($CDCl_3$) δ 1.4 (d, 3 H, J = 3 Hz), 1.48 (s, 3 H), 1.50 (s, 3 H), 3.75–4.35 (m, 2 H), 9.75 (d, 1 H); MS, m/z 162 (M^+), 159, 129, 115, 99, 85, 73, 59; IR (liquid film) 1730, 1760, 3450 cm^{-1}.

(b) From D-Threonine (See Preparation of the 4*S*-Trans Enantiomer from L-Threonine).

(4*S*)-*trans*-2,2,5-Trimethyl-1,3-dioxolane-4-carboxaldehyde (1c). L-Threonine (220 g, 1.85 mol) suspended in 500 mL of water at −5 °C was treated simultaneously while stirring with a solution of 138 g of $NaNO_2$ (2 mol) in 200 mL of water and 55.7 mL of concentrated H_2SO_4 (1 mol) in 150 mL of water. The two solutions were added at such a rate that the temperature remained between 0 and 5 °C. The solution was then stirred at room temperature overnight. The water was evaporated under vacuum and the remaining mixture treated with 300 mL of EtOH. The salts were then filtered and the solution evaporated to dryness again. Absolute MeOH (200 mL) was then added and the solution saturated with gaseous HCl and refluxed for 6 h. Evaporation of the solvent gave a crude dihydroxy ester which was directly transformed into the 1,3-dioxolane derivative by treatment with 200 mL of acetone, 200 mL of 2,2-dimethoxypropane, and 1 g of *p*-toluenesulfonic acid. After 2 h at room temperature the solution was evaporated. Partition between water and ethyl acetate and conventional treatment of the organic phase gave a crude product, which after distillation [70–75 °C (1 mm)] gave 177 g (55%) of (4*S*)-*trans*-2,2,5-trimethyl-4-(methoxycarbonyl)-1,3-dioxolane: $[\alpha]^{20}_D$ −16.4° (*c* 1, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 1.4 (d, 3 H), 1.48 (s, 6 H), 3.8 (s, 3 H), 4–4.4 (m, 2 H); MS, m/z 174 (M^+), 173, 159, 131, 115, 99, 97, 85; IR (liquid film) 1850 cm^{-1}. Anal. Calcd for $C_8H_{14}O_4$: C, 55.16; H, 8.10. Found: C, 54.91; H, 7.96.

The ester (25 g, 0.143 mol) in 200 mL of anhydrous ethyl ether was treated under nitrogen with 145 mL of a 1 M solution of DIBAH in hexane at −78 °C. The solution was stirred 1 h at −40 °C, cooled again at −78 °C, and 75 mL of water added dropwise. The mixture was allowed to come to room temperature. The solid part separated by filtration and washed with ether. Evaporation of the solvent and bulb-to-bulb distillation gave 18.2 g (88%) of the aldehyde **1c** mainly in its hydrated form, $[\alpha]^{20}_D$ −28.2° (*c* 1, $CHCl_3$) (−10.8° for the cyclohexylidene analogue).

(4*S*,5*S*)-[2-(1,3-Dioxolan-2-yl)ethenyl]-2,2,5-trimethyl-1,3-dioxolane (5). To a stirred mixture of 34 g of (1,3-dioxolan-2-ylmethyl)triphenylphosphonium bromide (85.6 mmol) in dry THF (70 mL) was added 171 mL of a 0.5 M solution of potassium *tert*-butoxide in anhydrous THF (85.6 mmol) dropwise at room temperature. The mixture was stirred for an additional 30 min, and the aldehyde **1b** (7 g, 4.3 mmol) was added in 10 mL of THF. The mixture was stirred at room temperature for 24 h. After conventional treatment (evaporation of the solvent, partition between water and methylene chloride) the crude extract was purified by flash chromatography, yielding **5** (6.2 g, 67%) as a 9:1 mixture of cis and trans isomers: $[\alpha]^{20}_D$ −16.2° (*c* 1, EtOH); ^1H NMR (300 MHz, $CDCl_3$) δ 1.29 (d, 3 H), 1.41 (s, 3 H), 1.42 (s, 3 H), 3.79 (m, 1 H), 3.90 and 4.01 (2 m, 5 H), 4.38 (m, 1 H), 5.53–5.58 (m, 1 H), 5.66–5.71 (m, 1 H); MS, m/e 199 (M^+ − 15), 183, 152, 139, 107, 87, 73. Anal. Calcd for $C_{11}H_{18}O_4$: C, 61.66; H, 8.47. Found: C, 61.57; H, 8.38. 4*R*,5*R* enantiomer of **5**: $[\alpha]^{20}_D$ +15.6° (*c* 1, EtOH).

