Nonplanarity of π Systems in 5,6-Bis(methylene)-7-oxanorborn-2-ene

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Received December 23, 1980

The predominant extension of the π-electron density toward the exo face of norbornene and norbornadiene has been invoked to explain the exo stereoselectivity of their additions,[1,2] but no experimental evidence for this structural problem has been reported so far. MINDO/3 calculations suggested a larger π anisotropy in 7-oxanorbornene than in norbornene derivatives.[3] We report here the synthesis, characterization, and X-ray crystal structure of a 5,6-bis(methylene)-7-oxanorborn-2-ene derivative (**3**) in which the substituents at $C_{2,3}$ deviate toward the endo face by ca. 10° with respect to the $C_{1,2,3,4}$ plane. A smaller, insignificant distortion is measured for the exocyclic diene at $C_{5,6}$.

The 2,3,5,6-tetrakis(methylene)-7-oxanorbornane (**1**), precursor of our doubly convergent synthesis of anthracyclinones,[4,5] reacts with 1 mol equiv of benzoquinone ($CHCl_3$, 80 °C, 5 h) to give the monoadduct **2** (mp 147 °C, dec. 95%). Only one isomer[4] is observed whose stereochemistry is determined below; no bis adduct is isolated unless a very large excess of benzoquinone is used.[6] The monoreduction of **2** with Bu_4NBH_4 in 1:1 CH_2Cl_2/MeOH (0.5 mol equiv, −78 °C, 1.5 h, workup with saturated aqueous solution of NH_4Cl, then H_2O_2) furnished **3** (94%) as a crystalline substance (mp 206–207 °C).

The structure of **3** was suggested by its elemental analysis and spectral data[7] and was confirmed by single-crystal X-ray diffraction.[8] The crystal structure contains four molecules per monoclinic unit cell [a = 13.053 (2), b = 8.427 (1), c = 13.211 (3) Å; β = 117.43 (1)°]. It consists of discrete molecular units joined together by a hydrogen bond between the alcohol group and the oxa bridge. The principal results of the X-ray analysis (final R value = 0.042) are summarized in Table I and by the ORTEP perspective[9] drawing (Figure 1).

In addition to the establishment of the stereoselectivity of the Diels–Alder addition of benzoquinone to **1** and the monoreduction of the adduct **2**, the structure of **3** allows one to reply to the following interesting questions: (1) How much is the endocyclic double bond in the 7-oxanorbornene **3** distorted from planarity (δ)? (2) How much is the exocyclic diene distorted from planarity (ϵ)? (3) Does the oxa bridge tilt toward the endocyclic double bond or toward the exocyclic diene? Answers to these three questions are given in Figure 2.

Scheme I

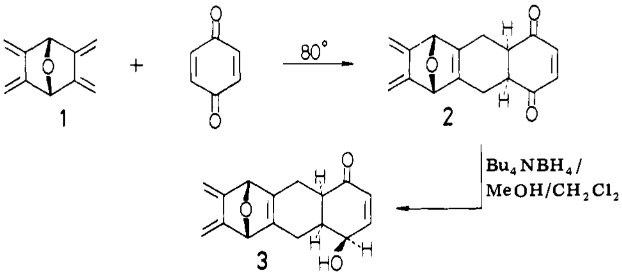

Table I. Selected Bond Lengths and Angles in **3**[a]

bond length, Å		bond angle, deg	
C_1–O_1	1.460 (4)	$C_{4,5,14}$	105.6 (3)
C_1–C_2	1.519 (4)	$C_{6,5,14}$	125.2 (3)
C_2–C_{15}	1.322 (6)	$C_{1,2,3}$	102.8 (3)
C_1–C_{14}	1.519 (5)	$C_{1,2,15}$	127.3 (4)
C_5–C_{14}	1.314 (5)	C_1,O_1,C_4	95.0 (2)
C_{11}–O_2	1.434 (5)	$C_{5,6,7}$	109.8 (3)

[a] For practical reasons, the numbering given in Figure 1 and here does not follow the IUPAC nomenclature rules.

