

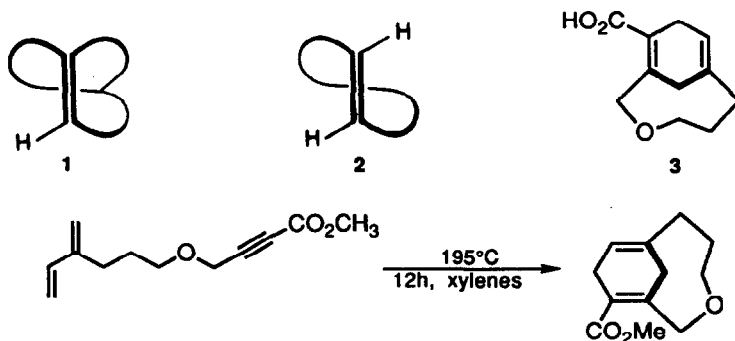
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STRUCTURAL STUDIES OF BRIDGEHEAD ALKENES. THE X-RAY CRYSTAL STRUCTURE OF 3-OXABICYCLO[5.3.1]DECA-1(10),7(8)-(ZZ)-DIENE-10-CARBOXYLIC ACID

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017 Summary: The X-ray crystal structure of 3-oxabicyclo[5.3.1]deca-1(10),7(8)-(ZZ)-diene-10-carboxylic acid, a highly strained bridgehead diene, is reported.

Bridgehead alkenes (1) comprise a subclass of *trans*-cycloalkenes (2), compounds that contain a distorted carbon-carbon double bond.¹ The magnitude of the distortion increases as the *trans*-cycloalkene ring size decreases. Despite considerable theoretical interest in these compounds,² there are few structural studies documenting the geometric distortions.^{3,4} We report the X-ray crystal structure of bridgehead diene 3, a compound containing two distorted bridgehead double bonds. Compound 3 constitutes the most highly strained isolable member of a homologous series of bridgehead dienes. The new structural data allows comparison of geometric distortions that occur upon progressive shortening of the tether by three methylene groups in the bridgehead diene series 3, 4, and 5.



The methyl ester of bridgehead diene 3 is prepared by intramolecular Diels-Alder cycloaddition (equation).^{5,6} Hydrolysis of the methyl ester cycloadduct (CH₃CN/H₂O/LiOH, nitrogen atmosphere) followed by acidification (HCl) to pH 3 and recrystallization from hexane/CH₂Cl₂ gave crystals suitable for X-ray analysis. An ORTEP drawing showing the molecular structure and labeling scheme for 3 is given in Figure 1.⁷

The crystal contains four carboxylic acid molecules arranged about a center of inversion. Two types of intermolecular hydrogen bonding interactions are present. The central pair 3a is characterized by a carboxylic acid hydrogen-bonded dimer ($R_2^2(8)$)⁸ (H3-O2 = 1.222 Å, H3-O3' = 1.411 Å, O-H...O = 178.6°). Each member of the dimer in turn is complexed in a simple hydrogen-bonding chain pattern at the ring ether oxygen

with a second carboxylic acid molecule **3b** ($H23-O23 = 0.929 \text{ \AA}$, $H23-O1 = 1.780 \text{ \AA}$, $O-H\cdots O = 169.2^\circ$). The geometries of the two acids are slightly different. Of particular interest are the distortions associated with the bridgehead double bonds. Two parameters are used to describe these deformations: the first is the torsion angle τ between the p-orbitals of the π -bond; the second is the pyramidalization angle χ of the constituent atoms of each double bond.⁹ The τ and χ values are given in the table, which includes a separate listing for the two forms of **3** in the crystal. For comparison the corresponding data for homologous acids **4** and **5** are also given.⁴

