observed. Localization is strongest where a single resonance structure can represent the maximum number of Clar sextets in a structure, as is the case for kekulene 1 and for 3. The MMPMI level of approximation thus finds that expectations of superaromaticity based on simple connectivity arguments for cycloarenes are unlikely, at least if full-perimeter bond delocalization is the criterion of superaromaticity.

Summary

Molecular mechanics with π-electron effects included (MMPMI) is an excellent tool by which to investigate the large, strained cycloarenes and related fully conjugated fused-ring aromatic systems. Semiempirical and ab initio computations on such systems are prohibitively expensive, whereas lower level connectivity-based and Hückel-type theories give no realistic geometric information. By use of MMPMI for synthetically likely cycloarenes, Clar-type structures are predicted in agreement with the limited experimental data to date. Given the recent interest in cycloarenes,[2-5] our findings indicate MMPMI to be a realistic, yet economical model for structural predictions for the potentially large number of such large, multiring π-systems. Finally, our results indicate that cycloarenes will *not* exhibit superaromatic geometric delocalization in general. Hopefully, crystal structure data for molecules such as 2 and 4 will become available in the near future to test these predictions and (we presume) strengthen trust in use of MMPMI and related algorithms for prediction of geometric and π-delocalization properties in very large aromatic systems. Finally, we hope that MMPMI will also prove useful in predicting the geometries of the open-ring precursors to cycloarenes and their abilities to be cyclized to the desired products, a problem that Staab and co-workers[3-5] have shown to be of much concern in planning syntheses of these fascinating molecules.

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Supplementary Material Available: MMPMI optimized cartesian coordinates and numbering schemes for all molecules, as well as ORTEP-type structural pictures (structural diagrams were produced by using a set of programs for IBM compatible personal computers, kindly provided by Professor John L. Ragle of the University of Massachusetts) (13 pages). Ordering information is given on any current masthead page.

A Practical Photochemical Synthesis of Bicyclo[1.1.1]pentane-1,3-dicarboxylic Acid

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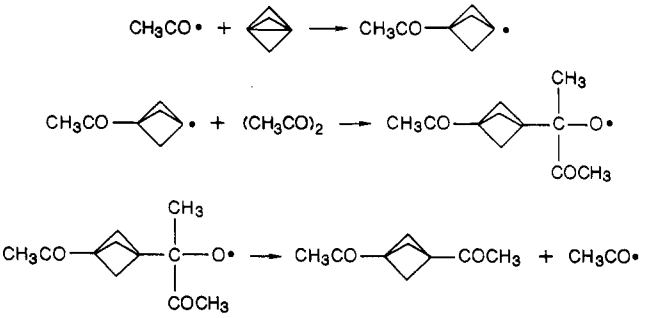
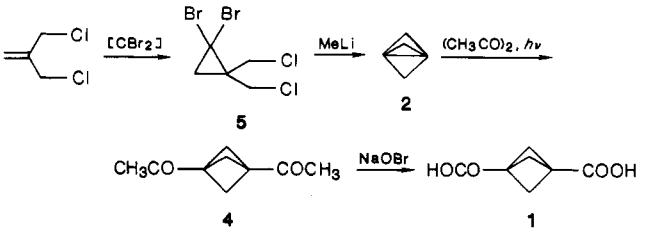
Bicyclo[1.1.1]pentane-1,3-dicarboxylic acid (1) represents a useful starting material for a variety of low molecular weight as well as polymeric structures containing the rigid and highly strained bicyclo[1.1.1]pentane moiety. The original route to 1 involved 12 steps and proceeded in a 2.3% overall yield from diethyl phenylmalonate.[1] Since [1.1.1]propellane[2] (2) has now become accessible in two easy steps from the commercially available methallyl dichloride,[3] and since radical addition across its central bond is facile,[3,4] efficient synthesis of 1 is merely a matter of an optimal choice of a reaction partner for radical addition. The choice of biacetyl is suggested by the report[3] that radical addition of acetaldehyde to 2 yields 1-acetyl-3-(1-hydroxyethyl)bicyclo[1.1.1]pentane (3), apparently via an addition of a bridgehead radical to the carbonyl group of acetaldehyde in preference to abstraction of the aldehydic hydrogen.

The hoped-for mechanism of the photoaddition of biacetyl is represented by the following chain process, where the key step is a β-fragmentation of an alkoxy radical:



Indeed, we find that irradiation of a solution of biacetyl and 2[5] in diethyl ether followed by hypobromite oxidation of the resulting diketone 4 yields the desired diacid 1 in an overall yield of 52% based on the starting tetrahalide[3] 5.



The diacid can also be prepared by hypohalite oxidation of 3, but the yield is less satisfactory. We now provide detailed descriptions of the recommended synthetic procedures for 1 and a few of its simple derivatives.

