Conformational Analysis of Organic Carbonyl Compounds. Part 8.† Conformational Properties of Aroyl Derivatives of Thiophene and Benzo[*b*]thiophene studied by *X*-Ray Crystallography, Nuclear Magnetic Resonance Lanthanide-induced Shifts Spectroscopy, and MO *Ab initio* Calculations

Rois Benassi,[a] **Ugo Folli,**[a] **Dario Iarossi,**[a] **Amos Musatti,**[b,c] **Mario Nardelli,**[c,d] **Luisa Schenetti,**[a] **and Ferdinando Taddei**[a]
[a] *Dipartimento di Chimica, Università, Via Campi 183, 41100 Modena, Italy*
[b] *Istituto di Strutturistica Chimica, Università, Viale delle Scienze, 43100 Parma, Italy*
[c] *Centro di Studio per la Strutturistica Diffrattometrica del CNR, Via M. D'Azeglio 85, 43100 Parma, Italy*
[d] *Istituto di Chimica Generale ed Inorganica, Università, Viale delle Scienze, 43100 Parma, Italy*

An investigation of the conformational properties in the solid state and in solution of 2- and 3-*p*-anisoyl derivatives of thiophene and of benzo[*b*]thiophene, compounds (**1b**) and (**2b**), and (**3**) and (**4**) respectively, is reported. *X*-Ray analysis of the compounds gave the following crystal data: (**1b**) space group *Pbca*, $a = 18.479(2)$, $b = 11.450(1)$, $c = 9.874(1)$ Å, $Z = 8$, $R = 0.0438$ for 1 611 observed reflections; (**2b**) space group *Pbca*, $a = 46.245(25)$, $b = 7.393(4)$, $c = 6.195(3)$ Å, $Z = 8$, $R = 0.0435$ for 1 153 observed reflections; (**3**) space group $P2_12_12_1$, $a = 14.039(2)$, $b = 12.469(2)$, $c = 7.457(1)$ Å, $Z = 4$, $R = 0.0697$ for 1 871 observed reflections; (**4**) space group $P2_1/a$, $a = 11.138(5)$, $b = 14.698(6)$, $c = 7.764(5)$ Å, $Z = 4$, $R = 0.0556$ for 1 983 observed reflections. In each of the molecules the rings are twisted with respect to the carbonyl plane, the heterocyclic ring is less twisted than the phenyl ring, and this deviation from planarity is particularly evident in the 2-substituted derivatives (**1b**) and (**3**). The orientation of the carbonyl group is of the S,O-*cis* and S,O-*trans* type in the 2-substituted and 3-substituted compounds; the former derivatives show the presence of attractive interactions between the sulphur and oxygen atoms. The conformational properties in chloroform were studied with the n.m.r. lanthanide-induced shifts (LIS) method (^{1}H and ^{13}C nuclei were employed). The preferred conformation (*ca.* 70%) found for derivatives (**1b**) and (**3**) is of the S,O-*cis* type, with the thiophene ring nearly coplanar with the carbonyl plane and the phenyl ring twisted. For derivative (**2b**) the preferred conformation in the equilibrium mixture is the S,O-*trans* type, yet in derivative (**4**) this conformation is almost exclusive. The heterocyclic and aryl rings show nearly the same degree of twist relative to the carbonyl plane. The conformational situation of derivatives (**1**)—(**4**) is compared with that of the corresponding furan and benzo[*b*]furan derivatives, and close conformational behaviour is found for the 3-substituted compounds. MO *Ab-initio* calculations in the minimal STO-3G basis set were also performed on the 2- and 3-benzoyl derivatives of thiophene, chosen as model compounds of those under investigation, and the conformations of minimum energy were located in the potential energy surface. For the 2-substituted compound (**1a**) the conformation of S,O-*cis* type was found to be the more stable conformer and a lower degree of twisting was found for the heterocycle than for the phenyl ring, in agreement with the experimental findings relative to compound (**1b**). For the 3-substituted derivative (**2a**) the results of calculations showed that the two conformers of the S,O-*cis* and S,O-*trans* type differ only slightly in energy content, the former being predicted to be more stable, in contrast with the experimental behaviour found for derivative (**2b**).

The conformational properties of carbonyl derivatives (aldehydes and ketones) of five-membered aromatic heterocycles have received much attention;[1,2] the relative orientation of the carbonyl oxygen and of the heteroatom X determines the existence of two conformers of X,O-*cis* and X,O-*trans* type. The geometrical features and population ratios of these conformers have been determined under different physical conditions.

Since 1973, the preferred conformation of thiophene-2-carbaldehyde in different solvents has been recognized[3–8] as the S,O-*cis* planar type (>90%). The same experimental behaviour has been found[9,10] for the corresponding benzo derivative. For 2-acetylthiophene the almost exclusive presence of the S,O-*cis* form, planar or nearly planar, is widely accepted,[1] and from low-temperature n.m.r. measurements this conformer appears[3] to be present in amounts greater than 95%. Even in the case of the 2-pivaloyl derivative the conformation of S,O-*cis* type is preferred and the molecule seems only slightly distorted from planarity.[3,11] The S,O-*cis* conformation is also largely preferred[9] for 2-acetylbenzo[*b*]thiophene. The higher stability of the S,O-*cis* conformer is determined by π-conjugative effects and, since this form is associated with greater polar character, its population is not expected to show any significant change on increasing the solvent polarity.[12]

For the 3-formyl and 3-acetyl derivatives of thiophene the S,O-*trans* conformer appears slightly more stable[12] and in

---

† For Part 7. see reference 21.

Supplementary data: (see Instructions for Authors, *J. Chem. Soc., Perkin Trans.*, 1987, issue 1, pp. xvii—xix). Lists of H-atom co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

solution an equilibrium is established between the conformers.[1] Benzo[*b*]thiophene derivatives show[9] a large preference for the S,O-*trans* form.

The planar conformation of the aroyl derivatives of five-membered heterocycles is sterically hindered[1] and one or both rings adopt a twisted orientation with respect to the carbonyl plane. Five-membered heterocycles are assumed[13,14] to have a higher conjugative ability with the C=O group than the phenyl ring and a higher degree of coplanarity is thus expected for the heterocyclic rings. For 2-benzoylthiophene the results of a number of investigations indicate that in solution the molecule has a preferred S,O-*cis* orientation[1,15–19] and the phenyl ring is more twisted than the 2-thienyl ring with respect to the carbonyl plane. The solid-state structure of closely related systems[20] confirms this preferred molecular orientation, the thienyl ring being almost coplanar and the phenyl ring severely twisted.

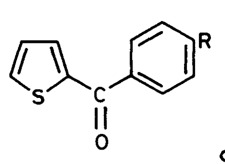
For 3-benzoylthiophene an equilibrium mixture of S,O-*cis* and S,O-*trans* forms exists in solution, and, in general, a higher degree of twist has been attributed to the phenyl ring, although these results have only led to qualitative conformational conclusions for this compound.

