Conformational Analysis of Organic Carbonyl Compounds. Part 11.* Conformational Properties of Difuryl, Dithienyl, and Furyl Thienyl Ketones studied by *X*-Ray Crystallography, N.M.R. Lanthanide-induced Shifts and *ab-initio* MO Calculations

Rois Benassi, Ugo Folli, Dario Iarossi, Luisa Schenetti, and Ferdinando Taddei
Dipartimento di Chimica, Università, Via Campi 183, 41100 Modena, Italy
Amos Musatti
Istituto di Strutturistica Chimica, Università, Centro di Studio per la Strutturistica Diffrattometrica del CNR, Viale delle Scienze, 43100 Parma, Italy
Mario Nardelli
Istituto di Chimica Generale ed Inorganica, Università, Centro di Studio per la Strutturistica Diffrattometrica del CNR, Viale delle Scienze, 43100 Parma, Italy

The conformational properties of the diheteroaryl ketones of the furan and thiophene series have been studied both experimentally, in the solid state and in solution, and with a theoretical *ab-initio* approach. *X*-Ray analysis of the samples which are solid at room temperature was possible only for the compounds which gave suitable crystals, *i.e.* di(2-thienyl) ketone (**2**), di(3-thienyl) ketone (**5**), 2-furyl 3-furyl ketone (**7**), 2-thienyl 3-thienyl ketone (**8**) and 3-furyl 2-thienyl ketone (**10**). The crystal data are: (**2**) space group $F\,dd2$, $a = 13.267(2)$, $b = 21.853(4)$, $c = 6.067(1)$ Å, $Z = 8$, $R = 0.0637$ for 388 observed reflections; (**5**) space group $P2_1/n$, $a = 6.174(1)$, $b = 11.184(3)$, $c = 13.203(2)$ Å, $Z = 4$, $R = 0.0776$ for 1 202 observed reflections; (**7**) space group $P2_1/c$, $a = 9.900(4)$, $b = 10.934(6)$, $c = 7.485(2)$ Å, $Z = 4$, $R = 0.0461$ for 984 observed reflections; (**8**) space group $P2_1/c$, $a = 6.183(1)$, $b = 11.109(1)$, $c = 13.379(2)$ Å, $Z = 4$, $R = 0.0732$ for 1 186 observed reflections; (**10**) space group $P\bar{1}$, $a = 13.799(2)$, $b = 10.039(2)$, $c = 6.084(1)$ Å, $Z = 4$, $R = 0.0639$ for 1 973 observed reflections. The crystal structures of compounds (**5**) and (**8**) are disordered: for the former the disorder concerns the position of one ring, whereas both rings are involved in the latter. For compound (**10**) the structure of the two crystallographically independent molecules is the same. From the n.m.r. LIS (lanthanide-induced shifts) measurements (on ^1H and ^{13}C) indicative information is obtained on the type of conformer and its relative population present in the solution equilibrium mixture. MO *ab-initio* calculations, performed by employing the 3-21G or 3-21G* (with d-orbitals on the sulphur atom) basis sets for the ground-state conformers of all the molecules considered, show that the solid-state structures are very similar to those calculated for the conformers with the lowest-energy content and the calculated conformer populations are in qualitative agreement with measurements in solution. As a general trend, the solid-state structures, the preferred conformations found in solution and those calculated for the free molecules show that the preferred orientation of one heterocyclic ring with respect to the carbonyl group is of the type found in the corresponding formyl and acetyl derivatives and is maintained in all the diheteroaryl ketones. For the molecules having conformers of similar energy content and different dipole moment, *i.e.* di(2-furyl) ketone (**1**), it was demonstrated, on the basis of the classical theory of the solvent effect, that the equilibrium mixture of conformers in the vapour phase is different from that in solution and changes in solvents of different polarity.

The relative orientation of the carbonyl oxygen and of the ring heteroatom in the acyl derivatives of furan and thiophene, in the solid state and in solution, has been widely studied.[1,2] Formyl and acetyl derivatives[1,2] have nearly planar ground-state conformations, the *O,O-trans* and *S,O-cis* orientation being preferred in 2-furyl and 2-thienyl derivatives, while the *X,O-trans* forms (X = O,S) are the more populated ones in the 3-substituted compounds. This situation refers to the molecules in the vapour phase or in solutions of low polarity.

For benzoyl derivatives, the carbonyl group and the rings are more or less distorted from coplanarity, for steric reasons, while the relative orientation of the carbonyl oxygen and ring heteroatom shows[3–5] the same type of preference found for the corresponding formyl and acetyl derivatives. The degree of twist is, as a general rule, higher for phenyl than for heterocyclic rings. This result should account for the extent of π-conjugation with the carbonyl group, which should be more efficient in the case of five-membered heterocycles than for the phenyl ring.[5]

The conformational behaviour of a number of difuryl, dithienyl and furyl thienyl ketones has been also reported.[1,2] For these molecules an equilibrium mixture between conformers was found in solution and the different studies have

---

* For part 10 see ref. 25.

Supplementary data: (see Instructions for Authors, *J. Chem. Soc., Perkin Trans. 2*, 1989, issue 1, pp. xvii–xix). Lists of H-atom co-ordinates, bond lengths and angles, and thermal paramters have been deposited at the Cambridge Crystallographic Data Centre.

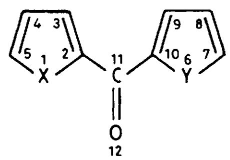
evidenced the difficulties of obtaining the correct structure of the conformers and their amount from the experimental techniques employed (n.m.r., dipole moments, Kerr constants). In particular, it was difficult to evidence the extent of coplanarity between the carbonyl group and the heterocyclic ring in the different conformations of the compounds and often the results from literature sources are not consistent. Hence it will be worthwhile to re-examine conclusions regarding the structure of the preferred conformers of diheteroaryl ketones and their populations.

From a qualitative point of view the results so far reported [6–16] enable one to conclude [2] that the preferred orientation of the carbonyl oxygen with respect to the heteroatom of one ring is roughly that found in the corresponding formyl and acetyl derivatives. From a quantitative point of view, the relative weight of the conformers in the equilibrium mixture, the effect of the medium on the equilibrium, and the geometrical details of preferred conformers are still poorly defined. This information is nevertheless useful for a better understanding of the importance of the electronic fine structure of these molecules in determining their conformational behaviour both in the vapour and in the condensed phase.

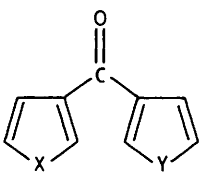
We report here a number of results, both experimental and from theoretical approaches, relative to the conformational analysis of all the isomers of difuryl, dithienyl, and furyl thienyl ketones. The aim is to set up a homogeneous comparison of the situation resulting from different techniques and referred to the molecules in different physical conditions. The *X*-ray diffraction method will be employed for the analysis of the molecules in the solid state, the n.m.r. (^{1}H and ^{13}C) method employing LIS (lanthanide-induced shift) simulation [17] for studying the behaviour in solution, and *ab-initio* MO calculations at an intermediate basis set extension level (3-21G and 3-21G*) with geometry optimisation to get the molecular structure and relative energy of all the conformers of the free molecules.

Results

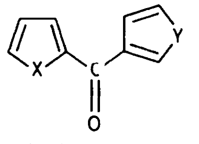
The compounds examined were (**1**)–(**10**). The relative orientation of the carbonyl oxygen and of the heteroatoms X, Y refers to:



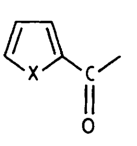
(**1**) X = Y = O
(**2**) X = Y = S
(**3**) X = O ; Y = S



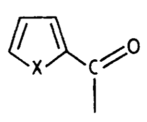
(**4**) X = Y = O
(**5**) X = Y = S
(**6**) X = O ; Y = S



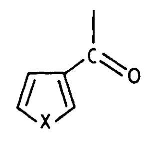
(**7**) X = Y = O
(**8**) X = Y = S
(**9**) X = O ; Y = S
(**10**) X = S ; Y = O



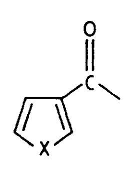
X, O-cis



X, O-trans



X, O-cis



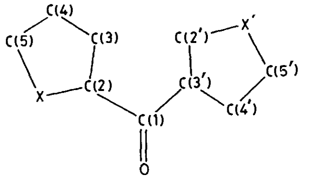
X, O-trans

X-*Ray Analysis.*—Only a limited number of compounds which are solid at room temperature gave crystals suitable for *X*-ray analysis, namely compounds (**2**), (**5**), (**7**), (**8**), and (**10**).

