were obtained with Rh than with Pd, even with lower Rh loading.

The high catalytic efficiency achieved with low precious metal loading and the excellent stability of these cathodes make them attractive for electrocatalytic hydrogenation of organic compounds. This work is currently being expanded to test new catalytic cathodes based on various combinations of redox polymers and metal catalysts.

Acknowledgment. We thank Professor G. Cauquis and Dr. C. Petrier for fruitful discussions.

Registry No. I, 100809-39-0; (poly$V^{2+}\cdot 2Cl^-$), 110589-61-2; (poly$V^{2+}\cdot 2ClO_4^-$), 110589-62-3; $PdCl_4^{2-}$, 14349-67-8; $PtCl_4^{2-}$, 13965-91-8; $RhCl_6^{3-}$, 21412-00-0; Pd, 7440-05-3; Pt, 7440-06-4; Rh, 7440-16-6; $PhCH{=}CHCO_2H$, 621-82-9; $PhC{\equiv}CPh$, 501-65-5; $PhNO_2$, 98-95-3; $PhCH_2CH_2CO_2H$, 501-52-0; $PhCH_2CH_2Ph$, 103-29-7; $PhNH_2$, 62-53-3; 4-isopropylcyclohex-2-en-1-one, 500-02-7; 3,5,5-trimethyl-2-cyclohexen-1-one, 78-59-1; 3-methoxybenzaldehyde, 591-31-1; 4-isopropylcyclohexanone, 5432-85-9; 3,3,5-trimethylcyclohexanone, 873-94-9; 3-methoxybenzenemethanol, 6971-51-3.

Dioxygen–Copper Reactivity: X-ray Structure and Characterization of an (Acylperoxo)dicopper Complex

Phalguni Ghosh, Zoltan Tyeklar, Kenneth D. Karlin,*
Richard R. Jacobson, and Jon Zubieta

Department of Chemistry
State University of New York (SUNY) at Albany
Albany, New York 12222

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The interaction and subsequent reactivity of dioxygen (O_2) with copper ions is of great interest due to the importance of dioxygen binding and/or activating proteins in biological systems and the utility of copper compounds in oxidative synthetic reactions.[1-3] In this communication, we report for the first time the synthesis and *X-ray structural characterization* of an (acylperoxo)dicopper(II) complex, a derivative of a coordinated dioxygen (peroxo) copper species.

We recently described a system in which O_2 reacts reversibly with a phenoxo-bridged dicopper(I) complex, $[Cu_2(XYL{-}O{-})]^+$ (**1**) (py = 2-pyridyl), in dichloromethane solution at low temperature to give an intensely purple (λ_{max} = 505 nm, ϵ = 6000 $M^{-1}\ cm^{-1}$) colored dioxygen complex, $[Cu_2(XYL{-}O{-})(O_2)]^+$ (**2**) ($Cu{:}O_2$ = 2:1) (Figure 1).[4] Resonance Raman[5] and extended X-ray absorption fine structure (EXAFS)[6] spectroscopic studies have established that **2** is best formulated as a (peroxo)dicopper(II) complex (ν_{O-O} = 803 cm^{-1}, Cu···Cu = 3.31 Å). The protonated form of **2**, $[Cu_2(XYL{-}O{-})(OOH)]^{2+}$ (**3**), can also be generated,[7] and while **3** can only be handled at low temperatures, we now report that a stable and crystalline analogue of **3**, the acylperoxo bridged dicopper(II) complex **5**, can be readily prepared by either the reaction of m-$ClC_6H_4C(O)OOH$ (MCPBA) with **4** or via the direct acylation of $[Cu_2(XYL{-}O{-})(O_2)]^+$ (**2**) with m-$ClC_6H_4C(O)Cl$, followed by a methathesis reaction (Figure 1).

