A Spectroscopic Study of Pivalophenone, 2-Pivaloylfuran, 2-Pivaloylthiophen and 2-Pivaloylselenophen, and their Sulphur Analogues

Claude G. Andrieu
Laboratoire des Composés Thio-organiques, Université de Caen, France *

Henri Lumbroso
Laboratoire de Chimie Générale, Université Pierre et Marie Curie, Paris, France **

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Infrared, ultraviolet, ^1H and ^{13}C nuclear magnetic resonance spectra were recorded for the title compounds. The infrared carbonyl-band frequencies and intensities, and the H_5 chemical shifts, of planar acetophenone, 2-acetylfuran, 2-acetylthiophen and 2-acetylselenophen indicate the order Phenyl < 2-Furyl < 2-Thienyl < 2-Selenyl for Aryl-carbonyl conjugation. Ultraviolet *K*-band absorption coefficients and carbon-13 chemical shifts provide an estimate of the twisting angle in the pivaloyl derivatives.

Introduction

Contrary to alkyl hetaryl ketones, which have been extensively examined by physico-chemical methods [1], there have been few studies on pivalophenethione [2], 2-thiopivaloylfuran and 2-thiopivaloylthiophen [3–4].

In the present work, with the aim of elucidating their solution-state conformations we have synthesized and examined by various spectroscopic methods ring-closed 2,2-dimethylindan-1-one and 1-thione (**1** and **1′**), 4,5-dihydro-5-methylcyclopenta[b]thiophen-6-one and 6-thione (**1**-a and **1′**-a), pivalophenone (**2**) and pivalophenethione (**2′**), 2-pivaloylfuran and 2-thiopivaloylfuran (**3** and **3′**), 2-pivaloylthiophen and 2-thiopivaloylthiophen (**4** and **4′**), 2-pivaloylselenophen and 2-thiopivaloylselenophen (**5** and **5′**) (cf. Figure 1). Our next paper will be devoted to the electric dipole moments of a number of acyl and thioacyl chalcogen-heterocycles including the compounds here examined.

Reprint requests to Prof. Dr. H. Lumbroso, Laboratoire de Chimie Générale, Université Pierre et Marie Curie, 4, Place Jussieu, F-75252 Paris Cedex 05, Frankreich.

* Esplanade de la Paix, F-14032 Caen Cedex.
** 4, Place Jussieu, F-75252 Paris Cedex 05.

Experimental

Materials

2,2-*Dimethylindan-1-one* (**1**), a novel compound, was synthesized by methylation of indan-1-one by using the procedure indicated by Gelin, Deshayes, and Gelin [5]. Methyl iodide (0.03 mole) was added dropwise to a solution of indan-1-one (0.02 mole) and sodium hydride (0.02 mole) in dimethyl sulphoxide (10 ml). The reaction mixture was kept for

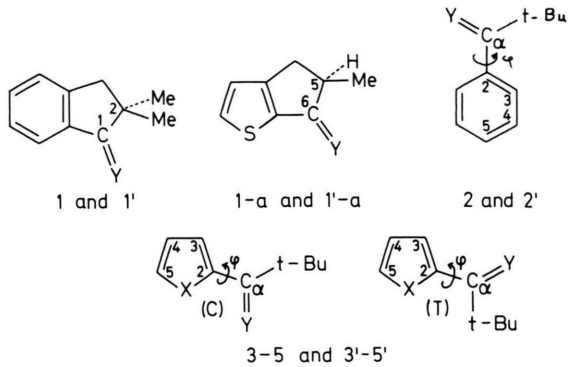

Fig. 1. **1** and **1′**: 2,2-Dimethylindan-1-one and 1-thione; **1**-a and **1′**-a: 4,5-dihydro-5-methylcyclopenta[b]thiophen-6-one and -6-thione; **2** and **2′**: pivalophenone and pivalophenethione; **3** and **3′**: 2-pivaloylfuran and 2-thiopivaloylfuran; **4** and **4′**: 2-pivaloylthiophen and 2-thiopivaloylthiophen; **5** and **5′**: 2-pivaloylselenophen and 2-thiopivaloylselenophen. X stands for O, S or Se, and Y for O or S.

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one hour at room temperature, then neutralized with dilute hydrochloric acid and extracted with ether. The oil obtained still contains some 2-methylindan-1-one which was separated by gas-phase chromatography: yield 35%; carbon-13 n.m.r. shifts (in p.p.m., from TMS) in $CDCl_3$, 211.2 (for C_1), 126.7, 134.9, 127.4, 135.4, 152.3.

4,5-*Dihydro-5-methylcyclopenta[b]thiophen-6-one* (**1**-a) was prepared as indicated by Meth-Cohn and Gronowitz [6]. Polyphosphoric acid (85 g), previously heated at 55 °C, was added to a mixture of thiophen (25 g), methacrylic acid (31 g) and methylene chloride (25 ml). The reaction mixture was stirred for 30 min at 55 °C, the solvent distilled and the residue hydrolyzed, then extracted with ether. Removal of the solvent gave an oil which, after drying with calcium chloride, was distilled: yield 40%, b.p. 138 °C at 17 mm Hg (lit. 137 °C at 15 mm Hg); carbon-13 n.m.r. shifts (in p.p.m., from TMS) in $CDCl_3$: 200.2 (for C_6), 140.9, 124.2, 140.0, 167.4.

