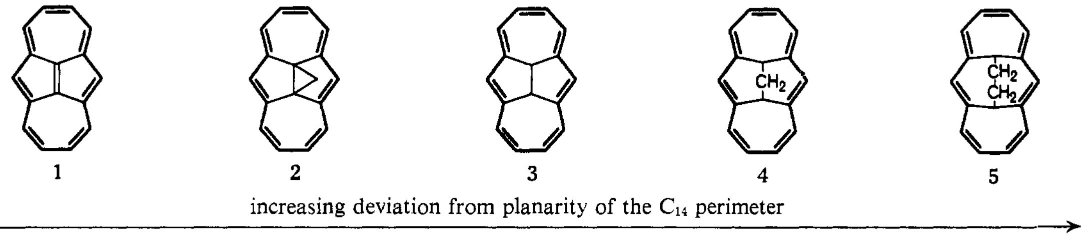
Bent [14]Annulenes. Synthesis of 1,6:8,13-Ethanediylidene[14]annulene

Sir:

The stepwise bending or deformation of an originally planar, cyclically conjugated $(4n + 2)$ π system commands considerable theoretical interest in that it would permit the geometrical prerequisite for aromaticity implicated in Hückel's rule to be subjected to experimental scrutiny.[1] Actually, several groups of investigators have already pursued the goal to enforce, by proper steric devices, a systematic departure of a benzene nucleus from planarity.[2,4,5] The difficulties encountered in these efforts strongly suggest, however, that higher aromatic benzene homologs, due to enhanced flexibility, might be better amenable to the proposed conformational alterations of the ring skeleton.[6a,b]

Chart I. Systematically Bent Bridged [14]Annulenes with an Anthracene Perimeter

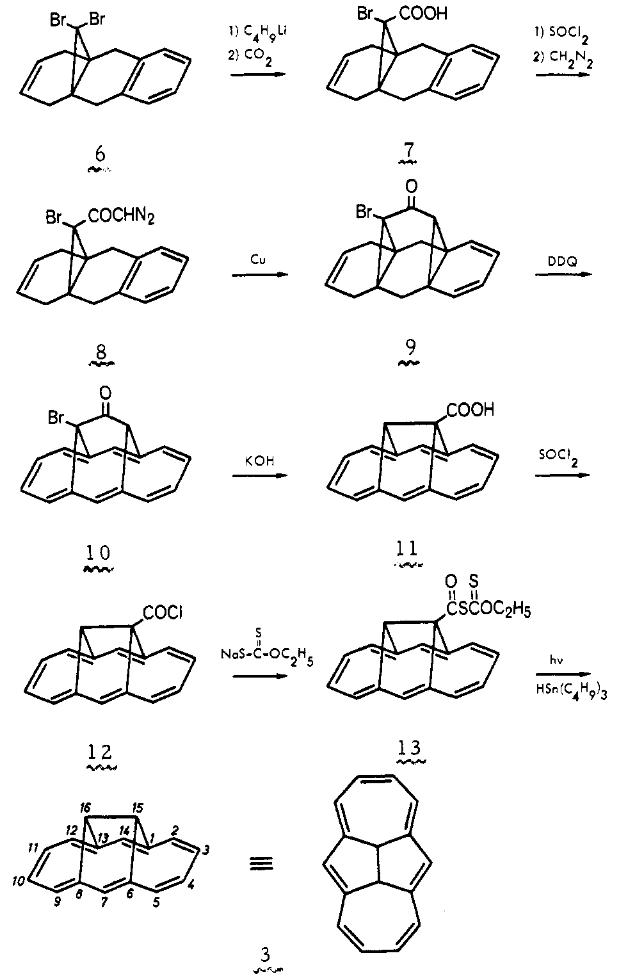


In the course of our research on bridged annulenes with a naphthalene or acene $C_{(4n+2)}$ perimeter[3a,b] it occurred to us that the [14]annulenes **2–5** which are formally derived from the as yet hypothetical planar dicyclohepta[*cd,gh*]pentalene (**1**)[7a–d] would constitute a series (Chart I), almost ideally suited for the correlation of the physical and chemical properties of a $(4n + 2)$ π system with changes in geometry of the $(4n + 2)$ carbon framework. As inferred from molecular models, the C_{14} perimeters of annulenes **2–5** experience progressive bending as one proceeds from left to right in the series.[8] Following the preparation of **4**[3a,b] and **5**,[3b] we now report the synthesis and some of the properties of 1,6:8,13-ethanediylidene[14]annulene (**3**) (Scheme I).

The approach to **3** encompassed three major stages: (1) the preparation of **10**, (2) generation of the 1,6:8,13-ethanediylidene bridge by a Favorski rearrangement of **10**, and (3) decarboxylation of **11** under the mildest possible conditions in order to avoid dehydrogenation.

