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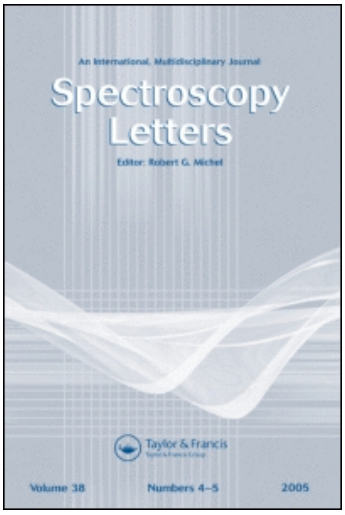

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

^{13}C-NMR Study of Some Substituted 9-Acridanone Derivatives

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To cite this Article Faure, Robert , Mahamoud, Abdallah , Galy, Jean-Pierre , Vincent, Emile-Jean , Galy, Anne-Marie and Barbe, Jacques(1981) '^{13}C-NMR Study of Some Substituted 9-Acridanone Derivatives', Spectroscopy Letters, 14: 3, 223 — 238
To link to this Article: DOI: 10.1080/00387018108062579
URL: http://dx.doi.org/10.1080/00387018108062579

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SPECTROSCOPY LETTERS, 14(3), 223-238 (1981)

^{13}C-NMR STUDY OF SOME SUBSTITUTED 9-ACRIDANONE DERIVATIVES

KEY WORDS : ^{13}C-NMR, Substituent effects, Molecular orbital calculations, Correlations, Acridanones.

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ABSTRACT : ^{13}C-NMR spectra of several 9-acridanones with different substituents both on the ring (R_1 = CH_3, OCH_3, NH_2, $N(CH_3)_2$, NO_2) and at the nitrogen atom (R_2 = H, CH_3 C_2H_5, CH_2-C_6H_5, C≡C-CH_3, $(CH_2)_2N(C_2H_5)_2$, CH=C=CH_2) have been recorded. The ^{13}C-NMR chemical shifts are discussed as a function of the nature of the substituent, the importance of peri steric interactions and the electronic structure of the acridanone ring. There is a good linear relationship between the total electronic density and the chemical shifts.

INTRODUCTION

Acridanone derivatives which are significant heterocyclic compounds in therapy, carry out polybiovalency. Over and above their

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antiviral[1], anti-allergy[2] or analeptic properties[3], these drugs can be used as radioprotectives[4] or antitumor agents[5]. In the latter case, a steric interaction with DNA is involved[6,7]. Consequently, the biological response is mainly dependent on the conformational structure[8], i.e. is governed by electronic and structural parameters. In connection with other researches into the subject[9-13], results about a ^{13}C-NMR study on some 9-acridanone derivatives are analysed below. This method indeed, is a suitable one, for stereochemical investigations[14,15]. The compounds studied are given in Table 1. The methodology is the same one already used with some other medicinal compounds[16-18].

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EXPERIMENTAL

^{13}C-NMR spectra were recorded in the FT mode on a Varian CFT-20 spectrometer. A 8 μsec pulse corresponding to a tilt angle of 45° was used. Accumulation of 5,000-50,000 transients - according to the solubility of the compounds - were made at a spectral width of 5,000 Hz. The compounds were studied as solutes in DMSO-d_6 at 28 ± 2°C. The latter was used either as lock or reference. Chemical shifts were measured in the decoupled noise mode in reference to the central line of the solvent. They were correlated to the TMS signal using the relation[19] $\delta_{TMS} = \delta_{DMSO\text{-}d_6} + 39.6$ in which δ is given in ppm. The accuracy of the measure of chemical shifts was better than 0.1 ppm.

Electronic densities were calculated by means of CNDO/2 MO method using a modified version[20] of QCPE 141[21]. Acridanone bond lengths and angles are specified in Figure 1.

From the point of view of an averaged time, it can be assumed that rings are belonging to a same plane because of the rapid nitrogen inversion. As for the values of substituent atomic distances and bond angles, they are those arising out of the litera-

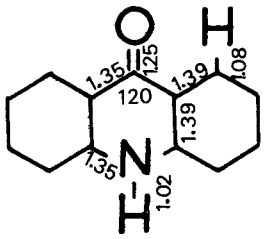

Figure 1. Atomic distances and bond angles of 9-acridanones.

ture[22]. Some of the compounds used were prepared and isolated according to a previously published process[11]. Synthesis of the other ones will be stated later[23].

