Conformations of Some 2-Substituted Furan and Thiophen Carbonyl Compounds

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Experimental dipole moments and molar Kerr constants are reported for the following as solutes in cyclohexane or carbon tetrachloride at 25°: furan-2-carbaldehyde, 2-acetylfuran, thiophen-2-carbaldehyde, 2-acetylthiophen, phenyl 2-furyl ketone, phenyl 2-thienyl ketone, mesityl 2-furyl ketone, mesityl 2-thienyl ketone, 1-naphthyl 2-thienyl ketone, 2-naphthyl 2-thienyl ketone, and di-2-thienyl ketone. Analysis of the data establishes the conformational preferences of these molecules.

THE conformational preferences of 2-substituted furan and thiophen carbonyl compounds have, during the last few years, attracted much attention, with virtually the complete armoury of physical-organic chemistry being brought to bear on the problem. A notable example is furan-2-carbaldehyde which has been the subject of more than thirty structural studies and, until recently [1,2] the source of much controversy because of apparently contradictory results obtained by different methods.

As part of a systematic investigation of the conformations of aromatic aldehydes and ketones we have applied considerations of molecular polarity and polarisability to a range of 2-substituted furans and thiophens. Experimental dipole moments and Kerr constants at 25° are here reported and analysed for the following as solutes in cyclohexane or carbon tetrachloride: furan-2-carbaldehyde (1), 2-acetylfuran (2), thiophen-2-carbaldehyde (3), 2-acetylthiophen (4), phenyl 2-furyl ketone (5), phenyl 2-thienyl ketone (6), mesityl 2-furyl ketone (7), mesityl 2-thienyl ketone (8), 1-naphthyl 2-thienyl ketone (9), 2-naphthyl 2-thienyl ketone (10), and di-2-thienyl ketone (11).

EXPERIMENTAL

Solutes.—Commercial samples of the following were purified by distillation immediately before use to give: furan-2-carbaldehyde, b.p. 90° at 65 mmHg, 162° at 760

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mmHg; 2-acetylfuran, b.p. 67° at 10 mmHg, 173° at 760 mmHg; thiophen-2-carbaldehyde, b.p. 59—61° at 2·5 mmHg; and 2-acetylthiophen, b.p. 64° at 1·5 mmHg.

Phenyl 2-furyl ketone was prepared by a modification of the method of Sugisawa *et al.*[3] as a pale yellow oil (54%), b.p. 99—101° at 0·4 mmHg, by the action of 2-furoyl chloride and aluminium chloride on an excess of benzene. The ketone darkens on exposure to the atmosphere. A low grade specimen of phenyl 2-thienyl ketone was passed through a silica column and eluted with benzene–light petroleum. Recrystallization from light petroleum gave needles, m.p. 55—57°.

The procedure described by Fuson and Wallingford[4] yielded mesityl 2-furyl ketone, which after vacuum sublimation had m.p. 103—103·5°; $\lambda_{max.}$ (EtOH) 278 nm (ε 13,200); $\nu_{max.}$ (CCl_4) 1668 cm^{-1}; τ (CCl_4) 2·45 (4 lines, J 1·7 and 0·9 Hz, H-5), 3·13 (4 lines, J 3·6 and 0·9, H-3), 3·21 (m, Ph), 3·55 (4 lines, J 3·6 and 1·7, H-4), 7·71br (s, 4-Me), and 7·88br (s, 2- and 6-Me); m/e 214 (M^+, 100), 91 (68), 185(43), 143(37), 171(34), and 186(34). Mesityl 2-thienyl ketone, obtained by the method of Kaper and de Boer,[5] after vacuum sublimation had m.p. 56·5—57·5°; $\lambda_{max.}$ (EtOH) 264 (ε 12,300) and 290 nm (11,900); $\nu_{max.}$ (CCl_4) 1656 cm^{-1}; τ (CCl_4) 2·43 (4 lines, J 4·8 and 1·2, H-5), 2·80 (4 lines J 3·8 and 1·2, H-3), 3·03 (4 lines, J 4·8 and 3·8, H-4), 3·23 (m, Ph), 7·71br (s, 4-Me), and 7·90br (s, 2- and 6-Me).

