4-Methoxydiphenylamine was prepared by the general procedure of Allen and McKee.[17] Purification by crystallization from aqueous ethanol followed by sublimation gave colorless crystals, mp 103.5–104 °C (lit.[18] mp 105–106 °C).

Acknowledgment. This research was supported by the National Science Foundation and by the Donors of the Petroleum Research Fund, administered by the American Chemical Society.

---

[17] Allen, C. F. H.; McKee, G. H. W. *Organic Synthesis*; Blatt, A. H., Ed.; Wiley: New York, 1943; Collect. Vol. II, p 15.

[18] Baltzly, R.; Harfenist, M.; Webb, F. *J. Am. Chem. Soc.* **1946**, *68*, 2673.

Sterically Congested Polycyclic Aromatic Hydrocarbons with Nonoptimal Geometries. 4,5-Didehydroacenaphthene as a Precursor for the Synthesis of 7,14-Diphenyl-8,9-(1′,8′-naphthenylene)acephenanthrene

Benjamin F. Plummer,* Steven J. Russell, and W. Gregory Reese

Department of Chemistry, Trinity University, San Antonio, Texas 78212

William H. Watson and Mariusz Krawiec

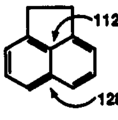
Department of Chemistry, Texas Christian University, Fort Worth, Texas 76129

Received November 12, 1990

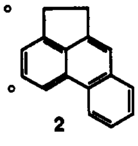
A multistep synthetic route for the synthesis of the reactive intermediate 4,5-didehydroacenaphthene (**15**) is described. A mixture of *N*-1-, *N*-2-, and *N*-3-aminoacenaphtho[4,5-*e*]triazoles is produced, which is oxidized by lead tetraacetate (LTA) to the corresponding aryne. The *N*-2-triazole is oxidized by LTA to 7-cyano-1-(cyanomethylene)indan (**18**), whose structure was verified by X-ray analysis. Intermediate **15** was trapped by 7,9-diphenyl-8*H*-cyclopenta[*a*]acenaphthylen-8-one (acecyclone) to produce the congested hydrocarbon 7,14-diphenyl-8,9-(1′,8′-naphthenylene)acephenanthrene (**20**). There is a small deviation from planarity for **20**, and this is modeled by MMX calculations and verified by X-ray crystallographic analysis of the structure.

Introduction

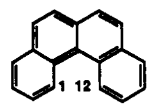
We are studying the effects of distortion and strain on the geometries of selected polycyclic aromatic hydrocarbons (PAH). Perifused cyclopentene PAHs such as acenaphthene (**1**) and annelated derivatives like acephenanthrene (**2**) are expected to have significant ring strain due to a deformation of the sp^2 bonds from the optimal geometry of a normal PAH. The strain energy for **1** is calculated to be 6.7 kcal/mol.[1] The internal bond angle in the cyclopentene-fused ring of **1** is reduced to 112.4° from an optimal 120°, while the external angle is opened to 128.4°.[2] The discovery of molecules that are twisted or deformed from planarity allows chemists to explore the limits of stability and reactivity.[3] The compound benzo[*c*]phenanthrene (**3**) epitomizes this effect. Because of the butressing of the hydrogen atoms at positions 1 and 12, this molecule is distorted by a 30° out-of-plane deformation as verified by X-ray crystallographic analysis.[4] Wittig and co-workers showed how deformation from planarity caused enhanced chemical reactivity at the cross-linking double bond in the naphthalene chromophore of dibenzo[*g*,*p*]chrysene (**4**).[5] Recently, **5** (9,18-diphenyltetrabenz[*a*,*c*,*h*,*j*]anthracene) was synthesized and exhibited a severe twist of the anthracene moiety of nearly 60° out of plane so that steric congestion would be reduced.[6-8] Given the extreme deformation in **5**, a legitimate concern is whether or not the anthracene moiety can still be considered to conform to the properties of an aromatic anthracene nucleus. As Clar first described, the effect of annelation often leads to a significant reduction in the aromaticity of specific rings in a PAH.[9,10]



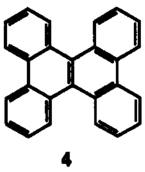
1



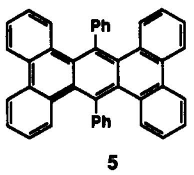
2



3



4



5

Herndon[11] has reported that there exists a large subclass of benzenoid PAH that are nonplanar. He also concluded that the modeling program MMX[12] is better at calculating

---

[1] Boyd, H. H.; Christensen, R. L.; Pua, R. *J. Am. Chem. Soc.* **1973**, *87*, 715.

[2] Balasubramani, V. *Chem. Rev.* **1966**, *66*, 567.

[3] Greenberg, A.; Liebman, J. F. *Strained Organic Molecules*; Academic Press: New York, 1978.

[4] Harnik, E.; Herbstein, T.-H.; Schmidt, G. M. J.; Hirshfeld, F. L. *J. Chem. Soc.* **1954**, 3302.

