Pyramidalized Olefins: Ab Initio Study and X-ray Structure Determination of Bicyclo[2.2.2]octadienes

Richard Vaughan Williams,* W. Daniel Edwards, and
Vijay R. Gadgil

*Department of Chemistry, University of Idaho,
Moscow, Idaho 83844-2343*

Michael E. Colvin*

*Computational Biochemistry Group,
Biology and Biotechnology Research Program,
Lawrence Livermore National Laboratory, Mailstop L-452,
Livermore, California 94550*

Edward T. Seidl

*Distributed Computing Department,
Sandia National Laboratories, California, P.O. Box 969,
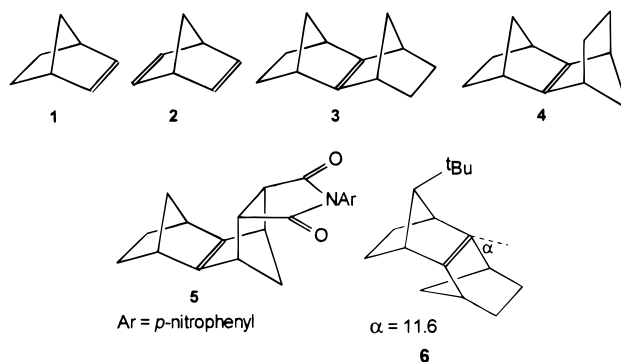Livermore, California 94551*

Dick van der Helm and M. Bilayet Hossain

*Department of Chemistry, University of Oklahoma,
Norman, Oklahoma 73019*

Strained alkenes (those with the R−C=C bond angle less than 120°) of low symmetry have a tendency to adopt a pyramidal geometry.[1] The force constant for the butterfly bending of the double bond decreases with decreasing R−C=C bond angle, and even for ethylene a pyramidal geometry is favored at H−C=C angles of less than 100°.[2] The double bond(s) in norbornene (**1**) and norbornadiene (**2**) are pyramidal, the deviation from planarity is about 7° and about 2–4°, respectively.[3–5] Similarly, it is not at all surprising that *syn*-sesquinorbornene (**3**), in agreement with calculations,[5,6] possesses a pyramidal double bond.[7] In contrast, the situation for *anti*-sesquinorbornene (**4**) was much less clear.[1,5] Continuing our interest in highly strained bridged polycyclic olefins,[8] we used high-order ab initio methods to study *anti*-sesquinorbornene and its derivatives. As we were

completing our investigations of **4**, an essentially identical study, by Holthausen and Koch,[5] appeared in the literature. We had reached the same conclusions as Holthausen and Koch; viz. *anti*-sesquinorbornene (**4**) has a planar ground state with a very low barrier to butterfly bending of the double bond. In addition, since the torsional energy surface is so flat, it is reasonable to postulate that unsymmetrically substituted analogues of **4** should have a pyramidal ground-state structure. In support of this prediction the imide **5** has been shown to be pyramidal by X-ray crystallography,[9] and our Hartree−Fock (HF)/6-31G** optimized structure of the *tert*-butyl derivative **6** has a bent minimum with a 168.4° butterfly angle.

Another strained system with potentially pyramidal double bonds is the bicyclo[2.2.2]octadienyl nucleus. This nucleus is less well-studied than the norbornenyl systems. Results from a recent relatively low-order ab initio calculation which did not include electron correlation indicate the double bonds in the parent bicyclo[2.2.2]-octadiene (**7**) to be planar.[10] The importance of a large basis set and electron correlation was amply demonstrated for **1**, **3**, and **4** in the work of Holthausen and Koch.[5] Therefore a reinvestigation of **7**, with a large basis set and including correlation, is essential. We are particularly interested in **7** in light of our recent investigation of the Diels−Alder cycloaddition to this nucleus.[8]

The stereochemistry of electrophilic, nucleophilic, radical, and pericyclic reactions on the norbornenyl nuclei (related to **1** and **2**) has been extensively studied.[11] The observed *exo* stereoselectivities in the norbornyl nuclei and π-facial selectivities in general have been rationalized in a variety of ways[12] including alkene pyramidalization.[3,13]

In contrast with the norbornenyl nucleus, the few electrophilic,[14] chelotropic,[15] and [2 + 2] cycloaddition[16]