TABLE 1

Polarisations, refractions, dipole moments, and molar Kerr constants at 25° from observations of incremental dielectric constants, densities, refractive indices, and birefringences of solutions [a]

Molecule	$\alpha\varepsilon_1$	β	$\gamma'n_1^2$	$_{\infty}P_2$/cm^3	R_D/cm^3	$10^{30}\mu$/C m [b]	γ	δ	$10^{27}{}_{\infty}({}_mK_2)$/m^5 V^{-2} mol^{-1}
(1)	9·93 ± 0·19	0·267 ± 0·001		252 ± 4	25·4 ± 0·1 [c]	11·07 ± 0·11	0·018 ± 0·002	475 ± 2	+676 ± 3
(2)	6·51 ± 0·13	0·244 ± 0·002	0·087 ± 0·009	199 ± 3	29·7 ± 0·3	9·56 ± 0·10	0·022 ± 0·002	260 ± 4	+423 ± 7
(3)	8·50 ± 0·09	0·346 ± 0·004	0·24 ± 0·02	253 ± 2	30·6 ± 0·6	10·95 ± 0·06	0·060 ± 0·005	426 ± 7	+708 ± 12
(4)	7·13 ± 0·06	0·306 ± 0·002	0·21 ± 0·01	245 ± 2	35·2 ± 0·3	10·63 ± 0·05	0·051 ± 0·003	248 ± 3	+462 ± 6
(5)	4·80 ± 0·04	0·317 ± 0·003		237 ± 2	49·7 ± 0·5 [c]	10·02 ± 0·05	0·092 ± 0·007	71 ± 3	+178 ± 8
(6)	5·37 ± 0·02	0·362 ± 0·003	0·37 ± 0·06	282 ± 1	56 ± 3	11·01 ± 0·07	0·089 ± 0·014	60 ± 4	+163 ± 11
(7)	5·10 ± 0·03	0·257 ± 0·001	0·28 ± 0·02	314 ± 2	67 ± 1	11·52 ± 0·04	0·068 ± 0·005	−117 ± 4	−380 ± 13
(8) [d]	4·65 ± 0·03	0·285 ± 0·004	0·28 ± 0·02	311 ± 2	70 ± 1	11·37 ± 0·05	0·069 ± 0·005	−88 ± 9	−309 ± 30
(9) [e]	10·23 ± 0·13	−0·248 ± 0·002	1·03 ± 0·03	313 ± 3	78·5 ± 0·8	11·19 ± 0·08	0·241 ± 0·006	−159 ± 3	−386 ± 7
(10) [e]	10·72 ± 0·05	−0·251 ± 0·004	1·02 ± 0·03	325 ± 1	78·3 ± 0·8	11·50 ± 0·04	0·240 ± 0·008	135 ± 4	+310 ± 9
(11) [e]	13·65 ± 0·09	−0·138 ± 0·001	0·86 ± 0·02	321 ± 2	56·6 ± 0·4	11·94 ± 0·04	0·203 ± 0·005	173 ± 3	+323 ± 6

[a] See ref. 7 for details of apparatus, procedures, symbols, solvent constants, *etc.* For each solute a set of solutions (usually five or six) having weight-fraction concentrations < *ca.* 1·5% was examined. The solvent was cyclohexane, except for compounds (9)—(11), where carbon tetrachloride was used. Quoted random errors were derived from standard deviations of observed properties; the absolute accuracy of the Kerr constants is limited by systematic errors estimated as ±5%. [b] Calculated assuming $_DP = 1{\cdot}05\,R_D$. [c] Calculated from refractive indices and densities of pure liquids. [d] Only two solutions studied because of small quantity of solute available. [e] Solvent carbon tetrachloride.

Literature methods[6] were used to obtain 1-naphthyl 2-thienyl ketone as an oil, b.p. 188° at 25 mmHg, 2-naphthyl 2-thienyl ketone as off-white crystals, m.p. 87° (lit.,[6] 87°), and di-2-thienyl ketone as chromatographically uniform yellow-brown needles, m.p. 86·5—87° (lit.,[6] 87°).

Apparatus, Results, etc.—Details of procedures, symbols, solvents constants, *etc.* have been given by LeFèvre and LeFèvre.[7] The results are summarized in Table 1. It should be noted that in this paper dipole moments (μ), molar Kerr constants ($_mK$), and polarisabilities (b) are expressed in S.I. units. Relevant conversion factors, for comparisons with literature data are: 1 C m = 0·2998 × 10^{30}D (dipole moment), 1 m^5 V^{-2} mol^{-1} = 0·8988 × 10 ^{15} e.s.u. mol^{-1} (molar Kerr constant), and 1 C m^2 V^{-1} = 0·8988 × 10^{16} cm^3 (polarisability). In the discussion which follows, dipole moments are, for convenience, quoted as 10^{30} μ/C m and molar Kerr constants as 10^{27} $_mK$/m^5 V^{-2} mol^{-1}.