To a dry dichloromethane solution of $[Cu_2(XYL{-}O{-})(OH)]Y_2$ (**4**)[8] (Y = ClO_4^- or PF_6^-) and 2 equiv of 2,2-dimethoxypropane at −80 °C under Ar was added 1.3 equiv of MCPBA, and by addition of dry diethyl ether, a dark green precipitate was isolated. Recrystallization by slow diffusion of diethyl ether into an acetonitrile solution of the product at −20 °C afforded the complexes $[Cu_2(XYL{-}O{-})(m\text{-}ClC_6H_4C(O)OO)]^{2+}$ (**5**) in >90% yield (Figure 1, reaction d).[9] Acylation of $[Cu_2(XYL{-}O{-})(O_2)]^+$ (**2**) m-$ClC_6H_4C(O)Cl$ also generated complexes **5** as shown by UV–vis and IR spectroscopy (Figure 1, reaction b). $[Cu_2(XYL{-}O{-})(m\text{-}ClC_6H_4CO)O_2)]^{2+}$ (**5**) exhibits a strong absorption at 395 nm (ϵ = 5500–5900 $M^{-1}\ cm^{-1}$) and a d–d band at 650 nm (ϵ = 420 $M^{-1}\ cm^{-1}$) in the UV–vis as well as a carbonyl absorption at 1745 cm^{-1} in an IR spectrum.[9]

X-ray quality crystals of $[Cu_2(XYL{-}O{-})(m\text{-}ClC_6H_4C(O)OO)](ClO_4)_2\cdot CH_3CN$ were grown from the reaction of MCPBA with **4**, as described above, and the structure of the dication **5** is shown in Figure 2.[10,11] The structure is very similar to that already described for complexes $[Cu_2(XYL{-}O{-})(X)]^{2+}$ (X = OH^-,[8,12] N_3^-,[12,13] and halide[12]), consisting of a phenoxo and X^- doubly bridged dicopper(II) species. Each Cu(II) ion is coordinated with equatorial binding to O1, O2, the amine N atom (N1, N4), one pyridyl N donor (N3, N5), and a longer axial interaction from the other pyridine donor (N2, N6) in a distorted square-based pyramidal geometry. The acylperoxo group is coordinated through O2 in a μ-1,1-fashion, occupying the position X found in the other related structures. The acylperoxo O2–O3 bond length is 1.463 (12) Å and compares with a closely structurally related (μ-1,1-hydroperoxo)dicobalt(III) complex (O–O = 1.42 Å)[14] and with distances observed in recently reported terminally bound t-$BuOO^-{-}M$ complexes (M = Co,[15] Hf[16]). The Cu···Cu distance in **5** is 3.197 Å, ca. 0.1 Å longer than that observed in **4**. The steric effect of the bulky MCPBA unit also results in larger Cu–O–Cu angles about the Cu_2O_2 unit (109.8 (3) and 108.3 (4) compared to 102.5 (5) and 104.4 (5) in **4**).

Unlike the hydroperoxo complex $[Cu_2(XYL{-}O{-})(OOH)]^{2+}$ (**3**), which oxygenates PPh_3 to $O{=}PPh_3$ stoichiometrically while forming the dicopper(II) product $[Cu_2(XYL{-}O{-})(OH)]^{2+}$ (**4**),[7] the dioxygen (peroxo) complex $[Cu_2(XYL{-}O{-})(O_2)]^+$ (**1**) does not oxidize PPh_3.[4,17] Consistent with its apparent closer relationship to the hydroperoxo complex **3**, the acylperoxo complex $[Cu_2(XYL{-}O{-})(m\text{-}ClC_6H_4C(O)OO)]^{2+}$ (**5**) reacts with PPh_3 to give a quantitative yield of $O{=}PPh_3$ and the carboxylato complex

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[9] $[Cu_2(XYL{-}O{-})(m\text{-}ClC_6H_4C(O)OO)](ClO_4)_2\cdot CH_3CN$: IR (Nujol) ν(CO), 1745 cm^{-1}, ν(CN), 2250 cm^{-1}. Anal. Calcd for $C_{45}H_{46}Cu_2Cl_3O_{12}N_7$: C, 48.66; H, 4.15; N, 8.83. Found: C, 48.65; H, 4.25; N, 8.70. $[Cu_2(XYL{-}O{-})(m\text{-}ClC_6H_4C(O)OO)](PF_6)_2$: IR (Nujol) ν(CO), 1745 cm^{-1}. Anal. Calcd for $C_{43}H_{43}Cu_2ClF_{12}N_6O_4P_2$: C, 44.49; H, 3.70; N, 7.24. Found: C, 43.93; H, 3.57; N, 6.98. An unambiguous assignment for the peroxide ν(O–O) cannot be made at this time due to the presence of ligand absorptions in the 700–850-cm^{-1} region.