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reactions investigated on bicyclo[2.2.2]octadiene (**7**) display a pronounced *endo* selectivity. We recently carried out the Diels−Alder cycloaddition between bicyclo[2.2.2]-octa-2,5-diene-2,3-dicarboxylic anhydride (**8**) and cyclopentadiene.[8] Of the eight possible products, we obtained only **9** and **10** (5:1) in 78% isolated yield. This is the first example demonstrating the stereoselectivity for the Diels−Alder addition to a simple bicyclo[2.2.2]octadiene. Again, in contrast with the norbornenyl system, there is a distinct preference for attack from the *endo* face.
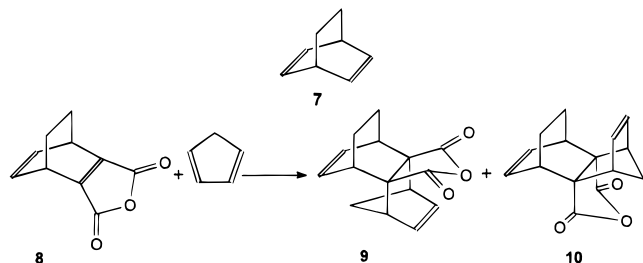
Differential steric factors are much less important in the bicyclo[2.2.2] systems **7** and **8** (ethano vs etheno bridges) than in the norbornenes **1** and **2** (methano vs etheno or ethano bridges). Face-selective torsional effects are also minimal in **7** and **8** as is apparent from consideration of molecular models and the optimized structure of **7**. We therefore carried out ab initio calculations on **7** in order to investigate the factors controlling the observed π-facial selectivity.

The Gaussian 92 suite of programs[17a] was used for calculations at the HF/6-31G* and second-order Møller−Plesset (MP2)/6-31G** levels on bicyclo[2.2.2]octadiene (**7**) and Gaussian 94[17b] for all calculations at the 6-31G** level on compounds **8**−**10**, **12**, and **13**. Even at the HF level of theory the olefinic hydrogens displayed an approximately 2° deviation (in the *exo* direction) from planarity. Including electron correlation resulted in a 3.18° *exo* pyramidalization. It should be noted that Holthausen and Koch,[5] using the MP2/6-31G** level of theory, obtained almost exact agreement with the experimentally determined pyramidalization in a norbornene derivative. Previous, lower-level calculations all underestimated this pyramidalization. In one of the very few structural studies of the bicyclo[2.2.2]octadiene nucleus, it is reported that the two carboxyl groups in **11** are twisted relative to each other.[18] Both carboxyls bend away from planarity in the *exo* direction. To obtain further confirmation for our predicted pyramidalization

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Table 1. Positional and Equivalent Isotropic Thermal Parameters for Non-Hydrogen Atoms[a]

atom	x	y	z	U_{eq}
O1	0.9978(1)	0.0227(2)	0.78412(7)	0.0304(3)
O2	1.1296(1)	0.0596(2)	0.90859(8)	0.0362(4)
O3	0.8081(2)	0.0445(2)	0.68076(7)	0.0395(4)
C1	1.0119(2)	0.0977(2)	0.8672(1)	0.0253(4)
C2	0.8619(2)	0.2149(2)	0.88486(9)	0.0202(4)
C3	0.7991(2)	0.3436(2)	0.95656(9)	0.0226(4)
C4	0.6306(2)	0.2533(3)	0.9700(1)	0.0277(5)
C5	0.5336(2)	0.2505(3)	0.9013(1)	0.0298(5)
C6	0.6123(2)	0.3378(3)	0.82333(9)	0.0266(4)
C7	0.7661(2)	0.2122(2)	0.81643(9)	0.0221(4)
C8	0.8480(2)	0.0909(2)	0.7505(1)	0.0271(4)
C9	0.7753(2)	0.5880(3)	0.9215(1)	0.0268(4)
C10	0.6646(2)	0.5843(3)	0.8448(1)	0.0267(4)

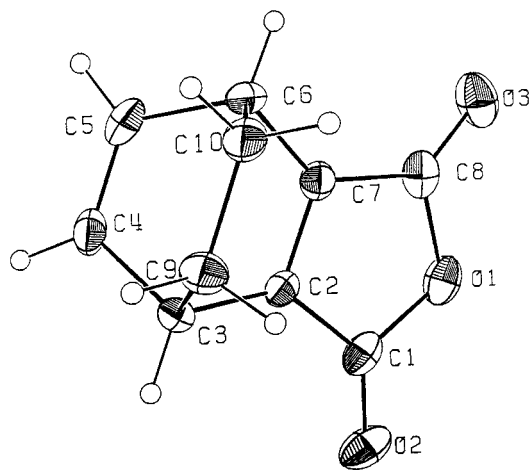[a] $U_{eq} = (1/3)\sum_i\sum_j U_i U_j a_i^* a_j^* a_i \cdot a_j$.