Previous Measurements.—Dipole moments obtained from observations on dilute solutions in benzene or carbon tetrachloride are already on record[8–19] for many of the molecules listed in Table 1. Our results with cyclohexane as solvent are uniformly lower than such literature data, as would be predicted from the treatment of the solvent effect for furan-2-carbaldehyde.[1] The dipole moments of 2-acetylfuran, mesityl 2-furyl ketone, mesityl 2-thienyl

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ketone, and the two naphthyl 2-thienyl ketones have not previously been determined. Kerr constant measurements have been reported only for furan-2-carbaldehyde, and results from the two previous studies [18,19] are notably divergent. The value (+757) given by Cureton *et al.*[18] for this substance dissolved in benzene (in which solute–solvent association can be expected to occur [20]) is somewhat larger than that found in the present work (+676) with cyclohexane as solvent. The molar Kerr constants found by Sheinker *et al.*[19] for furan-2-carbaldehyde in carbon tetrachloride (+464) and in benzene (+523) appear to be much too low. Conclusions from both previous studies are at variance with our findings.

DISCUSSION

Analysis of Dipole Moments and Kerr Constants.—Our procedure [7,21] is to use known bond and group dipole moment and polarisability components, together with standard computational methods, to predict dipole moments and Kerr constants for possible structures of each molecule. Comparison of the experimental data with the range of calculated values normally indicates the effective molecular conformation. Bond angles for the 2-formyl- and 2-acetyl-furans and -thiophens (1)—(4) were taken from the microwave structures of furan-2-carbaldehyde [22] and thiophen.[23] For the remaining molecules (5)—(11), we assumed regular valence angles of 120° around the carbonyl carbon atom. The moments of the *cis* (A) and *trans* (B) conformations of furan-2-carbaldehyde are available from the microwave spectral analysis.[22] In all other cases molecular moments were considered to be approximately calculable as the resultants of components μ_1 (furan, 2·40 [24]; thiophen, 1·80 [25]) collinear with the symmetry axis of the heterocyclic ring and μ_2 (9·90, from data for benzaldehyde,[26] acetophenone,[27] and benzophenone [28]) directed along the C=O bond. Anisotropic polarisabilities used in obtaining the theoretical Kerr constants are given in Table 2. Exaltations of refraction and polarisability are shown in Table 3.

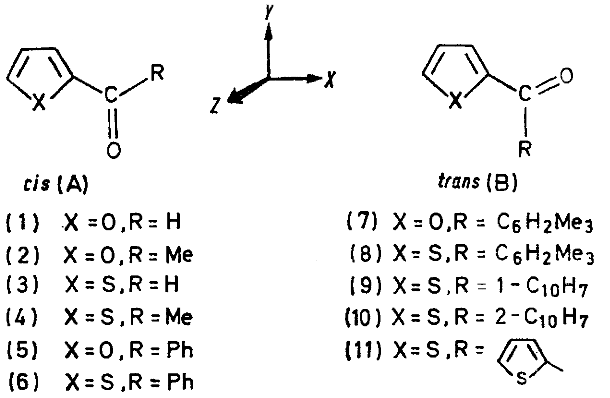

FIGURE 1

TABLE 2

Polarisability components (expressed as $10^{40}b$/C m^{2}V^{-1}) for bonds and groups [a]

	b_L	b_T	b_V
C–H [b]	0·72	0·72	0·72
C–C [b]	1·08	0·29	0·29
C=O [b]	2·56	1·56	0·51
Furyl [c]	7·55	9·17	5·25
Thienyl [c]	10·57	10·56	6·73
Phenyl [b]	11·69	11·69	7·56
Mesityl [d]	18·35	18·35	13·00
Naphthyl [e]	17·75	23·53	11·85

[a] Note that for the furyl and thienyl groups, b_L is collinear with the C_2 axis of the heterocycles; for the naphthyl group, b_L coincides with the inter-ring bond. [b] Ref. 7. [c] Ref. 25. [d] P. H. Gore, J. A. Hoskins, R. J. W. LeFèvre, L. Radom, and G. L. D. Ritchie, *J. Chem. Soc.* (*B*), 1969, 485. [e] R. J. W. LeFèvre and L. Radom, *J. Chem. Soc.* (*B*), 1967, 1295.

