MAGNETIC RESONANCE IN CHEMISTRY
Magn. Reson. Chem. **36**, 548–550 (1998)

Reference Data

^{1}H and ^{13}C NMR chemical shifts of some thienyl-substituted chromenes

C. Moustrou,[1]* N. Rebiere,[1] M. Frigoli,[1] E. Pottier,[1] R. Guglielmetti[1] and R. Faure[2]

[1] ERS CNRS 158, Laboratoire de Chimie et Matériaux Organiques, Modélisation, Université d'Aix–Marseille II, Case 901, 163 Avenue de Luminy, 13288 Marseille Cédex 09, France
[2] ESA CNRS 6009, Université d'Aix–Marseille III, Avenue Escadrille Normandie-Niemen, 13397 Marseille Cédex 20, France

Received 11 December 1997; accepted 25 February 1998

ABSTRACT: The complete assignment of the ^{1}H and ^{13}C NMR spectra of eight thienyl-substituted chromenes was achieved by the concerted application of homonuclear (gs-COSY), ^{1}H-detected heteronuclear one-bond (gs-HMQC) and long-range (gs-HMBC) gradient-selected correlation experiments. © 1998 John Wiley & Sons, Ltd.

KEYWORDS: NMR; ^{1}H NMR; ^{13}C NMR; gs-2D NMR; [3*H*]-naphtho[2,1-*b*]pyran; thienylchromenes

INTRODUCTION

Organic photochromic compounds undergo a reversible color change on UV irradiation owing to the existence of two interconvertible isomers.[1,2] In recent years, research in the area of photochromic compounds has increased significantly, especially in the field of optical technology and for the design of new conducting materials. In this context, we have synthesized a variety of [2*H*]-chromenes linked to a thiophene moiety. The introduction of the thienyl group allows subsequent preparation, through electrochemical polymerization or copolymerization,[3,4] of photochromic and electrochromic materials, which are strong candidates for photomodulated molecular devices.

In this paper, we report the complete ^{1}H and ^{13}C NMR chemical shift assignments obtained from one- and gradient-selected two-dimensional NMR techniques for eight thienyl-substituted [3*H*]-naphtho[2,1-*b*]pyrans (Fig. 1).

EXPERIMENTAL

Materials

Compounds **1a–d** and **2** were prepared by a mild 'one-pot' esterification.[5] Compounds **3a–c** were obtained through condensation of 2-(6-hydroxy-1-naphthyl)thiophene with the appropriate propargylic alcohols. This condensation took place at room temperature under acidic catalysis.[6] The products were purified by column chromatography on silica gel. All new compounds gave satisfactory C, H, S elemental analyses.

NMR spectra

All experiments were performed on a Bruker AMX-400 spectrometer in $CDCl_3$ solutions and tetramethylsilane (TMS) was used as an internal standard. Resonance multiplicities for ^{13}C were established via the acquisition of DEPT[7] spectra. For the DEPT sequence, the width of ^{13}C 90° pulse was 4.5 μs, that of a ^{1}H 90° pulse was 10 μs and the $(2J)^{-1}$ delay was set at 3.4 ms. 1D-COSY[8] experiments were obtained with Gaussian pulses of 80 ms for semi-selective excitation of selected proton. For two-dimensional experiments an inverse probehead incorporating a shielded *Z*-gradient was used. The gradients were shaped by a waveform generator and were amplified by a Bruker B-AFPA-10 amplifier. gs-COSY spectra were obtained using a pulse sequence (cosy 11 gs in the Bruker operating software), which includes