Figure 1. Perspective view of an ORTEP plot of a single molecule of anhydride **8**.

in the bicyclo[2.2.2]octadiene systems, we calculated the structure of our previously prepared[8] anhydride **8** and also determined its X-ray structure. Of most interest is the close agreement between the calculated (3.8°) and experimental (∼3°) deviations from planarity about the anhydride double bond.

X-ray Structure of Compound 8. The final atomic parameters are listed in Table 1. A perspective ORTEP plot of a single molecule of compound **8** is shown in Figure 1. Overall, the molecule has an approximate mirror symmetry. In the bicyclic system, the mean least-squares planes through C3, C4, C5, C6; C3, C2, C7, C6; C3, C6, C9, C10 form dihedral angles of nearly 120° with each other (123.4°, 118.8°, 117.8°). Each six-membered ring adopts a boat conformation, with a slightly flattened C2, C3, C4, C5, C6, C7 ring ($|\tau| = 52.2°$) and slightly puckered conformations for the other two rings ($|\tau| = 57.4°$, 57.6°). The five-membered anhydride ring is perfectly planar, with root-mean-square deviation of 0.003 Å. The atoms C3 and C6 both lie slightly out of this plane on the same side as the C9, C10 bridging atoms, with deviations of 0.072 and 0.079 Å, respectively. These deviations translate into an inclination of approximately 3° for the C2−C3 and C7−C6 bonds with the anhydride ring. The overall geometry of the bicyclic system is, in general, comparable to other known structures.[18−20] However, the elongations of the C3−C9

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Table 2. Calculated Total and Relative Electronic Energies[a] for Compounds 8–10, 12, 13, and 1,3-Cyclopentadiene

compd	HF/6-31G*//HF/6-31G* (rel E)	HF/6-31G**//HF/6-31G* (rel E)	MP2/6-31G**//HF/6-31G* (rel E)	MP2/6-31G**//MP2/6-31G** (rel E)
8	−607.914 194	−607.926 969	−609.767 70	−609.776 41
9	−800.731 721	−800.754 36	−803.305 54	−803.314 39
	(0.00)	(0.00)	(0.00)	(0.00)
10	−800.730 58	−800.753 19	−803.304 86	−803.313 76
	(0.72)	(0.74)	(0.43)	(0.39)
12	−800.728 59	−800.751 22	−803.303 73	−803.312 95
	(1.96)	(1.97)	(1.14)	(0.90)
13	−800.732 61	−800.755 16	−803.305 16	−803.313 76
	(−0.56)	(−0.50)	(0.24)	(0.39)
cyclopentadiene	−192.791 72	−192.802 41	−193.471 74	−193.473 26

[a] Total energies in Hartrees, relative energies (rel E) in kcal/mol.

Table 3. Heats of Reaction (kcal/mol) for 1,3-Cyclopentadiene + 8 → 9 or 10 or 12 or 13

compd	HF/6-31G*//HF/6-31G*	HF/6-31G**// HF/6-31G*	MP2/6-31G**//HF/6-31G*	MP2/6-31G**//MP2/6-31G**
9	−16.19	−15.68	−41.48	−40.61
10	−15.47	−14.94	−41.05	−40.22
12	−14.23	−13.71	−40.34	−39.71
13	−16.75	−16.18	−41.24	−40.22

Table 4. Thermodynamic Data

| compd	H[a] (kcal/mol)	S (cal/deg/mol)	G_{rel} @ 298 K[b] (kcal/mol)
8	112.39	92.10	
9	179.95	102.70	0.00
10	180.20	102.06	0.83
12	179.87	102.75	0.80
13	180.17	102.27	0.74

[a] Zero-point vibration energy and thermal corrections to enthalpy. [b] Using E(MP2//6-31G**).

(1.580 Å) and C6−C10 (1.578 Å) bonds observed in the present case are significantly larger than those observed in other related structures. It is also interesting to note that the C9−C10 bond is shorter (1.519 Å) than a normal C−C single bond.

The agreement between our calculated and experimental results is excellent with both methods demonstrating an approximately 3° (in the *exo* direction) pyramidalization of the olefinic substituents. In general, the facial selectivity of attack on a pyramidalized olefin parallels the pyramidalization.[6a,13,21] The π-facial selectivity observed in the [2.2.2] systems parallels the double-bond pyramidalization (this study) and also results in the minimization of steric interactions by approaching from the same face as the etheno bridge rather than the ethano bridge.