In a previous paper we have studied[21] the conformational properties of aroyl derivatives of furan and benzo[*b*]furan in the solid state and in solution; the conformational preference of 2-substituted derivatives differs in the single ring with respect to the benzo condensed system and under different physical conditions, though for 3-substituted compounds benzo condensation determines only shifts in the conformer populations of the aqueous equilibrium, their relative stability being preserved.

We now discuss the conformational properties of the 2- and 3-*p*-anisoyl derivatives of thiophene and benzo[*b*]thiophene under different physical conditions and compare our results with those obtained for the corresponding derivatives of furan and benzo[*b*]furan.[21]

Results

The strategy adopted to investigate the conformational properties of the aroyl derivatives of thiophene and benzo[*b*]thiophene (**1**)—(**4**) has been described.[21] In the solid state *X*-ray crystallographic analysis was used, whereas in solution the n.m.r. lanthanide-induced shifts (LIS) method[22] was employed. Derivatives (**1b**), (**2b**), (**3**), and (**4**) were chosen for ^{1}H measurements since they have simple spectra. The presence of a substituent (R) in the phenyl ring is not assumed to significantly effect the conformational preference of the two rings of compounds (**1b**) and (**2b**), in accord with results for *p*-substituted acetophenones.[23] The choice of compounds (**1a**) and (**2a**) for theoretical calculations was dictated by molecular size restrictions in relation to the time-consuming procedures necessary for constructing the potential energy surfaces of these molecules.

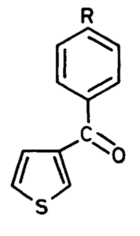


(**1a,b**)

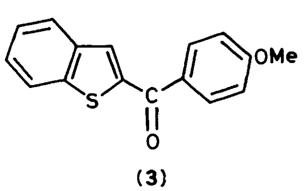
S,O-*cis*

a; R = H

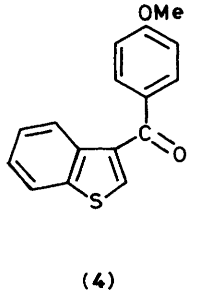
b; R = OMe



(**2a,b**)



(**3**)



(**4**)

X-Ray Analysis.—Bond distances, bond angles, and interatomic distances for derivatives (**1b**), (**2b**), (**3**), and (**4**) are given in Table 1 and the ORTEP drawings of the molecules are represented in Figure 1.

In these molecules the *O*-methyl group assumes an *s-trans* orientation with respect to the carbonyl oxygen and is nearly coplanar (twist angles within 4.5 and 12.3°) with the phenyl ring, as occurs in anisoles,[24] where a certain degree of conjugation between the ring and the methoxy substituent is present. This is also evidenced by the C–C bond distances in the phenyl ring, the C(*ortho*)–C(*meta*) bond being shorter than the others. The hydrogen atoms of the methoxy group assume a staggered conformation relative to the *ortho*-hydrogen atom of the ring. The carbonyl group is nearly planar as the central carbon atom forms sp^2 trigonal bonds. The two bond angles made by the rings with the exocyclic C–C(O) bond are very close to each other in the case of 3-substituted compounds (**2b**) and (**4**), while in the 2-substituted derivatives the angles S(1)–C(2)–C(6) in (**1b**) and S(1)–C(2)–C(8) in (**3**) are significantly smaller than the corresponding C(3)–C(2)–C(6) and C(3)–C(2)–C(8) bond angles. The phenyl ring makes slightly different angles with the C–C(O) bond which is thus not coincident with the binary axis passing across the ring: this situation is common to the four compounds examined and to the corresponding derivatives[21] of furan and benzo[*b*]furan. The exocyclic C–C(O) bond distances become shorter as the angle of twist of the ring with respect to the carbonyl plane decreases in a roughly linear trend, and with values that are close to that of a pure C(sp^2)–C(sp^2) bond (1.487 Å).

An approximate planar situation is found for the atoms of the rings while their planes are twisted with respect to the carbonyl plane. The heterocyclic ring is less twisted than the phenyl ring and the 2-substituted ring displays greater coplanar character than the 3-substituted rings. The conjugative ability of the thienyl ring, especially in the 2-position, is greater than that of the phenyl ring,[13,14] and may explain these structural differences. The two rings are rotated in the conrotatory sense, as occurs for the phenyl rings of the benzophenones.[25]

In the solid state compounds (**1b**) and (**3**) adopt the S,O-*cis* orientation; this conformation has also been found[26–28] for 2-formyl- and 2-acetyl-4-bromothiophene in the solid state. Derivatives (**2b**) and (**4**) exist in the S,O-*trans* orientation.

A number of attractive interactions have been found by examining the interatomic distances between non-bonded atoms; in compounds (**1b**) and (**3**) these include S(1)···O(7) [2.918(2) Å] and S(1)···O(9) [2.877(5) Å] and in compounds (**2b**) and (**4**) H(4)···O(7) [2.73(3) Å] and H(4)···O(9) [2.58(3) Å]. For compounds (**1b**) and (**3**) the S···O distance is significantly smaller than the sum of van der Waals radii (3.3 Å) and this is assumed[29] to be indicative of the presence of attractive interactions. These interactions cannot take place in the 3-substituted derivatives (**2b**) and (**4**) where, nevertheless, there occur those of C–H···O type which can act as weak hydrogen bonds.[30]

Packing energy calculations, performed with the OPEC program,[31] show that the groups attached to the central C=O carbonyl adopt positions of minimum steric interaction. As is found for the analogous series of furyl derivatives,[21] the total