TABLE 3

Observed [a] and calculated [b] molar refractions (R_D/cm^3) and exaltations [c] of polarisability (10^{40} Δb/C m^2 V^{-1})

Molecule	R_D(obs)	R_D(calc)	Δb
(1)	25·4	23·0	2·2
(2)	29·7	27·7	1·7
(3)	30·6	28·9	2·1
(4)	35·2	33·6	2·0
(5)	49·7	47·2	4·8
(6)	56	53·0	4·0
(7)	67	61·7	5·4
(8)	70	67·6	2·3
(9)	78·5	70·5	9·9
(10)	78·3	70·5	9·7
(11)	56·6	51·2	7·1

[a] From Table 1. [b] Evaluated from bond data tabulated in ref. 21*a* together with the following molar refractions (cm^3): furan, 18·4 and thiophen, 24·3 (B. Harris, R. J. W. LeFèvre, and E. P. A. Sullivan, *J. Chem. Soc.*, 1953, 1622); mesitylene, 40·8 (G. Thomson, *J. Chem. Soc.*, 1944, 404); and naphthalene, 43·6 (C. G. LeFèvre and R. J. W. LeFèvre, *J. Chem. Soc.*, 1955, 1641). [c] See ref. 21*a* for discussion of exaltation. Values shown are means of estimates from the equations $\Delta b = 0{\cdot}95\ (9\varepsilon_0/N_A)\ R_D\ (\text{obs}) - \Sigma b\ (\text{bonds})$ and $\Delta b = 0{\cdot}95\ (9\varepsilon_0/N_A)\ \Delta R_D$.

2-Formyl- and 2-Acetyl-furans and -thiophens.—The question of the conformational preference of furan-

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2-carbaldehyde has been studied using a wide variety of methods: Raman and i.r.,[29-36] far i.r.,[37] n.m.r.,[38-47] and microwave [22] spectroscopy; dipole moments [9,16-19,48] and molecular polarisabilities;[18,19] ultrasonic relaxation;[49] and theoretical studies.[1,50-55] Unfortunately much confusion has arisen because of the apparently contradictory results obtained by different techniques. The source of much of the difficulty has been a failure to recognize that the free energy difference between the conjugatively stabilized planer *cis*- and *trans*-conformations is markedly medium dependent. The explanation of this phenomenon lies in reaction field stabilization in dense media, relative to the vapour phase, of the more polar *cis*-isomer. In the case of furan-2-carbaldehyde the effect is so pronounced that although the *trans*-form is preponderant in the vapour phase,[22,37] the *cis*-isomer is undoubtedly the more abundant in polar solvents such as dimethyl ether and acetone.[1,2,41-47] The importance of solvent effects in determining the position of equilibrium between (1A) and (1B) was first recognized by Abraham and Siverns,[1] who used a quantitative, although approximate, theory to rationalize the range of experimental results.

Much less attention has been given to 2-acetylfuran, but n.m.r. studies [40,41,46,56] have confirmed that in polar solvents the *cis*-conformation (2A) is again present in the greater abundance. However, from the foregoing discussion of furan-2-carbaldehyde it might reasonably be expected that in the vapour phase or in a non-polar solvent such as cyclohexane the *trans*-isomer (2B) would be thermodynamically favoured.

The corresponding isomer abundances for thiophen-2-carbaldehyde (3) and 2-acetylthiophen (4) appear to be less dependent on the nature of the medium, and evidence from studies of fluid and condensed states shows that the *cis*-conformation is strongly preferred. Although the microwave spectrum [22] of (3) initially was interpreted as indicating predominance of the *trans*-form in the vapour, it has been suggested more recently [57] that in fact the experimental data favour the *cis*-conformation. N.m.r. investigations (coupling constants,[38,42,43,47,58] chemical shifts,[46,59,60] nuclear Overhauser effects,[44,46,60] lanthanide-induced shifts,[46,61] nematic phase studies [62]) and dipole moment measurements [11,12,48] on many 2-formyl- and 2-acetyl-thiophens in a variety of solvents have confirmed that the *cis*-isomer is the more abundant in the dissolved state. Studies of such solution equilibria by i.r. spectroscopy are complicated by the occurrence of Fermi resonance.[31-35,63,64] Crystallographic analyses of bromo-derivatives of (3) and (4) indicated *cis*-structures in the solid state.[42,65]

The enhanced stability of the *cis*-forms of 2-carbonylthiophens relative to the corresponding furan derivatives has been attributed to a stabilizing interaction between the sulphur and oxygen atoms, a view which is supported by theoretical studies.[42,43,46,62,66]

There are, as previous workers have recognized,[16,19,48] difficulties in analysing the experimental dipole moments and specially the Kerr constants of these four molecules in terms of the relative abundances of the conformers. Evidence from measured barrier heights for internal rotation (which of course exhibit a solvent effect) [1,22,37,49]

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and reaction rates,* together with theoretical studies [50,67] suggests that the electron-withdrawing carbonyl group conjugates more effectively with the 2-furyl and 2-thienyl rings than with a phenyl group. Because of strong mesomeric interactions the applicability of dipole moment and polarisability components, and in particular the assignment of polarisability exaltations, is somewhat uncertain. In addition only relatively small differences can be expected between the moments of the *cis*- and *trans*-isomers, since both furan and thiophen are of low polarity.