RESULTS AND DISCUSSION

Assigments were made in accordance with

(a) chemical shifts considerations[14], particularly about substituent effects in benzenic series[24],

(b) signal multiplicities determined from a coherent off-resonance decoupling,

(c) peak intensities,

(d) the assumption that, chemical shifts of an unsubstituted benzene ring are slightly changed by various substitutions, except if there are peri steric interactions. Chemical shifts are collected in Tables 2 and 3 whereas substituent effects are gathered in Table 4.

Substitution at the nitrogen atom

It can be generally pointed out that the shielding of the ring carbons is slightly affected by substitution at the nitrogen atom. However, the latter brings a shielding effect as far as the γ position is concerned - C-4 or C-5 - except with 39 in which such an effect is compensated by the deshielding one brought about by the

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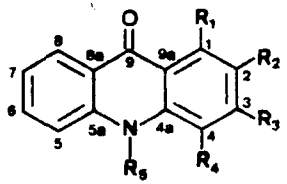
Table 1. - List and numbering of the 9-acridanones studied.



N°	R_1	R_2	R_3	R_4	R_5
1	H	H	H	H	H
2	CH_3	H	H	H	H
3	H	CH_3	H	H	H
4	H	H	CH_3	H	H
5	H	H	H	CH_3	H
6	H	OCH_3	H	H	H
7	H	H	H	OCH_3	H
8	H	H	H	H	CH_3
9	CH_3	H	H	H	CH_3
10	H	CH_3	H	H	CH_3
11	H	H	CH_3	H	CH_3
12	H	H	H	CH_3	CH_3
13	H	OCH_3	H	H	CH_3
14	H	H	H	OCH_3	CH_3
15	H	$N(CH_3)_2$	H	H	CH_3
16	H	CH_3	H	H	C_2H_5
17	H	OCH_3	H	H	C_2H_5

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18	H	H	H	OCH_3	C_2H_5
19	H	H	H	NO_2	C_2H_5
20	H	H	H	H	$CH_2C_6H_5$
21	CH_3	H	H	H	$CH_2C_6H_5$
22	H	CH_3	H	H	$CH_2C_6H_5$
23	H	H	CH_3	H	$CH_2C_6H_5$
24	H	H	H	CH_3	$CH_2C_6H_5$
25	H	H	H	H	$C\equiv C-CH_3$
26	H	CH_3	H	H	$C\equiv C-CH_3$
27	H	H	H	CH_3	$C\equiv C-CH_3$
28	H	NH_2	H	H	$C\equiv C-CH_3$
29	H	CH_3	H	H	$CH=C=CH_2$
30	H	H	H	CH_3	$CH=C=CH_2$
31	H	H	H	H	$CH_2CH_2N(C_2H_5)_2$
32	H	CH_3	H	H	$CH_2CH_2N(C_2H_5)_2$
33	H	H	H	OCH_3	$CH_2CH_2\overset{+}{N}H(C_2H_5)_2$
34	H	H	H	NO_2	$CH_2CH_2\overset{+}{N}H(C_2H_5)_2$
35	H	H	H	H	$(CH_2)_3OC_6H_5$
36	H	H	H	H	nC_3H_7
37	H	H	H	H	nC_4H_9
38	H	H	H	H	$(CH_2)_3N(C_2H_5)_2$
39	H	H	H	H	$CH(CH_3)_2$

Table 2. - Chemical shifts of the ring carbons of the 9-acridanones measured from DMSO-d_6 solutions.

