Preferred Conformations of Pivalophenone, (2-Pivaloyl)- and (2-Aroyl)-furans, (2-Pivaloyl)- and (2-Aroyl)-thiophens, (2-Pivaloyl)- and (2-Benzoyl)-selenophen, and their Sulphur Analogues

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Analysis of the dipole moments of the title compounds enables to elucidate their preferred conformations in benzene solutions. 2,2-Dimethylindan-1-one and -1-thione, 4,5-dihydro-5-methylcyclopenta[b]thione-6-one and -6-thione were taken as models for comparisons. In this work, thirty-eight dipole moments are measured and interpreted comprehensively.

Introduction

Unlike the 2-acyl chalcogen-heterocycles, which have been extensively studied [1–3], the 2-thioacyl analogues have been little examined [4, 5]. Therefore, a comparative study of these two families of compounds is still missing.

In the present work the electric dipole moments of the compounds quoted in Table 1 (where 2-Fu, 2-Th and 2-Sel designate one of the isomeric monovalent radicals from furan, thiophen and selenophen) were determined in benzene solution.

Whereas pivalophenone and pivalophenethione can exist in one conformation only, the 2-acyl and 2-thioacyl chalcogen-heterocycles can occur in two (or four) conformations which unequally contribute to the actual mixture of the compound dissolved in benzene (see Figures 1–4).

Experimental

Materials

R. P. Normapur benzene (for cryoscopy) and carbon tetrachloride (for spectroscopy), both from Prolabo (Paris), were distilled and dried with metallic sodium and molecular sieves, or with the latter only; at 30.0 °C, they presented the physical constants (d_4 and ε, the dielectric permittivity referred to that of benzene at 25.0 °C taken as 2.2741): 0.8687 and 2.2642, 1.5748 and 2.2208.

2-2-*Dimethylindan*-1-*one* and -1-*thione* (**1** and **1′**), *pivalophenone* (n_D 1.5045 at 30.0 °C, lit. 1.5094 at 20.0 °C [6]) and *pivalophenethione* (**2** and **2′**), 2-*pivaloylfuran* and 2-*thiopivaloylfuran* (**3** and **3′**), 2-*pivaloylthiophen* (n_D 1.5308 at 30.0 °C, lit. 1.5359 at 20.0 °C [7]) and 2-*thiopivaloylthiophen* (**4** and **4′**), 2-*pivaloylselenophen* and 2-*thiopivaloylselenophen* (**5** and **5′**), were all prepared and described as indicated in [5].

Parachloropivalophenone (**2**-a) (n_D 1.5229 at 30.0 °C, lit. 1.5309 at 16.0 °C [8]) was prepared as indicated by Tsatsas [9] for pivalophenone: b.p. 89–90 °C at 1 mm Hg (lit. 84–86 °C at 0.7 mm Hg [8]), and 2-*pivaloyl*(5-*chlorothiophen*) (**4**-a) as recommended by Hoch [10] for 2-pivaloylthiophen: m.p. 48 °C.

2-*Benzoylfuran* (**6**) was prepared as indicated by Gol'dfarb [11] (cf. [12]): b.p. 160 °C at 18 mm Hg (lit. 132–133 °C at 5 mm Hg [7]).

2-*Benzoylthiophen* (**7**) (b.p. 120 °C at 2 mm Hg, m.p. 57 °C; lit. b.p. 113–117 °C at 1.5 mm Hg, m.p. 56–57 °C [13]), 2-*benzoyl*(5-*chlorothiophen*) (**7**-a) (m.p. 64 °C, lit. 63–64 °C [14]), 2-(2′-*methylbenzoyl*)-*thiophen* (**7**-b) (b.p. 175 °C at 15 mm Hg, m.p. 75 °C; lit b.p. 180 °C at 18 mm Hg [15]), 2-(2′-*fluorobenzoyl*)*thiophen* (**7**-c) (b.p. 180 °C at 5 mm Hg,

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n_D 1.6149 at 20.0 °C), 2-(4′-*fluorobenzoyl*)*thiophen* (**7**-c′) (m.p. 95.5 °C, lit. 95.5–96.0 °C [16]), 2-(2′-*chlorobenzoyl*)*thiophen* (**7**-d) (b.p. 150 °C at 1 mm Hg, m.p. 42 °C; lit. b.p. 147 °C at 0.6 mm Hg [17]), 2-(4′-*chlorobenzoyl*)*thiophen* (**7**-d′) (m.p. 99 °C, lit. 99.5–100.0 °C [14]), and 2-(4′-*bromobenzoyl*)*thiophen* (**7**-e′) (m.p. 102 °C, lit. 103 °C [18]) were prepared as indicated in [19].

2-*Benzoylselenophen* (**8**) was synthesized by adding, at 0 °C, aluminium chloride (0.02 mol) to a mixture of benzoyl chloride (0.02 mol) and selenophen (0.02 mol) in carbon disulphide (100 ml). The reaction mixture was stirred for two hours at room temperature, then hydrolysed, washed with hydrochloric acid 1 N, soda 1 N, and water, and the ketone recrystallized in petroleum ether, m.p. 58 °C (lit. 57–58 °C [20]).

3-*Benzoylfuran* (**9**) (b.p. 145 °C at 15 mm Hg, lit. 105 °C at 1.8 mm Hg [21]), *di*-(2-*furyl*)*ketone*, (**10**) (b.p. 150 °C at 18 mm Hg, lit. 102 °C at 1 mm Hg [22]), 2-*furyl* 3-*furyl ketone* (**11**) (m.p. 57 °C), 2-*furyl* 2-*thienyl ketone* (**12**) (b.p. 133 °C at 3 mm Hg, lit. 134–136 °C at 3 mm Hg [23]), and 3-*furyl* 2-*thienyl ketone* (**13**) (m.p. 46 °C) were prepared after Fournié-Zaluski and Chatain-Cathaud [12], and *di*-(2-*thienyl*)*ketone* (**14**) (b.p. 159–160 °C at 1 mm Hg, m.p. 87 °C; lit. b.p. 189–190 °C at 10 mm Hg, m.p. 88–89 °C [24]) after Andrieu, Mollier and Lozac'h [19].