[10] Complex **5**-$(ClO_4)_2\cdot CH_3CN$ crystallizes in the monoclinic space group $C2/c$ with a = 23.149 (6) Å, b = 13.327 (3) Å, c = 32.935 (5) Å, β = 97.78 (2)°, V = 10067 (4) $Å^3$, and Z = 8. A Nicolet R3m diffractometer was used in the ω-scan mode to collect 4691 reflections of which 2459 reflections with $F_o \geq 6\ \sigma|F_o|$ were used in the solution and refinement. The positional parameters of the copper atoms were determined by the Patterson method. The remaining non-hydrogen atoms were located on subsequent difference Fourier maps. Hydrogen atoms were calculated and fixed at 0.96 Å from carbon; the phenyl and pyridyl rings were refined as rigid hexagons (d(C–C(N)) = 1.395 Å). The structure was refined to the current residual values of R = 0.0628 and R_w = 0.0670 (Mo Kα, λ = 0.71073 Å).

[11] Supplementary Material.

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[17] The reaction PPh_3 with $[Cu_2(XYL{-}O{-})(O_2)]^+$ (**1**) at −80 °C results in the quantitative evolution of O_2 and the production of a bis(triphenylphosphine)dicopper(I) adduct complex $[Cu_2(XYL{-}O{-})(PPh_3)_2]^+$, see ref. 4.

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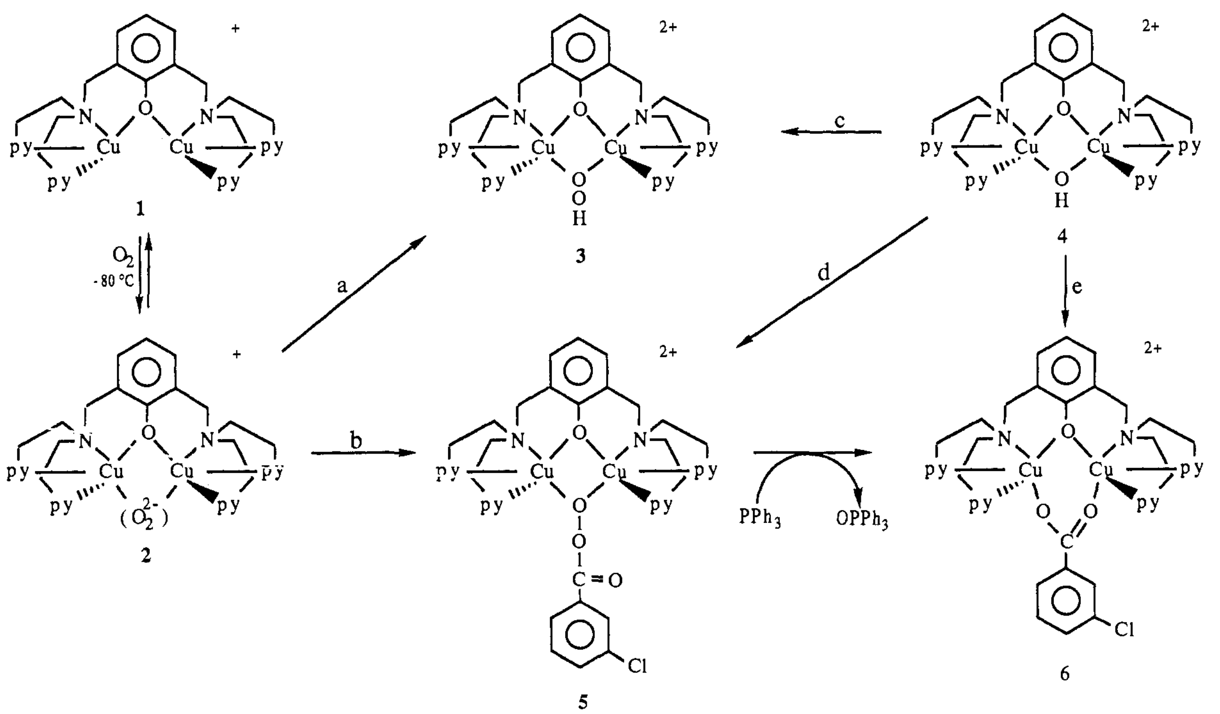