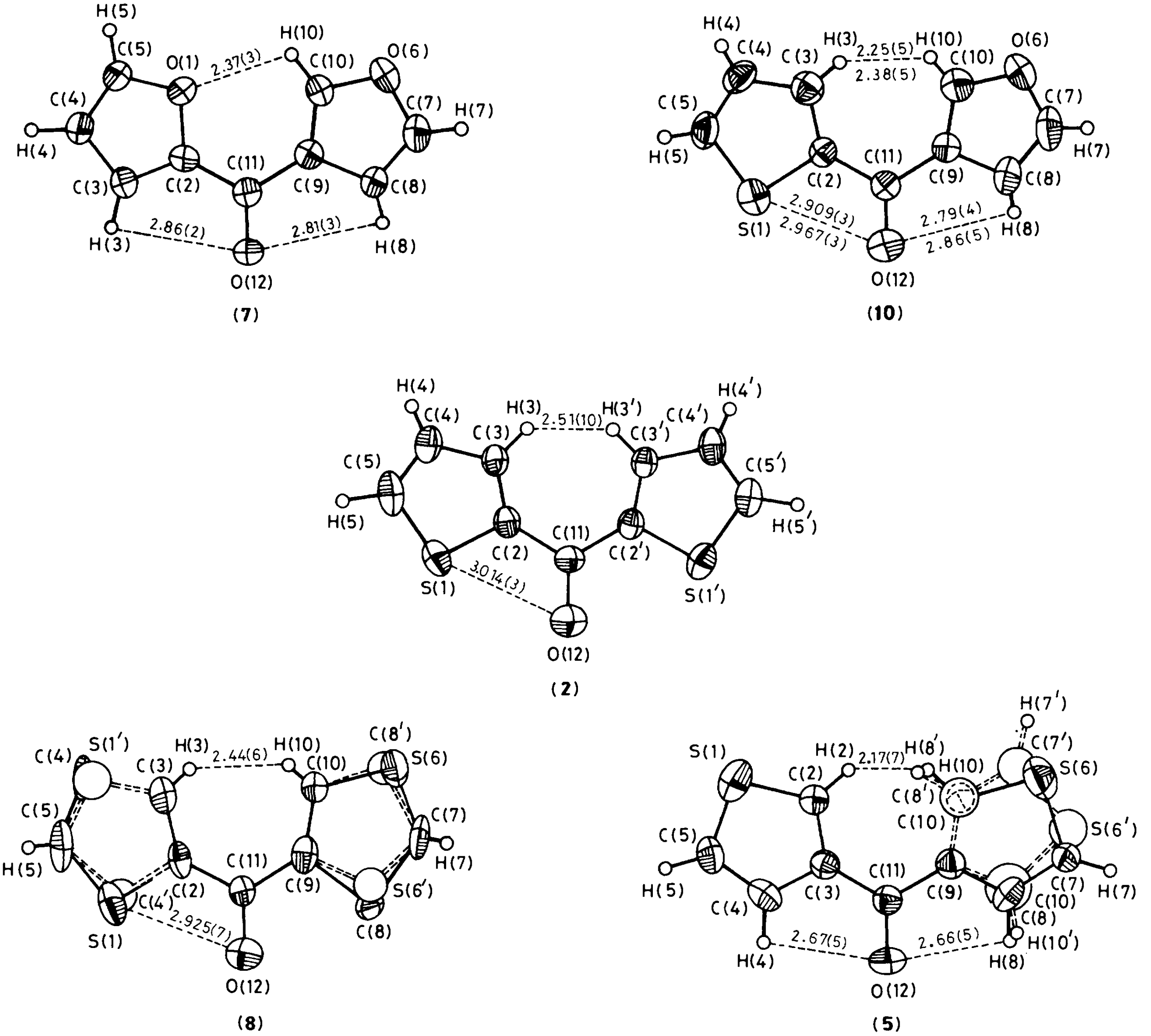
The averaged values of bond distances and angles are quoted in Table 1. These averages are weighted means calculated separately considering (*i*) the central C–CO–C group; (*ii*) the 2-substituted furan rings; (*iii*) the 3-substituted furan rings; (*iv*) the 2-substituted thiophene rings; (*v*) the 3-substituted thiophene rings. In calculating these averages, compounds of structure already described in the previous papers [4,5] were also considered when the heterocycle is not condensed. Owing to the inaccuracy of the results, the disordered rings found in the crystal structure of (**8**) and (**5**) were not considered in the averages.

In Table 1 the 2-substituted ring is represented by unprimed

Table 1. Averaged bond distances/Å and angles/° in ketones of the furan and thiophene series.



	X = O	X = S
C(1)–O	1.227(2)	
C(1)–C(2)	1.468(2)	
C(1)–C(3′)	1.472(3)	
C(2)–X	1.372(1)	1.716(3)
C(5)–X	1.363(1)	1.697(6)
C(5)–C(4)	1.328(2)	1.351(3)
C(4)–C(3)	1.416(2)	1.413(4)
C(2)–C(3)	1.344(2)	1.382(5)
C(2′)–X′	1.350(3)	1.700(7)
C(5′)–X′	1.367(4)	1.690(3)
C(5′)–C(4′)	1.323(5)	1.383(12)
C(4′)–C(3′)	1.428(7)	1.417(3)
C(2′)–C(3′)	1.344(3)	1.364(1)
O–C(1)–C(2)	118.7(5)	
O–C(1)–C(3′)	119.9(2)	
C(2)–C(1)–C(3′)	120.3(3)	
C(1)–C(2)–X	120.0(1)	118.0(4)
C(1)–C(2)–C(3)	130.4(4)	130.8(4)
C(2)–X–C(5)	105.8(2)	91.9(3)
C(4)–C(5)–X	111.3(1)	112.5(1)
C(5)–C(4)–C(3)	106.0(1)	112.6(3)
C(4)–C(3)–C(2)	107.2(2)	111.9(2)
C(3)–C(2)–X	109.4(4)	111.0(1)
C(1)–C(3′)–C(4′)	125.6(5)	122.3(2)
C(1)–C(3′)–C(2′)	128.8(5)	126.4(7)
C(2′)–X′–C(5′)	106.0(1)	93.0(5)
X′–C(5′)–C(4′)	110.6(3)	110.1(11)
C(5′)–C(4′)–C(3′)	106.9(4)	113.5(5)
C(4′)–C(3′)–C(2′)	105.5(3)	111.1(5)
C(3′)–C(2′)–X′	110.0(2)	112.1(5)



(7) (10) (2) (8) (5)

Figure 1. ORTEP[46] drawings of the molecules of compounds (**2**), (**5**), (**7**), (**8**), and (**10**). For compound (**10**) the figure actually refers to molecule A, and the quoted distances are: above for molecule A and below for molecule B. Ellipsoids at 40% probability level.

atoms, while primed atoms are for the 3-substituted ring. Examination of the data considered for calculating the averages shows that, in the case of bond distances, the differences between corresponding values are in general not significant (*i.e.* less than 3σ), whereas for the angles some significant (*i.e.* greater than 3σ) differences are observed. Hence the quoted averages for the angles correspond to a somewhat idealized geometry.

The crystal structure of compound (**5**) is disordered and the results of our analysis are in quite good agreement with those found for the same compound by Sheldrick *et al*:[12] one of the two rings is disordered into two positions, one obtained from the other by rotation of a ring about the C(9)–C(11) bond by 180°. As already observed by Sheldrick *et al.*,[12] the occupancy factors are relevantly different. The structure with S(6) on the same side as S(1) with respect to the C–CO–C central group, has an occupancy factor of 0.887(7), while that with C(9), C(8′), C(7′), C(6′), C(10′) ring-rotated (Figure 1) has an occupancy factor of 0.113(7).

The disorder found in compound (**8**) involves both rings according to a model different from that of compound (**5**). Now both rings are rotated by 180°, the S(1), C(2), C(3), C(4), C(5) ring about the direction along C(5) and the midpoint of the C(2)–C(3) bond with occupancy factors of 0.666(7) and 0.334(7), while the rotation of the S(6), C(7), C(8), C(9), C(10) ring is about the direction along C(7) and the midpoint of the C(9)–C(10) bond with occupancy factors of 0.650(6) and 0.350(6).

From Figure 1 it appears that, while in both 2- and 3-substituted furan derivatives the heteroatom of the ring is always on the opposite side with respect to C=O, in the cases of the thiophene derivatives this behaviour is observed only with 3-substituted derivatives. In the 2-substituted derivatives, sulphur is always on the same side of the C=O group (in the case of the disordered rings this is observed with the molecule showing the highest occupancy factor). This observation is in agreement with the presence of an attractive interaction between sulphur and oxygen.

Considering the averaged values of Table 1, no systematic differences are observed between corresponding bond distances in the 2- and 3-substituted rings and in every case the C(3)–C(4) bond is always longer than the other C–C distances in the ring. There are differences between the C–X bonds in each ring, but

Table 2. Torsion angles defining the orientation of the rings about the carbonyl group. Atomic labels according to the diagram given in Table 1.[a]

	X = O			X = S			
	(7)	**(10A)**	**(10B)**	**(10A)**	**(10B)**	**(2)**	**(5)**
X–C(2)–C(1)–O	176.4(2)	—	—	−13.6(4)	−17.2(4)	−21.6(8)	—
C(3)–C(2)–C(1)–O	−4.0(4)	—	—	162.9(4)	160.0(3)	152.6(6)	—
C(2′)–C(3′)–C(1)–O	174.8(3)	157.4(4)	151.6(4)	—	—	—	−156.5(6)
C(4′)–C(3′)–C(1)–O	−4.0(4)	−17.3(5)	−22.2(5)	—	—	—	17.5(9)

[a] **A** and **B** refer to the two crystallographically-independent molecules.

Table 3. ^{1}H N.m.r. chemical shifts (δ) in compounds (**1**)–(**10**) recorded in [^{2}H]chloroform solution. The ΔM are the LIS values and refer to Yb(fod)$_3$.