Parachloropivalophenethione (**2′**-a) (violet liquid, mass spectrum: *m/e* 212 (M^+), 155, 111, 101, 57), 2-*thiobenzoylfuran* (**6′**) (green oil), 2-*thiobenzoylthiophen* (**7′**) (green oil), 2-*thiobenzoyl*(5-*chlorothiophen*) (**7′**-a) (green crystals, m.p. 63 °C), 2-(4′-*fluorothiobenzoyl*)*thiophen* (**7′**-c′) (blue crystals, m.p. 70 °C), 2-(4′-*chlorothiobenzoyl*)*thiophen* (**7′**-d′) (blue crystals, m.p. 63 °C), 2-(4′-*bromothiobenzoyl*)*thiophen* (**7′**-e′) (blue crystals, m.p. 61 °C), and *di*-(2-*thienyl*)*thioketone* (**14′**) (green needles, m.p. 47 °C), were all prepared as indicated in [19]. All these compounds gave elemental analyses in accord with the expected ones. The ^1H and ^{13}C n.m.r. spectra were also recorded.

Measurements

The electric dipole moments were determined in benzene solution at 30.0 °C by using the well-known Debye refractivity method. The total polarization of the solute, extrapolated to infinite dilution, was calculated from the experimental ratios [25],

$$\alpha_0 = \lim_{w \to 0} \left[\frac{\varepsilon - \varepsilon_1}{w} \right] \quad \text{and} \quad \beta = \frac{\sum (v - v_1)}{\sum w},$$

where w is the weight fraction of the solute, ε and v are the dielectric permittivity and specific volume of the solutions, respectively, and subscript one refers to the pure solvent as used, i.e. made up in the same way as the solutions. The α_0 value was calculated from the linear function, $\alpha = \alpha_0 + \alpha' w$, obtained by least-squares analysis of the $\varepsilon(w)$ polynomial (quadratic) function.

The distortion polarization of the solute, ${}_EP + {}_AP$, was assumed to equal the molecular refraction for the sodium D line (R_D). Literature values, measured on the liquids, were adopted for indanone (39.14 $cm^3\,mol^{-1}$ [26]), pivalophenone (**2**) (50.02 [8]), 2-pivaloylthiophen (**4**) (48.88 [7]), 2-benzoylfuran (**6**) (50.17 [7]), 2-benzoylthiophen (**7**) (56.11 [27]), and 2-furyl 2-thienyl ketone (**12**) (48.14 [7]). The molecular refractions of the other components here examined (see Table 1) were calculated assuming additivity as follows (a parenthesis stands for R_D, in $cm^3\,mol^{-1}$): (thioketone) = (ketone) + (C=S) − (C=O) = (ketone) + 11.91 [28] − 3.32 [28]; (**1**) = 39.14 [26] + 2 × (CH_2) = 39.14 + 2 × 4.65 [29]; (**2** and **6**) = (**4** or **7**) + (furan) − (thiophen) + 0.63 = 48.88 [7] or 56.11 [27] + 18.37 [30] − 24.37 [31] + 0.63*; (**2**-a, **4**-a and **7**-a) = (**2**, **4** or **7**) + (2-ThCl) − (thiophen) = (**2**, **4** or **7**) + 29.32 [31] − 24.37 [31]; (**7**-b to **7**-d, **7**-c′ to **7**-e′) = (**7**) + (PhMe, PhF, PhCl or PhBr) − (benzene) = 56.11 [27] + (31.10, 25.98, 31.14 or 33.99 [28]) − 26.18; (**5** and **8**) = (**4** or **7**) + (selenophen) − (thiophen) = 48.88 [7] or 56.11 [27] + 27.96 [32] − 24.37 [31] − 0.63; (**10** and **14**) = (**12**) ± (furan) ∓ (thiophen) ± 0.63 = 48.14 [7] ± 18.37 [30] ∓ 24.37 [31] ± 0.63; (**9**, **11** and **13**) = (**6**, **10** or **12**) + (3-FuCHO) − (2-FuCHO) = (50.17 [7], 43.77 for (**10**), or 48.14 [7]) + 25.27 [33] − 25.37 [34]. Refractions determined in benzene solution were found to be in accord, within 0.3 − 0.5

* The mesomeric increase of the refraction is 0.63 or 1.29 $cm^3\,mol^{-1}$ greater for 2-acetylfuran than for 2-acetylthiophen and 2-acetylselenophen, respectively, since (2-FuCOMe) − (furan) = 29.66 [27] − 18.37 [30] = 11.29, (2-ThCOMe) − (thiophen) = 35.03 [7] − 24.37 [31] = 10.66, and (2-SelCOMe) − (selenophen) = 37.96 [20] − 27.96 [32] = 10.00. (2-Fu, 2-Th and 2-Sel stand for 2-furyl, 2-thienyl and 2-selenyle, respectively.)

Table 1. Physical data from dipole moment determinations[a].

