214 (17, $M^+ + 2$), 212 (17, M^+), 62 (100, Me_2S^+).

Anal. Calcd for $C_4H_9N_2OSBr$: C, 22.55; H, 4.26; N, 13.15. Found: C, 22.19; H, 4.21; N, 12.94.

***N*-(*N*-Iodomethoxycarbonimidoyl)-*S*,*S*-dimethylsulfilimine (4c).** *N*-Iodosulfilimine **4c** was obtained only in a low yield (6%) according to the same procedure described above. In methanol as a solvent, **4c** was prepared in 38% yield by the following procedure. To a stirred solution of 0.51 g (3 mmol) of **2** in 5 mL of methanol was gradually added a solution of 0.76 g (3 mmol) of iodine and 0.24 g (6 mmol) of sodium hydroxide in 20 mL of methanol below 5 °C. After being stirred about 20 min, the solution was mixed with water, and the mixture was extracted repeatedly with dichloromethane. After the extracts had been dried and concentrated, the remaining dark brown oily material was solidified with ether, and 0.30 g (38%) of crude **4c** was obtained. Recrystallization twice from dichloromethane–petroleum ether provided 0.15 g (19%) of **4c** as a yellow solid: mp 102.5–103.5 °C dec; IR (KBr) 1500 cm^{-1} (C=N); 60-MHz ^1H NMR ($CDCl_3$) δ 2.77 (s, 6 H, MeS), 3.83 (s, 3 H, MeO); mass spectrum (75 eV), m/e 260 (M^+), 62 (Me_2S^+).

Anal. Calcd for $C_4H_9N_2OSI$: C, 18.47; H, 3.49; N, 10.77. Found: C, 18.60; H, 3.43; N, 10.83.

Registry No. 2, 79373-16-3; **4a**, 79373-17-4; **4b**, 79373-18-5; **4c**, 79373-19-6; *N*-chloro-*O*-methylisourea, 19224-53-4.

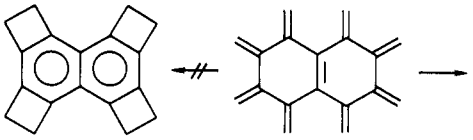
Tetracyclopentanaphthalene

Randolph P. Thummel* and Toshio Fuchigami

Department of Chemistry, University of Houston, Houston, Texas 77004

Received April 3, 1981

There has been a good deal of recent interest in the preparation and study of cyclobutene-fused aromatic molecules.[1] Hart and co-workers have reported the preparation of compound **3** via a pyrolytic dehydrochlorination which they suggest proceeds through the intermediate naphtharadialene **2**.[2] They find no evidence,



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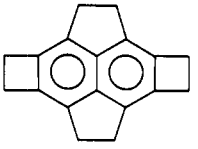

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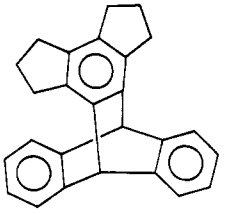
however, for the formation of tetracyclobutanaphthalene **1**. An earlier report on the the synthesis of hexaradialene by a similar route pointed out the absence of any detectable tricyclobutabenzene.[3] We have subsequently demonstrated that this molecule is quite stable when prepared under nonpyrolytic conditions.[4] Thus one might envision that a strategy similar to that used to prepare tricyclobutabenzene might lead to a successful synthesis of tetracyclobutanaphthalene. To test our Diels–Alder approach in the synthesis of a fully annelated naphthalene, we undertook the synthesis of the higher homologue, tetracyclopentanaphthalene (**8**).