Compound		2-H	3-H	4-H	5-H	7-H	8-H	9-H	10-H
(**1**)	δ		7.52	6.58	7.66	7.66	6.58	7.52	
	ΔM^a		19.00	7.24	8.73	8.73	7.24	19.00	
(**2**)	δ		7.89	7.16	7.68	7.68	7.16	7.89	
	ΔM		17.60	4.13	4.05	4.05	4.13	17.60	
(**3**)	δ		7.38	6.58	7.65	7.64	7.17	8.13	
	ΔM^a		20.28	5.41	8.51	5.81	5.98	20.54	
(**4**)	δ	8.00		6.85	7.47	7.47	6.85		8.00
	ΔM	19.66		21.50	5.85	5.85	21.50		19.66
(**5**)	δ	7.99		7.59	7.36	7.36	7.59		7.99
	ΔM	22.83		24.99	5.47	5.47	24.99		22.83
(**6**)	δ	7.99		6.88	7.49	7.36	7.58		8.01
	ΔM	18.33		20.05	5.17	5.38	23.70		21.65
(**7**)	δ		7.31	6.56	7.61	7.46	6.97		8.38
	ΔM		23.0^a	5.56^a	9.03^a	6.30	23.48		19.71
(**8**)	δ		7.78	7.15	7.68	7.37	7.61		8.07
	ΔM		23.46	6.29	5.90	5.06	24.72		23.35
(**9**)	δ		7.33	6.57	7.65	7.34	7.73		8.37
	ΔM		20.95^a	5.40^a	8.40^a	5.56	23.80		21.17
(**10**)	δ		7.78	7.15	7.66	7.49	6.90		8.09
	ΔM		23.60	6.27	6.12	5.26	21.11		19.58

[a] Chelate complex with the carbonyl and heterocyclic oxygen: not employed for conformational analysis.

these differences are not always significant and systematic. In the 2-substituted rings the C(1)–C(2)–X angle is relevantly less than the C(1)–C(2)–C(3) angle, while in the 3-substituted rings the corresponding C–C–C angles show smaller differences.

As observed in the previously described[4] benzo[*b*]furan aroyl derivatives the displacements from coplanarity of the 2- and 3-substituted rings are not significantly different. On the contrary, in the previously described furan aroyl derivatives[4] and in the aroyl derivatives[5] of benzo[*b*]thiophene and thiophene the displacements from coplanarity of the 2-substituted rings are less than those of the 3-substituted rings.

In Table 2, which gives the torsion angles defining the orientation of the rings about the carbonyl group, the disordered rings are not considered.

Results from N.M.R. spectra and LIS simulation.—The ^{1}H and ^{13}C n.m.r. chemical shifts, from spectra in [^{2}H]chloroform solution and LIS values are reported in Tables 3 and 4.

In comparison with those of the corresponding formyl[18a] and acetyl[19] derivatives, the chemical shifts show only small differences, restricted within 0.2 ppm for ^{1}H and 4 ppm for ^{13}C. It was previously observed that in substituted benzophenones[20] and acetophenones[21] the ^{13}C chemical shift of the C=O group can be employed for predicting the angle of twist between the phenyl ring and the carbonyl plane. A greater shielding of the carbonyl ^{13}C nucleus is observed in conjugated derivatives as compared with saturated ketones, owing to an increase of the electron density around that carbon.[21] For compounds (**1**)–(**10**) these chemical shifts span a range of *ca.* 14 ppm, that of di(2-furyl) ketone being at higher field, while that of di(3-furyl) and di(3-thienyl) derivatives is at lower field; these compounds, however, have this carbon at higher field than benzophenone (δ = 195.5).[20]

For our compounds difficulties arise when one tries to obtain quantitative indications of their conformational properties, since more than one variable, *i.e.* one or two angles of twist and the amount of *X,O-cis* and *X,O-trans* orientations, should be derived from a single experimental quantity in each compound. A number of interesting features is nevertheless observed. By taking the half of the chemical shift in the symmetrical compounds (**1**), (**2**), (**4**), and (**5**) and adding these quantities in pairs of different combinations, the calculated values are close (maximum deviation 0.7 ppm) to the chemical shifts relative to compounds (**3**), and (**6**)–(**10**). By employing the empirical correlation[21] between the torsional angle and the chemical shift of the carbonyl carbon, one can estimate that in benzophenones, a 90° rotation of one ring or a 45° rotation of both rings causes a low-field shift of the carbonyl carbon of *ca.* 8 ppm. If rotation of the heterocyclic rings has the same effect as does one phenyl ring on the ^{13}C carbonyl shielding, then the additivity found for our compounds seems to exclude strong conformational changes of the 2- and 3-substituted heterocyclic rings with respect to the carbonyl group in the different compounds.

A more quantitative approach to the description of the conformational equilibrium in solution can be gained with LIS simulation,[18] even though the large number of variables to be determined is expected to limit the precision of the results. The procedure employed is that described in a previous work.[3] The molecular geometry was derived from that determined experimentally for the rings and for the carbonyl group either from the *X*-ray results reported in this paper or from that of the corresponding aroyl derivatives of furan[4] and thiophene.[5] The LIS values (ΔM) were measured on the same sample for ^{1}H and

Table 4. ^{13}C chemical shifts (δ) in compounds (**1**)–(**10**) recorded in [^2H]chloroform solution, LIS values ΔM due to $Yb(fod)_3$ and corrected ($\Delta M - \Delta D$) for the complexation shift [18] in presence of $La(fod)_3$.

Compd.		C-2	C-3	C-4	C-5	C-7	C-8	C-9	C-10	C-11
(**1**)	δ	151.51	119.53	112.37	146.74	146.74	112.37	119.53	151.51	168.65
	ΔM^a	54.19	29.71	14.69	20.29	20.29	14.69	29.71	54.19	104.16
	($\Delta M - \Delta D$)	55.25	25.65	13.92	17.93	17.93	13.92	25.65	55.25	103.28
(**2**)	δ	143.02	133.13	127.96	133.43	133.43	127.96	133.13	143.02	178.75
	ΔM	36.58	22.46	8.90	10.04	10.04	8.90	22.46	36.58	80.92
	($\Delta M - \Delta D$)	39.03	18.56	8.26	7.36	7.36	8.26	18.56	39.03	78.88
(**3**)	δ	152.53	118.77	112.45	146.38	133.91	128.18	133.82	142.27	173.44
	ΔM^a	55.70	31.74	13.22	17.95	13.33	11.26	26.63	42.50	102.26
	($\Delta M - \Delta D$)	56.79	26.66	12.08	15.19	9.38	11.26	22.30	46.34	100.90
(**4**)	δ	146.84	127.71	109.62	144.17	144.17	109.62	127.71	146.84	181.69
	ΔM	28.53	52.35	27.40	12.45	12.45	27.40	52.35	28.53	115.58
	($\Delta M - \Delta D$)	24.38	53.88	27.40	12.45	12.45	27.40	53.88	24.38	110.42
(**5**)	δ	132.63	142.15	128.31	126.30	126.30	128.31	142.15	132.63	182.25
	ΔM	31.25	52.66	29.11	12.43	12.43	29.11	52.66	31.25	117.35
	($\Delta M - \Delta D$)	25.55	55.02	27.92	12.43	12.43	27.92	55.02	25.55	114.18
(**6**)	δ	147.47	127.37	110.06	144.00	126.54	127.80	142.42	131.85	182.47
	ΔM	27.21	50.05	26.26	11.92	11.68	27.06	48.53	29.33	109.75
	($\Delta M - \Delta D$)	22.68	51.43	26.26	11.92	11.68	25.99	51.16	23.21	105.25
(**7**)	δ	153.33	117.76	112.44	145.91	143.52	109.77	125.50	148.48	175.06
	ΔM	58.01^a	35.95^a	13.95^a	18.14^a	13.50	28.66	51.51	28.51	116.18
	($\Delta M - \Delta D$)	59.25^a	28.05^a	12.60^a	14.85^a	13.50	28.66	53.08	24.07	113.21
(**8**)	δ	144.03	133.55	127.98	133.62	126.35	128.27	141.22	132.17	181.18
	ΔM	50.04	29.67	12.27	13.72	11.50	28.37	52.37	30.95	113.85
	($\Delta M - \Delta D$)	53.69	24.93	12.27	10.16	11.50	27.38	53.98	25.61	111.36
(**9**)	δ	153.18	119.01	112.35	146.38	125.82	128.36	140.22	133.37	175.35
	ΔM	55.33^a	32.48^a	13.17^a	17.63^a	11.33	25.93	44.68	27.80	104.08
	($\Delta M - \Delta D$)	56.15^a	25.67^a	12.01^a	14.83^a	11.33	24.89	47.25	22.23	102.69
(**10**)	δ	144.08	132.48	128.02	133.36	143.97	110.11	126.59	147.06	180.24
	ΔM	49.41	30.18	12.45	14.03	12.17	27.37	53.18	29.29	113.98
	($\Delta M - \Delta D$)	53.22	25.13	11.70	10.85	12.17	26.82	54.03	25.15	110.56

[a] Chelate complex with the carbonyl and heterocyclic oxygens: not employed for conformational analysis.

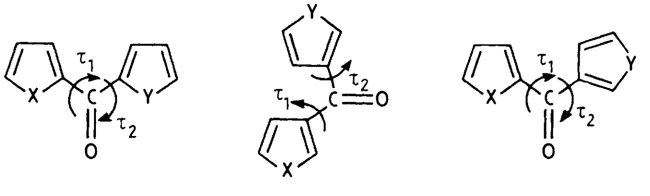


Figure 2. Definition of the angles of rotation τ_1 and τ_2 of the two heterocyclic rings around the exocyclic C–C(O) bonds. The all-planar situation depicted corresponds to $\tau_1 = \tau_2 = 0°$.