[5] Wittig, G.; Barendt, E.; Schoch, W. *Ann.* **1971**, *749*, 24–37.

[6] Pascal, R. B.; McMillan, W. D.; Van Engen, D.; Eason, R. G. *J. Am. Chem. Soc.* **1987**, *109*, 4660–4665.

[7] Pascal, R. A.; McMillan, W. D.; Van Engen, D. *J. Am. Chem. Soc.* **1986**, *108*, 5652–5653.

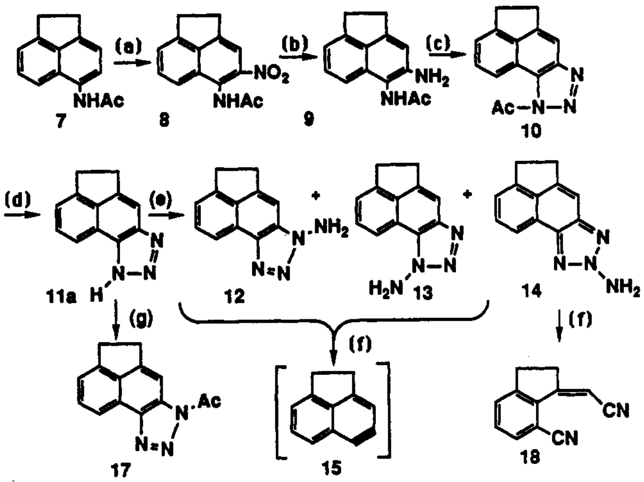
[8] Smyth, N.; Van Engen, D.; Pascal, R. A. *J. Org. Chem.* **1990**, *55*, 1937–1940.

[9] Gutman, I. *Pure Appl. Chem.* **1990**, *62*, 429–434.

[10] Clar, E. *Polycyclic Hydrocarbons* Academic Press, New York, 1964.

[11] Herndon, W. C.; Connor, D. A.; Lin, P. *Pure Appl. Chem.* **1990**, *62*, 436–444.

Scheme I[a]

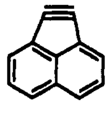


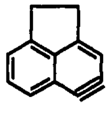
[a] Key: (a) $Cu(NO_3)_2$, HOAc; (b) H_2/Pt; (c) HONO; (d) H_2SO_4; (e) KOH, NH_2OSO_3H; (f) $Pb(OAc)_4$; (g) Ac_2O.

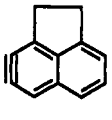
ΔH_f than is the AM1[13] program. We report here our results of trapping 4,5-didehydroacenaphthene (**15**) to produce a cyclopentene-fused polycyclic hydrocarbon as a prelude to the study of a variety of strained and deformed PAHs so that further understanding about aromaticity and conjugation in distorted rings can be probed.

Results and Discussion

Synthesis of 4,5-Didehydroacenaphthene. The chemistry of 1,2-didehydroacenaphthylene (**6**) was explored.[14-16] Its occurrence was inferred by trapping experiments and through matrix isolation spectroscopy. No report of the production of either **15** or 3,4-didehydroacenaphthene (**16**) is published. One of the potential


6


15


16

problems in the generation of **15** or **16** by normal elimination techniques using butyllithium on a haloaromatic is that the bridge protons in **1** are weakly acidic and undergo reaction with the base, thereby complicating the attempts to generate an aryne from derivatives of **1**. Our approach uses a technique developed by Rees[17] and Hart[18] to produce functionalized aryne intermediates. The reaction sequence is illustrated in Scheme I. For comparison purposes, we prepared the isomer of 3-(methylcarbonyl)-acenaphtho[4,5-*e*]triazole (**17**) through acetylation of the triazole (**11a**). The product is the less sterically encumbered derivative **17**. The ^{1}H NMR of **11a**, produced from the acid hydrolysis of **10**, was clean and did not suggest the presence of its tautomer **11b** at levels that we could detect.