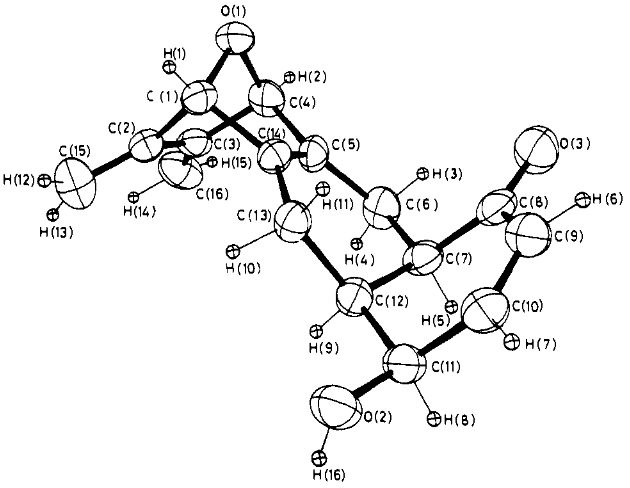

Figure 1. ORTEP plot of **3** (the H atoms are represented as spheres with an isotropic temperature factor artificially fixed at 0.004 Å^2).

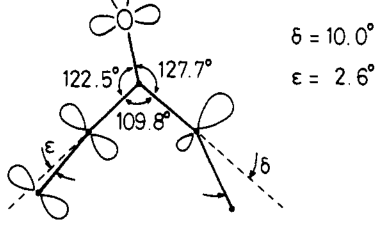

Figure 2. Angle between the $C_{1,4,5,14}$ and $C_{5,6,13,14}$ least-squares planes is denoted by δ. ϵ is the angle between the $C_{1,2,3,4}$ and $C_{2,3,15,16}$ least-squares planes; esd's are 0.3° (numbering, cf. Figure 1).

We feel that the π distortion of 10° observed for the endocyclic double bond of the 7-oxanorborn-2-ene **3** cannot be attributed only to lattice effects in the crystal or the bulk of the substituents (the exo face is less crowded than the endo face in bicyclo[2.2.1]heptane systems). Wagner et al.[10] have predicted that nonplanar ethylene (C_{2v}) becomes more stable than the planar geometry (D_{2h}) when all *four* CCH angles are reduced to a value <100°. The corresponding substituent angle deformations in **3** (see Table I) are not as large. Thus, if the above theoretical predictions[10] can be applied to 7-oxanorborn-2-enes, the 10° angle deviation from a

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[1] Inagaki, S.; Fukui, K. *Chem. Lett.* **1974**, *509*. Inagaki, S.; Fujimoto, H.; Fukui, K. *J. Am. Chem. Soc.* **1976**, *98*, 4054.

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[6] (E)- and (Z)-2-(chloromethylene)-3-methylene-7-oxanorbornane derivatives were found to add strong dienophiles preferentially onto their exo face: Avenati, M.; Hagenbuch, J. P.; Mahaim, C.; Vogel, P. *Tetrahedron Lett.* **1980**, 3167. Stereoselective labeling of one of the methylene hydrogen of **1** is necessary to determine the site of preferential attack by the dienophile.

[7] Data for **3**: IR ($CHCl_3$) 3510, 1790, 1685, 895 cm^{-1}; UV (CH_3CN) λ_{max} (log ϵ) 210 (4.31), 222 (4.21), 231 (4.15), 240 (4.01), 254 (3.66), 330 (1.64); mass spectrum, m/e (relative intensity) 256 (11), 182 (100).

[8] The crystal structure was determined by direct methods from diffractometer data. For details see supplementary material.

[9] Johnson, C. K., ORNL-3794, Oak Ridge National Laboratory, 1971.

[10] Wagner, H.-U.; Szeimies, G.; Chandrasekhar, J.; Schleyer, P.v.R; Pople, J. A.; Binkley, J. S. *J. Am. Chem. Soc.* **1978**, *100*, 1210.

