

Conformational Analysis of Organic Carbonyl Compounds. Part 7.† Conformational Properties of Aroyl Derivatives of Furan and Benzo[*b*]furan 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 Diffraattometrica del CNR, Viale delle Scienze, 43100 Parma, Italy

Mario Nardelli

Istituto di Chimica Generale ed Inorganica, Università; Centro di Studio per la Strutturistica Diffraattometrica del CNR, Viale delle Scienze, 43100 Parma, Italy

The conformational properties of 2- and 3-*p*-anisoyl derivatives of furan, compounds (**1b**) and (**2b**), and of benzo[*b*]furan, compounds (**3**) and (**4**), were studied in the solid state and in solution. X-Ray analysis was performed and the crystal data are: (**1b**) space group $P2_12_12_1$, $a = 11.001(3)$, $b = 22.266(5)$, $c = 4.034(1)$ Å, $Z = 4$, $R = 0.0387$ for 1 504 observed reflections; (**2b**) space group $P2_12_12_1$, $a = 24.526(3)$, $b = 10.094(1)$, $c = 4.058(1)$ Å, $Z = 4$, $R = 0.0478$ for 1 393 observed reflections; (**3**) space group $P\bar{1}$, $a = 11.236(4)$, $b = 9.110(3)$, $c = 6.302(2)$ Å, $\alpha = 76.59(2)$, $\beta = 100.52(2)$, $\gamma = 88.89(1)^\circ$, $Z = 2$, $R = 0.0426$ for 1 679 observed reflections; (**4**) space group $P2_1$, $a = 12.588(2)$, $b = 10.141(2)$, $c = 4.885(1)$ Å, $\beta = 95.83(2)^\circ$, $Z = 2$, $R = 0.0433$ for 1 097 observed reflections. In all the molecules examined the rings are distorted with respect to the carbonyl plane; the angle of twist in the 2-substituted compounds is higher for the *p*-anisoyl than for the heterocyclic ring while an almost equal degree of twist is observed in those 3-substituted. The orientation of the carbonyl and heterocyclic oxygens is of the O,O-*trans* type except in derivative (**3**), where packing forces provide a probable explanation for the adoption of the more polar O,O-*cis* conformation. The conformational properties in solution were studied with the n.m.r. lanthanide-induced shifts (LIS) method (^1H and ^{13}C nuclei were employed). In compounds (**1b**) and (**3**) a chelate complex is formed with the lanthanide atom and conformational information is thus not representative of these molecules; nevertheless the n.m.r. chemical shifts indicate that a situation close to that of the corresponding aldehydes, with an equilibrium between the O,O-*cis* and O,O-*trans* forms, should be present. For compounds (**2b**) and (**4**) the O,O-*trans* form is the preferred and the exclusive conformation in solution, while the rings are distorted from the carbonyl plane. MO *ab-initio* calculations in the minimal STO-3G basis set were also performed on the 2- and 3-benzoyl derivatives of furan, chosen as model compounds, and the conformations of minimum energy were located on the potential energy surface. The structural characteristics of these conformations were compared with those derived experimentally for compounds (**1b**) and (**2b**).

In the absence of steric effects, formyl and acetyl derivatives of five-membered heterocycles, in particular of furan and thiophene, assume planar ground-state conformations.¹⁻³ In the case of 2-substituted derivatives the orientation of the carbonyl group was almost exclusively of the S,O-*cis* type and biased conformational equilibria were found in solutions of different polarity for thiophene¹⁻³ and benzo[*b*]thiophene⁴ derivatives. For furan¹⁻³ and benzo[*b*]furan⁵ the less polar O,O-*trans* is the more stable conformation in the vapour phase and in non-polar solvents, while increasing amounts of the O,O-*cis* form appear in more polar media.

The benzoyl derivatives of furan and thiophene adopt¹ ground-state conformations where one or both rings are twisted with respect to the carbonyl plane for steric reasons. The orientation of the carbonyl group, examined mostly in solution for these compounds, is of the type found in the corresponding formyl and acetyl derivatives, and as reported in the literature for benzoylfurans⁶⁻¹⁰ and benzoylthiophenes.^{7,11-15} This general trend has been confirmed recently in a more quantitative context for benzo[*b*]furan and benzo[*b*]thiophene derivatives.¹⁶ The degree of twist of the rings with respect to the carbonyl plane in these derivatives should be regulated by the

extent of π -conjugation,¹⁷⁻¹⁹ and, in this respect, it is widely accepted^{8,20,21} that five-membered heterocycles are more efficient than the phenyl ring and approximately⁸ in the order: 2-furyl > 3-furyl \approx phenyl. In 2-benzoylfuran the angle of twist of the furyl ring is assumed to be near to zero, but in any case smaller than that of the phenyl ring, as shown by measurements taken for dipole moments,^{6,7,9} n.m.r.,⁸ and i.r. spectroscopy;²² a more quantitative estimate of the relative twist of the furyl and phenyl rings in this molecule has still to be reported, in view of possible variable behaviour of the molecular conformation and equilibrium in different physical conditions.

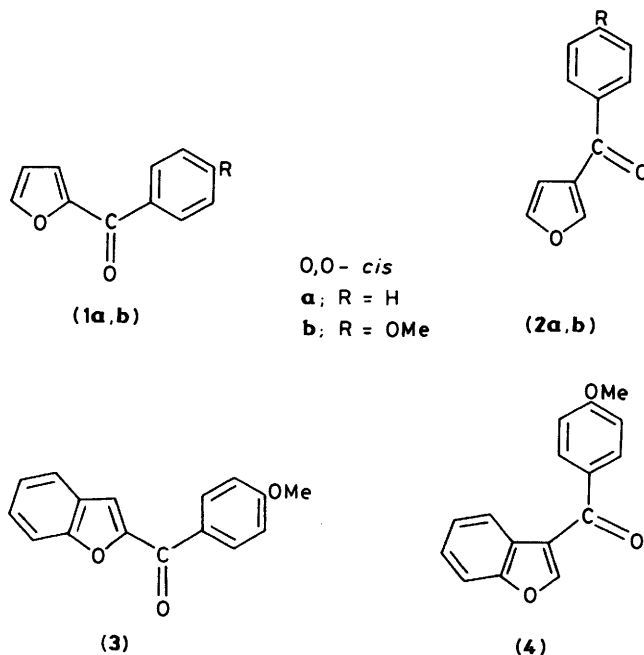
For 3-benzoylfuran n.m.r.^{8,10} and i.r.²² spectra were interpreted by assuming coplanarity of the furyl ring and carbonyl group and a significant degree of twist resulted for the phenyl ring, yet a close degree of twist for the two rings was in better agreement with the measurements taken from dipole moments.⁹

In the present paper we report an experimental study of the solid-state structure and of the conformational properties in solution of 2- and 3-aryoyl derivatives of furan and benzo[*b*]furan. The structural, energetic, and electronic properties of furan derivatives have also to be examined with a theoretical MO *ab-initio* approach, in a minimal AO basis set, in order to test the behaviour of these molecules in the absence of external perturbing factors.

† Part 6, ref. 38.

Results

The experimental study of the conformational properties of derivatives (1)–(4) was carried out by *X*-ray analysis in the solid state and by the ^1H and ^{13}C n.m.r. lanthanide-induced shifts (LIS) method²³ in solution. The compounds chosen for these measurements possess $\text{R} = \text{OMe}$, (1b), (2b), (3), and (4), which give simpler ^1H n.m.r. spectra for the phenyl ring multiplets, while *ab-initio* theoretical calculations were performed on compounds (1a) and (2a) in order to limit the molecular size as much as possible. The conformational properties of these compounds, in particular the relative orientation of the rings with respect to the carbonyl plane, should not be significantly influenced by the *para*-substituent in the phenyl ring, on account of results found in *para*-substituted acetophenones.²⁴



X-Ray Analysis.—The geometrical parameters, bond distances, and bond angles obtained from *X*-ray analysis of derivatives (1b), (2b), (3), and (4) are reported in Table 1 and the ORTEP drawings of the molecules are represented in Figure 1.

A number of structural features, beside those more pertinent to the relative orientation of the carbonyl bond with respect to the rings in these compounds, are present and are related to the conformational behaviour of these molecules. In all the compounds, except derivative (2b), the methyl group of the OMe substituent is *s-trans* oriented with respect to the carbonyl oxygen. Packing conditions involving contacts between the methyl hydrogens and the atoms of neighbour molecules may account for this difference in behaviour. The methyl carbon atom lies nearly in the plane of the phenyl ring, as occurs in anisole derivatives,²⁵ and a certain degree of π -conjugation between the methoxy group and the ring should be present: the fact that the $\text{C}_{ortho}\text{--C}_{meta}$ bond distance is shorter than the other C–C bond distances in the phenyl ring is probably also a consequence of this property. The methyl group is staggered with respect to the *ortho*-hydrogen directed toward the OMe substituent. The carbon atom of the carbonyl group shows substantial trigonal nature with bond angles near 120° , except in compound (1b) where the $\text{C}(2)\text{--C}(6)\text{--C}(8)$ angle is larger and that of $\text{C}(2)\text{--C}(6)\text{--O}(7)$ smaller than the corresponding angles in the other molecules examined: this behaviour seems related

to the interaction $\text{C}(13)\text{--H}(13)\cdots\text{O}(1)$, which is exclusive to this compound. The two exocyclic angles with the C–C(O) bond relative to the heterocyclic ring differ markedly in compounds (1b) and (3); they also appear to depend on the relative orientation of the carbonyl and furyl oxygen atoms. The geometry of the furan ring is only slightly influenced by the location of the carbonyl group, while the $\text{C}(4)\text{--C}(5)$ bond is significantly longer in the benzo-condensed derivatives [$\text{C}(4a)\text{--C}(7a)$]. The exocyclic C–C(O) bonds, which have a bond distance close to that of a pure single $\text{C}(sp^2)\text{--C}(sp^2)$ bond (1.487 Å), become longer as the twist of the relative ring increases, with a roughly linear trend.