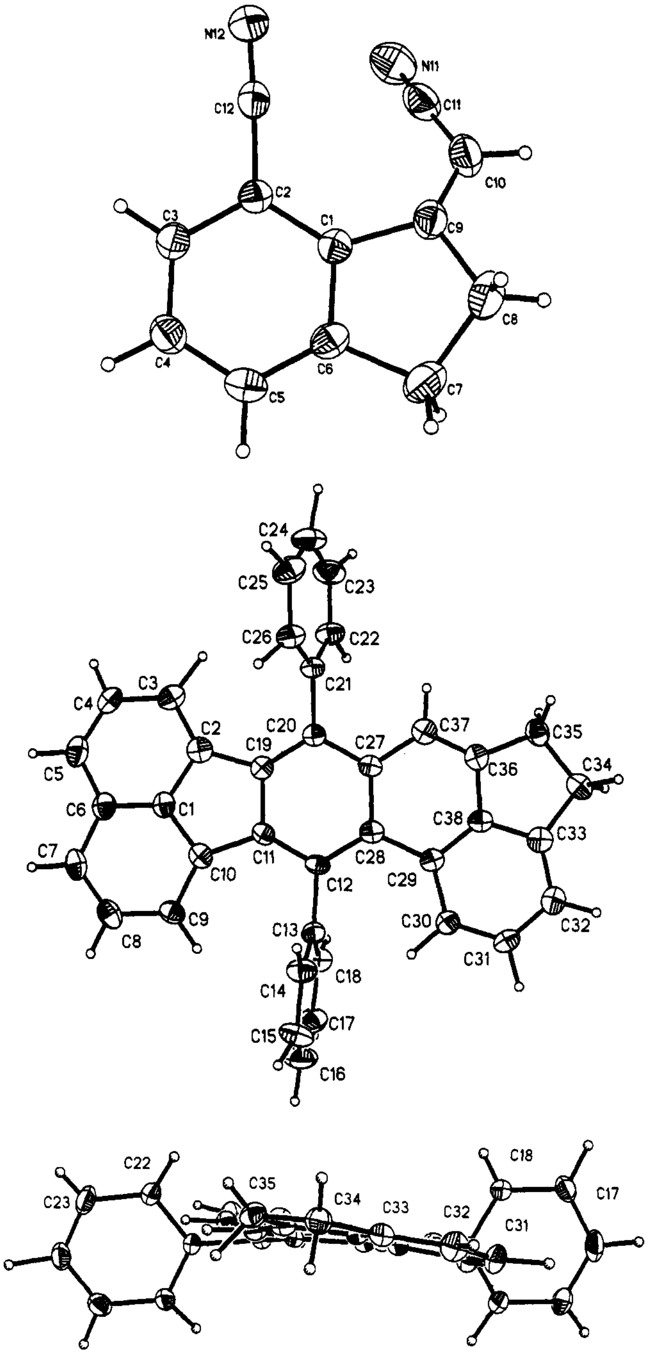
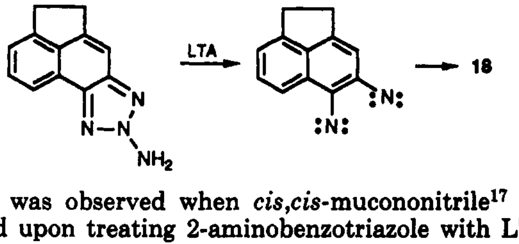


Figure 1. X-ray structures and *crystallographic* numbering schemes of (top to bottom) 7-cyano-1-(cyanomethylene)indan (**18**) and 7,10-diphenyl-8,9-(1′,8′-naphthenylene)acephenanthrene (**20**; two views). The thermal ellipsoids for carbon are drawn at the 30% probability level; hydrogen atoms are shown as spheres of arbitrary diameter.

The production of the mixture of N-aminated acenaphtho[4,5-*e*]triazoles **12**–**14** occurs readily. The crude mixture was not further separated but used directly in the next step to produce **15**. Lead tetraacetate (LTA) oxidation of **14**, however, does not lead to the aryne but instead produces the dinitrile **18** (eq 1). A similar cleavage re-



(1)

action was observed when *cis,cis*-mucononitrile[17] was formed upon treating 2-aminobenzotriazole with LTA. Campbell suggested that nitrene intermediates might be

---

(12) Gajewski, J. J.; Gilbert, K. E. *Serena software and MMX calculations, V 4.0* Serena Software: Bloomington, IN.

(13) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902–3909.

(14) Chapman, O. L.; Gano, J.; West, P. R.; Regitz, M.; Maas, G. *J. Am. Chem. Soc.* **1981**, *103*, 7033–7036.

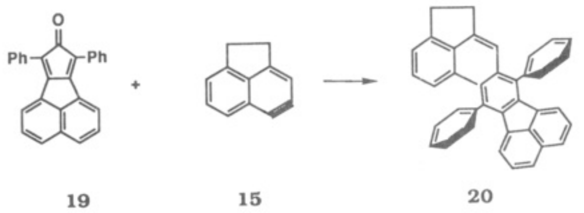
(15) Hartwig, J. F.; Andersen, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1989**, *111*, 2717–2719.

(16) Nakayama, J.; Ohshima, E.; Ishii, A.; Hoshino, M. *J. Org. Chem.* **1983**, *48*, 60–65.

(17) Campbell, C. D.; Rees, C. W. *J. Chem. Soc.* **1969**, 742–747.

(18) Hart, H.; Ok, D. *J. Org. Chem.* **1987**, *52*, 3835.

Scheme II



involved in the transformation. The structure of **18** is verified by its spectroscopic data (IR nitrile bands at 2229 and 2210 cm^{-1}) and by the X-ray crystallographic analysis (Figure 1). Because of the crowding of the terminus of the cyanomethylene moiety with the adjacent nitrile group, the double bond is bent out of plane and exhibits a slight twisting about the axis of the double bond.