Nr.	Compound[b]	t (°C)	w_{max}	α_0	$-\beta$	$P_{2\infty}$	R_D	μ/D
1	2.2-Dimethylindan-1-one	30.0	0.041	7.50	0.177	274.5	48.44	3.35[c]
1′	2.2-Dimethylindan-1-thione	30.0	0.017	6.40	0.235	262.1	57.03	3.19
2	PhCO-t-Bu (in benzene)	30.0	0.036	4.64	0.118	192.4	50.02	2.66[c]
2	PhCO-t-Bu (in CCl_4)	30.0	0.030	8.25	− 0.398	191.3	50.02	2.65
2-a	*P*-ClC_6H_4CO-t-Bu	30.0	0.075	3.15	0.250	170.2	54.98	2.39
2′	PhCS-t-Bu	31.0	0.015	3.90	0.133	185.8	58.60	2.52
2′-a	*P*-ClC_6H_4CS-t-Bu	30.0	0.008	2.45	0.238	156.5	63.56	2.15
3	2-FuCO-t-Bu	20.0	0.025	5.65	0.150	204.8	43.51	2.79
3′	2-FuCS-t-Bu	30.0	0.006	4.45	0.209	188.9	52.10	2.61
4	2-ThCO-t-Bu	25.0	0.032	6.24	0.220	243.8	48.88	3.09[d]
4-a	2-(5-ClC_4H_2S)CO-t-Bu	25.0	0.025	5.60	0.302	263.3	53.83	3.20[d]
4′	2-ThCS-t-Bu	30.0	0.010	5.45	0.242	240.5	57.47	3.02[d]
4′-a	2-(5-ClC_4H_2S)CS-t-Bu	27.6	0.013	4.73	0.367	246.3	62.42	3.01
5	2-SelCO-t-Bu	26.0	0.027	4.70	0.401	238.5	51.81	3.03
5′	2-SelCS-t-Bu	30.0	0.012	3.90	0.410	222.1	61.06	2.83
6	2-FuCOPh	25.0	0.016	7.41	0.319	282.1	50.17	3.37[e]
6′	2-FuCSPh	20.0	0.022	6.65	0.296	280.2	58.76	3.26
7	2-ThCOPh	25.0	0.037	7.10	0.345	299.7	56.11	3.45[e]
7-a	2-(5-ClC_4H_2S)COPh	20.0	0.025	6.73	0.373	329.8	61.06	3.63
7-b	2-ThCO(C_6H_4Me-2′)	25.0	0.044	6.21	0.303	286.9	61.03	3.32
7-c	2-ThCO(C_6H_4F-2′)	25.0	0.030	7.84	0.368	351.7	55.91	3.80
7-c′	2-ThCO(C_6H_4F-4′)	25.0	0.026	5.56	0.394	261.7	55.91	3.17
7-d	2-ThCO(C_6H_4Cl-2′)	25.0	0.038	8.40	0.407	400.6	61.07	4.08
7-d′	2-ThCO(C_6H_4Cl-4′)	25.0	0.019	5.15	0.403	264.7	61.07	3.16
7-e′	2-ThCO(C_4H_4Br-4′)	25.0	0.037	4.49	0.524	274.9	63.92	3.21
7′	2-ThCSPh	25.0	0.020	6.35	0.355	292.0	64.70	3.33
7′-a	2-(5-ClC_4H_2S)CSPh	20.0	0.032	5.70	0.369	307.9	69.65	3.39
7′-c′	2-ThCS(C_6H_4F-4′)	25.0	0.019	5.09	0.407	261.5	64.50	3.10
7′-d′	2-ThCS(C_6H_4Cl-4′)	27.6	0.013	4.85	0.448	268.5	69.66	3.13
7′-e′	2-ThCS(C_6H_4Br-4′)	25.0	0.042	3.90	0.543	258.4	72.51	3.02
8	2-SelCOPh	20.0	0.012	5.83	0.552	316.6	59.60	3.52
9	3-FuCOPh	25.0	0.042	4.51	0.280	190.4	50.07	2.62
10	2-FuCO(2-Fu)	25.0	0.021	9.06	0.355	314.4	42.77	3.65
11	2-FuCO(3-Fu)	25.0	0.015	5.15	0.314	197.2	42.67	2.75
12	2-FuCO(2-Th)	25.0	0.055	7.50	0.398	290.9	48.14	3.45
13	3-FuCO(2-Th)	25.0	0.033	6.10	0.351	246.5	48.04	3.12
14	2-ThCO(2-Th)	25.0	0.032	8.00	0.420	334.2	53.51	3.71
14′	2-ThCS(2-Th)	25.0	0.018	7.71	0.434	349.4	62.10	3.75

[a] In benzene solution, if not otherwise specified.
[b] Ph, 2-Fu, 2-Th, 2-Sel, t-Bu and Me stand for phenyl, 2-furyl, 2-thienyl, 2-selenyl, tertiobutyl and methyl, respectively.
[c] See [38] and [39] for literature values prior to 1971. — [d, e] Lit.: cf. [4] and [40], respectively.

$cm^3\,mol^{-1}$, with the values so calculated; the latter were adopted for the sake of homogeneity.

The techniques used for measuring the dielectric permittivities, specific volumes and refraction indices of solutions and solvent are described in [35] to [37].

Results

For each solute, the maximal value of w (given with only three decimal places though it is known to five to six), α_0, β (in $cm^3\,g^{-1}$), $P_{2\infty}$ and R_D (both in $cm^3\,mol^{-1}$), and μ (in Debye units) are listed in Table 1*.

Discussion

Pivalophenone and pivalophenethione, which do not present rotational isomerism, will be discussed first.

* 1 Debye (D) = 3.336×10^{-30} C m. In our opinion the Debye unit, which is still widely used, is more adequate to molecular structure data.

Twisted Conformations of Pivalophenone and Pivalophenethione

1) Since μ(Me−C) is equal to μ(H−C), the dipole moment of 2,2-dimethylindan-1-one (**1**) (3.35 D) is, as expected, close to that of indan-1-one (3.31 D [41]).

The dipole moments of **1** and its sulphur analogue **1′** (3.35 and 3.19 D) can be regarded as resultants of two vectors, μ(Alkyl−phenylene) and μ(Phenylene−CYR) = μ_0 (for Y=O) or μ_0' (for Y=S). The first vector makes an angle of 75° with the C=Y bond axis as determined on the X-ray structure of 5,7-dimethoxyindan-1-one [42], and it can be taken as the dipole moment of t-butylbenzene (0.70 D [43]); the second one likely acts (as the dipole moment of acetophenone, 2.95 D [44]) at 50° to the $C_{7a}-C_1$ bond axis [37] (see Fig. 1 for atom numbering). On these bases, calculations provide μ_0 = 3.16 D and μ_0' = 2.99 D. A comparison of these values with the (Phenylene−CYR) primary moments, μ(MeCO-t-Bu) = 2.70 D [45] and μ(MeCS-t-Bu) = 2.26 D [4], indicates that the m(Phenylene−CYR) mesomeric moment in **1′** is 1.6 times that in **1**, a result consistent with what is observed for other thiocarbonyl and carbonyl planar unsaturated systems [4, 46].

2) For obvious steric reasons, pivalophenone (**2**) and pivalophenethione (**2′**) likely occur in a twisted conformation, characterized by a rotational angle φ or φ' (see Figure 1).