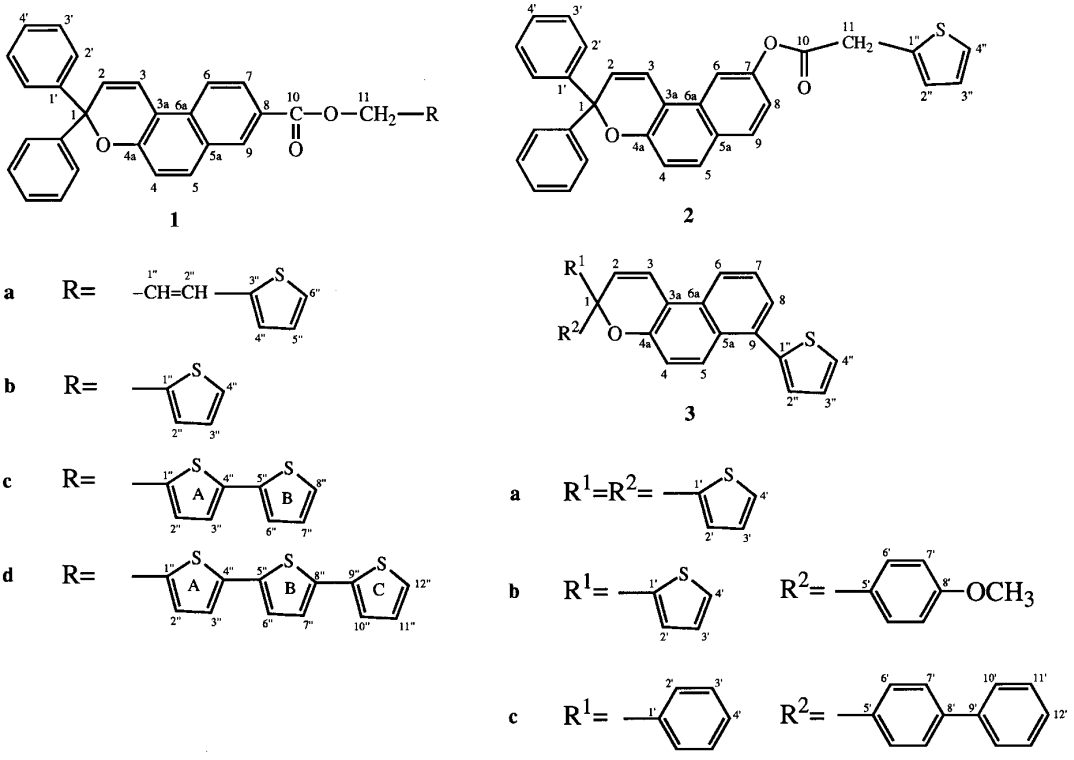

Figure 1. Structure of the compounds studied.

* *Correspondence to*: C. Moustrou, ERS CNRS 158, Laboratoire de Chimie et Matériaux Organiques, Modélisation, Université d'Aix–Marseille II, Case 901, 163 Avenue de Luminy, 13288 Marseille Cédex 09, France.

 CCC 0749-1581/98/070548–03 $17.50

Reference Data

Table 1. ^{13}C NMR chemical shifts of thienyl-substituted chromenes 1–3[a]

Atom	1a[b]	1b[c]	1c[d]	1d[e]	2[f]	3a[g]	3b[h]	3c[i]
C-1	83.11	83.11	83.13	83.12	82.76	78.69	80.27	82.58
C-2	128.12	128.11	128.12	128.12	127.92	127.08	127.74	128.02
C-3	119.16	119.13	119.15	119.12	119.44	120.08	119.73	119.88
C-3a	114.01	113.99	114.01	114.00	114.10	113.81	114.06	114.30
C-4	119.31	119.30	119.33	119.33	118.36	118.59	118.64	118.72
C-4a	152.69	152.71	152.75	152.75	151.27	150.12	150.43	150.74
C-5	131.48	131.48	131.53	131.51	129.72	128.22	128.00	128.02
C-5a	128.46	128.41	128.42	128.42	127.49	128.14	127.98	127.95
C-6	121.65	121.63	121.68	121.68	112.68	121.67	121.69	121.77
C-6a	132.31	132.34	132.37	132.38	130.53	130.26	130.37	130.47
C-7	126.26	126.26	126.26	126.24	149.39	126.27	126.13	126.19
C-8	125.24	125.00	124.92	124.88	118.49	126.44	126.28	126.30
C-9	131.86	131.98	132.03	132.04	130.11	133.23	133.16	133.21
C-10	166.58	166.50	166.54	166.53	169.13	—	—	—
C-11	65.34	61.17	61.33	61.30	35.71	—	—	—

