Conformational Analysis of Organic Carbonyl Compounds. Part 5.[1—4] *p*-Methoxybenzoyl Derivatives of Benzo[*b*]furan, Benzo[*b*]thiophene, and Naphthalene

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The conformational analysis of 2- and 3-(*p*-methoxybenzoyl)-benzo[*b*]furan and -benzo[*b*]thiophene and 1- and 2-(*p*-methoxybenzoyl)naphthalene was performed by the n.m.r. lanthanide-induced shift (LIS) method on ^1H and ^{13}C chemical shifts with $Yb(fod)_3$ as shift reagent. In the 2-substituted benzo[*b*]furan a chelate structure having the lanthanide atom bound to both carbonyl and furyl oxygens is formed, so the results do not represent useful information for the conformational properties of this molecule in solution. For the 2-benzo[*b*]thiophene derivative the S,O-*cis* (*Z*) conformation was found to be more abundant in the equilibrium mixture of the two nearly planar conformers. In the corresponding 3-substituted heterocycles the predominant conformation is that of X,O-*trans* type with a similar degree of distortion from planarity in the two compounds. In all these molecules the *p*-methoxyphenyl ring is twisted *ca.* 30° from the carbonyl plane. These systems thus demonstrate the tendency of the carbonyl group to adopt the characteristic orientation of the corresponding formyl and acetyl derivatives, with deviations from planarity due to steric factors. In the 1-naphthyl derivative the naphthyl group turns out to be perpendicular to the planar methoxybenzoyl group. The situation of 2-(*p*-methoxybenzoyl)-naphthalene resembles that of benzophenone and 4,4′-dimethoxybenzophenone: the latter compound was also analysed in the present work, with regard to its conformational properties, in order to test the degree of reliability of the experimental method employed when applied to relatively large molecular systems.

Formyl and acetyl derivatives of aromatic and heteroaromatic compounds were previously examined [1—4] in order to determine their conformational properties. For benzene, naphthalene, and heteroaromatic derivatives, the experimental results indicate that the most stable conformation of the carbonyl group corresponds to its almost coplanar orientation with respect to the aromatic ring, unless the aromatic ring contains substituents in the *ortho* position as in the case of 2,4,6-trimethylacetophenone,[5] where the planes of the carbonyl group and aromatic ring reach dihedral angles as large as 50—90°. In the case of anthracene-9-carbaldehyde the experimental evidence obtained from ^1H lanthanide-induced shifts (LIS) are not conclusive in differentiating between a perpendicular conformation and the presence of two equally populated all-planar conformers, though the latter situation seems more probable.

For the benzoyl derivatives of aromatic and heteroaromatic rings with respect to the plane of the carbonyl group should all-planar molecule represents a sterically impossible conformation. As a consequence, a certain degree of twist of one or both rings with respect to the plane of the carbonyl group should always be present. In benzophenones [6,7] this angle of twist is *ca.* 30° for the unsubstituted compound and increases to 45 and 90° when one and two *ortho*-substituents are introduced in at least one of the rings.

The conformational properties in aromatic ketones of the heterocyclic series have also received much attention. Regarding the furan and thiophene series, it has been reported [8—20] for thienyl phenyl ketones that, with respect to the carbonyl group, the heterocyclic ring tends to be nearly coplanar, while a significantly higher twist occurs for the phenyl ring. The degree of distortion from planarity in dithienyl,[14,20] difuryl,[10,11,21] and mixed thienyl furyl ketones [11,21] seems to admit of less generalization, since, although contradictory conclusions exist, it appears that the extent of departure from coplanarity between the carbonyl plane and heterocyclic ring depends on the pair of heterocycles involved and on the location of the C=O group. Independently of the extent of deviation from planarity in these molecules, the orientation of the carbonyl oxygen is of nearly exclusive S,O-*cis* type [10—13,15] and preferential O,O-*trans* type,[10,11,21,22] in the 2-thienyl and 2-furyl groups respectively.

Significant distortion from planarity is also found in benzoylpyridines [23] and, in the 2-pyridyl derivative, the N,O-*trans* distorted conformation is the more abundant one.

In the case of ketones R^1–C(O)–R^2 where R^1 is 2-thienyl [14] or phenyl [24] and R^2 1- or 2-naphthyl, the latter is rotated with respect to the carbonyl plane and this is more pronounced in the case of the 1-naphthyl group.