Methyl 2,3,6-Trideoxy-α-L-*threo*-hex-2-enopyranoside (2). **5** (1.6 g, 7.5 mmol) was dissolved at −78 °C in 90 mL of a cooled 0.1% HCl solution in anhydrous MeOH under nitrogen and kept at −78 °C for 72 h. The solution was then left at room temperature for 1 h. Sodium hydrogen carbonate was then added and the solvent evaporated in vacuum. Flash chromatography of the residue gave **2** as an oil (560 mg, 52%). The oily product was sublimed under reduced pressure to give white needles: mp 62–62.5 °C; $[\alpha]^{20}_D$ +130° (*c* 2, MeOH) [lit.[6b] $[\alpha]^{20}_D$ +139° (*c* 2, MeOH)]; ^1H NMR ($CDCl_3$) δ 1.3 (d, 3 H, J = 6 Hz), 1.9 (br s, 1 H, OH), 3.4 (s, 3 H), 3.3–3.8 (m, 1 H), 3.9–4.5 (dq, 1 H), 4.85 (d, 1 H, J = 3 Hz), 5.7–6.3 (m, 2 H); MS, m/z 144 (M^+), 127, 125, 113, 100, 95, 85, 83. Anal. Calcd for $C_7H_{12}O_3$: C, 58.31; H, 8.39 Found: C, 58.16; H, 8.31. **2a**: $[\alpha]^{20}_D$ −132° (*c* 2, MeOH).

(4*S*,5*S*)-4-[2-(1,3-Dioxolan-2-yl)ethyl]-2,2,5-trimethyl-1,3-dioxolane (6). **5** (850 mg, 3.97 mmol) in 15 mL of MeOH was hydrogenated in a Parr apparatus in the presence of 200 mg of 10% Pd/C during 20 min. Filtration and evaporation of the solvent gave crude **6** in nearly quantitative yield (845 mg): $[\alpha]^{20}_D$ −9.3° (*c* 2, MeOH); ^1H NMR ($CDCl_3$) δ 1.22 (d, 3 H), 1.35 (s, 3 H), 1.5–1.9 (m, 4 H), 3.5–4.0 (m, 6 H), 4.8 (m, 1 H); MS, m/z 216 (M^+), 201, 157, 141, 129, 115, 113, 99, 87, 73. Anal. Calcd for $C_{11}H_{20}O_4$: C, 61.09; H, 9.32. Found: C, 61.25; H, 9.16. 4*R*,5*R* enantiomer of **6**: $[\alpha]^{20}_D$ +8.1° (*c* 2, MeOH).

2,3,6-Trideoxy-L-*threo*-hexose (L-Rhodinose) (3). **6** (750 mg, 4.6 mmol) was dissolved in 8 mL of 50% acqueous acetic acid and heated at 60 °C for 2 h. The solvent was evaporated in vacuum and the residue purified by flash chromatography, yielding 322 mg of **3** (73%) as a mixture of four isomers as already observed by other authors:[9,10] $[\alpha]^{20}_D$ −13.6° (*c* 1, acetone); ^1H NMR (300 MHz, $CDCl_3$) δ 1.17, 1.19, 1.21, 1.26 (4 d, 2 H), 1.5–2.1 (m, 2 H), 3.49, 3.68, 3.95, 4.03 (m, 4 H), 4.77, 4.85, 5.52, 5.59 (m, 1 H); MS, m/z 132 (M^+), 115, 114, 99, 88, 87, 70, 69. Anal. Calcd for $C_6H_{12}O_3$: C, 54.55; H, 9.15. Found: C, 54.44; H, 9.07. D-Rhodinose: $[\alpha]^{20}_D$ +14.2° (*c* 1, acetone).