N°	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-4a	C-5a	C-8a	C-9a
1	126.0	121.0$_5$	133.5	117.4	117.4	133.5	121.0$_5$	126.0	176.8	140.9	140.9	120.5	120.5
2	140.5[a]	123.6	132.5	115.5	116.7	133.1	120.8	126.2$_5$	178.6	142.6	140.2[a]	121.8$_5$	122.9
3	125.0	129.9	134.7	117.1	117.1	133.0	120.5	125.9	176.5	139.0	140.8	120.5$_5$	120.5$_5$
4	126.0	122.8$_5$	143.8	116.6	117.3	133.2	120.8$_5$	126.0	176.4	141.1[a]	141.0[a]	120.8$_5$	118.7
5	124.0	120.5	133.9	125.8	118.6	133.0	121.1	125.8	177.4	141.6	141.6	120.5	120.8
6	104.8	153.7	124.0	118.9$_5$	117.1	132.7	120.4	125.7	175.9	135.5	140.3	120.8	119.5
7	118.3	120.5	112.4	147.8$_5$	117.2	133.1	121.2	125.8	176.6	131.9	140.7	120.5[a]	120.3[a]
8	126.5	121.2	134.0	116.1	116.1	134.0	121.2	126.5	176.9	142.3	142.3	121.6	121.6
9	140.9	124.2	132.7	114.0	115.6	133.4$_5$	120.8$_5$	126.5	178.6	144.0	141.8	123.1	124.2
10	125.8	130.3	135.2	116.0	116.0	133.8	120.8$_5$	126.6	176.4	140.4	142.2	121.5	121.5
11	126.5	122.7	144.5	115.6	116.0	133.7	120.8$_5$	126.5	176.6	142.3	142.3	(b)	(b)
12	124.0	121.8	137.3	127.0	117.3	133.7	121.2	125.9	177.5	145.9[a]	144.9[a]	122.1	124.3
13	105.9	153.8	123.7	117.9	115.8	133.5$_5$	120.7	126.5	175.9	137.0	141.8	122.3	120.6
14	117.9	122.0	116.8	149.8	116.0	133.7	121.2	125.9	176.7$_5$	135.0	145.1	121.2	124.6
15	106.0	145.2$_5$	120.1	117.0	115.6	133.1	121.4$_5$	126.6	176.0	134.5	141.5	122.5	120.6
16	126.0	130.2$_5$	135.5$_5$	115.6	115.6	133.9$_5$	120.8	126.8	176.3	139.3	141.0	121.6	121.6
17	106.2$_5$	153.9	124.1	117.6	115.4	133.8	120.8	126.8	175.8	135.9	140.7	122.4	120.8
18	118.3	122.0	116.7	149.8	116.1	133.9	121.3	126.3	176.7	134.4	144.1$_5$	121.7	124.7$_5$
19	131.7[a]	123.1	131.3[a]	138.0	119.1	134.3	121.2	126.4	176.0	140.9	142.4	124.4	124.4
20	126.7	121.5	134.2	116.1	116.1	134.2	121.5	126.7	176.6	142.1	142.1	121.7	121.7

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21	141.2	124.6	132.9	114.1	115.6	133.7	121.3	126.8	178.8	143.7	141.6	123.1	124.6
22	125.8	130.6	135.3	115.9[a]	115.7$_5$[a]	133.8	121.0	126.6	176.4	140.1	141.9	121.6	121.6
23	126.8	123.1	144.8	115.6	116.1	133.9	121.3	126.8	176.6	142.0[a]	142.3[a]	121.8	119.8
24	124.3	122.1	137.6	126.0	118.4	133.3	121.5	125.9	177.5	145.1[a]	144.9[a]	123.0	124.9
25	126.6	123.6	134.8	117.1	117.1	134.8	123.6	126.6	(b)	140.5	140.5	121.5	121.5
26	126.1	133.1	135.9$_5$	117.1	117.1	134.7	123.5	126.7	176.0	138.6	140.5	121.5	121.5
27	125.1$_5$	123.9	138.4	127.6	117.9$_5$	134.7$_5$	123.9	126.3	176.9	142.9	145.0	121.9	123.7
28	107.4	145.4	122.5	117.8	116.7	133.8	123.0	126.5	175.7$_5$	131.7	140.1	122.6	120.6
29	125.7	131.0	135.1	116.8	116.8	133.7	121.5	126.5	176.3	139.6	141.3	121.3	121.3
30	124.5	122.7	137.6	128.1	118.3	134.1	122.4$_5$	126.3	177.9	142.9	145.1	122.1	124.5
31	126.7	121.1	133.9	115.8	115.8	133.9	121.1	126.7	176.4	141.7	141.7	121.7	121.7
32	125.9	130.1	135.0	115.5	115.5	133.6	120.7	126.7	176.1	139.7	141.4	121.5	121.5
33	118.1	123.2	115.0	148.5	116.5	135.7	123.2	126.6	177.9	132.6	143.0	120.6	123.0
34	132.3	124.0	132.3	137.9	119.1	135.1	122.3$_5$	127.0	176.7	140.8	142.1	124.4	124.4
35	126.8	121.2$_5$	134.2	115.6	115.6	134.2	121.2$_5$	126.8	176.4$_5$	141.5	141.5	121.7	121.7
36	126.8	121.2	134.2	115.9	115.9	134.2	121.2	126.8	176.3	141.5	141.5	121.6	121.6
37	126.7	121.0	134.0	115.5$_5$	115.5$_5$	134.0	121.0	126.7	176.4	141.3	141.3	121.6	121.6
38	126.8	121.2	134.1	115.7$_5$	115.7$_5$	134.1	121.2	126.8	176.5	141.6	141.6	121.7	121.7
39	126.6	121.0$_5$	133.2	117.2$_5$	117.2$_5$	133.2	121.0$_5$	126.6	176.7	142.1	142.1	121.0	121.0

