^{13}C NMR Study of Substituted 10,10-Diphenyl-9-Phenanthrones. Structure Determination and Signal Assignment using 2D NMR Techniques

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The ^{13}C NMR spectrum of 10,10-diphenyl-9-phenanthrone was assigned unambiguously using 2D ^{13}C,^{1}H shift correlated NMR spectra, optimized either for one-bond or long-range ^{13}C–^{1}H couplings, and 2D RELAY NMR spectra. This information allowed the structures of a number of substituted 10,10-diphenyl-9-phenanthrones to be deduced from their ^{13}C NMR spectra. The results provide an insight into the mechanism of the reaction of 9-fluorenone with chlorodiphenylmethyllithium.

KEY WORDS ^{13}C   2D long-range ^{13}C,^{1}H shift correlation   2D RELAY   Substituted 9-phenanthrones

INTRODUCTION

Earlier work[1] on the reaction of 9-fluorenone (1; X = H) with a lithium carbenoid, chlorodiphenylmethyllithium (2), showed that the final product, 10,10-diphenyl-9-phenanthrone (3; X = H) appears to result from a seldom occurring type of rearrangement. Formally it is a 1,2-sigmatropic rearrangement, although it takes place in an electron-rich system. Unlike most apparently similar reactions reported in the literature,[2] it does not pass through an intermediate oxirane.

In order to obtain additional information on the reaction mechanism, we investigated this reaction starting from several monosubstituted fluorenones [1; X = 2-CH$_3$, 2-F, 2-Cl, 2-OCH$_3$, 2-N(CH$_3$)$_2$, 3-CH$_3$, 3-F, 3-Cl, 3-OCH$_3$] to study the nature of substituent effects.[3] Two different isomeric products are possible,

depending on which of the two rings migrates (see Table 1). In some cases two compounds could be isolated,

Table 1. List of compounds

Substituent X in 9-fluorenone (1)	Substituent X in each isomer of 10,10-diphenyl-9-phenanthrone (3)	Compound
H		3a
2-CH$_3$	2-CH$_3$ and 7-CH$_3$	3b
3-CH$_3$	3-CH$_3$ and 6-CH$_3$	3c
3-OCH$_3$	3-OCH$_3$ or 6-OCH$_3$	3d
3-Cl	3-Cl and 6-Cl	3e
2-F	2-F or 7-F	3f
2-OCH$_3$	2-OCH$_3$ or 7-OCH$_3$	3g
2-N(CH$_3$)$_2$	2-N(CH$_3$)$_2$ or 7-N(CH$_3$)$_2$	3h
2-Cl	2-Cl or 7-Cl	
3-F	3-F and 6-F	

1   2   3

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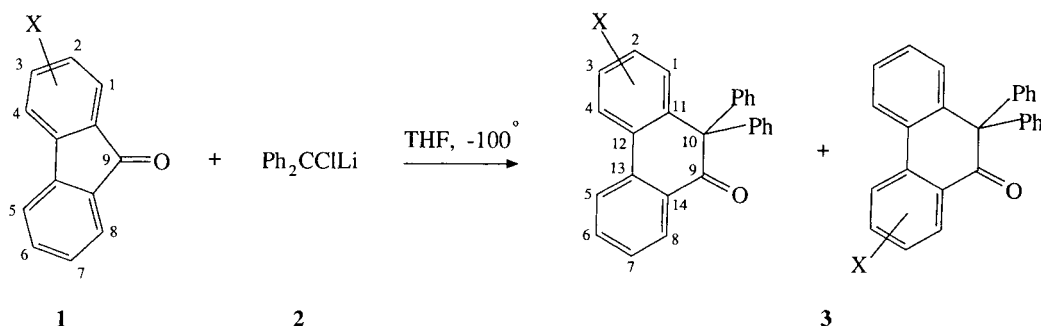
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whereas in other cases just one of the predicted isomers 3 was found. This raised the analytical problem of differentiating between the two possible isomers and assigning their structures. However, attempts to achieve this using various other spectroscopic methods were unsuccessful, and the only technique, apart from x-ray structural analysis, which provided the answer was ¹³C NMR. This paper reports details of this NMR analysis.

In order to assign the structures of the substituted phenanthrones, it was essential that the ¹³C NMR spectrum of 3a (X = H) be assigned unambiguously. This was achieved by 2D NMR techniques. For three of the substituted phenanthrones (3; X = 7-Cl, 6-F and 3-OCH₃), structural analyses by x-ray crystallography[4] confirmed the structures derived from ¹³C NMR.