The rings are twisted with respect to the carbonyl plane and the torsional angle is higher for the phenyl ring, yet this difference appears more evident in the case of benzo[*b*]furan derivatives (3) and (4). Rotation of the rings is in the conrotatory sense in all compounds as occurs in benzophenones.²⁶ The tendency to reach the coplanar orientation of the rings with the carbonyl group in order to have the highest degree of π -conjugation thus appears hindered by steric effects even in the solid state of these molecules. According to the accepted higher conjugative ability of the 2-furyl than the 3-furyl ring a higher coplanarity with the carbonyl bond is expected for the former derivative, but this trend is approximately verified only for derivatives (1b) and (2b).

An inspection of the non-bonded distances reported in Figure 2 shows the presence of attractive and repulsive interactions which are probably the origin of the solid-state conformation of these molecules. In compound (1b) two interactions of attractive origin,²⁷ namely $\text{C}(13)\text{--H}(13)\cdots\text{O}(1)$ [2.36(2) Å] and $\text{C}(9)\text{--H}(9)\cdots\text{O}(7)$ [2.52(2) Å] [angles $\text{C}(13)\text{--H}(13)\cdots\text{O}(1)$ $114(2)^\circ$ and $\text{C}(9)\text{--H}(9)\cdots\text{O}(7)$ $97(1)^\circ$ respectively], stabilize the molecule in the O,O-*trans* orientation, while in derivative (2b) only one such interaction, $\text{C}(9)\text{--H}(9)\cdots\text{O}(7)$ [2.56(3) Å] [angle $\text{C}(9)\text{--H}(9)\cdots\text{O}(7)$ $94(2)^\circ$], is present. In this molecule the atom O(1) is far from the hydrogen atoms of the phenyl ring for attractive interactions and it also seems that intermolecular interactions with oxygen atoms of the surrounding molecules can be excluded, since the shortest contact, with H(4) at $1 - x, y - \frac{1}{2}, \frac{1}{2} - z$, as appears in the molecular packing reported in Figure 2, is of 2.76(5) Å and thus higher than the sum of van der Waals radii (2.60 Å). The distance $\text{H}(2)\cdots\text{H}(13)$ in derivative (2b) is larger than that involved in a van der Waals interaction between hydrogen atoms (2.40 Å). Compounds (2b) and (4) show similar trends, in the latter derivative two interactions of attractive origin are revealed, $\text{C}(11)\text{--H}(11)\cdots\text{O}(9)$ [2.61(4) Å] and $\text{C}(4)\text{--H}(4)\cdots\text{O}(9)$ [2.63(4) Å].

Derivative (3) shows an orientation for the C=O bond opposite to that found in (1b): an interaction of repulsive origin seems to be present, since the $\text{O}(1)\cdots\text{O}(9)$ distance [2.708(2) Å] is lower than the sum of the van der Waals radii (2.80 Å). A contact of an attractive type, $\text{C}(11)\text{--H}(11)\cdots\text{O}(9)$ [2.51(2) Å], as found in compound (1b), is also present. It is known that the more polar O,O-*cis* form of furan-2-carbaldehyde is stable in polar solutions²⁸ and that the solid-state structure of 4-bromofuran-2-carbaldehyde²⁹ corresponds to the O,O-*cis* orientation. Nevertheless compounds (1b), (2b) and (4) adopt the O,O-*trans* conformation in the solid state in agreement with the presence of intramolecular C–H \cdots O attractive interactions; these are also the more stable forms in solution, if one excludes the behaviour expected for (1b) in polar solvents. For compound (3) where repulsive interactions between H \cdots H and O \cdots O atoms are present, the more polar O,O-*cis* conformation exists in the solid state. Probably, packing forces and electric fields characteristic of the crystal are sufficiently strong to reverse the relative orientation of the carbonyl bond in compounds (1b) and (3), in spite of the relatively low-energy difference between the ground states of 2-carbonyl derivatives

Table 1. Comparison of bond distances (Å), angles (°), and selected torsions (°) in compounds (**1b**), (**2b**), (**3**), and (**4**)

Compound	(1b)	(2b)	(3)	(4)
(a) Bond distances				
C(6)–O(7)	1.234(2)	1.223(3)	C(8)–O(9)	1.232(3)
C(2)–C(6)	1.477(3)		C(2)–C(8)	1.461(3)
C(3)–C(6)		1.482(3)	C(3)–C(8)	
C(6)–C(8)	1.459(3)	1.480(3)	C(8)–C(10)	1.472(3)
C(8)–C(13)	1.399(3)	1.392(3)	C(10)–C(15)	1.387(3)
C(8)–C(9)	1.405(3)	1.393(3)	C(10)–C(11)	1.399(3)
C(12)–C(13)	1.378(3)	1.372(3)	C(14)–C(15)	1.377(3)
C(9)–C(10)	1.365(4)	1.381(3)	C(11)–C(12)	1.362(4)
C(11)–C(12)	1.389(3)	1.390(3)	C(13)–C(14)	1.390(3)
C(10)–C(11)	1.391(3)	1.387(3)	C(12)–C(13)	1.392(3)
C(11)–O(14)	1.364(3)	1.360(3)	C(13)–O(16)	1.350(3)
O(14)–C(15)	1.433(4)	1.433(4)	O(16)–C(17)	1.408(4)
O(1)–C(2)	1.373(2)	1.343(3)	O(1)–C(2)	1.380(3)
O(1)–C(5)	1.364(3)	1.366(4)	O(1)–C(7a)	1.374(2)
C(2)–C(3)	1.342(3)	1.345(4)	C(2)–C(3)	1.345(3)
C(4)–C(5)	1.330(4)	1.322(4)	C(4a)–C(7a)	1.388(4)
C(3)–C(4)	1.419(4)	1.419(4)	C(3)–C(4a)	1.423(3)
			C(4a)–C(4)	1.400(3)
			C(7a)–C(7)	1.375(3)
			C(4)–C(5)	1.390(4)
			C(6)–C(7)	1.367(4)
			C(5)–C(6)	1.384(5)
				1.361(3)
				1.422(5)
				1.362(4)
				1.369(3)
				1.357(4)
				1.384(5)
				1.448(3)
				1.388(4)
				1.393(4)
				1.380(4)
				1.367(5)
				1.394(6)
(b) Bond angles				
C(2)–C(6)–O(7)	115.7(2)		C(2)–C(8)–O(9)	119.9(2)
C(3)–C(6)–O(7)		120.0(2)	C(3)–C(8)–O(9)	
C(8)–C(6)–O(7)	121.9(2)	120.4(2)	C(10)–C(8)–O(9)	120.9(2)
C(2)–C(6)–C(8)	122.4(2)		C(2)–C(8)–C(10)	119.2(2)
C(3)–C(6)–C(8)		119.6(2)	C(3)–C(8)–C(10)	
C(6)–C(2)–O(1)	120.0(2)		C(8)–C(2)–O(1)	116.3(2)
C(2)–C(3)–C(6)		127.7(2)	C(2)–C(3)–C(8)	
C(3)–C(2)–C(6)	130.1(2)		C(3)–C(2)–C(8)	132.8(2)
C(4)–C(3)–C(6)		126.5(2)	C(4a)–C(3)–C(8)	
C(6)–C(8)–C(13)	123.8(2)	122.9(2)	C(8)–C(10)–C(15)	123.7(2)
C(6)–C(8)–C(9)	118.6(2)	119.3(2)	C(8)–C(10)–C(11)	118.4(2)
C(9)–C(8)–C(13)	117.6(2)	117.8(2)	C(11)–C(10)–C(15)	117.9(2)
C(8)–C(13)–C(12)	121.4(2)	120.8(2)	C(10)–C(15)–C(14)	121.5(2)
C(8)–C(9)–C(10)	121.5(2)	122.2(2)	C(10)–C(11)–C(12)	121.1(2)
C(11)–C(12)–C(13)	119.6(2)	120.6(2)	C(13)–C(14)–C(15)	119.9(2)
C(9)–C(10)–C(11)	120.0(2)	118.9(2)	C(11)–C(12)–C(13)	120.6(2)
C(10)–C(11)–C(12)	120.0(2)	119.7(2)	C(12)–C(13)–C(14)	119.1(2)
C(12)–C(11)–O(14)	124.4(2)	115.1(2)	C(14)–C(13)–O(16)	125.3(2)
C(10)–C(11)–O(14)	115.7(2)	125.2(2)	C(12)–C(13)–O(16)	115.6(2)
C(11)–O(14)–C(15)	117.7(2)	117.9(2)	C(13)–O(16)–C(17)	118.4(2)
C(2)–O(1)–C(5)	105.6(2)	106.2(2)	C(2)–O(1)–C(7a)	105.9(2)
O(1)–C(2)–C(3)	109.8(2)	110.8(2)	O(1)–C(2)–C(3)	110.8(2)
C(2)–C(3)–C(4)	107.1(2)	105.6(2)	C(2)–C(3)–C(4a)	107.6(2)
C(3)–C(4)–C(5)	106.0(2)	107.0(2)	C(3)–C(4a)–C(7a)	105.3(2)
C(4)–C(5)–O(1)	111.4(2)	110.3(3)	C(4a)–C(7a)–O(1)	110.3(2)
			C(3)–C(4a)–C(4)	135.5(2)
			O(1)–C(7a)–C(7)	125.7(2)
			C(4)–C(4a)–C(7a)	119.2(2)
			C(4a)–C(7a)–C(7)	123.9(2)
			C(6)–C(7)–C(7a)	115.9(3)
			C(4a)–C(4)–C(5)	117.1(2)
			C(4)–C(5)–C(6)	121.4(3)
			C(5)–C(6)–C(7)	122.4(3)
				111.0(2)
				135.6(3)
				125.1(3)
				119.2(2)
				123.8(3)
				115.6(3)
				118.0(3)
				121.3(3)
				122.0(3)
(c) Torsion angles				
C(3)–C(2)–C(6)–O(7)	–15.7(4)		O(1)–C(2)–C(8)–O(9)	15.0(3)
C(4)–C(3)–C(6)–O(7)		–21.8(4)	C(4a)–C(3)–C(8)–O(9)	
O(1)–C(2)–C(6)–O(7)	160.6(2)		C(3)–C(2)–C(8)–O(9)	–161.6(3)
C(2)–C(3)–C(6)–O(7)		152.1(3)	C(2)–C(3)–C(8)–O(9)	
C(9)–C(8)–C(6)–O(7)	–17.2(3)	25.6(4)	C(11)–C(10)–C(8)–O(9)	29.5(3)
C(13)–C(8)–C(6)–O(7)	158.4(2)	151.4(3)	C(15)–C(10)–C(8)–O(9)	–147.9(2)
C(12)–C(11)–O(14)–C(15)	0.2(4)	–178.3(2)	C(14)–C(13)–O(16)–C(17)	–9.4(4)
C(10)–C(11)–O(14)–C(15)	179.6(2)	1.6(4)	C(12)–C(13)–O(16)–C(17)	170.3(2)