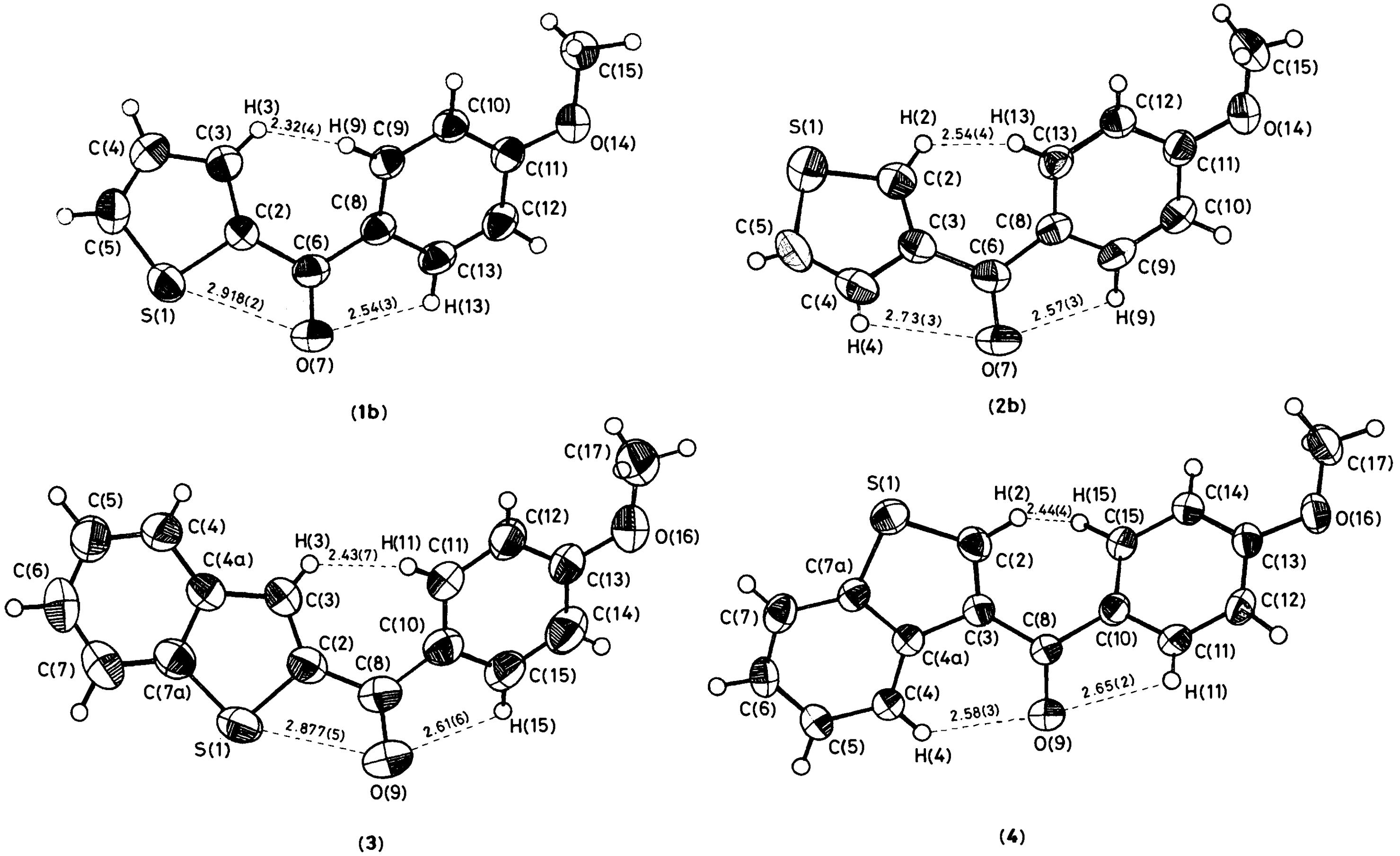


Figure 1. ORTEP drawings of the molecules of compounds (**1b**), (**2b**), (**3**), and (**4**). Ellipsoids at 50% probability level

Table 1. Comparison of bond distances (Å), angles (°), and torsions (°) in the four thiophene derivatives. *i* = *ipso*, *o* = *ortho*, *m* = *meta*, *p* = *para*. Benzo α, β, γ are for the position of the C–C bonds in the benzo ring with respect to the junction with the thiophene ring

Compd.	(**1b**)	(**2b**)	Compd.	(**3**)	(**4**)
S(1)–C(2)	1.718(2)	1.704(4)	S(1)–C(2)	1.737(6)	1.702(2)
S(1)–C(5)	1.703(2)	1.688(4)	S(1)–C(7a)	1.730(6)	1.727(2)
C(2)–C(3)	1.389(3)	1.365(4)	C(2)–C(3)	1.375(8)	1.348(3)
C(4)–C(5)	1.352(3)	1.377(5)	C(4a)–C(7a)	1.418(9)	1.392(3)
C(3)–C(4)	1.415(3)	1.415(5)	C(3)–C(4a)	1.439(8)	1.452(3)
		C–O(carbonyl)	1.223(4) av.		
		C(thiop.)–C(carbonyl)	1.476(2) av.		
		C(phen.)–C(carbonyl)	1.483(2) av.		
		C_i–C_o(phen.)	1.398(3) av.		
		C_o–C_m(phen.)	1.378(4) av.		
		C_m–C_p(phen.)	1.400(2) av.		
		C–O(Me)	1.367(2) av.		
		O–Me	1.434(5) av.		
			C–C(benzo, α)	1.394(3) av.	
			C–C(benzo, β)	1.365(6) av.	
			C–C(benzo, γ)	1.382(3) av.	
C(2)–C(6)–O(7)	119.3(2)	—	C(2)–C(8)–O(9)	118.3(6)	—
C(3)–C(6)–O(7)	—	119.0(3)	C(3)–C(8)–O(9)	—	120.2(2)
C(8)–C(6)–O(7)	121.2(2)	120.1(3)	C(10)–C(8)–O(9)	120.3(5)	120.2(3)
C(2)–C(6)–C(8)	119.5(2)	—	C(2)–C(8)–C(10)	121.4(5)	—
C(3)–C(6)–C(8)	—	120.9(2)	C(3)–C(8)–C(10)	—	119.5(2)
C(6)–C(2)–S(1)	117.8(1)	—	C(8)–C(2)–S(1)	116.4(4)	—
C(6)–C(3)–C(2)	—	126.0(3)	C(8)–C(3)–C(2)	—	123.3(2)
C(6)–C(2)–C(3)	130.8(2)	—	C(8)–C(2)–C(3)	130.6(6)	—
C(6)–C(3)–C(4)	—	122.4(3)	C(8)–C(3)–C(4a)	—	124.5(2)
C(6)–C(8)–C(9)	123.8(2)	118.4(2)	C(8)–C(10)–C(11)	123.2(5)	117.9(2)
C(6)–C(8)–C(13)	118.5(2)	123.7(3)	C(8)–C(10)–C(15)	118.4(5)	123.1(2)
C(10)–C(11)–O(14)	124.5(2)	115.6(3)	C(12)–C(13)–O(16)	125.2(5)	115.1(2)
C(12)–C(11)–O(14)	115.9(2)	124.4(3)	C(14)–C(13)–O(16)	114.4(5)	124.2(2)
C(11)–O(14)–C(15)	117.8(2) av.		C(13)–O(16)–C(17)	117.2(3) av.	
C(2)–S(1)–C(5)	92.0(4) av.		C(2)–S(1)–C(7a)	92.0(1) av.	
S(1)–C(2)–C(3)	111.3(2) av.		S(1)–C(2)–C(3)	113.6(4) av.	
C(2)–C(3)–C(4)	111.5(2) av.		C(2)–C(3)–C(4a)	111.7(2) av.	
C(3)–C(4)–C(5)	113.1(2) av.		C(3)–C(4a)–C(7a)	112.0(2) av.	
C(4)–C(5)–S(1)	111.9(7) av.		C(4a)–C(7a)–S(1)	110.9(2) av.	
		(C–C–C)$_i$(phen.)	120.1(3) av.		
		(C–C–C)$_o$(phen.)	121.3(2) av.		
		(C–C–C)$_m$(phen.)	119.5(2) av.		
		(C–C–C)$_p$(phen.)	118.2(3) av.		
S(1)–C(2)–C(6)–O(7)	12.2(2)	—	S(1)–C(2)–C(8)–O(9)	14.5(8)	—
C(4)–C(3)–C(6)–O(7)	—	22.1(5)	C(4a)–C(3)–C(8)–O(9)	—	−18.1(3)
C(13)–C(8)–C(6)–O(7)	30.4(3)	−150.4(3)	C(15)–C(10)–C(8)–O(9)	28.1(9)	144.8(2)
C(9)–C(8)–C(6)–O(7)	−147.3(2)	26.7(4)	C(11)–C(10)–C(8)–O(9)	−146.6(7)	−33.0(3)
C(10)–C(11)–O(14)–C(15)	−12.3(3)	−175.7(3)	C(12)–C(13)–O(16)–C(17)	5.2(10)	−177.1(2)
C(12)–C(11)–O(14)–C(15)	169.4(2)	4.5(5)	C(14)–C(13)–O(16)–C(17)	−176.7(7)	5.0(3)

