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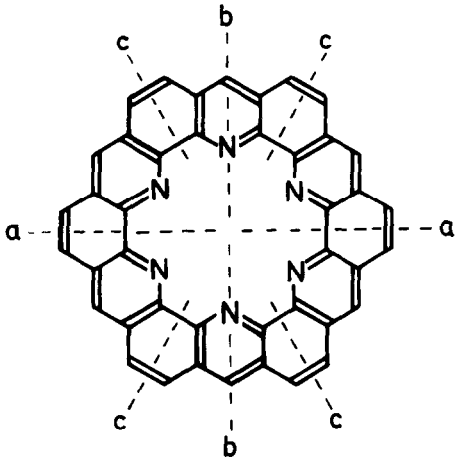
EN ROUTE TO HEXAAZA-KEKULENE

John E. Butler Ransohoff and Heinz A. Staab*

Abteilung Organische Chemie
Max-Planck-Institut für medizinische Forschung
Jahnstrasse 29, D-6900 Heidelberg

Abstract: As synthetic precursors of hexaaza-kekulene 1 the dibenzo[b,j]-[1,10]phenanthroline systems 2, 3, 4, 5 and 6 were prepared. From 6 via 7 a product was obtained for which the dodecahydrohexaaza-kekulene structure 8 is suggested on the basis of ^{1}H-NMR comparison with the dipyrido[3,2-c;2',3'-h]acridine (14) for which two syntheses are reported.

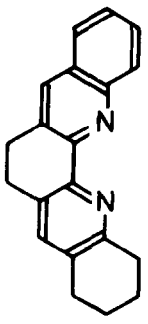
The first member of the cycloarene family kekulene (cyclo[d.e.d.e.d.e.d.e.d.e.d.e]dodecakisbenzene) has previously been synthesized in our group [1], and its molecular structure and spectroscopic properties were determined [2]. Of the heteroatomic analogues of kekulene so far only a dodecahydro-18,21-dioxonia-kekulene has been synthesized [3]. 19,20,21,22,23,24-Hexaaza-kekulene (1) with six coplanar nitrogen atoms forming the central cavity is of special interest (e.g., regarding its complexation behaviour). The synthesis of 1 has been tried following the strategies outlined as a, b, and c in formula 1. In this paper, we report on results achieved along route b.



1

2,3,4,5,7,8-Hexahydrodibenzo[b,j][1,10]phenanthroline (2) was prepared from 1,2,3,4,5,6,7,8-octahydroacridin-4-one following the two-step synthesis of Tilichenko et al. [4] with optimizing variations. The latter [4,5] was prepared from 1,2,3,4,5,6,7,8-octahydroacridine in two steps in analogy to a

known procedure [7] for the synthesis of 9. From 2 by catalytic hydrogenation (PtO_2, trifluoroacetic acid, 3.3 at H_2, 32 h, 20°C), 2,3,4,5,7,8,10,11,12,13-decahydrodibenzo[b,j][1,10]phenanthroline (3) [5] was obtained (~ quant., m.p. 163° -164°C). Condensation of 3 with benzaldehyde (acetic anhydride, 9.5 h, reflux) yielded the 2,13-dibenzylidene derivative 4 [5] (m.p. 208°C; 61%) which was ozonized in dichloromethane/methanol at -78°C to the diketone 5 [5] (m.p. 255°C, dec. 90%).



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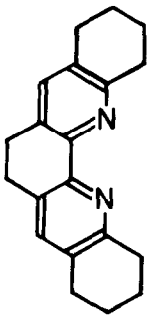

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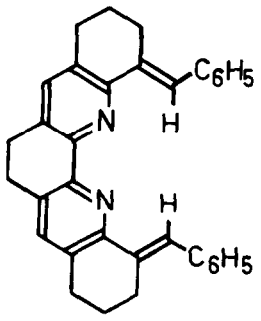
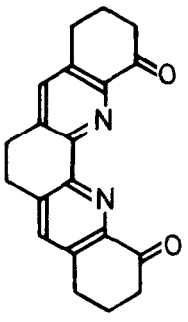


4

For the Vilsmeier reaction of 5 to 6, a solution of 5 in dry dichloromethane was added at 0 - 5°C to a reaction mixture prepared from dimethylformamide in dry dichloromethane by dropwise addition of freshly distilled phosphorous oxychloride. After 48 h stirring at 20°C and aqueous work up the β-chlorovinylaldehyde 6 [5] (m.p. 330°C, dec.) was obtained in 84% yield.



