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Twisted Imide Bond in Noncyclic Imides. Synthesis and Structural and Vibrational Properties of *N*,*N*-Bis(furan-2-carbonyl)-4-chloroaniline

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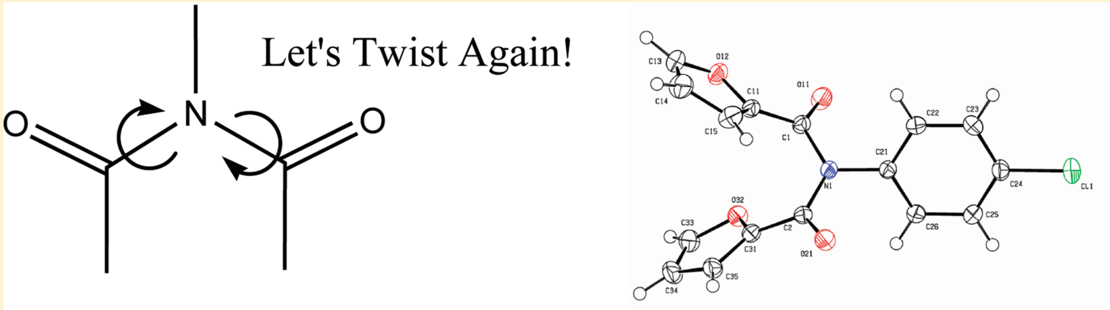
Supporting Information

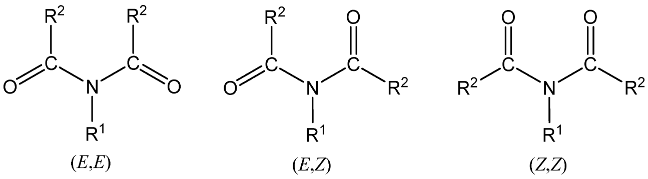


ABSTRACT: A novel imide compound ($C_{16}H_{10}ClNO_4$) was synthesized in a single step by the reaction of 2-furoic acid with 4-chloroaniline in a 2:1 molar ratio using carbonyldiimidazole (CDI) in dry THF. The structure was supported by spectroscopic and elemental analyses and the single-crystal X-ray diffraction data. Crystallographic studies revealed that the compound crystallized in a monoclinic system with space group $P2_1/c$ and unit cell dimensions a = 12.2575(5) Å, b = 7.7596(2) Å, c = 15.0234(7) Å, $\alpha = \gamma = 90°$, β = 92.771(4)°, V = 1427.25(10) Å^3, Z = 4. The imide bond is twisted, and the O═C−N−C(O) units deviate significantly from planarity with dihedral angles around the imide group reaching ca. −150.3° (C1−N1−C2−O21 = −148.8° and C2−N1−C1−O11 = −151.9°). The nonplanarity of the imide moiety and the related conformational properties are discussed in a combined approach that includes the analysis of the vibrational spectra together with theoretical calculation methods, especially in terms of natural bond orbital (NBO) calculations.

1. INTRODUCTION

The strong tendency for the amide bond to preserve planarity is usually explained in terms of the conjugation of the nitrogen lone pair with the C═O double bond. This interaction leads to a weakening of the C═O bond and to a partial double bond character of the N−C(O) motif, reflected in hindered internal rotation around this bond. Thus, the planarity of the amide bond usually includes also the directly bound neighbors. The same applied for symmetrical imide compounds [$R^1N(COR^2)_2$], and it was established that three planar conformations are stabilized by amide conjugation (see Scheme 1).[1] Two other factors, dipole−dipole interactions and steric interactions, are also of primary importance in determining conformational preferences of imides.[2]

Scheme 1. Planar Conformations Expected for Symmetrical Imide Compounds



Nevertheless, compounds with a twisted or distorted amide bond are very well-described, including several secondary and tertiary lactams,[3] including β-lactam antibiotics. Bicyclic amides adopt intrinsically nonplanar structures, and the tilt angles of *N*-aroyl-7-azabicyclo[2.2.1]heptanes range from 26 to 31° in the X-ray crystal structures.[4,5] Deviation from planarity is frequently accompanied by geometry changes at nitrogen. Thus, β-peptides containing β-amino acids bearing nonplanar amides display great flexibility of the backbone structure, promoted by facile *cis*−*trans* isomerization of the amide bonds.[6] Tertiary aromatic amides with hindered nitrogen substituents have been studied by Clayden and co-workers.[7] As recently remarked by Szostak and Aubé, there exists a strong motivation for organic chemists to prepare and study amides with a range of degrees of twist.[8]