Table 2. ^{1}H N.m.r. chemical shifts (δ values) in compounds (**1b**) and (**2b**) recorded in [^{2}H]chloroform. The Δ*M*s are the LIS values and refer to Yb(fod)$_3$

Compd.		2-H	3-H	4-H	5-H	2′-H	3′-H	OMe
(**1b**)	δ	—	7.65	7.13	7.69	7.91	6.99	3.87
	Δ*M*	—	21.98	6.06	5.30	29.29	5.53	2.02[a]
(**2b**)	δ	7.86	—	7.57	7.34	7.86	6.94	3.86
	Δ*M*	22.03	—	23.64	4.74	29.39	6.06	2.23[a]

[a] Not employed in LIS simulation.

intermolecular non-bonded energy increases by rotating the thienyl (or benzo[*b*]thienyl) groups (with the approximation of maintaining the remainder of the molecule and all adjacent molecules at rest) reaching maxima after 80° and 260° rotations and a minimum after 180° rotation in the case of compounds (**1b**), (**2b**) and (**3**). For the benzo derivatives these two maxima are exceedingly high and positive, and in the case of compound (**4**) this situation of very high positive values of energy is found over the whole angular region from 10—350°.

Results from N.M.R. LIS Simulation.—The ^{1}H and ^{13}C chemical shifts and LIS values for compounds (**3**) and (**4**) have been reported previously.[32] The ^{1}H and ^{13}C chemical shifts of compounds (**1b**) and (**2b**) recorded in [^{2}H]chloroform are given

Table 3. ^{13}C Chemical shifts (δ values) in compounds (**1b**) and (**2bH**) recorded in [^{2}H]chloroform, LIS values ΔM due to $Yb(fod)_3$ and corrected ($\Delta M - \Delta D$) for the complexation shift[6,33] in the presence of $La(fod)_3$

Compd.		C-2	C-3	C-4	C-5	C-1′	C-2′	C-3′	C-4′	C=O
(**1b**)	δ	143.92	133.91	127.75	133.32	130.83	131.60	113.76	163.19	186.76
	ΔM	50.33	28.57	11.78	13.14	51.35	30.24	11.50	10.26	113.57
	$\Delta M - \Delta D$	53.72	24.34	11.78	9.97	53.12	28.05	11.50	8.75	110.61
(**2b**)	δ	132.65	141.65	128.72	125.96	131.28	131.83	113.70	163.21	188.79
	ΔM	30.73	52.43	28.20	11.28	51.49	30.63	11.98	10.65	117.13
	$\Delta M - \Delta D$	24.69	54.77	26.75	11.28	53.98	27.77	11.98	8.91	113.04

Table 4. Results of LIS simulation: molecular geometry parameters for the complexes[a] and conformational properties for derivatives (**1b**), (**2b**), (**3**), and (**4**)

Compd.	$R_{cryst.}$	Sum–Diff. (p.p.m.)	R (Å)	φ	ψ	f	Population *endo*	Conformational angles[b] (°) θ	γ	%
(**1b**)	0.022	0.85	2.80	70	155	3 427	50	0	33	70
								180	33	30
(**2b**)	0.028	1.15	2.85	55	160	3 475	60	30	30	40
								150	30	60
(**3**)[c]	0.021	0.67	2.70	90	155	3 147	45	0	30	65—70
								180	30	35—30
(**4**)[c]	0.030	1.03	2.75	65	165	2 968	20	150	33	100

[a] For the symbols see references 6, 33, and 34. [b] These angles are defined in Figure 2; estimated error ±10°. [c] Results from reference 32.

in Tables 2 and 3 together with pseudocontact shifts (ΔM) obtained in presence of $Yb(fod)_3$ and corrections for complex formation[6,33,34] (ΔD) on ^{13}C shifts using $La(fod)_3$.

The close values of the difference in the chemical shifts from the parent heterocycles[35] found for 3-H, C-2, and C-3 in compounds (**1b**) and (**3**), and of 2-H, C-2, and C-3 in compounds (**2b**) and (**4**) and of the carbon atom of the carbonyl group, suggest that the presence of the condensed benzene ring does not affect the basic conformational trend in solution of the carbonyl group in 2- and 3-substituted derivatives. The low-field shift induced[35] by the C=O group on 3-H (0.6 p.p.m.) in compounds (**1b**) and (**3**), and on 2-H (0.6 p.p.m.) in compounds (**2b**) and (**4**), indicate a preferred S,O-*cis* and S,O-*trans* orientation in the former and latter compounds respectively, since higher shifts would be expected on these protons from the opposite orientation. From an approximate formulism[36] the contribution from the magnetic and electric dipoles of the C=O group to the screening constant of the protons can be derived. The calculated values of these contributions as a function of the angle of rotation defined in Figure 2, can be employed for a qualitative estimate of the conformation of the carbonyl group in derivatives (**1**)—(**4**). From the contribution to the screening of 3-H in derivatives (**1b**) and (**3**) the information obtained is inconclusive, since the experimental low-field shift is compatible both with the presence of 90—100% of the planar S,O-*cis* form and with lower amounts of this form distorted from planarity. In derivatives (**2b**) and (**4**) the contributions to the screening constants of 2-H and 4-H indicate that the S,O-*trans* conformer, slightly distorted from planarity (0—30°), is greatly preferred.

The LIS simulation procedure employed for obtaining conformational information has been used in our previous work[32] and is derived from literature sources.[6,33,34] The molecular geometry employed has been derived experimentally; minor changes in $R_{cryst.}$ (which indicates the best agreement between calculated and experimental values) and in the conformational conclusions are caused by choosing standard bond lengths and bond angles for the rings. Lanthanide-induced shifts (ΔM) for ^{1}H and ^{13}C were measured on the same sample. The LIRAS-3 computer program[34] was employed in the 'four-site' axially symmetric complexation model.

