strictions, especially for *trans*-4, cause conrotatory opening of dienes 4 to be mainly a scissors-opening motion with rotation about the C_7–C_8 bond.

Actually, the dianions are not "free"; they must be tightly coordinated with lithium ions. Such coordination could facilitate bond breaking. If a dimethylenecyclobutane dianion were coordinated with two lithium ions, both centered on the diene system, but one above and one below the molecular plane, con-
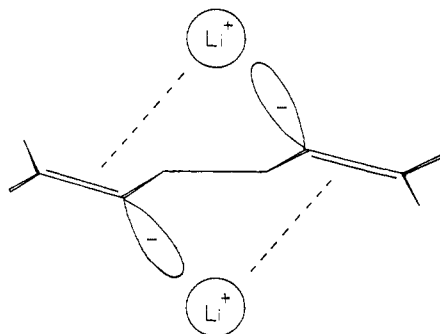
15

rotatory opening (to a dihedral angle of *ca.* 45°) would lead to a quadrupole-like structure, 15, an arrangement which should be energetically highly favorable. Additionally, in 15 each lithium ion would be close to and thus should be coordinated by the π electrons of the adjacent double bond.

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1,3,7,9,13,15,19,21-Octadehydro[24]annulene and Its Anions[1]

Sir:

We report the synthesis of the nonplanar 1,3,7,9,-13,15,19,21-octadehydro[24]annulene (5), and its conversion to the planar-delocalized radical anion 6 and dianion 7. The aromatic character of the 26 out-of-plane π-electron dianion 7, the first dianion of a dehydroannulene to be prepared,[2] is in contrast to the nonaromatic character of the neutral 26π-electron system tridehydro[26]annulene.[3]

A mixture of *trans*- and *cis*-3-hexene-1,5-diyne (2a–3a, $\sim$3:2) in ether solution, prepared from 1,5-hexadiyn-3-ol *p*-toluenesulfonate (1) as described previously,[4] was treated with ethylmagnesium bromide ($\sim$1.7 mol equiv) in tetrahydrofuran and then with chlorotrimethylsilane ($\sim$1.8 mol equiv) at room temperature. Distillation, followed by chromatography of the stereoisomeric

(1) Unsaturated Macrocyclic Compounds. LXXV. For part LXXIV, see G. M. Pilling and F. Sondheimer, *J. Amer. Chem. Soc.*, in press.

(2) For the synthesis of the radical anions of dehydroannulenes, see H. A. Staab and F. Graf, *Tetrahedron Lett.*, 751 (1966); *Chem. Ber.*, 103, 1107 (1970); N. M. Atherton, R. Mason, and R. J. Wratten, *Mol. Phys.*, 11, 525 (1966).

(3) C. C. Leznoff and F. Sondheimer, *J. Amer. Chem. Soc.*, 89, 4247 (1967). See also M. J. S. Dewar and G. J. Gleicher, *ibid.*, 87, 685 (1965).

(4) W. H. Okamura and F. Sondheimer, *ibid.*, 89, 5991 (1967).

2a, R = H
2b, R = SiMe$_3$

3a, R = H
3b, R = SiMe$_3$

5

4a, R = H
4b, R = SiMe$_3$
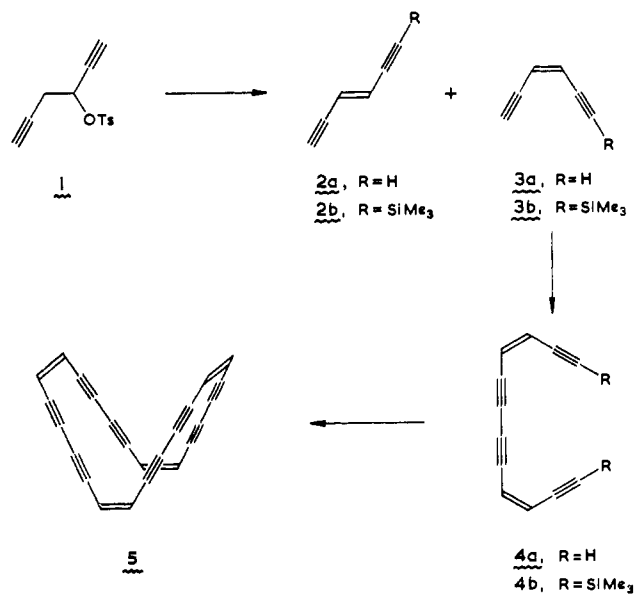
mono(trimethylsilyl) derivatives on silica gel, gave 25% (based on 1) of the trans compound 2b [liquid, >98% pure by glc; λ_{max}^{EtOH} 249 sh (ϵ 15,200), 254 sh (18,400), 261 (26,800), and 276 nm (25,600)][5] and then 14% (based on 1) of the cis compound 3b [liquid, >98 % pure by glc; λ_{max}^{EtOH} 249 sh (ϵ 10,200), 254 sh (11,400), 261 (16,400), and 276 nm (15,600)].[5,6] Substances 2b and 3b were much more stable than 2a and 3a, and are convenient derivatives for separation, storage, and further transformations.