Figure 1. Scheme showing the reactions of the dioxygen complex $[Cu_2(XYL\text{–}O\text{–})(O_2)]^+$ (**2**) and transformations involving the $[Cu_2(XYL\text{–}O\text{–})(OOR)]^{2+}$ complexes (R = H–, **3**; R = *m*-$ClC_6H_4C(O)$–, **5**) (py = 2-pyridyl). Reaction conditions are as follows: (a) $HBF_4{\cdot}Et_2O$, -80 °C in CH_2Cl_2; (b) *m*-$ClC_6H_4C(O)Cl$, -80 °C in CH_2Cl_2; $AgPF_6$ in CH_3CN; (c) excess H_2O_2 in CH_2Cl_2/DMF, -80 °C; (d) MCPBA, -80 °C in CH_2Cl_2 containing 2,2-dimethoxypropane; (e) *m*-ClC_6H_4COOH, room temperature in CH_2Cl_2. See text for further explanation.

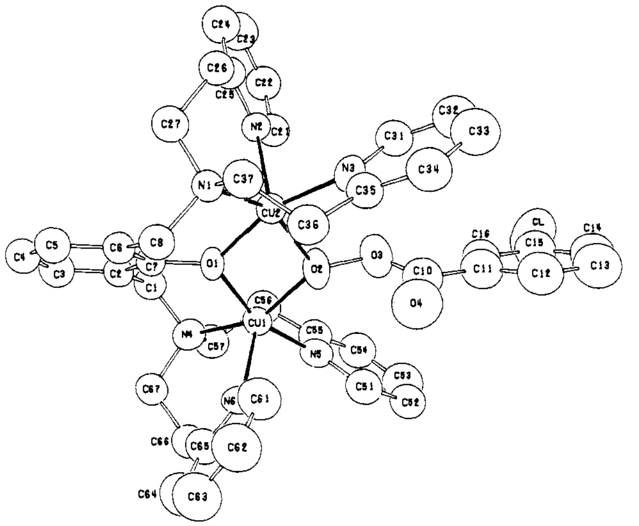

Figure 2. ORTEP diagram of the dicationic portion of $[Cu_2(XYL\text{-}O\text{-})(m\text{-}ClC_6H_4C(O)O_2)](ClO_4)_2{\cdot}CH_3CN$, **5**, showing the atom labeling scheme. Selected bond lengths (Å) and angles (deg) are as follows: Cu···Cu, 3.197; Cu1–O1, 1.948 (8); Cu1-O2, 1.971 (9); Cu1-N4, 2.069 (11); Cu1-N5, 1.949 (8); Cu1-N6, 2.165 (9); Cu2-O1, 1.959 (8); Cu2–O2, 1.973 (9); Cu2-N1, 2.049 (9); Cu2-N2, 2.158 (8); Cu2-N3, 1.948 (8); O2–O3, 1.463 (12); O1–Cu1–O2, 71.1 (3); O1-Cu1-N4, 94.7 (4); O2–Cu1-N4, 153.9 (4); O1-Cu1-N5, 161.0 (3); O2-Cu1-N5, 93.0 (4); N4–Cu1-N5, 95.7 (4); O1-Cu1-N6, 94.6 (3); O2-Cu1-N6, 106.5 (4); N4-Cu1-N6, 96.2 (4); N5-Cu1-N6, 100.1 (3); O1-Cu2-O2, 70.8 (3); O1-Cu2-N1, 93.5 (3); O2-Cu2-N1, 150.3 (4); O1-Cu2-N2, 99.9 (3); O2-Cu2-N2, 109.5 (4); N1-Cu2-N2, 97.7 (3); O1-Cu2-N3, 162.3 (3); O2-Cu2-N3, 94.3 (4); N1-Cu2-N3, 95.4 (4); N2-Cu2-N3, 94.1 (3); Cu1-O1-Cu2, 109.8 (3); Cu1-O2-Cu2, 108.3 (4); Cu1-O2-O3, 122.4 (7); Cu2-O2-O3, 123.3 (6).