The conformational results from the LIS approach are collected in Table 4, where the symbols are those adopted from previous papers.[6,32–34]

Compound (**1b**) in [^{2}H]chloroform indicates the presence of an equilibrium mixture of the S,O-*cis* and S,O-*trans* conformers, the S,O-*cis* form being preferred. The heterocyclic ring and the carbonyl plane are almost coplanar, yet $R_{cryst.}$ changes only slightly by varying θ up to 15°. The phenyl ring is twisted 33°. The conformational situation of compound (**1b**) is very similar to that of compound (**3**), as can be verified in Table 4.

For compound (**2b**) an equilibrium between the two distorted conformers is established, in which each ring is twisted about 30° with respect to the carbonyl plane, and the S,O-*trans* form is slightly preferred. Comparison with compound (**4**) shows that in the latter the preferred and the exclusive (*ca.* 100%) conformer is of the S,O-*trans* type despite the degrees of distortion of the rings being close in both compounds (see Table 4). This difference in the position of the conformational equilibrium in compounds (**2b**) and (**4**) has also been found in the corresponding derivatives of the oxygen heterocycles.[21]

Results from Theoretical Calculations.—Total molecular energy of model compounds (**1a**) and (**2a**) was calculated on a CRAY-X-MP12 computer using the Gaussian-82 program.[37] Only the STO-3G minimal basis set was adopted, since molecular size prevented any further basis expansion.

The potential energy surface was constructed with the procedure previously described[21] by employing energy values calculated in 30° steps by changing the θ and γ angles defined in Figure 2 in the intervals: $0° \leqslant \theta \leqslant 360°$, $0° \leqslant \gamma \leqslant 180°$. Geometry relaxation was allowed only for the parameters relative to the carbonyl group and was performed on the molecular conformations corresponding to the energy minima of the energy surface.[21] The geometries of the thienyl and phenyl

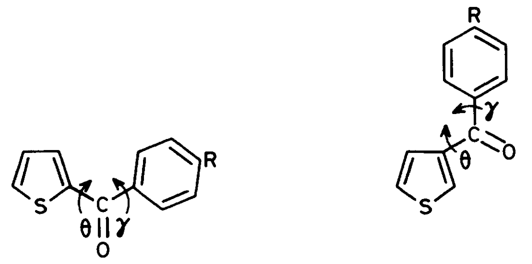


Figure 2. Definition of the angles of rotation θ and γ of the two rings around the exocyclic C–C(O) bonds in derivatives (**1**) and (**2**): the all-planar situation depicted corresponds to θ = γ = 0°

rings are those optimized for thiophene-2-carbaldehyde[38] and for benzophenone.[21] Four conformers are thus obtained, which represent two pairs of enantiomers.

In derivative (**1a**) both rings are twisted relative to the carbonyl plane, the angle of twist being greater for the phenyl ring. The two rings in derivative (**2a**) are almost equally rotated but the phenyl ring is slightly more twisted. Further, the angle of twist of the 3-thienyl ring is greater than that of the 2-thienyl ring. These results show that the degree of twist has an order inverse to that of the conjugative properties of the rings[13,14] and are in agreement with the trend of the conformational properties previously assigned[1,15–19] to these compounds.

The relative energy content of the two conformers of compound (**1a**) shows that the S,O-*cis* conformer is the more stable form ($\Delta E = 2.87$ kJ mol^{-1}), in agreement with the experimental behaviour,[1,15–19] though the energy difference is probably underestimated. Even for compound (**2a**) the S,O-*cis* conformer is slightly more stable ($\Delta E = 1.10$ kJ mol^{-1}) than the S,O-*trans* form. Experimental evidence[1] on 3-formyl- and 3-acetyl-thiophene indicates that small energy differences occur between the two conformers, but that the S,O-*trans* form is the more stable. The two conformers of thiophene-3-carbaldehyde have almost identical energy content from *ab-initio* MO calculations in the STO-3G basis set,[38,*] the S,O-*trans* form being only slightly more stable (0.26 kJ mol^{-1}); this relative stability increases when larger basis sets are employed.* Thus, considering that the experimental results relative to compounds (**2b**) and (**4**) show that the S,O-*trans* form is the exclusive conformer present in the solid state and the one preferred in solution, and in view of the theoretical results obtained for 3-benzoylfuran[21] which show that the calculated relative stability of the conformers of this compound is incorrectly predicted in the STO-3G approach, it appears that the higher stability of the S,O-*cis* form of compound (**2a**) is most probably an artifact due to the employment of contracted basis sets in the calculation of the energy content of this molecule. Unfortunately the large molecular size does not allow the basis set to be expanded in order to verify this point.

Discussion of the Results and Conclusions

Comparison of the results allows a number of conclusions to be drawn on the conformational properties of aroyl derivatives of thiophene and benzo[*b*]thiophene.

For compounds (**1b**) and (**3**) the S,O-*cis* orientation is preferred in the solid state and in solution, with the heterocyclic ring nearly coplanar or only slightly distorted from coplanarity with the carbonyl bond. In solution, an equilibrium between the two conformers is found, the S,O-*cis* form being preferred. Theoretical calculations on the model compound (**1a**) also show that the S,O-*cis* form is the more stable conformer, with the thienyl ring less twisted than the phenyl ring, in agreement with the experimental results relative to compound (**1b**). Thus, the 2-aroyl derivatives of thiophene and benzo[*b*]thiophene show very similar conformational properties. For the corresponding furan and benzo[*b*]furan derivatives, inversion of the O,O-orientation has been found[21] in the solid state and has been attributed to different packing requirements of the two molecules in view of the small difference in the energy content of the conformers and of their different polarity. In the solid state, it seems that repulsive and attractive interactions are of the utmost importance in determining the relative orientation of the ring heteroatom (S and O) and of the carbonyl oxygen of these molecules; the S,O-*cis* orientation of the 2-aroyl derivatives of thiophene and of benzo[*b*]thiophene corresponds to attractive interactions between the S and O atoms, evidenced by the short S$\cdots$O non-bonded distance. This is probably one of the factors contributing to the almost exclusive presence of the more stable and more polar S,O-*cis* form in solution, even though this kind of interaction appears insignificant on the basis of the charge density on the sulphur and oxygen atoms calculated[39] with the CNDO/2 method in thiophene-2-carbaldehyde. The *ab-initio* total charge densities S(+0.273) and O(−0.223) of the S,O-*cis* conformation of compound (**1a**) favour the presence of an attractive electrostatic interaction.

