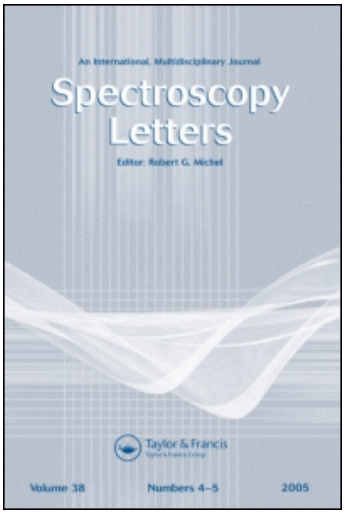

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STRUCTURAL ELUCIDATION OF NAPHTHACRIDONES AND 1-PHENYLACRIDONES BY ^{1}H-NMR, MASS, AND IR SPECTROSCOPY

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ABSTRACT

Structural elucidation with the help of ^{1}H-NMR and Mass spectroscopy could be achievable in the case of different varieties of naphthacridones i.e., naphth[2,1-*a*]- and naphth[2,3-*a*]- acridones. Similarly IR spectroscopy comes handy in the elucidation of structure of 1-phenylacridones, which have been reported for the first time.

Key Words: Naphthacridones; 1-Phenylacridones; Structural elucidation; ^{1}H-NMR; Mass spectroscopy; IR spectroscopy

INTRODUCTION

The pharmacological properties of acridine systems have attracted considerable attention towards themselves, in the last few years.[1–3] In our laboratory a methodology has been developed towards the synthesis of several fused acridones, by the treatment of 4-hydroxy-2-methylquinoline

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with some aldehydes followed by photocyclisation.[4–6] Here we report the structural elucidation of naphthacridones by ^{1}H-NMR and 1-phenylacridones by IR spectroscopy.

EXPERIMENTAL

Reagent grade aniline, ethylacetoacetate, acetic anhydride, diphenylether and aldehydes were used after usual purification methods. The solvents petroleum ether, ethylacetate, chloroform and methanol were purified by standard procedure. The naphthacridones and 1-phenylacridones were synthesized from 4-hydroxy-2-methyl-quinoline as previously reported[6] and the reactions were performed under free atmosphere. The IR spectra were recorded on a Shimadzu FTIR-8000 as KBr discs. ^{1}H-NMR spectra were recorded in DMSO-d_6 at 400 MHz on a Varian AMX 400 spectrometer using tetramethylsilane (TMS) as an internal reference. The mass spectra were recorded on a Jeol JMS-D 300 Mass spectrometer.

RESULTS AND DISCUSSION

The ^{1}H-NMR spectrum of all the 2-substituted-4-quinolones (**2a**, **4a** and **7a**) invariably showed the presence of singlet at 6.10–6.80 accountable for the free C_3-proton. Photocyclization of these intermediates gave respective products **3a**, **5a** and **8a** whose ^{1}H-NMR spectra showed the disappearance of the above singlet.

Table 1 lists the ^{1}H-NMR spectral data of compound **3a–c** with the assignment of chemical shifts. The ^{1}H-NMR spectrum of the product **3a** (Sch. 1) showed a significant down field shift of some signals at δ

Table 1. ^{1}H-NMR Spectral Data of Compounds **3a**, **3b** and **3c**

	Chemical Shift, δ ppm (J, Hz)					
Compd.	Ar-H	C_{11}-H	C_4-H	C_5-H	C_{13}-H	NH
3a	7.36–8.15 (m, 8H)	8.40–8.42 d, J = 8.25	8.88–8.90 d, J = 8.41	9.22–9.24 d, J = 8.92	10.38–10.40 d, J = 8.90	12.20 s
3b*	7.56–8.14 (m, 8H)	8.20 s	8.87–8.89 d, J = 8.16	9.18–9.21 d, J = 8.40	10.39–10.42 d, J = 8.64	12.10 s
3c**	7.17–8.05 (m, 8H)	8.20–8.22 d, J = 8.85	8.80–8.83 d, J = 8.26	9.13–9.16 d, J = 8.55	10.26–10.29 d, J = 8.85	10.87 s