$[Cu_2(XYL\text{-}O\text{-})(m\text{-}ClC_6H_4CO_2)]^{2+}$ (**6**) ($\nu_{asym}(COO)$ = 1545 cm^{-1}) (Figure 1).[18] The latter exhibits UV–vis and IR properties identical with that of the carboxylato compound independently synthesized by the addition of *m*-chlorobenzoic acid to $[Cu_2(XYL\text{-}O\text{-})(OH)]^{2+}$ (**4**) (Figure 1, reaction e).[18b]

The close similarity of the UV–vis spectral properties of the μ-1,1-acylperoxo-bridged complex **5** to the μ-hydroxo complex **4** and the hydroperoxo species **3** indicates that **3** is likely to possess a μ-1,1-OOH moiety. The enhanced reactivity of the protonated and the acylated peroxo complexes **3** and **5** toward PPh_3 oxidation suggests that such derivatives or O–O cleavage products derived from these may be important intermediates in copper-mediated oxidation/oxygenation processes.[19] Previously, it has been shown that Pt–O_2[20] and other M–peroxo[21] complexes can be activated toward substrate oxidation reactions upon treatment with electrophiles. The electrophilic activation of (porphyrin)M–O_2 complexes has also been reported,[22] and studies on O–O bond-breaking in porphyrin-containing and other LM–OOR species have shown that heterolytic and/or homolytic cleavage processes can lead to active metal-oxo oxidizing agents.[22,23] We expect that similar effects may be seen in copper ion chemistry, and we are investigating the reactions of Cu$_n$–OOR species both in the presence and absence of substrates.

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[18] (a) $[Cu_2(XYL\text{-}O\text{-})(m\text{-}ClC_6H_4CO_2)](ClO_4)_2$. Anal. Calcd for ($C_{43}H_{43}Cu_2Cl_3N_6O_{11}$) C, 49.01; H, 4.08; N, 7.97. Found: C, 48.52; H, 4.12; N, 7.83. (b) Acetato and benzoato derivatives of **4** have been previously synthesized and characterized; see ref 12.

[19] For PPh_3 oxidation, further mechanistic work is required to distinguish between (i) a metal–complex-based reaction and (ii) a pathway involving displacement of –OOR followed by direct attack on the PPh_3 substrate. (a) Sen, A.; Halpern, J. *J. Am. Chem. Soc.* **1977**, *99*, 8337–8339. (b) Read, G.; Urgelles, M. *J. Chem. Soc., Dalton Trans.* **1986**, 1383–1387.

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Supplementary Material Available: Listings of atomic coordinates and temperature factors, bond lengths, bond angles, anisotropic temperature factors, and hydrogen coordinates and temperature factors (11 pages). Ordering information is given on any current masthead page.

Coupling of Internal Motions in Bicyclobutane Radical Cation: The Effect of a Positive Charge on a Radical Center[1]

Shmaryahu Hoz,* Harold Basch, and Drora Cohen

Department of Chemistry, Bar-Ilan University
Ramat-Gan, Israel 52100

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Although bicyclobutane has been known for almost 30 years,[2] reports regarding its radical cation have appeared only in the last few years.[3] Recently, we have found that bromination of bicyclobutane derivatives occurs by an electron-transfer mechanism involving the radical cation of bicyclobutane as a reaction intermediate.[4] Consistency with the stereochemistry observed for the reaction requires that the postulated intermediate be stable in a highly puckered geometry. In order to test this assumption, an ab initio UHF/SCF study at the 3-21G level[5] was conducted in which the angle α was varied between 115° and 180° (see Figure 1) with full geometrical optimization at each α value. The results obtained confirmed the stability of the radical cation in its puckered form with $\alpha = 122°$.[4] In addition, interesting and unexpected couplings among the various geometrical parameters of the radical cation accompanying the variation in α were revealed. These latter results are given in Table I.

From Figures 1 and 2 it can be seen that other bond lengths and angles of the molecular geometry change significantly as α increases from 140° (r = 1.85 Å) to 160° (r = 2.1 Å). A particularly dramatic change is observed in the lengths of the side bonds r_1 and r_2 which become unequal. This result is due to a change in electronic structure from a symmetric (C_{2v}) delocalized charge distribution to a charge localized structure having C_s symmetry.[6] Localization of the positive charge on $C_{(1)}$ induces the shortening of r_1. The lengthening of r_2 results from a decrease of the bonding charge density in r_2 due to the hyperconjugative interaction between the σ bond orbital associated with r_2 and the vacant orbital on $C_{(1)}$.