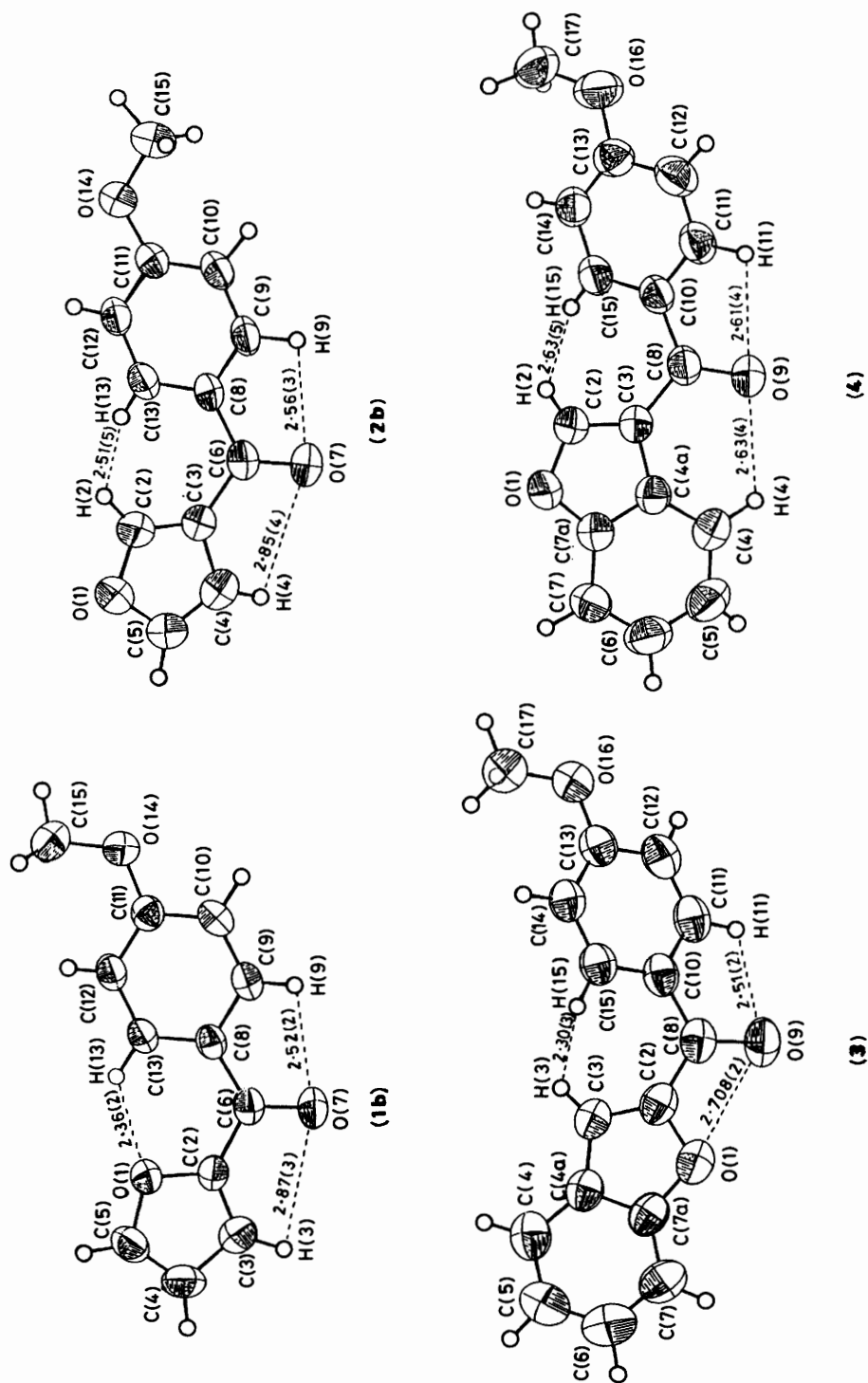


Figure 1. ORTEP drawings of the molecules of compounds (1b), (2b), (3), and (4). Ellipsoids at 50% probability level