The solid-state orientation of compounds (**2b**) and (**4**) is of the S,O-*trans* type and the angle of twist of the heterocycle is smaller than that of the phenyl ring but still greater than that of the 2-substituted rings. In solution, the S,O-*trans* form, with an almost equal degree of twist for the heterocycle and phenyl ring, is still the more stable conformer. Theoretical calculations on the model compound (**2a**) do not reproduce the experimental stability trend of these molecules even though the twist of the rings is in agreement with that found in the solid state. In [^{2}H]chloroform compounds (**2b**) and (**4**) differ in the amount of the S,O-*trans* conformer; almost exclusive for compound (**4**). The same situation has been revealed[21] for the corresponding derivatives of the oxygen heterocycles and the explanation given for those compounds[21] should apply here. It thus appears that 3-substituted derivatives of condensed five-membered heterocycles and of naphthalene[40] have qualitatively similar structural properties which favour the X,O-*trans* orientation of the carbonyl group. For compound (**2b**) and the analogous furan derivative[21] preference for the X,O-*trans* form in solution reflects the higher stability of this conformer which should be as well the form associated with lower polar character. This is expected on the basis of the experimental behaviour found for the corresponding formyl and acetyl derivatives,[1,12] but it is not predicted by MO *ab-initio* calculations in the minimal basis set. Studies of the medium effect on the conformational equilibrium of these compounds could probably throw light on this point.

Experimental

Compounds.—2- and 3-(*p*-anisoyl)thiophene (**1b**) and (**2b**),[41] 2- and 3-(*p*-anisoyl)benzo[*b*]thiophene (**3**) and (**4**)[42] were prepared according to literature methods. Samples for *X*-ray analysis were obtained by slow crystallization of the pure products from cyclohexane (**1b**), hexane (**2b**), and 95% ethanol (**3**) and (**4**).

Crystal Structure Analysis.—Data concerning the crystal structure analysis are reported in Table 5. The lattice parameters were determined by measuring numbers of accurately centred reflections at high θ by using the Cu-K_{α_1} ($\lambda = 1.540\,562$ Å) radiation at room temperature (294 K). For all the compounds, intensity data were collected on a SIEMENS AED diffractometer using the Cu-$K_{\bar{\alpha}}$ radiation, and the θ—2θ

---

* Results not yet published from our laboratories relative to thiophene-3-carbaldehyde.

Table 5. Experimental data for the crystallographic analyses

Compound	**(1b)**	**(2b)**	**(3)**	**(4)**
Formula	$C_{12}H_{10}O_2S$	$C_{12}H_{10}O_2S$	$C_{16}H_{12}O_2S$	$C_{16}H_{12}O_2S$
M	218.27	218.27	268.33	268.33
Space group	*Pbca*	*Pbca*	$P2_12_12_1$	$P2_1/a$
a/Å	18.479(2)	46.245(25)	14.039(2)	11.138(5)
b/Å	11.450(1)	7.393(4)	12.469(2)	14.698(6)
c/Å	9.874(1)	6.195(3)	7.457(1)	7.764(5)
β/°	90	90	90	90.86(2)
U/Å^3	2 089.2(4)	2 118(2)	1 305.2(4)	1 271(1)
Z	8	8	4	4
D_x/Mg m^{-3}	1.388	1.369	1.365	1.402
V_m/Å^3	184.5	182.4	226.9	229.0
V_{occ}/Å^3	1 476.2	1 529.4	950.3	915.9
S_m/Å^2	218.5	216.7	262.6	264.0
V_{free}/Å^3	613.0	658.6	397.6	355.1
C_K	0.707	0.689	0.695	0.721
Reflections for lattice parameters: number	30	30	30	30
Reflections for lattice parameters: θ range/°	20—38	21—39	22—37	26—40
F(000)	912	912	560	560
Crystal size/mm	0.27 × 0.31 × 0.51	0.25 × 0.27 × 0.30	0.20 × 0.24 × 0.35	0.19 × 0.26 × 0.35
μ/mm^{-1}	2.500	2.466	2.104	2.161
Extinction param. g	$6.0(1) \times 10^{-8}$	$2.3(2) \times 10^{-8}$	$5.6(5) \times 10^{-8}$	$8.7(2) \times 10^{-8}$
θ range/°	3—70	3—70	3—70	3—70
h range	0/22	0/49	−16/17	−13/13
k range	0/13	0/8	0/15	0/17
l range	0/12	0/7	0/8	0/9
Standard reflection	0 6 2	28 2 0	4 5 1	$\bar{8}$ 0 2
Intensity variation	None	None	None	None
No. of measured reflections	4 403	4 736	2 800	2 712
Conditions for observed reflections	$I > 2\sigma(I)$	$I > 3\sigma(I)$	$I > 3\sigma(I)$	$I > 3\sigma(I)$
No. reflections used in refinement	1 611	1 153	1 871	1 983
R(int)	0.041	0.015	0.019	0.020
Max. L.S. shift to error ratio	0.11	0.57	0.05	0.09
Min./max. height in final $\Delta\rho$/e Å^3	−0.44/0.19	−0.17/0.08	−0.31/0.13	−0.49/0.30
No. of refined parameters	176	176	220	220
$R = \Sigma\lvert\Delta F\rvert/\Sigma\lvert F_o\rvert$	0.0438	0.0435	0.0697	0.0556
$R' = [\Sigma w(\Delta F)^2/\Sigma wF_o^2]^{\frac{1}{2}}$	0.0708	0.0647	0.0888	0.0768
$S = [\Sigma w(\Delta F)^2/(N - P)]^{\frac{1}{2}}$ *	0.5910	0.3193	1.2269	0.4047
k, g ($w = k/[\sigma^2(F_c) + gF_o^2]$)	1.0, 0.0141	0.26, 0.1016	1.0, 0.0000	1.0, 0.0384

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

scan mode, scan speed 3—12° min^{-1}, scan width 1.2 + $\Delta\lambda/\lambda \tan\theta$). The individual reflections profiles were analysed following the method of Lehman and Larsen,[43] and the intensity data were corrected for Lorentz and polarization effects, but not for absorption. Extinction was considered according to Zachariasen.[44]

The structures were solved by the direct methods implemented in the SHELX 76[45] program and refinements were carried out by full-matrix least squares using the same program, anisotropically for the non-hydrogen atoms, isotropically for hydrogens whose starting co-ordinates were obtained from ΔF calculations. For compound (3), whose space group is polar, the attempts made to define the absolute polarity did not give reliable results, the intensity data being insufficiently accurate to give significant differences due to the anomalous scattering effects.

Crystal packing analysis was carried out using the OPEC[31] program. The molecular volume V_m, the total volume occupied in the cell V_{occ}, the free volume V_{free}, and the Kitaigorodski[46] packing coefficient C_K, of the four compounds are compared in Table 5.

Thermal motion was analysed in terms of the rigid-body LTS method of Schomaker and Trueblood.[47] Acceptable fits of U_{ij}s are obtained for compounds (**1b**) ($R_{wU} = [\Sigma(w\Delta U)^2/\Sigma(wU_o)^2]^{\frac{1}{2}} = 0.096$) [$\Delta U = U_{ij}(\text{obs.}) - U_{ij}(\text{calc.})$], (**2b**) ($R_{wU} = 0.098$) and (**3**) ($R_{wU} = 0.094$), while for compound (**4**) ($R_{wU} = 0.155$) the agreement is rather poor, indicating that internal motions are relevant particularly for this last compound.