Vector triangulation of the dipole moments of *p*-chloropivalophenone (**2**-a) and *p*-chloropivalophenethione (**2′**-a) (2.39 and 2.15 D), in terms of μ(**2**) or μ(**2′**) (2.66 and 2.52 D) and μ(PhCl) = 1.59 D [47], provides the angle (62.5 or 58.0°) that μ(**2**) and μ(**2′**) make with the Ph−CY bond axis.

A significant value for the mesomeric moment of **2** (m*) is obtained by comparing its dipole moment (2.66 D) with that of 2,4,6-trimethylpivalophenone (2.50 D [45]) since the latter ketone (like 2,4,6-trimethyl-3-pivaloylbenzoic acid, characterized by a φ-angle of 89.9° [48]) should occur in an orthogonal conformation with no mesomeric moment. This leads to m*(**2**) = 0.24 D (see [37] for details of the calculation)*. Comparing this value with the mesomeric moment of planar acetophenone (m_0 = 0.46 D [37]) and solving the equation [49, 36],

$$m^* = m_0 \cos^2 \varphi, \tag{1}$$

yields $\varphi = 44 \pm 5°$, to be compared with the determinations from UV spectra (34° [50], 33° [51] or 33° [5]), ^{13}C n.m.r. spectra (25° [52] or 45° [5])**, dipole moments (63° [45], by a different method), IR spectra (33° [51]), molar refractions (37° [53]), and Kerr-constants (49 ± 5° [54]).

Calculation of the mesomeric moment (m'*) of **2′** is less straightforward. The primary moment can be taken as μ(MeCS-t-Bu) = 2.26 D [4] and the moment for hypothetic, planar pivalophenethione as μ_0' = 2.99 D from μ(**1′**) (*vide supra*). It follows that m'^* = 0.35 D and m_0' = 1.07 D, whence $\varphi' = 55 \pm 5°$, a value which compares well with that (55°) drawn from ultraviolet spectroscopy [5].

The observation $\varphi' > \varphi$ (55 as against 49°) shows that the steric effect, being greater in the sulphur derivative in similar conditions (see [55]), outweighs its stronger mesomeric effect in determining the conformations of **2′** and **2**. Similarly, the twisting angle has been found to be greater in 2,4,6-tri-t-butylthiobenzaldehyde (φ' = 89.1° [56]) than in 2,4,6-tri-t-butylbenzaldehyde (φ = 65° [55]).

Conformations of 2-pivaloyl and 2-thiopivaloyl chalcogen-heterocycles

2-Pivaloylfuran (**3**), 2-pivaloylthiophen (**4**) and 2-pivaloylselenophen (**5**), and their sulphur analogues (**3′** to **5′**), can occur in two twisted *C*- and *T*-conformations with the (C=Y) group being close to, or away from, the heterocyclic heteroatom (Figure 2).

It has been recognized that 2-furyl and 2-thienyl conjugating abilities are superior to that of phenyl

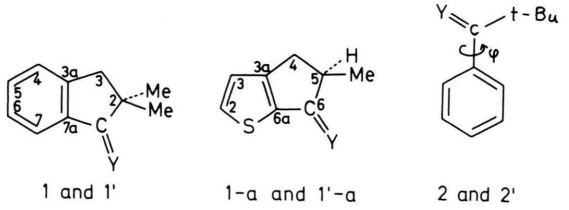

Fig. 1. **1** and **1′**: 2,2-Dimethylindan-1-one and -1-thione; **1**-a and **1′**-a: 4,5-dihydro-5-methylcyclopenta[b]thiophen-6-one and -6-thione; **2** and **2′**: pivalophenone and pivalophenethione. Y stands for O or S.

* In Ref. [37], p. 174, line 16 should read "where τ is the angle that the vector $\boldsymbol{m}_0$ makes with the $C_{ar}-C$ bond axis". A better value for τ is 16.8° instead of 15°; this does not change the results given before.

** The first value from the carbonyl-carbon shift [52], the second one as derived from the *para*-carbon shift by employing an original method [5].

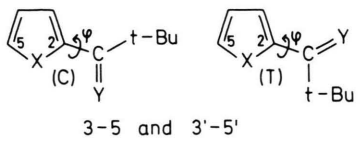

Fig. 2. **3** and **3'**: 2-Pivaloylfuran and 2-thiopivaloylfuran; **4** and **4'**: 2-pivaloylthiophen and 2-thiopivaloylthiophen; **5** and **5'**: 2-pivaloylselenophen and 2-thiopivaloylselenophen. X stands for O, S or Se, and Y for O or S.

in similar conditions [4, 5]. The barriers to rotation of the formyl-group are 45.6, 42.5 and 32.2 kJ mol^{-1} in 2-formylfuran [57], 2-formylthiophen [58] and benzaldehyde [59], respectively. As a consequence, m(Het.–CO) for Het. = 2-Fu, 2-Th and, presumably, 2-Sel (see [5]), should be superior to m(Ph–CO) and equal to $(45/32) \times (l/L) \times m(\text{Ph–CO}) \sim 1.2\, m(\text{Ph–CO})$, where l and L are the actual lengths of the mesomeric moments in Het.–CO (3.3–3.6 Å) and Ph–CO (3.8 Å).

Although the twisting angles for **3** (12 ± 5 or 45° [5], or 15 ± 15° [3]), **4** (20 ± 5 or 45° [5], or 27 ± 10° [3]) and **5** (20 or 60° [5]), and **4'** (30° [5]), are smaller than those for **2** (40 ± 5°) or **2'** (55°) (*vide supra*), it seems unlikely that the difference $\Delta m = m(\text{Het.–CY}) - m(\text{Ph–CY})$ exceeds 0.05 D. Such a low value is consistent with the observation that the dipole moments of ring-closed 4,5-dihydro-5-methylcyclopenta[b]thiophen-6-one (**1**-a) and -6-thione (**1'**-a) (3.87 [60] and 3.87 D [61]) are close to the values (3.90 and 3.77 D) calculated from those of 2,2-dimethylindan-1-one and -1-thione (**1** and **1'**), and the pertinent angles from 5,7-dimethoxyindan-1-one [42] and thiophen [62]. For the sulphur derivatives, the derived value for Δm *is* $(0.2) \times \cos^2 55° = 0.06$ D only. In the following the Δm differences were then neglected.

