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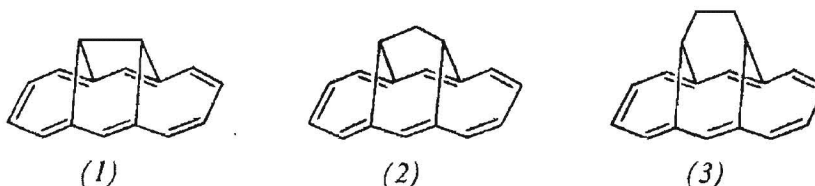
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REPRINT

1,6:8,13-Butanediylidene[14]annulene^[1]

By Emanuel Vogel, Wolfgang Sturm, and
Hans-Dieter Cremer^[*]

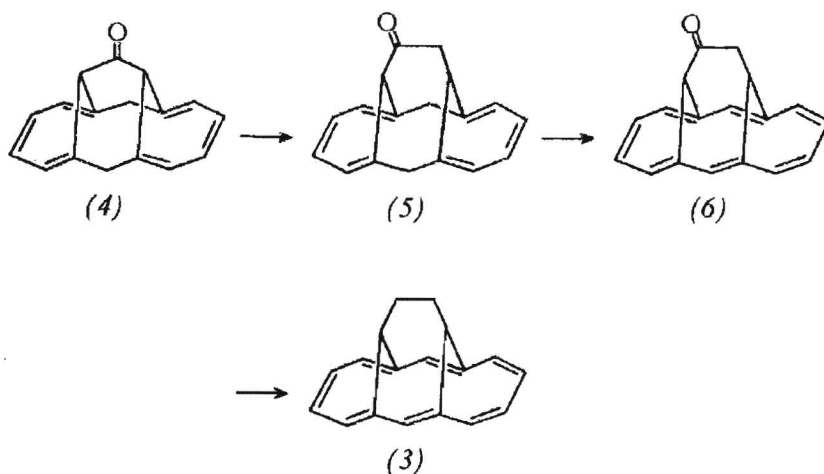
Replacement of the two inner bridge-protons in the as yet unknown syn-1,6 : 8,13-bismethano[14]annulene by one or more CH₂ groups — and, in the simplest case, direct linkage of the two bridging C atoms — leads to the series (1), (2), (3), etc. of bridged [14]annulenes, of which one member, 1,6 : 8,13-propanediylidene[14]annulene (2)^[2], has already been described.



From consideration of molecular models it can be predicted that (2) has an approximately planar annulene ring^[3], whereas for the higher analogs of (2) the (CH₂)_n intermediate bridges will compel progressive bending and/or zig-zagging of the peripheral C₁₄ skeleton. According to the models it is probable that the lower homolog of (2), *i.e.* 1,6 : 8,13-ethanediylidene[14]annulene (1), will fulfill the steric requirements for delocalization of the π -electrons even better than (2) itself. Thus the [14]annulene series (1), (2), (3), etc., opens up the possibility of studying the properties of a cyclic conjugated system in relation to the geometry of the ring skeleton.

The starting point for the synthesis of 1,6 : 8,13-butanediylidene[14]annulene (3) was the dihydro[14]annulene ketone

(4) [2]. Treatment of a solution of the ketone (4) in methanol-methylene dichloride (1 : 1) with ethereal diazomethane led to, amongst other products, the required homologous ketone (5) [m.p. 131–132 °C; NMR (CDCl₃), $\tau = 3.5$ –4.2 (multiplet consisting of two partially superimposed AA'XX' systems, 8 C=CH), 6.41 and 7.01 (AB system with $J = 13$ Hz, 2 allylic CH₂), 6.87 (d with $J = 3.5$ Hz, bridge-CH₂), 7.22 (s, 1 bridge-CH), 7.80 (t with $J = 3.5$ Hz, 1 bridge-CH); UV (cyclohexane), $\lambda_{\max} = 224$ ($\epsilon = 30300$), 261 nm (7100)], which could be isolated in 7% yield by chromatography on silica gel with methylene dichloride-hexane (2 : 1). 2,3-Dichloro-5,6-dicyano-*p*-benzoquinone dehydrogenated (5) in boiling anisole (24 h) to (6) [m.p. 164–165 °C; yield 60%; NMR (CCl₄), $\tau = 2.05$ (s, 2 arom. CH), 2.25–2.95 (multiplet consisting of two partially superimposed AA'BB' systems, 8 arom. CH), 8.78 (d with $J = 4.0$ Hz, bridge-CH), 9.87 (s, 1 bridge-CH), 10.87 (t with $J = 4.0$ Hz, 1 bridge-CH₂); UV (cyclohexane), $\lambda_{\max} = 272$ ($\epsilon = 8570$, sh), 305 (121000), 333 (12900, sh), 360 (7780), 478 (195), 484 (205), 490 (205), 498 nm (170, sh); IR (KBr), C=O 1708 cm⁻¹]. Finally, reducing (6) by the Huang-Minlon modification of the Wolff-Kishner reaction afforded the stable yellow hydrocarbon (3), m.p. 175–176 °C, in 66% yield.