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planar endocyclic double bond together with the tilt of the oxa bridge must be attributed to homoconjugative and hyperconjugative interactions.[11,12] The smaller π distortion (ca. 3°) of the exocyclic diene must be considered as insignificant at the moment. We are presently preparing other bicyclic olefinic systems and performing extensive calculations to approach a rationale for the nonplanarity of olefins with two nonequivalent faces. The present work shows that the π-electron anisotropy could be due to other factors than geometric constraints.[11,13,14] It demonstrates also the high stereoselectivity of the reactions **1** → **2** and **2** → **3**.

Acknowledgment. We are grateful to the Hoffmann-La Roche Co., Basel, the "Swiss National Science Foundation" (FN. 2.456-0.79) and the "Fonds Herbette", Lausanne, for generous support.

Supplementary Material Available: Spectral data, elemental combustion analyses of compounds **2** and **3**, and tables of atomic positions and isotropic temperature parameters (20 pages). Ordering information is given on any current masthead page.

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[12] Photoelectron spectra of unsaturated 7-oxanorbornanes suggested, however, little importance of the n(O)-π interactions: Bain, A. B.; Bünzli, J. C.; Frost, D. C.; Weiler, J. *J. Am. Chem. Soc.* **1973**, *95*, 291. Pfeffer, H.-U.; Klessinger, M.; Erker, G.; Roth, W. R. *Chem. Ber.* **1975**, *108*, 2923. Mohraz, M.; Batich, C.; Heibronner, E.; Vogel, P.; Carrupt, P. A. *Recl. Trav. Chim. Pays-Bas* **1979**, *98*, 361. See also: Neijzen, B. J. M.; Schmitz, R. F.; Klumpp, G. W.; DeLange, C. A. *Tetrahedron* **1975**, *31*, 873. Brown, R. S. *Can. J. Chem.* **1976**, *54*, 805. Schmidt, H.; Schweig, A.; Anastassiou, A. G.; Wetzel, J. C. *Tetrahedron* **1976**, *32*, 2239.

[13] Greenhouse, R.; Borden, W. T.; Hirotsu, K.; Clardy, J. *J. Am. Chem. Soc.* **1977**, *99*, 1664. Viavattene, R. L.; Greene, F. D.; Cheung, L. D.; Majeste, R.; Trefonas, L. M. *Ibid.* **1974**, *96*, 4342. See also: Liebman, J. F.; Greenberg, A. *Chem. Rev.* **1976**, *76*, 311. Shea, K. J. *Tetrahedron* **1980**, *39*, 1683, and references therein.

[14] The benzene ring in a 1,4-diphenyl-7-oxabenzo[*b*]norborn-2-ene derivative was found to deviate by ca. 5° toward the endo face, perhaps because of the torsional effects between the phenyl substituents and the benzo group. Szeimies-Seebach, U.; Szeimies, G.; Van Meersche, M.; Germain, G.; Declerq, J.-P. *Nouv. J. Chim.* **1979**, *3*, 357. We thank Professor G. Szeimies, Munich, for a listing of the X-ray data. If torsional effects due to the bridgehead hydrogens were responsible for the observed deviations, the exocyclic diene would have been expected to bend toward the endo face by about 10° also.

Oxygenation Reactions of Adamantylideneadamantane Cation Radical

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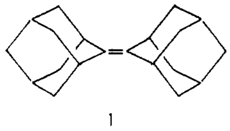
Received November 6, 1980