The key step in our preparation of this molecule involves the cycloaddition of 3,4:5,6-dicyclopentabenzyne (**5**) to 1,1′-bicyclopentenyl (**6**), (Scheme I). All four of the required cyclopentene rings are preformed in the reacting partners. Considering the relief of strain involved in the cycloaddition and the resonance stabilization gained in the final oxidation step, the energetics of this approach appear quite favorable. A related Diels–Alder reaction has been employed in the preparation of octamethylnaphthalene.[5]

A suitable benzyne precursor appeared to be the amino acid **4** which could be obtained by hydrolysis of the corresponding amino nitrile. This amino nitrile has been reported as the product of a condensation between cyclopentylidenecyclopentanone and malononitrile.[6] The Diels–Alder addition of **5** and **6**, however, proceeded in only 11% yield. To probe the efficiency of the cycloaddition step, we decided to examine the reaction of both the diene and dienophile with partners of established reactivity. The attempted addition of **6** to benzyne was unsuccessful, and none of the expected adduct was obtained. Benzyne **5** was added to anthracene, and the triptycene adduct **9** was obtained in less than 6% yield. It appears that both **5** and **6** are poor partners in [4 + 2] cycloadditions of this type, and the low yield of **7** is understandable.



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The oxidation of **7** to **8** could be effected with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) in benzene. It seemed likely that **8** might form a charge-transfer complex with unreacted DDQ. This complex should be cleaved by treatment with hydrazine, but even on employment of this technique the oxidation yield was only 20%.

Tetracyclopentanaphthalene is a solid which melts with decomposition at 273–274 °C. The ultraviolet spectrum of this compound shows an absorption at 246 nm which is substantially less intense (ϵ 2240) than the corresponding absorption for compound **3** [240 nm (ϵ 47 500)] or octamethylnaphthalene [251 nm (ϵ 50 120)]. The proton NMR spectrum shows two triplets at 3.50 and 2.90 ppm and a quintet at 2.12 ppm. In a study of the NMR spectra of a series of methyl-substituted naphthalenes, it has been established that *peri*-methyl groups (1,8 or 4,5) are significantly deshielded.[7] On this basis we assign the lower field triplet to the α-methylene groups. Examination of a model of the molecule indicates that its fairly rigid conformation imposes a serious nonbonded interaction between the methylene groups at peri positions. This

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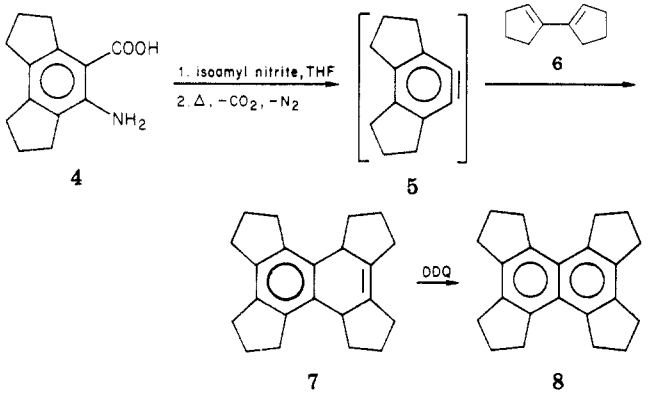
Scheme I



4 5 7 8

interaction would account for the unusual deshielding of these protons. The carbon-13 NMR spectrum shows peaks at 137.7, 137.5, 35.1, 31.7, and 24.8 ppm.[8] For the same reasons stated above the lower field resonance at 35.1 ppm is assigned to the α-methylene carbon.

Experimental Section

Proton and carbon nuclear magnetic resonance spectra were obtained on a Varian Associates T-60 or FT-80 spectrometer, and chemical shifts are reported in parts per million downfield from Me_4Si. Infrared spectra were obtained on a Beckman IR-4250 spectrometer. Ultraviolet spectra were obtained on a Cary-14 spectrometer. Mass spectra were obtained by direct sample introduction into a Hewlett-Packard 5933 A gas chromatograph–mass spectrometer system. High-resolution mass spectral analyses were performed by Dr. J. Hudson at the Department of Chemistry, University of Texas at Austin, on a Du Pont 21-110C double-focusing magnetic sector spectrometer at 70 eV and by Dr. David Hachey at the Baylor College of Medicine on a Finnegan MAT-212 double-focusing magnetic sector spectrometer at 70 eV. Exact masses were determined by peak matching. Combustion analysis was carried out by the Microanalytical Department of Sandoz, Inc. All melting points are uncorrected.