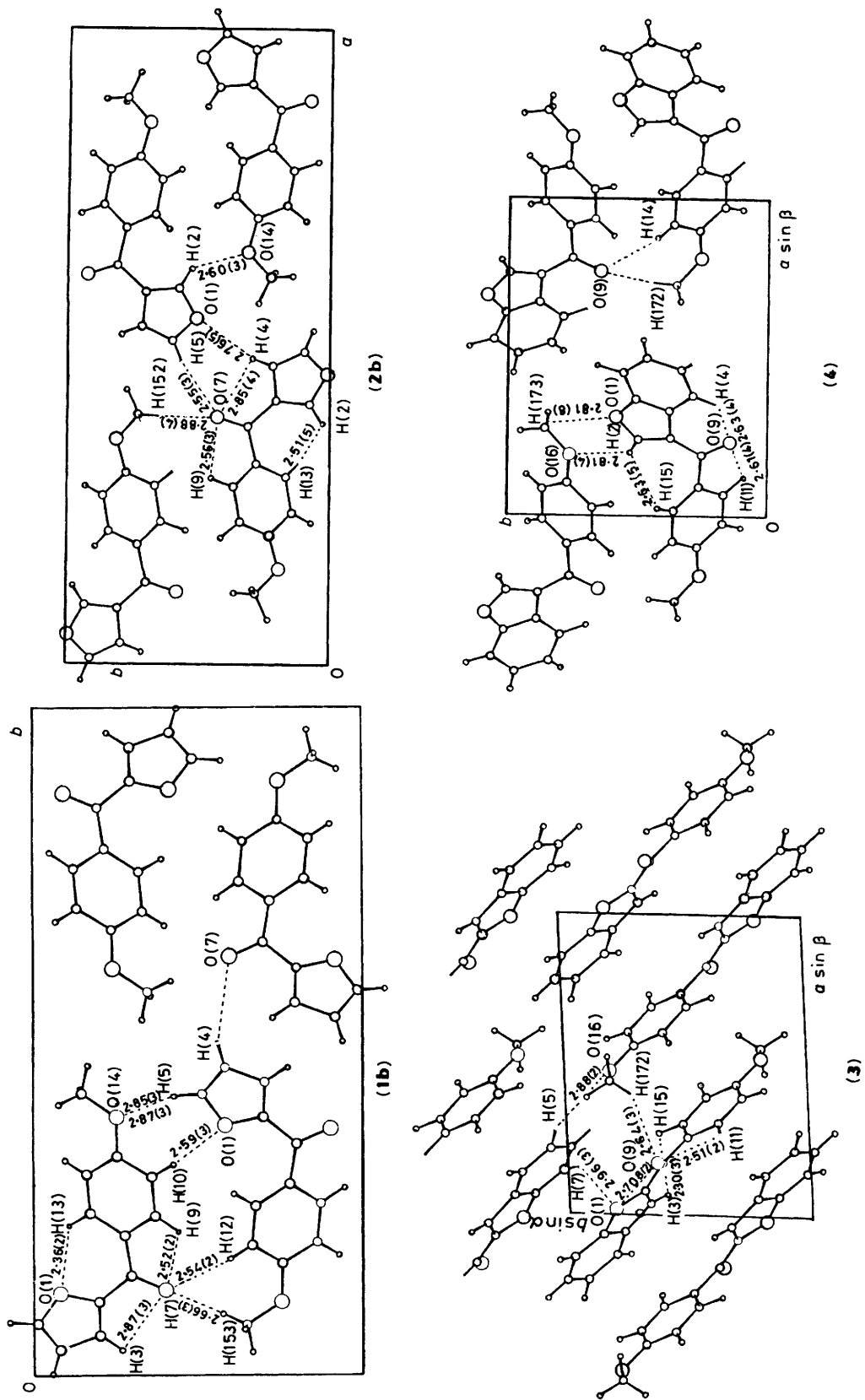


Figure 2. PLUTO drawings of the molecular packings in compounds (1b), (2b), (3), and (4)

of furan,^{28,30,31} confirmed by theoretical calculations in this paper.

Results from N.m.r. LIS Simulation.—The ¹H and ¹³C n.m.r. spectra and the conformational results from n.m.r. LIS simulation of compounds (3) and (4) have been reported previously.¹⁶

The ¹H and ¹³C chemical shifts of compounds (1b) and (2b) would seem to indicate that the conformational properties of the *p*-anisoyl group should not significantly change on going from the single-ring to condensed heterocyclic derivatives (see Tables 2 and 3). This is shown by the small differences between the chemical shifts found for 3-H, C-2, C-3 in derivatives (1b) and (3), and for 2-H, C-2, C-3 in derivatives (2b) and (4), and by the chemical shift of the carbon atom of the C=O group.³² In compounds (1b) and (3) the 3-H is shifted 0.9 p.p.m. to lower field by the aryl group, while 2-H moves to lower field by only 0.6 p.p.m. in derivatives (2b) and (4). In comparison with the corresponding low-field shifts found for formyl and acetyl derivatives^{5,33} of these heterocycles, these results suggest a preferred *O,O*-*trans* orientation of the carbonyl group in the 3-substituted compounds and an equilibrium mixture of the two forms in the 2-substituted derivatives in chloroform solution. Calculations of the contribution to the screening constant from the magnetic and electric dipoles of the C=O group with an approximate formalism³⁴ indicates, from the contribution to the screening of 2-H in derivative (2b) and of 2-H and 4-H in derivative (4), that the orientation of the carbonyl group should be of the *O,O*-*trans* type, with a distortion of the carbonyl group which may be restricted within 0–30°. As regards 3-H in

derivatives (1b) and (3), it is difficult to distinguish between a mixture of the two planar conformers in equivalent quantities and a conformation of the *O,O*-*cis* type with an angle of twist of 30–40° between the planes of the heterocycle and the carbonyl bond.

The procedure adopted in order to obtain conformational results on these molecules by employing the LIS method is that described in previous Parts.¹⁶ The molecular geometries employed are those derived experimentally, although minor changes are found for the final conformational results when standard geometries for the ring are adopted. Simultaneous use of ¹H and ¹³C chemical shifts was made, by measuring the LIS values ΔM , reported in Tables 2 and 3, in the presence of Yb(fod)₃ and by removing the ¹³C diamagnetic complexation shift³⁵ by use of La(fod)₃. The LIRAS-3 computer program³⁵ was employed in the 'four-site' axially symmetric complexation model for processing the experimental LIS values. The conformational results obtained are in Table 4, and the symbolism is the same as appears in previous works.^{16,35,36}

For the 2-*p*-anisoyl derivative (1b), the conformational result refers to a chelate complex with the lanthanide atom bonded to the heterocyclic and carbonyl oxygens and, very likely, does not correspond to the conformational situation of this molecule in the absence of complexing agents. The same behaviour has been previously found¹⁶ for derivative (3). For compound (2b) the lowest R_{cryst} (which indicates the best agreement between calculated and experimental LIS values) was found for a mixture of two non-planar conformations of *O,O*-*cis* and *O,O*-*trans* type (angle of twist of the heterocyclic and phenyl ring with respect to the carbonyl plane near to 30°), with the latter form more abundant (70–80%). In compound (4) the amount of the *O,O*-*trans* form, with a distortion comparable to that found in compound (2b), was¹⁶ nearly 100%.

Results from Theoretical Calculations.—MO *ab-initio* calculations were performed on derivatives (1a) and (2a) with the Gaussian-80 and Gaussian-82 computer programs.³⁷ The basis set employed was the minimal STO-3G and molecular size prevented further basis set implementation.

The approach was firstly applied to the benzophenone mole-

Table 2. ¹H N.m.r. chemical shifts (δ values) in compounds (1b) and (2b) recorded in [²H]chloroform solution. The ΔM are the LIS values and refer to Yb(fod)₃

Compound		2-H	3-H	4-H	5-H	9-H	10-H	OMe
(1b)	δ	7.20	6.55	7.65	8.01	6.95	3.86	
	ΔM		22.15	6.86	10.30	27.50	6.45	2.62 ^a
(2b)	δ	7.89	6.86	7.45	7.87	6.95	3.86	
	ΔM	18.74		20.01	4.89	29.70	6.33	2.37 ^a

^a Not employed in LIS simulation.

Table 3. ¹³C Chemical shifts (δ values) in compounds (1b) and (2b) recorded in [²H]chloroform solution, LIS values ΔM due to Yb(fod)₃, and corrected ($\Delta M - \Delta D$) for the complexation shift^{9,11} in the presence of La(fod)₃

Compound		C-2	C-3	C-4	C-5	C-8	C-9	C-10	C-11	C=O
(1b)	δ	152.82	119.50	112.04	146.45	129.95	131.74	113.76	163.37	181.07
	ΔM	66.48	35.80	16.37	23.59	45.59	28.35	11.93	10.67	113.36
	($\Delta M - \Delta D$)	67.34	30.19	15.33	20.87	48.57	26.14	11.93	9.07	111.77
(2b)	δ	147.66	126.63	110.47	143.72	131.56	131.21	113.84	163.31	187.97
	ΔM	28.26	53.43	27.21	11.79	50.59	30.39	12.10	10.89	116.10
	($\Delta M - \Delta D$)	23.92	54.67	26.39	11.79	53.47	27.64	12.10	8.95	111.05

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

Compound	R_{cryst}	Sum-dif. (p.p.m.)	R (Å)	ϕ	ψ	f	Population <i>endo</i>	Conformational angles (°) ^b		%
								θ	γ	
(1b)	0.030 ^c	1.22	<i>c</i>	<i>c</i>	<i>c</i>	<i>c</i>	<i>c</i>	0	0	100
(2b)	0.029	1.15	2.85	65	155	3 520	60	150	30	70–80
								30	30	20–30
(3) ^d	0.032 ^c	1.23	<i>c</i>	<i>c</i>	<i>c</i>	<i>c</i>	<i>c</i>	0	0	100
(4) ^d	0.031	1.17	3.00	50	160	3 714	25	150	28	100

^a For the symbols see refs. 35 and 36. ^b The torsional angles are defined in Figure 3: estimated error $\pm 10^\circ$. ^c Chelate structure with the lanthanide atom bonded to the carbonyl and furyl oxygens: R , ϕ , ψ , and population *endo* refer to a 'dummy' oxygen atom.¹⁶ ^d Results from ref. 16.