^{13}C resonances in presence of $Yb(fod)_3$. Corrections due to the diamagnetic shifts for complex formation [18] (ΔD) were made on ^{13}C LIS values, by using $La(fod)_3$. The LIRAS-3 computer program [18] was employed in the 'four-site' axially symmetric complexation model.

For the derivatives containing the 2-furyl group [compounds (**1**), (**3**), (**7**), and (**9**)] a chelate complex is formed, with the lanthanide atom bonded to the heterocyclic and carbonyl oxygens, as also observed previously for structurally related compounds.[3,4] For these derivatives the conformational situation derived from this approach probably does not correspond to that occurring in the absence of the complexing agent. Nevertheless the conformational behaviour of the partner heterocyclic ring was derived, and is reported in Table 5 as an indicative trend. Furthermore, the conformational results from the LIS approach refer to the relative orientation of one heterocyclic ring and of the carbonyl group, therefore only the upper limits of the amounts of the conformations of the whole molecules could be derived, not definite values.

The conformational results from the LIS approach are collected in Table 5 and the symbols have their usual meaning.[3,18] The conformational angles τ_1 and τ_2 are defined in Figure 2.

Concerning the 2-furyl ring, the result relative to compound (**1**) shows that the *O,O-trans* (nearly planar) is the one largely preferred. The 2-thienyl ring seems to assume preferentially the *S,O-cis* orientation, as emerges from compounds (**2**), (**3**), (**8**), and (**10**). The 3-substituted heterocycles prefer the *X,O-trans* orientation although, for these compounds, the amount of the single conformers seems to be decided also by the relative orientation of the two rings.

Results from MO ab-initio *Calculations*.—A number of structural and other physical features of the molecules here examined were also obtained from MO *ab-initio* calculations. The GAUSSIAN-82 package[22] was employed. Calculations were performed[23] at the 3-21G level, 3-21G* (with 3d functions on sulphur) for thienyl derivatives.

For symmetrical compounds [(**1**), (**2**), (**4**), (**5**)] geometry relaxation was allowed at the 3-21G level for the parameters reported in Table 6 and for torsional angles τ_1, τ_2, for each ground-state conformer, whereas the ring geometry was that optimized at the same level for the ground states of the corresponding aldehydes.[24,25] For compounds containing the sulphur atom, calculations were performed at the 3-21G* level with 3-21G relaxed geometry (3-21G*//3-21G). The trend of the bond lengths and angles for the *X,O-cis* and *X,O-trans* orientations of the rings is very close in all the conformers of the same compound. This indicates that the second ring does not significantly perturb the geometrical characteristics of the bonds made by the first ring with the carbonyl group.

Relaxation of the geometrical parameters chosen turned out to be extremely time consuming even for the fast supercomputer

Table 5. Results of LIS simulation: molecular geometry parameters for the complexes[a] and conformational properties for derivatives (**1**)–(**10**).

Compound	$R_{cryst.}$	Sum difference ppm	R/Å	φ°	ψ°	f	Population *endo*	Conformational angles/°[b]		%[c]
								τ_1	τ_2	
(**1**)	0.017[d]	0.745[d]	1.20[d]	15[d]	25[d]	1 457[d]	40[d]	0	180	80[e]
								0	0	20[e]
(**2**)	0.013	0.439	3.15	40	170	2 825	50	30	30	⩽75
								0	180	⩽50
								180	180	⩽25
(**3**)	0.028[d]	0.995[d]	1.30[d]	25[d]	60[d]	1 972[d]	25[d]	0	0	*ca.* 100
(**4**)	0.022	1.018	2.95	55	155	3 636	50	30	30	⩽20
								30	150	⩽40
								150	150	⩽80
(**5**)	0.022	1.088	2.85	55	160	3 503	50	30	30	⩽40
								30	150	⩽80
								150	150	⩽60
(**6**)	0.031	1.169	2.95	55	155	3 468	50	30	30	⩽20
								30	150	⩽20
								150	30	⩽40
								150	150	⩽60
(**7**)	0.035[d]	1.391[d]	1.25[d]	25[d]	65[c]	2 221[c]	25[d]	0	150	*ca.* 100
(**8**)	0.025	0.981	3.05	45	160	3 803	40	0	30	⩽40
								0	150	⩽60
								180	30	⩽30
								180	150	⩽30
(**9**)	0.041[d]	1.482[d]	1.30[d]	25[d]	60[d]	2 012[d]	25[d]	0	30	⩽20
								0	150	⩽80
(**10**)	0.022	0.837	2.90	65	155	3 616	60	0	30	⩽20
								0	150	⩽70
								180	30	⩽20
								180	150	⩽30

[a] For the symbols see refs. 3 and 18. [b] These angles are defined in Figure 2: estimated error ±10°. [c] Refers to the maximum value that can assume the amount of each conformer. [d] Chelate structure with lanthanide atom bonded to the carbonyl and furyl oxygens: R, φ, ψ and population *endo* refer to a 'dummy' atom.[3] Internuclear distances R of the two oxygen atoms from the lanthanide atom are 1.7–1.8 (heterocyclic oxygen) and 1.9–2.0 Å (carbonyl oxygen). [e] The lanthanide atom was assumed to be completely localized near the oxygen atom of one heterocyclic ring ($\tau_1 = 0°$) while the second ring was allowed freedom to assume preferred orientations.

Table 6. Optimized geometrical parameters[a] for compounds (**1**), (**2**), (**4**), and (**5**).

Compound	Conformer	C(11)–O(12)/Å	C(2)–C(11) or C(3)–C(11)/Å	C(2)–C(11)–O(12) or C(3)–C(11)–O(12)/°	X–C(2)–C(11) or C(2)–C(3)–C(11)/°
(**1**)	*O,O-cis,O,O-cis*	1.211	1.466	122.20	116.22
	O,O-cis,O,O-trans	1.216	1.458;[b] 1.462[c]	122.56;[b] 119.26[c]	115.60;[b] 122.03[c]
	O,O-trans,O,O-trans	1.221	1.456	119.42	122.65
(**2**)	*S,O-cis,S,O-cis*	1.217	1.469	120.92	117.48
	S,O-cis,S,O-trans	1.221	1.467;[b] 1.478[c]	119.04;[b] 118.09[c]	115.20;[b] 127.93[c]
	S,O-trans,S,O-trans	1.221	1.474	118.23	127.55
(**4**)	*O,O-cis,O,O-cis*	1.222	1.467	120.24	121.95
	O,O-cis,O,O-trans	1.218	1.469;[b] 1.466[c]	120.45;[b] 122.03[c]	120.11;[b] 130.72[c]
	O,O-trans,O,O-trans	1.220	1.468	120.50	130.40
(**5**)	*S,O-cis,S,O-cis*	1.217	1.483	120.72	119.91
	S,O-cis,S,O-trans	1.218	1.483;[b] 1.481[c]	120.86;[b] 119.79[c]	119.73;[b] 126.92[c]
	S,O-trans,S,O-trans	1.218	1.481	119.96	126.99

[a] For the atom numbering see the general formulas of the compounds. [b] Referring to the ring with the *X,O-cis* orientation. [c] Referring to the ring with the *X,O-trans* orientation.

we employed (CRAY-X-MP48). For the unsymmetrical derivatives an even larger number of variables is necessary in order to define the molecular geometry. A simplification was thus introduced in order to reduce the computing times; this turned out to be quite reasonable, in the light of the following results. For compound (**7**), in the *O,O-cis,O,O-cis* conformation we allowed all the parameters (nine) defining the carbonyl group to relax. The results were compared with those obtained by optimizing only the twist angles τ_1 and τ_2 and assuming the remaining parameters to be the same as in the parent symmetrical derivatives. For the C=O bond distance and C–C(O)–C bond angle the average value of those in the two parent compounds was adopted. The comparison showed that the SCF energies from the two calculations differ by 5.9818×10^{-5}au (0.15 kJ mol^{-1}), bond distances and angles within 4×10^{-4} Å and 0.6°. For the unsymmetrical derivatives [(**3**), (**6**), (**7**)–(**10**)] we therefore followed the latter approach.

The calculated twist angles τ_1 and τ_2, relative energies, dipole moments and populations of the conformers for compounds (**1**)–(**10**) are reported in Table 7. Comparison with the experimental geometrical parameters reported in Table 1 shows that the calculated quantities are close to them (within 0.01 Å

Table 7. Calculated relative energies kJ mol^{-1}[a] referred to the most stable conformer (absolute total energy is expressed in au), populations, dipole moments 10^{-30}C m and angles of twist (τ_1, τ_2)[b] for the conformers of compounds (**1**)–(**10**).

