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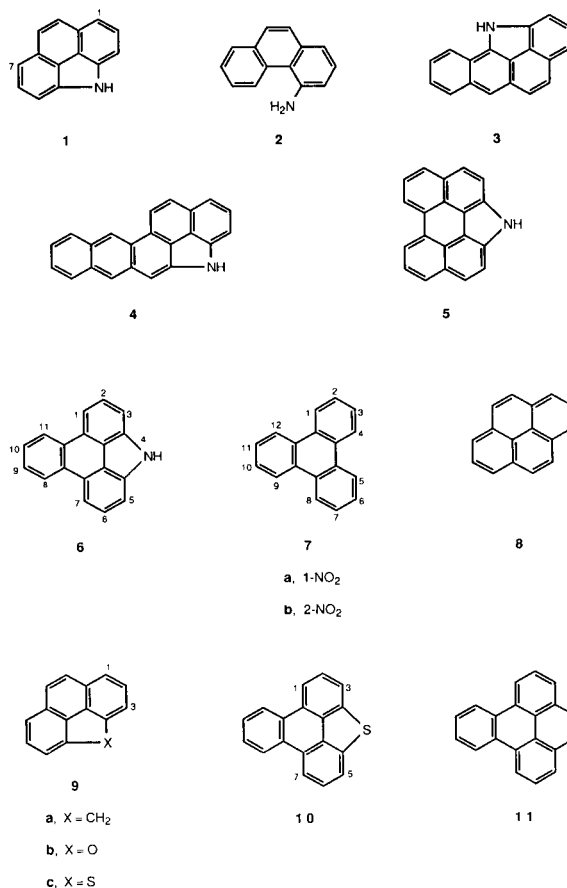
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Reaction of 1-nitrotriphenylene (**7a**) with triethylphosphite (Cadogan reaction) produces 4*H*-naphtho[1,4-*def*]carbazole, a likely component of fossil fuels. Surprisingly **7a** and its 2-isomer are obtained from treatment of triphenylene with sulfuric acid/trifluoroacetic anhydride in nitromethane. Correlation between ultraviolet spectra and substitution reactions in *peri*-condensed pyrroles and thiophenes is presented.

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The simplest *peri*-condensed pyrrole, 4*H*-benzo[*def*]carbazole (**1**), was probably synthesized by Bizzari in 1891 by heating carbazole with acetic acid or acetamide and either anhydrous zinc chloride or phosphorus pentoxide at 150° [2]. In 1954 Kruber and Grigoleit isolated **1** from coal tar and also prepared it by passing 4-aminophenanthrene (**2**) over calcium oxide at 400° [3,4]. Compound **1** has subsequently been identified in various other samples of coal tar, in diesel fuel, in tobacco smoke, in air pollutants, in river sediments and in fish [5,6]. In 1977 Schweighardt *et al.* reported that a sample of liquefied coal appeared to contain molecules bearing the parent system **1** itself, as well as other *peri*-condensed pyrroles with five to seven rings [7]. A benzo derivative of **1** or an isomer of it was identified in coke oven pitch and air pollutants from the coking process [6]. Air samples from an aluminum reduction plant contained numerous pollutants including **1** and several of its derivatives (bromo, methyl, formyl), probably isomeric benzo-**1** parent molecules and formyl derivatives, and a *peri*-condensed pyrrole of six rings [8]. A search of the literature revealed that only compounds **3-5** of the possible parent aromatic penta- to heptacyclic molecules in this series have been synthesized [9-11]. We now report the preparation and characterization of another example, 4*H*-naphtho[1,4-*def*]carbazole (**6**), an isomer of **3**.

Compound **6** was obtained in low yield (12%) by treatment of 1-nitrotriphenylene (**7a**) with triethyl phosphite at 110° (Cadogan reaction) [12]. In fact, the precursor triphenylene (**7**) was nitrated by two different methods. One involved repetition of the conventional procedure of Barker *et al.*, who used nitric acid/acetic anhydride at 60° [13]; while the other method, surprisingly, resulted from an unsuccessful attempt to sulfonylate **7** by means of sulfuric acid/trifluoroacetic anhydride in nitromethane-conditions reported by Weigel *et al.* to give diaryl sulfones from benzene and various substituted benzenes [14]. Instead of isolating any sulfone from our reaction mixture we obtained a mixture of **7a** and its isomer **7b** (27% com-



bined yield) in a ratio of about 1:1 [15,16]. This same ratio results from other methods of nitration which, however, give combined yields as high as 59% [17].

Imine **6** sublimes readily, has a high melting point (250°) [18], and shows a close doublet (3398 and 3375 cm⁻¹) for N-H stretching in the solid state [19]. Its electron-impact mass spectrum is characterized by an intense molecular ion plus four prominent doubly-charged ions.