The corrections for bond distances due to vibrational motion are in the range 0.001—0.011, av. 0.004 Å and do not change the observed trends so the discussion based on the data of Table 1 need not consider these corrections.

The atomic scattering factors were taken from reference 48. The final atomic co-ordinates are quoted in Table 6. The calculations were performed on the GOULD-SEL 32/77 computer of the 'Centro di Studio CNR per la Strutturistica Diffrattometrica' (Parma). In addition to the quoted programs, LQPARM,[49] PARST,[50] THMV,[51] ORTEP,[52] and PLUTO[53] programs have been used.

N.M.R. Measurements.—The spectra were recorded at 200.058 MHz for ^{1}H and 53.3088 MHz for ^{13}C by employing a Varian XL-200 spectrometer. The shift reagent employed is Yb(fod)$_3$ dried *in vacuo* on 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. The correlation coefficients for the plots relating chemical shifts to the

Table 6. Atomic fractional co-ordinates (× 10^4)

	Compound (**1b**)			Compound (**2b**)		
Atom	*x*	*y*	*z*	*x*	*y*	*z*
S(1)	2 914(0)	1 606(1)	2 972(1)	376(0)	−540(2)	615(2)
C(2)	3 494(1)	1 674(2)	4 328(2)	729(1)	−644(4)	1 391(5)
C(3)	3 377(1)	752(2)	5 216(2)	769(1)	20(4)	3 426(4)
C(4)	2 815(1)	11(2)	4 758(3)	505(1)	633(5)	4 328(5)
C(5)	2 523(1)	362(2)	3 570(2)	273(1)	425(5)	2 962(6)
C(6)	3 972(1)	2 701(2)	4 437(2)	1 043(1)	−5(4)	4 665(4)
O(7)	3 860(1)	3 551(1)	3 708(2)	1 033(1)	−22(4)	6 614(4)
C(8)	4 563(1)	2 704(2)	5 451(2)	1 326(1)	−49(4)	3 543(4)
C(9)	4 955(1)	1 710(2)	5 824(2)	1 562(1)	−856(4)	4 603(5)
C(10)	5 511(1)	1 759(2)	6 761(2)	1 831(1)	−859(4)	3 709(5)
C(11)	5 681(1)	2 825(2)	7 367(2)	1 877(1)	−31(4)	1 712(4)
C(12)	5 304(1)	3 834(2)	6 985(2)	1 648(1)	776(4)	629(5)
C(13)	4 762(1)	3 771(2)	6 045(2)	1 375(1)	733(4)	1 542(4)
O(14)	6 214(1)	2 976(1)	8 306(2)	2 156(0)	−92(3)	955(3)
C(15)	6 527(1)	1 955(2)	8 898(3)	2 219(1)	836(8)	−994(7)

	Compound (**3**)			Compound (**4**)		
Atom	*x*	*y*	*z*	*x*	*y*	*z*
S(1)	−3 257(1)	−2 765(1)	1 307(3)	1 436(1)	777(0)	637(1)
C(2)	−2 176(4)	−3 153(4)	2 233(9)	2 495(2)	5(1)	1 261(3)
C(3)	−2 169(4)	−4 206(5)	2 780(11)	3 461(2)	379(1)	2 051(2)
C(4a)	−3 068(4)	−4 725(4)	2 448(10)	3 345(2)	1 360(1)	2 187(2)
C(4)	−3 333(5)	−5 786(5)	2 809(11)	4 108(2)	1 999(1)	2 943(3)
C(5)	−4 230(5)	−6 125(6)	2 366(12)	3 802(2)	2 904(1)	2 903(3)
C(6)	−4 873(5)	−5 430(7)	1 543(12)	2 750(2)	3 202(1)	2 126(3)
C(7a)	−3 731(4)	−4 033(5)	1 599(10)	2 277(2)	1 672(1)	1 442(2)
C(7)	−4 640(4)	−4 382(6)	1 158(12)	1 984(2)	2 597(2)	1 388(3)
C(8)	−1 428(4)	−2 335(5)	2 297(10)	4 566(2)	−134(1)	2 465(3)
O(9)	−1 654(4)	−1 398(3)	2 050(9)	5 532(1)	256(1)	2 543(3)
C(10)	−420(4)	−2 620(4)	2 675(9)	4 503(2)	−1 136(1)	2 696(2)
C(11)	−4(4)	−3 576(5)	2 109(11)	5 469(2)	−1 662(2)	2 111(3)
C(12)	946(4)	−3 783(5)	2 454(11)	5 473(2)	−2 588(1)	2 318(3)
C(13)	1 491(4)	−3 037(5)	3 296(10)	4 516(2)	−3 018(1)	3 165(2)
C(14)	1 091(5)	−2 072(5)	3 870(13)	3 547(2)	−2 512(1)	3 775(3)
C(15)	153(5)	−1 867(5)	3 504(13)	3 547(2)	−1 574(1)	3 516(3)
O(16)	2 435(3)	−3 153(4)	3 706(8)	4 639(2)	−3 938(1)	3 376(2)
C(17)	2 910(6)	−4 084(8)	3 091(19)	3 656(3)	−4 416(2)	4 162(4)

lanthanide/substrate ratio were always found $\geqslant 0.999$ and the intercepts identical to the unshifted spectra.

Acknowledgements

The authors are grateful to the Centro di Calcolo of Modena University and CINECA for computing facilities, to the Centro Strumenti of Modena University for the use of the XL-200 spectrometer and to the Italian Ministry of Education for financial support. They are also indebted to Professor C. Guastini (Parma University) for collection of intensity data.

