your numbers with those obtained by the authors (using a somewhat different molecular mechanics calculation than MMX). Use molecular models to help you see the characteristics of the conformations.
[Bodwell, G. J.; Ernst, L.; Hopf, H.; Jones, P. G.; McNally, J. P.; Schomburg, D. *Chem. Ber.* **1990***, 123,* 2381.]

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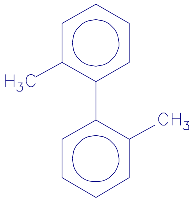

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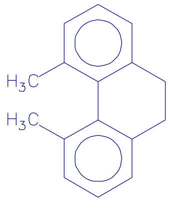

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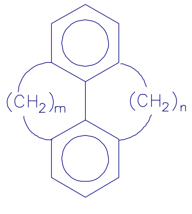


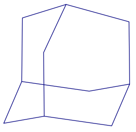
4

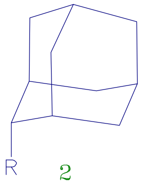
37. The first "triumph" of the earliest crude version of molecular mechanics was the calculation of the rotation barrier around the central bond of hindered biphenyls. Using the newer calculation methods (e.g. MMX) along with personal computers, more sophisticated calculations on larger structures can be done. For compounds **1**, **2**, and **3**, compute the energy and dihedral angle of the most stable (twisted) conformation and the energy of the forced all-planar conformation (which is the "transition state" for rotation). Do the same for selected values of m and n in structure **4**. Compare your answers with the experimental and theoretical values given in the reference.
[Müllen, K.; Heinz, W.; Klärner, F.-G.; Roth, W. R.; Kindermann, I.; Adamczak, O.; Wette, M.; Lex, J. *Chem. Ber.* **1990***, 123*, 2349.]

38. Steric effects can play a large role in the rate of S_N1 reactions of tertiary alkyl halides and related R_3C-X compounds. Use MMX to determine the steric energy difference between R-OH and R^+ for the series R- = Me_3C-, Me_2(t-Bu)C-, Me$(t\text{-}Bu)_2$C-, and $(t\text{-}Bu)_3$C-. Then plot the experimental rate data (in logarithmic form) vs. ΔE^{st}; see the cited article for details.
[Müller, P.; Mareda, J. *J. Comp. Chem.* **1989***, 10,* 863.]

39. Do the same (as suggested in Problem 38) for the series 1-R-1-OH-cycloalkane where R is CH_3 or t-Bu and the cycloalkane varies from five-to six- to seven-membered. See the same reference for details and for the experimental rate data.

40. Adamantane (**1**) is a rigid molecule consisting of four cyclohexanes in chair conformations; make a model if you don't see this. An alkyl substituent (as in **2**) is, therefore, axial in one six-membered ring, equatorial in another. Do MM calculations to see how the geometry and heat of formation vary as R changes from methyl to ethyl to isopropyl to tert-butyl; compare these numbers with those from axial-alkyl-cyclohexane and equatorial-alkyl-cyclohexane along the same series of alkyl groups. Then, for compound **3**, compute the energy difference between the isomer shown (R = methyl through tert-butyl) and the epimer with R oriented away from the axial methyl. Compare your calculated geometries with those reported for **2**, R = t-Bu and **3**, R = t-Bu (see article).
[Duddeck, H.; Rosenbaum, D. *J. Org. Chem.* **1991***, 56*, 1707.]


1



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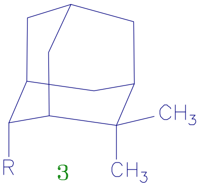
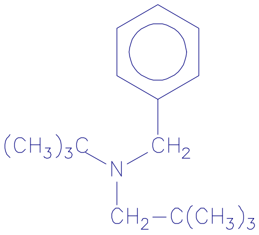
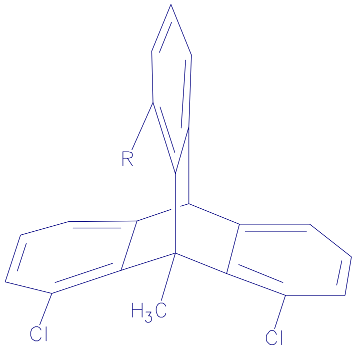


