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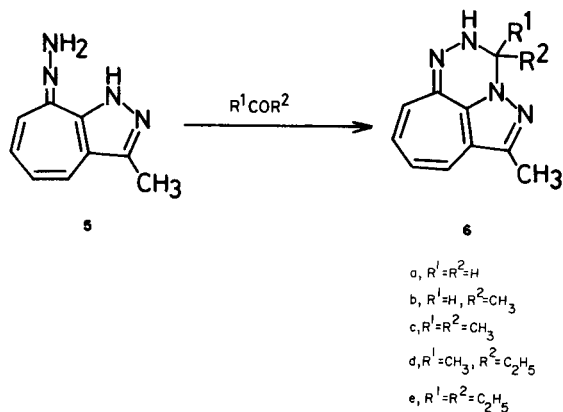
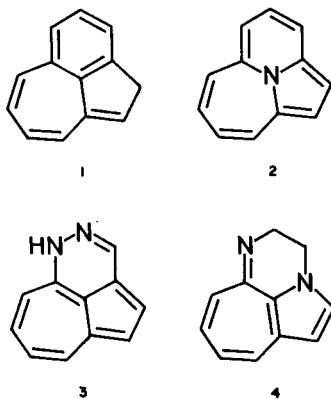
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3-Methyl-1,8-dihydrocycloheptapyrazol-8-one hydrazone (**5**) reacted with triethyl orthoformate, orthoacetate and orthopropionate to afford 2,2a,4,5-tetraazabenz[cd]azulene derivatives (**7a-c**). 3-Methyl- (**7b**) and 3-phenyl-substituted compounds (**7d**) were also obtained by the reactions of **5** with acetyl and benzoyl chlorides, respectively.

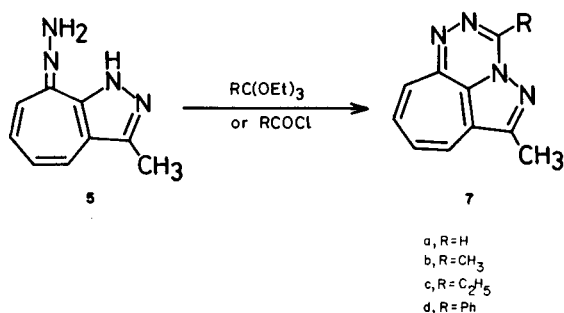
J. Heterocyclic Chem., **17**, 1057 (1980).

Numerous nonbenzenoid polycyclic-condensed hydrocarbons containing the azulene skeleton have been synthesized by peri-annulation of one or two 5- and 7-membered ring to azulene (**1**). 2*H*-Benz[cd]azulene (**1**) (**2**) is one of them. However, little is known about aza-analogs, except for cycl[4.3.2]azine (**2**) (**3,4**). Recently, 4,5-diaza (**3**) (**5**) and 2a,5-diaza derivatives (**4**) (**6**) were reported. We also reported that 3-methyl-1,8-dihydrocycloheptapyrazol-8-one hydrazone (**5**) (**7**) reacted with aliphatic aldehydes or ketones to give 3,4-dihydro-2,2a,4,5-tetraazabenz[cd]azulene derivatives (**6**) (**8**).



The present paper deals with the synthesis of 2,2a,4,5-tetraazabenz[cd]azulene derivatives (**7**) by the reactions

of the hydrazone (**5**) with orthoesters or with acyl halides.

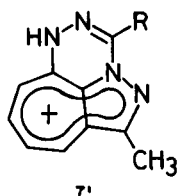


Refluxing of a mixture of the hydrazone (**5**) and triethyl orthoformate for 2 hours gave 1-methyl-2,2a,4,5-tetraazabenz[cd]azulene (**7a**) in 81% yield. The reactions of **5** with triethyl orthoacetate and with triethyl orthopropionate in refluxing methanol also afforded the tricyclic compounds (**7b** and **7c**) in 85 and 64% yields, respectively.

On the other hand, the hydrazone (**5**) reacted with acetyl chloride in refluxing chloroform to afford the compound (**7b**). The yield (13%) is lower than that in the reaction with triethyl orthoacetate. Similarly, the reaction of **5** with benzoyl chloride gave the 3-phenyl derivative (**7d**) in 10% yield.

The nmr spectrum in deuteriochloroform of the compound **7a** shows peaks at δ 2.30 (s, 3H) for 1-CH₃, 5.60 (ddd, 1H, $J = 10.8, 6.0, 2.4$ Hz) for H-8, 5.8-6.3 (m, 3H) for H-6,7,9 and 8.30 ppm (s, 1H) for H-3. The signals of the seven-membered ring protons are observed at considerably high field. These data indicate bond alternation in the seven-membered ring. The spectrum in trifluoroacetic acid shows shift of the seven-membered ring protons by *ca.* 1.1-1.3 ppm and that of 1-CH₃ protons by *ca.* 0.3 ppm towards lower field. However, the signal for H-3 does not shift. These results reveal that the positive charge of the cation is delocalized over both the seven-membered ring and the pyrazole ring and that the C=N bond at 3- and 4-positions in the triazine ring is localized.