Table 5. Structural parameters,^a bond lengths, and bond angles of the optimized conformations in the MO *ab-initio* calculations applied to compounds (1a), (2a), and to benzophenone

(1a)			(2a)			Benzophenone ^b	
	O,O- <i>cis</i>	O,O- <i>trans</i>		O,O- <i>cis</i>	O,O- <i>trans</i>		
C=O	1.226	1.227	C=O	1.226	1.226	C=O	1.225
C(6)-C(8)	1.525	1.525	C(6)-C(8)	1.527	1.528	C(6)-C(8)	1.527
C(2)-C(6)	1.514	1.514	C(3)-C(6)	1.515	1.514	C(8)-C(9)	1.392
O(7)-C(6)-C(8)	121.25	120.94	O(7)-C(6)-C(8)	120.65	120.56	C(9)-C(10)	1.385
C(6)-C(8)-C(9)	122.47	117.76	C(6)-C(8)-C(9)	118.58	118.44	C(10)-C(11)	1.387
O(7)-C(6)-C(2)	120.63	119.26	O(7)-C(6)-C(3)	120.77	120.57	C(9)-H(9)	1.083
O(1)-C(2)-C(6)	115.91	120.25	C(2)-C(3)-C(6)	124.81	128.83	C(10)-H(10)	1.083
						C(11)-H(11)	1.083
						O(7)-C(6)-C(8)	120.46
						C(6)-C(8)-C(9)	118.61
						C(8)-C(9)-C(10)	120.45
						C(9)-C(10)-C(11)	120.03
						C(10)-C(11)-C(10')	119.90
						C(8)-C(9)-H(9)	119.54
						C(9)-C(10)-H(10)	119.90
						C(10)-C(11)-H(11)	120.05

^a Differences in the structural parameters in the enantiomers (see text) of the molecules (1a) and (2a) range within 0.0002 Å for the bond lengths and 0.02° for bond angles. ^b Angle of twist of the phenyl ring with respect to the C=O plane $\pm 33.05^\circ$.

cule, and full geometry optimization was performed including the torsional angles of the phenyl rings with respect to the carbonyl plane. This angle turned out to be $\pm 33^\circ$ and the rings were twisted in the conrotatory sense, in satisfactory agreement with experimental observations.²⁶ The optimized geometry of benzophenone is reported in Table 5; the structural parameters obtained for the phenyl ring in this molecule were transferred in the calculations relative to compounds (1a) and (2a) and kept constant. The geometry of the furyl ring was derived from that of furan-2-carbaldehyde fully optimized³⁸ in the STO-3G approach (STO-3G//STO-3G) and also kept constant.

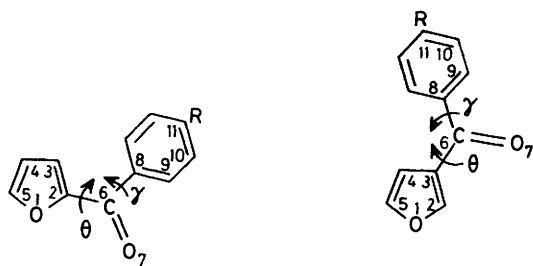


Figure 3. Definition of the angles of rotation θ and γ of the two rings around the exocyclic C-C(O) bonds in derivatives (1) and (2); the all-planar situation depicted corresponds to $\theta = \gamma = 0^\circ$

The procedure of deriving the energy surface by employing energy values obtained from geometrical relaxation turned out to be extremely time-consuming even on a fast computer like the CRAY-X-MP12, so we followed a different method. A portion of the energy-map relative to compound (2a) was obtained for $0^\circ \leq \theta \leq 180^\circ$ and $0^\circ \leq \gamma \leq 90^\circ$ (by varying the torsional angles θ and γ defined in Figure 3 in 30° steps) either by optimizing the geometrical parameters at each point, or without geometry optimization. The two energy maps, interpolated with the GPC program,³⁹ are shown in Figure 4. Comparison of the corresponding portions shows that, even though the energy values differ (they are about eight times smaller when geometry relaxation is allowed) the trends are quite similar and the

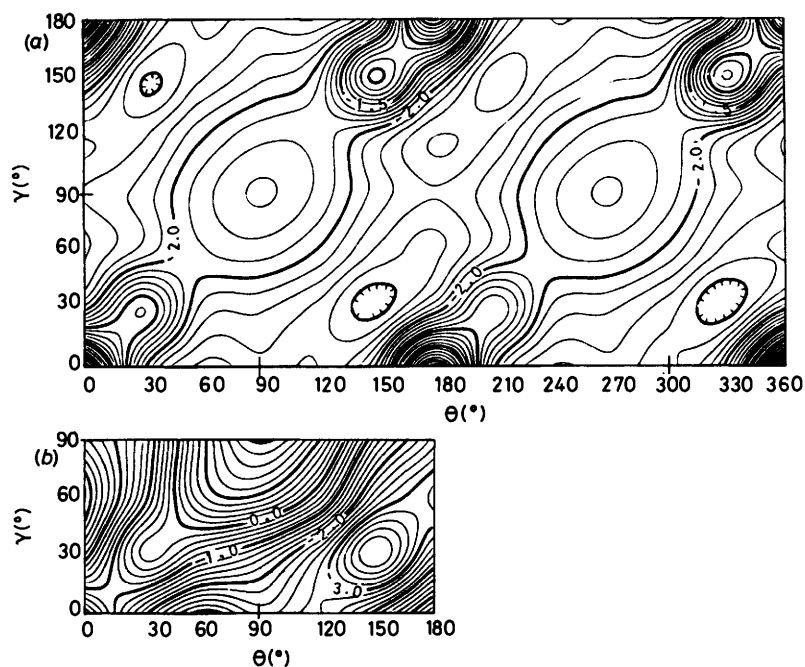
maxima and minima occur at close values of θ and γ . On the basis of this result we calculated the full energy surface by employing STO-3G energy points in the intervals $0^\circ \leq \theta \leq 360^\circ$ and $0^\circ \leq \gamma \leq 180^\circ$; optimization of the geometrical parameters (only those listed in Table 6, which include torsional angles) was performed in the regions of energy minimum. Four of these regions were located for each compound and, as the procedure above reported, four conformers are distinguished, corresponding to two pairs of enantiomers. The geometrical characteristics, the relative energy content, and dipole moments of these conformers are given in Table 6.

The preferred conformations of compounds (1a) and (2a) are not fully planar, and a certain degree of twist with respect to the carbonyl plane is found for both rings. For derivative (1a) it is observed that in both conformers, of O,O-*cis* and O,O-*trans* type, the phenyl ring is more twisted than the furyl ring, and the angle of twist of the phenyl ring is comparable with that found in benzophenones.²⁶ Comparison between derivatives (1a) and (2a) shows that the twist of the 3-furyl ring is more pronounced than that of the 2-furyl ring: these results are in agreement with the widely accepted^{20,21} conjugative properties of the 2-furyl, 3-furyl, and phenyl rings. In derivative (1a) the O,O-*trans* orientation turns out to be more stable than the O,O-*cis* type, as occurs for the corresponding planar conformations of 2-formyl and 2-acetyl derivatives in the vapour phase¹ and according to *ab initio* STO-3G calculations.^{30,31,40} For compound (2a) the O,O-*cis* form is predicted to be slightly more stable and this same result is obtained,^{31,40} by calculation, in agreement with results for 3-formyl- and 3-acetyl-furan, but in contrast with their experimental behaviour.¹ In an attempt to clarify this point we have determined⁴¹ the energy content of the two planar conformers of furan-3-carbaldehyde in more extended basis sets (3-21G and 6-31G) and their relative stability is effectively reversed with respect to the STO-3G approach. Further, we have observed⁴¹ that basis set implementation does not appreciably modify the molecular geometry, if one excludes the exocyclic C-C(O) bond, which is shorter (1.45 Å) in the expanded basis set with respect to the contracted STO-3G (1.50 Å), as we also observed³⁸ in the case of furan-2-carbaldehyde. This behaviour probably characterizes compound (2a) as well, but, unfortunately, this molecule cannot be tackled with larger basis sets owing to the large molecular size.

Table 6. Torsional angles,^a relative total energy, dipole moments, and π -bond orders (η) for the C(6)–C(n)^b and C(6)–C(8) bonds^c for the conformers of compounds (**1a**) and (**2a**) from *ab-initio* STO-3G calculations

Compd.	Conformation	θ^d	γ^d	$\Delta E/\text{kJ mol}^{-1}$	μ (10^{-30} Cm)	$\eta[\text{C}(6)\text{--C}(n)]^b$	$\eta[\text{C}(6)\text{--C}(8)]$
(1a)	O,O- <i>cis</i>	+21.68 –21.73	+34.53 –34.49	5.175	8.24	0.1062	0.0826
	O,O- <i>trans</i>	+165.13 –165.16	–26.31 +26.21	0.0	5.77	0.1130	0.0927
(2a)	O,O- <i>cis</i>	+28.54 –28.55	+31.70 –31.82	0.0	6.73	0.0938	0.0860
	O,O- <i>trans</i>	–156.01 +156.00	+34.45 –34.39	0.690	5.18	0.0962	0.0825

^a Defined in Figure 3. ^b *n* refers to atom 2 in compound (**1a**) and to atom 3 in compound (**2a**). ^c The calculated π -bond orders differ in the fourth decimal in the two enantiomeric forms. ^d The entries in the two rows refer to enantiomeric forms.

**Figure 4.** Map of the total energy calculated with the *ab-initio* MO STO-3G approach: (a) without geometry optimization; (b) with optimization of the parameters relative to the carbonyl group (see Table 6). Calculations refer to compound (**2a**)

In Table 6 the calculated π -bond orders relative to the exocyclic C–C(O) bonds are also reported. In comparison with experimental bond lengths of derivatives (**1b**) and (**2b**) they show a roughly inverse proportionality; a large deviation is observed for derivatives (**1a,b**) since the experimental length of C(6)–C(8) was unexpectedly small, the shortest of the exocyclic C–C bond distances. Calculations predict a lower degree of twist of the phenyl ring in the O,O-*trans* orientation of compound (**1a**), but not as low as is found in the crystal structure of compound (**1b**). In each molecule a higher value is found for the bond joining the carbonyl group to the heterocyclic ring, and this is higher for the 2-furyl derivative than for the 3-furyl. These quantities are in line with the conjugative properties of the groups involved, as pointed out above, and resolve the degree of coplanarity of the carbonyl and ring planes on a predominantly conjugative basis.