Methyl 2,3,6-Trideoxy-L-*threo*-hexopyranoside (7). **2** (820 mg, 5.7 mmol) in 15 mL of anhydrous MeOH in the presence of 200 mg of 10% Pd/C was shaken with hydrogen in a Parr apparatus during 30 min. The solution was filtered and the residue purified by flash chromatography to give 710 mg of **7** (87%) as a mixture of α and β anomers: $[\alpha]^{20}_D$ −32° (*c* 1, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 1.29 (d, 3 H, J = 6 Hz), 1.7–2.0 (m, 4 H), 2.1 (m, 1 H, OH), 3.4 and 3.5 (2 s, 3 H), 2.55 (m, 1 H), 3.95 (q, 1 H), 4.53 and 4.62 (2 d, 1 H, J = 3 Hz); MS, m/z 146 (M^+), 145, 144, 119, 118, 113, 101, 87, 75, 71, 59, 55. Anal. Calcd for $C_7H_{14}O_3$: C, 57.51; H, 9.65. Found: C, 57.63; H, 9.49. **7a**: $[\alpha]^{20}_D$ +36.4° (*c* 1, $CHCl_3$).

Elemental Analysis of the Products of the D Series. Anal. Calcd for the 4*R*,5*R* enantiomer of **5**, $C_{11}H_{18}O_4$: C, 61.66; H, 8.47. Found: C, 61.44; H, 8.52. Anal. Calcd for **2a**, $C_7H_{12}O_3$: C, 58.31; H, 8.39. Found: C, 58.46; H, 8.41. Anal. Calcd for the 4*R*,5*R* enantiomer of **6**, $C_{11}H_{20}O_4$: C, 61.09; H, 9.32. Found: C, 60.98; H, 9.23. Anal. Calcd for D-rhodinose, $C_6H_{12}O_3$: C, 54.55; H, 9.15. Found: C, 54.48; H, 9.08. Anal. Calcd for **7a**, $C_7H_{14}O_3$: C, 57.51; H, 9.65. Found: C, 57.48; H, 9.73.

A New Synthesis of Azulene-5-carboxylic Acid

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In connection with our studies on the base-catalyzed rearrangement of oxy-Cope system,[1] we were interested in synthesizing a five-carbon fragment. Recently, we reported[2] the synthesis and Michael acceptor properties of ethyl α-propargylacrylate and its use in cycloheptenone annulation leading to the synthesis of a homo-Wieland–Mieschler ketone.[3] However, our initial attempts to synthesize the title compound utilizing the above synthon were hampered by several poor-yielding reactions. We report herein a modified route in which several of the above difficulties are alleviated. This paper deals with the synthesis of a modified synthon and its utility toward the first synthesis of the title compound via a cycloheptenone annulation.

Alkylation of triethyl phosphonoacetate with the ethylene ketal of bromoacetone[4] with sodium hydride in THF at room temperature for 6 h and then at reflux for 3 h gave the alkylated compound **3** as a colorless liquid in 76% yield. The Wittig–Horner reaction of compound **3** with 30% formalin in the presence of saturated aqueous

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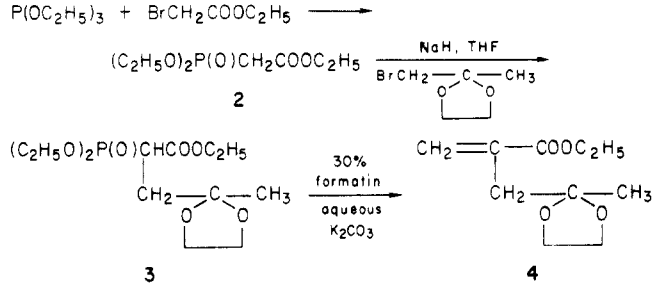
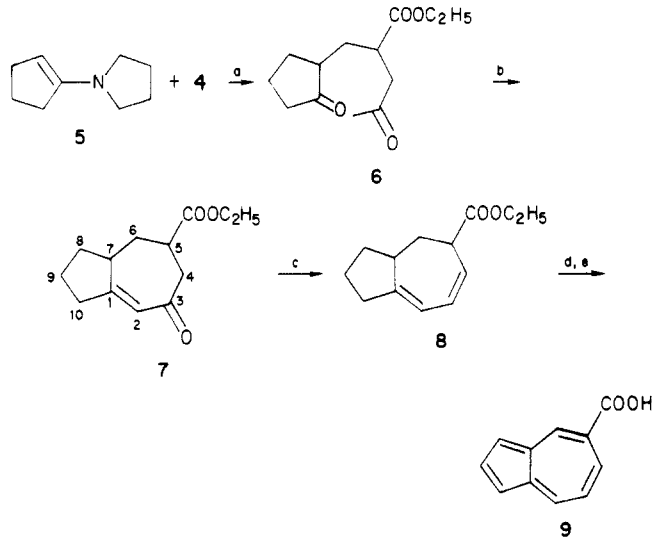
potassium carbonate[5] gave compound 4 as a colorless liquid in 68% yield.