With these justified assumptions, the dipole moments of the twisted *C* and *T*-conformers of **3**–**5**, and **3'**–**5'**, can be calculated from μ(**2** or **2'**), μ(furan) = 0.72 D, μ(thiophen) = 0.54 D or μ(selenophen) = 0.52 D [1], and the angle that the latter make with the C_2–CY bond axis (62.7, 73.8 or 77.5° [1]). For 2-pivaloyl(5-chlorothiophen) (**4**-a) and 2-thiopivaloyl(5-chlorothiophen) (**4'**-a), a C_5–Cl effective moment of 1.24 D (from μ(2-ThCl) = 1.48 D [63]) was taken into account. The results are listed in Table 2.

The dipole moments in benzene solution of **3**, **4** and **5** (2.79, 3.09 and 3.02 D) support what follows.

2-Pivaloylfuran likely exists as a mixture of both *C*- and *T*-conformers with $(T)/(C) = 64/36$, whereas both 2-pivaloylthiophen and 2-pivaloylselenophen mostly occur as *C* with $(T) \sim 10\%$.

Literature results for **3** to **5** in other solvents than benzene are not strictly comparable. The greater reaction-field stabilization of the more polar conformer (here shaped as *C*) relative to the other depends on the dielectric permittivity of the medium, the more so as its value is higher [64]. Further, there is a possibility of formation of a solute ... solvent complex whose enthalpy may differ for both conformers for steric reasons. Thus a specific solvation effect has been invoked to explain the *C*-preference of 2-pivaloylthiophen dissolved in benzene [65]. Carbon tetrachloride (and tetrachlor-

Table 2. Calculated dipole moments for the *C*- and *T*-conformers of 2-pivaloyl and 2-thiopivaloyl, 2-benzoyl and 2-thiobenzoyl chalcogen-heterocycles[a, b].

Ketone	$M(C)$	$M(T)$	μ_{exp}	Thioketone	$M(C)$	$M(T)$	μ_{exp}
2-FuCO-t-Bu	3.27	2.47	2.79	2-FuCS-t-Bu	3.05	2.48	2.61
2-ThCO-t-Bu	3.14	2.50	3.09	2-ThCS-t-Bu	2.92	2.45	3.02
2-(5-ClC$_4$H$_2$S)CO-t-Bu	3.37	1.68	3.20	2-(5-ClC$_4$H$_2$S)CS-t-Bu	3.01	1.81	3.01
2-SelCO-t-Bu	3.12	2.46	3.03	2-SelCS-t-Bu	2.90	2.43	2.83
2-FuCOPh	3.80	2.74	3.37	2-FuCSPh	3.68	2.64	3.26
2-ThCOPh	3.60	2.72	3.45	2-ThCSPh	3.49	2.62	3.33
2-(5-ClC$_4$H$_2$S)COPh	3.90	1.70	3.63	2-(5-ClC$_4$H$_2$S)CSPh	3.76	1.56	3.39
2-ThCO(C$_6$H$_4$F-4')	3.11	2.47	3.17	2-ThCS(C$_6$H$_4$F-4')	3.00	2.46	3.10
2-ThCO(C$_6$H$_4$Cl-4')	3.10	2.50	3.16	2-ThCS(C$_6$H$_4$Cl-4')	2.99	2.48	3.13
2-ThCO(C$_6$H$_4$Br-4')	3.11	2.47	3.21	2-ThCS(C$_6$H$_4$Br-4')	3.00	2.46	3.02
2-SelCOPh	3.58	2.71	3.52	–	–	–	–

[a] $\varphi = 40°$ for 2-pivaloyl compounds, $\varphi' = 55°$ for 2-thiopivaloyl compounds.
[b] 2-Furyl, 2-thienyl and 2-selenyl groups assumed to be coplanar with the C–CY–C plane for 2-benzoyl and 2-thiobenzoyl compounds.

ethylene by analogy) could form a weak complex with ketones, with a C=O ... CCl_4 bonding [66].

Infrared spectra in tetrachlorethylene [5] and carbon tetrachloride [65], and the ^1H n.m.r. spectrum in CCl_4 [65], showed that 2-pivaloylthiophen mostly occurs as *C* in these media, and such is also observed for 2-pivaloylselenophen in carbon tetrachloride [5]. The Kerr-constants of 2-pivaloylfuran and 2-pivaloylthiophen in CCl_4 suggest mixtures of the conformers (in which $\varphi = 15 \pm 15°$ or $27 \pm 10°$), with $(T)/(C) \sim 3.3$ and $(C)/(T) \sim 2.7$, respectively [3].

Like 2-pivaloylthiophen (**4**), its 5-chloro derivative **4**-a ($\mu = 3.20$ D) principally exists as *C*, with $(T) = 22\%$.

Comparison of the dipole moments in benzene of thiopivaloyl compounds **3′** (2.61 D), **4′** and **4′**-a (3.02 and 3.01 D), and **5′** (2.83 D), with the calculated values for *C*- and *T*-conformers suggests that **3′** prefers to occur as *T* (with $(C) \sim 20\%$), while **4′**, **4′**-a and **5′** essentially exist in the *C*-conformation with $(T) \leqq 5\%$.

Preferred Conformations of 2-Benzoyl and 2-Thiobenzoyl chalcogen-heterocycles

Two twisting angles, $\varphi' = \varphi$(Hetaryl) and $\varphi'' = \varphi$(Phenyl) are needed to characterize the conformers

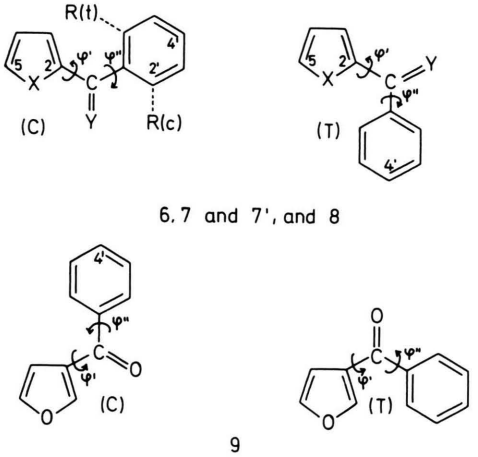

Fig. 3. **6**: 2-Benzoylfuran; **7** and **7′**: 2-benzoylthiophen and 2-thiobenzoylthiophen; **8**: 2-benzoylselenophen; **9**: 3-benzoylfuran. X stands for O, S or Se, Y for O or S, and R for Me, F or Cl.