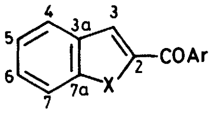
In the absence of steric effects, the different degree of coplanarity of aromatic and heteroaromatic rings with the carbonyl plane has been attributed [8,12,14,22,25,26] to the extent of π-conjugation, in view of the widely accepted higher ability of five-membered heterocycles, with respect to a phenyl ring, to propagate π-conjugation [8,9,11,14] and transmit substituent effects to a reaction centre.[27]

With this general situation concerning carbonyl compounds containing aromatic and heteroaromatic rings, our intention in the present study has been to bring a quantitative and comparative experimental approach to the knowledge of the conformational properties of aroyl derivatives of five-membered heterocycles, furan and thiophene, condensed with the benzene ring, of naphthalene, and of benzene. This in order to compare results given by the same experimental technique and to attempt a homogeneous analysis of the effects contributing to determine the conformations of these molecules.

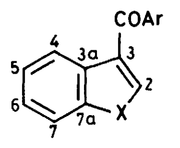
Results and Discussion

The derivatives examined are (**1**)—(**5**). The *p*-methoxyphenyl group has been chosen in the place of phenyl in order to have simpler ^1H n.m.r. spectra. We also assume that the relative orientation of the rings with respect to the carbonyl plane should not be significantly influenced by the *para*-substituent in the phenyl ring, on account also of the conformational results found in *para*-substituted acetophenones.[5b] The chemical shifts of the compounds examined, both at the frequency of ^{1}H and ^{13}C nuclei, are reported in Tables 1—4.

The analysis of the ^{1}H multiplets was carried out with the aid of the MIMER program[28] in order to obtain a complete set of chemical shifts and proton–proton coupling constants. The latter quantities, not reported in Tables 1 and 2, include the inter-ring coupling constants as well, relative to the heterocycle and naphthalene ring, and are close to those reported in the literature[4,29] for similar compounds. The ^{1}H n.m.r. spectra were recorded in two different solvents, namely [^{2}H]chloroform and [$^{2}H_6$]acetone, in order to observe whether the solvent shift may add further information concerning the conformational situation of these molecules and, in particular, to check the influence of solvent polarity on the conformer populations: for formyl and acetyl derivatives of furan[30] and benzo[*b*]furan[4] these were found to be significantly solvent-dependent. For ^{13}C n.m.r. only the spectra in chloroform solution are reported, since acetone causes rather small solvents shifts (restricted within 1 p.p.m.), in agreement with the well known low sensitivity of carbon shielding to solvent effects.

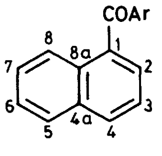


(1)

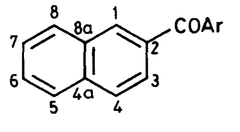


(2)

a; X = O
b; X = S



(3)

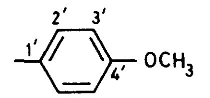


(4)

Ar — CO — Ar

(5)

Ar =



The ^{1}H chemical shifts which should significantly change upon conformational changes in the carbonyl group are 3-H in 2-substituted and 2- and 4-H in 3-substituted benzo[*b*]furan and benzo[*b*]thiophene. The shifts relative to the unsubstituted heterocycles for 3-H due to the ArCO and CH_3CO groups are similar, while in the corresponding 3-substituted derivatives the ArCO group causes smaller low-field shifts on 2- and 4-H than the CH_3CO substituent. For the acetyl group, the coplanarity of the carbonyl plane and heterocyclic ring is widely accepted and deshielding of the heterocyclic protons seems to be caused[31,32] by magnetic anisotropy and the electric field effects of the carbonyl group. At a preliminary stage of approximation this behaviour suggests that the carbonyl plane should only slightly deviate from coplanarity with the heterocyclic ring in 2-substituted derivatives (**1a** and **b**), while deviations of higher order or equilibrium mixtures of conformers should be present in the 3-substituted heterocycles (**2a** and **b**). In 1-(*p*-methoxybenzoyl)naphthalene (**3**) the chemical shift differences for 2- and 8-H with respect to the corresponding CH_3CO derivative[33] are even more pronounced, and a large deviation[34] from

Table 1. ^{1}H N.m.r. chemical shifts (δ values) in compounds (**1**) and (**2**) recorded in [^{2}H]chloroform and [$^{2}H_6$]acetone (0.3M). ΔM are the LIS values and refer to $Yb(fod)_3$ in $CDCl_3$