5-Amino-4-cyano-1,2,3,6,7,8-hexahydro-*as*-indacene. A mixture of 21.1 g (0.14 mol) of 2-cyclopentylidenecyclopentanone (Aldrich Chemical Co.), 9.4 g (0.14 mol) of malononitrile, 6.8 g (0.09 mol) of ammonium acetate, 2.1 g (0.03 mol) of acetic acid, and 80 mL of benzene was heated under a reflux condenser equipped with a Dean–Stark water separator until the separation of water ceased. After the mixture cooled, 50 mL of benzene and 50 mL of water were added to the reaction mixture, and the insoluble matter was removed by filtration. The organic layer was separated, washed with saturated $NaHCO_3$ solution, and dried over magnesium sulfate. After filtration, benzene and unreacted ketone were removed by distillation [150–160 °C (4–5 mm)]. The resulting dark, viscous oil was slowly dissolved in 100 mL of ice-cold concentrated sulfuric acid. The solution was refrigerated for 2 h and then poured onto 700 mL of crushed ice. The resulting dark brown solution was extracted twice with 200 mL of dichloromethane. The extracts were dried over magnesium sulfate and filtered, and the solvent was evaporated to provide a yellow solid. This solid was first washed with a small amount of cold ethanol and then recrystallized from ethanol to afford 6.1 g (22%) of amino nitrile: mp 122–124 °C (lit.[6] mp 124 °C); IR (KBr) 3455, 3395, 3365, 2200 cm^{-1}.

5-Aminobenzo[1,2:3,4]dicyclopentene-6-carboxylic Acid (4). A solution of 1.00 g (5 mmol) of the above described amino nitrile and 10 g (250 mmol) of sodium hydroxide in 8 mL of water and 12 mL of 2-methoxyethanol was refluxed for 10 h. After the mixture cooled, 20 mL of water was added and the precipitate collected by filtration (1.22 g). This solid was dissolved in 30 mL of water, and the pH of the solution was adjusted to 7.2 by the addition of hydrochloric acid to provide 1.07 g (100%) of the crude amino acid 4, mp 198 °C. This material was purified by recrystallization from methanol: mp 205 °C; IR (KBr) 3500, 3380, 1645 cm^{-1}; 60-MHz ^1H NMR (Me_2SO-d_6) δ 4.0 (br, shifts and sharpens upon dilution with D_2O), 3.08 (t, 4 H), 2.65 (t, 4 H) 2.0 (t, 4 H). Anal. Calcd for $C_{13}H_{15}NO_2$: C, 71.9; H, 7.0; N, 6.4. Found: C, 71.8; H, 7.1; N, 6.5.

Tetracyclopenta-1,4-dihydronaphthalene (7). To a stirred solution of 1.41 g (6.5 mmol) of amino acid 4 in 15 mL of THF was added dropwise 1.22 g (10.4 mmol) of isoamyl nitrite, and the solution was stirred for 45 min at 20 °C. To the resulting dark suspension was added a solution of 1.39 g (10.4 mmol) of 1,1′-bicyclopentenyl[10] in 10 mL of dichloromethane, and the mixture was refluxed for 1 h. The reaction mixture was concentrated under reduced pressure, and the remaining dark residue was chromatographed on 30 g of silica gel (60–200 mesh). Elution with hexane provided 0.21 g (11%) of the dihydronaphthalene 7 as a white solid: mp 265 °C dec; 80-MHz ^1H NMR ($CDCl_3$) δ 3.44 (AB q, 2), 3.0–2.7 (overlapping t, 12), 2.4–1.7 (overlapping m, 12); IR (KBr) 2960, 2355, 1563, 1544, 1100, 936, 900 cm^{-1}; mass spectrum, (70 eV) m/e (relative intensity) 290 (100, parent), 262 (21), 248 (20), 247 (75), 128 (20), 91 (39), 77 (21), 41 (43); calcd for $C_{22}H_{26}$ m/e 290.2035, found 290.2059.