The spectra of (3) all indicate the presence of an aromatic compound. The NMR spectrum (CCl₄) (Fig. 1) shows the annulene protons as a singlet at $\tau = 2.14$ (H-7, H-14) and as an AA'BB' system with $\tau_A = 2.43$ and $\tau_B = 2.88$ (H-2 to H-5, and H-9 to H-12), and the bridge protons as two groups of signals at $\tau = 9.48$ (2 H-16, 2 H-17) and 10.96 (H-15, H-18) which, to a first approximation, can be regarded as a triplet and a quintuplet ($^3J = 2.4$ Hz and $^4J = 1.9$ Hz), respectively (relative intensities 2 : 8 : 4 : 2). The coupling constants of the annulene protons H-2 to H-5 (and of H-9 to H-12) are $J_{AB} = 9.24$ Hz, $J_{BB'} = 9.31$ Hz, $J_{AB'} = 0.21$ Hz, $J_{AA'} = 1.53$ Hz. The absorptions of the annulene- and the bridge-

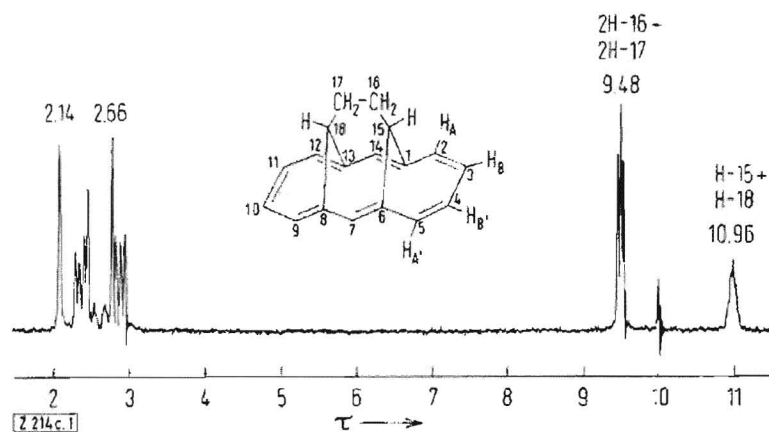


Fig. 1. NMR spectrum of 1,6:8,13-butanediylidene[14]annulene (3) (in CCl_4 ; 60 MHz; tetramethylsilane as internal standard).

protons at relatively low and relatively high field, respectively, together with the symmetry of the spectrum, indicate that the π -electron system of the hydrocarbon is delocalized. The UV spectrum of (3) can be interpreted in the same terms [$\lambda_{\text{max}} = 302$ ($\epsilon = 145000$), 320 (25800, sh), 360 (7450), 373 (7220, sh), 467 (270, sh), 473 (295), 480 (285), 486 (275), 492 nm (215, sh) (in cyclohexane)].

An X-ray structure analysis of 1,6 : 8,13-butanediylidene[14]-annulene (3) is not yet available⁽⁴⁾, but the geometry of the molecule is already evident from a comparison of its NMR spectrum with that of (2)^(2,5). The two compounds have almost identical chemical shifts for the annulene and CH -bridge protons; furthermore, they have virtually the same coupling constants for the annulene protons. However, for (3) the signals of the CH_2 -bridge protons lie approximately 1.1 ppm farther downfield than for (2). Thence it follows that the annulene ring of (3) has almost the same, nearly planar conformation as in (2), and that — contrary to the predictions based on models — it is rather the bridge moiety than the annulene ring that experiences deformation. In the spectrum of (3) the absorption of the CH_2 protons is at comparatively low field, indicating that the intermediate $\text{CH}_2\text{—CH}_2$ bridge is largely forced out of the space between C atoms 15 and 18. That the conformations of the annulene rings of (3) and (2) are very similar also follows from the close agreement of the UV spectra of the two hydrocarbons. As far as can be seen, considering the small quantity of (3) available up to the present, (3) corresponds to its homolog (2) also in its chemical behavior.

The spectra of (3) show that the tendency of the 14π -electron system for maximal p-orbital overlap determines the geometry of the molecule to a much greater extent than was assumed from consideration of models. Thus, intermediate bridges that are appreciably more rigid and more space-filling than a $\text{CH}_2\text{—CH}_2$ grouping will be required to enforce

the intended bending of the annulene ring of bridged [14]-annulenes of the present type.

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[*] Prof. Dr. E. Vogel, Dr. W. Sturm, and H.-D. Cremer
Institut für Organische Chemie der Universität
5 Köln 1, Zülpicher Strasse 47 (Germany)

[1] Previously named 1,6:8,13-butano[14]annulene.

[2] *E. Vogel*, Proc. Robert A. Welch Foundation Conferences on Chemical Research, XII. Organic Synthesis, Houston, Texas 1968, p. 215; *E. Vogel, A. Vogel, H.-K. Kübbeler, and W. Sturm*, *Angew. Chem.* 82, 512 (1970); *Angew. Chem. internat. Edit.* 9, 514 (1970).

[3] This expectation has meanwhile been confirmed by X-ray structure analysis of (2): *G. Casalone, A. Gavezzotti, A. Mugnoli, and M. Simonetta*, *Angew. Chem.* 82, 516 (1970); *Angew. Chem. internat. Edit.* 9, 519 (1970).

[4] An X-ray structure analysis is currently being performed by Professor *M. Simonetta* at the University of Milan (Italy).

[5] For an NMR analysis of (2) see *W. Bremser, J. D. Roberts, and E. Vogel*, *Tetrahedron Letters* 1969, 4307.