Synthesis of 1-Arylacenaphtho[1,2-*d*]pyrazoles and 5,7-Dehydro-5*H*,7*H*-benzo[*b*]acenaphtho[1,2-*e*]-1,3a,6a-triazapentalenes

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2-Benzoyl- **5** and 2-acetylacenaphthenone **6**, prepared from the corresponding 1-acyl-2-(1-pyrrolidinyl)-acenaphthylenes **2** and **3**, reacted with arylhydrazines **8** under acidic conditions to give the corresponding 1-arylacenaphtho[1,2-*d*]pyrazoles **9** and **10**. Novel heteropentalene mesomeric betaines, 5,7-dehydro-5*H*,7*H*-benzo[*b*]acenaphtho[1,2-*e*]-1,3a,6a-triazapentalenes **13** and **14** were prepared by reductive cyclization of 1-(*o*-nitrophenyl)acenaphtho[1,2-*d*]pyrazoles **9d** and **10d**, respectively.

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It has been demonstrated that there are 10 general types of neutral heteropentalenes which are isoconjugate with the pentalenyl dianion [1], and in Ramsden's classification [1b,d] four of these general types are conveniently described as heteropentalene mesomeric betaines of Types **A-D** [2]. These compounds are intrinsically interesting, particularly from the point of view of their electronic structure and their participation in 1,3-dipolar cycloaddition reactions. We have previously reported the synthesis and 1,3-dipolar cycloaddition reactions of some heteropentalene mesomeric betaines, thieno[3,4-*c*][1,2,5]oxadiazoles (Type **A**) [3], pyrazolo[1,2-*a*][1,2,3]triazoles (Type **B**) [4], and imidazo[1,2-*c*]thiazoles (Type **C**) [5].

Two different periselectivities have been observed in the cycloadditions of pyrazolo[1,2-*a*][1,2,3]triazoles (hereinafter described as 1,3a,6a-triazapentalenes [6]) with acetylenic dipolarophiles: Dibenzo[*b*,*e*]-1,3a,6a-triazapentalenes react as azomethine imines [4d,e], whereas substituted bicyclic 1,3a,6a-triazapentalenes [7] and phenazino[*b*]-1,3a,6a-triazapentalenes [8] function as azomethine ylides. We are thus interested in other 1,3a,6a-triazapentalene systems.

The object of this study is to prepare novel heteropentalene betaines, 5,7-dehydro-5*H*,7*H*-benzo[*b*]acenaphtho-[1,2-*e*]-1,3a,6a-triazapentalenes (abbreviated as acenaphtho-1,3a,6a-triazapentalenes) [6]. In this connection the preparation of 1-arylacenaphtho[1,2-*d*]pyrazoles is also described.

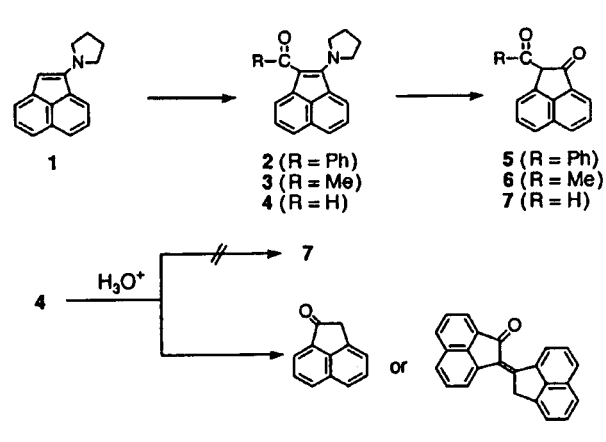
Results and Discussion.

One of the convenient methods for synthesis of benzo[*b*]-1,3a,6a-triazapentalene systems is the reductive cyclization of appropriate 1-(*o*-nitrophenyl)pyrazoles with triethyl phosphite [4a,b,9]. Thus, we have first studied the preparation of 1-arylacenaphtho[1,2-*d*]pyrazoles including 1-(*o*-nitrophenyl) derivatives as precursors of acenaphtho-1,3a,6a-triazapentalenes.