In the present work, the novel *N*,*N*-bis(furan-2-carbonyl)-4-chloroaniline species has been prepared by the condensation

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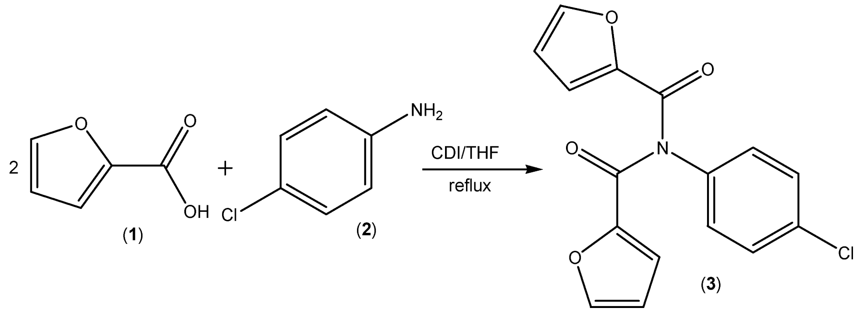
Scheme 2. Synthesis of the *N*,*N*-Difuran-2-carbonyl-4-chloroaniline



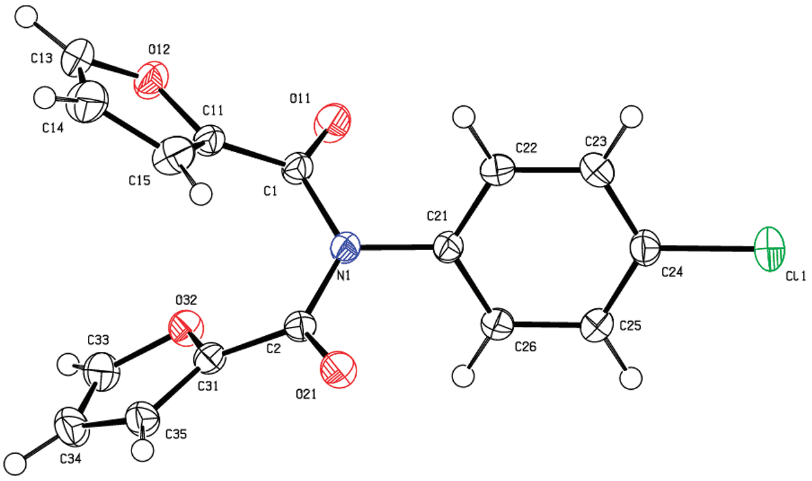


Figure 1. Molecular structure with atom numbering for *N*,*N*-bis(furan-2-carbonyl)-4-chloroaniline. Displacement ellipsoids are shown at the 50% probability level.

reaction between 2-furoic acid with 4-chloroaniline in the presence of carbonyldiimidazole. The title compound belongs to N,N-disubstituted anilines, a unique class of compounds. It contains an N,N-disubstituted benzamide structure, a well-known class of drugs that contain many analogues having radio- and chemosensitizing and bioactive properties.[9] Furan, a 5-membered unsaturated oxygen heterocycle, is the basic ring structure found in industrially significant products and in a large number of biologically active natural products.[10,11]

In order to gain additional experimental and theoretical information about the structural properties of imides, we also report here an X-ray diffraction study for the title species, drawing on its vibrational spectra (IR and Raman). Moreover, quantum chemical calculations have been performed in order to assist the interpretation of the experimental data, and the natural bond orbital (NBO) population analyses were applied to rationalize the effect of electronic interaction in the structural, conformational, and configurational properties around the imide group.