Compound	Solvent	2-H	3-H	4-H	5-H	6-H	7-H	2′-H	3′-H	OCH_3[a]
(**1a**)	$CDCl_3$		7.51	7.72	7.32	7.48	7.63	8.10	7.01	3.90
	ΔM		23.19	1.02[a,b]	1.13[a,b]	1.87[a,b]	3.73[a,b]	29.44	6.59	2.96
	$(CD_3)_2CO$		7.66	7.84	7.37	7.54	7.68	8.13	7.11	3.92
(**1b**)	$CDCl_3$		7.84	7.87	7.41	7.47	7.90	7.95	7.01	3.90
	ΔM		21.42	3.43	1.54	1.80	2.22	27.64	5.22	2.14
	$(CD_3)_2CO$		8.04	8.03	7.47	7.54	8.04	7.98	7.12	3.92
(**2a**)	$CDCl_3$	8.07		8.18	7.38	7.40	7.56	7.91	7.00	3.89
	ΔM	19.54		24.86	1.14[a,b]	2.05[a,b]	4.39	27.54	4.33	1.19
	$(CD_3)_2CO$	8.46		8.17	7.40	7.45	7.65	7.97	7.09	3.91
(**2b**)	$CDCl_3$	7.94		8.44	7.48	7.43	7.90	7.90	6.98	3.89
	ΔM	19.87		30.25	1.12	1.04	3.61	24.06	3.73	1.03
	$(CD_3)_2CO$	8.25		8.41	7.50	7.48	8.05	7.90	7.08	3.91

[a] Not included in LIS simulation. [b] Uncertain values.

Table 2. ^{1}H N.m.r. chemical shifts (δ values) in compounds (**3**)—(**5**) recorded in [^{2}H]chloroform and [$^{2}H_6$]acetone (0.3M). ΔM are the LIS values and refer to $Yb(fod)_3$ in $CDCl_3$

Compd.	Solvent	1-H	2-H	3-H	4-H	5-H	6-H	7-H	8-H	2′-H	3′-H	OCH_3[a]
(**3**)	$CDCl_3$		7.54	7.50	7.97	7.90	7.51	7.47	8.01	7.85	6.91	3.85
	ΔM		24.30	5.47	4.52	3.05	1.10	1.20	32.71	25.17	4.78	1.72
	$(CD_3)_2CO$		7.56	7.58	8.07	8.00	7.55	7.50	7.94	7.79	7.02	3.88
(**4**)	$CDCl_3$[b]	8.23		7.88	7.92	7.89	7.59	7.55	7.90	7.88	6.99	3.89
	ΔM	26.63[c]		26.92[c]	4.54	2.18	1.49[a,c]	1.30[a,c]	3.15	26.20	5.07	2.21
	$(CD_3)_2CO$	8.27		7.86	8.03	8.00	7.60	7.65	8.05	7.87	7.09	3.91
(**5**)	$CDCl_3$									7.79	6.95	3.89
	ΔM									27.04	5.07	2.20

[a] Not included in LIS simulation. [b] The chemical shifts in $CDCl_3$ were obtained by direct inspection of the multiplets owing to the complexity of the spectrum, restricted within a narrow frequency range: the chemical shifts of 5- and 8-H may also be reversed. [c] Uncertain values.

Table 3. ^{13}C Chemical shifts (δ values) in compounds (**1**) and (**2**) recorded in [^{2}H]chloroform, LIS values ΔM due to $Yb(fod)_3$ and corrected ($\Delta M - \Delta D$) for the complexation shift[37] in the presence of $La(fod)_3$

Compd.		C-2	C-3	C-4	C-5	C-6	C-7	C-3a	C-7a	C-1′	C-2′	C-3′	C-4′	C=O	OCH_3
(**1a**)	δ	152.89	115.34	123.15	123.89	127.97	112.47	127.13	155.87	129.92	131.99	113.90	163.69	182.73	55.53
	ΔM	62.10	35.23	4.64	3.09	2.99	6.16	13.20	16.91	49.82	31.05	12.84	11.23	118.27	3.13
	$\Delta M - \Delta D$	62.10	30.32	4.64	3.09	2.99	6.16	13.20	15.87	51.92	28.54	12.84	9.54	116.37	3.13
(**1b**)	δ	143.40	131.06	125.87	124.97	127.13	122.84	139.14	142.46	130.56	131.72	113.87	163.41	188.02	55.52
	ΔM	48.83	28.82	5.55	3.35	3.66	3.79	10.90	11.38	49.17	29.32	10.89	9.62	110.68	
	$\Delta M - \Delta D$	52.28	24.54	5.55	3.35	2.68	3.79	10.90	9.49	50.51	27.12	10.89	8.22	107.14	
(**2a**)	δ	150.94	121.47	122.89	124.32	125.65	111.45	125.65	155.65	132.07	131.15	113.97	163.40	188.57	55.49
	ΔM	27.90	52.45	19.06	5.66[a]	4.51[a]	6.40	28.62	13.63	50.28	28.51	9.62	8.43	114.67	2.05
	$\Delta M - \Delta D$	23.11	53.37	19.06	5.66	4.51	6.40	30.16	13.63	53.31	25.46	9.62	6.79	109.12	2.05
(**2b**)	δ	136.05	135.36	125.07	125.43	125.43	122.34	137.75	140.12	131.94	131.94	113.79	163.34	189.61	55.51
	ΔM	26.17	46.56	19.83	6.48	4.16	5.73	26.76	11.98	46.47	25.93	8.86	8.38	102.58	1.36
	$\Delta M - \Delta D$	21.47	47.46	19.83	6.48	4.16	5.73	27.74	11.98	48.46	23.66	8.86	6.96	98.49	1.36

[a] Uncertain values, not included in LIS simulation.