Pivalophenone (**2**) was prepared as indicated by Tsatsas [7]: b.p. 105 °C at 17 mm Hg (lit. 102–104 °C at 14 mm Hg); carbon-13 n.m.r. chemical shifts (in p.p.m., from TMS) for the compound in $CDCl_3$: δ_α 208.8, δ_2 139.8, δ_3 128.2, δ_4 128.0, δ_5 130.8 (see Fig. 1 for atom numbering).

2-*Pivaloylfuran* (**3**) was prepared after Heathcock et al. [8]: b.p. 87 °C at 16 mm Hg (lit. 67 °C at 10 mm Hg); ^1H n.m.r. shifts (p.p.m.) in CCl_4: δ_3 7.12, δ_4 6.48, δ_5 7.51; carbon-13 shifts (in p.p.m., from TMS) in $CDCl_3$; δ_α 194.7, δ_2 152.9, δ_3 117.8, δ_4 111.8, δ_5 144.9.

2-*Pivaloylthiophen* (**4**) was synthesized according to Hoch [9]: b.p. 115 °C at 17 mm Hg (lit. 115–116 °C at 16 mm Hg); ^1H n.m.r. shifts (p.p.m.) in CCl_4: δ_3 7.78, δ_4 7.13, δ_5 7.57 (lit. 7.68, 7.01 and 7.47, respectively [10]); carbon-13 shifts (in p.p.m., from TMS) in $CDCl_3$: δ_α 197.7, δ_2 142.2, δ_3 131.8, δ_4 127.4, δ_5 131.4.

2-*Pivaloylselenophen* (**5**), a novel compound, was prepared as follows. To a mixed solution of selenophen previously dried with metallic sodium (0.04 mole) and pivalic anhydride (0.04 mole), was added (with caution) a solution of perchloric acid (some drops) in pivalic anhydride (1 ml). The reaction mixture was stirred for 5 h, washed with a saturated solution of sodium bicarbonate for 12 h, then extracted with ether, and distilled. Rectification of the residue gave the pure product: yield 30%, b.p. 92 °C at 3 mm Hg; ^1H n.m.r. shifts (in p.p.m.) in CCl_4: δ_3 7.93, δ_4 7.29, δ_5 8.20; carbon-13 shifts (in p.p.m., from TMS) in $CDCl_3$: δ_α 199.2, δ_2 150.6, δ_3 138.5, δ_4 130.8, δ_5 133.5.

All the ketones here examined were controlled by gas-phase chromatography and gave elemental analyses in agreement with the expected ones. Ring-closed **1** and **1**-a are characterized by their infrared and ultraviolet spectra, and compounds **2** to **5** only by their infrared spectra (Tables I and II).

The corresponding thioketones **1′**, **1′**-a, **2′–5′** were prepared from the relevant ketones as follows.

Tetraphosphorous decasulphide (4 g) and some celite were added to a benzene solution of the ketone (1 g). The reaction mixture was heated for one hour with stirring, then cooled and filtered. The filtrate was washed with sodium bicarbonate and water, and the solvent quickly distilled. The oil obtained was purified by gas-phase chromatography at 200 °C by using a 3-meter column of SE30. Absence of the carbonyl band in the infrared spectra showed their purity. Ultraviolet spectra are given in Table II. Because of their instability, no elemental analysis has been possible for all thioketones. Compound **1′** and **1′**-a are red, **2′** is violet, **3′** and **4′** are blue, and **5′** is green. The ^1H n.m.r. shifts (in p.p.m.) are in CCl_4

3′: δ_3 7.45, δ_4 6.51, δ_5 7.70;
4′: δ_3 7.50, δ_4 7.05, δ_5 7.50;
5′: δ_3 7.81, δ_4 7.52, δ_5 8.39.

The carbon-13 n.m.r. shifts (in p.p.m., from TMS) in $CDCl_3$ are

1′: 254.7 (for C_1), 125.0, 134.9, 127.7, 126.3;
1′-a: 140.7, 124.2, 155.4, 165.7;
2′: δ_α 266.0, δ_2 151.4, δ_3 124.9, δ_4 128.1, δ_5 127.5;
3′: δ_α 234.2, δ_2 161.0, δ_3 120.0, δ_4 111.8, δ_5 145.3;
4′: δ_α 242.1, δ_2 154.2, δ_3 136.6, δ_4 127.6, δ_5 128.5;
5′: δ_α 218.2, δ_2 162.8, δ_3 143.4, δ_4 128.4, δ_5 132.2.

Measurements

The infrared spectra were recorded on a Perkin-Elmer 225 spectrometer calibrated with water vapour. The absolute error was smaller than 1 cm^{-1} and the reproducibility within 0.25 cm^{-1}. Integrated-intensity determinations were carried out using NaCl cells (0.1 or 1 mm thick) by means of a method which consists in measuring the band area with a planimeter. The apparent integrated-in-

tensity (in $cm^{-2}\,mol^{-1}\,l$) is calculated by the equation

$$A' = (1/c\,l) \cdot \int_{\nu_1}^{\nu_2} \log_e(T_0/T)\,d\nu\,, \qquad (1)$$

where c is the concentration of the solute in $mol^{-1}\,l$) l the cell thickness in cm, ν_1 and ν_2 are the band edges in cm^{-1}, and T_0 and T the transmission factors out of the band and at the maximum of absorption, respectively.

