SYNTHESIS OF 13,13,13a,15,15-PENTAMETHYL-*-6H,7H,13H,13aH,15H*-1,4-DIAZEPINO[1,7a : 4,5a']DIINDOLE AND THE STRUCTURE OF ITS PERCHLORATE

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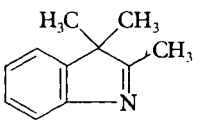
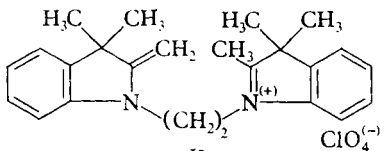
Condensation of 2,3,3-trimethyl-3*H*-indole (*I*) with 1,2-dibromoethane gave base *V*, affording perchlorate *III*. In strongly acid solutions both the base and its perchlorate got converted into disalt *IV*.

The reaction of 2,3,3-trimethyl-3*H*-indole (*I*) with dihalogenated alkanes was described by several authors[1-3]. The free base produced by the reaction of *I* with dibromoethane has not yet been obtained, but its perchlorate was isolated and assigned[2,3] the open structure *II*. The authors assume that in a dimethyl sulphoxide solution it is in equilibrium with the cyclic form *III*.



I



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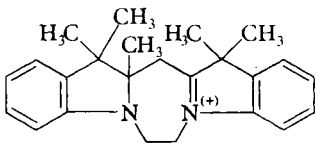
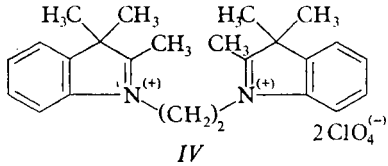
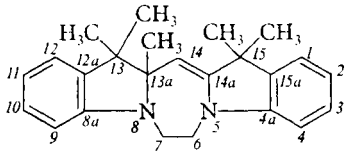


III



IV



V

We have now found that the free base is formed readily by the reaction of 1,2-dibromoethane with compound *I*, followed by alkalinization of the alkylation product with an alkali hydroxide. On the basis of its IR, ^{1}H NMR and ^{13}C NMR spectra, it has been identified as 13,13,13a,15,15-pentamethyl-6*H*,7*H*,13*H*,13a*H*,15*H*-1,4-diazepine[1,7a : 4,5a']diindole (*V*).

The different chemical shifts of carbon atoms of the individual methylene groups in the ^{13}C NMR spectrum, and the non-equivalence of protons in each of the methylene groups attached to nitrogen atoms suggest a rigid polycyclic structure. The presence of the enamine grouping is safely demonstrated by both the proton and the carbon spectra. The IR spectrum exhibits a strong absorption band at 1 680 cm^{-1}, which is characteristic of this grouping. To rule out the possibility of a wrong assignment and an erroneous interpretation of the relationships between the ^{1}H and the ^{13}C NMR spectra, we measured the ^{1}H ^{13}C shift-correlated 2D NMR spectrum, which enabled us to assign the signals of protons and carbon atoms in the aromatic region, and underlined the non-equivalence of geminal protons in the CH_2—N groups. An unequivocal identification of the methyl group signals, *C*, was deduced from the proton and the carbon spectra of the deuterated analogue. The assignment of the individual signals is given in Table I; we used the data from the 2D NMR spectrum and values reported for compounds of related types[3-5].

Neutralization of an ethanolic solution of compound *V* with perchloric acid gave a monoperchlorate which according to its melting point and ^{1}H NMR spectrum was identical with that described in the literature[2]. The ^{1}H NMR spectrum contained three methylene proton multiplets which were identified by means of the spin interaction. The determined constant of spin interaction of the isolated methylene group, 15 Hz, testifies to a cyclic structure of the salt *III*. If it had the open form *II*, the spin interaction of the terminal methylene group should not exceed 3 Hz. The IR spectrum of *III*, measured in a KBr pellet, had a weak absorption band at 1 625 cm^{-1}, associated with the $-N^{(+)}=\overset{|}{C}-$ bond. The absorption characteristic of an enamine grouping was absent. All this evidence suggests, at variance with the reported data[2], the cyclic structure *III*. The ^{1}H NMR spectra of compounds *III* and *V*, measured in trifluoroacetic acid (7·89 – 7·39 ppm (8 H, m, ArH); 5·31 ppm (4 H, s, CH_2CH_2); 2·94 ppm (6 H, 2,2'-CH_3); 1·64 ppm (12 H, 3,3,3',3'-CH_3)) were identical, and, in accordance with the literature[2], demonstrated the presence of compound *IV*. Alkalinization back-released the compound *V*.