Table 4. ^{13}C Chemical shifts (δ values) in compounds (**3**)—(**5**) recorded in [^{2}H]chloroform, LIS values ΔM due to $Yb(fod)_3$ and corrected ($\Delta M - \Delta D$) for the complexation shift[37] in the presence of $La(fod)_3$

Compd.		C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-4a	C-8a	C-1′	C-2′	C-3′	C-4′	C=O
(**3**)	δ	137.04	126.79	124.43	130.63	128.35	126.35	126.99	125.73	133.66	130.88	131.07	132.76	113.70	163.80	196.64
	ΔM	47.03	27.43	10.50	9.49	5.23	3.82	6.30	21.08	11.09	26.46	45.88	27.18	10.21	9.35	105.55
	$\Delta M - \Delta D$	48.67	25.78	10.50	8.49	5.23	3.82	6.30	21.08	11.09	26.46	47.29	25.00	10.21	7.91	100.98
(**4**)	δ	130.99	135.72	125.79	128.20	127.81	128.04	126.73	129.27	134.91	132.31	130.32	132.49	113.52	163.12	195.43
	ΔM	27.89	49.56	28.70	10.48	3.26	3.02	2.56	4.81	8.54	10.74	49.81	29.24	11.00	9.76	112.65
	$\Delta M - \Delta D$	25.06	51.66	27.64	9.08	3.26	3.02	2.56	4.81	8.54	10.74	51.88	26.24	11.00	7.79	107.13
(**5**)	δ											130.88	132.19	113.52	162.89	194.36
	ΔM											48.49	28.83	10.60	9.97	113.08
	$\Delta M - \Delta D$											50.66	26.20	10.60	7.94	108.40

coplanarity of the carbonyl and naphthyl groups should be present. In the 2-(*p*-methoxybenzoyl)naphthalene (**4**) these differences are small and the distortion is expected to be smaller than in the corresponding 1-aroyl derivative. This conclusion should nevertheless be regarded with caution, since the spectra of compounds (**4**) and of 2-acetylnaphthalene refer to different solvents.

The change of solvent polarity does not significantly affect the general behaviour of ^{1}H chemical shifts: the variations are significant only for 3-H in 2-substituted and for 2-H in 3-substituted derivatives, and of the same order of magnitude as those found for the acetylbenzo[*b*]furans[4] and for the formyl- and acetyl-furans and -thiophenes.[35,36] It is thus rather difficult to obtain information regarding the conformational requirements of these molecules from the ^{1}H solvent shifts: nevertheless it seems that conformational equilibria, where present, are influenced by solvents in a similar way in the different carbonyl derivatives of these heterocycles.

The ^{13}C chemical shifts of the ring carbons, reported in Table 3, differ slightly with respect to those of the corresponding acetyl derivatives of benzo[*b*]furan[4] and benzo[*b*]thiophene.[3] The differences are nevertheless small, within 2 p.p.m., and the highest values are found for the carbon atoms which are in the neighbourhood of the carbonyl substituent. The low sensitivity of ring-carbon atoms to conformational effects in substituted benzophenones and acetophenones has also been previously pointed out.[6]

The LIS method provides more quantitative information on the conformational properties of organic carbonyl compounds. Hitherto the method has been applied,[2–4] with satisfactory results, to the conformational analysis of formyl and acetyl derivatives of the heterocycles here considered. Recently, quantitative application of the LIS method by simultaneous use of ^{1}H and ^{13}C resonances, with the ^{13}C diamagnetic complexation shift removed by use of $La(fod)_3$, was reported[37] in the determination of conformational isomerism and structure of aromatic aldehydes and ketones, including sterically crowded compounds[5] where the carbonyl group turns out to be non-coplanar with the aromatic ring.