The ultraviolet spectra were recorded with a Beckman Acta MVI spectrometer calibrated with a film of holmium oxide. The absolute error and reproducibility were 0.1 nm, and the maximum error in absorbance was ≦ 3%.

The ^1H n.m.r. spectra were taken with a Varian A-60D spectrometer calibrated with chloroform. The frequency error was 0.02 p.p.m.

The carbon-13 n.m.r. spectra were recorded with a Bruker WP-60 spectrometer. The frequency error was 0.2 p.p.m. Tetramethylsilane was used as internal reference.

Results and Discussion

Infrared Spectra

1) Aryl-carbonyl conjugation, in augmenting the polarity of the carbonyl bond, decreases the carbonyl stretching frequency and increases the intensity of the carbonyl band [11]. For Ar−COR compounds this type of conjugation depends on the nature of Ar and R, and on the angle of twist (φ) of the (RCO)-group. It follows that only similar systems (with the same alkyl and φ-angle) can be compared.

Benzaldehyde [12], 2-formylfuran [13], 2-formylthiophen [14] and, by analogy, 2-formylselenophen, are planar in the gaseous state, and this is also observed for acetophenone [15], 2-formyl-4-bromofuran [16] and 2-acetyl-5-bromothiophen in the crystalline state [17]. Experimental evidence supports nonplanarity for the corresponding pivaloyl compounds **2** [18−22], **3** and **4** in solution [23].

Table I lists the frequencies and apparent integrated-intensities of the carbonyl band for PhCHO, 2-FuCHO, 2-ThCHO and 2-SelCHO, PhCOMe, 2-FuCOMe, 2-ThCOMe and 2-SelCOMe, PhCO-t-Bu, 2-FuCO-t-Bu, 2-ThCO-t-Bu and 2-SelCO-t-Bu (Ph, 2-Fu, 2-Th and 2-Sel stand for the monovalent radicals from benzene, furan, thiophen and selenophen, respectively).

As referred to aliphatic acetaldehyde in carbon tetrachloride ($\nu_s(C{=}O) = 1730.4\ cm^{-1}$ [24]), the carbonyl frequencies of PhCHO, 2-FuCHO, 2-ThCHO and 2-SelCHO are −21.4, −28.9, −40.4 and −51.4 cm^{-1}, respectively, indicating that the Aryl-carbonyl conjugation in the series follows the order Ph < 2-Fu < 2-Th < 2-Sel. The formyl-group rotational barriers are 32.22, 45.57 and 42.5 kJ mol^{-1} in benzaldehyde [25], 2-formylfuran [26] and 2-formylthiophen [27], respectively.

The carbonyl frequencies and carbonyl-band integrated intensities (in carbon tetrachloride) for PhCOMe, 2-FuCOMe, 2-ThCOMe and 2-SelCOMe can be compared to the values for acetone, $\nu_s(C{=}O) = 1718\ cm^{-1}$, $A' = 1.48 \times 10^{-4}\ cm^{-2}\,mol^{-1}\,l$ [24]. The frequency differences are −27.0, −29.0, −43.0 and −49.0 cm^{-1}, and the integrated-intensity ratios are 1.26, 1.28, 1.35 and 1.49, respectively. These observations support the Aryl−carbonyl conjugation order to be Ph < 2-Fu < 2-Th < 2-Sel. The acetyl-group rotational barriers are 22.4 and 38.25 kJ mol^{-1} in acetophenone [28] and 2-acetylfuran [29], respectively.

For the pivaloyl compounds **1**−**4** the carbonyl-band frequencies and intensities are not strictly comparable because the Ar−CO-t-Bu twisting angles may differ in the series. Relative to methyl t-butyl ketone ($\nu_s(C{=}O) = 1711\ cm^{-1}$, $A' = 1.50 \times 10^{-4}\ cm^{-2}\,mol^{-1}\,l$ [30]), they are −29.0, −36.5, −33.0 and −48.0 cm^{-1}, and 0.88, 0.87, 1.19 and 0.97,

Table 1. Stretching frequency and apparent integrated-intensity of the carbonyl band of aromatic aldehydes and ketones[a].

Compound	ν_s[b]	A'[c]	Compound	ν_s[b]	A'[c]	Compound	ν_s[b]	A'[c]
PhCHO	1709	2.02	PhCOMe	1691	1.87	PhCO-t-Bu	1679	1.33
2-FuCHO	1701.5	2.60	2-FuCOMe	1689	1.90	2-FuCO-t-Bu	1671.5	1.30
2-ThCHO	1690	2.46	2-ThCOMe	1675	2.00	2-ThCO-t-Bu	1665 1657	1.78
2-SelCHO	1679	2.96	2-SelCOMe	1669	2.20	2-SelCO-t-Bu	1659 1645.5	1.45

[a] In carbon tetrachloride, [b] in cm^{-1}, [c] in $10^{-4} \times cm^{-2}\,mol^{-1}\,l$.

for **1** to **4**, respectively. Clearly, the (Ar−CO)-conjugation for these hindered ketones is at variance with that observed for planar PhCOMe, 2-FuCOMe, 2-ThCOMe and 2-SelCOMe, showing the role played by twisting both on the carbonyl frequencies and the integrated-intensities.