Experimental Section

Bioling points are uncorrected. Melting points were determined with a Boetius PHMK05 apparatus with a microscope attachment at a heating rate of 4 °C/min. Melting points taken in a sealed capillary are uncorrected. NMR spectra were run on a Nicolet NT-360 instrument in $CDCl_3$ solvent unless specified otherwise. IR spectra were recorded on a Nicolet 60SXR FTIR instrument. Mass spectra were taken on a 5995 Hewlett-Packard instrument. Elemental analyses were performed by Atlantic Microlab.

1,3-Diacetylbicyclo[1.1.1]pentane (4). A mixture of 89.1 g (0.30 mol) of 5[3] and 90 mL of pentane was placed in a 1-L three-neck round-bottom flask equipped with a mechanical stirrer,

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(5) We have prepared and used amounts up to 0.3 mol in a single run in the form of a dilute solution in diethyl ether. Yield, estimated from isolated yields of various addition products, is over 90%. Further scale up appears quite straightforward.

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septum, and a side arm connected to a dry-ice condenser and flushed with dry argon. With vigorous stirring, 510 mL of a 1.4 M solution of methyllithium in diethyl ether (Aldrich, salts free) were added via cannula in 15 min at the dry ice–acetone bath temperature. When the addition was completed, the bath was replaced by an ice bath and the stirring was continued for 1 h. All volatiles were then vacuum-transferred to a cold trap equipped with a 1-L round-bottom flask receiver containing a magnetic stirring bar. When almost dry salts appeared in the flask, the transfer was discontinued and the apparatus was again filled with argon. The receiver containing the propellane solution was disconnected from the cold trap and stoppered with a septum, and 27 mL of freshly distilled biacetyl was added from a syringe. The solution was stirred at ice-bath temperature and irradiated in a Pyrex vessel for 8 h with a 450-W medium-pressure Hanovia mercury lamp under dry argon. Volatiles were evaporated, and the semicrystalline residue was distilled on a Kugelrohr apparatus (80–85 °C/0.4 mmHg), yielding 36.2 g of wet white to pale yellow crystals. Crystallization of the crude **4** from heptane afforded 26.4 g of pure **4** in a 58% overall yield based on **5**: mp 67–69 °C; ^{1}H NMR δ 2.14 (s, 6 H), 2.24 (s, 6 H); ^{13}C NMR δ 25.79, 43.10, 51.81, 205.01; IR (C=O) 1708; MS, m/z (relative intensity) 152 (1, M^+), 137 (11), 109 (43), 95 (10), 43 (100), 39 (25); HRMS, m/z (calcd for $C_9H_{12}O_2$ 152.0837) 152.0839. Anal. Calcd for $C_9H_{12}O_2$: C, 71.02; H, 7.95. Found: C, 71.01; H, 7.97.

Bicyclo[1.1.1]pentane-1,3-dicarboxylic Acid (1). A 26.4-g portion of **4** was dissolved in 125 mL of dioxane and added over a period of 2 h to a stirred solution of sodium hypobromite prepared from 65 mL (1.25 mol) of bromine, 140 g (3.5 mol) of sodium hydroxide, and 1050 mL of water at 0–3 °C. After the addition of the diketone was completed, the reaction mixture was stirred for 1 h at 0 °C and then for 3 h at room temperature and finally for 1 h at 50 °C. Next, 6 g of sodium bisulfite were added, and the reaction mixture was extracted with 3 × 300 mL of chloroform, acidified with 225 mL of concentrated hydrochloric acid, and extracted with ether in a continuous extraction apparatus for 30–50 h. The ether was evaporated, the residue was dried under reduced pressure, and the crude product was washed with 50 mL of boiling chloroform. Cold suspension of the product was filtered, giving 24.6 g (90% yield) of the diacid **1**: mp 305 °C rapid dec, sealed tube (lit.[1] mp >260 °C subl); ^{13}C NMR (acetone-d_6) δ 38.08; 53.04, 170.59.

Bicyclo[1.1.1]pentane-1,3-dicarboxylic Acid (1) via Addition of Acetaldehyde to 2. A solution of **2** in diethyl ether prepared by the above procedure (210 mL, 3% in **2** according to integrated ^{1}H NMR intensities), 150 mL of acetaldehyde, and 0.4 g of benzoyl peroxide was stirred and irradiated as above for 6 h. Evaporation of solvents and excess acetaldehyde at reduced pressure (at the end, 50 °C/0.8 mmHg) furnished 15.06 g of crude **3** in the form of a yellowish oil (about 80% pure by GC): ^{1}H NMR δ 1.05 (d, J = 6.4 Hz, 3 H), 1.81 (d, J = 9.0 Hz, 3 H), 1.87 (d, J = 9.0 Hz, 3 H), 2.06 (s, 3 H), 3.74 (q, J = 6.4 Hz, 1 H); ^{13}C NMR δ (major peaks) 19.17, 25.95, 42.70, 43.41, 48.49, 66.21, 206.90; GC–MS, m/z (relative intensity) 139 (24, M – Me), 121 (63), 111 (27), 95 (30), 93 (68), 91 (59), 77 (81), 71 (100). An attempt at purification by short-path distillation (110–115 °C/0.4 mmHg) led to partial decomposition. Crude **3** (7.5 g) diluted with 25 mL of dioxane was slowly added to a vigorously stirred solution of sodium hypobromite prepared by slow addition of 18.5 mL (0.36 mol) of bromine to a well-stirred solution of 40.0 g (1.0 mol) of sodium hydroxide in 300 mL of water. Temperature during preparation of the hypobromite as well as the addition of **3** was maintained below 5 °C. The reaction mixture was stirred for 1 h at ice-bath temperature and then for 3 h at room temperature and finally for 1 h at 50 °C. Excess hypobromite was destroyed by addition of 5 g of sodium bisulfite, the mixture was extracted with 3 × 50 mL of chloroform and acidified with 55 mL of concentrated HCl, and the product was extracted with ether for 10 h. Ether was evaporated, the residue was dried under reduced pressure, and the crude diacid **1** was washed with 10 mL of boiling chloroform. Filtering off the cold suspension gave 2.76 g (35% yield) of the product.