Horaguchi *et al.* noted similarities in shapes of the ultraviolet spectra of **1** and pyrene (**8**), though the latter spectrum shows considerably more fine structure [20]. These

authors also called attention to the fact that there is a bathochromic shift in the ultraviolet spectrum as one proceeds through the series of bridged phenanthrenes from **9a** to **9b** to **1** and that "consequently a difference in reactivity is expected upon electrophilic substitution" into these molecules. We have previously pointed out close similarities in the spectra of the thienolog-benzolog pairs **9c** plus **8**, and **10** plus **11**, where again the benzolog shows more fine structure in its spectrum [21,22]. It, thus, becomes of interest to compare the analogous heterocyclic pairs **1** plus **9c**, and **6** plus **10**, in both ultraviolet spectra (Figure 1) and electrophilic substitution reactions. Figure 1 shows closely similar spectra for **1** and **9c**, but with less fine structure in the spectrum of the imine and with bathochromic shift of its principal maxima when compared to the spectrum of the sulfur compound. For the pentacyclic systems **6** and **10** the two spectra show more variation, but again with less fine structure in that of the imine. Except for the deep minimum at 266 nm for **6** all four spectra are

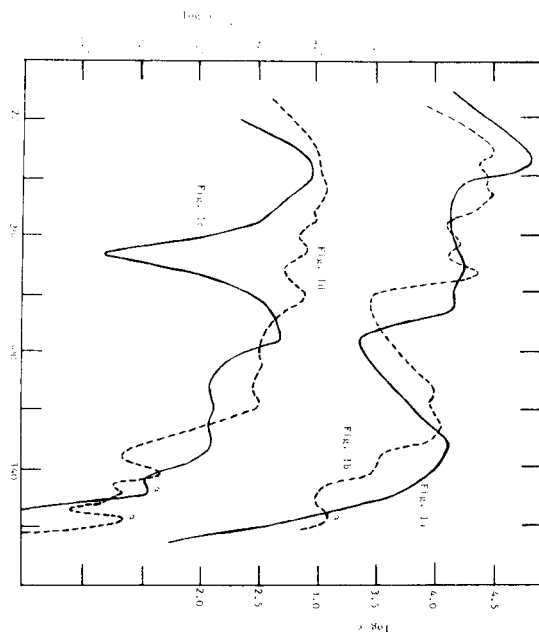


Figure 1. Ultraviolet absorption spectra of *peri*-condensed pyrroles and analogous *peri*-condensed thiophenes. Figure 1a—Compound **1** in 95% ethanol [20]. Figure 1b—Compound **9c** in 95% ethanol [21]. Figure 1c—Compound **6** in absolute ethanol. Figure 1d—Compound **10** in 95% ethanol [22]. The vertical scale on the right side of the graph refers to Figures 1a and 1b; that on the left side, to Figures 1c and 1d.

remarkably similar, with the long-wavelength *alpha* bands occurring in the same region of ca. 340–360 nm. No studies on substitution into **6** have yet been made. However, the *N*-acetyl derivative of imine **1** is reported to undergo nitration at C-1; and **1** itself, to give 1,7-diacetyl-**1** with acetyl chloride and aluminum chloride [23]. Similarly thiocompound **9c** undergoes nitration at C-1 and C-3 [24] plus

Friedel-Crafts acetylation at C-1 [25], while compound **10** yields 1-nitro, 3-nitro, and 1,7-dinitro derivatives [26] plus 3-acetyl and 3,5-diacetyl derivatives [27], respectively. Thus, *ortho-para* orientation with respect to the heteroatom occurs on electrophilic substitution in these three systems.

EXPERIMENTAL [28]

Nitration of Triphenylene.

(a) With Nitromethane [16].

A solution of 0.51 g (2.2 mmoles) of triphenylene (**7**) (Aldrich) in 100 ml of nitromethane (Matheson, Coleman, and Bell spectroquality) [16], 0.26 ml (4.7 mmoles) of 96% sulfuric acid, and 1.5 ml (10.5 mmoles) of trifluoroacetic anhydride (Aldrich) was maintained at 25–40° for 3 days and at 80° for 3 hours and then poured onto ice. The organic layer was combined with a nitromethane extract of the aqueous layer and steam distilled to remove the solvent. A chloroform extract of the distillation residue was dried (sodium sulfate) and chromatographed on 50 g of silica gel with benzene/cyclohexane (1:1) to yield three fractions (in order of elution): recovered **7** (74 mg), mixed products, and colored impurities. Rechromatography of the mixed products on 100 g of silica gel gave more **7** (70 mg, *R_f* 0.57), 1-nitrotriphenylene (**7a**) (33 mg, *R_f* 0.32, mp 167–168.5°), mixed **7a** (48 mg) and **7b** (69 mg) (analyzed by pmr), and 2-nitrotriphenylene (**7b**) (9 mg, *R_f* 0.27, mp 143.5–156°), combined yields: 14% of **7a**, 13% of **7b**. Crude **7b** was recrystallized from benzene-ethanol to give faintly yellow needles, mp 162–163°.

