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BI[18]ANNULENYL[1]

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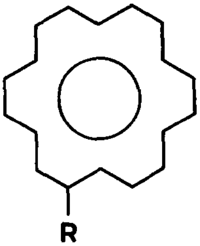
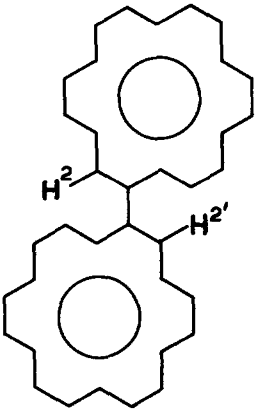
We report the synthesis of bi[18]annulenyl (bicyclooctadeca-1,3,5,7,9,11,13,15,17-nonaenyl) (3), the first example of a substance in which two macrocyclic annulenes are joined directly. Substance 3 has the same relationship to [18]annulene (1) as biphenyl has to benzene.

It has been shown by Kende *et al*[2] that tris(triphenylphosphine)nickel(0) [Ni(TPP)$_3$] in dimethylformamide cleanly causes coupling of phenyl-, vinyl- and allylic halides. Taking advantage of this discovery, we treated bromo[18]annulene (2)[3] with [Ni(TPP)$_3$] under various conditions. The best, though still very low, yield of bi[18]annulenyl (3) was obtained when the reaction was carried out in dimethylformamide at -30 °C, followed by warming to room temperature. The low yield is undoubtedly due to the instability of the [18]annulene system, which is completely destroyed by many reagents under relatively mild conditions.[4]



1, R=H
2, R=Br



3

Chromatography on alumina (Woelm, act. II), and elution with petroleum ether (bp 40-60 °C) - benzene (7 : 3) gave rise to *ca* 8 % of [18]annulene (1), produced by reduction of 2. Further elution with these solvents (4 : 6), and crystallization from benzene-ether, yielded 3.3 % of bi[18]annulenyl (3) as purple crystals, mp > 150 °C decomp. The electronic spectrum of (3) in benzene was complex, and showed λ_{max} 380 nm (ε 163,700),[5] *ca* 400 sh (102,600), ca 425 sh (59,800), 466 (46,400), and ca 510 sh (12,600).[6] The ^{1}H nmr spectrum of 3 at -60 °C in deuteriochloroform at 90 MHz [Bruker HFX-90 spectrometer, F.T., 1000 pulses] showed a 2 H doublet (J = 13.6 Hz) at τ 0.16 (H^2, $H^{2'}$), a 20 H multiplet at ca 0.4 - 1.2 (other outer protons), and a 12 H multiplet at ca 12.0 - 13.0 (inner protons).[7]

The mass spectrum of bi[18]annulenyl (3) could not be determined, due to its involatility and relative instability. However, the "dimeric" nature of 3 was confirmed by catalytic hydrogenation in ethyl acetate over a platinum oxide catalyst, which led to the corresponding saturated hydrocarbon [m/e 502.5475 (M^+); calcd. for $C_{36}H_{70}$, 502.5477].

Bi[18]annulenyl (3) is presumably non-planar, like biphenyl, due to hydrogen-hydrogen interaction in the planar molecule. However, each [18]annulene ring in 3 appears to have the same degree of planarity as [18]annulene itself[8] in view of the similarity of the ring currents [^{1}H nmr spectrum of [18]annulene (THF-d_8, -59.5 °C): τ 0.75 (outer H), 12.88 (inner H)].[9] The low field 2H band at τ 0.16 in the ^{1}H nmr spectrum of bi[18]annulenyl (3) must be due to the outer protons (H^2, $H^{2'}$) adjacent to the bond joining the two rings, since it is a doublet, and the J value (13.6 Hz) is essentially identical to that of the trans J value in [18]annulene itself (13.5 ± 0.2 Hz).[9]

REFERENCES AND NOTES

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4. See (a) I.C. Calder, P.J. Garratt, H.C. Longuet-Higgins, F. Sondheimer, and R. Wolovsky, J. Chem. Soc. (C), 1041 (1967); (b) F. Sondheimer, R. Wolovsky, and Y. Amiel, J. Amer. Chem. Soc., **84**, 274 (1962).
5. The ε values are minimum ones, due to the relatively unstable nature of 3.
6. By comparison, the electronic spectrum of [18]annulene (1) in benzene showed main maxima at 378 nm (ε 297,000) and 456 (28,400).[4b]
7. The ^{1}H nmr spectrum of 3 was temperature dependent, as that of related compounds,[3,4a] and at room temperature essentially only a complex band at ca τ 0.8 - 1.3 ("fixed" outer protons) could be observed.
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