We attempted to intercept **15** with furan by the expected Diels–Alder reaction analogous to the experiments reported by Hart.[18] The anticipated [4 + 2] cycloadduct was not isolated; instead, polymeric material and a low yield of **18** was recovered from the reaction mixture. Furan is recognized as one of the less reactive dienes in the Diels–Alder reaction, and it appears that any aryne formed diverted to intractable materials. The oxidation of the triazole mixture produced the dinitrile **18** in less than 15% yield, suggesting that **14** constitutes a small fraction of the aminated triazole mixture. Because **18** is easily separated from other reaction products, we chose to work with the mixture **12–14** in all subsequent reactions.

Synthesis and Structural Analysis of 7,14-Diphenyl-8,9-(1′,8′-naphthenylene)acephenanthrene (20). The aryne **15** was readily intercepted by 7,9-diphenyl-8*H*-cyclopent[*a*]acenaphthylen-8-one (acecyclone; **19**) to produce in 21% isolated yield compound **20** (Scheme II). Considering the steric constraints on the product, we consider this a satisfactory yield. Compound **20** is yellow, with a decomposition temperature greater than 300 °C. The crystals are monoclinic, space group $P2_1/c$, $Z = 4$. In the following text, the crystallographic structure and numbering scheme (Figure 1) is used as a basis for discussion. There is a ~3° twist along the long axis of the molecule causing the basic nuclear skeleton to be slightly nonplanar. The twist is the result of minimizing the nonbonded repulsion between covalent hydrogen–carbon electron density. The phenyl group at C20 (Figure 1) is bent out of plane along the C20–C21 covalent bond axis by 7° and exhibits a dihedral angle of 68°, while the phenyl at C12 (Figure 1) is bent slightly out of plane in the opposite direction by 3° with a dihedral angle of 81°. The central benzene ring exhibits a flattened half-chair conformation, while the fused phenyl (C27–C28 fusion) of the acenaphthene ring is in a flattened twist-boat conformation. Bond alternation is more pronounced in the naphthalene ring fused through C2–C19 and C10–C11, but some alternation occurs in the acephenanthrene portion of the skeleton. The C37–C36 bond in **20** is short compared to those expected for typical PAH molecules.

We tested the effectiveness of the MMX[12] molecular modeling program in simulating the structure of **20** (Figure 2). The modeling program simulates closely the geometry of the deformed compound. However, there are significant differences that occur between computed and measured values. In Table I selected measurements are compared. The computed bond distance C36–C37 is longer by 4.4 pm than the X-ray value. The distance computed for the similar bond in acephenanthrene is 138.0 pm, but no X-ray data is available for this compound. Given the substantial shortening of the C36–C37 bond found in crystalline **20**, we assume that the strain incurred leads to the shortening observed. It is interesting to note that the C5–C6–C7 and C28–C29–C30 angles of 126° and 128°, respectively, are very similar to that found for the comparable angle of 128° in **1**. The interior angles C36–C38–C33 and C2–C1–C10 are 110° and are only slightly smaller than the comparable 112° angle found in **1**.

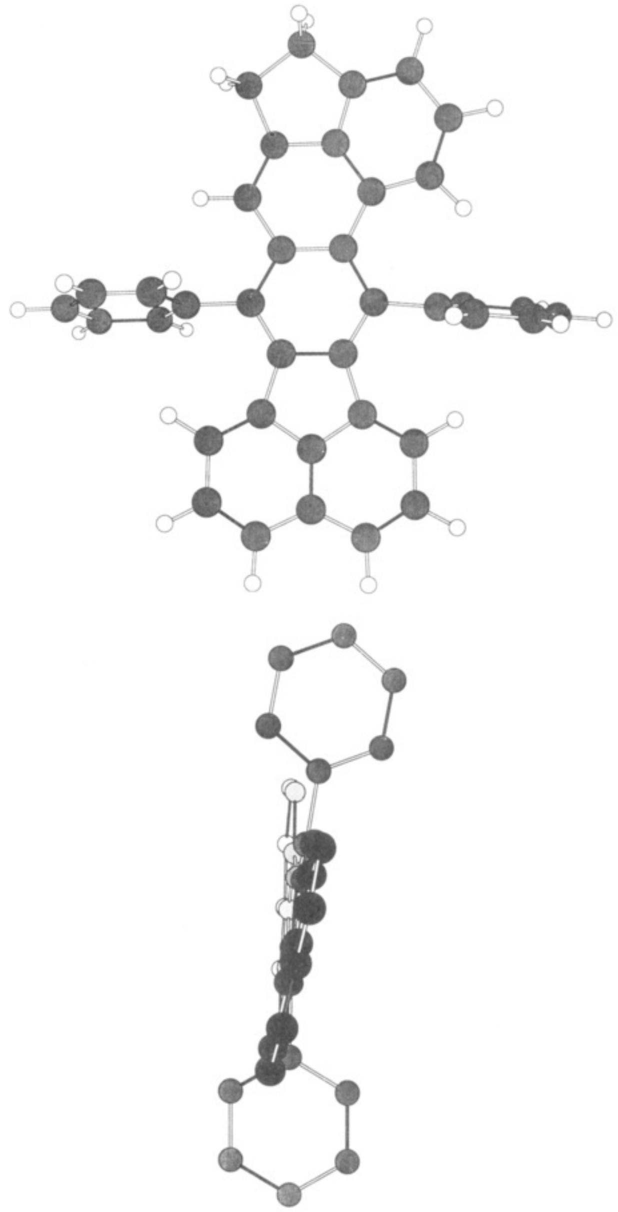


Figure 2. Simulated structures (two views) of 7,10-diphenyl-8,9-(1′,8′-naphthenylene)acephenanthrene (**20**) computed using the MMX program and drawn using Chem 3D. Hydrogen atoms are omitted in the edge-on view for clarity.