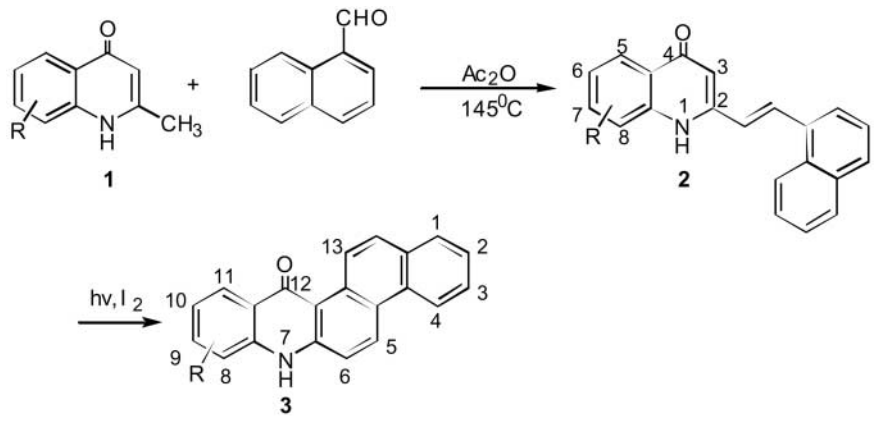
*C_{10}-CH_3 δ 2.50 (s, 3H).

**C_8-CH_3 δ 2.61 (s, 3H).

10.38–10.40, 9.22–9.24 and 8.88–8.90 ppm. The δ value at 10.38–10.40 is assigned to C_{13}-H as, in this structural environment, it must be anisotropically deshielded by >C=O[7] and the remaining values may be assigned for the protons C_5-H and C_4-H respectively (Fig. 1).

The mass spectrum of **3a** registered a molecular ion peak at m/z 295 (100%) and fragment ions at m/z 294 (22%), 267 (20%), 266 (19%) and 238 (5%) which exhibited a fragmentation pattern similar to that established for acridones[8] (Sch. 2).

Having realized the naphth[2,1-*a*]acridones, we experimented 2-naphthaldehyde in the synthesis of another naphthacridone system. Interestingly, in this case one could expect two cyclized products as shown in Sch. 3. Even though mass spectrum ($M^{+\cdot}$, 295) and elemental analysis could favour both the structures **5a** and **6a** the product formed was established as **5a**, only from its ^{1}H-NMR spectrum (Fig. 2). Table 2 lists the ^{1}H-NMR spectral data of compound **5a**–**5c.** The values of two low field singlets at δ 10.80 and 8.59 ppm accounted C_{14}-H and C_5-H respectively. This also ruled out the other possible structures, namely, naphth[1,2-*a*]acridone, in which case, there will be still a low field doublet expected for C_{14} proton. The multiplet



R	H	6-CH_3	8-CH_3
1-2	**a**	**b**	**c**
R	H	10-CH_3	8-CH_3
3	**a**	**b**	**c**

Scheme 1.