Acylation of 1-(1-pyrrolidinyl)acenaphthylene **1** [10], prepared from acenaphthenone and pyrrolidine, with benzoyl, acetyl chloride and formic-acetic anhydride gave the corresponding 1-acyl-2-(1-pyrrolidinyl)acenaphthylenes **2-4**, respectively. A tedious procedure was required, however, for the isolation of pure acetyl derivative **3**. Hydrolysis of **2-4** to the corresponding 2-acylacenaphthenones was studied under various conditions. It has been eventually found that hydrolysis of **2** with 3% sulfuric acid in refluxing ethanol gave 2-benzoylacenaphthenone **5** in 87% yield. 2-Acetylacenaphthenone **6** was formed in 58% yield by hydrolysis of **3** with 25% acetic acid in refluxing dioxane. However, one pot procedure consisted of acetylation of **1** followed by hydrolysis was convenient, since the isolation of **3** was rather tedious. Both the 2-acyl compounds **5** and **6** were found to exist as their enol forms in a solution, respectively. On the other hand, hydrolysis of **4** to 2-formylacenaphthenone **7** was unsuccessful. Surprisingly, hydrolysis of **4** with 3% hydrochloric acid or 25% acetic acid in dioxane under reflux afforded acenaphthenone or biacenaphthylidenone, respectively (Scheme 1)

The reaction of 2-acylacenaphthenones **5** and **6** with arylhydrazines **8** was studied. Both **5** and **6** reacted with phenylhydrazine **8a** in refluxing ethanol containing a catalytic amount of 36% hydrochloric acid gave the corresponding pyrazoles **9a** and **10a** in 80 and 77% yields,

Scheme 1



respectively. The other pyrazoles **9b-9d** and **10d** were prepared by the reaction of **5** and **6** with *p*-tolyl- **8b**, *p*-chlorophenyl- **8c** or *o*-nitrophenylhydrazine **8d** under acidic conditions (Scheme 2). Yields were as follows: **9b** 59%, **9c** 68%, **9d** 69%, **10d** 81%.

Scheme 2

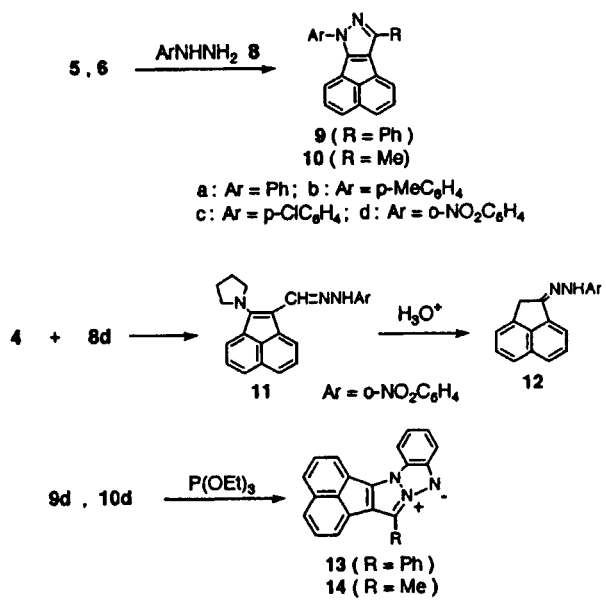


Table 1

Absorption Maxima of **9d**, **10d**, **13**, **14**, **15**, and **16**

Compound	Absorption λ max (ε) nm
9d	348 (8,360), 322 (9,740), 283 (19,800), 234 (54,720)
10d	340 (9,720), 320 (9,260), 267 (12,820), 233 (52,920)
13	529 (7,850), 518 (8,040), 396 (27,860), 387 (27,540), 313 (19,050), 303 (23,990), 256 (31,990)
14	513 (9,660), 506 (10,350), 490 (9,550), 390 (5,250), 358 (19,720), 349 (18,200), 307 (19,500), 300 (18,620), 252 (25,700)
15	390 (2,510), 365 (17,380), 328 (3,310), 312 (2,450), 307 (2,750), 301 (3,710), 294 (3,390), 289 (3,800), 274 (3,090), 248 (28,840)
16	402 (38,300), 362 (23,300), 323 (4,110), 308 (2,850), 255 (63,000)

