Tetrahedron Vol. 23, pp 4419 to 4424. Pergamon Press Ltd. 1967. Printed in Great Britain

THE ABSORPTION SPECTRA AND SYNTHESIS OF SOME 2,2'-BITHIENYL DERIVATIVES

R. F. CURTIS and G. T. PHILLIPS*

Department of Chemistry, University College of Swansea, Singleton Park, Swansea

(*Received* 14 *November* 1966; *accepted for publication* 17 *February* 1967)

Abstract—The IR and UV absorption spectra of 2,2'-bithienyl derivatives have been correlated, and are shown to have maxima which are characteristic of the substitution pattern. In the IR, 2,2'-bithienyl shows maxima at 835, 690 cm^{-1}; 5-substituted derivatives at 840, 800 and 690 cm^{-1} and 5,5'-disubstituted derivatives at 800 cm^{-1}. In the UV region the characteristic maximum of 2,2'-bithienyl at 301 mμ (ε, 12,800) undergoes bathochromic shifts of ca. 30 mμ or ca. 50 mμ when single or conjugated chromophores are substituted in the 5-position. These correlations give a good guide to the substitution pattern of naturally occurring 2,2'-bithienyl systems. Syntheses of 5-methyl-, 5,5'-diformyl- and 5-formyl-5'-iodo-2,2'-bithienyl are recorded.

IN THE course of our investigations of naturally occurring thiophens[1-3] we have examined the IR and UV absorption spectra of a large number of 2,2'-bithienyl derivatives. We can now record correlations which are useful for establishing the pattern and nature of the substituents frequently observed in natural products based on this skeleton.

These correlations are particularly useful since 2,2'-bithienyl derivatives are generally unstable to chemical degradation and occur in low abundance as natural products.

Infrared spectra

Numerous papers have been published on the vibrational spectra of thiophen and its derivatives and these have been summarized in a recent publication by Lippincott *et al.*[4] In addition to the correlations now available for mono-substituted thiophens,[4] Schulte[5] has studied numerous 2,5-disubstituted thiophens and has shown that a strong band at 800 ± 15 cm^{-1} is especially characteristic of these compounds. The results of our comparable observations in the 2,2'-bithienyl series, in which the base skeleton contains both a 2-substituted and a 2,5-disubstituted thiophen nucleus, are presented in Table 2.

It is clear that the absorption bands between 850 and 670 cm^{-1} are characteristic of the substitution pattern. Thus 2,2'-bithienyl(**I**) shows intense bands at 835 and 690 cm^{-1}; 5-substituted-2,2'-bithienyl derivatives (II) show bands at 840, 800 and

---

* Present address: The Chemical Laboratory, University of Sussex, Falmer, Brighton.

[1] R. E. Atkinson, R. F. Curtis and G. T. Phillips, *J. Chem. Soc.* 7109 (1965).

[2] R. E. Atkinson, R. F. Curtis and G. T. Phillips, *J. Chem. Soc.* 1101 (1966).

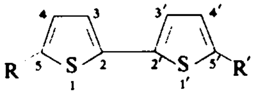
[3] R. E. Atkinson, R. F. Curtis and G. T. Phillips, *Chem. & Ind.* 2101 (1964); *J. Chem. Soc.* in press (1967).

[4] M. Horak, I. J. Hyams and E. R. Lippincott, *Spectrochim. Acta* **22**, 1355 (1966).

[5] K. E. Schulte, A. Kreutzberger and G. Bohn, *Chem. Ber.* **97**, 3263 (1964).

690 cm^{-1}, and 5,5'-disubstituted-2,2'-bithienyl derivatives (III) show only a single band at 800 cm^{-1}. These observations are summarized in Table 1, and listed in detail in Table 2.