Comparison of the calculated and measured dipole moments, the latter being root-mean-square values, leads to estimates of isomer abundances as shown in Table 4. For furan-2-carbaldehyde, the microwave dipole moments for the two conformers are notably higher than predicted from the simple model. The discrepancy can be attributed to enhanced conjugative interaction, which would be expected to be greater in the 2-formyl than in the 2-acetyl compounds. Conclusions from our analysis of dipole moments are consistent with information from other sources. Abraham and Siverns' theory [1] of the solvent effect on rotational isomerism in furan-2-carbaldehyde predicts that in cyclohexane the relative abundance of the *trans*-form should be *ca.* 75%. Agreement is therefore satisfactory when account is taken of approximations in both the theory and in our treatment of dipole moment data. The 2-acetyl compounds appear in each case to be conformationally similar to the respective 2-formyl derivatives.

TABLE 4

Predicted dipole moments (μ_c, μ_t), derived percentage abundances of the *trans*-isomer at 25° and calculated Kerr constants (${}_{\rm m}K_c$, ${}_{\rm m}K_t$) for *cis* (*c*) and *trans* (*t*) conformations of 2-formyl- and 2-acetyl-furans and -thiophens [a]

Molecule	μ_c	μ_t	% *trans*	${}_{\rm m}K_c$	${}_{\rm m}K_t$	% *trans* [b]
(1)	13·1	10·8	88 ± 5	+786	+658	(86)
(2)	12·3	8·9	83 ± 10	+141	+448	(92)
(3)	11·6	8·8	27 ± 10	+767	+244	(11)
(4)	11·6	8·8	39 ± 10	+540	+332	(38)

[a] Dipole moments quoted as $10^{30}\mu/\text{C m}$; molar Kerr constants as $10^{27}{}_{\rm m}K/\text{m}^5\text{V}^{-2}\text{ mol}^{-1}$. [b] Calculated molar Kerr constants for (1)—(4) are unusually dependent on apportionment of exaltation (Table 3). Values quoted here incorporate an arbitrary distribution (see text) of exaltation which yields results consistent with the isomer proportions obtained from dipole moments. The bracketted isomer abundances are given merely to show that theoretical and experimental Kerr constants can be reconciled with dipole moment results.

For reasons already mentioned comparisons of observed and calculated molar Kerr constants do not provide a reliable means of discriminating between the *cis*- and *trans*-conformations of these molecules, the main problem being the distribution in the *XY*-plane of the exaltation of polarisability. Trial calculations have shown, however, that the measured Kerr constants are consistent with the isomer abundances suggested by the analysis of dipole moments, provided the predicted Kerr constants incorporate the following apportionments of exaltation:

(1) $\Delta b_{xx} = 1{\cdot}5,\ \Delta b_{yy} = 0{\cdot}7$

(2) $\Delta b_{xx} = 1{\cdot}7,\ \Delta b_{yy} = 0$

(3) $\Delta b_{xx} = 0,\ \Delta b_{yy} = 2{\cdot}1$

(4) $\Delta b_{xx} = 1{\cdot}3,\ \Delta b_{yy} = 0{\cdot}7$

In summary, it appears that although the *trans*-form of the furan derivatives is favoured in cyclohexane, the corresponding thiophens exhibit a strong preference for the *cis*-conformation. For the furans this is readily explicable in terms of minimization of dipole–dipole interaction energy, while for the thiophens it may be indicative of a stabilizing interaction between the sulphur and oxygen atoms.