EXPERIMENTAL

The melting points were not corrected. The IR spectra were measured employing a spectrometer Perkin-Elmer 325. The ^{1}H NMR spectra were measured with spectrometers Varian XL-100 (100 MHz, 31°C) and Varian XL-200 (200 MHz, 25°C), ^{13}C NMR spectra with an apparatus Tesla BS 567 (25·14 MHz, 25°C) and Varian XL 200 (50 MHz, 25°C), tetramethylsilane being

used as internal standard. The shift-correlated 2 D NMR spectra were measured in C^2HCl_3 at 25°C, employing the apparatus XL-200.

13,13,13a,15,15-*Pentamethyl*-6H,7H,13H,13aH,15H-1,4-*diazepino*[1,7a : 4,5a']*diindole* (V): A mixture of *I* (191 g, 120 mmol) and 1,2-dibromoethane (33·8 g, 180 mmol) was heated 5 h to 130 °C, cooled down, stirred up with boiling ethanol and filtered. The solid (11 g) was dissolved in water and alkalinized with 10% potassium hydroxide. The separated substance was taken into ether, the solution was dried with calcium chloride, the ether was distilled off and the residue was crystallized from acetone–hexane; yield 3·0 g (14·5%) of *V*, m.p. 121—122°C. For $C_{24}H_{28}N_2$ (344·5) calculated: 83·68% C, 8·19% H, 8·13% N; found: 83·64% C, 8·12% H, 8·20% N.

The deuterated analogue was obtained by dissolving the product in ^2H_2O, and alkalinization with anhydrous potassium carbonate; m.p. 117—118°C (acetone). The ^1H NMR spectrum measured in C^2HCl_3 was identical with that of non-deuterated *V*, except that the signals at 1·07 and 4·23 ppm were lacking.

Perchlorate III: 0·345 g (1 mmol) of *V* in 2 ml of ethanol was neutralized with 60% perchloric acid; yield 0·41 g (92%) of *III*, m.p. 132—133°C. After crystallization from acetonitrile the m.p. was unchanged. For $C_{24}H_{29}ClN_2O_4$ (445·0) calculated: 64·78% C, 6·57% H, 6·30% N, 7·97% Cl; found: 64·92% C, 6·69% H, 6·38% N, 7·91% Cl. ^1H NMR spectrum (C^2H_3CN) 1·14 (3 H, s, CH_3), 1·23 (3 H, s, CH_3), 1·34 (3 H, s, CH_3), 1·45 (3 H, s, CH_3), 1·60 (3 H, s, CH_3), 3·11—3·67 (2 H, m, 14, 14 H), 3·74—3·98 (2 H, m, 7, 7 H), 4·61—4·84 (2 H, m, 6, 6 H), 6·50—6·84 (8 H, m, ArH).

TABLE I
^{13}C NMR and ^1H NMR spectra of compound *V*

Signal assignment	^{13}C NMR spectrum[a]		^1H NMR spectrum[b] (mult. J_{H-H})	
A, B	20·9	26·6	1·09 (s); 1·30 (s)	
C	18·6		1·07 (s)	
D, E	29·9	31·1	1·32 (s); 1·34 (s)	
1, 12	121·6	121·8	6·98 (d, d, d; 0·4; 1·3; 7·4)	
2, 11	116·5	118·6	6·62 (dt, 1·0; 7·4)	
			6·77 (dt, 1·0; 7·4)	
3, 10	127·0	127·4	7·13 (dt, 1·3; 7·5)	
			7·05 (dt, 1·4; 7·4)	
4, 9	104·5	105·6	6·36 (bd, 7·4), 6·53 (bd, 7·5)	
4a, 8	147·0	147·3	—	
12a, 15a	137·3	137·6	—	
13	44·9		—	
13a	73·4		—	
14	95·7		4·23 (s)	
14a	151·6		—	
15	47·0		—	
6	47·6		3·51 (m)	3·77 (m)
7	40·1		3·51 (m)	3·77 (m)

[a] Measured in C^2HCl_3, 0·1 ppm; [b] 0·01 ppm, $J = 0·1$ Hz.

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