Compounds **7a** and **7b** were identified by ir, pmr, and mass spectra, including direct comparison with authentic samples prepared in part (b).

(b) With Nitric Acid/Acetic Anhydride.

This synthesis followed a literature procedure [13]. Isomers of nitrotriphenylene were separated by column chromatography. The first fraction, largely 1-nitrotriphenylene (**7a**), was recrystallized from benzene-ethanol, mp 159.5–163°, used directly in the synthesis of **6** (*vide infra*). Further crystallization raised the melting point to 164.5–166.5°; ir: 1519 and 1356 (nitro group), 761, 739, 728 cm^{-1} ; pmr (hexadeuterioacetone): δ 9.10 (d, $J_{3,4} = 9$ Hz, 1H, H-4), 8.8–9.0 (m, 3H, H-5, H-8, H-9), 8.03 (2d, 2H, H-2 and H-12), 7.88 (t, H-3) which overlaps 7.7–7.95 (m, 4H total, H-6, H-7, H-10), 7.64 (t, $J = 8$ Hz, 1H, H-11); pmr (deuteriochloroform): (360 MHz [29]) δ 8.705 (split dd, $J_{2,4} = 1.2$ Hz, $J_{3,4} = 8.2$ Hz, 1H, H-4), 8.576 (dt, $J_{\text{meta}} = 1.5$ –2 Hz, $J_{\text{ortho}} = 7.7$ Hz, 2H, H-8 and H-9), 8.497 (dd, $J_{5,7} = 2.0$ Hz, $J_{5,6} = 7.7$ Hz, 1H, H-5), 8.007 (split dd, $J_{9,12} \cong 1.0$ Hz, $J_{11,12} \cong 8$ Hz, 1H, H-12), 7.794 (dd, $J_{2,3} = 7.7$ Hz, 1H, H-2), 7.617 (t, H-3) which overlaps 7.61–7.71 (m, 4H total, H-6, H-7, H-10), 7.522 (ddd, $J_{10,11} = 7.2$ Hz, 1H, H-11). Assignments of signals in the 360 MHz spectrum were consistent with a COSY nmr obtained on the same sample [29,30].

4*H*-Naphtho[1,4-*def*]carbazole (**6**) [31].

A mixture of the preceding sample (0.45 g, 1.6 mmoles) of 1-nitrotriphenylene from part (b) and 15 ml (88 mmoles) of triethyl phosphite (Aldrich) was stirred and heated at 110° in an oven-dried flask, fitted with a long condenser and a drying tube and kept in a good hood, for 20 hours while nitrogen gas was passed into the flask at a very slow rate. Excess triethyl phosphite was removed at 110° by rotary evaporation, including use of two successive additions of 8 ml of xylene as chaser. The brown liquid residue (about 1 ml) was chromatographed (90 g of silica gel, 60–200 mesh/chloroform) and the fraction which showed one spot at *R_f* 0.58 was collected. This fraction was rechromatographed on alumina (80 g) with benzene and then benzene-ether (1:1) as eluent. Compound **6**, 49.3 mg (12%), mp 238–245°, was isolated from a fraction which showed one spot at *R_f* 0.36 with alumina/benzene-ether (9:1). Recrystallization from benzene plus sublimation at 150° (0.5 mm) gave white, fluffy needles, mp 248.5–251.5°; ir (potassium bromide wafer): 3398 and 3375 (strong, NH), 1594, 1438, 1320, 750 (very strong) cm^{-1} ; pmr (deuteriochloroform): δ

8.76 (2 overlapping d, 2H, H-8 and H-11), 8.24 (broad s, NH) which partially overlaps 8.20 (d, J = 7.7 Hz, 2H, H-1 and H-7), 7.84 (t, 2H, H-2 and H-6), 7.76 (2 overlapping d, 2H, H-9 and H-10), 7.59 (d, J = 7.7 Hz, 2H, H-3 and H-5); uv (absolute ethanol): λ max (log ϵ) 238 (4.46), 253 shoulder (4.07), 285 shoulder (4.19), 295 (4.18), 319 (3.61), 330 (3.60), 348 (3.08); ms: m/e (relative intensity) 242 (26), 241 (M⁺, 100), 240 (30), 213 (M⁺ - H₂CN, 11), 120.5 (M⁺, 31), 119.5 (12), 106.5 (22), 105.5 (16), 94 (11).

Anal. Calcd. for C₁₈H₁₁N: C, 89.60; H, 4.60; N, 5.81. Found: C, 89.73; H, 4.37; N, 5.82.

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