2-Pivaloylfuran (**3**) in tetrachlorethylene exhibits a well-symmetrical band centred at 1671.5 cm^{-1}, contrary to what is observed for 2-formylfuran, 2-acetylfuran and 2-benzoylfuran in the same medium [31]. This observation, however, may indicate rotational isomerism with one of the conformers to be predominant (≧ 70%), the more so as the compound shows an asymmetrical band in benzene, tetrahydrofuran and chloroform, at 1668, 1661 and 1661 cm^{-1}. In carbon tetrachloride and carbon disulphide a symmetrical band is observed at 1671.5 and 1668 cm^{-1}, respectively.

Both 2-pivaloylthiophen (**4**) and 2-pivaloylselenophen (**5**) exhibit a doublet in carbon tetrachloride (ν_s = 1665 and 1657 cm^{-1}, ν_s = 1659 and 1645.5 cm^{-1}, respectively), benzene (1665 and 1653, 1648 and 1643), tetrahydrofuran (1665 and 1652, 1658 and 1643), chloroform (1665 and 1647, 1653 and 1639), and carbon disulphide (1665 and 1652, 1658 and 1643). These facts can be due either to Fermi resonance with an overtone or to rotational isomerism with a small amount of one of the conformers. To gain more information in this respect, the infrared spectra in the range 1600−1700 cm^{-1} of ^{18}O-enriched compounds **4** and **5** were recorded in tetrachlorethylene at room temperature (Figures 2 and 3).

The infrared spectrum of ^{18}O-enriched **4** shows two distinct doublets, the first (ν_s = 1634.5 and 1623.0, $\Delta\nu_s$ = 11.5 cm^{-1}) from the isotopic ketone and the second (1665 and 1657, $\Delta\nu_s$ = 8.0 cm^{-1}) from the natural ^{16}O-compound. As the $\Delta\nu_s$ separations and intensity ratios of the components differ, such a splitting should be attributed to Fermi resonance with an overtone (or a combination band), the more so as a very weak band at 1634 cm^{-1} is observed in the spectrum of natural ketone. However, rotational isomerism cannot be precluded: if two conformers (*C* and *T*) occur they are likely to give both a doublet in the same frequency region, and the two bands observed could well be the superimposition of the bands of two conformers. As a matter of fact, the less abundant conformer-population does not exceed 20−30%. The dipole of **4** in benzene indicates a *C*-population of 90% [32],

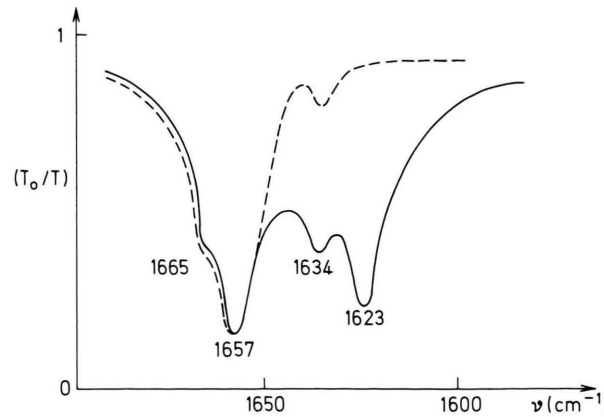

Fig. 2. Infrared spectra in the range of 1600−1700 cm^{-1} of ^{18}O-enriched and natural 2-pivaloylthiophen (**4**) in tetrachlorethylene; the dotted curve refers to the latter.

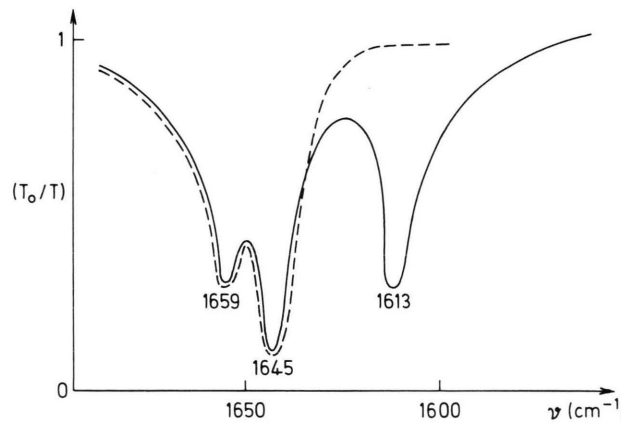

Fig. 3. Infrared spectra in the range of 1600−1700 cm^{-1} of ^{18}O-enriched and natural 2-pivaloylselenophen (**5**); the dotted curve refers to the latter.

while the Kerr-constant in carbon tetrachloride suggests a *C*-amount of (70 ± 20)% [23] (see Fig. 1 for the shapes of the conformers).

The infrared spectrum of ^{18}O-enriched **5** contains one band at 1613 cm^{-1} from the isotopic compound and a doublet (ν_s = 1659.0 and 1645.5, $\Delta\nu_s$ = 13.5 cm^{-1}) from the natural ketone, clearly indicating that the doublet is due to Fermi resonance. As temperature increases from 200 to 370 K, one of the doublet components remains at 1658 cm^{-1} while the other moves from 1640 to 1643.5 cm^{-1}: now only pure carbonyl bands behave like that with increasing temperature [33]. All these facts are consistent with a small amount of the less stable conformer. The dipole moment of **5** in benzene (3.03 D) suggests a *C*-population of 90% [32].