Since the synthesis of 2-formylacenaphthenone **7** was unsuccessful, an alternate approach to the 3-unsubstituted 1-(*o*-nitrophenyl)acenaphthopyrazole was attempted: Hydrolysis of 1-formyl-2-(1-pyrrolidinyl)acenaphthenone *o*-nitrophenylhydrazone **11**, prepared from **4** and **8d**, however, gave none of the expected pyrazole, but strangely formed acenaphthenone o-nitrophenylhydrazone **12**. We were thus obliged to give up the preparation of 3-unsubstituted pyrazole.

Finally, reductive cyclization of pyrazoles **9d** and **10d** was carried out. When a solution of **9d** or **10d** and triethyl phosphite in *m*-xylene was refluxed for 11 or 15 hours under a stream of nitrogen, the expected acenaphtho-1,3a,6a-triazapentalene **13** or **14** both as violet needles, was obtained in 71 or 53% yield, respectively (Scheme 2).

The mesomeric structures of **13** and **14** are in agreement with spectroscopic and microanalytical data, and the results of their participitation in 1,3-dipolar cycloaddition reactions [11]. Both **13** and **14** display strong uv-visible absortion. The absorption maxima of **13** and **14** are given in Table 1, together with those of pyrazoles **11d**, **12d**, tetrahydrodibenzo-1,3a,6a-triazapentalene **15** [4b], and dibenzo-1,3a,4,6a-tetraazapentalene **16** [12]. The absorptions of novel triazapentalenes **13** and **14** show an appreciable shift to longer wavelengths compared to other polyazapentalenes **15** and **16**, particularly in the long-wavelength region.

EXPERIMENTAL

Melting points were determined on a Yanagimoto micro-apparatus and are uncorrected. Mass spectra were obtained on a Nippon Denshi JMS-AX500 mass spectrometer at 75 eV using a direct inlet system. The ^{1}H- and ^{13}C-nmr spectra were recorded on a JNM-EX 90 FT-NMR spectrometer using tetramethylsilane as an internal standard in deuteriochloroform, unless otherwise stated. The ir spectra were measured on a Nippon-bunko FT-IR 7000 spectrophotometer as potassium bromide pellets, and uv-visible spectra were recorded on a Hitachi U-2000 spectrophotometer in ethanol. Column chromatography was carried out on silica gel (Wako gel, C-300).

1-(1-Pyrrolidinyl)acenaphthylene **1** and 1-benzoyl-2-(1-pyrrolidinyl)acenaphthylene **2** were prepared according to the previously reported method [10].

1-Acetyl-2-(1-pyrrolidinyl)acenaphthylene **3**.

To a solution of the enamine **1** (6.0 g) and triethylamine (6.8 g) in benzene (60 ml) was added dropwise with stirring acetyl chloride (3.4 g) in benzene (4 ml) at room temperature, and then the mixture was stirred for 3 hours at the same temperature. The reaction mixture was filtered to remove triethylamine hydrochloride, and the filtrate was evaporated *in vacuo* to leave reddish viscous residue, which was extracted with petroleum ether. The extract was concentrated *in vacuo* to leave the residue, which was again extracted with *n*-hexane using a Soxhlet extracter. The extract was concentrated *in vacuo* to leave red solid, which on recrystallization from *n*-hexane gave 3.1 g (43%) of **3** as red needles.

This compound had mp 134-135°; ir: 1601 cm^{-1}; ^{1}H-nmr: δ 1.97-2.18, 3.66-3.78 (each 4H, m), 2.63 (3H, s), 7.24-8.08 (6H, m); ms: m/z (relative intensity) 263 (M^+, 100), 220 (90).