The calculated dipole moments of the conformers of compounds (**1a**) and (**2a**) are also given in Table 6. The O,O-*cis* form is the more polar conformation for both molecules. Even

for the corresponding formyl derivatives theoretical calculations show^{30,38,41} that the O,O-*cis* form is the more polar in agreement with experimental results;^{9,28} for furan-2-carbaldehyde the STO-3G calculated values appear^{30,38} underestimated. The experimental dipole moment of compound (**1a**) amounts to 10.84 and 10.02 (10^{-30} Cm) from two different literature sources^{6,7} and for compound (**2a**) to 9.57 (10^{-30} Cm);⁹ the calculated values thus appear underestimated and, according to the empirical values assigned^{7,9} to the two conformers of each compound, *ca.* 0.6 times smaller.

Discussion

Comparison of the results obtained for derivatives (**1**)–(**4**) enables a number of conclusions regarding conformational properties of these molecules to be drawn.

For derivatives (**1b**) and (**3**) the results from the LIS method fail to provide useful information for their behaviour in solution owing to bidentate complex formation. Nevertheless, the n.m.r.

Table 7. Experimental data for the crystallographic analyses

Compound	(1b)	(2b)	(3)	(4)
Formula	C ₁₂ H ₁₀ O ₃	C ₁₂ H ₁₀ O ₃	C ₁₂ H ₁₂ O ₃	C ₁₆ H ₁₂ O ₃
<i>M</i>	202.27	202.27	252.27	252.27
Space group	P2 ₁ 2 ₁ 2 ₁	P2 ₁ 2 ₁ 2 ₁	P $\bar{1}$	P2 ₁
<i>a</i> /Å	11.001(3)	24.526(3)	11.236(4)	12.588(2)
<i>b</i> /Å	22.266(5)	10.094(1)	9.110(3)	10.141(2)
<i>c</i> /Å	4.034(1)	4.058(1)	6.302(2)	4.885(1)
α /°	90	90	76.59(2)	90
β /°	90	90	100.52(2)	95.83(2)
γ /°	90	90	88.89(1)	90
<i>U</i> /Å ³	988.1(5)	1 004.6(3)	615.6(4)	620.4(2)
<i>Z</i>	4	4	2	2
<i>D_x</i> /Mg m ⁻³	1.359	1.337	1.361	1.350
<i>V_m</i> /Å ³	175.5	175.6	219.3	218.0
<i>V_{occ}</i> /Å ³	702.2	702.3	438.6	436.0
<i>S_m</i> /Å ²	211.8	211.2	256.7	255.6
<i>V_{free}</i> /Å ³	285.9	302.3	177.0	1 884.4
<i>C_K</i>	0.711	0.699	0.712	0.703
Reflections for } number	26	30	30	29
lattice parameter } θ range/°	23–34	21–37	23–35	22–40
<i>F</i> (000)	424	424	264	264
Crystal size/mm	0.10 × 0.26 × 0.40	0.15 × 0.28 × 0.35	0.19 × 0.27 × 0.40	0.18 × 0.25 × 0.38
μ /mm ⁻¹	0.767	0.755	0.726	0.670
Extinction param. <i>g</i>	2.42(4) × 10 ⁻⁷	6.5(5) × 10 ⁻⁸	1.49(7) × 10 ⁻⁷	4.3(2) × 10 ⁻⁷
Scan speed/° min ⁻¹	3–12	3–12	3–12	3–12
Scan width/°	1.2 + $\Delta\lambda/\lambda \tan \theta$	1.2 + $\Delta\lambda/\lambda \tan \theta$	1.2 + $\Delta\lambda/\lambda \tan \theta$	1.2 + $\Delta\lambda/\lambda \tan \theta$
θ range/°	3–70	3–70	3–70	3–70
<i>h</i> range	–13/13	–28/29	–13/13	–14/15
<i>k</i> range	0/26	0/12	–10/10	0/12
<i>l</i> range	0/4	0/4	0/7	0/5
Standard reflection	3 7 0	2 4 0	$\bar{1}$ 2 3	3 2 2
Intensity variation	none	none	none	none
No. of measured reflections	2 203	2 279	1 679	1 388
Conditions for observed reflections	<i>I</i> ≥ 2σ(<i>I</i>)	<i>I</i> ≥ 3σ(<i>I</i>)	<i>I</i> ≥ 2σ(<i>I</i>)	<i>I</i> ≥ 3σ(<i>I</i>)
No. of reflections used in refinement	1 504	1 393	1 679	1 097
<i>R</i> (int)	0.009	0.056		0.029
Max. L.S. shift to error ratio	0.07	0.01	0.03	0.007
Min./Max. height in final $\Delta\rho/e \text{ \AA}^{-3}$	–0.34/0.20	–0.14/0.22	–0.02/0.02	–0.10/0.12
No. of refined parameters	176	176	220	220
<i>R</i> = $\Sigma \Delta F /\Sigma F_o $	0.0387	0.0478	0.0426	0.0433
<i>R'</i> = $[\Sigma w(\Delta F)^2/\Sigma w F_o^2]^{1/2}$	0.0451	0.0593	0.0473	0.0502
<i>S</i> = $[\Sigma w(\Delta F)^2/(N - P)]^{1/2}$ *	1.2533	0.6577	1.7319	0.7035
<i>k</i> , <i>g</i> (<i>w</i> = $k/[\sigma^2(F_o) + g F_o^2]$)	1.0, 0.0005	1.0, 0.0072	1.0, 0.0005	1.0, 0.005

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

spectra suggest, from a qualitative point of view, that compounds (1b) and (3) have close conformational properties in chloroform solution, with the forms corresponding to the two orientations of the carbonyl group (probably nearly coplanar with the heterocyclic ring) almost equally populated. In the solid state the O,O-*trans* form is adopted by compound (1b), while the O,O-*cis* form is found in compound (3). Calculations on the model compound (1a) show that the O,O-*trans* form is the more stable of the two conformations. The angles of twist of the rings differ in the solid-state structure of compounds (1b) and (3) and this can be linked to the different O,O-*cis/trans* orientation of both compounds: in each molecule, the angle of twist of the furyl ring being the smaller one. The comparison with the calculated angles of twist of the conformers of (1a) shows that an angle of twist significantly higher than that found experimentally in compound (1b) is present only for the phenyl ring in the O,O-*trans* form; it is nevertheless close to that measured for derivative (3).

In principle, the different orientations found for the carbonyl group in compounds (1b) and (3) in the solid state may be attributed to a different electronic interaction between the carbonyl group and the two different (furan and benzo[*b*]furan)

rings, exchanging the relative ground-state stabilities. We thus determined the energy content of the planar ground-states of benzo[*b*]furan-2-carbaldehyde in the STO-3G approach. The O,O-*trans* form turned out to be more stable even for this molecule and the difference in energy content of the ground-states is 3.31 kJ mol⁻¹, compared with 3.45 kJ mol⁻¹ calculated⁴⁰ for furan-2-carbaldehyde. Thus, the orientation of the carbonyl group in derivative (3) with respect to the other compounds in the solid state is mainly dependent on packing forces or electric field effects, and also on account of the relatively small energy content and upon the different polarity of the two possible conformers.

To test the presence of driving forces for the molecular conformation within the crystal, we performed empirical calculations of the packing energies for these molecules. van der Waals lattice energy, and intermolecular electrostatic packing energy were calculated with the OPEC program.⁴² The results show that the groups attached to the carbonyl bond adopt positions of minimum steric interaction: the total intermolecular non-bonded energy increases by rotating the furyl (or benzofuryl) groups from the minimum found in the crystal structure (assuming that the remainder of the molecule and all adjacent

Table 8. Atomic fractional co-ordinates ($\times 10^4$)

Atom	(1b)			(2b)		
	x	y	z	x	y	z
O(1)	829(1)	1 225(1)	619(5)	4 554(1)	73(2)	3 079(8)
C(2)	2 002(2)	1 103(1)	-333(6)	4 083(1)	735(3)	3 488(9)
C(3)	2 032(2)	592(1)	-2 093(7)	4 135(1)	2 001(2)	2 503(7)
C(4)	821(3)	375(1)	-2 287(8)	4 681(1)	2 130(3)	1 399(11)
C(5)	143(2)	767(1)	-624(9)	4 913(1)	956(3)	1 741(12)
C(6)	3 004(2)	1 498(1)	757(7)	3 726(1)	3 078(2)	2 780(7)
O(7)	4 032(1)	1 278(1)	612(6)	3 875(1)	4 231(2)	2 988(8)
C(8)	2 800(2)	2 114(1)	1 854(6)	3 138(1)	2 748(2)	2 802(6)
C(9)	3 731(2)	2 408(1)	3 601(7)	2 773(1)	3 608(2)	4 326(7)
C(10)	3 623(2)	2 994(1)	4 547(7)	2 218(1)	3 376(2)	4 364(7)
C(11)	2 576(2)	3 315(1)	3 769(7)	2 017(1)	2 255(2)	2 802(7)
C(12)	1 646(2)	3 040(1)	2 001(7)	2 375(1)	1 400(2)	1 208(7)
C(13)	1 758(2)	2 447(1)	1 080(6)	2 926(1)	1 636(2)	1 227(6)
O(14)	2 552(1)	3 897(1)	4 822(5)	1 483(1)	1 897(2)	2 671(6)
C(15)	1 495(3)	4 247(1)	4 060(12)	1 091(1)	2 755(4)	4 190(10)