(a) These assignments may be reversed in a same compound.

(b) Unobserved signals.

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Table 3. - Chemical shifts of the substituent carbons of the 9-acridanones measured from DMSO-d_6 solutions.

N°	Substituent Carbons
2	R_1:23.8
3	R_2:20.4
4	R_3:21.6
5	R_4:17.9
6	R_2:55.1
7	R_4:56.3
8	R_5:33.7
9	R_1:24.2 ; R_5:34.5
10	R_2:20.3 ; R_5:33.6
11	R_3:22.0 ; R_5:33.6
12	R_4:22.5_5 ; R_5:42.3
13	R_2:55.4 ; R_5:33.6_5
14	R_4:56.4 ; R_5:41.2
15	R_2:40.4 ; R_5:33.3
16	R_2:20.2 ; R_5(CH_2:40.3 ; CH_3:12.4)
17	R_2:55.4 ; R_5(CH_2:40.6 ; CH_3:12.5)
18	R_4:56.5_5 ; R_5(CH_2:46.9 ; CH_3:15.2_5)
19	R_5(CH_2:47.4 ; CH_3:13.5)

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20	R_5(CH$_2$:49.0$_5$; C1':136.3 ; C2':125.8 ; C3':128.8$_5$; C4':127.2$_5$)
21	R_1:24.2 ; R_5(CH$_2$:50.0 ; C1':136.3 ; C2':125.8 ; C3':128.8$_5$; C4':127.2)
22	R_2:20.0 ; R_5(CH$_2$:48.9 ; C1':136.2$_5$; C2':125.6$_5$; C3':128.7 ; C4':127.1)
23	R_3:21.9 ; R_5(CH$_2$:48.9 ; C1':136.3 ; C2':125.8 ; C3':128.8$_5$; C4':127.2)
24	R_4:22.3 ; R_5(CH$_2$:55.4 ; C1':137.6 ; C2':126.2 ; C3':128.3 ; C4':126.9)
25	R_5(Cα:(a) ; Cβ:(a) ; CH$_3$:3.0)
26	R_2:20.4 ; R_5(C :68.5 ; C :74.9 ; CH$_3$:3.0)
27	R_4:21.9 ; R_5(C :73.2$_5$; C :71.2 ; CH$_3$:2.9)
28	R_5(Cα:68.9 ; Cβ:74.2 ; CH$_3$:3.1)
29	R_2:20.3 ; R_5(CH:95.1 ; C:208.8 ; CH$_2$:84.2)
30	R_4:23.4 ; R_5(CH:102.3 ; C:206.8 ; CH$_2$:84.3)
31	R_5(CH$_2$(α):44.7 ; CH$_2$ (β):49.8 ; CH$_2$:47.0 ; CH$_3$:11.9)
32	R_2:20.1 ; R_5(CH$_2$(α):44.6 ; CH$_2$(β):49.7 ; CH$_2$:47.0 ; CH$_3$:11.9)
33	R_4:56.7 ; R_5(CH$_2$(α):47.0$_5$; CH$_2$(β):51.1 ; CH$_2$:49.0 ; CH$_3$:9.2)
34	R_5(CH$_2$(α):46.9 ; CH$_2$(β):48.2 ; CH$_2$:46.6 ; CH$_3$:8.3)
35	R_5(CH$_2$(α):42.4 ; CH$_2$(β):26.7 ; CH$_2$(γ):64.6$_5$; C1':158.3 ; C2':114.6 ; C3':129.5 ; C4':120.8)
36	R_5(CH$_2$(α):46.6 ; CH$_2$(β):20.2 ; CH$_3$:10.8)
37	R_5(CH$_2$(α):45.0 ; CH$_2$(β):28.8 ; CH$_2$(γ):19.3 ; CH$_3$:13.6
38	R_5(CH$_2$(α):43.7 ; CH$_2$(β):24.8 ; CH$_2$(γ):49.7 ; CH$_2$:46.6 ; CH$_3$:12.0
39	R_5(CH:51.1 ; CH$_3$:20.3)