Phenyl and Mesityl 2-Furyl and 2-Thienyl Ketones.—The conformations of molecules (5)—(8) are determined by the best compromise, in relation to energy minimization, between two opposing factors: conjugative interactions and steric repulsions. Since the uniplanar forms are sterically impossible, the heterocyclic group and the phenyl ring necessarily compete for more effective conjugation with the carbonyl group. Reference has already been made to the greatly superior conjugating abilities, relative to phenyl, of both the 2-furyl and 2-thienyl rings. Therefore it can be inferred that the dihedral angle, ϕ, between the plane of the phenyl or mesityl ring and that of the C–CO–C group will be larger than the corresponding angle for the heterocycle. Experimental evidence (dipole moments,[10,14,17,48] u.v.,[5,68-70] i.r.,[70,71] and n.m.r.[59,60,72]

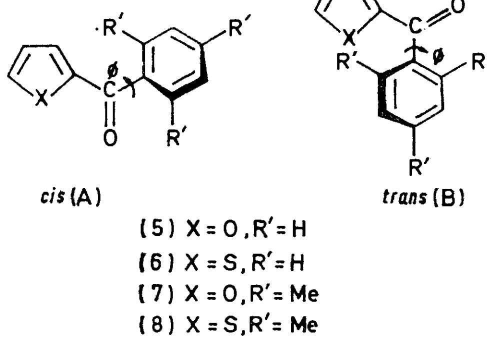

FIGURE 2

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* Estimates of the enhanced conjugating abilities of 2-furyl and 2-thienyl groups can be derived from the near linear plot of free valence index, F_1, against the logarithm of rate constants for anionotropy of allyl alcohols in 60% dioxan solution at 30° (E. A. Braude and J. S. Fawcett, *J. Chem. Soc.*, 1952, 4158; E. A. Braude, *Quart. Rev.*, 1950, **4**, 404). Results (relative to phenyl) emerge as 2-furyl, 1·9 and 2-thienyl, 1·7.

[67] J. de Heer, *J. Amer. Chem. Soc.*, 1954, **76**, 4802.

[68] L. Kaper, J. U. Veenland, and T. J. de Boer, *Spectrochim. Acta*, 1967, **23A**, 2605.

[69] L. Kaper and T. J. de Boer, *Spectrochim. Acta*, 1971, **27A**, 261.

[70] A. Arcoria, E. Maccarone, G. Musumarra, and G. Romano, *Spectrochim. Acta*, 1973, **29A**, 161.

[71] C. Andrieu and Y. Mollier, *Bull. Soc. chim. France*, 1969, 831.

[72] C. Andrieu, M. L. Martin, and G. J. Martin, *Bull. Soc. chim. France*, 1968, 703.

spectra) supports this prediction and suggests, furthermore, that the heterocyclic ring is coplanar, or near-coplanar, with the C–CO–C plane. Because of severe steric hindrance arising from the *o*-methyl groups, it can be anticipated that (6) and (8) will have structures in which the dihedral angle between the mesityl and C–CO–C planes is close to 90°.

In our analysis it was assumed, on the basis of the evidence cited, that the favoured conformations of (5)—(8) are those in which the heterocyclic ring and the C–CO–C group are coplanar. To establish the equilibrium proportions of the *cis* (A) and *trans* (B) isomers the observed dipole moments were analysed in conjunction with the simple model already described. Predicted dipole moments are: (5A) and (7A), 12·3; (5B) and (7B), 8·9; (6A) and (8A), 11·7; (6B) and (8B), 8·8. The apparent isomer abundances are shown in Table 5. With the exception of mesityl 2-furyl ketone, the results are similar to those for the corresponding 2-formyl- and 2-acetyl-furans and -thiophens: in cyclohexane at 25° the preferred conformations are, respectively, *trans* for the furans, and *cis* for the thiophens. In the case of mesityl 2-furyl ketone, the expected *trans*-structure appears to be destabilized relative to the predominant *cis*-form.

TABLE 5

Percentage abundances at 25° of *cis* (A) and *trans* (B) isomers (predicted from dipole moments), and calculated molar Kerr constants * for conformations of phenyl and mesityl 2-furyl and 2-thienyl ketones

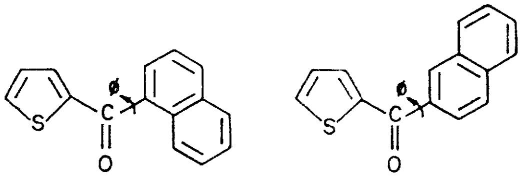
	Abundance	Calculated molar Kerr constant			
Structure	(%)	$\phi = 0°$	$\phi = 30°$	$\phi = 60°$	$\phi = 90°$
(5A)	30 ± 10	+602	+422	+62	−118
(5B)	70 ± 10	+501	+381	+143	+23
		(+531)	(+393)	(+119)	(−19)
(6A)	75 ± 10	+764	+605	+289	+130
(6B)	25 ± 10	+450	+340	+119	+8
		(+686)	(+539)	(+247)	(+100)
(7A)	75 ± 10	+409	+179	−282	−512
(7B)	25 ± 10	+610	+456	+147	−8
		(+459)	(+248)	(−175)	(−386)
(8A)	90 ± 10	+456	+255	−147	−349
(8B)	10 ± 10	+563	+420	+134	−9
		(+467)	(+272)	(−119)	(−315)