3

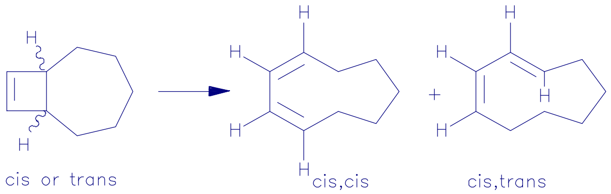
41. Consider the case of N-tert-butyl-N-neopentylbenzylamine (shown to the right). According to a recent article, "The anti arrangement of the t-BuNCH$_2$-t-Bu part of the molecule greatly limits the space available for the benzyl substituent, and only one conformation about the N-benzyl bond is populated. Molecular mechanics calculations suggest that the benzyl group occupies a pocket or cleft ... " The assignment here is to confirm or disprove the preceding assertion and to examine other tertiary amines of the type PhCH$_2$-N-(t-alkyl)(CH$_2$-t-alkyl).
[Anderson, J. E.; Tocher, D. A.; Casarini, D.; Lunazzi, L. *J. Org. Chem.* **1991,** *56*, 1731; Anderson, J. E.; Casarini, D.; Lunazzi, L. *J. Chem. Soc., Perkin Trans. 2* **1991,** 1431.]



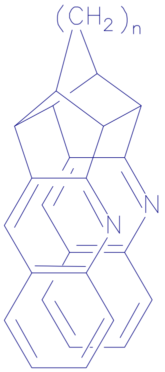
42. In substituted 9-methyltriptycenes (shown to the right), there is restricted rotation about the C-CH$_3$ bond. Whereas butane has a barrier of about 5 kcal/mol about the central bond, these triptycenes have experimentally measured barriers of 10 - 15 kcal/mole. Calculate the energy of the most stable and least stable conformations for R = H, F, OCH$_3$, CH$_3$, and t-Bu. Compare your numbers with the experimental values and with the calculated values in the cited article. Comment on which of the parameters that make up the MMX energy are the most important in determining the barrier to rotation.
[Yamamoto, G.; Oki, M. *Bull. Chem. Soc. Jpn.* **1990,** *63,* 3550.]



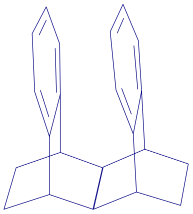
43. The electrocyclic opening (with heat or with light) of cis- or trans-bicyclo[5.2.0]non-8-ene can produce cis,cis and/or cis,trans-1,3-cyclononadiene. Calculate the ground-state geometries and energies of both stereoisomers of the bicyclic reactant. Then, calculate the energies and geometries of both the cis,cis and cis,trans monocyclic dienes, not only in their lowest energy form but also in the conformation in which the four carbons of the diene are coplanar. See the cited article (Scheme II and p. 1578, left column) for details on this.
[Leigh, W. J.; Zheng, K.; Clark, K. B. *J. Org. Chem.* **1991***, 56*, 1574.]

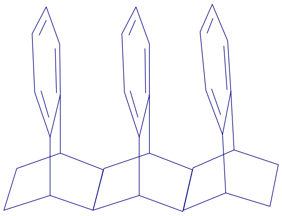


44. Although most of the interest in cyclophanes has been devoted to the para,para and meta,meta types (see Problem 3), ortho,ortho-cyclophanes are also intriguing molecules when they are constructed on rigid frameworks which force the aromatic rings to be parallel (or nearly so) to one another. Consider the molecules shown to the right in which two quinolines are held in close proximity. Do calculations of geometry and energy for the cases n = 1, 2, and 3. Compare your answers for the internuclear distances with those found in Table II and in the discussion on p. 1495 in the cited article.
[Lim, J.-L.; Chirayil, S.; Thummel, R. P. *J. Org. Chem.* **1991,** *56,* 1492; Taffarel, E.; Chirayil, S.; Thummel, R. P. *J. Org. Chem.* **1994**, *59* 823.]

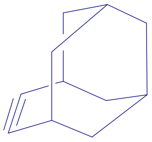


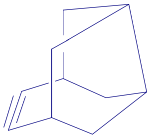
45. Another pair of molecules which have approximately parallel benzene rings in close proximity is shown to the right. Use MM calculations to determine the separation between carbon atoms of the rings; determine the degree of planarity of each ring. Compare your answers with the experimental values from the X-ray crystal structures in the cited article.
[Grimme, W.; Kämmerling, H. T.; Lex, J.; Gleiter, R.; Heinze, J.; Dietrich, M. *Angew. Chem., Int. Ed. Engl.* **1991***, 30,* 205.]

