0.9 g of $ZnCl_2$ was refluxed for 1 h, cooled, and treated with 10 mL of water, and 5.0 g of powdered $K_2Cr_2O_7$ was added at once. This mixture was refluxed for 1 h, then cooled, and poured into ice and 20 mL of concentrated H_2SO_4. After the usual workup and crystallization from benzene was obtained 4.1 g (90%) of yellow **11b**: mp 258–259 °C; m/e 335.979 286, calcd for $C_{18}H_9BrO_2$ 335.978 640.

2-Bromo-7,12-dihydro-7,12-dihydroxy-7,12-dimethylbenz[*a*]anthracene (12b). To a suspension of 1.00 g of **11b** in 40 mL of benzene and 10 mL of THF was added 7.2 mL of 2.5 M methylmagnesium bromide in ether (Aldrich) and the mixture was held at reflux for 16 h and worked up as usual to give 0.972 g (89%) of crude diol, which on trituration with 10 mL of benzene followed by washing with hexane gave 0.345 g (32%) of **12b**: mp 218–219 °C dec. In the IR there was strong OH absorption and no carbonyl band: m/e 353.018 597, calcd for $C_{20}H_{17}BrO_2$ 353.017 763.

2-Bromo-7,12-dimethylbenz[*a*]anthracene* (3). To the clear solution of 1.7 g of $SnCl_2$ in 30 mL of ether containing 1.5 mL of concentrated HCl was added 300 mg of **12b** in two portions during 5 min. After 20 min the mixture was worked up as usual, chromatographed over basic alumina, and crystallized from EtOH–CH_2Cl_2 to obtain 0.16 g (59%) of **3**: mp, 91–92.5 °C.

3-Bromo-7,12-benz[*a*]anthraquinone (11c). By treatment of 2.5 g of **9c** essentially as described for **9b** was obtained 2.20 g (89%) of **11c** (mp 219–220 °C; m/e 335.9764, calcd for $C_{18}H_9BrO_2$ 335.9785) after chromatography over basic alumina ($CHCl_3$).

3-Bromo-7,12-dimethylbenz[*a*]anthracene* (4). To a solution of 1.00 g of **11c** in 40 mL of THF under nitrogen was added 4.5 mL of 1.48 M methyllithium in ether. After 20 h at room temperature the mixture was treated with water and worked up as usual to yield a mixture containing dimethyl diol. A solution of the crude diol in 20 mL of ether was added to a stirred solution of 5.0 g of $SnCl_2$ and 3 mL of concentrated HCl in 20 mL of ether. After 20 min, the products, isolated as usual, were chromatographed over basic alumina to yield **4**, which was purified by vacuum sublimation to give 0.33 g (33% from **11c**) of **4**: mp 159–160 °C.

Registry No. 1, 86456-53-3; 1·picrate, 86456-54-4; **2**, 86456-55-5; **3**, 78302-37-1; **4**, 78302-38-2; **5a**, 85864-82-0; **6b**, 81830-59-3; **7c**, 86456-56-6; **8a**, 86456-57-7; **8b**, 86470-91-9; **8c**, 86456-58-8; **9a**, 86456-59-9; **9a** (acid chloride), 86456-73-7; **9b**, 81846-82-4; **9c**, 86456-60-2; **9c** (acid chloride), 86456-72-6; **10a**, 86456-61-3; **10c**, 86456-62-4; **11b**, 49600-95-5; **11c**, 78302-29-1; **12b**, 86456-63-5; **12c**, 86456-64-6; **13**, 20005-55-4; **14**, 86456-65-7; **15**, 86456-66-8; **16**, 31042-07-6; **17**, 51644-34-9; **18**, 86456-67-9; **19**, 86456-68-0; **20**, 86456-69-1; **20**·hexamethylenetetramine, 86456-70-4; *p*-bromoacetophenone, 99-90-1; 3-(4-bromophenyl)butanoic acid, 53086-46-7; 1-(4-bromophenyl)ethyl bromide, 24308-78-9; diethyl malonate, 105-53-3; diethyl 2-[1-(4-bromophenyl)ethyl]malonate, 59771-11-8; 4,4-dimethyl-2-phenyl-2-oxazoline, 19312-06-2; 6-bromo-α-[2-(4,4-dimethyl-2-oxazolin-2-yl)phenyl]-1-naphthalenemethanol, 86456-71-5; 8-bromo-1-naphthoic acid, 1729-99-3; anhydro-8-hydroxymercuric-1-naphthoic acid, 6314-27-8; (8-bromo-1-naphthyl)methanol, 14938-58-0; methyl bromide, 74-83-9.