RESULTS

Assignment of the ¹³C NMR spectrum of 3a

The resonances of the phenyl groups were identified by their relative intensities. The signals due to C-10 (68.3 ppm) and the carbonyl carbon C-9 (200.2 ppm) are readily assigned from their chemical shifts.

The connectivities of those carbon atoms directly attached to protons were obtained from a 2D ¹H–¹H–¹³C relayed coherence spectrum,[5,6] which allows adjacent protonated ¹³C nuclei to be identified. This

establishes that the carbon signals at 128.0, 128.3, 134.0 and 122.8 and those at 124.2, 127.9, 128.5 and 132.1 ppm arise from the two chains of carbon atoms —(CH)₄— (i.e. C-1–C-4 and C-5–C-8), although it does not show which chain is which, or the direction of the sequences (see Fig. 1).

To locate these chains in the molecule and to obtain information on the quaternary carbons, a 2D ¹³C,¹H shift correlated spectrum[7] (for general references, see Ref. 6; long-range heteronuclear shift correlations have recently been reviewed by Martin and Zektzer[8]) using polarization transfer via long-range couplings [optimized for $^nJ(C,H)$ of the order of 10 Hz] was recorded (see Fig. 2). The main cross-peaks on the contour plot arise from coupling between carbon nuclei and protons three bonds removed, since for carbon nuclei in aromatic rings[9] $^3J(CH) > {}^2J(CH) \approx {}^4J(CH)$.

The signals at 136.6 and 131.4 ppm must be assigned to C-13 and C-12 since they couple with protons from both rings (C-12: H-1, H-3 and H-5; C-13: H-6, H-8 and H-4). This also fixes the order of the proton signals H-1–H-8, although the CH group adjacent to the carbonyl group has yet to be identified. In the proton-coupled ¹³C NMR spectrum the signal of the carbonyl resonance C-9 is a doublet owing to coupling with H-8 [$^3J(C-9,H-8) = 3$ Hz]. A long-range correlated ¹³C,¹H 2D NMR spectrum and selective irradiation experiments identified the signal due to H-8, thus completing and confirming the assignment of the ¹H and the ¹³C spectra. All details of the 2D NMR spectrum are fully consistent with the complete assignment given in Table 2.
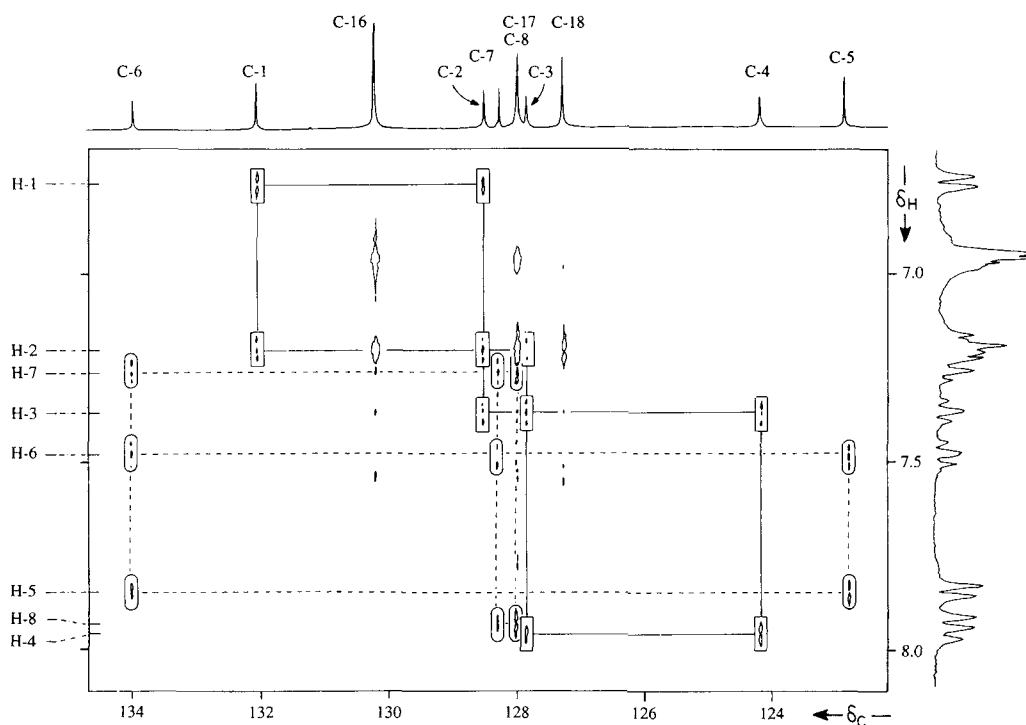