References

1 V. N. Sheinker, A. D. Garnovskii, and O. A. Osipov, *Russ. Chem. Rev.* (*Engl. Transl.*), 1981, **50**, 336 and references cited therein.
2 D. J. Chadwick and I. A. Cliffe, *Khim. Geterotsikl. Soedin.*, 1984, 579 (*Chem. Abstr.*, 1984, **101**, 71823) and references cited therein.
3 D. Casarini, L. Lunazzi, and D. Macciantelli, *J. Chem. Soc., Perkin Trans. 2*, 1985, 1839.
4 C. Chatgilialoglu, L. Lunazzi, D. Macciantelli, and G. Placucci, *J. Am. Chem. Soc.*, 1984, **106**, 5252.
5 S. R. Salman, *Org. Magn. Reson.*, 1982, **20**, 151.
6 R. J. Abraham, D. J. Chadwick, and F. Sancassan, *Tetrahedron*, 1982, **38**, 1485.
7 P. Finocchiaro, A. Recca, P. Maravigna, and G. Montaudo, *Tetrahedron*, 1974, **30**, 4159.
8 G. Montaudo, S. Caccamese, V. Librando, and P. Maravigna, *Tetrahedron*, 1973, **29**, 3915.
9 Part 3, R. Benassi, U. Folli, D. Iarossi, L. Schenetti, and F. Taddei, *J. Chem. Soc., Perkin Trans. 2*, 1983, 911.
10 C. G. Andrieu and A. Ruwet, *Bull. Soc. Chim. Fr.*, 1972, 1008.
11 D. Mirarchi and G. L. D. Ritchie, *J. Mol. Struct.*, 1984, **116**, 377.
12 J. Kao and L. Radom, *J. Am. Chem. Soc.*, 1979, **101**, 311.
13 M. Fiorenza, A. Ricci, G. Sbrana, G. Pirazzini, C. Eaborn, and G. Stamper, *J. Chem. Soc., Perkin Trans. 2*, 1978, 1232.
14 M. C. Fournié-Zaluski, B. P. Roques, and C. Chatain-Cathaud, *Org. Magn. Reson.*, 1975, **7**, 167.
15 V. N. Sheinker, A. S. Kuzharova, V. F. Lavrushin, N. F. Pedchenko, and O. A. Osipov, *Khim. Geterotsikl. Soedin.*, 1979, 1327 (*Chem. Abstr.*, 1980, **92**, 93794).
16 R. Abu-Eittah and R. Hilal, *Bull. Chem. Soc. Jpn.*, 1978, **51**, 2718.
17 C. G. Andrieu, P. Metzner, D. Debruyne, D. M. Bertin, and H. Lumbroso, *J. Mol. Struct.*, 1977, **39**, 263.
18 C. L. Cheng, I. G. John, G. L. D. Ritchie, P. H. Gore, and L. Farnell, *J. Chem. Soc., Perkin Trans. 2*, 1975, 604.
19 L. Kaper and Th. De Boer, *Spectrochim. Acta, Part A*, 1970, **26**, 2161.
20 W. F. Hoffman, O. W. Woltersdorf, Jr., F. C. Novello, E. J. Cragoe, Jr., J. P. Springer, L. S. Watson, and G. M. Fanelli, Jr., *J. Med. Chem.*, 1981, **24**, 865.
21 Part 7, R. Benassi, U. Folli, D. Iarossi, A. Musatti, M. Nardelli, L. Schenetti, and F. Taddei, *J. Chem. Soc., Perkin Trans. 2*, in press.

22 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. L. Eliel, Wiley (Interscience), New York, 1976, vol. 9, p. 111; F. Inagaki and T. Mijazawa, in 'Progress in NMR Spectroscopy,' eds., J. W. Emsley, J. Feeney, and L. H. Sutcliffe, Pergamon Press, Oxford, 1982, vol. 14, p. 67; R. J. Abraham, *Anal. Proc.* (*London*), 1981, **18**, 364.

23 K. S. Dhami and J. B. Stothers, *Can. J. Chem.*, 1965, **43**, 479.

24 A. Di Rienzo, A. Domenicano, G. Portalone, and A. Vaciago, *Proc. Yugosl. Cent. Crystallogr.*, Suppl. to vol. 11, 1976, **A102**—**A104**; P. Domiano, M. Nardelli, A. Balsamo, B. Macchia, and F. Macchia, *Acta Crystallogr., Sect. B*, 1979, **35**, 1363.

25 G. W. Buchanan, G. Montaudo, and P. Finocchiaro, *Can. J. Chem.*, 1973, **51**, 1053 and references cited therein.

26 B. Roques, S. Combrisson, C. Riche, and C. Pascard-Billy, *Tetrahedron*, 1970, **26**, 3555.

27 B. Roques and M. C. Fournié-Zaluski, *Org. Magn. Reson.*, 1971, **3**, 305.

28 H. J. Sheurman and H. Schenk, *Recl. Trav. Chim. Pays-Bas*, 1970, **89**, 392.

29 C. Cohen-Addad, M. S. Lehmann, P. Becker, L. Parkanyi, and A. Kalman, *J. Chem. Soc., Perkin Trans. 2*, 1984, 191.

30 R. Taylor and O. Kennard, *J. Am. Chem. Soc.*, 1982, **104**, 5063; Z. Berkovitch-Yellin and L. Leiserowitz, *Acta Crystallogr., Sect. B*, 1984, **40**, 159.

31 A. Gavezzotti, *J. Am. Chem. Soc.*, 1983, **105**, 5220; *ibid.*, 1985, **107**, 962.

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

33 R. J. Abraham, D. J. Chadwick, and F. Sancassan, *Tetrahedron*, 1982, **38**, 3245.

34 R. J. Abraham, M. J. Bovill, D. J. Chadwick, L. Griffiths, and F. Sancassan, *Tetrahedron*, 1980, **36**, 279.

35 T. J. Batterham, 'NMR of Simple Heterocycles,' John Wiley and Sons, New York, 1973; E. Breitmaier, G. Haas, and W. Voelter, 'Atlas of Carbon-13 NMR Spectra,' Heyden and Son Ltd., London, 1979; K. D. Bartle, D. W. Jones, and R. S. Mathews, *Tetrahedron*, 1971, **27**, 5177; M. Platzer, Jr., J. Basselier, and P. Demerseman, *Bull. Soc. Chim. Fr.*, 1974, 905.

36 H. M. McConnell, *J. Chem. Phys.*, 1963, **38**, 2803; J. I. Musher, *ibid.*, 1962, **37**, 34; A. D. Buckingham, *Can. J. Chem.*, 1960, **38**, 300; V. M. S. Gil and J. N. Murrell, *Trans. Faraday Soc.*, 1964, **60**, 248; J. Niwa, *Bull. Chem. Soc. Jpn.*, 1977, **50**, 979.

37 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, USA.

38 Part 6, R. Benassi, U. Folli, L. Schenetti, and F. Taddei, *J. Chem. Soc., Perkin Trans. 2*, in press.

39 L. Lunazzi and A. Veracini, *J. Chem. Soc., Perkin Trans. 2*, 1973, 1739.

40 J. Seita, J. Sandström, and T. Drakenberg, *Org. Magn. Reson.*, 1978, **11**, 239; Part 2, R. Benassi, U. Folli, D. Iarossi, L. Schenetti, and F. Taddei, *J. Chem. Soc., Perkin Trans. 2*, 1981, 228.

41 D. R. Arnold and R. J. Birtwell, *J. Am. Chem. Soc.*, 1973, **95**, 4599.

42 R. Royer, P. Demerseman, J. P. Lechartier, and A. Cheutin, *J. Org. Chem.*, 1962, **27**, 3808.

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

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

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

46 A. I. Kitaigorodski, 'Organic Chemical Crystallography,' Consultants Bureau: New York, 1961; 'Molecular Crystals and Molecules,' Academic Press, New York, 1973.

47 V. Schomaker and K. N. Trueblood, *Acta Crystallogr., Sect. B*, 1968, **24**, 63.

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

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

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

51 K. N. Trueblood, THMV, University of California, Los Angeles (USA), 1984.

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

53 W. D. S. Motherwell and W. Clegg, PLUTO, University of Cambridge, 1976.

Received 20*th November* 1986; *Paper* 6/2236