Following the crystallographic numbering scheme, two protons in the ^{1}H NMR spectrum of **20** appear as doublets upfield at δ 6.25 and 6.47, while the rest of the aromatic protons are grouped between δ 7.1–7.8. The protons on C30, C37, C3, and C9 are the closest in proximity to the anisotropic shielding cone of the phenyl groups. H37 is ruled out because it should be a singlet. From the crystallographic and modeling data, it appears that protons H30 and H3 are the most highly shielded but specific assignments will require a more detailed spectral analysis using 2D NMR. The ethylene bridge protons at δ 3.7 exhibit the characteristic multiplicity found in most of these ace-PAHs. Each phenyl substituent exhibits significant splitting, suggesting that the protons are located

Table I. Comparison between Measured and Calculated Values for 20[a]

	computed	measured
Bond Length (pm)		
C(2)–C(3)	138.4	138.0 (6)
C(27)–C(28)	143.3	145.3 (5)
C(11)–C(19)	143.1	145.3 (5)
C(36)–C(37)	136.1	131.7 (6)
C(33)–C(34)	150.5	151.3 (6)
C(35)–C(36)	150.6	150.4 (5)
Bond Angle (deg)		
C(35)–C(36)–C(38)	112.0	109.3 (3)
C(2)–C(19)–C(20)	130.5	132.5 (4)
C(30)–C(29)–C(38)	112.2	114.7 (3)
C(32)–C(33)–C(34)	128.9	130.7 (4)
C(28)–C(29)–C(30)	131.2	128.1 (3)
C(35)–C(36)–C(37)	129.5	132.9 (4)
C(33)–C(38)–C(36)	107.7	110.0 (3)
C(3)–C(2)–C(19)	135.6	135.0 (3)
C(9)–C(10)–C(11)	136.0	135.5 (3)
C(2)–C(1)–C(10)	111.2	110.2 (3)
C(5)–C(6)–C(7)	127.2	126.4 (4)

[a] Numbering scheme taken from X-ray data in Figure 1.

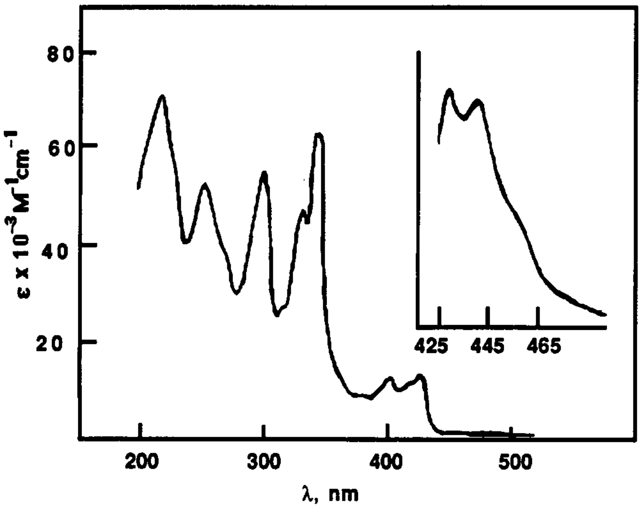


Figure 3. Absorption spectrum of 7,10-diphenyl-8,9-(1′,8′-naphthenylene)acephenanthrene (**20**) dissolved in cyclohexane. The inset shows the fluorescence spectrum of **20** when the excitation wavelength is 422 nm.

in a diastereotopic environment that causes their nonequivalent behavior in **20**. The rotational freedom of the phenyl substituents ultimately will be studied by temperature-dependent NMR techniques.

The absorption and emission spectrum of **20** is shown in Figure 3. A long wavelength absorption band in cyclohexane at 425 nm accounts for the yellow color. When this band is excited, **20** produces an intense structured emission with peaks at 428 and 455 nm and a shoulder at 485 nm. The excitation spectrum verifies that the emission originates from **20**. The polar solvents methanol, acetonitrile, and glycerol cause a merging of the peaks in the emssion spectrum and some loss of fine structure as is expected for polar effects on such emissions.

Summary

We have shown that 4,5-didehydroacenaphthene can be produced by oxidation of a mixture of N-aminated acenaphtho[4,5-*e*]triazoles and that the aryne can be trapped by acecyclone to produce 7,14-diphenyl-8,9-(1′,8′-naphthenylene)acephenanthrene. The 2-aminoacenaphtho[4,5-*e*]triazole that is contained in the mixture is oxidized and cleaved to form 7-cyano-1-(cyanomethylene)indan. We have not successfully trapped aryne **15** with furan or with anthracene. Other cyclone traps are expected to be successful in trapping the aryne and are currently being investigated. Molecular modeling calculations of the structure of **20** are in reasonable agreement with the X-ray crystallographic analysis. It seems likely that such simulations can be used to predict anticipated geometries of distorted PAH in lieu of X-ray data when poor crystal habitat prevents a successful crystallographic analysis.