Table 2. Infrared spectra in the range of 1000–1300 cm^{-1} for 2-pivaloylfuran and 2-thiopivaloylfuran, 2-pivaloylthiophen and 2-thiopivaloylthiophen, 2-pivaloylselenophen and 2-thiopivaloylselenophen [a].

2-FuCO-t-Bu	2-FuCS-t-Bu	2-ThCO-t-Bu	2-ThCS-t-Bu	2-SelCO-t-Bu	2-SelCS-t-Bu
1291 (s) [b]	1290 (m)	1276 (s)	–	1273 (m)	–
–	–	–	1258 (s)	–	1258 (s)
1220 [c]	–	1231 (m) 1220 [c]	–	1231 (m)	1232 (w)
–	–	–	–	–	1199 (w)
–	–	1176 (s)	1180 (m)	–	–
1162 (sh.)	1160 (m)	1162 (sh.)	–	1169 (s)	1172 (s)
1151 (s)	1152 (sh.)	–	–	–	–
–	1124 (m) 1102 (m)	–	1119 (m) 1099 (m)	–	1095 (m)
1080	1082 (s)	1078 (w)	–	1076 (s)	1073 (m)
–	–	1057 (s)	1062 (s)	–	–
1046	–	1040 (w)	–	1046 (m)	1047 (s)
1009	1018 (s)	1020 (w)	1020 (w)	–	1018 (w)

[a] As pure liquids. [b] s, m, w, and sh, stand for strong, medium, weak, and a shoulder. [c] Three overlapping bands.

2) Comparison of the infrared spectra in the range 1000–1300 cm^{-1} of thiopivaloyl compounds **3′**, **4′** and **5′** with those of the corresponding ketones **3**, **4** and **5** shows that the skeletal ring-vibrations occur at a similar frequency for homologous compounds (Table 2). The intense band, centred at 1220 cm^{-1}, not observed in the spectra of thioketones, must then be attributed to the carbonyl group. Further, **3′** and **4′** both exhibit a doublet (ν_s = 1124 and 1102 cm^{-1}, ν_s = 1119 and 1099 cm^{-1}) and **5′** a singlet at 1095 cm^{-1}, which obviously must be ascribed to the thiocarbonyl group. The thiocarbonyl stretching frequency occurs at 1269 cm^{-1} for propanethione [30], at 1160–1180 cm^{-1} for various thiochromones [34], and at 1186–1195 cm^{-1} for several 2-thiobenzoylthiophens [35].

Even in the simple case of propanethione the skeletal (CCC)-vibration and (C=S)-vibration are strongly coupled [36], and this likely occurs for the ring-vibration and (C=S)-vibration of aromatic thioketones. As a consequence, no attempt has been made to interpret the vibration band at about 1200 cm^{-1} of thiopivaloyl compounds **2′**, **3′** and **4′** in terms of Aryl–thiocarbonyl conjugation and/or rotational isomerism.

Ultraviolet Spectra

An intramolecular charge-transfer absorption band (*K*-band), at about 240 nm, is observed in the ultraviolet spectra of aromatic ketones dissolved in hexane [37], the intensity of which is indicative of the magnitude of Aryl–carbonyl conjugation [18].

When passing from planar acetophenone to twisted pivalophenone (**2**) and from planar 2-acetylfuran, 2-acetylthiophen and 2-acetylselenophen to the 2-pivaloyl analogues (**3**, **4** and **5**), a small hypsochromic shift and a much greater hypochromic effect is observed, and this also occurs on going from planar 2,2-dimethylindane-1-thione (**1′**) to pivalophenethione (**2′**) and from 4,5-dihydro-5-methylcyclopenta[b]thiophene-6-thione (**1′**-a) to 2-thiopivaloylthiophen (**4′**) (see Table 3).

Since the energy of charge-transfer transitions in twisted acetophenones depends on the angle of twist (φ) as E (in eV) = (0.65) $f(\varphi)$ + 3.65 [38] with $f(\varphi) = \cos^2\varphi$ [21], it can be inferred that both the maximum absorption intensity (ε_{max}) and oscillator strength (f) vary as

$$\varepsilon = \varepsilon_0 \cos^2\varphi\,, \tag{2}$$

$$f = f_0 \cos^2\varphi\,. \tag{3}$$

Equation (2) has been applied by Braude and Sondheimer [18] and by Katritzky et al. [21], and (3) by Rekker and Nauta [39]. Ketones (and thioketones) to be compared must exhibit absorption bands at close wave-lengths, which is nearly true for **2** and acetophenone (and ring-closed **1**), **3** and 2-acetylfuran, **4** and 2-acetylthiophen (and ring-closed **1**-a), **5** and 2-acetylselenophen, **2′** and ring-closed **1′**, **4′** and ring-closed **1′**-a.

Taking the acetyl ketone as the reference compound calculation provides $\varphi = 35°$ (from (2)) and $\varphi = 31°$ (from (3)) for pivalophenone (**2**), $\varphi = 12$ and 12° for 2-pivaloylfuran (**3**), $\varphi = 18$ and 23° for

Table 3. Ultraviolet *K*-band absorption of aromatic and heteroaromatic ketones and thioketones [a, b].