Michael addition of the pyrrolidine enamine of cyclopentanone[6] to the synthon 4 was carried out in an efficient manner and in fairly good yield only in the presence of a solvent like Me_2SO to give the keto ester 6 in 52% yield. Cyclization was effected with pyrrolidine in benzene to give the enone 7 in 81% yield.



(a) Me_2SO, room temperature, 16 h; 80 °C, 3-4 h; (b) pyrrolidine, benzene, 80 °C, 8 h; (c) $NaBH_4$, C_2H_5OH, room temperature, 6 h; 15% HCl, 4 h; (d) DDQ, benzene, 14 h; (e) NaOH, H_2O, 4 h

Sodium borohydride reduction of the enone ester 7 gave the hydroxy ester which on refluxing with 15% dilute hydrochloric acid gave the diene 8 in 78% yield. Dehydrogenation of compound 8 with DDQ gave ethyl azulene-5-carboxylate which on saponification gave the title compound 9[7] in 65% yield.

Experimental Section

All syntheses were performed with high purity grades of commercially available materials. Me_2SO was distilled from calcium hydride under reduced pressure, and tetrahydrofuran was distilled from sodium benzophenone ketyl immediately prior to use. Distillation temperatures are uncorrected. All glassware was oven-dried at 150 °C before use. Fluka sodium hydride (50–60% in oil) was used and washed twice with THF in the reaction flask under a static pressure of nitrogen. Column chromatography was performed with 200–400-mesh ACME silica gel with petroleum ether (60–80 °C), benzene, and ethyl acetate as eluents. TLC was run on glass plates coated (0.25 mm) with silica gel G (ACME) and visualized with iodine. Infrared spectra were recorded on a Perkin-Elmer 598 spectrophotometer as solutions in $CHCl_3$ or CCl_4 and are reported in reciprocal centimeters (cm^{-1}). Proton magnetic resonance spectra were obtained on a Varian EM 390 spectrometer with tetramethylsilane as an internal standard. Chemical shifts are expressed in parts per million (δ), and peaks are integrated in units of protons (H). Significant ^1H NMR data are tabulated in the following order: number of protons, multiplicity (s, singlet; d, doublet; t, triplet; q, quartet, m, multiplet). Microanalyses were performed with a Perkin-Elmer 240B elemental analyzer.

Preparation of 3. To a suspension of oil-free NaH (2.4 g, 0.1 mol) in 25 mL of THF was added dropwise with cooling, triethylphosphonoacetate[8] (22.4 g, 0.1 mol. After addition, the solution was stirred for 1 h or until the gas evolution ceased. The ethylene ketal of bromoacetone[4] (18.1 g, 0.1 mol) was dissolved in 75 mL of THF and was added slowly over a period of 30 min. The solution was stirred for 6 h and then refluxed on a water bath for 3 h. The reaction mixture was then cooled and filtered, and the filtrate was concentrated under reduced pressure. The residue was distilled under pressure to give a colorless liquid (24.62 g, 76%): bp 95–99 °C (0.8 mm); IR ($CHCl_3$) 1720 cm^{-1}; ^1H NMR (CCl_4) δ 1.2 (t, 9 H), 1.3 (s, 3 H), 3.0 (d, 2 H), 3.1 (br s, 1 H), 4.1–4.4 (q, 5 × OCH_2, 10 H).

Anal. Calcd for $C_{13}H_{25}O_7P$: C, 48.15; H, 7.72. Found: C, 48.12; H, 7.70.

Preparation of 4. To a mixture of compound 3 (3.24 g, 0.01 mol) and 30% aqueous formalin (4 mL, 0.02 mol) agitated at room temperature was added slowly (20 min) a saturated solution of potassium carbonate (2.82 g, 0.02 mol). At the end of the addition, the temperature reached 50–55 °C, and the agitation was continued for another 1 h. Saturated NH_4Cl solution (40 mL) was added, and the mixture was thoroughly extracted with ether (4 × 50 mL). The combined organic phases were washed with brine and dried (Na_2SO_4). The solvent was removed under reduced pressure, and the residual oil was vacuum distilled (1.36 g, 68%): bp 68–70 °C/3 mm; IR ($CHCl_3$) 1715, 1630 cm^{-1}; ^1H NMR (CCl_4) δ 1.3 (t, 3 H), 1.4 (s, 3 H), 3.4 (br s, 2 H), 4.0–4.3 (q, 3 × OCH_2, 6 H), 5.9 (s, 1 H), 6.3 (s, 1 H).