TABLE 1



Substitution pattern	Characteristic frequencies (cm^{-1})
I. R = R' = H	835, 690 cm^{-1}
II. R ≠ H, R' = H	840, 800, 690 cm^{-1}
III. R ≠ H, R' ≠ H	800 cm^{-1}

The recent results of Lippincott *et al.*[4] suggest that the bands in the region of 835 cm^{-1} and 690 cm^{-1} are probably due to C—H out-of-plane vibrations rather than "ring breathing" and CH out-of-plane deformations as originally assigned by Katritzky.[6] The band which appears at 800 cm^{-1} in the mono- and di-substituted bithienyls is clearly characteristic of a 2,5-disubstituted thiophen ring and was assigned to a "ring breathing" absorption by Schulte.[5]

Absorption bands characteristic of aromatic systems were also observed, e.g. 5-substituted-2,2'-bithienyl derivatives showed a weak but sharp absorption at 3050 ± 50 cm^{-1} which is probably due to the C—H stretching mode[4,7] of the C—H bond in the 5'-position. An even weaker band at 2950 cm^{-1} was also observed in some 5,5'-disubstituted-2,2'-bithienyl derivatives; it is probably, therefore, the C—H stretching mode of the C—H bond in the β-positions of the thiophen rings.

Strong peaks were observed in the 1400–1450 cm^{-1} region in all the compounds examined. These were localized near 1510, 1450 and 1425 cm^{-1} and are probably connected with a ring-stretching absorption.[4]

The usefulness of these correlations is illustrated by the IR absorption frequencies of compounds **2**, **7**, **10** and **11** isolated from *Tagetes minuta*,[1,2] which were clearly shown to be 5-substituted-2,2'-bithienyl derivatives from the consistent absorptions at 840, 800 and 690 cm^{-1}. In contrast to these, the closely-related synthetic intermediates **27** and **28** and the naturally occurring acetate **29**,[3,8] showed absorptions only at ca. 800 cm^{-1} in agreement with the above correlations. We have already pointed out[1] that the absorption at 690 cm^{-1} can be confused with a *cis* double bond; in a 2,2'-bithienyl derivative an absorption at 690 cm^{-1} more likely to be indicative of a 5-substituted-2,2'-bithienyl derivative, rather than the presence of an isolated *cis* double bond.

Ultraviolet absorption spectra

The UV absorption spectra of 5- and 5,5'-disubstituted-2,2'-bithienyl derivatives show three main absorption bands. First, a broad band at ca. 330–360 mμ, (ε_{max} ca. 20,000) characteristic of an electron transfer[9] transition. This may be subdivided

[6] A. R. Katritzky and A. J. Boulton, *J. Chem. Soc.* 3500 (1959).

[7] L. J. Bellamy, *The Infrared Spectra of Complex Molecules* p. 64. Methuen, London (1960).

[8] F. Bohlmann and K.-M. Klein, *Chem. Ber.* **96**, 1229 (1963).

[9] J. Murrell, *J. Chem. Soc.* 3779 (1956).

into two distinct types, the first of which may involve an electronic transition from the π orbital of the aromatic ring into the π* orbital of the chromophoric group (Fig. 1). The bathochromic shifts characteristic of this type, relative to the local π-π* excitation of the parent 2,2'-bithienyl nucleus are shown in Table 2 (section A).

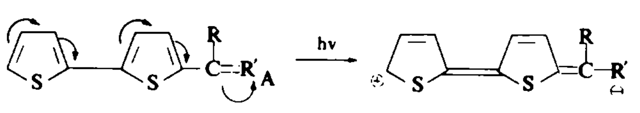


FIG. 1

The second type is shown by the compounds listed in Table 3 (section B), and possibly represents transitions between the p-orbital of the substituent and the antibonding π* orbital of the heterocyclic rings (Fig. 2).

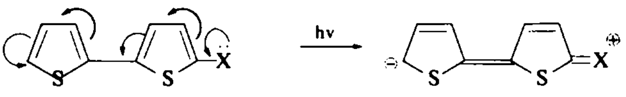


FIG. 2

In addition, compounds which have substituents representing both auxochromes and chromophores on the same nucleus are listed in Section C.