Atom	(3)			(4)		
	x	y	z	z	y	z
O(1)	175(1)	8 087(2)	4 020(2)	3 091(2)	5 801(3)	7 347(4)
C(2)	803(2)	6 868(2)	3 691(4)	2 372(2)	4 963(3)	5 996(6)
C(3)	379(2)	6 633(3)	1 667(3)	2 437(2)	3 724(3)	7 051(5)
C(4A)	-577(2)	7 751(2)	587(4)	3 281(2)	3 771(3)	9 296(4)
C(4)	-1 360(2)	8 113(3)	-1 488(4)	3 757(2)	2 871(4)	11 181(6)
C(5)	-2 194(2)	9 340(3)	-1 905(5)	4 577(3)	3 309(4)	13 050(7)
C(6)	-2 233(3)	10 185(3)	-352(5)	4 927(3)	4 614(5)	13 042(7)
C(7A)	-660(2)	8 628(2)	2 091(4)	3 642(2)	5 062(3)	9 365(5)
C(7)	-1 467(2)	9 863(3)	1 670(5)	4 466(2)	5 527(4)	11 234(6)
C(8)	1 729(2)	6 061(2)	5 563(4)	1 899(2)	2 532(3)	5 907(5)
O(9)	1 745(2)	6 267(2)	7 432(3)	2 306(2)	1 445(0)	6 442(5)
C(10)	2 617(2)	4 985(2)	5 189(3)	891(2)	2 639(3)	4 059(5)
C(11)	3 080(2)	3 736(3)	6 930(4)	672(2)	1 671(3)	2 046(6)
C(12)	3 934(2)	2 729(3)	6 709(4)	-253(2)	1 698(4)	328(6)
C(13)	4 382(2)	2 932(2)	4 750(3)	-1 009(2)	2 676(4)	595(5)
C(14)	3 935(2)	4 169(2)	3 006(3)	-824(2)	3 631(3)	2 584(6)
C(15)	3 058(2)	5 167(2)	3 233(3)	137(2)	3 599(3)	4 300(6)
O(16)	5 232(2)	1 874(2)	4 721(3)	-1 896(2)	2 594(4)	-1 237(5)
C(17)	5 585(3)	1 878(4)	2 688(5)	-2 725(3)	3 528(5)	-1 010(13)

molecules remain at rest) reaching maxima after 60–80 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) very high positive energy values are found for the whole angular region from 20–330°. The introduction of electrostatic dipole effects does not significantly alter the calculated values.

In solution, derivatives (2b) and (4) show a preference for the O,O-*trans* conformation, as revealed by the LIS method and from the inspection of ¹H and ¹³C chemical shifts: the distortion of the rings with respect to the carbonyl plane is comparable in the two compounds, while derivative (4) is almost exclusively in the O,O-*trans* form. The close structural similarity of this molecule to 1-carbonyl-substituted naphthalenes^{43,44} should favour the O,O-*trans* conformation,¹⁶ both in view of the *trans* arrangement of the carbonyl bond and the adjacent double bond of the ring with higher π -electron density, and for the attractive *peri*-interaction of the carbonyl oxygen and the hydrogen H(4): this conformation in the corresponding formyl and acetyl derivatives is nearly planar,⁵ while in derivative (4) the large size of the aroyl substituent deviates the carbonyl group from the heterocyclic plane. In compound (2b) an equilibrium is found between the two conformers, where the

phenyl ring and the 2-furyl group are almost equally twisted, and the O,O-*trans* form prevails (70–80%). The solid-state structure of these molecules indicates that they have the O,O-*trans* orientation, with a twist slightly higher for the anisoyl ring: the carbonyl group is more deviated from the plane of the heterocyclic ring in the single-ring derivative (2b). MO calculations on the model compound (2a) show a slight preference for the more polar O,O-*cis* form, and this is in contrast with experimental results for (2b) in the solid state and in solution. Probably, the *ab-initio* calculations in the minimal basis set STO-3G, while correctly indicating that the conformers should differ only slightly in their energy content, do not properly reproduce their order of stability as also occurs for the corresponding 3-formylfuran.⁴¹ This result emphasizes caution in considering the order of stability of conformers of carbonyl compounds when they differ in energy content by < 3.5–4.0 kJ mol⁻¹, calculated in minimal basis sets, and upon attempting to verify the results as a function of basis set implementation.

Experimental

Compounds.—2- and 3-(4-methoxybenzoyl)benzo[*b*]furan (3) and (4) were prepared as previously described.¹⁶ Samples for X-ray analysis were obtained by slow crystallization of the pure

products from 95% ethanol and isopropyl alcohol, respectively. 2- and 3-(4-methoxybenzoyl)furan (**1b**) and (**2b**) were obtained from furan-2- (Merck) and -3-carboxylic acid (Janssen), respectively, by the procedure previously described¹⁶ for compound (**4**). Compound (**1b**) (57%) had m.p. 62–63 °C (di-isopropyl ether) (lit.,²¹ m.p. 63 °C). Compound (**2b**) (78%) had m.p. 75–77 °C (cyclohexane) (Found: C, 71.3; H, 5.3. Calc. for C₁₂H₁₀O₃: C, 71.3; H, 5.0%). Samples for X-ray analysis were obtained by slow crystallization of the pure products from di-isopropyl ether and cyclohexane, respectively.

Crystal Structure Analysis.—The most relevant data concerning the crystal structure analysis are reported in Table 7. The lattice parameters were determined by measuring numbers of accurately centred reflections at high θ by using the Cu-K_α ($\lambda = 1.540562$ Å) radiation, at room temperature (294 K). For all the compounds, intensity data were collected on a Siemens AED diffractometer using the Cu-K_α radiation, and the $\theta - 2\theta$ scan mode. The individual reflection profiles were analysed following the method of Lehman and Larsen,⁴⁵ and the intensity data were corrected for Lorentz and polarization effects, but not for absorption. Extinction was considered according to Zachariasen.⁴⁶

The structures were solved by the direct methods implemented in the SHELX76⁴⁷ program, excepting compound (**4**) whose structure was obtained by the MULTAN⁴⁸ program. Refinements were carried out by full-matrix least-squares using the SHELX76 program, anisotropically for the non-hydrogen atoms, isotropically for hydrogens whose starting co-ordinates were obtained from ΔF calculations. In the case of polar space groups no attempts were made to define the absolute polarities, the anomalous scattering effects of the non-hydrogen atoms being too small to be detectable.

Crystal packing analysis was carried out using the OPEC⁴² program. The molecular volume, V_m , the total volume occupied in the cell, V_{occ} , the molecular free surface,⁴⁹ S_m , the free volume V_{free} , and the Kitaigorodski⁵⁰ packing coefficient, C_K , for the four compounds are compared in Table 7.

Thermal motion was analysed in terms of the rigid-body LTS method of Schomaker and Trueblood.⁵¹ Acceptable fits of $U_{i,j}$ values are obtained for compounds (**1b**) ($R'_U = [\sum(w\Delta U)^2/\sum(wU_O)^2]^{-1/2} = 0.090$), (**2b**) ($R'_U = 0.075$), and (**3**) ($R'_U = 0.095$), while for compound (**4**) ($R'_U = 0.171$) the agreement is rather poor, indicating that internal motions are relevant particularly for this last compound. The corrections for bond distances due to vibrational motions does 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 52. The final atomic co-ordinates are quoted in Table 8. The calculations were performed on the GOULD-SEL 32/77 computer of the 'Centro di Studio CNR per la Strutturistica Diffraattometrica' (Parma). In addition to the quoted programs, LQPARM,⁵³ PARST,⁵⁴ THMV,⁵⁵ ORTEP,⁵⁶ and PLUTO⁵⁷ programs were used.

N.m.r. measurements.—The spectra were recorded at 200.058 MHz for ¹H and 53.3088 MHz for ¹³C by employing a VARIAN XL-200 spectrometer. The reagent shift employed is Yb(fod)₃ dried *in vacuo* on phosphorus pentaoxide, added in known and increasing amounts to [²H]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 lanthanide:substrate ratio were always found ≥ 0.999 and the intercepts identical with the unshifted spectra. For MO *ab-initio*

calculations the VAX-750 and CRAY-X-MP12 computers were employed.