Anal. Calcd. for $C_{18}H_{17}NO$: C, 82.10; H, 6.51; N, 5.32. Found: C, 82.39; H, 6.65; N, 5.29.

1-Formyl-2-(1-pyrrolidinyl)acenaphthylene **4**.

The mixed anhydride of formic and acetic acid [13] (9.0 g) was added dropwise to a stirred solution of **1** (8.7 g) in dioxane (80 ml) at room temperature. After 4 hours, water (4 ml) was added and the solution was stirred for another one hour. The solution was poured into water (400 ml), and filtration gave an orange solid, which was recrystallized from benzene to afford **4** (5.2 g, 53%).

This compound was obtained as orange needles, mp 220-221°; ir: 1610 cm^{-1}; ^1H-nmr: δ 1.75-1.97, 3.30-3.51 (each 4H, m), 7.15-8.30 (6H, m), 9.69 (1H, s); ms: m/z (relative intensity) 249 (M^+, 100), 233 (18), 232 (89), 220 (40), 150 (37).

Anal. Calcd. for $C_{17}H_{15}NO$: C, 81.90; H, 6.06; N, 5.62. Found: C, 82.10; H, 6.14; N, 5.63.

2-Benzoylacenaphthenone **5**.

A solution of **2** (15.1 g) in ethanol (80 ml) was stirred with 3% sulfuric acid (75 ml) under reflux for 11.5 hours. The reaction mixture was concentrated *in vacuo*, and the residue was recrystallized from *n*-hexane to give **5** as yellow needles (11.0 g, 87%).

This compound had mp 101-102°; ir: 1640, 1620 cm^{-1}; ^1H-nmr: δ 7.12-8.12 (11H, m), 14.14 (1H, brs); ms: m/z (relative intensity) 272 (M^+, 100), 195 (30), 194 (97), 139 (27), 105 (19).

Anal. Calcd. for $C_{19}H_{12}O_2$: C, 83.80; H, 4.44. Found: C, 84.04; H, 4.53.

2-Acetylacenaphthenone **6**.

1) To a solution of **3** (1.2 g) in refluxing dioxane (20 ml) was added dropwise with stirring 25% acetic acid (14 ml). The reaction mixture was refluxed for 8 hours, and poured into water (300 ml). The precipitate was filtered and recrystallized from *n*-hexane to give **6** as yellow needles (0.56 g, 58%).

This compound had mp 118-119°; ir: 1659, 1618 cm^{-1}; ^1H-nmr: δ 2.48 (3H, s), 7.25-8.10 (6H, m), 14.10 (1H, brs); ms: m/z (relative intensity) 210 (M^+, 100), 195 (86), 192 (52), 168 (16), 139 (42).

Anal. Calcd. for $C_{14}H_{10}O_2$: C, 79.98; H, 4.79. Found: C, 79.96; H, 5.00.

2) To a solution of **1** (39.2 g) and triethylamine (42.2 g) in benzene (300 ml) was added dropwise, at room temperature, with stirring a solution of acetyl chloride (19.6 g) in benzene (32 ml) for 30 minutes. After the reaction mixture was stirred for 3 hours at the same temperature, the precipitated triethylamine hydrochloride was filtered off and then the filtrate was concentrated *in vacuo* to leave the residue. A solution of the residue in dioxane (250 ml) was heated with 25% acetic acid (250 ml) under reflux for 3.5 hours. After being cooled to 20°, filtration gave crude product (23.8 g), which on recrystallization from *n*-hexane using active carbon afforded **6** as yellow needles (14.0 g). The filtrate was poured into water (1000 ml) and extracted with *n*-hexane (100 ml x 4) . The extract was washed with water, dried over magnesium sulfate, and evaporated *in vacuo* to leave the residue: Recrystallization of the residue from *n*-hexane using active carbon gave **6** as yellow needles (3.3 g). Total yield was 17.3 g (47%).