* Exaltation of polarisability was distributed isotropically for (5) and (6) and as follows for (7) and (8): (7), $\Delta b_{xx} = 2{\cdot}4$, $\Delta b_{yy} = 0{\cdot}5$, $\Delta b_{zz} = 2{\cdot}4$; (8), $\Delta b_{xx} = 2{\cdot}9$, $\Delta b_{yy} = 0$, $\Delta b_{zz} = 2{\cdot}9$. Note also that for (8) the observed molar refraction appears to be too low.

To determine the orientation of the phenyl or mesityl group in these molecules we compared the measured Kerr constants with those calculated for appropriate mixtures of *cis*- and *trans*-isomers having particular values of the dihedral angle, ϕ. Predicted Kerr constants for some conformations are shown in Table 5; the values in parentheses are those expected on the basis of the isomer abundances obtained from the analysis of dipole moments.

From the calculations for (5) and (6), in which isotropic distributions of exaltation were made, conformational angles emerge as *ca.* 53 ± 10° for phenyl 2-furyl ketone and 71 ± 10° for phenyl 2-thienyl ketone. These results, which seem sterically reasonable, may be compared with the recently reported value of 70 ± 10° for phenyl pyrrol-2-yl ketone.[73] The observed molar Kerr constants for the mesityl derivatives (7) and (8) are considerably more negative than those of the corresponding phenyl compounds (5) and (6), so that larger conformational angles can be expected in the former molecules. In order to obtain sufficiently negative Kerr constants it proved necessary to make an anisotropic apportionment of exaltation (see Table 5), and there seems little doubt that (7) and (8) have near-orthogonal structures (*i.e.* ϕ *ca.* 90°). It is noteworthy that mesityl phenyl ketone, which is similar to (7) and (8), also was found to have a conformation in which the planes of the mesityl and C–CO–C groups are approximately perpendicular.[28,74]

1- *and* 2-*Naphthyl* 2-*Thienyl Ketones*.—These molecules, whose conformations have not previously been determined, can be expected to show structural similarities with the phenyl and mesityl 2-thienyl ketones, although the naphthyl group gives rise to additional steric factors. It is clear from the measured dipole moments (Table 1) of (9) and (10) that the *cis*-isomer is again strongly, and in the case of (10) perhaps exclusively, favoured. To simplify the analysis of Kerr constants we therefore consider only the conformations of the predominant *cis*-isomers (9A) and (10A), it being assumed that in each case the 2-thienyl and C–CO–C groups are coplanar. Trial calculations confirm that results are virtually unaffected by inclusion of the small amounts (<20%) of *trans*-conformers indicated by the dipole moments.



(9A) (10A)

FIGURE 3

Particular structures of (9A) and (10A) can be defined by the conformational angle, ϕ, between the plane of the 1- or 2-naphthyl groups and the plane containing the carbonyl group. The reference (*i.e.* $\phi = 0$) structures are the sterically impossible uniplanar forms shown in Figure 3, and values of ϕ refer to clockwise rotations when the rotation axis is viewed from C (ring) to C (carbonyl). Some calculated Kerr constants for (9A) and (10A) are shown in Table 6. The large exaltations of polarisability exhibited by these molecules were distributed isotropically, since no information regarding more correct apportionments is available.

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[73] C. L. Cheng, I. G. John, G. L. D. Ritchie, and P. H. Gore, *J.C.S. Perkin II*, 1974, 1318.

[74] P. H. Gore, J. A. Hoskins, R. J. W. LeFèvre, L. Radom, and G. L. D. Ritchie, *J. Chem. Soc.* (*B*), 1969, 227.

Comparison of observed and predicted Kerr constants, which span a very wide range, indicates that in 1-naphthyl 2-thienyl ketone, as in mesityl-2-thienyl ketone, the planes of the naphthyl and C–CO–C groups are approximately perpendicular (ϕ *ca.* 90°). In the case of 2-naphthyl 2-thienyl ketone, concordance is achieved when the dihedral angle is *ca.* 65° or, alternatively, 145°. The Kerr effect cannot differentiate between these possible stereostructures, but the former ($\phi = 65 \pm 10°$), which is the less hindered, is analogous to the apparent conformation of the sterically similar phenyl 2-thienyl ketone ($\phi = 75 \pm 10°$).

