

152–155°C, which is recycled to (3a) by phosgene in the presence of a tertiary amine. 3,4-Dichloroaniline reacts with (3a) even at ca. 20°C, giving the monothiotriuret (6a), m.p. 163°C. (3a) can be prepared from (1a) and phenoxycarbonyl isocyanate in boiling toluene even in absence of a tertiary base.

Experimental:

A solution of (1a) (11.6 g, 0.1 mol) in methylene chloride (40 ml) is added, with cooling, to one of *N*-chlorocarbonyl isocyanate (10.5 g, 0.1 mol) in methylene chloride (60 ml). The white precipitate of (2a) that is immediately formed is filtered off and dried. M. p. 222°C. Yield 19.5 g (95%).

A solution of (2a) (22.15 g, 0.1 mol) in water (50 ml) is added dropwise with cooling, to one of *N,N*-dimethylaniline (12.1 g, 0.1 mol) in methanol (50 ml). The white precipitate is filtered off and washed with water, giving 70% (13 g) of (3a), m.p. 210–211°C.

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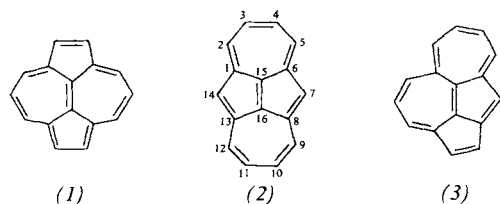
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Dicyclohepta[cd,gh]pentalene— A New Pyrene Isomer^[**]

By Henning Reel and Emanuel Vogel^[*]

Dedicated to Professor Otto Bayer on the occasion of his 70th birthday

HMO calculations^[1] on the three non-alternant pyrene isomers consisting only of five- and seven-membered rings dicyclopenta[ef,kl]heptalene (1), dicyclohepta[cd,gh]pentalene (2), and pentaleno[2,1,6-def]heptalene (3) which, like pyrene, have Kekulé structures with a peripheral 14π Hückel system and a central double bond yield the relatively high resonance energies (R_E) of 6.05 β, 6.03 β, and 5.95 β respectively (pyrene: R_E = 6.51 β). Accordingly, compound (1) which has very recently been synthesized by two independent routes^[2] and the longer known 9-methyl derivative of (3)^[3] are thermodynamically



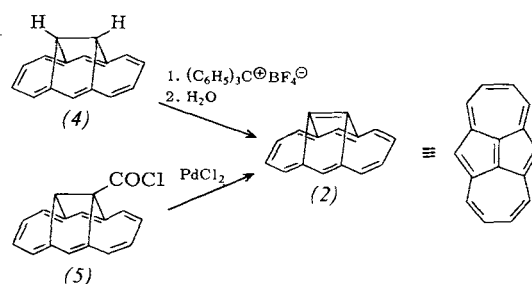
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[**] To facilitate comparison, the numbering chosen for (2) corresponds to that of bridged [14]annulenes having an anthracene perimeter.

stable hydrocarbons deserving the designation aromatic. The hitherto elusive pyrene isomer (2)—which has long been the goal of synthetic efforts^[4] and the subject of quantum mechanical calculations^[1, 4–8]—has now been prepared in our laboratory.

Dicyclohepta[cd,gh]pentalene (2) attracted our interest since it is to be regarded as the parent of the bridged [14]annulenes possessing an anthracene perimeter: 1,6;8,13-ethanediylidene[14]annulene (4)^[9], 1,6;8,13-propanediylidene[14]annulene^[10], 1,6;8,13-butanediylidene[14]annulene^[11] etc.^[8, 12]

As can be readily seen, this series of [14]annulenes is derived from the above Kekulé structure of (2) by replacement of its formal central double bond by the $\text{>CH}-(\text{CH}_2)_n-\text{CH}<$ grouping with $n=0,1,2$, etc. The recently described 1,6;8,13-ethanediylidene[14]annulene (4)^[9] thus represents the *cis*-15,16-dihydro derivative of (2). This relationship prompted experimental efforts to convert (4) into (2) by dehydrogenation.



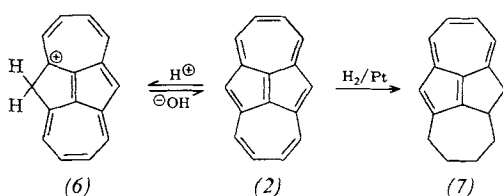
Contrary to expectation, dehydrogenation of (4) by the usual methods ran into difficulties; either no reaction took place (with noble metal catalysts in boiling decalin!) or decomposition occurred (with 2,3-dichloro-5,6-dicyanobenzoquinone). The desired transformation eventually became possible when we observed that a bridge hydrogen is abstracted as hydride ion when (4) is treated with triphenylmethyl tetrafluoroborate in acetonitrile (at ca. 50°C). Treatment of the resulting stable carbenium ion, *i.e.* protonated (2), with water effects deprotonation to give (2) [yield 70% based on (4)]^[13]. The interesting question whether the aforementioned carbenium ion intermediate is the primary product of hydride abstraction [(2) protonated in position 15] or the hydride-shift product (6)^[14] is still open since the poor solubility of the ion has so far hampered NMR studies.