The pathway taken to **10** started out from the adduct of dibromocarbene to 1,4,5,8,9,10-hexahydroanthracene.[3a,b] Heating of the adduct with 3,4-dichloro-5,6-dicyanobenzoquinone (DDQ) in benzene readily effected dehydrogenation to give **6**, mp 148°, in 85% yield. When **6** was metallated in tetrahydrofuran (THF) with 1 equiv of *n*-butyllithium at −90°, and the intermediate α-bromolithium compounds decomposed with carbon dioxide, there was obtained in 85% yield a 3:1 mixture of the two stereoisomeric α-bromocarboxylic acids with **7** representing the major isomer.

Scheme I



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(1) The steric condition for a cyclically conjugated $(4n + 2)$ π system to be aromatic, *i.e.*, the presence of a planar or near-planar ring skeleton, manifests itself most dramatically in the purely olefinic properties of the few known $[4n + 2]$annulenes with severely bent or distorted skeletons, notably 2,2a,3,3a,4,5-hexahydro-1*H*-cyclopent[*jkl*]-*as*-indacene (a bent [6]annulene)[2] and *anti*-1,6:8,13-bismethano[14]-annulene.[3a,b]

(2) H. Rapoport and G. Smolinsky, *J. Amer. Chem. Soc.*, **82**, 1171 (1960).

(3) For reviews, see (a) E. Vogel, *Proc. Robert A. Welch Found. Conf. Chem. Res.*, **12**, 215 (1968); (b) *Pure Appl. Chem.*, **28**, 355 (1971).

(4) D. J. Cram, C. S. Montgomery, and G. R. Knox, *J. Amer. Chem. Soc.*, **88**, 515 (1966).

(5) Bent and battered benzene rings in cyclophane chemistry have been the subject of an illuminating recent review by D. J. Cram and J. M. Cram, *Accounts Chem. Res.*, **4**, 204 (1971).

(6) For reviews on annulenes, see (a) F. Sondheimer, *Proc. Robert A. Welch Found. Conf. Chem. Res.*, **12**, 125 (1968); (b) F. Sondheimer, *Accounts Chem. Res.*, **5**, 81 (1972).

(7) For theoretical calculations on **1**, see (a) E. R. Hanna, K. T. Finley, W. H. Saunders, Jr., and V. Boekelheide, *J. Amer. Chem. Soc.*, **82**, 6342 (1960); (b) R. Zahradnik, *Angew. Chem.*, **77**, 1097 (1965); (c) D. E. Jung, *Tetrahedron*, **25**, 129 (1969); (d) P. Baumgartner, E. Weltin, G. Wagnière, and E. Heilbronner, *Helv. Chim. Acta*, **48**, 751 (1965).

(8) An X-ray structure analysis of **4** has been reported by G. Casalone, A. Gavezzotti, A. Mugnoli, and M. Simonetta, *Angew. Chem.*, **82**, 516 (1970), and of **5** by C. M. Gramaccioli, A. Mugnoli, T. Pilati, M. Raimondi, and M. Simonetta, *Chem. Commun.*, 973 (1971).

Separation of pure **7**, mp 232–233° dec, was achieved by fractional crystallization from ethanol. Treatment of **7** with thionyl chloride in THF in the presence of sodium carbonate and a catalytic amount of dimethylformamide produced the corresponding acid chloride which, by reaction with diazomethane, led to the diazo ketone **8**. Without isolation, **8** was subjected to copper-catalyzed thermolysis in cyclohexane to furnish **9** as white crystals, mp 196–197° dec (the overall yield from **7** to **9** was *ca.* 50%). Aromatization of **9** could be carried out with excess DDQ in refluxing chlorobenzene, affording **10** as orange needles (THF), mp 282–284° dec, in 45% yield.

The conversion of **10** to **11** by a Favorskii rearrangement smoothly occurred when **10** was heated with 20% KOH in methanol–water (50:50) at 90° (1 hr). Compound **11**, obtained as red cubes, mp 238–239° (THF), in 95% yield, was best characterized as its methyl ester, mp 153–154°: nmr ($CDCl_3$) multiplet at τ 1.55–2.30 (H_2–H_5 and H_9–H_{12}) and three singlets at 1.98 (H_7, H_{14}), 7.30 (methyl protons), and 11.69 (H_{16}).

Not too surprisingly, the decarboxylation of **11** proved to be the most demanding step. As conventional thermal methods failed to generate **3**, photochemical reactions were envisaged. Our attention chiefly focused on Barton's[9] photolysis of *S*-acyl xanthates, a reaction that in general leads to *S*-alkyl xanthates. Since the *S*-alkyl xanthates on hydrolysis afford thiols, the decarboxylation problem would in theory then be reduced to the task of desulfurization.

The *S*-acyl xanthate **13**, prepared from **12** and sodium *O*-ethyl xanthate, rapidly decarbonylated upon irradiation in benzene with a high-pressure mercury lamp (Philips HPK 125). Interestingly, the product obtained was not the anticipated *S*-alkyl xanthate but rather the desired hydrocarbon **3** (30% yield). Execution of the decarbonylation reaction in the presence of tri-*n*-butyltin hydride afforded **3** in yields as high as 60%. 1,6:8,13-Ethanediylidene[14]annulene (**3**) thus produced forms scarlet red plates, mp 118–119° (methanol), and is a perfectly stable compound.