The pseudocontact shift (ΔM) in the presence of $Yb(fod)_3$ and the effect of complex formation[37,38] (ΔD) on ^{13}C using $La(fod)_3$ are collected in Tables 1—4. The experimental LIS were processed by employing the McConnell–Robertson equation,[39] assuming an axially symmetric 1 : 1 lanthanide–substrate complex. The LIRAS-3 computer program[38] was employed and the 'four-site' model for complexation adopted. The procedure followed and the symbols appearing in the LIS simulation results are those described in previous papers.[3,4]

In order to achieve better understanding of the reliability limit to be attributed to the results obtained with this method applied to the compounds here chosen, we shall first discuss the case of 4,4′-dimethoxybenzophenone (**5**). This molecule was chosen as a reference compound since the conformations of benzophenone and substituted benzophenones are known.[6,40] The molecular geometry of compound (**5**), for LIS simulation, was constructed from regular hexagons for the benzene ring, while for the carbonyl group, perfect trigonal geometry was assumed, with bond distances C=O of 1.22 and C–Ar of 1.458 Å. This geometry was also adopted for the *p*-methoxybenzoyl group in all the compounds examined. The localization of the lanthanide atom bonded to the carbonyl group requires three co-ordinates[39] (R, φ, and ψ), while the '*endo*' or '*exo*' position on the oxygen lone-pairs with respect to the aryl ring is equally probable (*endo* population 50%) for complexation owing to the symmetry of the molecule. The normalizing factor (f) is the fourth unknown of the problem and, together with the angle of twist γ of the aryl ring with respect to the carbonyl plane, five unknowns have to be determined. The system is overdetermined since seven experimental shifts are available (two for ^{1}H and five for ^{13}C, the ^{1}H and ^{13}C chemical shifts of the OCH_3 group were

Table 5. Results of LIS simulation: molecular geometry parameters for the complexes[a] and conformational properties for derivatives (**1**)—(**5**)

Compound	$R_{\text{cryst.}}$	Sum-Diff (p.p.m.)	R(Å)	φ(°)	ψ(°)	f	Population *endo*	Conformational angles (°)[b]		Amount (%)
								θ	γ	
(**1a**)	0.032[c]	1.23	*c*	*c*	*c*	*c*	*c*	0	0	100
(**1b**)	0.021	0.67	2.70	90	155	3 147	45	0	30	65—70
								180	30	35—30
(**2a**)	0.031	1.17	3.00	50	160	3 714	25	30	28	100
(**2b**)	0.030	1.03	2.75	65	165	2 968	20	30	33	100
(**3**)	0.028	0.85	2.80	85	150	3 127	50	90	0	100
(**4**)	0.030	0.94	2.70	90	155	3 141	50	30	30	65—70
								150	30	35—30
(**5**)	0.014	0.66	2.80	50	170	3 199	50	30	30	100

[a] For the symbols see refs. 37 and 38. [b] The angles are defined in Figure 1: estimated error ±10°. [c] Chelate structure with the lanthanide atom bonded to the carbonyl and furyl oxygens: R, φ, and ψ are not reported since they refer to the dummy atom (see text).

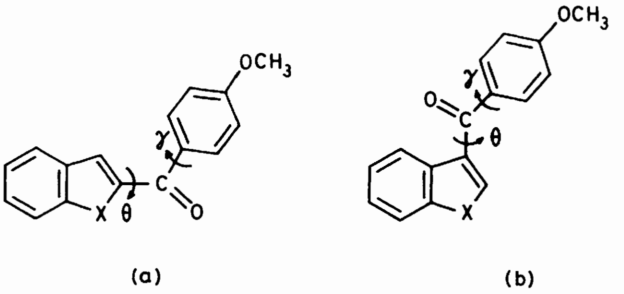
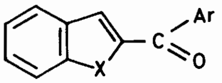
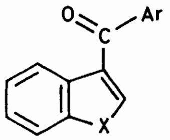


Figure 1. Representation of a general formalism for the compounds examined defining the angles of rotation θ and γ of the Ar rings around the Ar–C(O) bonds: the all-planar situation depicted corresponds to θ = γ = 0. Formula (a) applies to 2-benzo[*b*]furan (X = O), 2-benzo-[*b*]thiophene (X = S), and 2-naphthyl (X = CH=CH) derivatives; formula (b) applies to 3-benzo[*b*]furan (X = O), 3-benzo[*b*]thiophene (X = S), and 1-naphthyl (X = CH=CH) derivatives



X, O-*cis*



X, O-*trans*

excluded from LIS simulation). The best agreement between calculated and experimental LIS values, expressed as $R_{\text{cryst.}}$ in Table 5, is found for an angle of twist of 30°, in satisfactory agreement with results from different techniques.[6,40]

For compounds (**1**) and (**2**) we employed either the molecular geometry constructed from that of the heterocyclic rings[41] and that of the *p*-methoxybenzoyl group employed in the case of compound (**5**), or experimental molecular geometry:[42] the results of LIS simulation were not critically related to the choice of one or other of these two sets of structural parameters as regards $R_{\text{cryst.}}$ and the final values of the angles of twist (θ, γ) defined in Figure 1.