The oxidation chemistry of the title olefin (**1**) has been of sustained interest since Wynberg and co-workers[1a] showed that its reaction with singlet oxygen gives the remarkably stable dioxetane **2** (half-life of 30 min at 160 °C[2]). The epoxide **3**[1b] is often obtained as well as **2**,[3] and careful work on the sensitizer dye, solvent, and additive effects by Jefford and Boschung showed that in addition to a singlet oxygen pathway to **2**, there is a parallel pathway to **3** involving electron transfer and radical intermediates. Electron-transfer reactions giving products once thought to be characteristic of singlet oxygen are topics of great current interest.[4] Barton and others[5] have shown that the diene to endoperoxide conversion will occur in a chain reaction of ground-state (triplet) O_2 with diene cation radical, the adduct being reduced to endoperoxide by another molecule of diene. Foote et al.[6] and Schaap et al.[7] have emphasized that dioxetanes are formed from several olefins in nonsinglet oxygen reactions when easily reduced sensitizers such as 9,10-dicyanoanthracene are employed and have shown that a very rapid (if inefficient) production of dioxetane occurs when olefin radical cation is quenched by superoxide (generated from rapid reaction of sensitizer radical anion with oxygen). They also note that olefin radical cation reacts with triplet oxygen in a reaction that is slow on the time scale at which they are working. We point out here that the reaction of triplet oxygen with $\mathbf{1}^{+\cdot}$ is rapid enough to lead to interesting oxygenation chemistry which does not involve electronically excited states.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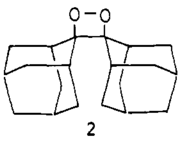
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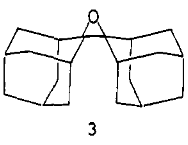
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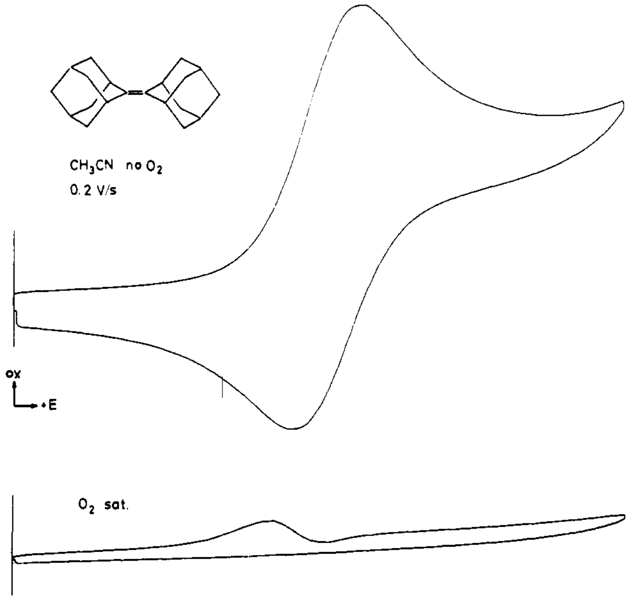

Figure 1. CV of **1** in the absence of oxygen (above) and in oxygen-saturated (below) acetonitrile containing 0.1 M tetra-*n*-butylammonium perchlorate, scanned from 1.15 to 1.75 V vs. SCE at 200 mV/s.

Our interest in the reaction of triplet oxygen with $\mathbf{1}^{+\cdot}$ was piqued by our observation that $\mathbf{1}^{+\cdot}$ solutions are extremely air sensitive;[8] many radical cations are not particularly sensitive to oxygen. To see if a chemically useful product sensitivity might result, we examined the reaction of **1** with three one-electron oxidants in the presence of oxygen. Most interestingly, high yields of three

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[4] For a brief review, see: Bartlett, P. D. *ACS Symp. Ser.* **1978**, *No. 69*, 15–32.

[5] (a) Barton, D. H. R.; LeClerc, G.; Magnus, P. D.; Menzies, I. D. *J. Chem. Soc., Perkin Trans. 1* **1975**, 2055. (b) Haynes, R. K. *Aust. J. Chem.* **1978**, *31*, 121, 131. (c) Haynes, R. K.; Probert, M. K.; Wilmot, I. D. *Ibid.* **1978**, *31*, 1737. (d) Tang, R.; Yue, H. J.; Wolf, J. F.; Mares, F. *J. Am. Chem. Soc.* **1979**, *100*, 5248.

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