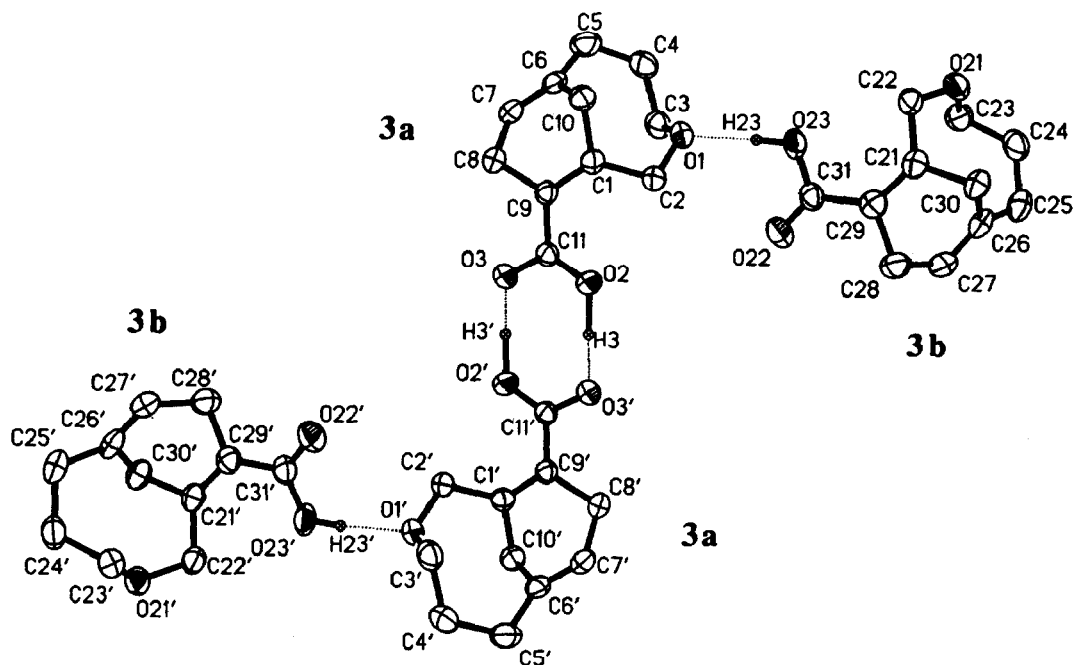


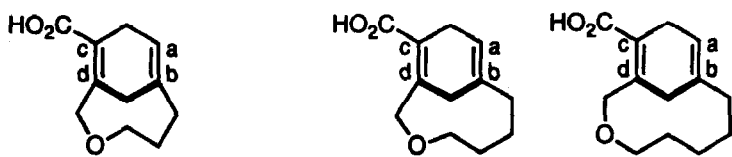
Figure 1. ORTEP plot showing arrangement of molecules in crystal of bridgehead diene **3**.

Each double bond in **3a** and **3b** reveals extensive distortions from planarity. The bridgehead atoms C_b and C_d are significantly pyramidalized because they are subject to the topologic constraints of the bicyclic framework of **3**. While not subject to the same geometric requirements, atoms C_a and C_c are also significantly pyramidalized. This effect is attributed to a favorable reduction of the π -orbital misalignment which occurs when the unconstrained atoms are pyramidalized.¹⁰ An indication of the relative ease of deformation of the conjugated and non-conjugated alkenes is the extent of their distortions: χ_d is greater than χ_b , and $|\tau_{cd}|$ is greater than τ_{ab} . Both effects may be understood in terms of the partial single bond C_c-C_d character arising from the zwitterionic resonance form of the enacid.

While the trend is toward increasing distortions in the series $5 \rightarrow 4 \rightarrow 3$, the progression is generally not uniform: significant increases in χ_b and τ_{cd} are observed upon removal of the first methylene of the tether to give **4** from **5**; yet only a slight increase is observed in those two parameters upon removal of a second methylene to give **3** from **4**. On the other hand, χ_c exhibits similar values for **4** and **5**, but a much larger value for **3**. Only χ_d

exhibits a uniform progression in the series. The inherent asymmetry of the molecules makes it difficult to assess the origins of these varying progressions of distortion. The C=C bond distances are not a sensitive function of the geometric deformations as they do not experience a statistically significant elongation with increasing distortions.