[a] In ppm from TMS; $CDCl_3$ as solvent.
[b] δ C-1′ = 144.70 ppm; δ C-2′ = 127.08 ppm; δ C-3′ = 128.28 ppm; δ C-4′ = 127.78 ppm; δ C-1″ = 122.96 ppm; δ C-2″ = 127.58 ppm; δ C-3″ = 141.34 ppm; δ C-4″ = 126.64 ppm; δ C-5″ = 127.53 ppm; δ C-6″ = 125.06 ppm.
[c] δ C-1′ = 144.67 ppm; δ C-2′ = 127.07 ppm; δ C-3′ = 128.27 ppm; δ C-4′ = 127.78 ppm; δ C-1″ = 138.27 ppm; δ C-2″ = 128.27 ppm; δ C-3″ = 126.95 ppm; δ C-4″ = 126.95 ppm.
[d] δ C-1′ = 144.70 ppm; δ C-2′ = 127.09 ppm; δ C-3′ = 128.30 ppm; δ C-4′ = 127.81 ppm; δ C-1″ = 137.17 ppm; δ C-2″ = 129.10 ppm; δ C-3″ = 123.40 ppm; δ C-4″ = 139.10 ppm; δ C-5″ = 137.21 ppm; δ C-6″ = 124.12 ppm; δ C-7″ = 127.95 ppm; δ C-8″ = 124.81 ppm.
[e] δ C-1′ = 144.67 ppm; δ C-2′ = 127.07 ppm; δ C-3′ = 128.27 ppm; δ C-4′ = 127.78 ppm; δ C-1″ = 137.28 ppm; δ C-2″ = 129.14 ppm; δ C-3″ = 123.28 ppm; δ C-4″ = 138.77 ppm; δ C-5″ = 135.94 ppm; δ C-6″ = 124.65 ppm; δ C-7″ = 124.43 ppm; δ C-8″ = 136.66 ppm; δ C-9″ = 137.12 ppm; δ C-10″ = 123.89 ppm; δ C-11″ = 127.99 ppm; δ C-12″ = 124.68 ppm.
[f] δ C-1′ = 144.71 ppm; δ C-2′ = 127.07 ppm; δ C-3′ = 128.19 ppm; δ C-4′ = 127.65 ppm; δ C-1″ = 134.37 ppm; δ C-2″ = 127.31 ppm; δ C-3″ = 127.07 ppm; δ C-4″ = 125.46 ppm.
[g] δ C-1′ = 148.57 ppm; δ C-2′ = 126.09 ppm; δ C-3′ = 126.55 ppm; δ C-4′ = 126.29 ppm; δ C-1″ = 141.83 ppm; δ C-2″ = 127.58 ppm; δ C-3″ = 127.29 ppm; δ C-4″ = 125.77 ppm.
[h] δ C-1′ = 149.62 ppm; δ C-2′ = 126.31 ppm; δ C-3′ = 126.42 ppm; δ C-4′ = 126.26 ppm; δ C-5′ = 136.56 ppm; δ C-6′ = 127.86 ppm; δ C-7′ = 113.50 ppm; δ C-8′ = 159.27 ppm; δ OCH_3 = 55.32 ppm; δ C-1″ = 141.89 ppm; δ C-2″ = 127.52 ppm; δ C-3″ = 127.25 ppm; δ C-4″ = 125.70 ppm.
[i] δ C-1′ = 144.83 ppm; δ C-2′ = 127.13 ppm; δ C-3′ = 128.31 ppm; δ C-4′ = 127.76 ppm; δ C-5′ = 143.91 ppm; δ C-6′ = 127.23 ppm; δ C-7′ = 127.60 ppm; δ C-8′ = 140.56 ppm; δ C-9′ = 140.76 ppm; δ C-10′ = 127.02 ppm; δ C-11′ = 128.86 ppm; δ C-12′ = 127.45 ppm; δ C-1″ = 141.97 ppm; δ C-2″ = 127.60 ppm; δ C-3″ = 127.32 ppm; δ C-4″ = 125.76 ppm.

a 1:1 gradient combination.[9] The spectral widths were about 6 ppm and the spectra were collected as 1 K × 256 blocks of data. Zero filling was applied in F_1 in order to have a symmetrical matrix of 512 × 512 real data points, which was processed by unshifted sinusoidal windows in each dimension. The gs-HMQC spectra (inv 4gs in the Bruker software) resulted from a 1024 × 128 data matrix size with 4–16 scans per t_1 depending on the sample concentration, an inter-pulse delay of 3.5 ms and a 5:3:4 gradient combination.[10] gs-HMBC spectra were acquired using a pulse sequence (hmbcgs in the Bruker library) optimized on ^2J or ^3J couplings (inter-pulse delay for the evolution of long-range couplings = 50 ms) and the same gradient ratio as described above for HMQC experiments.[11] In this way, direct responses (^1J couplings) were not completely removed.