Figure 1. Contour plot of the two-dimensional ¹³C,¹H RELAY spectrum of the aromatic region of 3a showing the cross-peaks arising from the transfer of magnetization between coupled protons. Those from C-1–C-4 are indicated by the full lines and square boxes and those for C-5–C-8 by dashed lines and rounded boxes. A 2D ¹³C,¹H chemical shift correlated NMR spectrum optimized for direct couplings confirmed that the more intense peaks are due to direct coupling.
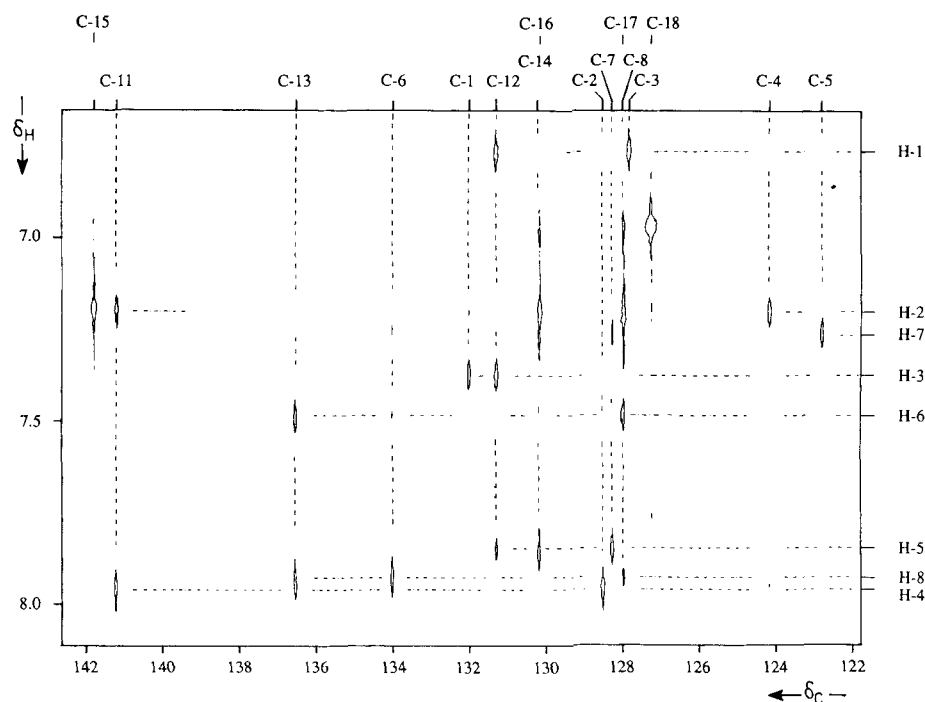
Figure 2. Contour plot of the two-dimensional $^{13}C,^1H$ correlated NMR spectrum of **3a** in the same region as Fig. 1, optimized for long-range couplings [^3J(CH) = 10 Hz]. Thus C-1 (δ_C = 132.1) has just one cross-peak (with H-3), but C-13 (δ_C = 136.6) has three (correlation with H-4, H-6 and H-8).

Assignment of the ^{13}C NMR spectra of 3b–3h

For several of the substituted phenanthrones, only a few milligrams of material were available. The structural assignments were made by estimating the ^{13}C chemical shifts for both possible isomers and determining which set of values was in better agreement with the observed values. These chemical shift estimates were made based on the chemical shifts of **3a** together with the corresponding substituent chemical shifts (SCS) for the

appropriate substituent [CH_3, Cl, F, OCH_3 or $N(CH_3)_2$] in arenes[10] [the following substituent chemical shifts (ppm) were employed: CH_3, S_{ipso} = 9.2, S_{ortho} = 0.7, S_{meta} = −0.1, S_{para} = −3.0; F, 34.8, −13.0, 1.6, −4.4; Cl, 6.3, 0.4, 1.4, −1.9; CH_3O, 31.4, −14.4, 1.0, −7.7; $(CH_3)_2N$, 22.5, −15.4, 0.9, −11.5].