Tetracyclopentanaphthalene (8). To a stirred solution of 200 mg (0.69 mmol) of 7 in 40 mL of dry benzene was slowly added a solution of 200 mg (0.88 mmol) of DDQ in 60 mL of dry benzene. The mixture was refluxed for 2.5 h and cooled, and 600 mg (17.8 mmol) of 95% hydrazine was added to the reaction mixture. The resulting precipitate was removed by filtration, and the filtrate was concentrated by evaporation. The residue was chromatographed on 10 g of silica gel (60–200 mesh), eluting with hexane, to give a white solid which was recrystallized from dichloromethane to give 40 mg (20%) of tetracyclopentanaphthalene: mp 273–274 °C dec; 80-MHz ^1H NMR ($CDCl_3$) δ 3.50 (t, 8, J = 7.2 Hz, Ar CH_2), 2.91 (t, 8, J = 7.4 Hz, Ar CH_2), 2.12 (quintet, 8, J = 7.3 Hz, Ar CH_2CH_2); 20-MHz ^{13}C NMR ($CDCl_3$) δ 137.7, 137.5, 35.1, 31.7, 24.8; IR (KBr) 2960 (w), 2910 (w), 2840 (w), 1575 (m), 1560 (m), 1270 (m), 1100 (s), 935 (s), 900 (s) cm^{-1}; UV (95% ethanol) λ_{max} 246 nm (ϵ 2440); mass spectrum (70 eV), m/e (relative intensity) 288 (100, parent), 287 (18), 286 (19), 260 (9), 259 (9), 202 (7); calcd for $C_{22}H_{24}$ m/e 288.1878, found 288.1883.

Reaction of 3,4:5,6-Dicyclopentabenzyne with Anthracene. A solution of 430 mg (2 mmol) of amino acid 4 in 5 mL of THF was added during 20 min to a refluxing mixture of 300 mg (2.6 mmol) of isoamyl nitrite and 710 mg (4 mmol) of anthracene in 15 mL of dichloromethane. After the addition, the reaction mixture was refluxed for 10 min and concentrated, and 4 g of maleic anhydride in 30 mL of xylene was added. The mixture was refluxed for 1 h and cooled, and 50 mL of water and 30 mL of dichloromethane were added. The organic layer was separated, washed twice with 15% aqueous sodium hydroxide, and evaporated to dryness. The residue was chromatographed on 30 g of silica gel (60–200 mesh), eluting with ether–hexane (1:2) to provide 40 mg (6%) of a white solid. Sublimation of impurities at 90 °C (0.3 mm) left the desired triptycene as a residue: mp 193–201 °C; 80-MHz ^1H NMR ($CDCl_3$) δ 7.14 (A_2B_2 pattern, 8, Ar H), 5.44 (s, 2, Ar–CH–Ar), 3.05 (t, 4, Ar CH_2), 2.71 (t, 4, Ar CH_2), 2.05 (quintet, 4, $CH_2CH_2CH_2$); 20-MHz ^{13}C NMR ($CDCl_3$) δ 145.7, 138.6, 136.3, 124.9, 123.5, 51.5, 31.3, 30.3, 25.4; mass spectrum (70 eV), m/e (relative intensity) 334 (100, parent), 306 (43), 305 (37), 291 (23), 289 (25); calcd for $C_{26}H_{22}$ m/e 334.1722, found 334.1753.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Robert A. Welch Foundation for support of this research. We also thank Dr. Sandor Barcza for assistance with the combustion analysis.

Registry No. 4, 79373-20-9; 5, 79373-21-0; 6, 934-02-1; 7, 79373-22-1; 8, 79373-23-2; 9, 79373-24-3; malononitrile, 109-77-3; 2-cyclopentylidenecyclopentanone, 825-25-2; 5-amino-4-cyano-1,2,3,6,7,8-hexahydro-*as*-indacene, 36039-03-9.

(8) Limited solubility and a long relaxation time made it difficult to observe the central naphthalene carbons (C-9 and C-10). Similar observations have been made previously.[2a,7]

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