Compound 3b in acetone containing N,N,N',N'-tetramethylethylenediamine and cuprous chloride was coupled by shaking with oxygen at room temperature.[7] Chromatography on silica gel gave 70% of the "dimer" 4b as a yellow oil, homogeneous to tlc: $\lambda_{max}^{C_6H_{12}}$ 257 sh (ϵ 18,700), 265 (22,400), 279 (20,900), 295 (24,800), 302 sh (18,700), 312 (22,300), 317 (22,300), 324 sh (18,700), 340 (30,400), and 366 nm (29,700); mass spectrum, m/e 294.127 (calcd for $^{12}C_{18}{}^1H_{22}{}^{28}Si_2$: 294.126).[5]

Removal of the protecting groups of 4b by the silver nitrate–potassium cyanide method[8] led to the unstable dienetetrayne 4a [λ_{max}^{ether} (>300 nm) 302.5 (ϵ 15,800), 310 sh (12,100), 323.5 (22,000), and 347 nm (21,200)[9]], which was coupled directly in ether and pyridine (1:1) with cupric acetate[10] at room temperature for 2 hr. Chromatography on alumina then yielded 20% (based on 4b) of the octadehydro[24]annulene (5) as yellow-orange crystals (bright yellow in concentrated solution): explosion point $\sim$130° (capillary); λ_{max}^{ether} 243 (ϵ 50,600), 248 (50,400), 307 sh (27,400), 317 sh (29,500), 329 (38,900), 341 (38,300), and 352 nm (45,100); $\nu_{max}^{CHCl_3}$ 2110 (w) cm^{-1} (C≡C); nmr spectrum (THF-d_8, 100 MHz), τ 3.85 (sharp s). The solid substance was

(5) The nmr and infrared spectra, as well as the elemental analysis or high-resolution mass spectrum, were in accord with the assigned structure.

(6) Further amounts of 3b could be obtained by photolysis of 2b in pentane with a Hanovia low-pressure mercury vapor lamp at 0°, which led in $\sim$80 , yield to an equilibrium mixture of 2b and 3b ($\sim$2:3).

(7) See A. S. Hay, *J. Org. Chem.*, 27, 3320 (1962); R. Eastmond and D. R. M. Walton, *Chem. Commun.*, 204 (1968).

(8) J. F. Arens and H. M. Schmidt, *Recl. Trav. Chim. Pays-Bas*, 86, 1138 (1967).

(9) The ϵ values represent minimum ones, due to the instability of the substance.

(10) See G. Eglinton and A. R. Galbraith, *J. Chem. Soc.*, 889 (1959).

very unstable (*e.g.*, it detonated with a flash on being rubbed), but could be stored in ether solution at 0°. A satisfactory elemental analysis or mass spectrum could not be obtained for this reason, but the assigned structure follows from the method of synthesis, the spectral data, and the fact that catalytic hydrogenation in ethyl acetate over platinum gave cyclotetracosane (mass spectrum, m/e 336).

The octadehydro[24]annulene (**5**) is formally derived from cyclooctatetraene by insertion of four 1,3-diyne rods, and, like this substance, appears to be nonplanar. This follows from the general similarity of the electronic spectrum to that of the precursor **4a** (both in λ_{max} and ϵ values, taking into account that **5** is made up of two units of **4a**), and especially from the fact that the position of the proton resonance in the nmr spectrum (τ 3.85 in THF-d_8) is not shifted upfield compared with linear models (*e.g.*, **3a**, τ 4.11 in CCl_4; **4b**, τ 4.06 in THF-d_8). This is in contrast to the presumably more planar 1,7,13,19-tetradehydro[24]annulene[11] and 1,3,9,-11,17,19-hexadehydro[24]annulene,[12] in which the outer protons are shifted appreciably upfield due to a paramagnetic ring current. The fact that **5** is nonplanar is probably due to the presence of four cis double bonds and the comparative rigidity imposed by the four 1,3-diyne units.

Contact of a solution of the octadehydro[24]annulene (**5**) in THF-d_8 with a potassium mirror at room temperature *in vacuo* resulted in the immediate disappearance of the nmr signal. The esr hyperfine spectrum of the deep blue solution in THF consisted of nine equally spaced lines, and these had the approximate relative intensities expected for the hyperfine splittings of a symmetrical radical anion with eight equivalent protons. The line width was about 0.15 G,[13] and a value of 1.66 G was found for a^H, the hyperfine interaction. The small value of a^H compared to that observed for the cyclooctatetraenyl radical anion (3.21 G)[13] indicates that the electron spends part of the time on the acetylenic carbon atoms.