2. RESULTS AND DISCUSSION

2.1. Synthesis and Characterization. The reaction of 2-furoic acid (**1**) with 4-chloroaniline (**2**) in a 2:1 molar ratio using carbonyldiimidazole (CDI) in dry THF produces *N*,*N*-bis(furan-2-carbonyl)-4-chloroaniline (**3**) according to Scheme 2 in 85% yield. This one-pot method is important because it does not require the conversion of acids to acid chloride.[12]

The new compound is an air-stable brownish prismatic solid with mp = 157−159 °C. The molecular formula was confirmed by elemental analysis and GC−mass spectral data. ^{1}H and ^{13}C NMR and infrared spectroscopic data were in complete agreement with the proposed structure (see Table S1 in the Supporting Information). The main absorption bands in the infrared spectrum at 1665(vs), 1337(s), 1275(m), 1138(s), and 769(s) cm^{-1} allow to identify the main functional groups, as will be discussed below.

The ^{1}H NMR of compound **3** as $CDCl_3$ solution shows 10 aromatic hydrogen signals between 6.47 and 7.47 ppm. Thus, double doublets integrating for two hydrogens at δ 7.08 (d, J = 3.3 Hz, 2H, H-3′) and another for one hydrogen at 6.47 ppm (J_1 = 1.8, J_2 = 1.8 Hz, 2H, H-4′) are assigned to the furan ring, and doublets at 7.19 ppm (d, 2H, J = 8.7 Hz H-3,H-5), 7.38 (H-3,H-5) and a coupling constant of 8.7 Hz are assigned to the aromatic protons.

The ^{13}C NMR study of **3** in $CDCl_3$ showed nine chemical shifts indicating nine unequivalent carbons. Of these, five were assigned to the quaternary carbons including that at δ 161.04 ppm for carbonyl and four to the tertiary aromatic carbons. The benzene aromatic carbons have chemical shifts of δ 119.84 (C2, C6, Ar), 129.79 (C3, C5, Ar), 134.07 (C4, Ar), and 137.40 (C1, Ar) ppm, and the carbons of the furan ring have chemical shifts of δ 112.41 (C4′) 115.58 (C′3), 146.44 (C5′), and 147.31 (C2′) ppm, respectively.

The GC chromatogram shows a peak at retention times of 19.7 min with a very simple mass spectrum that was assigned to the expected ionic fragments from logical ruptures of the corresponding $M^{\bullet+}$ molecular ions (see Table S1 in the Supporting Information). A second, less intense peak was found at 15.5 min probably corresponding to the monosubstituted 4-chloroaniline, with a molecular ion with m/z = 221, in agreement with $C_{11}H_8ClNO_2$.

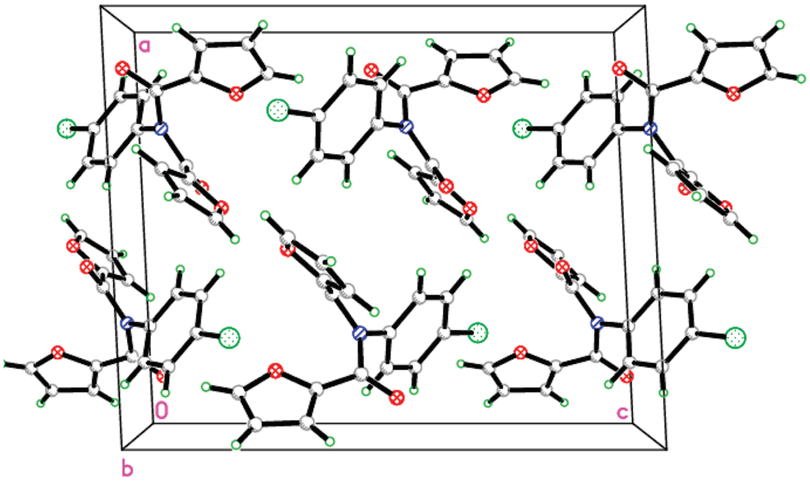


Figure 2. Crystal packing of *N,N*-bis(furan-2-carbonyl)-4-chloroaniline.

2.2. -X-ray Analysis and Molecular Structure. The molecular structure for the title compound, showing the atomic numbering, as determined in the crystalline phase is shown in Figure 1. The crystal packing (Figure 2) of title compounds is stabilized by several nonbonded interactions. The molecules are associated by weak hydrogen bonding C−H(furan)···O as well as pseudo-offset-stacked parallel aromatic interactions involving the chlorophenyl group.[13] In this compound, the tertiary nitrogen atom is not involved in intermolecular interactions.