				Dipole moment				Angles of twist/°	
Compd.	Conformer	Relative energy	Populations	Calculated		Experimental	From equation (1)	τ_1	τ_2
(**1**)	*O,O-cis,O,O-cis*	31.577	0	18.44	11.47[c]	12.17;[d] 12.14[e]	10.68;[f] 11.61[g]	22.41	22.41
	O,O-cis,O,O-trans	0.(−565.656 19)	0.58	14.22				0	180
	O,O-trans,O,O-trans	0.749	0.42	7.77				180	180
(**2**)	*S,O-cis,S,O-cis*	0.(−1 208.124 847)	0.71	17.11	15.08[c]	11.94;[h] 12.34;[i] 12.37[d]	12.32;[f] 12.88[g]	24.01	24.01
	S,O-cis,S,O-trans	2.841	0.22	11.58				0	−179.76
	S,O-trans,S,O-trans	5.820	0.07	5.59				180	180
(**3**)	*O,O-cis,S,O-cis*	31.46	0	17.79	13.40[c]	11.41;[e] 11.51[d]	11.37[f]	24.09	22.00
	O,O-cis,S,O-trans	33.08	0	12.51				15.46	−165.11
	O,O-trans,S,O-cis	0.(−866.896 721)	0.88	14.23				179.98	0.01
	O,O-trans,S,O-trans	3.97	0.12	7.21				180	−179.76
(**4**)	*O,O-cis,O,O-cis*	0.163	0.33	11.84	8.56[c]		8.64[f]	19.34	19.34
	O,O-cis,O,O-trans	0.(−565.651 809)	0.35	8.60				21.05	−162.67
	O,O-trans,O,O-trans	0.188	0.32	5.20				−159.07	−159.07
(**5**)	*S,O-cis,S,O-cis*	3.682	0.13	10.86	7.39[c]		7.99[f]	26.56	26.56
	S,O-cis,S,O-trans	1.954	0.27	8.52				30.03	−159.30
	S,O-trans,S,O-trans	0.(−1 208.124 440)	0.60	6.10				−155.44	−155.44
(**6**)	*O,O-cis,S,O-cis*	2.318	0.15	11.34	7.94[c]		8.30[f]	20.55	26.00
	O,O-cis,S,O-trans	0.375	0.32	8.9				22.64	−158.92
	O,O-trans,S,O-cis	2.184	0.15	8.16				−162.38	29.05
	O,O-trans,O,O-trans	0.(−866.888 190)	0.38	4.90				−159.07	−155.44
(**7**)[j]	*O,O-cis,O,O-cis*	34.597	0	15.47	9.87[c]	9.17;[d] 9.37[e]	9.38[f]	18.93	21.66
	O,O-cis,O,O-trans	34.225	0	12.13				22.09	−159.37
	O,O-trans,O,O-cis	3.335	0.21	12.27				−180.01	0.00
	O,O-trans,O,O-trans	0.(−565.661 569)	0.79	9.26				180.00	180.00
(**8**)[j]	*S,O-cis,S,O-cis*	1.757	0.25	14.26				18.31	31.96
	S,O-cis,S,O-trans	0.(−1 208.124 752)	0.52	11.90	11.57[c]		10.34[f]	22.01	−153.59
	S,O-trans,S,O-cis	5.962	0.05	9.79				−164.16	24.98
	S,O-trans,S,O-trans	2.535	0.18	7.41				−163.30	−161.02
(**9**)	*O,O-cis,S,O-cis*	33.212	0	15.04	10.19[c]		9.56[f]	18.73	29.50
	O,O-cis,S,O-trans	30.945	0	12.59				22.41	−155.44
	O,O-trans,S,O-cis	7.372	0.10	12.19				180.00	0.10
	O,O-trans,S,O-trans	0.(−866.896 542)	0.90	9.97				180.00	180.00
(**10**)	*S,O-cis,O,O-cis*	0.297	0.33	14.68	11.44[c]	10.37;[e] 10.41[d]	10.27[f]	18.90	24.21
	S,O-cis,O,O-trans	0.(−886.888 505)	0.37	11.41				21.78	−157.31
	S,O-trans,O,O-cis	3.448	0.09	10.11				−169.20	12.70
	S,O-trans,O,O-trans	1.418	0.21	6.95				−166.13	−165.61

[a] The values in parentheses are the calculated total energies (au). [b] Referred to Figure 2. [c] Weight-averaged value, obtained from calculated populations. [d] Ref. 15. [e] Ref. 8. [f] From the dipole moment calculated for the vapour phase. [g] From the dipole moment calculated in benzene solution (see Table 8). [h] Ref. 13. [i] Ref. 10. [j] The sequence of ring heteroatoms refers to *X,O-cis*, *Y,O-cis* and analogously for the other conformers.

for bond lengths and 2° for bond angles). This agreement emerges only when the experimental geometry is matched with the calculated conformer which corresponds to that found in the solid state: differences of the C–C(O) bond lengths and relative angles made by those bonds with the rings for the different orientations of the carbonyl group are significant, as can be seen in Table 6.

Discussion

From the experimental behaviour of compounds (**1**)–(**10**) and from theoretical results, a number of conclusions regarding their conformational trends are possible, which can also be drawn by comparisons with previous studies.

For compound (**1**) *ab-initio* calculations show that the *O,O-cis,O,O-trans* form is slightly more stable than the *O,O-trans,O,O-trans* form and are both planar. No definite conclusions can be reached from LIS studies, even though the ring not involved in chelate formation prefers the *O,O-trans* orientation. A mixture of these conformers was indicated[9] as the result of a ^{1}H chemical-shift interpretation, the prevailing presence of the *O,O-cis,O,O-trans* conformer emerged[8,15] from dipole moments and this form, slightly distorted from planarity, is also in agreement with i.r. spectra.[11] The results of MO calculations on the free molecule thus seem to agree with experimental trends. For 2-acyl derivatives of furan a solvent dependent conformational behaviour should be expected, since, as occurs for furan-2-carbaldehyde,[24,26] the less polar forms are the more stable ones and the energy difference between the *cis,trans* and *trans,trans* is relatively small. The former is thus likely to become more stable in solvents of increasing polarity.

The *S,O-cis* orientation prevails in acyl derivatives of thiophene[1,2] and this also occurs in derivative (**2**), in the solid state and in solution. Calculations show (Table 7) that the amount of the *S,O-cis,S,O-cis* conformer is greater than 70% and this does not disagree with the results of the LIS measurements in solution. The solid-state conformation, of *cis,cis* type, shows also that the twist angle of the rings from the carbonyl plane is close to that found in the theoretical approach. This conformation has been previously reported as being more

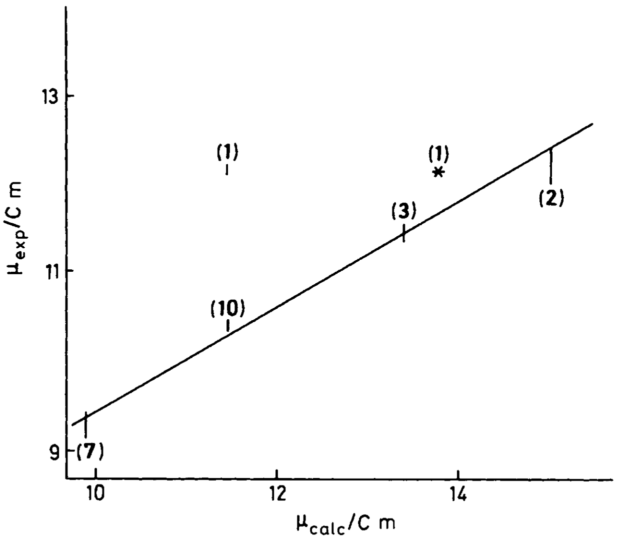


Figure 3. Plot of known experimental dipole moments *vs.* calculated values referred to the free molecules. For compound (**1**) the two calculated values refer to the free molecule (|) and to the benzene solution (*).

stable in solution, on the basis of dipole moments[10,13,15] and Kerr constant measurements,[13] with a twist angle somewhat higher than that found in this study.

The *O,O-trans* and *S,O-cis* preferred orientation is maintained even in compound (**3**), at least from the results of MO calculations. The chelate structure involving the furyl ring in presence of the lanthanide atom did not enable us to have information on the conformational trend of this molecule in solution, even if, indicatively, it would seem that the *S,O-cis* orientation is preferred. The largely preferred conformer, according to calculation, is that found in previous studies with dipole moments,[8,15] ^{1}H chemical shifts,[9] and i.r. spectra,[11] all made in solution.

Small energy differences are calculated between the conformers of compound (**4**), the *O,O-trans* and *O,O-cis* orientations being almost energetically equivalent. The furyl ring is twisted and this agrees with the molecular geometry given in solution by LIS simulation, while, according to this technique, the *trans–trans* conformer should be preferred. Owing to the small energy differences which are expected on 3-acyl derivatives of furan[25,27] it is likely that either the results from calculations are unable to define clearly the conformational preference or the position of the equilibrium determined experimentally can change in different media.

The *S,O-trans,S,O-trans* conformer is predicted as the more stable one for compound (**5**) and, from a qualitative point of view, the *S,O-trans* orientation appears to be preferred even from LIS measurements. In the solid state, the molecule adopts the *trans–trans* conformation with the rings twisted, in agreement with LIS simulation and calculated structures. The small energy difference between the *S,O-cis* and *S,O-trans* orientation of one ring when the other is *S,O-trans*, is the origin of the disorder found for one ring in the crystal structure.

In the unsymmetrical derivative (**6**) the *S,O-trans* and *O,O-trans* orientations are preferred in solution: from the calculations the *X,O-trans* orientation is more stable in the case of the thienyl than the furyl ring.