Table 2 shows that the bathochromic shift contributed by auxochromes (relative to 2,2'-bithienyl) is from 6–14 mμ, decreasing in the series I > Br > Cl > CH_3 and consistent with the dihalogenated series. The bathochromic shift contributed by a carbonyl chromophore is ca. 50 mμ and decreases in the order CHO > COMe > CO_2Me. Comparisons in any halogenated series, with a corresponding series containing a carbonyl chromophore (e.g. the halogenated-2,2'-bithienyls and the 5-halogenated-5'-methoxycarbonyl derivatives) show that the sum contribution of the auxochrome and chromophore differ from the sum of their individual contributions by only ±2 mμ.

These correlations are useful to determine the substitution pattern and the nature of the conjugation in naturally occurring, 2,2'-bithienyl derivatives, such as compounds **2**, **7**, **10**, **11**, **28** and **29** in Table 2. The weaker conjugative effect of an acetylenic bond, relative to a *cis* or *trans* double bond is shown by the absorption maxima of the alcohols **8**, **9** and **10**.

A second major band of moderate intensity (ε_{max} 5000–9000) occurs at ca. 240–250 mμ, and may be due to the π-π* local excitation transition of the heteroaromatic nucleus. This band is characteristic, but not diagnostic of, a 2,2'-bithienyl nucleus.

The absorption band at 207 ± 3 mμ may be due to the η-σ^* transition of the p electrons of the heteroatom and the antibonding σ orbital.

All of the compounds discussed were prepared by the standard methods indicated in Table 2. 5-Methyl-2,2'-bithienyl was prepared in excellent yield by Wolff–Kishner reduction of 5-formyl-2,2'-bithienyl,[13] and the latter compound was prepared by formylation of 2,2'-bithienyl with phosphorus oxychloride dimethyl formamide.

---

[10] J. H. Uhlenbroek and J. D. Bijloo. *Rec. Trav. Chim.* 79, 1181 (1960).

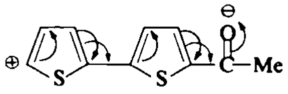
[11] R. F. Curtis and G. T. Phillips. *J. Chem. Soc.* 5134 (1965).

[12] G. Carpanelli and G. Leandri. *Ann. Chim., Italy* 57, 187 (1961).

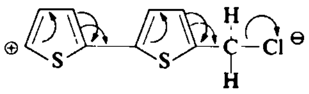
[13] E. Lescot, Jr., Ng. Ph. Bûû-Hoi and N. D. Xuong. *J. Chem. Soc* 3234 (1959).

TABLE 2

Compound	η-σ^* λ_{max} mμ(ε)	Local energy band π-π^* λ_{max} mμ(ε)	Electron transfer band λ_{max} mμ(ε)	C—H out-of-plane deformation ~840 cm^{-1}	Ring "breathing" mode ~800 cm^{-1}	C - H out-of-plane deformation ~690 cm^{-1}
Section A						
2,2'-Bithienyl (**1**)[12]	206 (4,200)	246 (6,400)	301 (12,800)	835	—	690
2,2'-5,2''-Terthienyl (**2**)[1]	210 (12,420)	252 (9,220)	350 (22,650)	835	800	690
5-Formyl-2,2'-bithienyl (**3**)[13]	207 (7,960)	244 (7,240)	350·5 (22,400)	840	808	705
5-Acetyl-2,2'-bithienyl (**4**)[14]	207 (9,730)*	245 (8,710)	348 (21,900)	848	795	700
5-Dichloromethyl-2,2'-bithienyl (**5**)* [1]	210 (10,100)	248·5 (8,150)	342 (20,560)	840	805	705
5-Methoxycarbonyl-2,2'-bithienyl (**6**)[15]	206 (8,720)	257 (5,610)	332 (19,700)	845	792	695
5-(But-3-en-1-ynyl)2,2'-bithienyl (**7**)[1]	210 (12,645)	249 (8,820)	341 (22,930)	835	800	693
trans-5-(4-Hydroxybut-1-enyl)2,2'-bithienyl (**8**)[1]	210 (9,860)	245 (8,630)	339–341 (20,300)	840	796	694
cis-5-(4-Hydroxybut-1-enyl)2,2'-bithienyl (**9**)[1]	207 (12,700)	243 (9,330)	333–337 (20,900)	840	800	690
5-(4-Hydroxybut-1-ynyl)2,2'-bithienyl (**10**)[1]	207 (8,270)	242 (6,580)	328 (22,060) 334 (22,280)	840	800	695
5-(4-Chloro-3-hydroxy-but-1-ynyl)2,2'-bithienyl (**11**)[2]	214 (9,540)	245 (9,120)	331 (25,120)	840	800	694
5,5'-Diformyl-2,2'-bithienyl (**12**)	207 (11,100)	260 (6,310)	336 (25,570) 358 (24,000)	—	800	—
5,5'-Diacetyl-2,2'-bithienyl (**13**)[14]	208 (12,800)	260 (7,410)	357 (29,500)	—	790	—