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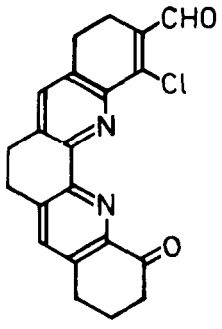
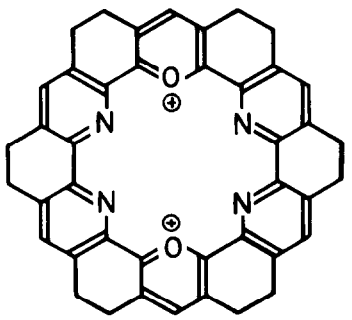


6

Cyclisation of 6 to the dodecahydro-19,20,22,23-tetraaza-21,24-dioxonia-kekulene 7 was achieved with perchloric acid/acetic acid (2.5 h, 20°C). The extremely insoluble product isolated (dec. > 300°C; ~ 94%), according to elemental analysis, is 7-tetraperchlorate. Under corresponding conditions 7-tetrakis(tetrafluoroborate) [5] was obtained. Reaction of 7-tetraperchlorate with ammonia in acetonitrile (18 h, reflux) yielded, by dichloromethane extraction of the residue obtained after evaporation of the acetonitrile, a product as pale-yellow powder in 3% yield. Mass spectra [CI: m/z 617 (20%, $[M - H]^+$),

FAB: m/z 619 (70%, $[M + H]^+$) do not rule out structure 8. Of more significance, however, is the ^{1}H-NMR spectrum (360 MHz, CD_2Cl_2) which shows only two singlets at 3.090 (4H) and 7.599 (1H) as expected for the D_{6h}-symmetrical dodecahydro-19,20,21,22,23,24-hexaaza-kekulene 8.



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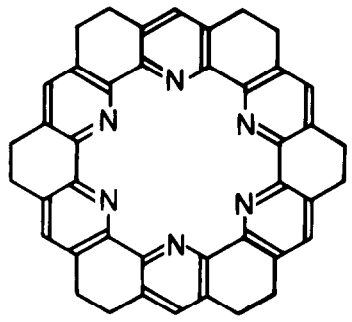
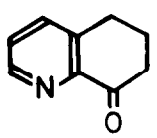


8

Since, so far, the assumption of structure 8 is essentially based on ^{1}H-NMR, the comparison of the δ-values obtained for 8 with those of 5,6,8,9-tetrahydrodipyrido[3,2-c;2',3'-h]acridine (14) is of special interest. 14 was synthesized from 5,6,7,8-tetrahydroquinolin-8-one (9) in two different ways: By condensation of 9 with p-tolualdehyde (piperidine, ethanol; 2 h, reflux) 7-(4-methylbenzylidene)-5,6,7,8-tetrahydroquinolin-8-one (10) [5] was obtained (m.p. 176 - 177°C; 67%) which with 9 on heating with trifluoromethanesulfonic acid (5 h, 100°C) yielded 5,6,8,9-tetrahydrodipyrido[3,2-c;2',3'-h]xanthylium trifluoromethanesulfonate 13 [5] (m.p. 118°C; 29%). From 13 on heating with aqueous ammonia/ethanol (1 h, reflux) 14 [5] was obtained (m.p. 229°C; 21%). For an alternative synthesis of 14 from 9, 7-hydroxymethylene-5,6,7,8-tetrahydroquinolin-8-one (11) was prepared from 9 by condensation with ethyl formate (EtONa, ether; 12 h, 20°C; 94%); 11 [5] (m.p. 106°C) was converted by reaction with ammonia in chloroform into the aminomethylene derivative 12 which without purification was reacted with 9 (ammonium acetate, 12 h, 120°C) to yield 14 in 22% yield. Two independent syntheses of the hitherto unknown 14 were very recently reported [6].



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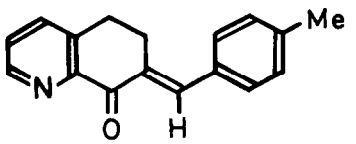

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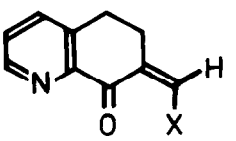
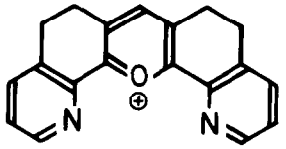
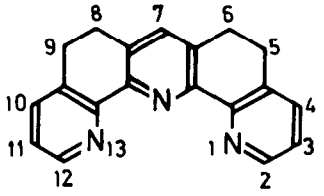


11: X = OH
12: X = NH_2



$F_3CSO_3^{\ominus} \cdot F_3CSO_3H$

13



14

The ^{1}H-NMR spectrum (360 MHz, CD_2Cl_2) shows the following signals: δ = 3.009 ('s', 8H; 5,6,8,9-H), 7.230 (dd, J = 7.6 and 4.7 Hz, 2H; 3,11-H), 7.451 (s, 1H; 7-H), 7.579 (dd, J = 7.6 and 1.5 Hz, 2H; 4,10-H), 8.683 (dd, J = 4.7 and 1.5 Hz, 2H; 2,12-H). The excellent agreement of the signals for 7-H and 5,6,8,9-H of 14 with the two signals of 8 are a strong indication for the structure suggested. - Dehydrogenation to hexaaza-kekulene 1 is in progress.

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5) Correct elemental analyses and spectroscopic data are in accordance with the structures suggested.

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