Table 1 gives a comparison between the experimental values of the most important geometrical parameters and the optimized structure at the B3LYP/6-311++G** level of approximation. The agreement between the experimental and computed results is very good, especially for the central imide group.

Table 1. Selected Experimental (X-ray) and Computed (B3YLP/6-311++G) Bond Lengths (Å) and Angles (deg) around the Imide Moiety of the Title Compound**

geometrical parameter[a]	exptl[b]	calcd[c]
N(1)−C(2)/N(1)−C(1)	1.4087(13)/1.4134(12)	1.416/1.428
N(1)−C(21)	1.4383(13)	1.442
C(1)−O(11)/C(2)−O(21)	1.2103(13)/1.2177(12)	1.208/1.216
C(1)−C(11)/C(2)−C(31)	1.4552(14)/1.4588(14)	1.469/1.470
C(2)−N(1)−C(1)	124.87(9)	125.5
C(2)−N(1)−C(21)/C(1)−N(1)−C(21)	117.42(8) /117.69(8)	117.1/117.4
O(11)−C(1)−N(1)/O(21)−C(2)−N(1)	121.02(10)/121.06(9)	121.5/121.6
O(11)−C(1)−C(11)/O(21)−C(2)−C(31)	122.99(9)/121.39(9)	122.9/120.3
N(1)−C(1)−C(11)/N(1)−C(2)−C(31)	115.77(9)/117.37(9)	115.1/118.0
C(2)−N(1)−C(1)−O(11)/C(1)−N(1)−C(2)−O(21)	−151.94(11)/−148.83(11)	−146.5/−152.4
C(21)−N(1)−C(1)−O(11)/C(21)−N(1)−C(2)−O(21)	29.74(15)/ 29.50(15)	32.5/28.6
C(2)−N(1)−C(1)−C(11)/C(1)−N(1)−C(2)−C(31)	33.33(14)/36.00(14)	31.8/39.6
C(21)−N(1)−C(1)−C(11)/C(21)−N(1)−C(2)−C(31)	−144.99(10)/−145.68(9)	−141.4/−147.2

[a] For atom numbering, see Figure 1. [b] For complete crystallographic information, see the Supporting Information. [c] Syn−anti conformer computed at the B3YLP/6-311++G** level of approximation.

The C−N imide bond lengths equal 1.4087(13) and 1.4134(12) Å, distances which are considerably shorter than that expected for the single C(sp2)−N(sp2) bond length (average value of 1.472(5) Å.[14]) while the carbonyl bond lengths are in the range expected for imide carbonyl bonds. These facts have been usually attributed to the importance of the resonance form in the amide-like structures, a point that will be discussed in a next section. However, it should be noted that much shorter C−N amide bond distances (typically ca. 1.32 Å) have been found for related compounds.[15,16]

The N atom shows a trigonal planar coordination (sum of the bond angles around N 360°). The observed C(1)−N(1)−C(2) bond angle is higher [124.87(9)°] than the ideal value, the same is valid for the vacuum isolated computed structure (125.5°). Thus, is it plausible that steric hindrance between the 2-carbonyl furan rings is acting in the title species. This effect is also reflected in the torsion angles of the O═C−N−C(O) units, which deviate significantly from planarity [C(1)−N(1)−C(2)−O(21) = −148.8° and C(2)−N(1)−C(1)−O(11) = −151.9°] and neither of the furan rings is coplanar with the imide unit [torsion angles: N(1)−C(1)−C(11)−C(15) = 21.7°; N(1)−C(2)−C(31)-C(35) = −167.2°]. The phenyl ring is almost perpendicular to both furan rings (dihedral angles between the ring planes are 92.0° and 89.0°).

The central R^2−O═C−N(R^1)−C═O−R^2 (R^1 = C_6H_4Cl, R^2 = 2-furan) imide group adopts a nonplanar *E,E*-like configuration. As remarked previously by Noe and Raban,[2] the *Z,Z* configuration might have been anticipated to be favored in simple imides;[17] however, it is also expected that imide substitution strongly affect the balance between dipole−dipole and steric interactions and thus the conformational behavior.[18] To better understand how the substituents affect the conformational preference for the sterically congested compound here studied, quantum chemical calculations have been applied. Several attempts to characterize the *Z,Z* form have been made without success, probable due to steric repulsion between the furan groups. Indeed, the optimization procedure converges to the *E,E* form in many trails. Both, the intermediate *E,Z*-like and the *E,E* conformers have been determined as a true minimum in the conformational space for the title compound, having very similar electronic energies. The computed difference in the electronic energy (ΔE^0, corrected by zero-point vibrational energies), ΔE^0, amounts to 0.2 kcal/mol at the B3LYP/6-311++G** level of approximation, the *E,E* form being the most stable one. Thus, taking into account these results for the vacuum-isolated species, which are in perfect agreement with the conformer observed in the crystalline phase, the following discussion will be centered in the most stable *E,E* form for the imide group.