For all compounds, the agreement between the spectra and the estimated chemical shifts of one of the isomers was excellent, and in each case the structure assignment was unambiguous. The multiplicities of the

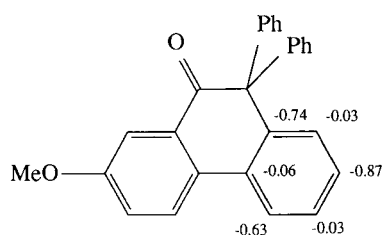**Table 2.** ^{13}C NMR data for 10,10-diphenyl-9-phenanthrone derivatives[a]

X	3a H	3b 2-CH_3	3c 3-CH_3	3d 3-OCH_3	3e 6-Cl	3f 7-F[b]	3g 7-OCH_3	3h 7-$N(CH_3)_2$
C-1	132.07	132.65	132.07	133.34	132.24	132.20	132.04	131.93
C-2	128.54	138.62	129.48	114.05	128.57	128.54	127.67[d]	126.64
C-3	127.86	128.77[c]	137.49	159.37	128.08	128.07	127.83[d]	127.65
C-4	124.17	124.16	124.82	109.93	124.37	124.08	123.54	122.81
C-5	122.79	122.59	122.75	122.78	123.09	125.20 (7.3)	124.55	124.09
C-6	134.01	134.02	133.96	133.90	140.66	121.32 (22.4)	121.91	118.13
C-7	128.31	127.89[c]	128.21	128.44	129.27	162.71 (249.2)	159.81	150.29
C-8	128.04	128.18[c]	128.12	128.09	129.76	114.21 (22.4)	110.56	110.00
C-9	200.18	200.41	200.43	200.12	199.15	199.22	200.25	201.03
C-10	68.33	68.38	68.07	67.83	68.37	68.58	68.46	68.45
C-11	141.29	141.30	138.42	133.57	141.73	140.86	140.55	140.01
C-12	131.39	128.81	131.19	132.60	130.30	130.85	131.44[e]	132.15
C-13	136.60	136.88	136.79	136.55	138.29	133.03 (3.1)	129.93	125.33
C-14	130.28	130.13	130.48	130.66	128.64	132.2 (ca. 7)[f]	131.46[e]	130.95
CH_3		21.47	21.30	55.46			55.52	40.22

[a] The phenyl resonances fall in the following ranges: C_{ipso}, 142.51–141.49; C_{ortho}, 130.32–130.22; C_{meta}, 128.16–127.94; C_{para}, 127.51–127.11.
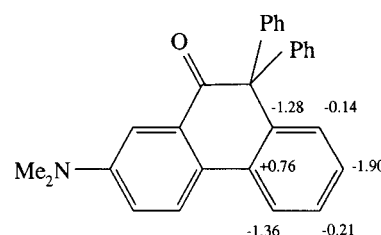[b] $J(^{19}F,^{13}C)$ in parentheses.
[c,d,e] Assignments may be interchanged.
[f] Signal partially obscured.

Ph
O   Ph
                -0.74 -0.03
MeO—   -0.06   -0.87
                -0.63   -0.03

3g

Ph
O   Ph
                -1.28 -0.14
Me₂N—   +0.76   -1.90
                -1.36   -0.21

3h

signals, determined from DEPT spectra, were taken into account when comparing the observed spectra with the calculated spectra. Where sufficient material was available for a proton-coupled spectrum to be recorded, the fine structure of the multiplets provided additional support for the spectral assignment; for example, when a compound has a substituent in the 2-position, the signal due to C-4 appears as a sharp doublet with no resolved fine structure because ^3J(C-4,H-2) is no longer present.

A 2D RELAY experiment was carried out to assist the assignment of the ¹³C NMR spectrum of 3g, since the chemical shifts in both rings are affected by the substituent (see Discussion).

DISCUSSION

The increments for substituents in arenes predicted accurately the chemical shifts in the substituted ring. To a first approximation the resonances of the carbon atoms in the other ring are generally not significantly different from those of 3a. The exceptions are 3g and 3h, where delocalization of charge from the substituent into the second ring can take place and small upfield shifts

relative to the corresponding signals of 3a are observed for C-2, C-4 and C-11.

EXPERIMENTAL

All ¹³C NMR measurements were carried out at 40 °C in CDCl₃ at 75.5 MHz on a Bruker WM-300 NMR spectrometer. Chemical shifts are given relative to internal TMS. The 2D NMR spectra of the aromatic region were recorded using the programs described in Refs 5 and 7. The f_2 spectral width was 2000 Hz over 4K points, giving a resolution of 1.0 Hz per point; 128 spectra with t_1 incremented by 0.001 s gave an f_1 width of 500 Hz, which after zero filling gave a resolution of 1.95 Hz per point. For the 2D RELAY experiment the delay for transferring magnetization between protons was set to 0.0125 s. The delays Δ_1 and Δ_2 in the long-range shift correlation experiment were 0.05 and 0.025 s, respectively.

Acknowledgements

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