With increasing α the bridgehead substituent at $C_{(1)}$ moves first inward (decreasing β) and then, starting at α around 145°, tilts in the reverse direction. This unusual flip motion has been previously observed in neutral bicyclobutane.[7] Its origin apparently

Table I. Selected Geometrical Parameters for the Radical Cation as a Function of α[a]

fixed α (deg)	optimized β (deg)	γ (deg)	r_1 (Å)	r_2 (Å)
115	159.7	159.7	1.518	1.518
120	157.2	157.2	1.515	1.515
122.68	156.0	156.0	1.515	1.515
125	154.9	154.9	1.515	1.515
130	152.8	152.8	1.514	1.514
140	149.2	149.2	1.515	1.515
150	151.2	146.6	1.491	1.551
153	160.6	148.8	1.489	1.561
157.5	174.9	196.7	1.497	1.548
160	175.9	196.7	1.496	1.547
170	178.3	192.1	1.496	1.541
179.9	180.0	180.7	1.496	1.538

[a] See Figure 1 for the assignment of α, β, γ, r_1, and r_2.

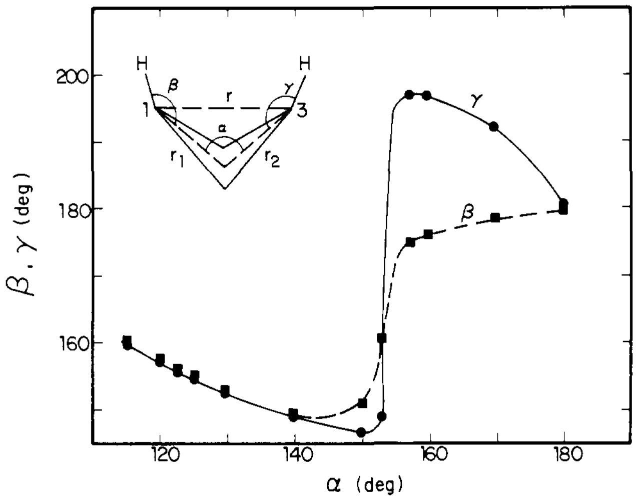


Figure 1. Optimum values of the angles β and γ for fixed values of the angle α.

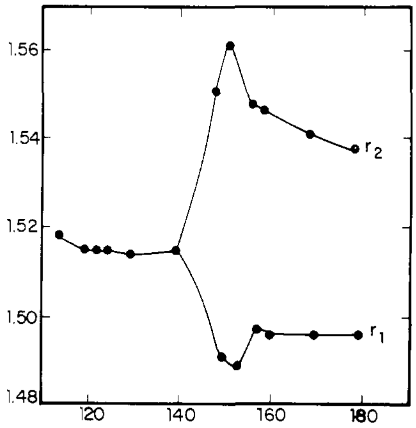
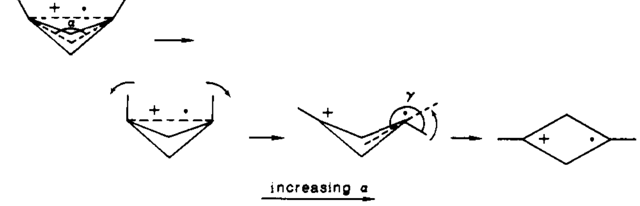


Figure 2. Optimum values of the side C–C bond lengths r_1 and r_2 for fixed values of the angle α.

Scheme I



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(1) (a) This is part 14 in the series Cyclobutane–Bicyclobutane System. For part 13 see ref 4.

(2) For a relevant review of the chemistry of bicyclobutane, see: Hoz, S. In *The Chemistry of the Cyclopropyl Group*; Rappoport, Z., Ed.; Patai, S., series, Ed; Wiley, New York, 1987; Chapter 19.

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(6) (a) At the α value points which showed C_{2v} symmetry for the molecular wave function, in moving from point to point induced distortions to lower symmetry of the molecular skeleton disappeared as the system relaxed back to C_{2v} symmetry in the geometry optimization. (b) See, also: Liebman, J. F.; Greenberg, A. In *The Chemistry of The Cyclopropyl Group*; Rappoport, Z., Ed.; Patai, S., series Ed.; Wiley, New York, 1987. (c) Relaxation of the symmetry of the charge localized structure to C_1 shows the bicyclic form of the cation to be a local minimum. (d) Geometry optimization at the UMP2 level also gives a change in the electronic structure from C_{2v} to C_s but at an α value that is larger by ~15° than in the UHF calculations.

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