RESULTS AND DISCUSSION

The results for compounds **1**–**8** are given in Tables 1 and 2. The assignment of ^1H and ^{13}C chemical shifts for phenyl and thiophene rings located at C-1 was trivial on the basis of signal intensities and chemical shift considerations.[12] In the 400 MHz ^1H NMR spectra, the protons of the [3*H*]-naphtho[2,1-*b*]pyran skeleton would constitute two AX and one AMX spin systems. Unfortunately, some ^1H signals of this heterocycle show strong overlap with substituent protons, which precludes the accurate measurement of chemical shifts for these resonances. However, the latter information can be obtained indirectly from the 1D-COSY pulse sequence in which the semi-selective excitation of selected coupled protons was achieved with Gaussian-shaped pulses. Although a ^1H intercoupling network can be obtained from 2D-COSY experiments, complete ^1H assignment of this heterocycle cannot be realized from the above results. Therefore, assignment of the ^1H and ^{13}C resonances of the [3*H*]-naphtho[2,1-*b*]pyran moiety was deduced from the concerted application of both direct and long-range heteronuclear chemical shift correlation experiments. One-bond proton–carbon chemical shift correlations were established using the HMQC sequence and the CH_n groups were unambiguously characterized from the analysis of long-range correlation responses over two and three bonds (^2J or ^3J couplings) using the HMBC technique. Long-range ^1H–^{13}C connectivities found for this heterocycle are presented in Table 3. These data are in good agreement with those reported previously for other [3*H*]-naphtho[2,1-*b*]pyran derivatives.[13]

Two-dimensional and 1D-COSY experiments were also applied to the assignment of ^1H and ^{13}C chemical shifts of thienyl and biphenyl (**3c**) substituents. It should be noted that the magnitude of the ^1H–^1H splittings in the thiophene group was in fair agreement with the literature data.[14]

REFERENCES

1. R. Guglielmetti, in *Photochromism: Molecules and Systems*, edited by H. Dürr and H. Bouas-Laurent, p. 314. Elsevier, Amsterdam (1990).
2. J. Crano and R. Guglielmetti (Eds), *Organic Photochromic and Thermochromic Compounds*. Plenum, New-York, in press.

Reference Data

Table 2. ^{1}H NMR chemical shifts of thienyl-substituted chromenes 1–3[a]

Atom	1a[b]	1b[c]	1c[d]	1d[e]	2[f]	3a[g]	3b[h]	3c[i]
H-2	6.28	6.27	6.28	6.27	6.23	6.32	6.28	6.33
H-3	7.28	7.27	7.27	7.27	7.16	7.35	7.32	7.35
H-4	7.24	7.22	7.23	7.23	7.16	7.18	7.18	7.22
H-5	7.75	7.73	7.73	7.74	7.61	8.06	8.04	8.04
H-6	7.96	7.94	7.94	7.95	7.64	8.00	7.98	7.99
H-7	8.06	8.03	8.05	8.04	–	7.49	7.47	7.47
H-8	—	—	—	—	7.04	7.42	7.40	7.41
H-9	8.48	8.46	8.47	8.47	7.69	—	—	—
H-11	4.97	5.53	5.50	5.49	4.11	—	—	—