Hydrolysis of **4**.

1) After a solution of **4** (0.2 g) in dioxane (5 ml) was refluxed with 3% hydrochloric acid (24 ml) for 30 minutes, the reaction mixture was poured into water (500 ml) to give acenaphthenone, mp 120-121° (mp 121-121.5° [14]), as colorless needles (84 mg, 62%).

2) After a solution of **4** (0.2 g) in dioxane (5 ml) was refluxed with 25% acetic acid (2.4 ml) for 7 hours, filtration gave biacenaphthylidenone, mp 261° (mp 262° [15]), as golden yellow needles (31 mg). The filtrate was poured into water (60 ml) to give unreacted **4** (82 mg, 41%).

1,3-Diphenylacenaphtho[1,2-*d*]pyrazole **9a**.

A solution of **5** (0.40 g) and **8a** (0.25 g) in ethanol (10 ml) containing 36% hydrochloric acid (2 drops) was refluxed for 8 hours. After being cooled to room temperature, filtration gave crystals, which on recrystallization from cyclohexane afforded **9a** as yellow needles (0.41 g, 80%).

This compound had mp 203-204°; ir: 1598, 1510 cm^{-1}; ^1H-nmr: δ 7.16-8.20 (m); ms: m/z (relative intensity) 344 (M^+, 100), 241 (21).

Anal. Calcd. for $C_{25}H_{16}N_2$: C, 87.18; H, 4.68; N, 8.13. Found: C, 86.98; H, 4.89; N, 8.16.

3-Phenyl-1-(*p*-tolyl)acenaphtho[1,2-*d*]pyrazole **9b**.

A similar reaction of **5** (0.30 g) with the hydrazine **8b** (0.20 g) in refluxing ethanol containing 36% hydrochloric acid (2 drops) for 6 hours to that described above gave **9b** as yellow needles (acetonitrile) (0.23 g, 59%).

This compound had mp 209-210°; ir: 1608, 1520 cm^{-1}; ^1H-nmr: δ 2.42 (3H, s), 7.16-8.12 (16H, m); ms: m/z (relative intensity) 358 (M^+, 100), 255 (19).

Anal. Calcd. for $C_{26}H_{18}N_2$: C, 87.12; H, 5.06; N, 7.82. Found: C, 87.23; H, 5.15; N, 7.80.

1-(*p*-Chlorophenyl)-3-phenylacenaphtho[1,2-*d*]pyrazole **9c**.

A similar reaction of **5** (0.20 g) with the hydrazine **8c** hydrochloride (0.20 g) in refluxing ethanol (10 ml) containing 36% hydrochloric acid (2 drops) for 6 hours to that decribed above afforded **9c** (0.19 g, 68%) as yellow needles (cyclohexane).

This compound had mp 117-118°; ir: 1595, 1510 cm^{-1}; ^1H-nmr: δ 7.20-8.10 (m); ms: m/z (relative intensity) 380 (M^+, 34), 378 (M^+, 100), 277 (3), 275 (9).

Anal. Calcd. for $C_{25}H_{15}N_2Cl$: C, 79.26; H, 3.99; N, 7.40. Found: C, 79.34; H, 4.27; N, 7.38.

1-(*o*-Nitrophenyl)-3-phenylacenaphtho[1,2-*d*]pyrazole **9d**

A similar reaction of **5** (2.93 g) with the hydrazine **8d** (1.99 g) in ethanol (150 ml) containing concentrated sulfuric acid (0.25 ml) for 5 hours to that described above gave **9d** (2.89 g, 69%) as yellow prisms (ethyl acetate).

This compound had mp 191-192°; ir: 1607, 1537, 1365 cm^{-1}; ^1H-nmr: δ 7.41-8.09 (m); ^{13}C-nmr: δ 120.31, 121.31, 121.92, 125.59, 125.65, 125.89, 126.05, 126.11, 126.96, 128.59, 128.72, 128.92, 130.30, 130.41, 132.80, 133.14, 133.29, 134.45, 144.73, 148.03, 149.07; ms: m/z (relative intensity) 389 (M^+, 100), 343 (19), 342 (20), 240 (15).