Experimental Section

Melting points are uncorrected and were determined on a Mel-Temp apparatus. Proton NMR spectra were determined in $CDCl_3$ on a Varian EM-360L or a Varian VXR 300 spectrometer, and chemical shifts are in δ downfield from TMS. Infrared spectra were measured from KBr pellets on a Perkin-Elmer FT-IR 1600 spectrophotometer. Electronic absorption spectra were recorded on a Cary 2315 UV–Visible-NIR spectrophotometer with a Cary DS-15 stand-alone data station running Varian Multiscan software. Excitation and emission spectra were obtained on a Perkin-Elmer MPF-44B fluorescence spectrophotometer with use of an excitation slit width of 5 nm and emission slit width of 10 nm and a photomultiplier detector type R928. Mass spectra were determined on a Hewlett-Packard 5995-C gas chromatographic mass spectrometer at 70-eV ionizing radiation. Elemental analyses were performed by Texas Analytical Laboratories. 5-Nitroacenaphthene (**21**)[19] and acecyclone (**19**)[20] were prepared by literature methods.

5-Aminoacenaphthene (22). A suspension of 20.0 g (0.10 mol) of **21** in 300 mL of absolute ethanol with 1.0 g of 10% Pd/C catalyst was charged into a 500-mL bottle and shaken in a Parr hydrogenation apparatus at 60 psi. After 1 h, the resulting clear solution was filtered to remove the catalyst and the amine was forced out of the ethanol by the addition of an equal volume of cold water. The product was collected by vacuum filtration to give 15.5 g (91%) of crude **22**. It was recrystallized from cyclohexane to give clear needles, mp 103–104 °C (lit.[21] mp 104 °C).

5-Acetamidoacenaphthene (7). To a solution of 10.0 g (59 mmol) of **22** in 100 mL of pyridine at room temperature was added 20 mL of acetic anhydride dropwise over 15 min. The mixture was heated at reflux for 15 min then poured into 300 mL of ice–water to give an off-white solid. The product was collected by vacuum filtration to give 11.8 g (95%) of **7**. It was recrystallized from ethanol/water to give a white powder, mp 188–189 °C (lit.[22] mp 188–189 °C).

4-Nitro-5-acetamidoacenaphthene (8). To a 1-L round bottom flask with a mechanical stirrer attached was added a slurry of 12.0 g (57 mmol) of **7** in 400 mL of acetic acid. The mixture was cooled to 11 °C, and 27.0 g (114 mmol) of copper nitrate trihydrate was added in three portions during 15-min intervals. The green slurry was stirred for 2 h at 20 °C, and then 400 mL of water was added. Vacuum filtration produced a yellow product that was recrystallized from 2-butanone to give 9.7 g (67%) of yellow needles of **8**, mp 244–246 °C dec (lit.[22] mp 253 °C).

4-Amino-5-acetamidoacenaphthene (9). A suspension of 11.0 g (46 mmol) of **8** in 300 mL of methanol was mixed with 0.5 g of 10% Pd/C catalyst and shaken 2 h in a 500-mL Parr hydrogenator bottle at 60 psi of hydrogen. The resulting suspension was added to an additional 200 mL of warm methanol to dissolve the product, and the mixture was filtered while hot to remove the catalyst. The filtrate was rotary evaporated to produce 9.0 g (93%) of 4-amino-5-(methylcarboxamido)acenaphthene (**9**) as an off-white solid, mp 228–230 °C (lit.[23] mp 231–233 °C).

1′-(Methylcarbonyl)acenaphtho[4,5-*e*]triazole (10). To a suspension of 9.0 g (40 mmol) of **9** in 500 mL of ethanol in a 1-L, three-necked flask equipped with a mechanical stirrer was added

---

[19] Jones, L. A.; Joyner, C. T.; Kim, H. K.; Kyff, R. A. *Can. J. Chem.* **1970**, *48*, 3132–3135.

[20] Dilthey, W.; ter Horst, I.; Schommer, W. *J. Prakt. Chemie* **1935**, *143*, 189–207.

[21] Cava, M. P.; Merkel, K. E.; Schlessinger, R. H. *Tetrahedron* **1956**, *21*, 3059.

[22] Mosebach, G.; Sachs, F. *Chem. Ber.* **1911**, *44*, 2852.

[23] Jones, L. A.; Kim, H. K.; Watson, R. *J. Chem. Soc. C* **1971**, 3891–3893.