[a] In ppm from TMS; $CDCl_2$ as solvent.
[b] δ H-2′ = 7.46 ppm; δ H-3′ = 7.32 ppm; δ H-4′ = 7.25 ppm; δ H-1″ = 6.26 ppm; δ H-2″ = 6.88 ppm; δ H-4″ = 7.01 ppm; δ H-5″ = 6.96 ppm; δ H-6″ = 7.18 ppm.
[c] δ H-2′ = 7.45 ppm; δ H-3′ = 7.31 ppm; δ H-4′ = 7.25 ppm; δ H-2″ = 7.18 ppm; δ H-3″ = 7.01 ppm; δ H-4″ = 7.33 ppm.
[d] δ H-2′ = 7.47 ppm; δ H-3′ = 7.32 ppm; δ H-4′ = 7.26 ppm; δ H-2″ = 7.08 ppm; δ H-3″ = 7.06 ppm; δ H-6″ = 7.17 ppm; δ H-7″ = 6.99 ppm; δ H-8″ = 7.20 ppm.
[e] δ H-2′ = 7.45 ppm; δ H-3′ = 7.31 ppm; δ H-4′ = 7.24 ppm; δ H-2″ = 7.08 ppm; δ H-3″ = 7.04 ppm; δ H-6″ = 7.05 ppm; δ H-7″ = 7.06 ppm; δ H-10″ = 7.15 ppm; δ H-11″ = 7.00 ppm; δ H-12″ = 7.20 ppm.
[f] δ H-2′ = 7.44 ppm; δ H-3′ = 7.29 ppm; δ H-4′ = 7.23 ppm; δ H-2″ = 7.06 ppm; δ H-3″ = 7.00 ppm; δ H-4″ = 7.25 ppm.
[g] δ H-2′ = 7.08 ppm; δ H-3′ = 6.94 ppm; δ H-4′ = 7.29 ppm; δ H-2″ = 7.17 ppm; δ H-3″ = 7.15 ppm; δ H-4″ = 7.40 ppm.
[h] δ H-2′ = 6.94 ppm; δ H-3′ = 6.91 ppm; δ H-4′ = 7.27 ppm; δ H-6′ = 7.48 ppm; δ H-7′ = 6.86 ppm; δ OCH_3 = 3.77 ppm; δ H-2″ = 7.16 ppm; δ H-3″ = 7.14 ppm; δ H-4″ = 7.39 ppm.
[i] δ H-2′ = 7.53 ppm; δ H-3′ = 7.34 ppm; δ H-4′ = 7.26 ppm; δ H-6′ = 7.55 ppm; δ H-7′ = 7.55 ppm; δ H-10′ = 7.55 ppm; δ H-11′ = 7.40 ppm; δ H-12′ = 7.28 ppm; δ H-2″ = 7.17 ppm; δ H-3″ = 7.14 ppm; δ H-4″ = 7.39 ppm.

3. A. Yassar, C. Moustrou, H. Korri Youssoufi, A. Samat, R. Guglielmetti and F. Garnier, *J. Chem. Soc., Chem. Commun.* 471 (1995).
4. A. Yassar, C. Moustrou, H. Korri Youssoufi, A. Samat, R. Guglielmetti and F. Garnier, *Macromolecules* **28**, 454 (1995).
5. A. Hassner and V. Alexanian, *Tetrahedron Lett.* **46**, 4475 (1978).
6. B. Van Gemert, M. Bergomi and D. Knowles, *Mol. Cryst. Liq. Cryst.* **246**, 67 (1994).
7. D. M. Doddrell, D. T. Pegg and M. R. Bendall, *J. Magn. Reson.* **48**, 323 (1982).
8. H. Kessler, S. Mronga and G. Gemmecker, *Magn. Reson. Chem.* **29**, 527 (1991).
9. R. E. Hurd, *J. Magn. Reson.* **87**, 422 (1990).
10. R. E. Hurd and B. K. John, *J. Magn. Reson.* **91**, 648 (1991).
11. W. Wilker, D. Leibfritz, R. Kerssebaum and W. Bermel, *Magn. Reson. Chem.* **31**, 287 (1993).
12. H. O. Kalinowski, S. Berger and S. Braun, *Carbon-13 NMR Spectroscopy*. Wiley, New York (1988).
13. C. Barberis, M. Campredon, V. Lokshin, G. Giusti and R. Faure, *Magn. Reson. Chem.* **33**, 977 (1995).
14. E. Pretsch, T. Clerc, J. Seibl and W. Simon, *Tables of Spectral Data for Structure Determination of Organic Compounds*, p. H265. Springer, New York (1989).

Table 3. Long-range proton–carbon correlations found in the HMBC spectra for [3*H*]naphtho[1,2-*b*]pyran ring compounds 1–3

Carbon	Protons showing HMBC correlation (^2J and ^3J couplings)
1	H-2; H-3
3a	H-2; H-4
4a	H-3; H-5
5a	H-6; H-8 (in **2** and **3**)
6	H-8 (in **2** and **3**)
6a	H-7 (in **1** and **3**); H-9 (in **1** and **2**)
7	H-9 (in **1** and **2**)
8	H-6
9	H-7 (in **1** and **3**)