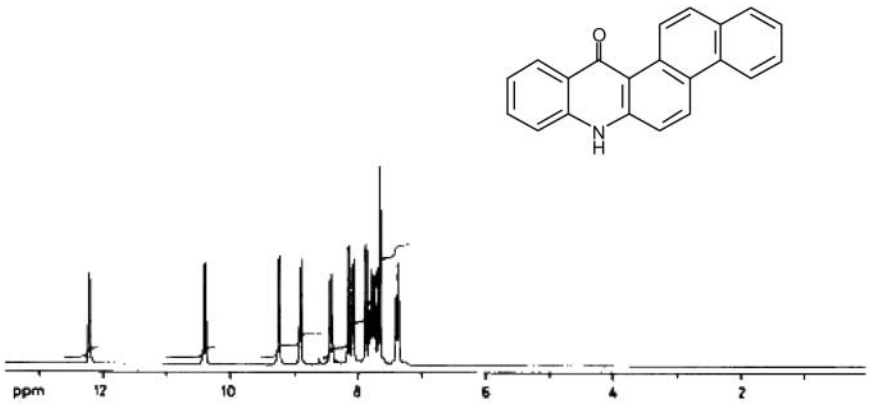
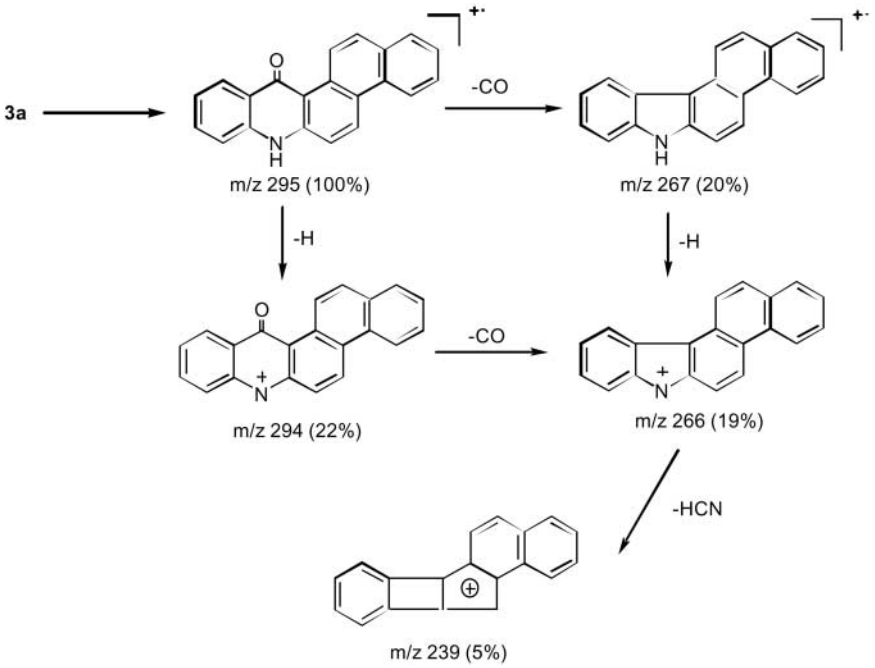
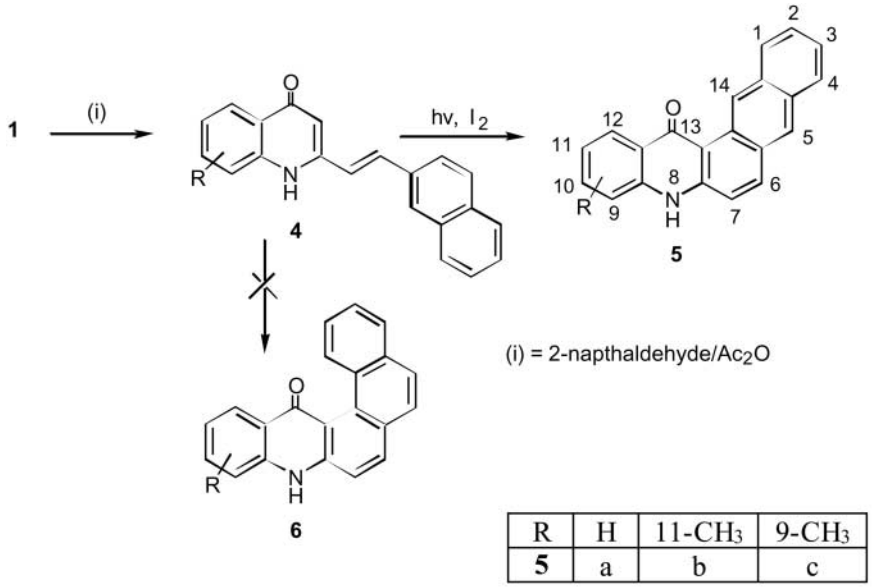


Figure 1. ^{1}H-NMR spectrum of naphth[2,1-*a*] acridin-12(*7H*)-one (400 MHz).



Scheme 2.



R	H	11-CH_3	9-CH_3
5	a	b	c

Scheme 3.