For naphthalene derivatives (**3**) and (**4**), the geometry was constructed from that of the parent hydrocarbon.[43]

In the case of ketones with two different rings, the best agreement in LIS simulation requires the localization parameters of the lanthanide atom and a double rotation minimization as a function of θ and γ angles. Further, conformational equilibria involving different amounts of planar and distorted X,O-*cis* and X,O-*trans* conformations were also taken into account. The same degree of distortion was assumed for the two weight-averaged conformations.

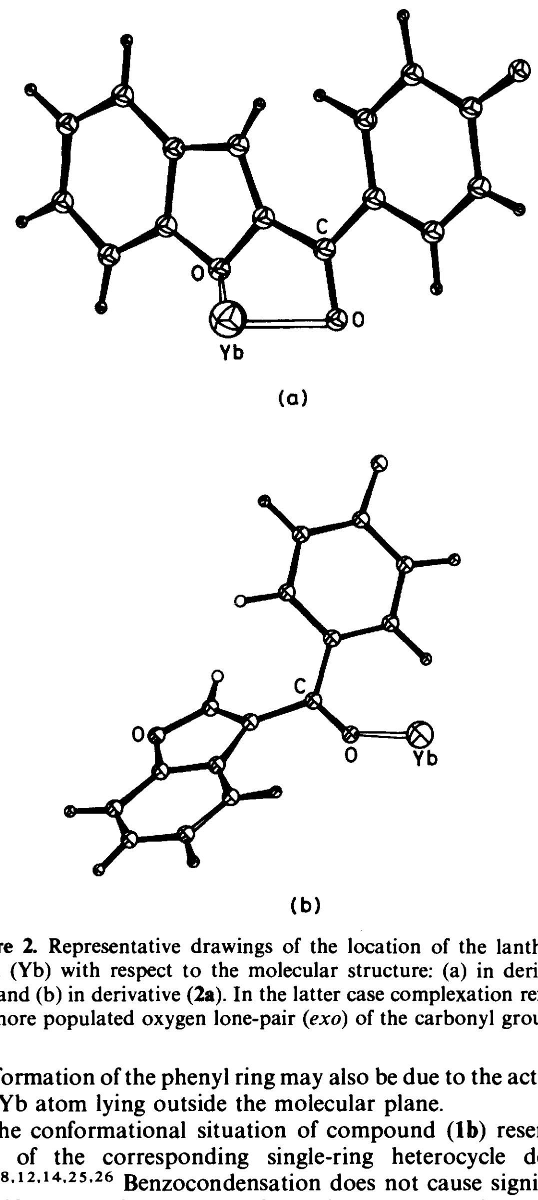
In the case of compound (**1a**) the experimental LIS values for the carbon nuclei directly bonded to the carbonyl group (C-2 and C-1′) differ by >8 p.p.m. This difference could not be reproduced by the calculated LIS values whichever geometry was adopted for the molecule. Since the anomalous LIS value seems to be that of C-2, by comparison also with compound (**1b**), it could, in principle, be supposed that complexation of the lanthanide atom should also involve the heterocyclic oxygen. Accordingly, the presence of a fictitious oxygen atom lying among the carbonyl and furyl oxygens was simulated and the positions of this atom and of the lanthanide were moved until the best agreement between calculated and experimental LIS was reached. In this way it was possible to reproduce the experimentally induced shifts on C-2 and C-1′ (the lowest $R_{\text{cryst.}}$ obtained amounts to 0.032, employing 16 chemical shift values and excluding those of 4-, 5-, 6-, and 7-H which are largely undetermined). In the complex of (**1a**) with Yb(fod)_3 the Yb•••O(=C) bond distance is 1.91 and Yb•••O(furyl) is 1.84 Å; the two oxygen atoms were found in the plane of the heterocyclic ring and O,O-*cis* oriented and the Yb atom is 1.178 Å out of this plane. The phenyl ring was coplanar with the carbonyl plane. A drawing of the location of the lanthanide atom with respect to the molecular structure is shown in Figure 2a.

In the case of compound (**1b**), the lowest deviation between calculated and experimental LIS values was found by averaging conformations of S,O-*cis* and S,O-*trans* type. As shown in Table 5, the amount of the S,O-*cis* form is more abundant, while the averaged conformation is nearly planar (±10°).