The situation corresponding to the *O,O-trans* orientation of the 2-furyl ring and *X,O-trans* for the 3-substituted heterocycles is clearly preferred as the results of the calculations applied to compounds (**7**) and (**9**) show. From LIS measurements only a qualitative evidence of the *trans* orientation of the latter rings is gained. The conformation of compound (**7**) in the solid state is *trans,trans*, nearly planar, in agreement with the calculated structure. For this compound, previous studies[8,9,11,15,16] in solution reported different conclusions and, together with the preferred *trans,trans* conformer, smaller amounts of the *O,O-trans,O,O-cis* conformer (the first orientation is referred to the 2-substituted ring) are found.[15,16] The presence of this form is also predicted on the basis of calculated energies, Table 7, and its amount in solution is likely to increase owing to the higher polarity with respect to the *trans,trans* form.

The *S,O-cis* orientation of the 2-thienyl ring is preferred even in compounds (**8**) and (**10**), while the 3-substituted rings can adopt both orientations. These results, from MO calculations, are in agreement with indications from LIS measurements. In the solid state, ignoring at this level the disorder found in (**8**), the conformers of the molecules are clearly of *S,O-cis,Y,O-trans* type, with the rings twisted from the carbonyl plane, in agreement with the calculated structures. For compound (**10**) a number of results obtained in solution with different experimental techniques show that the *S,O-cis,O,O-trans* conformer is preferred, and in the equilibrium mixture the *S,O-cis,O,O-cis* form is also present, the amounts varying in the different literature sources. The results of Table 7 are in agreement with these conclusions.

Calculated dipole moments for the conformers of compounds (**1**)–(**10**) were also obtained and are collected in Table 7. By employing the conformer populations of Table 7, a weight-averaged value of the dipole moment of each molecule can be obtained and compared with known experimental results. Calculated values are higher than experimental ones, as found previously[24] also for the formyl derivatives of furan and thiophene, and, as is shown in the plot of Figure 3, the two quantities are roughly proportional.

Compound (**1**) deviates sharply from this behaviour and the calculated value seems largely underestimated. Owing to the small difference in the stability between the *cis,trans* and *trans,trans* conformers the amount of the more polar *cis,trans* conformer can increase[26] in solution. We tried to reach an approximate estimate of the contributions of solvent effects in changing conformer populations. Classical theory of solvent effect[24,28] was employed and restricted to the evaluation of the electrostatic contribution to solvation energy. Dipole moments and molecular geometries are from MO *ab-initio* calculations. The results, reported in Table 8, show that for compound (**1**), *cis,trans* conformer increases considerably in solution with respect to the vapour phase. The dipole moment of the equilibrium mixture should thus become greater in solution, whereas in more polar media it is expected not to increase further to any great extent. The calculated dipole moment for the equilibrium mixture in benzene or chloroform solution now fits the plot of Figure 3 better, as is indicated by the asterisk, relative to compound (**1**). For compound (**2**), calculations at the same level, show that the solvent increases the amount of the *S,O-cis,S,O-cis* conformer, which is also more abundant in the vapour phase, but the change is less enhanced than for compound (**1**). Similar changes probably also occur for the remaining compounds when small differences in the energy of the conformers occur and when their polar character differs.

From the plot of Figure 3 an approximate linear correlation between experimental and calculated (3-21G or 3-21G*) dipole moments can be derived in the form of equation (1) (r =

$$\mu_{exp.} = 0.56\mu_{calc.} + 3.83 \qquad (1)$$

0.9897). The values calculated with this empirical expression are collected in Table 7 and compare satisfactorily with known experimental values in spite of solvent effects. These calculated

Table 8. Relative energy, ΔE kJ mol^{-1} and populations n of the conformers and weight-averaged dipole moments in different solvents for compounds (**1**) and (**2**).

		Vapour phase			Cyclohexane			Benzene			Chloroform			Acetone		
Compd.	Conformer	ΔE	n	$\bar{\mu}$	ΔE	n	$\bar{\mu}$	ΔE	n	$\bar{\mu}$	ΔE	n	$\bar{\mu}$	ΔE	n	$\bar{\mu}$
(**1**)	*O,O-cis,O,O-cis*	31.58	0	11.47	31.74	0	13.68	31.77	0	13.82	31.91	0	14.14	32.05	0	14.20
	O,O-cis,O,O-trans	0	0.58		0	0.92		0	0.94		0	0.99		0	1.00	
	O,O-trans,O,O-trans	0.75	0.42		5.92	0.08		6.76	0.06		11.06	0.01		15.25	0	
(**2**)	*S,O-cis,S,O-cis*	0	0.71	15.08	0	0.81	15.98	0	0.82	16.08	0	0.87	16.38	0	0.90	16.54
	S,O-cis,S,O-trans	2.84	0.22		3.79	0.18		3.95	0.17		4.74	0.13		5.51	0.10	
	S,O-trans,S,O-trans	5.82	0.07		9.96	0.01		10.63	0		14.08	0		17.43	0	

Table 9. Experimental data for the crystallographic analyses.

Compound	(**7**)	(**10**)	(**2**)	(**8**)	(**5**)
Formula	$C_9H_6O_3$	$C_9H_6O_2S$	$C_9H_6OS_2$	$C_9H_6OS_2$	$C_9H_6OS_2$
M	162.1	178.2	194.3	194.3	194.3
Space group	$P2_1/c$	$P\bar{1}$	$Fdd2$	$P2_1/c$	$P2_1/n$
a/Å	9.900(4)	13.799(2)	13.267(2)	6.183(1)	6.174(1)
b/Å	10.934(6)	10.039(2)	21.853(4)	11.109(1)	11.184(3)
c/Å	7.485(2)	6.084(1)	6.067(1)	13.379(2)	13.203(2)
α/°	—	86.63(1)	—	—	—
β/°	109.96(2)	100.08(1)	—	102.38(1)	101.24(2)
γ/°	—	94.31(1)	—	—	—
U/Å^3	761.6(6)	826.6(2)	1 759.0(5)	897.6(2)	894.2(3)
Z	4	4	8	4	4
D_x/Mg m^{-3}	1.414	1.432	1.467	1.438	1.443
Diffractometer	PHILIPS PW1100	SIEMANS AED	SIEMENS AED	SIEMENS AED	PHILIPS PW1100
Reflections for lattice parameters number	25	30	30	30	24
Reflections for lattice parameters θ range/°	20.9–26.2	22.6/34.7	27.0/39.5	27.5/43.9	17.4/24.4
Radiation	Mo-K_α $\lambda = 0.71069$	Cu-K_α $\lambda = 1.541\ 78$	Cu-K_α $\lambda = 1.541\ 78$	Cu-K_α $\lambda = 1.541\ 78$	Mo-K_α $\lambda = 0.710\ 69$
F(000)	336	368	800	400	400
Crystal size/mm	0.3 × 0.4 × 0.6	0.2 × 0.3 × 0.5	0.2 × 0.3 × 0.6	0.3 × 0.4 × 0.4	0.3 × 0.3 × 0.5
μ/mm^{-1}	0.100	0.304	4.961	4.861	4.880
Extinction parameter g	$4.1(3) \times 10^{-8}$	$2.31(4) \times 10^{-7}$	$3.1(1) \times 10^{-8}$	$1.6(1) \times 10^{-7}$	—
Scan speed/° min^{-1}	6	3–12	3–12	3–12	6
Scan width/°	1.8	$1.2 + \Delta\lambda/\lambda \tan\theta$	$1.2 + \Delta\lambda/\lambda \tan\theta$	$1.2 + \Delta\lambda/\lambda \tan\theta$	1.8
θ range/°	3/27	3/70	3/70	3/70	3/30
h range	−12/11	−16/16	0/16	−7/6	−8/8
k range	0/12	−12/12	0/26	0/13	0/14
l range	0/9	0/7	0/6	0/16	0/17
Standard reflection	3 3 4	1 5 1	6 0 2	1 5 0	0 0 10
Intensity variation	None	None	None	None	None
No. of measured reflections	1 832	3 141	499	1 969	2 873
Condition for observed reflections	$I > 3\sigma(I)$	$I > 3\sigma(I)$	$I > 3\sigma(I)$	$I > 3\sigma(I)$	$I > 2\sigma(I)$
No. of reflections used in refinement	984	1 973	388	1 186	1 202
R(int)	0.030	—	—	0.060	0.031
Max. LS shift to error ratio	0.003	0.026	0.070	0.014	0.022
Min./Max. height in final Δρ/e Å^{-3}	−0.15/0.11	−0.46/0.27	−0.34/0.19	−0.32/0.24	−0.17/0.19
No. of refined parameters	133	265	67	143	110
$R = \Sigma\lvert\Delta F\rvert/\Sigma\lvert F_o\rvert$	0.0461	0.0639	0.0637	0.0732	0.0776
$R' = [\Sigma w(\Delta F)/\Sigma w F_p]^{\frac{1}{2}}$	0.0547	0.0738	0.0726	0.0890	0.0739
$S = [\Sigma w(\Delta F)/(N - P]^{\frac{1}{2}}$ *	7.543	0.308	0.658	2.867	1.160
k, g ($w = k/[\sigma^2(F_c) + gF_o{}^2]$)	22.9, 0.0002	1.0, 0.0627	1.0, 0.0129	1.0, 0.0005	1, 0

* P = number of parameters, N = number of observations.

values should represent a reasonable prediction for unknown experimental situations

Experimental

Compounds.—Di(2-furyl) ketone (**1**),[29] di(2-thienyl) ketone (**2**),[30] 2-furyl 2-thienyl ketone (**3**),[31] di(3-thienyl) ketone (**5**),[32] 2-furyl 3′-furyl ketone (**7**),[33] 2-thienyl 3′-thienyl ketone (**8**),[34] and 3-furyl 2-thienyl ketone (**10**)[33] were prepared according to literature methods and their physical properties agreed with those reported.