Anal. Calcd. for $C_{25}H_{15}N_3O_2$: C, 77.12; H, 3.86; N, 10.79. Found: C, 77.33; H, 4.09; N, 10.56.

3-Methyl-1-phenylacenaphtho[1,2-*d*]pyrazole **10a**.

A similar reaction of **6** (0.20 g) with **8a** (0.16 g) in ethanol (5 ml) containing 36% hydrochloric acid (2 drops) for 30 minutes to that described for **9a** afforded **10a** (0.21 g, 77%) as yellow needles (*n*-hexane).

This compound had mp 103°; ir: 1601, 1516 cm^{-1}; ^1H-nmr: δ 2.51 (3H, s), 7.09-7.78 (11H, m); ms: m/z (relative intensity) 282 (M^+, 100), 241 (15), 164 (3).

Anal. Calcd. for $C_{20}H_{14}N_2$: C, 85.08; H, 5.00; N, 9.92. Found: C, 84.84; H, 5.13; N, 9.76.

3-Methyl-1-(*o*-nitrophenyl)acenaphtho[1,2-*d*]pyrazole **10d**.

A similar reaction of **6** (3.0 g) with **8d** (2.5 g) in ethanol (75 ml) containing concentrated sulfuric acid (0.45 ml) for 24 hours to that described for **9d** gave **10d** (3.74 g, 81%) as yellow plates (benzene).

This compound had mp 175-176°; ir: 1607, 1535, 1371 cm^{-1}; ^{1}H-nmr: δ 2.52 (3H, s), 7.39-7.98 (10H, m); ^{13}C-nmr: δ 13.16, 120.28, 120.80, 125.41, 125.50, 126.01, 126.90, 127.72, 127.93, 128.31, 128.54, 130.20, 130.53, 133.21, 133.27, 134.12, 144.51, 144.85, 148.27; ms: m/z (relative intensity) 327 (M^+, 100), 281 (4), 240 (10).

Anal. Calcd. for $C_{20}H_{13}N_3O_2$: C, 73.38; H, 4.00; N, 12.84. Found: C, 73.48; H, 4.20, N, 12.70.

1-Formyl-2-(1-pyrrolidinyl)acenaphthylene *o*-Nitrophenylhydrazone **11**.

A solution of **4** (0.5 g) and **8d** (0.4 g) in dioxane (20 ml) was refluxed for 10 hours. The reaction mixture was concentrated *in vacuo* to leave the residue, which was chromatographed to give **11** as blue violet needles from benzene elution (0.46 g, 60%).

This compound had mp 225-226°; ir: 3295, 1615, 1574, 1524, 1346 cm^{-1}; ^{1}H-nmr: δ 1.94, 3.63 (each 4H, m), 6.54-8.33 (11H, m), 10.89 (1H, s); ms: m/z (relative intensity) 384 (M^+, 25), 382 (29), 247 (100), 246 (45).

Anal. Calcd. for $C_{23}H_{20}N_4O_2$: C, 71.85; H, 5.25; N, 14.58. Found: C, 71.80; H, 5.22; N, 14.41.

Hydrolysis of **11**.

A solution of **11** (0.3 g) in tetrahydrofuran (15 ml) containing 3% hydrochloric acid (1 ml) was refluxed for 3 hours. After being cooled to room temperature, filtration gave crystals, which on recrystallization from chloroform afforded acenaphthenone o-nitrophenylhydrazone **12**, mp 210-211°, as red needles. This compound was identical with an authentic sample prepared from the reaction of acenaphthenone with **8d**; ir: 3298, 1618, 1576, 1342, 1328 cm^{-1}; ^{1}H-nmr: δ 4.01 (2H, s), 6.72-8.22 (10H, m), 10.85 (1H, s); ms: m/z (relative intensity) 303 (M^+, 32), 151 (100).