Table II. Crystallographic Data for 18 and 20

compd	18	20
formula	$C_{12}H_8N_2$	$C_{38}H_{24}$
space group	$P2_1/n$	$P2_1/c$
a (Å)	7.215 (2)	10.097 (6)
b (Å)	16.705 (4)	13.244 (8)
c (Å)	8.168 (2)	18.723 (8)
β (deg)	107.70 (2)	95.86 (4)
V (Å^3)	938.1 (4)	2491 (2)
Z	4	4
D_{calc} (g cm^{-1})	1.27	1.28
crystal size (mm)	0.45 × 0.45 × 0.23	0.45 × 0.23 × 0.18
u (Mo Kα)(cm^{-1})	0.74	0.67
2θ range (deg)	3–55	3.50
reflections measured	2763	6549
unique obsd reflections	1476	2676
parameters	160	439
least-squares refinement	block-cascade	block-cascade
(*wR*)	0.0473	0.0655
goodness to fit	1.602	1.873

40 mL of concd HCl and 10 mL of water. To the resulting solution maintained at 4 °C under nitrogen was added dropwise a solution of 10.0 g (145 mmol) of sodium nitrite in 50 mL of water over 30 min. After an additional 30 min of stirring, the white precipitate was collected by vacuum filtration to give 7.8 g (82%) of **10**, which was recrystallized from ethanol: mp 174–175 °C; NMR ($CDCl_3$) δ 8.87 (d, 1 H, *J* = 8.4 Hz), 7.71 (t, 1 H, *J* = 1.4 Hz), 7.62 (dd, 1 H), 7.5 (dd, 1 H, *J* = 7.0 Hz), 3.45 (m, 4 H), 3.10 (s, 3 H); IR (KBr) 3854, 3751, 3122, 3067, 3008, 2923, 2426, 1706, 1606, 1560, 1542, 1516, 1411 cm^{-1}. Anal. Calcd for $C_{14}H_{12}N_3O$: C, 70.57; H, 5.08; N, 17.64. Found: C, 70.78; H, 4.71; N, 17.80.

3′-(Methylcarbonyl)acenaphtho[4,5-*e*]triazole (17). To a solution of 500 mg (2.5 mmol) of **11a** and 60 mL of pyridine was added all at once 0.5 mL of acetic anhydride. The mixture was stirred and refluxed for 30 min and then poured into 75 mL of ice–water. The crude yellow precipitate of **17** was collected by vacuum filtration, dried, and recrystallized from ethanol to yield 400 mg (70%). A tenacious brown impurity was removed by column chromatography on silica with CH_2Cl_2 as an eluate. After rotary evaporation, the off-white residue was recrystallized from cyclohexane to produce fibrous, white crystals: mp 153–155 °C; NMR ($CDCl_3$) δ 8.40 (d, 1 H, *J* = 8.1 Hz), 8.12 (s, 1 H), 7.76 (dd, 1 H), 7.51 (d, 1 H, *J* = 7.1 Hz), 3.56 (m, 4 H), 3.13 (s, 3 H); IR (KBr) 3852, 3750, 3122, 3066, 3009, 2921, 2425, 1704, 1606, 1560, 1542, 1516, 1411 cm^{-1}. Anal. Calcd for $C_{14}H_{12}N_3O$: C, 70.57; H, 5.08; N, 17.64. Found: C, 70.82; H, 4.65; N, 17.78.

Acenaphtho[4,5-*e*]triazole (11a). A suspension of 8.5 g (36 mmol) of **10** in 250 mL of 50% aqueous ethanol mixed with 2 mL of concd sulfuric acid contained in a 500-mL round-bottom flask with an attached condenser was refluxed under nitrogen for 2 h. The mixture was poured into 500 mL of ice–water and the resulting tan solid collected to give 5.6 g (80%) of **11a**: mp 260 °C dec; NMR ($CDCl_3$) δ NMR 15.7 (br s, 1 H, NH), 8.16 (d, 1 H, *J* = 7.5 Hz), 7.68 (dd, 1 H), 7.57 (s, 1 H), 7.49 (d, 1 H, *J* = 7.3 Hz), 3.45 (m, 2 H, CH_2), 3.39 (m, 2 H, CH_2); IR (KBr) 3854, 3751, 3122, 3067, 3008, 2923, 2426, 1606, 1560, 1542, 1516, 1411 cm^{-1}. Anal. Calcd for $C_{12}H_{10}N_3$: C, 73.83; H, 4.65; N, 21.52. Found: C, 73.76; H, 4.68; N, 21.48.

***N*-Aminoacenaptho[4,5-*e*]triazole 12–14.** To 25 mL of 8% KOH stirred at 60 °C under nitrogen was added 0.8 g (4 mmol) of **11a**. To this mixture was added portionwise during 1 h 1.9 g (17 mmol) of hydroxylamine-*O*-sulfonic acid. When the mixture was cooled, the precipitate was collected by vacuum filtration to give 300 mg of a tan solid. The filtrate was continuously extracted with ether for 36 h, and the ether was rotary evaporated to dryness to give 100 mg to produce 47% (1.9 mmol) combined yield of **12–14**. TLC indicated the presence of three components (presumed to be 1-, 2-, and 3-aminoacenaptho[4,5-*e*]triazole) in addition to trace impurities. This crude mixture was used without further purification in all subsequent experiments.