Di(3-*furyl*) *ketone* (**4**). Butyl-lithium (1.6 mol dm^{-3} in hexane; 18.6 cm^3; 29 mmol) was added (15 min) with a syringe through a silicone rubber septum to a THF solution (55 cm^3) of 3-iodofuran[35] (5 g, 28 mmol) and the mixture was stirred at −70 °C under a nitrogen atmosphere. After 30 min at −70 °C, the milky suspension was slowly transferred under nitrogen pressure into a THF solution (100 cm^3) of 3-furoyl chloride[36] (7.33 g, 56 mmol) stirred at −70 °C. After 2 h at −70 °C the mixture was allowed to warm slowly to room temperature. Most of the THF solvent was removed *in vacuo* and the residue was treated with 5% NaOH (to hydrolyse the excess of acyl

Table 10. Atomic fractional co-ordinates (× 10^4).

Atom	*x*/*a*	*y*/*b*	*z*/*c*
Compound (**7**)			
O(1)	−26(2)	6 651(1)	1 729(2)
O(6)	−3 852(2)	5 169(2)	−1 836(3)
O(12)	−2 328(2)	9 096(1)	−527(3)
C(2)	−478(2)	7 821(2)	1 174(3)
C(3)	603(3)	8 605(2)	2 008(4)
C(4)	1 786(3)	7 905(3)	3 145(4)
C(5)	1 355(3)	6 749(3)	2 936(4)
C(7)	−4 892(3)	6 023(3)	−2 633(4)
C(8)	−4 376(3)	7 131(3)	−2 163(4)
C(9)	−2 915(2)	7 018(2)	−969(3)
C(10)	−2 666(3)	5 811(2)	−831(4)
C(11)	−1 935(2)	8 039(2)	−136(3)
Compound (**10**) molecule **A** (for *S* × 10^5)			
S(11)	20 850(8)	48 973(10)	2 929(18)
O(61)	−920(3)	756(3)	3 174(5)
O(121)	697(2)	2 901(3)	−2 008(4)
C(21)	1 099(2)	4 065(3)	1 249(5)
C(31)	939(3)	4 596(3)	3 164(6)
C(41)	1 624(3)	5 672(4)	3 832(7)
C(51)	2 278(3)	5 929(4)	2 445(7)
C(71)	−1 343(3)	476(5)	1 003(9)
C(81)	−899(3)	1 222(4)	−486(8)
C(91)	−142(2)	2 064(3)	848(5)
C(101)	−191(3)	1 724(4)	3 018(7)
C(111)	555(2)	2 995(3)	−94(5)
Compound (**10**) molecule **B** (for *S* × 10^5)			
S(12)	−27 930(7)	−15 263(10)	58 735(15)
O(62)	−4 269(3)	3 495(2)	933(5)
O(122)	−3 651(2)	867(3)	7 193(4)
C(22)	−3 506(2)	−406(3)	4 188(5)
C(32)	−3 789(2)	−870(3)	2 065(5)
C(42)	−3 423(3)	−2 111(4)	1 851(7)
C(52)	−2 869(3)	−2 566(4)	3 760(7)
C(72)	−4 730(3)	3 874(4)	2 593(7)
C(82)	−4 639(3)	2 979(4)	4 296(7)
C(92)	−4 087(2)	1 940(3)	3 701(5)
C(102)	−3 896(3)	2 308(3)	1 658(6)
C(112)	−3 744(2)	795(3)	5 167(5)
Compound (**2**) (for *S* × 10^5)			
S(1)	34 889(10)	−8 608(7)	0(−)
O(12)	5 000(−)	0(−)	2 038(13)
C(2)	4 191(3)	−305(3)	−1 215(10)
C(3)	3 826(3)	−176(3)	−3 283(10)
C(4)	2 964(4)	−538(3)	−3 820(13)
C(5)	2 720(4)	−932(3)	−2 147(15)
C(11)	5 000(−)	0(−)	−10(17)
Compound (**8**)			
S(1)	118(10)	−3 142(4)	4 926(4)
S(6)	5 321(12)	869(5)	7 879(5)
O(12)	−1 289(6)	−1 105(3)	6 018(3)
C(2)	1 619(8)	−1 908(3)	5 374(3)
C(3)	3 525(9)	−1 830(4)	5 002(3)
C(4)	3 864(39)	−3 066(16)	4 308(12)
C(5)	1 809(14)	−3 634(6)	4 285(4)
C(7)	2 946(12)	1 456(5)	7 815(4)
C(8)	520(19)	860(9)	7 147(7)
C(9)	2 106(7)	−196(3)	6 681(3)
C(10)	4 408(8)	−253(4)	7 056(3)
C(11)	699(8)	−1 068(3)	6 020(3)
S(1′)	3 834(21)	−2 823(10)	4 299(9)
S(6′)	1 207(11)	893(7)	7 161(6)
C(4′)	414(68)	−2 988(34)	4 996(33)
C(8′)	5 361(76)	634(32)	7 840(31)
Compound (**5**)			
S(1)	2 385(4)	690(2)	2 961(2)
S(6)	597(4)	−2 887(3)	−827(2)
O(12)	7 382(7)	−1 133(5)	1 025(4)
C(2)	2 655(10)	−379(6)	2 092(5)
C(3)	4 562(9)	−280(5)	1 724(4)
C(4)	5 807(10)	718(5)	2 182(5)
C(5)	4 807(10)	1 362(5)	2 880(4)
C(7)	3 171(10)	−3 638(6)	−782(5)
C(8)	4 718(13)	−2 970(7)	−94(6)
C(9)	3 921(9)	−1 926(5)	336(4)
C(10)	1 693(11)	−1 798(7)	−9(5)
C(11)	5 422(9)	−1 113(5)	1 030(4)
S(6′)	22 620(0)	−36 651(0)	−8 052(0)
C(7′)	3 291(0)	−25 661(0)	−5 538(0)
C(8′)	16 044(0)	−17 054(0)	−631(0)
C(10′)	44 604(0)	−29 681(0)	−1 002(0)

chloride), and then extracted with ether. After the extract had been dried ($MgSO_4$) and the solvent evaporated, the residue was chromatographed on a SiO_2 column using light petroleum–ethyl ether (95:5) as the eluant. This yielded a white solid (1.5 g, 33% based on 3-iodofuran), m.p. 129–131 °C. Crystallization of this from cyclohexane (60 cm^3) did not change the m.p. (Found: C, 67.5; H, 3.7. Calc. for $C_9H_6O_3$: C, 66.7; H, 3.7%).

3-*Furyl* 3-*thienyl ketone* (**6**). This was obtained from lithiated 3-iodofuran[35] and 3-thenoyl chloride[37] (b.p. 85 °C/14 mmHg, m.p. 53–54 °C) by the same procedure used for di(3-furyl) ketone; 24% yield after column chromatography, m.p. 76–77 °C; crystallization from cyclohexane did not change the m.p. (Found: C, 61.0; H, 3.4; S, 18.0. Calc. for $C_9H_6O_2S$: C, 60.7; H, 3.4; S, 18.0%).

2-*Furyl* 3-*thienyl ketone* (**9**). To a benzene solution (110 cm^3) of 3-thenoyl chloride[37] (16.1 g, 110 mmol) and furan (30 g, 440 mmol), was added slowly tin tetrachloride (12.66 cm^3; 110 mmol) (30 min) with stirring at 0 °C. Stirring was continued for 2 h at 0 °C and 48 h at room temperature. The complex was decomposed by the slow addition of HCl (2 mol dm^{-3}; 110 cm^3), allowing the internal temperature to reach 40–45 °C. The copious, dark insoluble material was removed by filtration on Celite and washed with ether. The filtered liquid phases were separated, and the organic phase was washed with ether. The combined organic extracts and washings were dried ($MgSO_4$) and evaporated, and the residue was chromatographed on a SiO_2 column [light petroleum–diethyl ether (95:5) as the eluant] and further purified by distillation. This gave an oily material (2.74 g, 14% based on thenoyl chloride), b.p. 95 °C/0.05 mmHg, $n_D^{17.5}$ = 1.6337, $\nu_{C=O}$(film) 1 630 cm^{-1}. A low-melting solid (*ca.* 35 °C) was obtained by storage in a refrigerator.

Crystal Structure Analysis.—Table 9 gives the experimental data concerning the crystal structure analyses. The lattice parameters were determined by measuring numbers of accurately centred reflections at high θ by using the *K*-α_1 radiation (Cu: λ = 1.540 562 Å, Mo: λ = 0.709 300 Å), at room temperature (294 K). The individual reflection profiles were analysed following the method of Lehman and Larsen,[38] and the intensity data were corrected for Lorentz and polarization effects, but not for absorption. When considered, extinction was corrected according to Zachariasen.[39]

The structures of compounds (**5**), (**7**), and (**10**) were solved by the direct methods of the SHELX 86 program,[40] that of compound (**2**) by the Patterson methods of the same program and that of compound (**8**) by the MULTAN[41] program. The hydrogen atoms were located by Fourier difference calculations and refined isotropically. The refinements were carried out by anisotropic least-squares on F using the SHELX 76[42] program. No attempt was made to define the absolute polarity of the structure of compound (**2**) the crystals of which belong to a polar space group.