and



---

* This dichloromethyl derivative has been included at this point at the suggestion of a referee who pointed out the close similarity between the data for **4** and **5** and further suggested an analogy represented as:

TABLE 2—*continued*

Compound	η-σ^* λ_{max} mμ(ε)	Local energy band π-π^* λ_{max} mμ(ε)	Electron transfer band λ_{max} mμ(ε)	C—H out-of-plane deformation ~840 cm^{-1}	Ring "breathing" mode ~800 cm^{-1}	C—H out-of-plane deformation ~690 cm^{-1}
Section B						
5-Chloro-2,2′-bithienyl (**14**)[11]	207 (7,210)	247 (5,880)	311 (13,800)	845	790	694
5-Bromo-2,2′-bithienyl (**15**)[11]	209 (5,590)	249 (5,400)	311 (13,660)	840	790	692
5-Iodo-2,2′-bithienyl (**16**)[11]	210 (6,570)	248 (5,640)	314 (15,700)	840	795	697
5-Methyl-2,2′-bithienyl (**17**)	210 (5,570)	245 (5,820)	308 (13,230)	840	795	695
5,5′-Dichloro-2,2′-bithienyl (**18**)[10, 16]	206 (5,060)	250 (6,300)	318 (16,500)	—	795	—
5,5′-Dibromo-2,2′-bithienyl (**19**)[17]	208 (6,320)	255 (6,910)	318 (15,210)	—	795	—
5,5′-Diiodo-2,2′-bithienyl (**20**)[18]	209 (9,650)	246 (6,740)	324 (19,880)	—	800	—
5-Iodo-5′-methyl-2,2′-bithienyl (**21**)[19]	204 (9,370)	239·5 (6,770)	320 (17,070)	—	790	—
Section C						
5-Chloro-5′methoxycarbonyl-2,2′-bithienyl (**22**)[11]	207 (11,780)	245 (7,774)	339 (18,820)	—	785	—
5-Bromo-5′-methoxycarbonyl-2,2′-bithienyl (**23**)[11]	210 (8,490)	245 (5,950)	339 (22,230)	—	795	—
5-Iodo-5′-methoxycarbonyl-2,2′-bithienyl (**24**)[11]	210 (10,380)	251 (6,750)	344 (23,090)	—	800	—
5-Formyl-5′-iodo-2,2′-bithienyl (**25**)	210 (11,950)	258 (11,222)	357 (25,120)	—	795	—
5-(But-3-en-1-ynyl)5′-methyl-2,2′-bithienyl (**26**)[3]	207 (14,710)	252 (9,210)	350 (27,300)	—	790	—
5-(But-3-en-1-ynyl)5′-methoxycarbonyl 2,2′-bithienyl (**27**)[3]	207 (15,600)	263 (9,010)	358 (23,730)		790	
5-(But-3-en-1-ynyl)5′-hydroxymethyl-2,2′-bithienyl (**28**)[3]	207 (12,100)	252 (5,220)	348 (24,400)	—	805	—
5-Acetoxymethyl-5′-(but-3-en-1-ynyl)2,2′-bithienyl (**29**)[3]	208 (16,700)	252 (9,700)	348 (28,200)	—	800	—

The first two examples of disubstitution in this reaction have recently been recorded;[20] a further example is the isolation of 5,5′-diformyl-2,2′-bithienyl in significant yield in this reaction.