The hydrocarbon (2) was subsequently found to be more readily accessible by degradation of 1,6;8,13-ethanediylidene[14]annulene-15-carboxylic acid^[9] than by the two-step dehydrogenation of (4) *viz.* a) by heating the acyl chloride (5) with palladium chloride in decalin to 170–180°C (yield 25%) and b) by reaction of (5) with sodium azide in acetone/water and subsequent heating of the resulting carbonyl azide in ethanol (yield 50%)^[14]. Compound (2) is relatively stable towards air and crystallizes from cyclohexane (yellowish-brown solution) as greenish black needles of m.p. 141–142°C (partial decomposition).

The NMR spectrum of the pyrene isomer (2) (0.35 mol in CS_2/TMS) consists only of an AA'BB' system at $\tau_A = 1.34$ ($\text{H}^2, \text{H}^5, \text{H}^9, \text{H}^{12}$) and $\tau_B = 1.92$ ($\text{H}^3, \text{H}^4, \text{H}^{10}, \text{H}^{11}$) with the coupling constants $J_{2,3} = 9.91$ Hz, $J_{2,4} = 0.44$ Hz, $J_{2,5} = 0.80$ Hz, and $J_{3,4} = 10.23$ Hz, and a singlet at $\tau = 1.94$ ($\text{H}^7, \text{H}^{14}$)^[15]. The shape and coupling constants of the spectrum thus correspond to those of the spectra

of the bridged [14]annulenes derived from (2). The pronouncedly downfield position of the proton resonances can be rationalized by assuming an important contribution by the Kekulé structures with a peripheral 14π system—as inferred from the theoretically determined bond orders in (2)^[4]. An alternative interpretation of the observed chemical shifts derives from ring-current calculations by Jung^[6], which predict diamagnetic ring currents in the five- and seven-membered rings of (2) and of the isomers (1) and (3). Support for the conclusions drawn from the NMR spectrum and MO calculations regarding the π -electron structure of (2) should come from an X-ray structural analysis of the hydrocarbon that is currently in progress^[16].

The absorption bands of the UV spectrum of (2) [(in cyclohexane): $\lambda_{\max} = 235$ ($\epsilon = 27\,000$, sh), 284 (181 300), 296 (33 750 sh), 310 (26 500), 321 (6 950, sh), 363 (6 200, sh), 367 (8 700), 374 (4 750, sh), 383 (6 780), 387 (12 200), 427 (720, sh), and 486 nm (4 660)] are in satisfactory agreement with the values calculated by a simplified Pariser-Parr-Pople method^[5].



The prediction, based on HMO calculations^[4], that electrophiles will preferentially attack (2) in position 7 (or 14) has meanwhile been confirmed for protonation. (2) dissolves in trifluoroacetic acid or in 50% sulfuric acid to form the stable carbenium ion (6) [NMR spectrum (in CF_3COOH): complex multiplet at $\tau = 0.52 - 1.58$ (9H) and singlet at 4.30 (2H)], from which the hydrocarbon can be regenerated, albeit with some losses, by addition of dilute sodium hydroxide solution at 0°C.

By analogy with the catalytic hydrogenation of the 9-methyl derivative of (3)^[3], treatment of (2) with Pt/H_2 in ethanol yields an azulene derivative (together with other hydrogenation products); the compound designated structure (7) has so far become available in only very small quantities so that its characterization has been limited to UV and mass spectrometry.

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[16] Professor M. Simonetta, Milan, is currently engaged with the X-ray structure analysis of (2).

Unusual Oxidation States of Metalloporphyrins: Octaethylporphinosilver(III) Perchlorate^[**]

By Karl Kadish, Donald G. Davis, and Jürgen H. Fuhrhop^[*]

During a comprehensive survey of the redox potentials of some 30 different metalloporphyrin compounds certain anomalies were noticed which indicated the formation of some unusual oxidation states of the central metal ion. It has been shown that for the case of a simple derivative, such as tetraphenylporphinatozinc(II) or the corresponding etioporphyrin compound, the porphyrin ring can be oxidized in two successive, reversible, one-electron steps^[1–3] (yielding π cation radicals and dications) and reduced in two successive, reversible, one-electron steps^[4–6] (yielding π anion radicals and dianions). In several metalloporphyrins, such as those involving Mn, Co, and Fe, the central metal ion itself may undergo an oxidation state change $\text{M}^{\text{II}} \rightleftharpoons \text{M}^{\text{III}}$. The decision as to whether a given reaction is that of the ring or the metal ion can often be made on the basis of visible and/or ESR spectra^[1, 3, 5, 6].

Another criterion for differentiating between metal and ring reactions is provided by electrochemical potentials. During a cyclic voltammetric study^[7] we observed that the absolute redox potentials of ring oxidations and reductions fall into well defined patterns: the numerical difference between the half-wave potential ($E_{1/2}$) for the first ring oxidation (in butyronitrile) and the first ring reduction (in dimethyl sulfoxide) remained constant at $E_{1/2\text{ox}} - E_{1/2\text{red}} = 2.25 \pm 0.15$ V, regardless of the charge on the central metal ion. This was true for the M^{2+} ions of Mg, Ca, Cu, Ni, Pd,

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