This phenomenon is also observed in the compounds (7b-d).



The electronic spectrum of the tricyclic compound (7a) is shown in Figure I together with that of its 3,4-dihydro derivative (6a). The absorption band of 7a in the visible region is characteristic and is strikingly similar in pattern and intensity to those of azulene. This might indicate that the electronic transition is due to pyrazolo[1,2-d][1,2,4]triazine moiety, which is isoelectronic to azulene, as shown in the structure (7'). However, introduction of the electronegative nitrogen atoms caused a noticeable hypsochromic shift in the visible band. Thus, the seven-membered ring is isolated from the 10 π -electronic system and shows olefinic character as described in the nmr spectrum in deuteriochloroform.

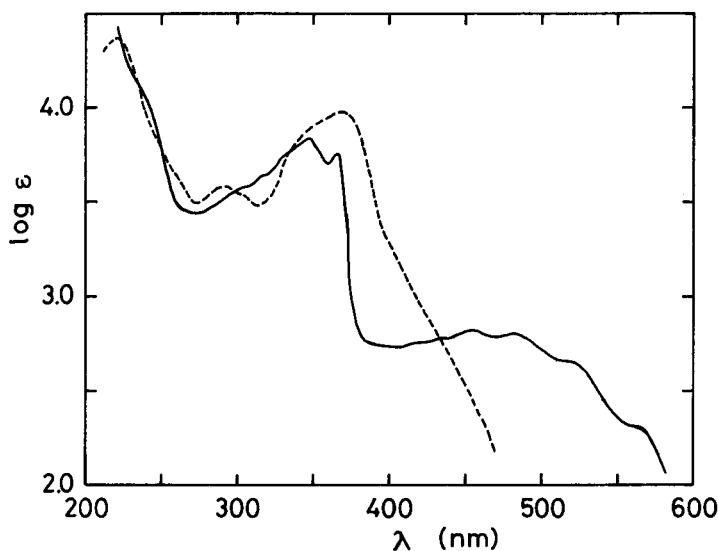
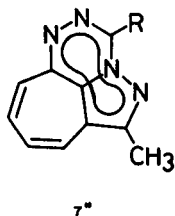


Figure I. Electronic spectra

----- 6a
 ——— 7a



EXPERIMENTAL

Melting points were determined with a Yanagimoto MP-S2 melting point measuring apparatus and are uncorrected. Ir spectra were taken on a JASCO IRA-1 spectrophotometer and uv spectra on a Hitachi EPS-3T spectrophotometer. Nmr spectra were recorded with a Hitachi R-24 spectrometer (60 MHz) with TMS as an internal standard. Analyses were done by the Elemental Analysis Center of Kyushu University.

1-Methyl-2,2a,4,5-tetraazabenz[cd]azulene (7a).

3-Methyl-1,8-dihydrocycloheptapyrazol-8-one hydrazone (5) (870 mg., 5 mmoles) and triethyl orthoformate (10 ml.) was boiled under reflux for 2 hours. After evaporation of an excess of triethyl orthoformate under reduced pressure, the residue was recrystallized from benzene-cyclohexane (1:1) to afford 1-methyl-2,2a,4,5-tetraazabenz[cd]azulene (7a) as reddish brown prisms, yield 745 mg. (81%), m.p. 176-178°; ir (chloroform): 1632 (C=N), 1556 cm^{-1} (C=C); uv (methanol): 348 (log ϵ 3.84), 365 (3.75), 430 sh (2.77), 454 (2.82), 484 (2.80), 516 sh (2.66), 560 sh nm (2.32); nmr (deuteriochloroform): δ 2.30 (s, 3H, CH₃), 5.4-5.75 (m, 1H), 5.8-6.3 (m, 3H), 8.30 ppm (s, 1H, H-3); nmr (trifluoroacetic acid): δ 2.60 (s, 3H, CH₃), 6.5-6.8 (m, 2H), 7.1-7.6 (m, 2H), 8.40 ppm (s, 1H, H-3).

Anal. Calcd. for C₁₀H₈N₄: C, 65.20; H, 4.38; N, 30.42. Found: C, 65.02; H, 4.35; N, 30.29.