Conformations with the phenyl and heterocyclic rings twisted with respect to the carbonyl plane were found for compounds (**2a** and **b**). The C=O bond is directed towards the six-membered ring of the heterocyclic moiety. Unacceptably higher $R_{\text{cryst.}}$ values were found when an equilibrium mixture between planar or distorted conformations was taken into account. The low value of the *endo* population found for these molecules seems reasonable since complexation on this lone-pair is more hindered, being at the side of the condensed ring. The location of the lanthanide atom in derivative (**2a**), referred to the more populated lone-pair (*exo*), is reported in Figure 2b.

Conformational Results and Conclusions.—From the results in Table 5 and referring to the conformational properties of single-ring heterocycles reported in the literature, the following conclusions can be drawn.

For derivative (**1a**) the LIS result cannot be employed for assigning the conformational properties to the molecule in solution, owing to bidentate complex formation. The planar



(a)

(b)

Figure 2. Representative drawings of the location of the lanthanide atom (Yb) with respect to the molecular structure: (a) in derivative (**1a**) and (b) in derivative (**2a**). In the latter case complexation refers to the more populated oxygen lone-pair (*exo*) of the carbonyl group

conformation of the phenyl ring may also be due to the action of the Yb atom lying outside the molecular plane.

The conformational situation of compound (**1b**) resembles that of the corresponding single-ring heterocycle derivative.[8,12,14,25,26] Benzocondensation does not cause significant modifications in the conformational properties of 2-thienylcarbonyl derivatives, on account of the results found for the acetyl and formyl derivatives.[3,4]

The results of Table 5 show the same conformational trend in compounds (**2a** and **b**) with a similar degree of twist for the heterocycle and phenyl rings. Concerning the situation of the 3-furyl group, the following conclusions were reached for different ketones: the 3-furyl group is distorted from planarity in 2-thienyl 3-furyl ketone,[11] the molecule of 2-furyl 3-furyl ketone[11] is completely planar, while the position is contradictory in the case of 3-benzoylfuran.[10,11,16,21] Taking into account the *peri*-interaction of the carbonyl group and the 4-H atom which differentiates compounds (**2a** and **b**) from the corresponding single-ring derivatives, the conformational situation should resemble that of the corresponding 1-naphthyl derivative (**3**), where, nevertheless, the carbonyl group and naphthalene ring are mutually perpendicular. The carbonyl group, twisted 30 ± 10° with respect to the heterocyclic ring, is directed toward the six-membered ring, recalling the X,O-*trans* planar conformation which is present, almost exclusively, in the corresponding 3-acetyl and 3-formyl derivatives.[3,4]

The conformation found for derivative (**3**) shows that the naphthyl ring is perpendicular to the carbonyl plane and, in this situation, the phenyl ring is in the same plane as the carbonyl group. The result coincides with that obtained[24] from the Kerr constant of 1-benzoylnaphthalene and can be compared with the conformation found[14] for 2-thienyl 1-naphthyl ketone, which shows closely similar characteristics and where the 2-thienyl ring is coplanar with the carbonyl group. In the case of 2-naphthyl derivative (**4**) the rings are equally distorted. Previous results for 2-benzoylnaphthalene[24] and 2-naphthyl 2-thienyl ketone[14] indicate distortion of the naphthyl group in these two molecules even greater than that found for compound (**4**), while for the phenyl and 2-thienyl rings the reported twist is negligible. We deem, nevertheless, that distortion of the phenyl ring should be reasonable since the molecule of compound (**4**) is expected not to differ greatly, from a conformational point of view, from that of benzophenone.

Diaryl ketones should assume a preferred conformation where energy minimization is a result of a compromise of different and somewhat opposing factors: steric repulsion, dipole–dipole interactions (stabilizing or destabilizing), conjugative stabilization between the rings and the carbonyl group. A higher conjugative ability of the 2-furyl and 2-thienyl groups with respect to the phenyl ring has been invoked to explain[11] the higher energy barriers for internal rotation in the 2-formyl and 2-acetyl derivatives of furan and thiophene (38—46 kJ mol^{-1}) with respect to the corresponding benzene and 3-acetylfuran derivatives (25—33 kJ mol^{-1}). This property is also shown in chemical reactivity[27] when the transmitting ability of substituent effects to a reaction centre of these rings is compared. In compound (**1b**) the higher stability of the S,O-*cis* (*Z*) conformation should have the same electronic origin[14,36,44] as in the corresponding formyl and acetyl derivatives. In 3-substituted benzo[*b*]furan (**2a**) and benzo[*b*]thiophene (**2b**) and in 1-naphthyl (**3**) derivatives, the relative twist of these rings with respect to the carbonyl plane should result from steric interactions simultaneously involving the C=O bond and the *peri* hydrogen and 2- and 2′-H of the rings. The tendency to give conformations with the C=O group facing the neighbouring six-membered ring is maintained with respect to the corresponding acetyl and formyl derivatives:[2–4] the coplanarity with the carbonyl group is increasingly hindered in the derivatives of heterocycles and of naphthalene. Molecular geometries show that in the planar X,O-*trans* conformation the distances 2-H ··· 2′-H and C=(O) ··· H_{peri} are significantly smaller in the naphthyl derivative.