Once *endo* selectivity has taken place in the [2.2.2] system, the orientation of the attacking cyclopentadiene molecule is again determined so as to minimize steric interactions leading to 9 rather than 12. While, no doubt, kinetic control dominates in determining the products of this Diels−Alder reaction, it is interesting to note that the observed selectivity parallels the thermodynamic stability of the adducts (Table 2). The heats of reaction for 8 + cyclopentadiene to give 9, 10, 12, or 13 (Table 3) are very similar at each level of theory. The thermodynamic corrections to the enthalpy at 298 K (H) (including zero-point vibrational motion) and the entropy (S) are shown in Table 4. The HF/6-31G* optimizations and frequencies for compounds 8–10, 12, and 13 were carried out with MPQC,[22] a parallel quantum chemical program.

The relative free energies of isomers 9, 10, 12, and 13, calculated using the MP2//6-31G** electronic energy and the HF/6-31G* thermal corrections and entropy, are given in the last column of Table 4. Isomer 9 is predicted to be favored by less than 1 kcal/mol over the other isomers, reinforcing the notion that these reactions are kinetically controlled.

Preferred direction of attack
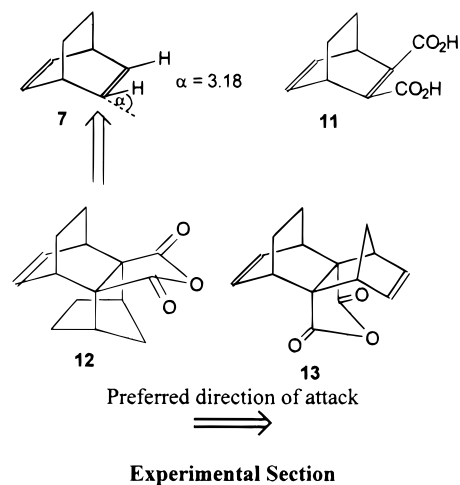
Experimental Section

The anhydride 8[8] was crystallized from hexane. A prismatic crystal size, 0.40 × 0.22 × 0.15 mm, was selected for all crystallographic measurements. Cell dimensions were obtained by least-squares fit to ±2θ values of 25 reflections measured at 223 K using Mo Kα₁ radiation. All X-ray measurements were carried out on an Enraf-Nonius CAD-4 diffractometer equipped with a liquid N₂ low-temperature device.

Crystal data: $C_{10}H_8O_3$, MW = 176.2, monoclinic, $P2_1/c$; a = 8.396(3), b = 5.999(9), c = 16.051(5) Å; β = 91.86(4)°, V = 808.0 Å³, z = 4, D_x = 1.194 g cm⁻³; $F(000)$ = 368, λ(Mo Kα) = 0.710 73 Å, μ(Mo Kα) = 0.65 cm⁻¹.

The intensity data of all the unique reflections within 2θ range 0−60° were collected at 223 ± 2 K using Mo Kα radiation and employing θ − 2θ scan technique with a variable scan width of (0.90 + 0.20 tan θ)° and horizontal aperture of (3.0 + 0.86 tan θ) mm. Three standard reflections were monitored every 2 h of

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X-ray exposure, and they showed maximum variation of 1.0%. The crystal orientation was checked regularly by three control reflections. A total of 2294 unique reflections were recorded of which 1737 reflections were considered 'observed' on the basis $I > 2\sigma(I)$. The intensities were corrected for Lorentz and polarization factors, but no absorption correction was made. The structure was solved by direct methods and the use of the program SHELXS-86[23] and refined by a full-matrix least-squares routine SHELX76[24] in which the quantity $\Sigma w(F_o - F_c)^2$ is minimized, where $w = 1/\sigma^2(F_o)$. All the hydrogen atoms were located from difference Fourier maps, and hydrogen parameters were refined. In the final stages of refinement, non-hydrogen atoms were given anisotropic thermal parameters. The refinement converged to a final $R = 0.047$, $R_w = 0.053$ for 1737 observations and 150 parameters, $S = 1.7$, $\Delta/\sigma = 0.05$, electron density in the final difference map ± 0.3 e/Å^3.

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Supporting Information Available: Table S2, bond distances, bond angles, and selected torsion angles for **8**; Table S3, anisotropic thermal parameters for **8**; and Table S4, hydrogen atom parameters for **8** (3 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information. Complete calculated data (structure and energy) for *tert*-butyl derivative **6** and the other systems studied in this work are available from: colvin@gutenberg.llnl.gov.

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