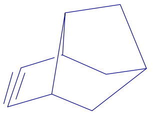


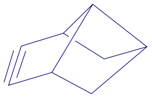


46. The tricyclic alkyne $C_{11}H_{14}$ shown to the right has two cycloheptyne units in its structure. Nevertheless, it is stated that MM calculations show that it is more like cyclohexyne than cycloheptyne in its structure and strain energy. Do complete MM calculations of the structure and energy of cycloheptyne, cyclohexyne, and the four tricyclic alkynes from $C_{11}H_{14}$ through C_8H_8.
[Komatsu, K.; Kamo, H.; Tsuji, R.; Masuda, H.; Takeuchi, K. *J. Chem. Soc., Chem. Commun.* **1991***,* 71.]


$C_{11}H_{14}$

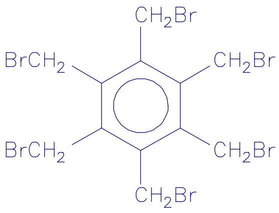

$C_{10}H_{12}$


C_9H_{10}

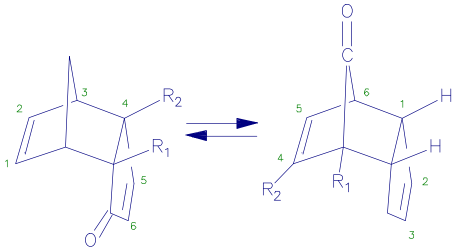

C_8H_8

47. Ammonia has a nearly perfect tetrahedral shape with a 107° angle between any pair of H-N bonds. It is alleged that highly crowded amines flatten out, such that the bond angles approach 120°. Use MM to calculate the geometry of R_3N: where R = CH_3 or CH_2CH_3 or $CH(CH_3)_2$ or $C(CH_3)_3$. Compare your answers with the calculated and experimental values for triisopropylamine in the cited article; also compare with the analogous series $R_3O:^+$ and R_3C-H where, again, R can vary from methyl to t-butyl.
[Bock, H.; Goebel, I.; Havlas, Z.; Liedle, S.; Oberhammer, S. *Angew. Chem., Int. Ed. Engl.* **1991,** *30,* 187.]

48. Consider the case of hexakis(bromomethyl)benzene, whose structure is shown to the right. There are eight distinctly different conformations for this compound (see Figure 4 in the cited reference for a shorthand notation). Compute the relative energies of these eight conformations; compare your values with those in the article; assign the variation in conformational energy to the responsible factors.
[Golan, N. Z. O.; Biali, S. E. *J. Org. Chem.* **1991***, 56*, 2444.]



49. When heated, the structures shown to the right equilibrate by a Cope rearrangement mechanism; the numbered carbons should help you to see the necessary bond-making and bond-breaking changes which occur. The position of equilibrium in this reaction (as a function of substituents) has been discussed in a recent article. Use MM to calculate the relative energies of the equilibrating partners for the parent case ($R_1 = R_2 = H$); for the monomethyl derivative ($R_1 = CH_3$, $R_2 = H$); and for two esters ($R_1 = H$, $R_2 = COOCH_3$; $R_1 = CH_3$, $R_2 = COOCH_3$). Compare your results with the experimental results and with the MM calculations cited (see p. 1496, 2nd paragraph).
[Lange, J. H. M.; Klunder, A. J. H.; Zwanenburg, B. *Tetrahedron* **1991***, 47,* 1495.]



50. The heats of reduction of a series of carbonyl compounds (aldehydes and ketones) to the corresponding alcohols have been measured; from these, the heats of formation of the oxidized and reduced species have been determined. Use molecular mechanics to compute the heats of formation of (a) aldehydes ethanal, propanal, butanal, and 2-methylpropanal; (b) ketones acetone and the five cycloalkanones from the 4- through the 8-membered rings; and (c) the alcohol reduction products. Compare your answers with the experimental values and the computed MM3 values cited in the article.
[Wiberg, K. B.; Crocker, L. S.; Morgan, K. M. *J. Am. Chem. Soc.* **1991***, 113,* 3447.]

51. meta,meta-Cyclophane conformations **A** and **B** equilibrate at room temperature, presumably via unstable conformation **C**. Use molecular mechanics (a) to calculate the energies of these three conformations for comparison with the experimental equilibrium values and (b) to determine the various bond lengths and dihedral angles for comparison with the calculated and experimental values in Table **III** of the cited article.
[Nishimura, J.; Horikoshi, Y.; Wada, Y.; Takahashi, H.; Sato, M. *J. Am. Chem. Soc.* **1991,** *113,* 3485.]