Table I. Geometric Distortions and Bond Lengths of Bridgehead Dienes.



	3a	3b	4	5
χ_a	11.0	9.7	0.7 ^a	0.1 ^a
χ_b	11.2	10.9	10.1	2.4
χ_c	7.6	7.8	1.4	1.7
χ_d	16.4	14.5	6.1	1.6
τ_{ab}	5.6	6.9	7.0 ^a	4.6 ^a
τ_{cd}	-12.5	-10.9	-10.0	-3.1
d C=C(H) (Å)	1.316(3)	1.322(4)	1.322(5)	1.323(4)
d C=C(CO ₂ H) (Å)	1.344(3)	1.335(3)	1.336(4)	1.342(3)

(a) Angles determined using calculated hydrogen atom positions.

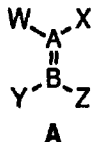
The progression of distortions that is observed in the homologous series 5 → 3 manifests itself in terms of increased chemical reactivity with both electrophiles and nucleophiles. Under conditions where both 4 and 5 are unreactive (25°C, 30 min), diene 3 undergoes base catalyzed Michael addition and addition of protic acids to the conjugated and nonconjugated double bonds, respectively. The next lower homologue in this series has a half-life of only several hours at room temperature in dilute solution.⁶ More quantitative relationships between olefin distortion and chemical reactivity are currently under investigation.¹¹

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7. X-ray diffraction data for $C_{11}H_{12}O_3$: The crystals belong to the monoclinic system with unit cell parameters at 296K: $a = 18.015(4)$, $b = 12.722(3)$, $c = 8.682(1)\text{\AA}$, $\beta = 92.34(1)^\circ$, and $V = 1988.2(9)\text{\AA}^3$. The space group is $P2_1/a$ with $Z = 8$ formula units / unit cell and D (calc.) = 1.23 g/cm^3 . Intensity data (4945 total) were collected on a Syntex $P2_1$ diffractometer system using monochromatized $MoK\alpha$ radiation ($\bar{\lambda} = 0.710730\text{\AA}$) using a $\theta - 2\theta$ scan technique.^{7a} Those 2514 reflections with $|F_o| > 6.0\sigma(|F_o|)$ were considered observed. The structure was solved by direct methods and refined by full-matrix least-squares techniques.^{7b,c} Hydrogen atoms were located from a difference-Fourier map and included with isotropic temperature factors. At convergence $R_F = 4.4\%$, $R_{wF} = 5.7\%$, and $GOF = 1.60$ for 365 variables. A final difference-Fourier map was featureless, $\rho(\text{max}) = 0.41\text{e}\text{\AA}^{-3}$. The ORTEP plot is shown at the 40% probability level. (7a) Sams, D. B.; Doedens, R. J. *J. Inorg. Chem.* **1979**, *18*, 153. (7b) Gilmore, C. J. *Appl. Cryst.* **1984**, *17*, 4246. (7c) UCLA Crystallographic Computing Package, University of California, Los Angeles, 1981, C. Strouse, personal communication.
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9. Winkler, F. K.; Dunitz, J. D. *J. Mol. Biol.* **1971**, *59*, 169-182. For a distorted double bond A the pyramidalization angle χ_B is found by defining the plane ZBA and measuring its acute angle to the plane YBA. Note that for a planar sp^2 - sp^2 double bond $\chi \approx 0^\circ$; for a fully pyramidalized (sp^3) atom $\chi \approx 60^\circ$. The p-orbital torsion angle τ_{A-B} is the average of the four-atom torsion angles Φ_{WABY} and Φ_{XABZ} . When there is no π -orbital misalignment $\tau = 0^\circ$.



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