Ketone [c]	λ_{max}	ε_{max}	f	Thioketone [c]	λ_{max}	ε_{max}	f
1	237	13 530	0.225	**1′**	308	11 700	0.224
PhCOMe	237	12 720	0.215				
PhCO-t-Bu	235	8 500	0.159	PhCS-t-Bu	291	3 510	0.068
2-FuCOMe	261	15 070	0.267				
2-FuCO-t-Bu	264	14 470	0.255				
1-a	259	11 100	0.228	**1′**-a	332	11 300	0.199
2-ThCOMe	255	10 000	0.219				
2-ThCO-t-Bu	258	9 020	0.187	2-ThCS-t-Bu	355	8 140	0.150
2-SelCOMe	265	11 020	0.237				
2-SelCO-t-Bu	269	9 580	0.206				

[a] In hexane.
[b] λ_{max} in nm, ε_{max} in cm^{-1} mol^{-1} l, and f (the oscillator strength) $= (4.32 \times 10^{-9})$. $\varepsilon_{max} \Delta\nu_{1/2}$.
[c] See Fig. 1 for the formulae of **1** and **1′**, **1**-a and **1′**-a.

Table 4. ^{1}H n.m.r. spectra of heterocyclic aldehydes, ketones and thioketones [a].

Compound	δ_3	δ_4	δ_5	Compound	δ_3	δ_4	δ_5
2-FuCHO [b]	7.45	6.74	7.94	2-FuCO-t-Bu [c]	7.12	6.48	7.51
2-ThCHO [b]	7.93	7.30	7.96	2-ThCO-t-Bu [c]	7.78	7.13	7.57
2-SelCHO [b]	8.17	7.54	8.68	2-SelCO-t-Bu [c]	7.93	7.29	8.20
2-FuCOMe [b]	7.32	6.65	7.81	2-FuCS-t-Bu [c]	7.45	6.51	7.70
2-ThCOMe [b]	7.80	7.17	7.80	2-ThCS-t-Bu [c]	7.50	7.05	7.50
2-SelCOMe [b]	8.02	7.43	8.52	2-SelCS-t-Bu [c]	7.80	7.52	8.39

[a] Chemical shifts (δ) in p.p.m.; see Fig. 1 for atom numbering.
[b] In hexadeuterioacetone [40].
[c] In carbon tetrachloride ($v/v \sim 0.2$).

2-pivaloylthiophen (**4**), and $\varphi = 21$ and 21° for 2-pivaloylselenophen (**5**). With ring-closed **1** or **1′** as reference, calculation yields 37 and 33° for **2**, and 57 and 57° for **2′**. Taking ring-closed **1**-a or **1′**-a as reference leads to 26 and 25° for **4**, and to 32 and 30° for **4′**.

The ultraviolet spectra of 2-thiopivaloylfuran (**3′**) and 2-thiopivaloylselenophen (**5′**) cannot be interpreted in a similar manner because attempts to synthesize the relevant ring-closed analogues of **1′**-a were unsuccessful.

^{1}H and ^{13}C nuclear magnetic resonance spectra

1) Only a qualitative discussion of the ^{1}H n.m.r. spectra of the carbonyl and thiocarbonyl derivatives listed in Table IV will be attempted.

Both the H_3 and H_5 chemical shifts of 2-acylfurans, 2-acylthiophens and 2-acylselenophens depend on the π-electron density at relevant carbon atom, C_3 or C_5 (see Figure 4). Since the H_3 shift also undergoes the effect of magnetic anisotropy and electric field of the adjacent carbonyl bond (which may differ in both *C*- and *T*-conformers), only the H_5 shift will be considered here.

The H_5 shifts of 2-formylfuran, 2-formylthiophen and 2-formylselenophen, relative to the H_2 shift of the relevant heterocycle (7.46, 7.40 and 8.10 p.p.m. in hexadeuterioacetone [40]), are 0.48, 0.56 and 0.58 p.p.m., respectively. A similar trend is observed for the H_5 shifts of 2-acetylfuran (0.35 p.p.m.), 2-acetylthiophen (0.40 p.p.m.) and 2-acetylselenophen (0.42 p.p.m.). This supports that, for planar 2-acyl chalcogen-heterocycles, the ring–carbonyl conjugation follows the order 2-Fu < 2-Th ≦ 2-Sel in accordance with what is concluded from infrared spectroscopy (p. 1331).

The fact that the H_5 shifts are (by 0.13, 0.16 and 0.16 p.p.m.) higher for 2-formylfuran, 2-formylthio-

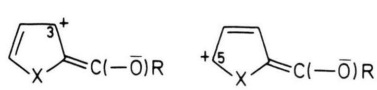

Fig. 4. Valence bond structures for 2-acyl and 2-thiopivaloyl chalcogen-heterocycles with a unitary π-charge at the C_3 and C_5 carbon atoms.

phen and 2-formylselenophen than for the 2-acetyl analogues, respectively, is indicative of greater ring-formyl conjugation. The (RCO)-group rotational barriers in benzaldehyde and 2-formylfuran are higher than in acetophenone and 2-acetylfuran, respectively.