1,3-Bis(chlorocarbonyl)bicyclo[1.1.1]pentane (6). A 24.6-g portion (0.157 mol) of the diacid **1** and 45 mL of thionyl chloride were refluxed until a clear solution was formed (about 10 h). Excess thionyl chloride was evaporated, and the crystalline residue was distilled on a Kugelrohr apparatus (120 °C/12 mmHg), giving 26.92 g (89% yield) of **6**: mp 55–57 °C; ^{1}H NMR δ 2.58 (s); ^{13}C NMR δ 44.57, 54.80, 169.55; IR (C=O) 1794; MS, m/z (relative intensity) 159 (1.4, M – Cl), 157 (4.4, M – Cl), 131 (1.3), 129 (4.0), 103 (11.6), 101 (32.4), 65 (100); HRMS, m/z (calcd for $C_7H_6ClO_2$ 157.0056) 157.0054. Anal. Calcd for $C_7H_6Cl_2O_2$: C, 43.55; H, 3.13; Cl, 36.74. Found: C, 43.48; H, 3.14; Cl, 36.76.

Dimethyl Bicyclo[1.1.1]pentane-1,3-dicarboxylate (7). First, 26.92 g (0.139 mol) of **6** was slowly added to 75 mL of stirred anhydrous methanol. Then, when the addition was completed, the mixture was refluxed for 30 min. Evaporation of methanol gave a crystalline solid, which after short-path distillation (125–130 °C/12 mmHg) gave 25.24 g (99% yield) of **7**: mp 92 °C; ^{1}H NMR δ 2.30 (s, 6 H), 3.67 (s, 6 H); ^{13}C NMR δ 37.46; 51.45, 52.68, 169.31; IR: 1739, 1211; MS, m/z (relative intensity) 153 (31, M – OMe), 152 (57), 125 (51), 124 (80), 96 (100), 66 (70), 64 (59); HRMS, m/z (calcd for $C_8H_9O_3$ 153.0552) 153.0549. Anal. Calcd for $C_9H_{12}O_4$: C, 58.69; H, 6.57. Found: C, 58.78; H, 6.58.

3-Methoxycarbonylbicyclo[1.1.1]pentane-1-carboxylic Acid (8). To a gently refluxed and stirred solution of 25.24 g (0.137 mol) of the dimethyl ester **7** in 200 mL of methanol, a solution of 5.50 g (0.137 mol) of sodium hydroxide in 50 mL of methanol was added during 1.5 h. When the addition was completed, the mixture was stirred and refluxed for 1 h. Methanol was evaporated, and the white sodium salts were vacuum dried. The salts were dissolved in 150 mL of water, unreacted **7** was extracted with 4 × 50 mL of methylene chloride (3.00 g of **7** was recovered), and the aqueous phase was acidified with 12 mL of concentrated hydrochloric acid. The product was extracted with 4 × 50 mL of methylene chloride, and the extracts were dried with sodium sulfate. Evaporation of the solvent gave 18.12 g (88% yield corrected for recovered **7**) of crude product **8** (mp 137.5–140 °C). Crystallization from heptane–chloroform gave pure **8**: mp 139.5–140 °C (lit.[1] mp 139.5–140.2 °C); ^{1}H NMR δ 2.35 (s, 6 H), 3.69 (s, 3 H); ^{13}C NMR δ 37.43, 51.80, 52.69, 169.61, 174.73; MS, m/z (relative intensity) 153 (1, M – OH), 152 (4), 139 (13), 138 (14), 125 (10), 124 (16), 111 (17), 110 (31), 96 (53), 93 (22), 83 (29), 82 (100), 67 (52), 66 (62), 65 (98).

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Heterogeneous Acid-Catalyzed Amination of Isobutene to *tert*-Butylamine

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Despite extensive studies on direct amination of lower alkenes[2,3] to form the corresponding alkylamines, this transformation has been achieved in a single step only by treatment with alkali metal amide catalysts.[3,4] While amination of ethene proceeds satisfactorily, isomerization and polymerization of the alkene substrate complicate the synthesis of propyl and butylamines.[5] We recently re-

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