5-Formyl-5-iodo-2,2′-bithienyl (**25**) was prepared by direct iodination of the formyl derivative **3**.

EXPERIMENTAL

IR spectra were measured with a Perkin-Elmer spectrophotometer Model 237 at a concentration of ca. 1% with potassium bromide discs, or where appropriate as films. UV absorption spectra were measured in EtOH soln with a Unicam SP 800 spectrophotometer.

5,5′-Diformyl-2,2′-bithienyl (**12**). $POCl_3$ (41·3 g) was added in small portions to 2,2′-bithienyl (30 g) and dimethyl formamide (24 g) in dry toluene (450 ml). After the exothermic reaction the mixture was heated on a steam bath for 2·5 hr, cooled and warm saturated aqueous AcONa (600 ml) added. The organic layer was worked up in the usual way and the residue on evaporation fractionally crystallized from benzene light petroleum (b.p. 40–60°) (1:5) to give *5,5′-diformyl-2,2′bithienyl* (**12**; 1·0 g) as yellow plates, m.p. 217–8°. (Found: C, 54·0; H, 3·2. $C_{10}H_6O_2S_2$ requires: C, 54·0; H, 2·8%.)

The mother liquors were evaporated and the residue crystallized from benzene light petroleum (b.p. 60–80°; 1:10) to give **3** (25·7 g) as yellow plates, m.p. 58–59° (lit.[13] m.p. 59°). (Found: C, 55·6; H, 3·3. Calc for $C_9H_6OS_2$: C, 55·6; H, 3·1%.)

5-Methyl-2,2′-bithienyl (**17**). The preceding formyl derivative (10 g) and hydrazine (100%, 13 ml) in ethylene glycol (50 ml) were heated under reflux for 30 min, cooled and KOH (13 g) added. After heating under reflux for 30 min the product was poured into water, extracted with pentane (3 × 100 ml), dried (Na_2SO_4) and evaporated. The residual orange oil was passed through alumina (30 × 4 cm) in pentane solution, the solvent recovered and the residue distilled to give **17** as a colourless oil (7·7 g; 83%), b.p. 50°/0·006 mm; lit.[19] 145–146 17 mm. (Found: C, 60·2; H, 4·6. Calc for $C_9H_8S_2$: C, 60·0; H, 4·5%.)

5-Formyl-5′-iodo-2,2′-bithienyl (**25**). Iodine (9·1 g) and yellow HgO (7·7 g) were added alternatively to a stirred soln of 5-formyl-2,2′-bithienyl (7 g) in benzene (70 ml) at 40° during 2 hr. Over this period a buff ppt appeared. The whole reaction mixture was shaken with ether (300 ml) and sat. KI aq (300 ml) and the ethereal layer separated, washed and dried (Na_2SO_4). Evaporation gave *5-formyl-5′-iodo-2,2′-bithienyl* (**25**) as plates from $CHCl_3$ pentane, m.p. 186° (9·0 g). (Found: C, 33·6; H, 1·6; S, 20·5. C_9H_5IOS requires: C, 33·8; H, 1·2; S, 20·0%.)

Acknowledgement – We are grateful to the S.R.C. for financial support (G.T.P.) and Professor C. H. Hassall for laboratory facilities.

---

[14] M. C. Rebstock and C. D. Stratton, *J. Am. Chem. Soc.* **77**, 3082 (1955).

[15] H. Wynberg and A. Bantjes, *J. Am. Chem. Soc.* **82**, 1447 (1960).

[16] A. Töhl and O. Eberhard, *Chem. Ber.* **26**, 2945, 2947 (1893).

[17] W. Steinkopf and J. Roch, *Liebigs Ann.* **482**, 260 (1930).

[18] W. Steinkopf and W. Köhler, *Liebigs Ann.* **522**, 17 (1936).

[19] W. Steinkopf, R. Leitsmann and K. H. Hoffmann, *Liebigs Ann.* **546**, 180 (1941).

[20] C. Grundmann and J. M. Dean, *Angew. Chem.* (Int. Ed.) **11**, 955 (1965).