Synthesis of 7-Cyano-1-(cyanomethylene)indan (18). Attempted Trap of 15 with Furan. To a two-necked, round-bottom flask with an attached condenser and a nitrogen atmosphere was added 30 mL of freshly distilled furan and 200 mg (0.9 mmol) of crude aminotriazole mixture. A suspension of 0.93 g (2.1 mmol) of $Pb(OAc)_4$ in 20 mL of furan was added dropwise over 30 min. The mixture was stirred for an additional 30 min, diluted with 300 mL of water, and extracted with 3 × 25 mL of CH_2Cl_2. The combined organic layers were rotary evaporated. The residual dark red oil was purified by radial chromatography using gradient elution with hexane/CH_2Cl_2. The major product was a tan solid, 40 mg (17% yield) of **18**. It was recrystallized from methanol and then toluene/hexane to give an off-white powder: mp 159–160 °C; IR (KBr) 3428, 3046, 2977, 2229, 2210, 1619, 1474, 1436, 1360, 1322, 1283, 1102, 836, 802, 744 cm^{-1}; NMR (^1H $CDCl_3$) δ 3.0 (4 H, m, $-CH_2CH_2$), 5.68 (1 H, t, vinyl), 7.50 (1 H, dd, ArH), 7.59 (1 H, d, ArH), 7.66 (1 H, d, ArH); (^{13}C, $CDCl_3$) δ 161.2, 150.4, 139.1, 132.9, 131.3, 129.7, 117.4, 116.4, 109.1, 93.1, 36.9, 30.4; LRMS (EI, 70 eV) *m/z* (relative intensity) 125 (10), 126 (11), 140 (100), 141 (12), 152 (22), 153 (34), 165 (10), 179 (28), 180 (53), 181 (7): CI (methane) *m/z* MH^+ at 181 with the expected adduct from $CH_3CH_{2^+}$ at 209; UV λ_{max} (cyclohexane) (ϵ) 227 (24 500), 266 (9600), and a broad peak at 310 (7300) nm; exact mass $C_{12}H_8N_2$ 180.066 80, measured mass 180.0689.

7,10-Diphenyl-8,9-(1′,8′-naphthenylene)acephenanthrene (20). Trap with 7,9-Diphenyl-8*H*-cyclopent[*a*]-acenaphthylen-8-one (Acecyclone; 19). To a three-necked 250-mL round-bottom flask with attached condenser and nitrogen bleed tube was added a solution of 0.2 g (10 mmol) of crude **12–14** and 0.34 g (1 mmol) of **19** dissolved in 100 mL of purified THF. The solution was degassed for 1 h with nitrogen and then heated to 40 °C. A suspension of 5.0 g (11 mmol) of $Pb(OAc)_4$ in 60 mL of THF was added portionwise during 30 min. The mixture was magnetically stirred for 20 min and poured into 500 mL of water, and the resulting mixture extracted 3 × 100 mL CH_2Cl_2. The combined organic layers were washed 2 × 50 mL of saturated aqueous $NaHCO_3$ and 2 × 50 mL of saturated aqueous NaCl, dried over $MgSO_4$, and rotary evaporated to dryness. Yellow fluorescent **20** (95 mg, 21%) was isolated by radial chromatography with hexanes on a 1-mm silica rotor and recrystallized from cyclohexane: mp 300 dec (thermochromism); NMR ($CDCl_3$) δ 7.1–7.8 (m, H), 6.47 (d, 1 H, *J* = 7.1 Hz), 6.28 (d, 1 H, *J* = 7.1 Hz) 3.8 (m, 2 H), 3.6 (m, 2 H); λ_{max}(cyclohexane) (ϵ) 425 (12 000), 405 (11 300), 338 (62 700), 335 (62 600), 328 (46 400), 294 (54 700), 264 (sh) (36 700), 245 (51 700), 220 (sh) (53 400), 210 (71 300); IR (KBr) 3166, 2931, 2825, 1640, 1420, 1399, 1396, 1114, 751, 700 cm^{-1}. Anal. Calcd for $C_{38}H_{24}$: C, 94.97; H, 5.03. Found: C, 94.51; H, 5.13.

X-ray Crystallography. Single crystals of compound **18** were formed upon slow evaporation of a 10:1 toluene/hexane solution. Single crystals of compound **20** were obtained by slow recrystallization of a chromatographed sample from cyclohexane. Crystallographic measurements were made by using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å) on a Nicolet R3m/μ update of a $P2_1$ diffractometer. The data were collected at 298 °C. The crystallographic data and details of data collection are reported in Table II.

Acknowledgment. This work was funded in part by the Petroleum Research Fund, administered by the American Chemical Society (B.F.P.), in part by NSF Grant No. CHE-8922685 (B.F.P.), and in part by the R. A. Welch Foundation (W.H.W.).

Supplementary Material Available: X-ray data for **18** and **20** including atomic coordinates, bond lengths and angles, and anistropic thermal parameters (10 pages). Ordering information is given on any current masthead page.