TABLE 6

Calculated molar Kerr constants for *cis*-conformations of 1-naphthyl 2-thienyl ketone (9A) and 2-naphthyl 2-thienyl ketone (10A)

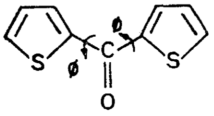
Molecule	$\phi = 0°$	30°	60°	90°	120°	150°	180°
(9A)	+1396	+948	+53	−395	+53	+948	+1396
(10A)	+1476	+1128	+398	−112	−56	+347	+565

TABLE 7

Calculated dipole moments and molar Kerr constants for conformations of di-2-thienyl ketone

	$\phi = 0°$	30°	60°	90°	120°	150°	180°
μ	13·40	13·00	11·90	10·40	8·91	7·81	7·41
$_{\mathrm{m}}K$	+966	+532	−176	−367	−96	+208	+326

Di-2-thienyl Ketone.—It has been inferred from previous dipole moment studies [10,48] that the preferred conformation of this molecule is a non-planar variant of the *cis–cis*-structure shown in Figure 4. Di-2-thienyl ketone (11) can be expected to resemble benzophenone, which is believed to exist as a conrotatory structure in which the angle, ϕ, between the planes of the phenyl and C–CO–C groups is *ca.* 42°.[28,75] In analysing the observed dipole moment and Kerr constant of (11) we therefore consider only the analogous conrotatory forms, *i.e.* the 2-thienyl rings are equivalently rotated from the C–CO–C plane with retention of a C_2 molecular axis.



(11)

FIGURE 4

For this molecule, the predicted values of both the dipole moment and the Kerr constant depend on the dihedral angle, ϕ. Our calculations, which incorporate an isotropic distribution of the polarisability exaltation, are summarized in Table 7. From the measured dipole moment, ϕ emerges as *ca.* 59°, while comparison of the observed and predicted Kerr constants suggests a value of 38°. It may be noted from the data in Table 7 that the molecular dipole moment exhibits a relatively small dependence on ϕ, because of the low polarity of the thiophen rings. However the molar Kerr constant again shows a very large variation, so that this property should yield the more reliable estimate of the interplanar angle. We therefore conclude that the preferred conformation of di-2-thienyl ketone has a dihedral angle of *ca.* 45 ± 10°.

General Conclusions.—Measurements of dipole moments and Kerr constants have provided confirmatory evidence that in cyclohexane at 25° the *trans*-conformations of 2-substituted furan carbonyl compounds are the more abundant, while for the thiophen derivatives the *cis*-isomers are strongly preferred. The enhanced stability of the *trans*-form of the furans can be attributed to an energetically favourable alignment of the furan and carbonyl group dipoles. Studies of the analogous 2-substituted pyrroles [73] and pyridines [76] similarly established the importance of dipole–dipole interactions in determining the conformational preferences of these molecules. Since the large dipole moment of pyrrole acts along the H–N bond towards the ring (in contrast to the moments of furan and thiophen, which are oppositely directed) the *cis*-structures of the 2-acylpyrroles are very strongly favoured. The predominance of the *trans*-forms of pyridine-2-carbaldehyde and related molecules is likewise explicable in terms of dipole–dipole interactions. For the corresponding thiophens, however, a different explanation is required, and a stabilizing interaction between the sulphur and oxygen atoms has been suggested. It is of interest to note also that the *cis*-conformation of various substituted 2-vinyl-furans and -thiophens has been shown [77] to be the preferred structure, possibly because of a favourable relative orientation of the highly polarisable C=C bond and the dipole moment of the heterocyclic ring.

The conformations of phenyl 2-furyl ketone and other molecules having two different aromatic rings attached to the carbonyl group are determined by the best compromise between competing steric and mesomeric effects. There is compelling evidence to suggest that the 2-furyl, 2-thienyl, and pyrrol-2-yl groups, in marked

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[75] R. Hoffmann and J. R. Swenson, *J. Phys. Chem.*, 1970, **74**, 415.

[76] C. L. Cheng and G. L. D. Ritchie, *J.C.S. Perkin II*, 1973, 1461.

[77] T. N. Huckerby, *Tetrahedron Letters*, 1971, 353.

contrast to the 2-pyridyl group, conjugate much more effectively than a phenyl substituent with the electron-withdrawing carbonyl group. In consequence, the five-membered heterocycle retains the coplanar *cis*- or *trans*-arrangement with the C–CO–C unit, and steric repulsions are accommodated by relatively large rotations of the phenyl, mesityl, or naphthyl groups from this plane.

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