The Synthesis and Ultraviolet and Nuclear Magnetic Resonance Spectra of Some 9-Substituted 9,10-Dihydroacridines

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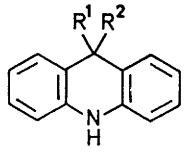
The n.m.r. spectra of a series of 9-substituted 9,10-dihydroacridines are consistent with a molecular conformation in which a central boat-shaped ring has the larger substituent in the pseudo-axial orientation. The u.v. spectra of 9,10-dihydro-9-t-butylacridine and its derivatives show absorption maxima absent from the spectra of other 9,10-dihydroacridines.

DURING an attempt to solve the long-standing problem of the preferred conformation of 9-substituted 9,10-dihydroanthracenes, a series of 9-substituted 9,10-dihydroacridines was synthesised and their n.m.r. spectra were examined. Since the publication of our preliminary communication,[1] a paper by Brinkmann and his co-workers has appeared [2] on 9-substituted 9,10-dihydroanthracenes which supersedes our work. This group has reported the observation of nuclear Overhauser effects which show that in the 9,10-dihydroanthracene series the preferred conformation is that in which a bulky 9-substituent occupies a pseudo-axial orientation. We have attempted to observe a nuclear Overhauser effect between aromatic protons and the methyl group of 9-methyl-9,10-dihydro-9-t-butylacridine but have failed, and 9,10-dihydro-9-t-butylacridine is too sparingly soluble to permit double irradiation experiments. We therefore report here the synthetic and spectroscopic data, conclusions based upon the latter, in accord with Brinkmann's results for the dihydroanthracene series, having already been described.[1] We have also measured the u.v. spectra of the compounds in the hope that increasing population of near-planar conformations might show itself in long-wavelength absorption arising from interaction between the two aromatic rings. Although additional absorption bands are present in the spectra of the 9-t-butyl derivatives, their absence from the spectrum of 9,10-dihydro-9,9-di-isopropylacridine shows that they are not attributable to this cause. The u.v. spectrum of a 10% solution of 9,10-dihydro-9,9-dimethylacridine shows only a very faint inflection at long wavelength; nothing corresponding to the reported long-wavelength absorption of 9,10-dihydro-9-methylacridine [3] could be found. We have measured the u.v. absorption of an ethanolic 2% solution of freshly recrystallised 9,10-dihydro-9-methylacridine and have observed only a very weak shoulder at 383 nm, with an intensity corresponding to log ε 1·83 if due to the dihydroacridine.

The n.m.r.[a] and u.v.[b] spectra of some 9,10-dihydroacridines



		τ(R¹)				τ(R²)			
R¹	R²	H	CH	CH_2	CH_3	CH	CH_2	CH_3	$\lambda_{max.}$/nm (log ε)
H	H *	6·01							
H	Me	5·98						8·68	
H	Et	6·18					8·39	9·24	
H	Pr^i	6·34				8·21		9·23	284 (4·22)
H	Bu^t *	6·44						9·21	251s (3·46), 282 (4·21), 315s (3·63)
Me	Me				8·46			8·46	287 (4·21), 385s (1·52)
Me	Et				8·39		8·19	9·40	289 (4·27)
Me	Pr^i				8·31	8·19		9·29	287 (4·21)
Me	Bu^t				8·24			9·24	253 (3·46), 286 (4·21), 357s (1·03)
Et	Et			8·12	9·41		8·12	9·41	290 (4·30)
Et	Pr^i			7·81	9·34	8·23		9·30	289 (4·26)
Et	Bu^t			7·69	9·34			9·24	245s (3·84), 253 (4·16), 286 (4·20) 359 (2·95), 368s (2·75), 387 (2·53)
Pr^i	Pr^i		7·53		9·11	7·53		9·11	292 (4·30), 316s (3·90)

[a] Measured with a Varian HA100 spectrometer for 0·05M-solutions in carbon tetrachloride at 30° (tetramethylsilane as internal standard). All compounds showed NH absorption between τ 4·05 and 4·25 and aromatic proton absorption between τ 2·4 and 3·7. All coupling constants involving R¹ and R² lie between 6·5 and 7·5 Hz. [b] Measured for ethanolic solutions of analytically pure compounds with a Unicam SP 700C or Cary 14 spectrometer.

* N.m.r. spectra measured for saturated solutions in carbon tetrachloride of concentration less than 0·05M.

[1] G. A. Taylor and S. A. Procter, *Chem. Comm.*, 1969, 1379.
[2] A. W. Brinkmann, M. Gordon, R. G. Harvey, P. W. Rabideau, J. B. Stothers, and A. L. Ternay, *J. Amer. Chem. Soc.*, 1970, **92**, 5912.
[3] A. Kellmann, *J. Chim. phys.*, 1957, **54**, 469; 'Organic Electronic Spectral Data,' Interscience, New York, 1966, vol. III, p. 454.

However the dihydroacridine solution undergoes oxidation when exposed to air, and the spectrum of the resulting 9-methylacridine has a shoulder at 382 nm (log ε 3·5), so we are reluctant to assign the weak absorption to the dihydroacridine. The weak, long-wavelength absorption of 9,10-dihydro-9,9-dimethylacridine might also be due to impurity.