Anal. Calcd. for $C_{18}H_{13}N_3O_2$: C, 71.27; H, 4.33; N, 13.86. Found: C, 71.47; H, 4.41; N, 13.84.

7-Phenyl-5,7-dehydro-5*H*,7*H*-benzo[*b*]acenaphtho[1,2-*e*]-1,3a,6a-triazapentalene **13**.

A solution of **9d** (5.18 g) and triethyl phosphite (9.5 g) in *m*-xylene (60 ml) was refluxed for 11 hours under a stream of nitrogen. After being cooled to room temperature, filtration gave violet crystals, which were recrystallized from benzene to give **13** as violet needles (4.1 g, 71 %).

This compound had mp 261-263°; ir: 1603, 1406, 1367, 1348, 1311, 1160, 816, 766, 725 cm^{-1}; ^{1}H-nmr: δ 7.07-8.42 (m) [16]; ms: m/z (relative intensity) 357 (M^+, 100), 329 (39), 328 (89), 254 (18), 165 (12), 164 (23).

Anal. Calcd. for $C_{25}H_{15}N_3$: C, 84.01; H, 4.23; N, 11.76. Found: C, 83.82; H, 4.44; N, 11.76.

7-Methyl-5,7-dehydro-5*H*,7*H*-benzo[*b*]acenaphtho[1,2-*e*]-1,3a,6a-triazapentalene **14**.

A solution of **10d** (6.9 g) and triethyl phosphite (21.0 g) in *m*-xylene (200 ml) was refluxed for 15 hours under a stream of nitrogen. A similar procedure to that described above gave **14** as violet needles (3.32 g, 53%).

This compound had mp 239-241°; ir: 2920, 1605, 1458, 1437, 1367, 1344, 1307, 1145, 814, 770, 725 cm^{-1}; ^{1}H-nmr: δ 2.34 (3H, s), 6.61-7.69 (10H, m) [16]; ms: m/z (relative intensity) 295 (M^+, 100), 280 (2), 267 (26), 266 (57), 254 (48), 165 (4), 154 (11).

Anal. Calcd. for $C_{20}H_{13}N_3$: C, 81.33; H, 4.44; N, 14.23. Found: C, 81.11; H, 4.39; N, 14.04.

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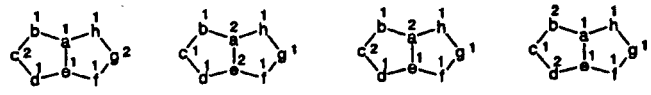
[1] For the reviews on chemical and physical properties of heteropentalene mesomeric betaines, see: [a] M. P. Cava and M. V. Laksmikantham, *Acc. Chem. Res.*, **8**, 139 (1975); [b] C. A. Ramsden, *Tetrahedron*, **33**, 3203 (1977); [c] C. A. Ramsden, In Comprehensive Heterocyclic Chemistry, Vol VI, A. R. Katritzky and C. W. Rees, eds, Pergamon Press, Oxford, 1984, pp 1027-1048; [d] W. D. Ollis, S. P. Stanforth, and C. A. Ramsden, *Tetrahedron*, **41**, 2239 (1985).

[2] General formulas of Types **A-D**, in which a-h represent suitably substituted carbon or heteroatoms and the superscripts indicate the origin of the 10π -electrons, are as follows:



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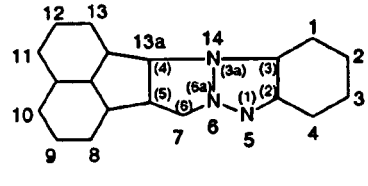
[6] The triazapentalene nomenclature is employed in this paper to emphasize the role of the annular nitrogens of the central rings in providing the unusual properties of this novel system. The following numbering system has been adopted.



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[16] The ^{13}C nmr spectra of triazapentalenes **13** and **14** were not measured because of their slight solubility in deuterated solvents.