Anal. Calcd for $C_{10}H_{16}O_4$: C, 60.00; H, 8.00. Found: C, 60.02; H, 8.03.

2-(2-Carbethoxy-4-oxopentyl)cyclopentanone (6). To a stirred solution of 1-(cyclopent-1-enyl)pyrrolidine (5) (27.4 g, 0.2 mol) in 75 mL of Me_2SO was added 40.0 g (0.2 mol) of synthon 4 in 75 mL of Me_2SO over a period of 45 min. The solution was stirred for 16 h at room temperature, then warmed at 80 °C for 3–4 h, finally cooled, and added slowly to an excess of crushed ice saturated with NH_4Cl. The mixture was extracted thoroughly with ether (6 × 100 mL), and the combined ether extracts were washed repeatedly with water and concentrated. The residue was taken up in benzene (100 mL), water (30 mL) and glacial acetic acid (10 mL) were added to it, and the mixture was refluxed for 2 h, then cooled, diluted with ether, washed with $NaHCO_3$ solution, water, and brine, and dried (Na_2SO_4). Concentration and distillation under reduced pressure gave 6 as a pale yellow liquid (24.5 g, 52%): bp 116–119 °C (1 mm); IR (CCl_4) 1740, 1720 (br) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.26 (t, 3 H), 2.0 (s, 3 H), 2.3–3.1 (m, 12 H), 4.2 (q, 2 H).

Anal. Calcd for $C_{13}H_{20}O_4$: C, 65.00; H, 8.33. Found: C, 65.05, H, 8.30.

5-Carbethoxy-3-oxobicyclo[5.3.0]dec-1-ene (7). A solution of compound 6 (4.8 g, 0.02 mol) and pyrrolidine (1 mL) in dry benzene (50 mL) was stirred under reflux for 8 h under nitrogen with removal of water with a Dean–Stark water separator. The mixture was cooled diluted with ether, washed with ice-cold dilute hydrochloric acid and water, dried (Na_2SO_4), and concentrated. The crude product was purified by chromatography on silica gel (9:1 petroleum ether–benzene) to afford 7 as a viscous liquid (3.61 g, 81%): IR ($CHCl_3$) 1720, 1700, 1630 cm^{-1}[^1H NMR ($CDCl_3$) δ 1.25 (t, 3 H), 2.3–3.0 (m, 12 H), 4.1 (q, 2 H), 5.9 (s, 1 H).

Anal. Calcd for $C_{13}H_{18}O_3$: C, 70.27; H, 8.11. Found: C, 70.22; H, 8.14.

3-Carbethoxybicyclo[5.3.0]deca-4,6-diene (8). To an ice-cooled solution of the enone 7 (4.44 g, 0.02 mol) in ethanol (50 mL) was added sodium borohydride (0.40 g, 0.01 mol) in portions. Stirring was continued for 6 h, and the mixture was left overnight

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at room temperature. The complex was the decomposed with glacial acetic acid, and the solvent was removed under reduced pressure. Water (20 mL) was added, and the mixture was extracted with $CHCl_3$ (3 × 25 mL). To the combined extracts was added 15% hydrochloric acid (25 mL), and the mixture was refluxed for 4 h and then cooled, and the organic layer was separated. The aqueous layer was extracted once with $CHCl_3$, and the combined extracts were washed with saturated brine, dried (Na_2SO_4), and concentrated. Chromatography on silica gel (10:1 petroleum ether–EtOAc) gave 3.22 g (78%) of pure **8**: IR ($CHCl_3$) 1720 cm^{-1}; ^1H NMR (CDCl3) δ 1.19 (t, 3 H), 2.1–3.1 (m, 10 H), 4.0 (q, 2 H), 5.8 (m, 3 H).

Anal. Calcd for $C_{13}H_{18}O_2$: C, 75.73; H, 8.74. Found: C, 75.78; H, 8.78.

Azulene-5-carboxylic Acid (9). A mixture of diene **8** (2.06 g, 0.01 mol) and DDQ (100 mg) in benzene (75 mL) was refluxed for 14 h. The solution was cooled, filtered, diluted with ether, and washed with aqueous $NaHCO_3$ solution. A 20% NaOH solution (25 mL) was added to the organic phase, and the solution was stirred at 25 °C for 4 h. The organic layer was separated, and the aqueous phase was extracted once with benzene. The combined extracts were washed successively with water, dilute hydrochloric acid, and water, then dried (Na_2SO_4), and concentrated. The residue was crystallized (EtOAc–petroleum ether) to give violet crystals of **9** (1.2 g, 65%): mp 202–203 °C (lit.[9] mp 206–207 °C).