In the 2-naphthyl derivative (**4**) molecular geometry shows that the interatomic distances between hydrogen atoms of the two rings (1- and 3-H of the naphthyl ring and 2′-H of the phenyl ring) are not significantly different from the equivalent distances in benzophenone. From this point of view, the conformational properties of compound (**4**) should not greatly differ from those of benzophenones. The results of Table 5 show that the two distorted conformations, of *Z*-(θ 150°) and *E*-(θ 30°) type are present in different amounts and the more abundant *E*-distorted form shows the same kind of orientation for C=O found for the corresponding 2-formyl[2,45] and 2-acetyl[2] derivatives. In these molecules the conformational preference should be governed by π-electron interactions involving a *trans*-arrangement of the C=O and C=C bond of the naphthalene ring having the higher π-electron density.[2,45]

Experimental

The n.m.r. spectra of compounds (**1**)—(**5**) were recorded in solution of the selected solvent (0.3M) at 200.058 MHz for ^{1}H and 50.3088 MHz for ^{13}C by employing a Varian XL-200 spectrometer. The reagent shift employed is $Yb(fod)_3$ dried *in vacuo* over phosphorus pentaoxide, added in known and increasing amounts to [^{2}H]chloroform solutions (0.3M) of the substrate examined. The maximum molar ratio between $Yb(fod)_3$ and the substrate was 0.1. The experimental LIS values were measured on the same sample (employing the ^1H decoupling coil of the broad-band probe) at 20.15 MHz for ^{13}C and 80 MHz for ^1H on a Bruker WP80 spectrometer. For the compounds not allowing an accurate analysis of ^1H LIS values at 80 MHz, owing to strong coupling conditions, the spectra at 200 MHz were also recorded and the latter data were normalized to the former ones. The ^1H spectrum of compound **(4)** is quite complex even at 200 MHz, some of the chemical shifts are thus rather undetermined, and the LIS values of 1- and 3-H uncertain. The correlation coefficients for plots relating chemical shifts to the lanthanide:substrate ratio were always $\geqslant 0.999$ and the intercepts identical to the unshifted spectra. All calculations were performed on Cyber-76 CDC and VAX-750 computers.

Compounds.—Commercial (Aldrich) 4,4′-dimethoxybenzophenone **(5)** was crystallized from 95% ethanol. 2-(4-Methoxybenzoyl)benzo[*b*]furan[46] **(1a)**, 2- and 3-(4-methoxybenzoyl)benzo[*b*]thiophene[47] **(1b)** and **(2b)**, and 1-(4-methoxybenzoyl)naphthalene[48] **(3)** were prepared according to literature methods.

3-(4-*Methoxybenzoyl*)*benzo*[b]*furan* **(2a)**. Benzo[*b*]furan-3-carboxylic acid[4] (3.24 g, 20 mmol) and thionyl chloride (6.5 ml, 90 mmol) were refluxed for 2 h and the excess of thionyl chloride was removed under reduced pressure. The crude acyl chloride and anisole (2.71 g, 25 mmol) were dissolved in dry carbon disulphide and aluminium chloride (3.21 g, 24 mmol) was added in portions at 15 °C. The mixture was stirred at 15 °C overnight, decomposed by careful addition of dilute hydrochloric acid, and extracted with ether. The ether solution was washed with dilute sodium carbonate, dried ($MgSO_4$), and evaporated. The residue was crystallized from isopropyl alcohol, yielding product (2.2 g, 44%), m.p. 89—90 °C (Found: C, 76.1; H, 4.9. Calc. for $C_{16}H_{12}O$: C, 76.2; H, 4.8%).

2-(4-*Methoxybenzoyl*)*naphthalene* **(4)**. A Grignard reagent from 2-bromonaphthalene[49] and magnesium powder in THF was allowed to react with a THF solution of 4-methoxybenzoyl chloride[50] at −78 °C according to a general procedure of ketone synthesis.[51] The crude product was purified by column chromatography (SiO_2, light petroleum–diethyl ether 90:10) and by crystallization from cyclohexane, 46% yield, crystals, m.p. 91—93 °C (lit.,[52] 91—92; lit.,[53] 93 °C).

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