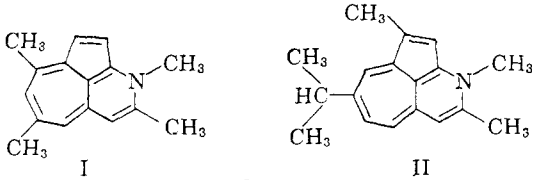
COMMUNICATIONS TO THE EDITOR

1*H*-CYCLOHEPTA[d,e]-1-PYRINDINE, A NEW CONJUGATE-UNSATURATED HETEROCYCLIC SYSTEM

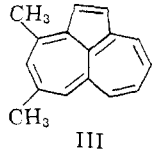
Sir:

In the course of studies on heterocyclic compounds which are iso-π-electronic with non-benzenoid aromatic hydrocarbons,[1] the synthesis of two derivatives (I and II) of the hitherto unknown 1*H*-cyclohepta[d,e]-1-pyrindine has been achieved. This new ring system is a π-excessive[2] heteroanalog of the interesting hydrocarbon (III) recently reported by Hafner.[3]



I

II



III

The 1,2,5,7-tetramethyl derivative (I) was prepared from 1-nitro-4,6,8-trimethylazulene.[4] Reductive acetylation[5] of this nitro compound afforded the corresponding 1-acetylamino derivative (IV) in nearly quantitative yield as blue needles, m.p. 178–181°. Found for $C_{15}H_{17}NO$: C, 78.76; H, 7.30; N, 6.46. Visible: λ_{max} 563 mμ (ϵ 524); infrared, 2.94 μ (NH); 5.93 μ.[6] Treatment of IV with sodium hydride followed by the addition of methyl iodide gave 95% of the N-methyl compound (V) as purple crystals, m.p. 162–164° (softening at *ca.* 155°). Found for $C_{16}H_{19}NO$: C, 79.70; H, 7.89; N, 5.82. Visible: λ_{max} 553 mμ (ϵ 525); infrared, 6.01 μ. As anticipated,[7] the intramolecular condensation of V was effected by reaction with sodium N-methylanilide and a 68% (93% net) yield of I[8] was obtained as green needles, m.p. 210–212° (evac. capillary). Found for $C_{16}H_{17}N$: C, 85.96; H, 7.43; N, 6.31. The infrared spectrum showed no peaks corresponding to NH or carbonyl groups. The ultraviolet and visible spectra were quite similar to those reported for III[3] and showed maxima in mμ (log ϵ) at 236 (4.52), shoulder at 243(4.47), 270(4.51), 290(4.26), 358(3.99), 387(3.74), 399(3.81), 423(3.56), shoulder at 630(2.56), 688(2.71), 766(2.72), and 869(2.43).

The pronounced basicity of I was evidenced by complete protonation in 10% sulfuric acid (maxima in mμ (log ϵ) at 238(4.33), shoulder at 253(4.20), 278(4.06), 292(4.04), 301(4.02), shoulder at 323-(3.87), 456(3.10), 481(3.10), and a shoulder at 510-(3.03)) and in formic acid to form red solutions.[9]

A parallel reaction sequence led to II. 3-Acetylaminoguaiazulene[10] was converted to the N methyl derivative (VI), obtained as blue crystals, m.p. 75–77.5°, in 56% yield. Found for $C_{18}H_{23}NO$: C, 80.31; H, 8.67; N, 5.26. Visible: λ_{max} 610 mμ (ϵ 490); infrared, 6.00 μ. Treatment of VI with sodium N-methylanilide gave 61% of II as red-brown needles, m.p. 179–180.5°. Found for $C_{18}H_{21}N$: C, 85.77; H, 8.51; N, 5.73. The ultraviolet and visible spectra of II showed maxima in mμ (log ϵ) at 238(4.47), 253(4.43), 270(4.49), shoulder at 300(3.84), 361(4.12), 398(3.69), 422-(3.62), 449(3.43), shoulder at 690(2.38), 763(2.50), 862(2.50) and 996(2.22). The infrared spectrum showed no absorption corresponding to NH or carbonyl groups.

I and II are fairly stable in crystalline form but decompose on alumina and slowly in solution. Their n.m.r. spectra were consistent with the proposed structures.

Acknowledgment.—We thank the National Science Foundation for support of this work under Grant G 7397.

(1) A. G. Anderson, Jr., W. F. Harrison, R. G. Anderson and A. G. Osborne, *J. Am. Chem. Soc.*, **81**, 1255 (1959); A. G. Anderson, Jr., and W. F. Harrison, *Tetrahedron Letters*, [2], 11 (1960).

(2) A. Albert, "Heterocyclic Chemistry," Essential Books, Fair Lawns, N. J., 1959.

(3) K. Hafner and J. Schneider, *Ann.*, **624**, 37 (1959).

(4) K. Hafner and C. Bernhard, *ibid.*, **625**, 108 (1959).

(5) A. G. Anderson, Jr., J. A. Nelson and J. J. Tazuma, *J. Am. Chem. Soc.*, **75**, 4980 (1953).

(6) Ultraviolet, visible and near-infrared spectra were measured in cyclohexane solution and infrared spectra in carbon tetrachloride solution.

(7) The acidic nature of the methyl protons in 4-(8)methylazulenes is well established; *cf.* ref. 3.

(8) None of the presumed intermediate tricyclic hydroxy compound was isolated or detected in the reaction mixture.

(9) The basicity of I is in accord with the observation that 2-phenyl-2-pyrindine is appreciably more basic than azulene; A. G. Anderson, Jr., and W. F. Harrison, unpublished results.

(10) K. G. Scheibli, Doctoral Thesis, Eidgenössischen Technischen Hochschule, Zürich, Switzerland, 1952, p. 35.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF WASHINGTON ARTHUR G. ANDERSON, JR.
SEATTLE 5, WASHINGTON LANNY L. REPLOGLE

RECEIVED JUNE 13, 1961

AGARITINE: AN IMPROVED ISOLATION PROCEDURE AND CONFIRMATION OF STRUCTURE BY SYNTHESIS

Sir:

In a recent communication[1] structure I (R = CH_2OH) was proposed for agaritine isolated from *Agaricus bisporus*. We have isolated agaritine in yields of *ca.* 1 g./10 lb. of mushrooms by a different process and have confirmed its structure as β-N-(γ-L(+)-glutamyl)-4-hydroxymethylphenylhydrazine by synthesis.

Buttons from two- to three-day old mushrooms[2] were homogenized in methanol (700 g. in 1350

(1) B. Levenberg, *J. Am. Chem. Soc.*, **83**, 503 (1961).

(2) Supplied by the Michigan Mushroom Co., Niles, Michigan.