EXPERIMENTAL

9,10-Dihydroacridine, 9,10-dihydro-9-methylacridine, and 9-ethyl-9,10-dihydroacridine were prepared by lithium aluminium hydride reduction of the corresponding acridines. 9,10-Dihydro-9,9-dimethylacridine was prepared from acetone and diphenylamine by use of Craig's method.[4]

9,10-*Dihydro*-9-*isopropylacridine*.— 9-Isopropylacridine was prepared from isobutyric acid, diphenylamine, and zinc chloride by use of recorded procedures.[5] The crude oily product was mixed with twice its weight of picric acid in hot ethanol and the precipitated solid was collected, washed with ethanol, and shaken with benzene and aqueous 10% ethanolamine solution.[6] Evaporation of the benzene solution and distillation of the residue gave 9-isopropylacridine, b.p. 160—170° at 0·2 mmHg, as yellow crystals, m.p. 69° [from light petroleum (b.p. 40—60°)] (Found: C, 86·9; H, 6·8; N, 6·3. Calc. for $C_{16}H_{15}N$: C, 86·9; H, 6·8; N, 6·3%).

Reduction of 9-isopropylacridine with lithium aluminium hydride in ether followed by the normal work-up gave the *dihydroacridine* as needles, m.p. 160° (from aqueous methanol) (Found: C, 86·4; H, 7·6; N, 6·3. $C_{16}H_{17}N$ requires C, 86·1; H, 7·6; N, 6·3%).

General Method of Preparation of 9,9-*Dialkyl*-9,10-*dihydroacridines*.—The 9-alkylacridine (5 g) was added to an ethereal solution of an alkylmagnesium halide [from magnesium (5 g)] followed by dry dibutyl ether (100—200 ml). Diethyl ether was distilled off and the residue was heated under reflux on a steam-bath for 1—2 h and then cooled. After decomposition of excess of Grignard reagent by cautious addition of water, the mixture was shaken with dilute hydrochloric acid and ether. Work-up of the ethereal solution gave orange-brown oils which crystallised slowly. The following compounds were prepared by this method.

9-*Ethyl*-9,10-*dihydro*-9-*methylacridine*, from ethylmagnesium bromide and 9-methylacridine, plates, m.p. 93—94° (from aqueous methanol) (Found: C, 85·7; H, 7·4; N, 6·1. $C_{16}H_{17}N$ requires C, 86·1; H, 7·6; N, 6·3%).

9,10-*Dihydro*-9-*isopropyl*-9-*methylacridine*, from isopropylmagnesium bromide and 9-methylacridine, needles, m.p. 110° (from ethanol) (Found: C, 86·0; H, 8·5; N, 6·0. $C_{17}H_{19}N$ requires C, 86·1; H, 8·0; N, 5·9%).

9,10-*Dihydro*-9-*methyl*-9-*t-butylacridine*, from t-butylmagnesium chloride and 9-methylacridine, needles, m.p. 149—152° (decomp.) [from light petroleum (b.p. 60—80°)] (Found: C, 85·5; H, 8·3; N, 5·5. $C_{18}H_{21}N$ requires C, 86·1; H, 8·4; N, 5·6%).

9,9-*Diethyl*-9,10-*dihydroacridine*, prisms, m.p. 92—93° (from aqueous methanol) (Found: C, 86·0; H, 8·4; N, 6·1. $C_{17}H_{19}N$ requires C, 86·1; H, 8·0; N, 5·9%).

9-*Ethyl*-9,10-*dihydro*-9-*isopropylacridine*, from isopropylmagnesium bromide and 9-ethylacridine, needles, m.p. 107—108° (from light petroleum followed by aqueous methanol) (Found: C, 85·8; H, 8·7; N, 5·3. $C_{18}H_{21}N$ requires C, 86·1; H, 8·4; N, 5·6%).

9-*Ethyl*-9,10-*dihydro*-9-*t-butylacridine*, from t-butylmagnesium chloride and 9-ethylacridine, needles, m.p. 150—153° (decomp., sintering at 130°) (Found: C, 86·0; H, 8·6; N, 5·5. $C_{19}H_{23}N$ requires C, 86·0; H, 8·7; N, 5·3%).

9,10-*Dihydro*-9,9-*di-isopropylacridine*, needles, m.p. 120—123° (from light petroleum) (Found: C, 86·1; H, 8·3; N, 5·6. $C_{19}H_{23}N$ requires C, 86·0; H, 8·7; N, 5·3%).

9,10-*Dihydro*-9-*t-butylacridine*.—This compound was prepared by the method already described from acridine and t-butylmagnesium chloride. On acidification of the reaction mixture and filtration the crude acridan was left as a white residue. Recrystallisation from ethanol gave the *dihydroacridine* as needles, m.p. 227—230° (decomp., sintering at 190°) (from ethanol) (Found: C, 85·8; H, 7·7; N, 5·8. $C_{17}H_{19}N$ requires C, 86·1; H, 8·0; N, 5·9%). This compound is very sparingly soluble in cold organic solvents.

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[4] D. Craig, *J. Amer. Chem. Soc.*, 1938, **60**, 1458.
[5] N. P. Buu-Hoi and J. Lecocq, *Rec. Trav. chim.*, 1945, **64**, 250; O. Tsuge, M. Nishinohara, and M. Tashiro, *Bull. Chem. Soc. Japan*, 1963, **36**, 1477.
[6] I. A. Kaye, J. C. Kogan, and W. Burlant, *J. Amer. Chem. Soc.*, 1950, **72**, 5752.