Contact of **5** in THF-d_8 with the potassium mirror (with occasional shaking) for 2 hr resulted in the appearance of a new singlet at τ 3.88[14,15] (*i.e.*, at approximately the same position as that of **5**), which we attribute to the dianion. This signal slowly decreased in intensity on further contact with potassium. Quenching this solution with water gave only some **5** and a considerable amount of polymer.

The course of the reduction of **5** in THF with a potassium mirror could be followed most conveniently by examination of the electronic spectrum. After shaking for 1 min, the spectrum showed λ_{max} (>380 nm) 389 (relative optical density 0.39), 428 (0.35), 441 (0.36), 446 (0.37), 468 (0.33), 564 (0.04), 582 (0.03), 595 (0.02), and 638 nm (0.07), as well as maxima due to **5**. After 10 min, the spectrum was similar but the optical den-

sities of the new bands were greater. The 468-nm maximum then increased in intensity at the expense of the other bands and gradually moved to higher wavelength, until after ∼1 hr the spectrum (>300 nm) consisted simply of one maximum at 476 nm. The spectrum after 1 min is considered to be due to mainly the radical anion, and the final spectrum to the dianion.[16]

The simple esr spectrum of the radical anion demands that the molecule has a high degree of symmetry, and this is most readily accommodated by the planar delocalized structure **6**, formally derived from the cyclo-

6   **7**
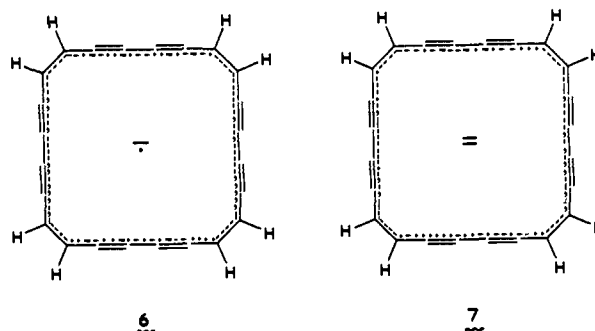
octatetraenyl radical anion[13] by elongation of alternate bonds. The proton chemical shift of the nmr spectrum of the dianion is at lower field than would be expected for a localized system having two excess electrons,[17] and is indicative of the planar delocalized structure **7**. The coincident position of the nmr signals of **5** and **7** is attributed to the balance between the deshielding effect of the diamagnetic ring current and the shielding due to the excess electron density, as has previously been observed for cyclooctatetraene and its dianion.[18]

(16) The fact that the electronic spectra of this type of radical anion is more complex than that of the corresponding dianion has been observed before (see N. S. Hush and J. R. Rowlands, *Mol. Phys.*, 6, 317 (1963).

(17) See G. Fraenkel, R. E. Carter, A. McLachlan, and J. H. Richards, *J. Amer. Chem. Soc.*, 82, 5846 (1960); T. Shaeffer and W. G. Schneider, *Can. J. Chem.*, 41, 966 (1963).

(18) T. J. Katz, *J. Amer. Chem. Soc.*, 82, 3784, 3785 (1960).

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(11) See F. Sondheimer, I. C. Calder, J. A. Elix, Y. Gaoni, P. J. Garratt, K. Grohmann, G. di Maio, J. Mayer, M. V. Sargent, and R. Wolovsky, *Chem. Soc. Spec. Publ.*, No. 21, 75 (1967).

(12) G. P. Cotterrell, G. H. Mitchell, and F. Sondheimer, unpublished experiments.

(13) For the method of measurement and its significance, see H. L. Strauss, T. J. Katz, and G. K. Fraenkel, *J. Amer. Chem. Soc.*, 85, 2360 (1963).

(14) Measured from the low-field band of THF, taken as τ 6.40.

(15) At the concentrations required for the nmr experiments, the formation of a black insoluble polymer occurred in a number of cases, and no new signal was observed.

Photodecomposition of *cis*- and *trans*-2,4-Dimethylcyclobutanones in the Gas Phase. Stereochemical Inversion in the Decarbonylation Process and Unimolecular Lifetime of the Hot Ground State[1]

Sir:

We have recently reported one aspect of the stereochemistry in the thermal and photolytic decomposition of *cis*- and *trans*-2,3-dimethylcyclobutanones (DMCB).[2]

(1) This research has been supported by National Science Foundation Grant No. GP 11390.

(2) H. A. J. Carless and E. K. C. Lee, *J. Amer. Chem. Soc.*, 92, 4482 (1970).