The 100-MHz nmr spectrum of **3** (0.35 *M* ($CDCl_3$); TMS), consisting of an AA′BB′ system at τ_A 1.83 (H_2, H_5 and H_9, H_{12}) and τ_B 2.18 (H_3, H_4 and H_{10}, H_{11}) ($J_{23} = 9.42$, $J_{24} = 0.47$, $J_{25} = 1.17$, and $J_{34} = 9.72$ Hz) and two singlets at τ 2.00 (H_7, H_{14}) and 11.82 (H_{15}, H_{16}), rigorously proves the assigned structure and, moreover, in agreement with the assumptions based on molecular models, indicates a noticeably stronger ring current effect for the compound than is observed for the higher homologs **4** and **5**. The uv spectrum of **3** [λ_{max} (cyclohexane) 308 (ϵ 202, 500), 339 (25, 100), 381 (10, 900), 398 sh (6000), 472 (350), and 551 nm (3700)] is similar to those of **4** and **5**, but shows a bathochromic shift and increased intensity for the band of longest wavelength.

A most remarkable chemical feature of **3** is its resistance toward dehydrogenation under a variety of conditions. Thus, the hydrocarbon remains essentially unaffected when treated with $Pd/BaSO_4$ in boiling decalin (*ca.* 200°!) for 2 hr, even though the anticipated product, **1**, has been postulated to be a stable aromatic molecule.[7a]

The relationship of **3** and its hypothetical trans isomer to Boekelheide's[10] *cis*- and *trans*-15,16-dihydropyrenes will be discussed in a forthcoming publication.

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(9) D. H. R. Barton, M. V. George, and M. Tomoeda, *J. Chem. Soc.*, 1967 (1962).

(10) For a review on 15,16-dihydropyrenes, see V. Boekelheide, *Proc. Robert A. Welch Found. Conf. Chem. Res.*, **12**, 83 (1968); see also, R. H. Mitchell and V. Boekelheide, *Chem. Commun.*, 1555 (1970).

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Circular Dichroism of Polypeptide Solutions in the Vacuum Ultraviolet

Sir:

Previous measurements of the circular dichroism (CD) of polypeptides have been limited to the wavelength region above 183 nm.[1,2] It is important to make measurements below this wavelength cutoff of commercial instruments, because theoretical calculations of the CD spectrum predict a large negative peak near 180 nm.[3,4] The predicted peak is assigned to the negative lobe of a CD band which has the shape of the derivative of an absorption curve.[5] This type of CD band is central to the correct interpretation and understanding of the CD of helical polymers.[6,7]

Figure 1 shows the measured CD of poly-L-glutamic acid as a helix (pH 4.5) and coil (pH 8), and of *N*-acetyl-L-alanine-*N*′-methylamide. The molecules were dissolved in water and adjusted to the required pH with NaOH; no other salt was added. All measurements were made on a vacuum ultraviolet CD spectrometer described elsewhere.[8] The spectrometer was calibrated using a value of $\epsilon_L - \epsilon_R = 2.20$ at 290.5 nm for *d*-10-camphorsulfonic acid in water.[1] Samples were prepared by putting 1 drop of solution with a concentration of about 5 mg/ml between polished, clean CaF_2 windows with no spacer. Windows were carefully chosen so that they mated with only a single fringe over most of their area. The sample thickness was about 1–10 μ and was controlled by the size of the drop put on the CaF_2 plate. Different path lengths were used for different wavelength regions, but the total absorbance of the cell, solvent, and sample was kept below 1.0 for all measurements. The sample thickness was determined from the known CD of the molecules in the near-ultraviolet. The helix CD at 190 nm and the coil CD at 195 nm were chosen as reference points.[9]

Instead of a negative peak below 180 nm, a positive shoulder is seen for the helix in Figure 1. This must be caused by a transition not previously considered in the theoretical analysis. Cassim and Yang[1] had inferred the absence of a negative peak near 180 nm from a careful comparison of their measured CD and ORD above 183 nm. They concluded that either the theory of the CD of polypeptides was in error, or an unexpected new band was cancelling the predicted trough.

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(1) J. Y. Cassim and J. T. Yang, *Biopolymers*, **9**, 1475 (1970).

(2) J. R. Parrish, Jr., and E. R. Blout, *ibid.*, **10**, 1491 (1971).

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(5) I. Tinoco, Jr., *J. Amer. Chem. Soc.*, **86**, 297 (1964).

(6) W. Moffitt, *J. Chem. Phys.*, **25**, 467 (1956).

(7) W. Moffitt, D. D. Fitts, and J. G. Kirkwood, *Proc. Nat. Acad. Sci. U. S.*, **43**, 1046 (1957).

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