(*C* and *T*) of 2-benzoylfuran (**6**), 2-benzoylthiophens (**7** and **7**-a, **7**-c′ to **7**-e′) and 2-benzoylselenophen (**8**), and their sulphur analogues (**6′**, **7′**, **7′**-a, **7′**-c′ to **7′**-e′) (see Table 1 and Figure 3).

As the carbonyl (and thiocarbonyl) groups conjugate more than phenyl with 2-furyl and 2-thienyl (and 2-selenyl) [5]), it can be inferred that the heterocyclic ring is coplanar, or near-coplanar, with the reference C−CY−C plane, and the phenyl-group is rotated by a finite angle which may attain 53 ± 10 and $71 \pm 10°$ in unsubstituted **6** and **7**, respectively [67]. Accordingly, m(Ph−CO) in these compounds can be equated to the value in benzophenone which, in solution, exists in a C_2 conrotatory conformation, with $\varphi' = -\varphi'' = 42°$ [68]. Comparison of the dipole moments of benzophenone (2.98 D [69]) with that of (presumably) diorthogonal 2,4,6;2′,4′,6′-hexachlorobenzophenone (2.81 D [70]) provides m(Ph−CO) = 0.14 D in the former, whence $\Delta m = m$(Het.−CO) − m(Ph−CO) is $(0.14)/(\cos^2 42°) - (0.14) = 0.11$ D at the most. The value of $\Delta m' = m$(Het.−CS) − m(Ph−CS) was taken as 0.15 D.

The dipole moments for the *C*- and *T*-conformers of **6**−**8** were calculated from $\mu(Ph_2CO) = 2.98$ D [69] or $\mu(Ph_2CS) = 2.86$ D [4], μ(heterocycle) = 0.72, 0.54 or 0.52 D [1], Δm or $\Delta m'$, and the C−CO−C and C−CS−C angles (122° [71] and 120° [72]). For 5-chloro compounds **7**-a and **7′**-a, $\mu(C_5-Cl)$ was taken as 1.24 D as before, while for 4′-halogeno-substituted derivatives **7**-c′ to **7**-e′, **7′**-c′ to **7′**-e′, $\mu(C_{4'}-F)$, $\mu(C_{4'}-Cl)$ and $\mu(C_{4'}-Br)$ were assumed to be 1.18, 1.21 or 1.17 D from the dipole moments of 4′-fluoro-, 4′-chloro and 4′-bromo-benzophenone (2.68, 2.71 and 2.67 D for ${}_EP + {}_AP = R_D$ [73]). The results of these calculations are given in Table 2. Comparison of the experimental and calculated moments supports the following:

2-Benzoylfuran and 2-thiobenzoylfuran likely occur as a mixture of both conformers with $(C)/(T) = 56/44$ or 55/45, whilst 2-benzoylthiophen, 2-thiobenzoylthiophen and 2-benzoylselenophen mainly exist as *C* with $(C) = 81$, 79 or 92%. *C*-preference for the latter is clearly indicated by the fact that the dipole moments of 4′-halogeno-substituted derivatives (**7**-c′ to **7**-e′, **7′**-c′ to **7′**-e′) are slightly superior to those calculated for the *C*-conformers (see Table 2).

The *T*-populations for 5-chloro derivatives (**7**-a and **7′**-a) result as 17 and 23%, respectively.

Strictly speaking, the literature results for other solvents are not comparable to ours in benzene.

The infrared spectrum of **6** in tetrachlorethylene indicates two conformers to be present [74], and the Kerr-constant in carbon tetrachloride a mixture of both forms with $(C)/(T) = 75/25$ [75–77] or $(30 \pm 10)/(70 \mp 10)$ [67]*. The ^{1}H n.m.r. spectrum in deuteriochloroform is consistent with an equimolecular mixture of both conformers [79].

The ^{1}H n.m.r. spectra of **7** and **7′** in carbon tetrachloride support a *C*-conformation [80, 65], while the Kerr-constant of the former in the same medium suggests a mixture of both forms with $(C)/(T) = (75 \pm 10)/(25 \mp 10)$ [67].

It can be inferred that, like 2-benzoylthiophen (**7**) mostly existing as *C* in benzene solution, its 2′-methyl-, 2′-fluoro- and 2′-chloro-substituted derivatives (**7**-b, **7**-c and **7**-d) occur in a *C*-conformation in which the thienyl-group is coplanar with the C–CO–C plane (i.e. $\varphi' = 0°$) and the 2′-substituted phenyl ring is rotated by a φ''-angle to be determined (Fig. 3). In the following calculations, effective μ^*(Ph–X) moments were taken as μ(toluene) = 0.37 D [81]; μ(fluorobenzene) = 1.45 D [82] and μ(chlorobenzene) = 1.59 D [47], or (as before) μ^*(Ph–F) = 1.18 D, μ^*(Ph–Cl) = 1.21 D (p. 1343). (μ^*(Ph–Me) and μ^*(Ph–Cl) values cannot be drawn from the 2-methyl- and 2-chlorobenzophenone moments (2.69 and 3.46 D [69]) because the actual structures of these compounds are not known.) On these bases the twisting φ''-angles, measured from the planar *Cc*-conformations with the 2′-substituent (or atom) being close to the carbonyl-oxygen atom, are 40° in **7**-b, 117 or 111° in **7**-c and 103 or 92° in **7**-d. The order Me < F < Cl found for the twisting angles in the series is at variance with that expected from the van der Waals radii of methyl (2.0 Å), chlorine (1.80 Å) and fluorine (1.35 Å) (all from [83]), giving the steric hindrance in both planar *Cc*- and *Ct*-conformers. This fact emphasizes the role played by the electrostatic potential between non-bonded atoms. If in *Cc*-conformations the (X, O) contact is repulsive for X = F and Cl and likely to be attractive for X = Me, in *Ct*-conformations the (X, H) contact is repulsive for X = Me and (possibly) attractive for X = F and Cl. This may account for the order Me < F < Cl observed. The (Me, O) attractive potential in **7**-b makes its twisting φ''-angle close to that in unsubstituted 2-benzoylthiophen (**7**), where φ'' is about 40° [84]. Interestingly, the dipole moment of 2-methylbenzophenone in benzene (2.69 [69] or 2.91 D [85]) supports a twisted [*cis*-(Me, O)]-conformation with φ(2-tolyl) = 41.5° (or 89.5°).