Molecular Geometries and Relative Stabilities of Acyclic π-Conjugated C_6H_8 Dianions. A Simple Prediction and ab Initio Molecular Orbital Study

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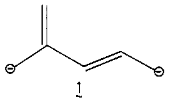
Received December 23, 1982

π-Conjugated dianions of acyclic hydrocarbons were recently subjected to theoretically and experimentally rigorous investigations.[1-8] The stability of the cross-conjugated trimethylenemethane dianion relative to the linearly conjugated butadiene dianion has been well established.[1-5] Attention is here concentrated on the relative stabilities and molecular geometries of the higher homologues. All isomers of acyclic C_6H_8 conjugated dianions, **1–4**, have been prepared by Bates et al.[5-7]



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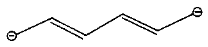

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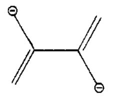

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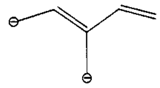

4

Recently, we showed[4] that *acyclic* conjugated molecules contain *cyclic* interactions among the orbitals of the component systems such as lone-pair electrons and bonds and that the extent of the electron delocalization is under the control of the orbital-phase continuity–discontinuity properties. The phase requirements for the delocalization are the same as those in cyclic conjugated systems: (i) the electron-donating (occupied) orbitals out of phase; (ii) the electron-accepting (unoccupied) oribitals in phase; (iii) the donating and accepting orbitals in phase. Two principles important for the present purpose can be drawn from the requirements. The electron delocalization from the geminal anionic centers to the double bond is favored by the orbital phase continuity as was shown for trimethylenemethane dianion while that from the vicinal ones as in butadiene dianion is disfavored by the phase discontinuity.[4] The difference is produced by the bond polarization allowed in the trimethylenemethane dianion and forbidden in the butadiene dianion. The electron delocalization from the anionic center to a distant bond across another is favored by the phase continuity for linear conjugation while disfavored by the phase discontinuity for cross-conjugation.

There are a number of Kekulē structures for each isomer. The two anionic centers are assumed to be separated from each other as far as possible in the main Kekulē structures as shown by **1–4**.[9] All contain butadiene structures with anionic centers in the different positions. The degree of electron delocalization is primarily determined by the delocalization of anionic lone-pair electrons to the adjacent double bonds. This delocalization is not restricted by the orbital-phase properties except for **4**. The Kekulē structure **4** contains a butadiene dianion unit where the delocalization is disfavored (the first principle). Therefore, **4** is predicted to be the least stable dianion. Secondarily, the whole delocalization is determined by the distant delocalization of the anionic lone pairs beyond a bond. The distant delocalization is depressed by the cross-conjugation for both anionic lone pairs in **3**, for one in **1**, and for neither in **2** (the second principle). The stability is then expected to increase in the order **3** < **1** <

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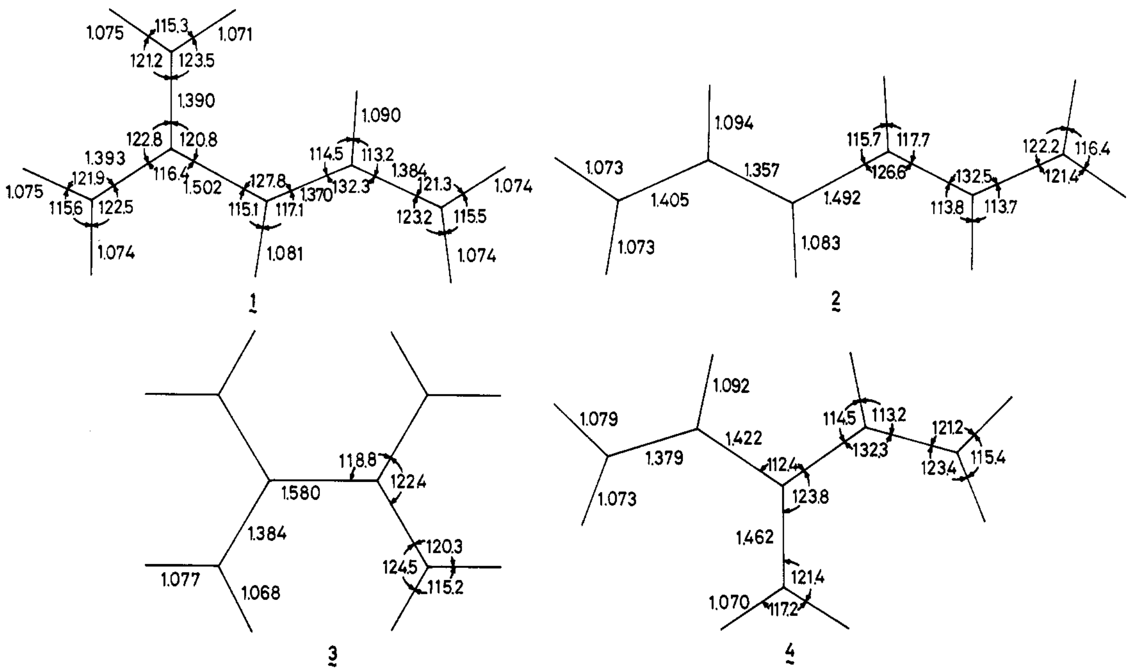

Figure 1. STO-3G optimized structures for the planar hexatriene dianion and its isomers.