The H_5 shifts for 2-pivaloyl compounds **3, 4** and **5** in carbon tetrachloride are lower (by 0.30, 0.23 and 0.32 p.p.m.) than those for 2-acetylfuran, 2-acetylthiophen and 2-acetylselenophen, respectively. This reflects twisting in the 2-pivaloyl chalcogen-heterocycles.

2-Thiopivaloyl compounds (**3′**, **4′** and **5′**) cannot be safely compared to the corresponding ketones (**3**, **4** and **5**) because the ring−thiocarbonyl conjugation is (for similar unsaturated systems) of greater magnitude [3, 41], and the twisting angles are markedly larger.

2) Amongst the carbon-13 chemical shifts of the ketones and thioketones listed in Table 5, only the side-chain carbon and 5-carbon shifts will be examined.

Dhami and Stothers [19, 44, 45] have shown that the side-chain carbon shifts (δ_α) of overcrowded acetophenones and pivalophenones are related to the magnitude of ring−carbonyl conjugation and, thereby, to the angle of twist (φ). For pivalophenone (**2**), they found that the carbonyl shielding is towards lower fields by −4.1 p.p.m. relative to isobutyrophenone (which can be regarded as having its Ph−COCH residue planar) while the difference in the carbonyl-carbon shift is 0.8 p.p.m. between 2-methylbutanone and 2,2-dimethylbutanone, and 0.2 p.p.m. only between diisopropyl ketone and di-t-butyl ketone. The part due to twisting in **2** should be $\Delta\delta_\alpha = -4.1 + [(0.8 + 0.2)/2] = -3.6$ p.p.m., and the twisting angle of 25°, calculated by solving the appropriate equation [19],

$$\cos^2\varphi = (\Delta\delta_\alpha + 20)/20 \,. \qquad (4)$$

A comparison of our δ_α value for **2** (208.8 p.p.m.) with the literature figure for acetophenone (196.9 p.p.m. [42]) leads to a φ-angle of 33°, taking into account the difference in the carbonyl-carbon shift (5.9 p.p.m. [46]) between acetone and 2,2-dimethylbutanone. This value compares well with that drawn from the ultraviolet spectrum of **2** in hexane (35 or 31°).

Equation (4) is not applicable to 2-pivaloyl and 2-thiopivaloyl chalcogen-heterocycles because the denominator term (20 p.p.m.) was calculated from the carbonyl-carbon shifts of benzene derivatives (see [44]). However, the observation that the differences in the carbonyl-carbon shifts between **3** and 2-acetylfuran (8.3 p.p.m.), **4** and 2-acetylthiophen (7.0 p.p.m.), **5** and 2-acetylselenophen (7.8 p.p.m.), are markedly higher than that (5.9 p.p.m.) between aliphatic 2,2-dimethylbutanone and acetone indicates twisting in the 2-pivaloyl compounds *.

It has been recognized that the para-carbon chemical shift of monosubstituted benzenes is proportional to the π-electron density [49]. The δ_5 chemical shifts of the ketones listed in Table 5, as referred to that of benzene (128.5 p.p.m. [42]) or the relevant heterocycle (δ_2(furan) = 142.7 [50], δ_2(thiophen) = 124.9 [51], δ_2(selenophen) = 131.4 [52]), are then indicative of the total π-electron density Q_π at the 5-carbon atom (see Fig. 1 for atom numbering). Now, Q_π can be regarded as the sum of two distinct terms (q_I and q_M), originating from the π-inductive effect and the φ-dependent mesomeric effect of the acyl-group, respectively, and $\Delta\delta_5$ can then be divided in two terms (τ_I and τ_M). Since q_M (at the *para*-carbon atom of acetophenones) is a fraction of the acyl mesomeric moment which varies as $m = m_0 \cdot \cos^2\varphi$ [48, 53, 54], τ_M should also vary as

$$\tau_M = \tau_M(0°)\cos^2\varphi \,. \qquad (5)$$

The τ_I term in acetophenones (and 2-acyl chalcogen-heterocycles) can be estimated as follows: for

Table 5. Carbon-13 n.m.r. spectra of aromatic and heteroaromatic ketones [a].

Compound [b]	δ_2	δ_3	δ_4	δ_5	δ_α
PhCOMe [c]	137.4	128.6	128.4	132.9	196.9
2-FuCOMe [d]	132.7	117.5	112.3	146.8	186.4
2-ThCOMe [d]	144.5	132.6	129.2	133.8	190.7
2-SelCOMe [e]	152.4	135.4	131.1	140.8	191.4
PhCO-t-Bu	139.9	128.1	128.0	130.8	208.8
2-FuCO-t-Bu	152.9	117.8	111.8	144.9	194.7
2-ThCO-t-Bu	142.2	133.6	127.4	129.6	197.7
2-SelCO-t-Bu	150.6	138.5	130.8	133.5	199.2

[a] In deuteriochloroform ($w/w \sim 0.25$).
[b] See Fig. 1 for atom numbering; the chemical shifts are in p.p.m., and δ_α refers to the carbonyl carbon shift.
[c–e] From Ref. [42], [43] and [40], respectively.

* Twisting raises the carbonyl-carbon shift: as referred to tetramethylsilane, δ_5 is 196.9 p.p.m. for planar acetophenone [42] and 208.4 p.p.m. for twisted 2,6-dimethylacetophenone [47], characterized by a twisting angle of 55° [48].