The steric hindrance in **7**-b, relative to **7**, is consistent with the ultraviolet and ^{1}H n.m.r. spectra of these compounds [80]. Nearly orthogonal φ''-twisted conformations are compatible with the ^{1}H n.m.r. spectra of 2-(2′-bromobenzoyl)thiophen and 2-(2′iodobenzoyl)thiophen [84], and with the infrared spectra of 2-(2′-fluorobenzoyl)thiophen, 2-(2′-chlorobenzoyl)thiophen and 2-(2′-bromobenzoyl)thiophen [60] (all the spectra recorded in carbon tetrachloride).

Although the 3-furyl–carbonyl conjugation is markedly weaker than the 2-furyl–carbonyl one in similar systems, it is sufficiently strong to impose a conformation with a near-coplanar (3-furoyl)-group for 3-benzoylfuran (**9**): the acetyl-group rotational barriers are between 26.4 and 29.7 kJ mol^{-1} in 3-acetylfuran [79], 37.7 kJ mol^{-1} in 2-acetylfuran [86], and 25.1 kJ mol^{-1} in acetophenone [87]. Note that the barriers to formyl-group rotation in 3-formyl-N-butylpyrrole [88] and 2-formyl-N-methylpyrrole [89] differ by ca. 8 kJ mol^{-1}.

The dipole moments of the *C*- and *T*-conformers of **9**, calculated from $\mu(Ph_2CO) = 2.98$ D [69], μ(furan) = 0.72 D [1] and the pertinent angles out of the microwave structure of furan [90], are $M(C) = 3.17$ D and $M(T) = 2.33$ D. The dipole moment of **9** in benzene (2.62 D) is then consistent either with a mixture of both conformers ($(T)/(C) = 69/31$) or with a strongly twisted *T*-conformation with φ(3-furyl) as high as 65°. The best solution is that 3-benzoylfuran (**9**) principally occurs in a slightly twisted *T*-conformation: assuming φ(3-furyl) = 30°, the *C*-population is calculated to be 28% (see Fig. 3 for the shapes of *C*- and *T*-conformers).

The infrared spectrum in tetrachlorethylene indicates that **9** (mainly) occurs in one conformation [74], which is *T*-shaped after the ^{1}H n.m.r. spectrum in deuteriochloroform [79].

* Note that unexpectedly (after [67]), 2-benzoylfuran principally occurs as *T* (~ 70%) and 2-(2′,4′,6′-trimethylbenzoyl)furan as *C* (~ 75%), while both thiophen relatives prefer to exist as *C* (with (*C*) ~ 75 or 90%). The analysis of Kerr-constants is fraught with difficulties in some cases and may lead to doubtful conclusions (cf. [78]).

Preferred Conformations for Di-(2-furyl)ketone, 2-Furyl 3-furyl ketone, 2-Furyl 2-thienyl ketone, 3-Furyl 2-thienyl ketone, Di-(2-thienyl)ketone and Di-(2-thienyl)thioketone

The title compounds (**10** to **14**, and **14'**) can occur in four conrotatory conformations (i*c'*, j*c''*), (i*c'*, j*t''*), (i*t'*, j*c''*) and (i*t'*, j*t''*), where i*c* and i*t* stand for (i-Fu−CY) (or (i-Th−CY)) shaped as *cis*-(X, Y) or *trans*-(X, Y) (see Figure 4). The dipole moments of the conformers can be calculated from $\mu(Ph_2CO)$ (or $\mu(Ph_2CS)$), μ(furan or thiophen) and a ΔM term (along the C=Y bond axis) originating from the fact that m(2-Fu−CO) and m(2-Th−CO) are higher than m(Ph−CO), and m(2-Th−CS) is greater than m(2-Th−CO). For conrotatory models with $\varphi' = \varphi'' = \pm 45°$, ΔM can be taken as 0.10 D for the ketones and 0.15 D for di-(2-thienyl)thioketone. With these assumptions, the calculations yield the results given in Table 3, where **11** and **13** are written as 3-FuCO(2-Fu) and 3-FuCO(2-Th) for the sake of homogeneity.

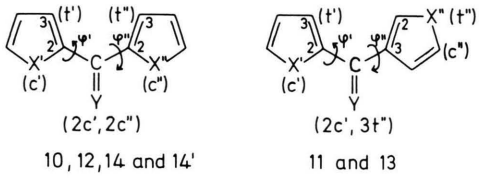

Fig. 4. **10**: Di-(2-furyl)ketone (X' = X'' = O, Y = O); **11**: 2-furyl 3-furyl ketone (X' = X'' = O, Y = O); **12**: 2-furyl 2-thienyl ketone (X' = O, X'' = S, Y = O); **13**: 3-furyl 2-thienyl ketone (X' = S, X'' = O, Y = O); **14** and **14'**: di-(2-thienyl)ketone and di-(2-thienyl)thioketone (X' = X'' = S, Y = O or S). *c'* and *t'* refer to the possible situations of X' relative to Y, and *c''* and *t''* to those of X'' with respect to the same atom.

For di-(2-furyl)ketone (**10**), di-(2-thienyl)ketone (**14**) and di-(2-thienyl)thioketone (**14'**), conformer (2*t*, 2*t*) can be discarded because of the repulsion between both heterocyclic heteroatom sp^2-hybridized lone-pairs.

The experimental dipole moment of **10** in benzene (3.65 D) supports a (2*c*, 2*t*)-model or, better, a mixture of (2*c*, 2*c*)-conformer and mixed conformers ((2*c*, 2*t*) and (2*t*, 2*c*)) with the latter being more abundant (73%).

A near-coplanar (2*c*, 2*t*)-model has been suggested to account for the infrared spectrum of **10** in tetrachlorethylene [74]. The ^{1}H n.m.r. spectrum of the compound in deuteriochloroform is consistent either with a nearly equimolecular mixture of (2*c*, 2*c*) and mixed conformers, or of (2*t*, 2*t*) and mixed forms [79]; the first solution, which leads to a calculated moment of 3.83 D, should be preferred to the second one leading to calculated 3.05 D only.