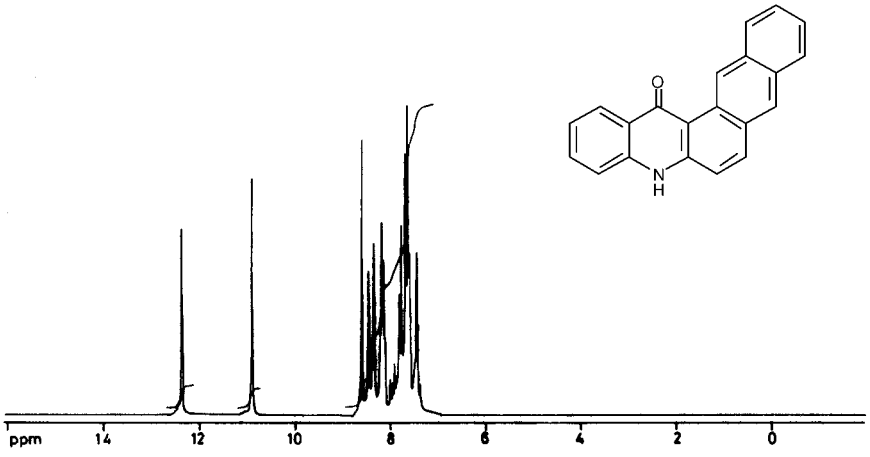


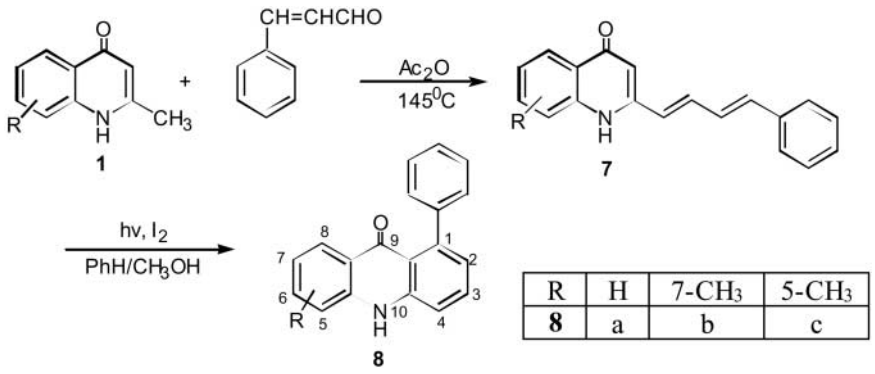
Figure 2. ^{1}H-NMR spectrum of naphth[2,3-*a*] acridin-13(8*H*)-one (400 MHz).

Table 2. ^{1}H-NMR Spectral Data of Compounds **5a**, **5b** and **5c**

Compd.	Chemical Shift, δ ppm			
	Ar-H	C_5-H	C_{14}-H	NH
5a	7.40–8.44 (m, 10H)	8.59 (s, 1H)	10.80 (s, 1H)	12.40 s
5b*	7.40–8.33 (m, 9H)	8.50 (s, 1H)	10.80 (s, 1H)	12.20 s
5c**	7.22–8.30 (m, 9H)	8.58 (s, 1H)	10.82 (s, 1H)	11.10 s

*C_{11}-CH_3 δ 2.52 (s, 3H).

**C_9-CH_3 δ 2.64 (s, 3H).



Scheme 4.

for aromatic protons appeared at δ 7.40–8.44 and singlet for NH, at δ 12.40 ppm.

In the case of 1-phenylacridones the IR absorption of the products gave some vital evidence regarding the cyclized products. Generally, the 9-acridones produce a carbonyl stretching frequency at 1645 cm^{-1} and a characteristic broad N-H stretching region at 3400–3200 cm^{-1}, obviously indicating strong intermolecular hydrogen bonding.[9] But in the case of 1-phenylacridone, the presence of phenyl group in the surrounding lattice prevents the formation of hydrogen bonding.[9] Hence, the increase in the absorption of carbonyl group at 1680 cm^{-1} and at 3292 cm^{-1} for NH group was shown by the photoproduct (see Sch. 4).

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