Acknowledgment. Financial support was provided by the Department of Science and Technology, and the Government of India is gratefully acknowledged. We also thank Dr. R. Balasubramanian for his help.

Registry No. **2**, 867-13-0; **3**, 99377-24-9; **4**, 99377-25-0; **5**, 7148-07-4; **6**, 99377-26-1; **7**, 99377-27-2; **8**, 99377-28-3; **9**, 1202-03-5; bromoacetone ethylene ketal, 33278-96-5.

An ab Initio Study of the Cyclobutadiene Dianion and Dication

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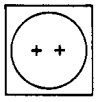
Hückel's rule predicts that both the dication (**1**) and dianion (**2**) of cyclobutadiene should be aromatic. Ion **1** contains two π electrons ($4n + 2$, $n = 0$) and ion **2** six π electrons ($4n + 2$, $n = 1$). However, more recent Hückel calculations with a Mulliken–Parr type of reference structure predict both to be nonaromatic (REPA = -0.001β).[1]



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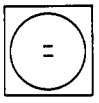
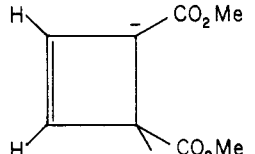


2

The little experimental evidence available seems to suggest that neither ion is particularly stable. While the parent dication **1** is unknown, Olah, Bollinger, White, and Mateescu have reported the synthesis of the tetramethyl and tetraphenyl derivatives (**3** and **4**).[2,3] However, their syntheses of **3** and **4** were later questioned by van der Hout-Lodder, de Haan, van de Ven and Buck because of the temperature dependence of the ^{13}C NMR spectrum of **4**.[4,5] They suggested that what Olah and co-workers had observed were the dications in equilibrium with their monocations. Olah and Staral subsequently published more details of the syntheses of **3** and **4** and reported the formation of first the monocations and subsequently the dications.[6] They concluded that if the equilibrium is present, the dication must be by far the dominant species. Perhaps the best evidence for the lack of strong π stabilization in **1** is an ab initio calculation reported in 1978.[7] It was found that the dication **1** is not planar but rather a puckered square (D_{2d}) with a dihedral angle of 144.2°.

McKennis, Brener, Schweiger, and Pettit[8] obtained evidence for the formation of dianion **2**; but they characterized it as being highly reactive since it apparently abstracted protons from THF. More recently Garratt and Zahler[9] measured the pK_a of **5** and concluded that the dianion formed from **5** has no special stabilization. They suggested that even the parent dianion **2** will be nonaromatic.



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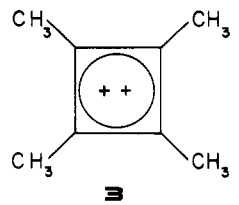
We have carried out an initial search of the potential surface of **2** with the 3-21G basis set.[10,11] Several geometries were examined: trapezoid (C_{2v}), rectangle (D_{2h}), puckered square (D_{2d}), rhombus (D_{2h}), square (D_{4h}). However, all led to a square geometry, which was the highest symmetry considered. The optimized square had a C–C bond distance of 1.470 Å and a C–H bond distance of 1.088 Å and an energy of −152.376 61 au. Reoptimization of the square with the 6-31G* basis[10] gave values of 1.455 and 1.077 Å and an energy of −153.245 73 au.

To be certain that the square structure was a minimum on the potential surface, a vibrational analysis was undertaken with the 6-31G* basis. It was found that for the E_g distortion (**6**) the energy decreased relative to the square structure and, thus, that indeed the square is not a minimum on the potential surface of the cyclobutadiene dianion. Structure **6** has lower symmetry (C_s) than any previously examined. Further optimization was then carried out with a C_s symmetry constraint. This was done with both the 3-21G and 6-31G* basis sets, and the results



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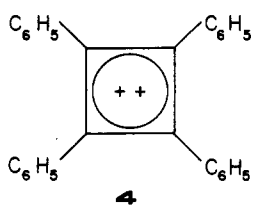

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(11) Although the 3-21G basis set was developed for neutral molecules, L. Radom (*Aust. J. Chem.* **1976**, *29*, 1635) has shown that with the similar 4-31G basis excellent agreement between calculated and experimental geometries was obtained for a number of mono- and dianions.

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