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References

- V. N. Sheinker, A. D. Garnovskii, and O. A. Osipov, *Russ. Chem. Rev. (Engl. Transl.)*, 1981, **50**, 336 and references quoted therein.
- D. J. Chadwick and I. A. Cliffe, *Khim. Geterotsikl. Soedin.*, 1984, 579, and references quoted therein.
- D. Casarini, L. Lunazzi, and D. Macciantelli, *J. Chem. Soc., Perkin Trans. 2*, 1985, 1839.
- Part 3, R. Benassi, U. Folli, D. Iarossi, L. Schenetti, and F. Taddei, *J. Chem. Soc., Perkin Trans. 2*, 1983, 911.
- Part 4, R. Benassi, U. Folli, D. Iarossi, L. Schenetti, and F. Taddei, *J. Chem. Soc., Perkin Trans. 2*, 1984, 1479.
- V. N. Sheinker, A. S. Kuzharov, Z. N. Nazarova, and O. A. Osipov, *Zh. Org. Khim.*, 1975, **11**, 2489.
- C. L. Cheng, I. G. John, G. L. D. Ritchie, P. H. Gore, and L. Farnell, *J. Chem. Soc., Perkin Trans. 2*, 1975, 744.
- M. C. Fournié-Zaluski, B. P. Roques, and C. Chatain-Cathaud, *Org. Magn. Reson.*, 1975, **7**, 160.
- D. M. Bertin, C. Chatain-Cathaud, and M. C. Fournié-Zaluski, *C. R. Hebd. Seances Acad. Sci.*, 1972, **C274**, 1112.
- G. Gacel, M. C. Fournié-Zaluski, and B. P. Roques, *Org. Magn. Reson.*, 1976, **8**, 525.
- V. N. Sheinker, A. S. Kuzharova, V. F. Lavrushin, N. F. Pedchenko, and O. A. Osipov, *Khim. Geterotsikl. Soedin.*, 1979, 1327.
- C. G. Andrieu, P. Metzner, D. Debruyne, D. M. Bertin, and H. Lumbruso, *J. Mol. Struct.*, 1977, **39**, 263.
- H. Lumbruso, D. M. Bertin, and P. Cagniant, *Bull. Soc. Chim. Fr.*, 1970, 1720.
- C. Andrieu and Y. Mollier, *Bull. Soc. Chim. Fr.*, 1969, 831.
- C. Andrieu, D. Bertin, and H. Lumbruso, *C. R. Hebd. Seances Acad. Sci.*, 1965, **260**, 131.
- Part 5, R. Benassi, U. Folli, D. Iarossi, L. Schenetti, and F. Taddei, *J. Chem. Soc., Perkin Trans. 2*, 1987, 351.
- L. Kaper and Th. De Boer, *Spectrochim. Acta, Part A*, 1971, **27**, 261.
- L. Kaper and Th. De Boer, *Spectrochim. Acta, Part A*, 1970, **26**, 2161.
- R. Abu-Eittah and R. Hilal, *Bull. Chem. Soc. Jpn.*, 1978, **51**, 2718.
- M. C. Fournié-Zaluski, B. P. Roques, and C. Chatain-Cathaud, *Org. Magn. Reson.*, 1975, **7**, 167.
- M. Fiorenza, A. Ricci, G. Sbrana, G. Pirazzini, C. Eaborn, and J. G. Stamper, *J. Chem. Soc., Perkin Trans. 2*, 1978, 1232.
- C. Andrieu, C. Chatain-Cathaud, and M. C. Fournié-Zaluski, *J. Mol. Struct.*, 1974, **22**, 433.
- 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 N.M.R. 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.
- K. S. Dhami and J. B. Stothers, *Can. J. Chem.* 1965, **43**, 479.
- A. Di Rienzo, A. Domenicano, G. Portalone, and A. Vacicagi, *Proc. Yugoslv. Cent. Crystallogr. Suppl. to Vol. 11*, 1976, **A102**; P. Domiano, M. Nardelli, A. Balsamo, B. Macchia, and F. Macchia, *Acta Crystallogr., Sect. B*, 1979, **35**, 1363.
- G. W. Buchanan, G. Montaudo, and P. Finocchiaro, *Can. J. Chem.*, 1973, **51**, 1053 and references cited therein.
- 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.
- R. J. Abraham and T. M. Sivers, *Tetrahedron*, 1972, **28**, 3015.
- B. Roques, S. Combrisson, C. Riche, and C. Pascard-Billy, *Tetrahedron*, 1970, **26**, 3555.

- 30 C. Petrongolo, *Chem. Phys. Lett.*, 1976, **42**, 512; P. Cremaschi, *Rend. Ist. Lomb. Acad. Sci. Lett.*, 1973, **A107**, 735.
- 31 I. G. John and L. Radom, *J. Am. Chem. Soc.*, 1978, **100**, 3981.
- 32 T. J. Batterham, 'N.M.R. of Simple Heterocycles,' Wiley, New York, 1973; E. Breitmaier, G. Haas, and W. Voelter, 'Atlas of C-13 N.M.R. Spectra,' Heyden, London, 1979; M. Platzer, jun., J. Basselier, and P. Demerseman, *Bull. Soc. Chim. Fr.*, 1974, 905.
- 33 S. Gronowitz, G. Sörlin, B. Gestblom, and R. A. Hoffmann, *Ark. Kemi*, 1962, **19**, 483; S. Nagata, T. Yamabe, K. Yoshikawa, and H. Kato, *Tetrahedron*, 1973, **39**, 2545.
- 34 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. W. ApSimon and H. Beierbeck, *Can. J. Chem.*, 1971, **49**, 1328; J. W. ApSimon, J. Elguero, A. Fruchier, D. Mathieu, and R. Phan-Tan-Luu, *ibid.*, 1974, **52**, 2296.
- 35 R. J. Abraham, M. J. Bovill, D. J. Chadwick, L. Griffiths, and F. Sancassan, *Tetrahedron*, 1980, **36**, 279.
- 36 R. J. Abraham, D. J. Chadwick, and F. Sancassan, *Tetrahedron*, 1982, **38**, 1485, 3245.
- 37 Gaussian-80. An *ab-initio* Molecular Orbital Program, J. S. Binkley, R. A. Whiteside, R. Krishnan, D. Seeger, D. J. De Fries, H. B. Schlegel, S. Topiol, L. R. Kahn, and J. A. Pople, QCPE 1981, **13**, 406.
- Gaussian-82. Release A: J. S. Binkley, K. Ragavachari, D. J. De Fries, H. B. Schlegel, R. A. Whiteside, G. Fluder, J. M. Frisch, R. Seeger, and J. A. Pople, Carnegie-Mellon University.
- 38 Part 6, R. Benassi, U. Folli, L. Schenetti, and F. Taddei, *J. Chem. Soc., Perkin Trans. 2*, 1987, 961.
- 39 GPC. A General Purpose Contouring Program, California Computer Products, Anaheim, California.
- 40 I. G. John, G. L. D. Ritchie, and L. Radom, *J. Chem. Soc., Perkin Trans. 2*, 1977, 1601.
- 41 R. Benassi and F. Taddei, unpublished work.
- 42 OPEC. Organic Packing Energy Calculations and Volume Analysis, A. Gavezzotti, Dipartimento di Chimica Fisica ed Elettrochimica, Centro CNR, Milan; A. Gavezzotti, *J. Am. Chem. Soc.*, 1983, **105**, 5220.
- 43 J. Seita, J. Sandström, and T. Drakenberg, *Org. Magn. Reson.*, 1978, **11**, 239.
- 44 Part 2, R. Benassi, U. Folli, D. Iarossi, L. Schenetti, and F. Taddei, *J. Chem. Soc., Perkin Trans. 2*, 1981, 228.
- 45 M. S. Lehman and F. K. Larsen, *Acta Crystallogr., Sect. A*, 1974, **30**, 580.
- 46 W. H. Zachariasen, *Acta Crystallogr.*, 1963, **16**, 1139.
- 47 G. M. Sheldrick, SHELX76, Program for Crystal Structure Determination, University of Cambridge, 1976.
- 48 P. Main, M. M. Woolfson, L. Lessinger, G. Germain, and G. P. Declercq, MULTAN 74, System of Computer Programs for Automatic Solution of Crystal Structures, Universities of York and Louvain, 1974.
- 49 A. Gavezzotti, *J. Am. Chem. Soc.*, 1985, **107**, 962.
- 50 A. I. Kitaigorodski, 'Organic Chemical Crystallography,' Consultants Bureau; New York, 1961; 'Molecular Crystals and Molecules,' Academic Press; New York, 1973.
- 51 V. Schomaker and K. N. Trueblood, *Acta Crystallogr., Sect. B*, 1968, **24**, 63.
- 52 'International Tables for X-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4, pp. 99 and 149.
- 53 M. Nardelli and A. Mangia, *Ann. Chim. (Rome)*, 1984, **74**, 163.
- 54 M. Nardelli, *Comput. Chem.*, 1983, **7**, 95.
- 55 K. N. Trueblood, THMV, University of California, Los Angeles, 1984.
- 56 C. K. Johnson, ORTEP, Report ORNL-3794, Oak Ridge National Laboratory, Tennessee, 1965.
- 57 W. D. S. Motherwell and W. Clegg, PLUTO, University of Cambridge, 1976.

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