The Synthesis of Circumanthracene

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ABSTRACT The synthesis of circumanthracene, a polycyclic aromatic hydrocarbon with an anthracene unit completely benzannelated around its periphery, is described.

Coronene (1, circumbenzene) and ovalene (2, circumnaphthalene) are the only two known circumarenes, polycyclic aromatic hydrocarbons (PAH's) which contain a fully circularly benzannelated arene subunit.¹ In 1956, Clar described the preparation of a third circumarene, circumanthracene (3), via a "controlled graphitization" process (Scheme 1).² The structure of 3 was assigned on the basis of the UV/Vis spectrum, elemental analysis, and a poorly refined X-ray crystal structure However, in 1981, Clar and Schmidt et al. published correlations between photoelectron spectra and structures of PAH's which clearly revealed that the material prepared earlier was not circumanthracene but rather compound 4.3 We became involved in the synthesis of 3 for several reasons: (i) Circumanthracene is an interesting material for which band structure calculations predict semiconductor properties.⁴ (ii) The photoelectron and UV/Vis spectra of 3 have been predicted by Clar and Schmidt et al. on the basis of extrapolations of the spectra for PAH's of known molecular structure.³ The preparation of 3 should provide a test for the accuracy of such predictions. (iii) Studies with 3 and other extended aromatic perimeters should provide insight into the transition from benzenoid to graphite-type properties which eventually occurs with increasing size of PAH's. (iv) Finally, investigation of the electronic properties of 3 should advance the understanding of the modes of π -electron delocalization in large aromatic hydrocarbons.⁵ Here, we describe an efficient synthetic route to circumanthracene which should be amenable to the preparation of large quantities of this material.





(a) (i) Isoprene, 150 °C, (ii) air oxidation, (iii) separation from the more soluble 2,7-isomer by recrystallization from EtOH; 76% (b) Na₂Cr₂O₇, H₂O, 250 °C, 7 h; 75% (c) Zn, CuSO₄, NH₄OH; 90%. (d) (i) SOCl₂, (ii) EtOH; 77%. (e) LiAlH₄, THF; 98%. (f) PBr₃, CH₂Cl₂; 89%. (g) PPh₃, DMF; 68%. (h) EtOH, EtONa; 34%. (i) hv, 450W Mercury arc lamp, toluene, Ar, I₂, 3 h, 93%. (j) DDQ, 1,2,4-trichlorobenzene, Ar, 90 °C, 15 h; $\approx 50\%$. (k) Oxygen from air and daylight, 20 °C; 93%.

The synthetic route to **3** is shown in Scheme 2 together with the 500 MHz ¹H NMR data for compounds **12-14** in CDCl₃.⁸ From the Wittig reaction of 2-formyl-7-methylnaphthalene with **11**, only the *cis-cis* isomer **12** [EI-MS: $M^+ = 510 (100\%)$] was isolated and fully characterized, since the two other isomers were insoluble in all common solvents. The fourfold photocyclization of **12** to **13** proceeded in an excellent yield of 93%. This yield is remarkable since the two initial "stilbene-to-phenanthrene-type" photocyclodehydrogenations of **12** could, in principle, have led to ten different products.⁹ Sequential photocyclizations similar to those leading from **12** to **13** have precedence as in the one-step formation of benzo[*ghi*]perylene from *cis*-1,2-bis(2-naphthyl)ethene.¹⁰ Compound **13** [EI-MS: $M^+ = 502 (100\%)$] is an orange (Fig.1), extremely light-sensitive material which can exist in two helical, *C*₂ and *C*₁-symmetrical conformations.¹¹ MMX force field calculations¹² suggest that the *C*₂-conformation with the two methyl groups on opposite sides.¹¹



The pentacene 13 reacts readily in daylight with oxygen from the air to give the stable endoperoxide 14 which was isolated by chromatography on SiO₂ [FAB-MS: 535 (M⁺ + 1, 32%), 503 (M⁺ + 1 - O₂, 100%)]. The UV/Vis spectrum in Fig.1 shows that, after 8 days, more than 90% of 13 is converted to 14.¹³ Upon formation of the endoperoxide, a large part of the torsional strain present in the helical precursor 13 is released. The MMX-optimized structure of 14 (Fig. 2) shows that the two benzopyrene moieties that are connected to the central dioxabicyclo[2.2.2]octadiene ring in the molecule are nearly planar.

The reaction of 7 mg of 13 with DDQ¹⁴ in 1,2,4-trichlorobenzene in the dark under Ar afforded 4 mg of an extremely insoluble crystalline precipitate which was washed with EtOAc to remove residual traces of quinone and hydroquinone.¹⁵ The EI mass spectrum of this poorly volatile material (source temperature > 350 °C) is remarkably simple and shows the molecular ion of circumanthracene (3) as the base peak at m/z = 496 together with the expected M⁺ + 1 peak at m/z = 497 The absence of signals above m/z = 497 indicates that the cyclodehydrogenation of 13 to 3 went to completion. No fragment ions were observed between m/z = 100 and



496. Fig. 3 shows the UV/Vis spectrum of a blue, intensively red-fluorescing dilute solution of 3 in 1,2,4-trichlorobenzene. The overall structure of the spectrum and the positions of the long-wavelength absorption maxima at $\lambda_{max} = 609, 582, 540, 502,$ 470, 380, and 364 nm are in good agreement with the data predicted for 3 by Clar and Schmidt et al. (Fig. 3, insert).³ Following this strong preliminary evidence for the formation of circumanthracene via a rational synthetic route, larger quantities are now being prepared for solid state NMR spectroscopy, X-ray crystallography, and evaluation of material properties.

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