Table I. Results of ab Initio Molecular Orbital Calculations

dianion	relative energies, kcal/mol STO-3G[a]	relative energies, kcal/mol 4-31G[a]
1	−53.4	−34.8
2	−52.2	−31.2
3	−36.1	−18.5
4	0.0	0.0

[a] The molecular geometries optimized at the STO-3G level were employed.

2. However, the first principle is not taken into account in the delocalizability estimation. This effect favors the vinylogue of the trimethylenemethane dianion 1 to that of the butadiene dianion 2. There are no existing theories available for predicting which principles govern the relative stability of 1 and 2. The problem remains to be solved here by the ab initio molecular orbital calculation. As a result, the stability is predicted to decrease in the order 1, 2 > 3 > 4.

The geometries were optimized by the ab initio SCF-MO calculations with minimal (STO-3G) basis sets.[10] The energy was calculated at the 4-31G level as well (Table I).[11] Both calculations show that the stability decreases in the order 1 > 2 > 3 > 4. The energy difference between 1 and 2 is far smaller (1.2 kcal/mol at STO-3G; 3.6 kcal/mol at 4-31G) than those (more than 16.1 kcal/mol at STO-3G and 12.7 kcal/mol at 4-31G) between any other pairs. This ordering is partially different from that predicted by the resonance energy per atom (1 > 3 > 2 > 4).[5] Just recently, experiments confirmed a part of the ordering. The cross-conjugated dianion 1 was found to be thermodynamically more stable than the linearly conjugated dianion 2.[12]

There is a noticeable feature in the optimized geometries (Figure 1). The dianions 1–3 are separated by a sizably long (1.50, 1.49 and 1.58 Å) bond into two allyl anions with shorter (less than 1.41 Å) bonds. Charge distribution is in agreement with the molecular composition. There is a significant negative charge on the terminal carbons of the "allyl" groups while the central carbons are almost neutral (Figure 2[13]). This is confirmed by the X-ray anaylsis for the dianion 2 ion paired with lithium–TMEDA.[14] In contrast, the dianion 4 is considered to be a combination of an isolated carbanion center and the pentadienyl anion with negative charges on the alternated carbons. This spearation is not so distinguishable as that for 1–3. The distance (1.46 Å) between the anionic moieties is closed to some of the bond lengths (1.42 Å) in the pentadienyl group.

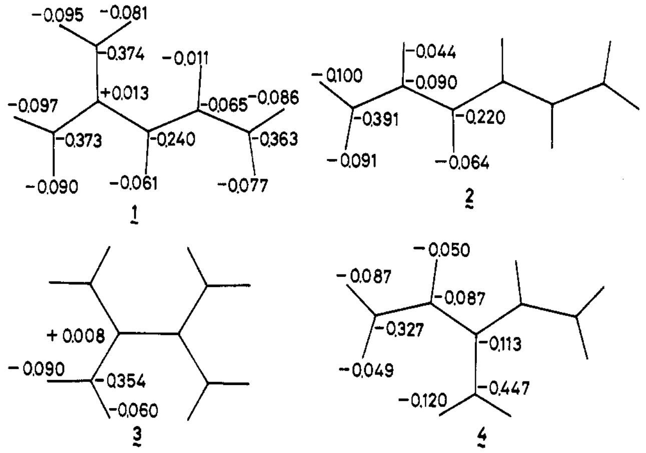

Figure 2. Charge distribution in the planar hexatriene dianion and its isomers.

Acknowledgment. The calculation was carried out on a HITAC-M200H computer, Institute for Molecular Science.

Registry No. 1, 64080-78-0; 2, 64080-77-9; 3, 69780-62-7; 4, 78831-99-9.

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[10] The IMSPACK program was employed.

[11] (a) Some high-lying occupied molecular orbitals of 1–4 have positive energy values. (b) The total energy of the reference species 4 is −228.3168 hartrees at STO-3G and −231.1155 hartrees at 4-31G.

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[13] The results of the STO-3G calculations are shown. The 4-31G calculations yielded similar charge distributions, although the charge separation is greater.

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