2,6-dimethylacetophenone, a twisted molecule in which the acetyl mesomeric effect (and the τ_M term) is strongly reduced because of large twisting ($\varphi = 55°$ [48]), the *para*-carbon shift (128.65 p.p.m. [47]) is, by 0.55 p.p.m. only, superior to the value for *meta*-xylene (128.10 p.p.m. [55]). It then follows that τ_I (for acetophenone) should be 0.55 at the very most. In the following calculations, τ_I has been taken as 0.3 ± 0.1; the assumed uncertainty leads to an error of $\pm 2°$ on calculated φ-angles. On these bases, calculation provides: $\varphi = 46°$ for pivalophenone (**2**), 45° for 2-pivaloylfuran (**3**), 44° for 2-pivaloylthiophen (**4**), and 64° for 2-pivaloylselenophen (**5**), which are all markedly higher than those drawn from the ultraviolet spectra of **2**–**5** in hexane (35, 12, 23 and 21°).

Conclusions

The infrared carbonyl-band frequencies and intensities indicate the order Ph < 2-Fu < 2-Th ≦ 2-Sel for the Aryl–carbonyl conjugation in planar benzaldehyde, 2-formylfuran, 2-formylthiophen and 2-formylselenophen, acetophenone, 2-acetylfuran, 2-acetylthiophen and 2-acetylselenophen. The same order is given by the ^{1}H n.m.r. spectra of these planar 2-acyl chalcogen-heterocycles. Because of twisting, the order may differ for the corresponding pivaloyl ketones (**3**–**5**).

Analysis of the carbonyl band of 2-pivaloylfuran (**3**), ^{18}O-enriched 2-pivaloylthiophen (**4**) and 2-pivaloylselenophen (**5**) enables a discussion of their conformational (*C*)/(*T*) ratios.

Ultraviolet and ^{13}C n.m.r. spectra (through the *para*-carbon or C_5 chemical shift) suggest the indicative twisting angles: 35 or 46° for **2**, 15 or 45° for **3**, 20 or 44° for **4**, and 20° or 64° for **5**, while the ultraviolet spectra of thiopivaloyl compounds **2′** and **4′** afford 57° in the former and 30° in the latter. The literature values for the twisting angles of **2** are 34 or 33° from UV spectra [18, 21], 25° from the ^{13}C n.m.r. carbonyl-carbon shift [19], 63 or 44° by dipole moment analysis [20, 32], 33° from the IR spectrum [21], 37° from the molecular refraction [56], and 49° from the Kerr-constant [22]; the electric birefringences of **3** and **4** are consistent with 15 and 27°, respectively [23], and dipole moment analysis of **2′** provides $55 \pm 5°$ [32].

Although (for analogous planar unsaturated systems) the Aryl–thiocarbonyl conjugation is greater [3, 41], pivalophenethione (**2′**) exists in a more twisted conformation than the oxygen analogue (**2**). This may be due to greater van der Waals repulsion between the sulphur and *ortho*-phenyl hydrogen atoms (the van der Waals radii of sulphur and oxygen are 1.85 and 1.40 Å [57]), and to stronger electrostatic attraction between the carbonyl oxygen and *ortho*-phenyl hydrogen atoms (see [58])*. As shown by the dipole moments of gaseous formaldehyde (2.34 D [61]) and thioformaldehyde (1.65 D [62]), the carbonyl moment (1.94 D, for μ(H–C) = 0.40 D) is much higher than the thiocarbonyl one (1.25 D) and, further, it includes a markedly lower trigonal-heteroatom hybridization moment (μ_h), nearly equal to half the resultant of the two heteroatom sp^2-hybridized lone-pair moments [63]: μ_h(O) = 1.6 D and μ_h(S) = 2.8 D [63], or (probably better) 0.48 and 0.83 D, respectively [64]. This results in the carbonyl oxygen being certainly much more negatively charged than the thiocarbonyl sulphur, the charge of which might be slightly positive [65]**. Thus, the steric factor plays a major role in the actual conformations of **2′** and **2**.

Larger Aryl–carbonyl conjugation and smaller (H_3,t-Bu) repulsion may explain why 2-pivaloylthiophen (**4**) and 2-pivaloylselenophen (**5**) (both mostly existing as *C*) are less twisted than pivalophenone (**2**), and this also holds for thiopivaloyl compounds **4′** and **2′**. Some electrostatic attraction likely occurs between the heterocyclic heteroatom (S or Se) and the carbonyl oxygen in both **4** and **5** as *C* (see [32]).

2-Pivaloylfuran (**3**) prefers to exist as *T* (66%) with a smaller twisting angle, principally because in *C* the (O,O)-repulsion outweighs the (C_3–C_2–C=O) chain being more stable as s-*trans* [32]; $\Delta G°$(anti-syn) is 8.62 kJ mol^{-1} for acrylaldehyde [66].

* Note that thioformanilide, unlike formanilide existing as a mixture of *cis*- and *trans*-forms with (*c*)/(*t*) = 55/45 [59], uniquely occurs as *cis* (i.e. *trans*-(Ph, S)) [60].

** $q(Y) = (\mu - \mu_h)/(4.8\, r) = 0.06$ or $0.25\, e$ for Y = O, and -0.20 or $+0.05\, e$ for Y = S, according to adopted $\mu_h(Y)$.

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