(a) Unobserved signals.

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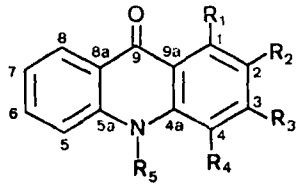
Table 4. - Substituent effects in the 9-acridanone series.



Compounds	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-4a	C-5a	C-8a	C-9a	R_5
	Substitution at the nitrogen atom													
8-1	0.5	0.1_5	0.5	-1.3	-1.3	0.5	0.1_5	0.5	0.1	1.4	1.4	1.1	1.1	CH_3
20-1	0.7	0.4_5	0.7	-1.3	-1.3	0.7	0.4_5	0.7	-0.2	1.2	1.2	1.2	1.2	$CH_2C_6H_5$
25-1	0.6	2.5_5	1.3	-0.3	-0.3	1.3	2.5_5	0.6	-	-0.4	-0.4	1.0	1.0	$C\equiv C-CH_3$
29-3	0.7	1.1	0.4	-0.3	-0.3	0.7	1.0	0.6	-0.2	0.6	1.1	0.7_5	0.7_5	$CH=C=CH_2$
31-1	0.7	0.0_5	0.4	-1.6	-1.6	0.4	0.0_5	0.7	-0.5	0.8	0.8	1.2	1.2	$(CH_2)_2N(C_2H_5)_2$
35-1	0.8	0.2	0.7	-1.8	-1.8	0.7	0.2	0.8	-0.3_5	0.6	0.6	1.2	1.2	$(CH_2)_3OC_6H_5$
36-1	0.8	0.1_5	0.7	-1.5	-1.5	0.7	0.1_5	0.8	-0.5	0.6	0.6	1.1	1.1	nC_3H_7
37-1	0.7	-0.0_5	0.5	-1.8_5	-1.8_5	0.5	-0.0_5	0.7	-0.4	0.4	0.4	1.1	1.1	nC_4H_9
38-1	0.8	0.1_5	0.6	-1.6_5	-1.6_5	0.6	0.1_5	0.8	-0.3	0.7	0.7	1.2	1.2	$(CH_2)_3N(C_2H_5)_2$
39-1	0.6	0.0	-0.3	-0.1_5	-0.1_5	-0.3	0.0	0.6	-0.1	1.2	1.2	0.5	0.5	$CH(CH_3)_2$
	Substitution on the ring													
	1-Methyl													
2-1	14.5	2.5_5	-1.0	-1.9	-0.7	-0.4	-0.2_5	0.2_5	1.8	1.7	-0.7	1.3_5	2.4	H
9-8	14.4	3.0	-1.3	-2.1	-0.5	-0.5_5	-0.3_5	0.0	1.7	1.7	-0.5	1.5	2.6	CH_3
21-20	14.5	3.1	-1.3	-2.0	-0.5	-0.5	-0.2	0.1	2.2	1.6	-0.5	1.4	2.9	$CH_2C_6H_5$