The atomic scattering factors were taken from ref. 43. The final atomic co-ordinates are quoted in Table 10. The calculations were performed on the GOULD-SEL 32/77 computer of the Centro di Studio del CNR per la Strutturistica Diffrattometrica (Parma). In addition to the programs quoted, LQPARM,[44] PARST,[45] and ORTEP[46] programs were used.

N.M.R. Measurements.—The spectra were recorded at 200.058 MHz for ^1H and 53.3088 MHz for ^{13}C by employing a Varian LX-200 spectrometer. The reagent shift employed was $Yb(fod)_3$, dried *in vacuo* on phosphorus pentaoxide, added in known and increasing amounts to [^2H]chloroform solutions (0.3 mol dm^{-3}) of the substrate examined. The maximum mole ratio between $Yb(fod)_3$ and the substrate was 0.1. The experimental LIS values on ^1H and ^{13}C nuclei were measured on the same sample. The correlation coefficients for the plots relating chemical shifts to the lanthanide:substrate ratio were always found to be $\geqslant 0.999$ and the intercepts identical with the unshifted spectra.

MO *ab-inito* calculations were performed on a CRAY-X-MP48 at the CINECA Computing Centre.

Acknowledgements

The Authors are grateful to the Centro di Calcolo of Modena University and to CINECA for computing facilities, to the Centro Strumenti of Modena University for the use of the XL-200 N.m.r. spectrometer and to the Italian Ministry of Education for financial support. Thanks are also due to Professor C. Guastini for collecting intensity data.

References

1 V. N. Sheinker, A. D. Garnovskii, and O. A. Osipov, *Russ. Chem. Rev. (Engl. Transl.)*, 1981, **50**, 336.

2 R. Benassi, U. Folli, L. Schenetti, and F. Taddei, *Adv. Heterocycl. Chem.*, 1987, **41**, 76.

3 Part 5. R. Benassi, U. Folli, D. Iarossi, L. Schenetti, and F. Taddei, *J. Chem. Soc., Perkin Trans. 2*, 1987, 351.

4 Part 7. R. Benassi, U. Folli, D. Iarossi, A. Musatti, M. Nardelli, L. Schenetti, and F. Taddei, *J. Chem. Soc., Perkin Trans. 2*, 1987, 1443.

5 Part 8. R. Benassi, U. Folli, D. Iarossi, A. Musatti, M. Nardelli, L. Schenetti, and F. Taddei, *J. Chem. Soc., Perkin Trans. 2*, 1987, 1851.

6 C. J. Leach and B. J. Tabner, *J. Chem. Soc. Perkin Trans. 2*, 1986, 1851.

7 C. J. Leach and B. J. Tabner, *J. Chem. Soc., Perkin Trans. 2*, 1986, 337.

8 D. M. Bertin, C. Chatain-Cathaud, and M.-C. Fournié-Zaluski, *C. R. Acad. Sci., Ser. C*, 1972, **274**, 1112.

9 M.-C. Fournié-Zaluski, B. P. Roques, and C. Chatain-Cathaud, *Org. Magn. Reson.*, 1975, **7**, 160.

10 C. Andrieu, D. Bertin, and H. Lumbroso, *C. R. Acad. Sci.*, 1965, **260**, 131.

11 C. G. Andrieu, C. Chatain-Cathaud, and M.-C. Fournié-Zaluski, *J. Mol. Struct.*, 1974, **22**, 433.

12 W. S. Sheldrick, W. Beker, and J. Engel, *Acta Crystallogr., Sect. B*, 1978, **34**, 3120.

13 C. L. Cheng, I. G. John, G. L. D. Ritchie, P. H. Gore, and L. Farnell, *J. Chem. Soc., Perkin Trans. 2*, 1975, 744.

14 C. G. Andrieu, P. Metzner, D. Debruyne, D. M. Bertin, and H. Lumbroso, *J. Mol. Struct.*, 1979, **39**, 263.

15 H. Lumbroso, C. Liégeois, and C. G. Andrieu, *Z. Naturforsch., Teil. A*, 1985, **40**, 1338.

16 G. Gacel, M.-C. Fournié-Zaluski, and B. P. Roques, *Org. Magn. Reson.*, 1976, **8**, 525.

17 P. Finocchiaro, A. Recca, P. Maravigna, and G. Montaudo, *Tetrahedron*, 1974, **30**, 4159; O. Hofer, in 'Topics in Stereochemistry,' eds. N. L. Allinger and E. Eliel, Wiley (Interscience), New York, 1976, vol. 9, p. 111; F. Inagaki and T. Mijazawa, in 'Progress in N.M.R. Spectroscopy,' eds. J. W. Emsley, J. Feeney, and L. Sutcliffe, Pergamon Press, Oxford 1982, vol. 14, p. 67; R. J. Abraham, *Anal. Proc. (London)*, 1981, **18**, 364.

18 (*a*) R. J. Abraham, D. J. Chadwick, and F. Sancassan, *Tetrahedron*, 1982, **38**, 1485, 3245; (*b*) R. J. Abraham, M. J. Bovill, D. J. Chadwick, L. Griffiths, and F. Sancassan, *ibid.*, 1980, **36**, 279.

19 S. Nagata, T. Yamabe, K. Yoshikawa, and H. Kato, *Tetrahedron*, 1973, **38**, 1485.

20 G. W. Buchanan, P. Finocchiaro, and G. Montaudo, *Can. J. Chem.*, 1973, **51**, 1053.

21 K. S. Dhami and J. B. Stothers, *Tetrahedron Lett.*, 1964, 631; *Can. J. Chem.*, 1965, **43**, 479.

22 GAUSSIAN-82. Release A: J. S. Binkley, K. Ragavachari, D. J. De Frees, H. B. Schlegel, R. A. Whiteside, G. Fluder, J. M. Frisch, R. Seeger, and J. A. Pople, Carnegie-Mellon University.

23 W. J. Hehre, L. Radom, and P. v. R. Schleyer, '*ab-initio* Molecular Orbital Theory,' Wiley, New York, 1986.

24 Part 6. R. Benassi, U. Folli, L. Schenetti, and F. Taddei, *J. Chem. Soc., Perkin Trans. 2*, 1987, 961.

25 Part 10. R. Benassi, U. Folli, L. Schenetti, and F. Taddei, *J. Chem. Soc., Perkin Trans. 2*, 1988, 1501.

26 R. J. Abraham and T. M. Siverns, *Tetrahedron*, 1972, **28**, 3015.

27 I. G. John and L. Radom, *J. Am. Chem. Soc.*, 1978, **100**, 3981; I. G. John, G. L. D. Ritchie, and L. Radom, *J. Chem. Soc., Perkin Trans. 2*, 1977, 1601.

28 D. L. Beveridge, M. M. Kelly, and R. J. Radna, *J. Am. Chem. Soc.*, 1974, **96**, 3769; F. Birnstock, H. J. Hofman, and H. J. Köler, *Theor. Chim. Acta*, 1976, **42**, 311.

29 T. Reichstein, *Helv. Chim. Acta*, 1930, **13**, 356.

30 A. Buzas and J. Teste, *Bull. Soc. Chim. France*, 1960, 793.

31 H. Gilman, L. W. Rowe, and J. B. Dickey, *Recl. Trav. Chim.*, 1933, **52**, 395.

32 S. Gronowitz and B. Eriksson, *Ark. Kemi*, 1963, **21**, 335.

33 M.-C. Fourniè-Zaluski and C. Chatain-Cathaud, *Bull. Soc. Chim. Fr.*, 1974, 1571.

34 E. Campaigne and H. L. Thomas, *J. Am. Chem. Soc.*, 1955, **77**, 5365.

35 S. Gronowitz and G. Sörlin, *Ark. Kemi*, 1962, **19**, 515.

36 S. Shiotani and H. Morita, *J. Heterocycl. Chem.*, 1982, **19**, 1207.

37 D. R. Arnold and R. J. Birtwell, *J. Am. Chem. Soc.*, 1973, **85**, 4599.

38 M. S. Lehman and F. K. Larsen, *Acta Crystallogr., Sect. A*, 1974, **30**, 580.

39 W. H. Zachariasen, *Acta Crystallogr.*, 1963, **16**, 1139.

40 G. M. Sheldrick, SHELX 86. Program for Crystal Structure Solution, University of Gottingen, Federal Republic of Germany, 1986.

41 P. Main, S. J. Fiske, S. E. Hull, L. Lessinger, G. Germain, J.-P. Declerq, and M. M. Woolfson, MULTAN 80. A System of Computer Programs for the Automatic Solution of Crystal Structures from *X*-Ray Diffraction Data, Universities of York, England and Louvain, Belgium, 1980.

42 G. M. Sheldrick, SHELX 76. Program for Crystal Structure Determination, University of Cambridge, 1976.

43 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, England, 1974, vol. 4, pp. 99 and 149.

44 M. Nardelli and A. Mangia, *Ann. Chim. (Rome)*, 1984, **74**, 163.

45 M. Nardelli, *Comput. Chem.*, 1983, **7**, 95.

46 C. K. Johnson, ORTEP. Report ORNL-3794, Oak Ridge National Laboratory, Tennessee, 1965.

Received 9*th May* 1988; *Paper* 8/01821I