1,3-Dimethyl-2,2a,4,5-tetraazabenz[cd]azulene (7b).

a)

A mixture of the hydrazone (5) (870 mg., 5 mmoles) and triethyl orthoacetate (1.62 g., 10 mmoles) in methanol (50 ml.) was refluxed for 2 hours. The solvent was evaporated off and the remaining product was recrystallized from cyclohexane to afford 1,3-dimethyl-2,2a,4,5-tetraazabenz[cd]azulene (7b) as reddish brown needles, yield 842 mg. (84%), m.p. 169-171°; ir (chloroform): 1638 (C=N), 1562 cm^{-1} (C=C); uv (methanol): 307 sh (log ϵ 3.60), 318 sh (3.66), 335 sh (3.77), 347 (3.84), 365 (3.71), 426 sh (2.66), 448 (2.72), 477 (2.71), 506 sh (2.59), 550 sh nm (2.28); nmr (deuteriochloroform): δ 2.30 (s, 3H, 1-CH₃), 2.47 (s, 3H, 3-CH₃), 5.3-5.7 (m, 1H), 5.8-6.3 ppm (m, 3H); nmr (trifluoroacetic acid): δ 2.61 (s, 3H, CH₃), 2.62 (s, 3H, CH₃), 6.5-6.8 (m, 2H), 7.1-7.5 ppm (m, 2H).

Anal. Calcd. for C₁₁H₁₀N₄: C, 66.65; H, 5.09; N, 28.27. Found: C, 66.60; H, 5.12; N, 28.19.

b)

The hydrazone (5) (435 mg., 2.5 mmoles) was also reacted with acetyl chloride (395 mg., 5 mmoles) in chloroform (50 ml.) under reflux to afford 7b, yield 65 mg. (13%).

3-Ethyl-1-methyl-2,2a,4,5-tetraazabenz[cd]azulene (7c).

A mixture of the hydrazone (5) (870 mg., 5 mmoles) and triethyl orthopropionate (1.76 g., 10 mmoles) in methanol (50 ml.) was refluxed for 2 hours. The reaction mixture was worked up as mentioned above and recrystallized from cyclohexane to afford 3-ethyl-1-methyl-2,2a,4,5-tetraazabenz[cd]azulene (7c) as reddish orange needles, yield 680 mg. (64%), m.p. 113-115°; ir (chloroform): 1638 (C=N), 1564 cm^{-1} (C=C); uv (methanol): 305 sh (log ϵ 3.59), 335 sh (3.79), 347 (3.86), 364 (3.75), 424 sh (2.37), 447 (2.80), 474 (2.78), 506 sh (2.63), 546 sh nm (2.29); nmr (deuteriochloroform): δ 1.33 (t, 3H, J = 7.2 Hz, CH₂-CH₃), 2.30 (s, 3H, 1-CH₃), 2.85 (q, 2H, J = 7.2 Hz, CH₂),

5.3-5.7 (m, 1H), 5.8-6.4 ppm (m, 3H); nmr (trifluoroacetic acid): δ 1.41 (t, 3H, $J = 7.2$ Hz, $\text{CH}_2\text{-CH}_3$), 2.66 (s, 3H, 1- CH_3), 3.06 (q, 2H, $J = 7.2$ Hz, CH_2), 6.5-6.8 (m, 2H), 7.1-7.5 ppm (m, 2H).

Anal. Calcd. for $\text{C}_{12}\text{H}_{12}\text{N}_4$: C, 67.90; H, 5.70; N, 26.40. Found: C, 67.80; H, 5.73; N, 26.44.

1-Methyl-3-phenyl-2,2a,4,5-tetraazabenz[cd]azulene (7d).

A solution of the hydrazone (5) (870 mg., 5 mmoles) and benzoyl chloride (1.40 g., 10 mmoles) in chloroform (100 ml.) was refluxed for 5 hours. After evaporation of the solvent, the residue was chromatographed on three Wakogel B-10 plates (30 x 30 cm^2) with chloroform and recrystallized from benzene-cyclohexane to afford 1-methyl-3-phenyl-2,2a,4,5-tetraazabenz[cd]azulene (7d) as dark red prisms, yield 130 mg. (10%), m.p. 189-191°; ir (chloroform): 1635 (C=N), 1562 cm^{-1} (C=C); uv (methanol): 271 ($\log \epsilon$ 3.93), 359 (3.71), 440 sh (2.89), 466 (2.95), 495 (2.93), 530 sh (2.77), 578 sh nm (2.42); nmr (deuteriochloroform): δ 2.28 (s, 3H, CH_3), 5.3-5.8 (m, 1H), 6.0-6.4 (m, 3H), 7.2-7.6 (m, 3H, H-3',4',5'), 8.2-8.5 ppm (m, 2H, H-2',6'); nmr (trifluoroacetic acid): δ 2.69 (s, 3H, CH_3), 6.5-7.4 (m, 4H), 7.5-7.8 (m, 3H), 8.1-8.3 ppm (m, 2H).

Anal. Calcd. for $\text{C}_{16}\text{H}_{12}\text{N}_4$: C, 73.83; H, 4.65; N, 21.53. Found: C, 73.68; H, 4.82; N, 21.42.

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