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	2-Methyl													
3-1	-1.0	8.8_5	1.2	-0.3	-0.3	-0.4	-0.5_5	-0.1	-0.3	-1.9	-0.1	0.0_5	0.0_5	H
10-8	-0.7	9.1	1.2	-0.1	-0.1	-0.2	-0.3_5	-0.1	-0.5	-1.9	-0.1	-0.1	-0.1	CH_3
22-20	-0.9	9.1	1.1	-0.2	-0.3_5	-0.4	-0.5	-0.1	-0.2	-2.0	-0.2	-0.1	-0.1	$CH_2C_6H_5$
26-25	-0.5	9.5	1.1_5	0.0	0.0	-0.1	-0.1	-0.1	-	-1.9	0.0	0.0	0.0	$C\equiv C-CH_3$
32-31	-0.8	9.0	1.1	-0.3	-0.3	-0.3	-0.4	0.0	-0.3	-2.0	-0.3	-0.2	-0.2	$(CH_2)_2N(C_2H_5)_2$
	3-Methyl													
4-1	0.0	1.8	10.3	-0.8	-0.1	-0.3	-0.2_5	0.0	-0.4	0.2	0.1	0.3_5	-1.8	H
11-8	0.0	1.5	10.5	-0.5	-0.1	-0.3	-0.3_5	0.0	-0.3	0.0	0.0	-	-	CH_3
23-20	0.1	1.6	10.6	-0.5	0.0	-0.3	-0.2	0.1	0.0	0.1	0.2	0.1	-1.9	$CH_2C_6H_5$
	4-Methyl													
5-1	-2.0	-0.5_5	0.4	8.4	1.2	-0.5	0.0_5	-0.2	0.6	0.7	0.7	0.0	0.3	H
12-8	-2.5	0.6	3.3	10.9	1.2	-0.9	0.0	-0.6	0.6	3.6	2.6	0.5	2.7	CH_3
24-20	-2.4	0.6	3.2	9.9	2.3	-0.9	0.0	-0.8	0.9	3.0	2.8	1.3	3.2	$CH_2C_6H_5$
27-25	-1.4_5	0.3	3.6	10.5	0.8_5	-0.1_5	0.3	-0.3	-	2.4	4.5	0.4	2.2	$C\equiv C-CH_3$
	2-Methoxy													
6-1	-21.2	32.6_5	-9.5	1.5_5	-0.3	-0.8	-0.6_5	-0.3	-0.9	-5.4	-0.6	0.3	-1.0	H
13-8	-20.6	32.6	-10.3	1.8	-0.3	-0.4_5	-0.5	0.0	-1.0	-5.3	-0.5	0.7	-1.0	CH_3
	4-Methoxy													
7-1	-7.7	-0.5_5	-21.1	30.4_5	-0.2	-0.4	0.1_5	-0.2	-0.2	-9.0	-0.2	0.0	-0.2	H
14-8	-8.6	0.8	-17.2	33.7	-0.1	-0.3	0.0	-0.6	-0.1_5	-7.3	2.8	-0.4	3.0	CH_3
	2-Amino													
28-25	-19.2	21.8	-12.3	0.7	-0.4	-1.0	-0.6	-0.1	-	-8.8	-0.4	1.1	-0.9	$C\equiv C-CH_3$
	2-Dimethylamino													
	-20.5	24.0_5	-13.9	0.9	-0.5	-0.9	0.2_5	0.1	-0.9	-7.8	-0.8	0.9	-1.0	CH_3
	4-Nitro													
19-8	5.2	2.1	-2.7	22.9	3.0	0.3	0.0	-0.1	-0.9	-1.4	0.1	2.8	2.8	CH_3/C_2H_5

methyl groups[25]. Moreover, there is an unexpected deshielding - $\Delta\delta$ = 2.5 ppm - at the C-2 or C-7 level with a propynyl substitution. In accordance to the good correlation between chemical shifts and electronic densities which will be emphasized below, such a deshielding can proceed from a decrease of the reactivity of these carbons towards electrophilic reagents.

Substitution on the ring

Substituent chemical shifts (SCS) for a few selected monosubstituted benzenes[24] are given in Table 5.

There is a grat similarity between these and those of the series studied. That is consistent with theoretical calculations[26] predicting a considerable delocalization of the ring π cloud. Consequently, the following molecular formula is allowed for the acridanone substituted derivatives :

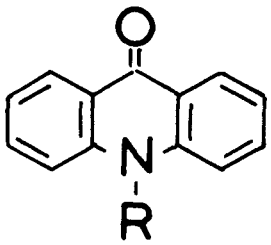

Table 5. - ^{13}C substituent chemical shifts in monosubstituted benzene for some selected compounds.