The dipole moment of 2-furyl 3-furyl ketone (**11**) in benzene (2.75 D) is consistent with a mixture of (3*c*, 2*t*)- and (3*t*, 2*t*)-forms, with the latter being slightly more abundant (55%), a conclusion in accord with the ^{1}H n.m.r. spectrum of **11** in deuteriochloroform [79].

By analogy with what is observed for 2-benzoylthiophen (**7**) essentially existing as *C*, both the (i*c'*, 2*t''*)- and (i*t'*, 2*t''*)-forms can be ignored for 2-furyl 2-thienyl ketone (**12**) and 3-furyl 2-thienyl ketone (**13**).

A mixture of conrotatory (2*t'*, 2*c''*)- and (2*c'*, 2*c''*)-conformers (76 and 24%) has a calculated dipole moment equal to that observed for **12** in benzene; with corresponding planar models (M = 3.23 and 4.35 D), the calculated (2*c'*, 2*c''*)-population becomes 17%. The infrared spectrum of the compound in tetrachlorethylene suggests that the (2*t'*, 2*c''*)-

Table 3. Calculated dipole moments for all conrotatory conformers of di-(2-hetaryl)ketones, 3-furyl 2-hetaryl ketones, and di-(2-thienyl)thioketone (Debye units)[a].

Compounds[b,c]	M(i*c'*, j*c''*)	M(i*c'*, j*t''*)	M(i*t'*, j*c''*)	M(i*t'*, j*t''*)	μ_{exp}
2-FuCO(2-Fu)	4.19	3.43	3.43	2.61	3.65
3-FuCO(2-Fu)	3.70	3.07	3.11	2.44	2.75
2-FuCO(2-Th)	4.03	3.43	3.25	2.60	3.45
3-FuCO(2-Th)	3.58	3.04	3.00	2.44	3.12
2-ThCO(2-Th)	3.88	3.24	3.24	2.60	3.71
2-ThCS(2-Th)	3.80	3.17	3.17	2.51	3.75

[a] For $\varphi' = -\varphi'' = 45°$.
[b] See Fig. 4 for the structural formulae of the conformers.
[c] i = 2 or 3, and j = 2.

form is more abundant [74], and the ^{1}H n.m.r. spectrum in deuteriochloroform indicates a mixture of (twisted) ($2t'$, $2c''$)-form (70%) and planar ($2c'$, $2c''$)-conformer [79].

The experimental dipole moment of **13** in benzene (3.12 D) shows that the ($3t'$, $2c''$)-conformer should be preferred, the population of ($3c'$, $2c''$) being 14% at the most. This result was expected since 3-benzoylfuran (**9**) principally occurs as *T* (p. 1344).

The dipole moments of di-(thienyl)ketone and di-(2-thienyl)thioketone (**14** and **14'**) in benzene solution (3.71 and 3.75 D) are consistent with a mixture of ($2c$, $2c$)-conformer and mixed conformers, with the former being more abundant (72 and 91%, respectively). The Kerr-constant of **14** in carbon tetrachloride suggests a conrotatory ($2c$, $2c$)-model, with $\varphi' = -\varphi'' = 45 \pm 10°$ [67]. See Fig. 4 for the shapes of these conformers.

Conclusions

Pivalophenone and pivalophenethione occur in a twisted conformation, with $\varphi = (40 \pm 5)°$ or $\varphi' = (55 \pm 5)°$ (Figure 1).

By contrast with 2-pivaloylfuran and 2-thiopivaloylfuran mostly existing as *T* (60 and 80%), 2-pivaloylthiophen, 2-thiopivaloylthiophen, 2-pivaloylselenophen and 2-thiopivaloylselenophen mainly occur as *C* (Figure 2). This is also observed for 2-benzoylfuran and 2-thiobenzoylfuran nearly equal divided into *C* and *T*, 2-benzoylthiophen, 2-thiobenzoylthiophen and 2-benzoylselenophen which predominantly exist as *C* (Figure 3). These facts can be explained as follows. The (C=C−C=O) chain prefers to occur in a s-*trans* conformation, as shown by the observed structure of acrylaldehyde [91] and of 3-benzoylfuran (this work). For the 2-furyl compounds, the (O, O) (or (O, S)) repulsion is high enough to change the more stable conformation of the (C=C−C=O) chain; against that, the (S, Y) and (Se, Y) contacts in 2-thienyl and 2-selenyl derivatives appear not to be sufficiently repulsive to cause such an effect. The net electron-density at the oxygen atom in furan is to be much greater (in modulum) than that at the sulphur (or selenium) atom(s) in thiophen and selenophen because of what follows: (i) the mesomeric moments of furan, thiophen and selenophen are 1.03, 1.35 and 1.29 D; (ii) the heteroatom hybridization-moment μ_h (defined by Gibbs [92]) is much higher for sulphur and selenium than for oxygen since the localized sp^2-hybridized lone-pair moment (μ_p) is 1.65 D for sulphur, 1.90 D for selenium and 0.95 D for oxygen [93], and $\mu_h \sim \mu_p/2$ [92]*.

Preferred conformations for di-(2-furyl)ketone, di-(2-thienyl)ketone, di-(2-thienyl)thioketone, 2-furyl 3-furyl ketone, 2-furyl 2-thienyl ketone, and 3-furyl 2-thienyl ketone, have been proposed. As a rule, 2-ThCO and 2-ThCS groups prefer to occur as twisted *C*, 3-FuCO as twisted *T*, while the 2-FuCO residue is divided into twisted *T* and *C* (see Figure 3).

* The dipole moments of furan, thiophen and selenophen (0.72, 0.54 and 0.52 D) are directed from the ring centre towards the heteroatom [1]. Their mesomeric moment, directed in the opposite sense, causes a positive π-charge at the heteroatom. The quoted heteroatom hybridization-moments, directed as the total dipole moment, here are only indicative but the actual values certainly follow the same order. Note that the hybridization-moment, though not altering the net charge of an atom, largely contributes to the molecular dipole moment (see [92]).

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