Substituents	Position				Solvent
	ipso	ortho	meta	para	
CH_3	9.0	0.6	-0.1	-3.0	DMSO
OCH_3	31.0	-14.4	1.2	-7.9	DMSO
NH_2	20.7	-14.3	0.5	-12.5	DMSO
$N(CH_3)_2$	22.6	-15.8	0.5	-12.0	aceton
NO_2	19.5	-4.9	1.6	7.0	DMSO

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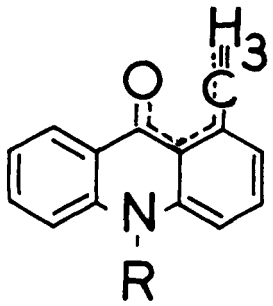
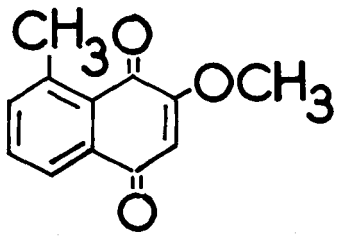
However, there are differences between the two series which are compared above owing to steric or electronic interactions non-existing in the benzenic compounds. As a matter of example, methylation in position 1 leads to a noticeable ipso effect of 14.5 ppm. That can be explained by a $\sigma-\pi$ interaction, i.e. hyperconjugation of the methyl group, as it is shown in the following scheme :



Besides, the shielding of the methyl carbon is in agreement with the proposal the more so as a similar behavior is observed with the 1,4-naphtoquinone. In the latter compound, the ipso effect of the methyl group is close to 15 ppm[27].



On the other hand, the unsymmetrical ortho effect noted with amino, dimethylamino and methoxy substituents can be ascribed to the favoured canonical structure B presented in the figure 2.

Finally, if there are peri steric interactions (5,7,12,14,19, 22,27) SCS are changed with regard to the benzenic series. The magnitude of the interaction can be portrayed by the deshielding of the α substituent carbons :

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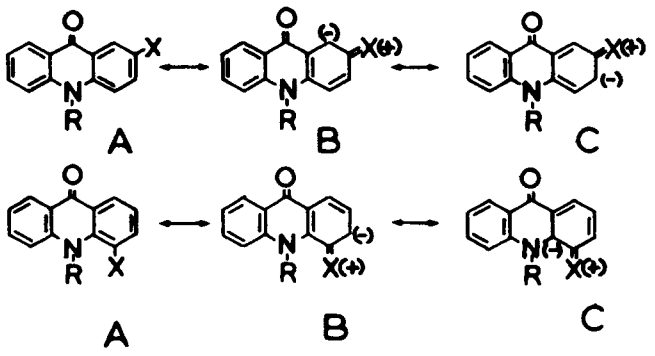
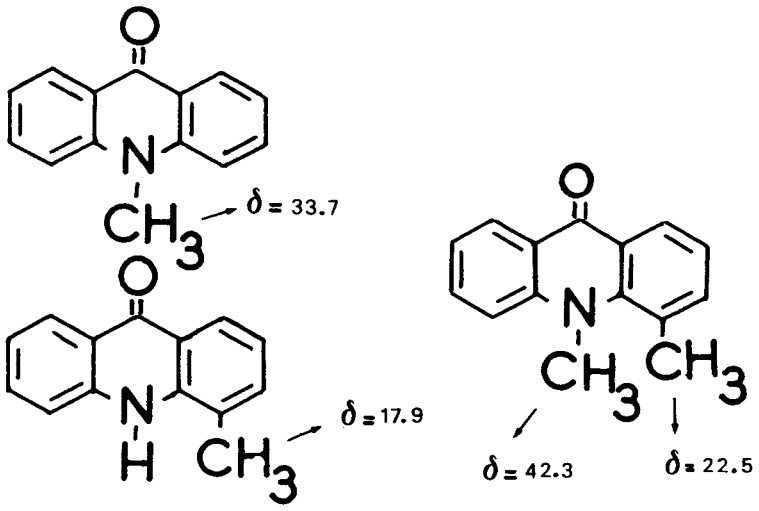


Fig. 2



Correlation between chemical shifts and the total electronic densities

An attempt for correlating chemical shifts of some 9-acridanone derivatives (1,2,5-10,12-15,22,25-27) with the total electronic densities calculated by means of a CNDO/2 method leads to the following good enough relationship :

$$\delta 13_C = (-108.2) \pm 2.5) Q_{\sigma+\pi} + 558.9 \pm 8.9$$

The correlation coefficient is 0.96.

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Received: December 29, 1980
Accepted: February 19, 1981

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