The conformational properties of carbonyl furans were studied, and two planar conformations have been identified. These planar forms are named as syn and anti, depending on the mutual orientation of the C═O double bond and the oxygen atom in the ring.[19,20] From early IR and variable-temperature NMR studies, it is known that the syn isomer of 2-furaldehyde is the more stable form in the gas phase and nonpolar solvents, with the anti conformer being about only 1 kcal/mol higher in energy.[21] Similar rotational isomerism has been observed for related 2-carbonylfuran species, and both experimental and theoretical results indicate that for all species the energy difference between the two planar configurations is small, with a low barrier to interconversion.[22]

For the title species, the X-ray structure analysis reveals that the 2-carbonyl furan groups are not equivalents in the solid phase, mainly differing in the conformation adopted by the C═O double bond with respect to the furan ring. Indeed, one of the 2-carbonyl furan is in syn while the second is clearly in anti orientation, as showed in the Figure 1. For better understand this conformational equilibrium, quantum chemical calculations have been performed for the three most relevant conformations for the title species: syn-syn, syn-anti and anti-anti. The B3LYP/6-311++G** (vacuum-isolated) optimized structures are shown in Figure 3.

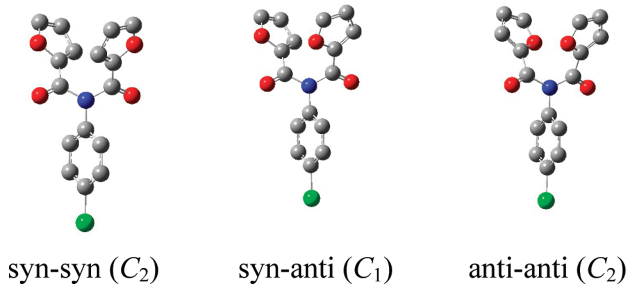


Figure 3. Molecular structure of the main conformers of the title species found theoretically (B3LYP/6-311++G**). Hydrogen atoms are omitted for clarity.

The computed differences in the electronic energy (ΔE^0, corrected by zero point vibrational energies) suggest that the most stable form corresponds to the anti–anti conformer, the least favorable conformer being the syn–syn form (ΔE^0 = 2.0 kcal/mol). The intermediate syn–anti conformation is only 1.1 kcal/mol above the anti–anti one. The same ordering is obtained when Gibbs free energies of the isolated structures are compared, with difference Gibbs free energy values of 1.5 and 2.5 kcal/mol for the syn–anti and syn–syn, with respect to the most stable anti–anti form, respectively. Thus, it is plausible that intermolecular interactions present in the crystal affect the conformational equilibrium described for the gas phase. In effect, the crystal packing for the title species shows distinct nonbonded interactions between the 2-carbonyl furan moieties and the furan hydrogen atoms In particular, a bifurcated hydrogen bond is observed between the furan hydrogen and the C═O and the furan oxygen mutually oriented in syn form, with nonbonded C═O(11)···C(13) and O(12)···C(13) [symmetry code: (1 − *x*, 1/2 + *y*, 1/2 − *z*)] distances of 3.387 and 3.495 Å, respectively (for further details see the Supporting Information).

2.3. Vibrational Analysis.

The FTIR and FT-Raman spectra for the title compound in the solid phase are shown in Figure 4. The observed and calculated (B3LYP/6-311++G**) wavenumbers, together with a tentative assignment of the bands, are given in Table 2. A tentative assignment of the observed bands has been carried out by comparison with theoretical wavenumbers, as well as on comparison with the reported data for related molecules, especially imides,[17] tertiary amides,[23−25] and 2-carbonylfuran species.[26] Very good agreement between the experimental and computed vibrational data support the proposed assignment.

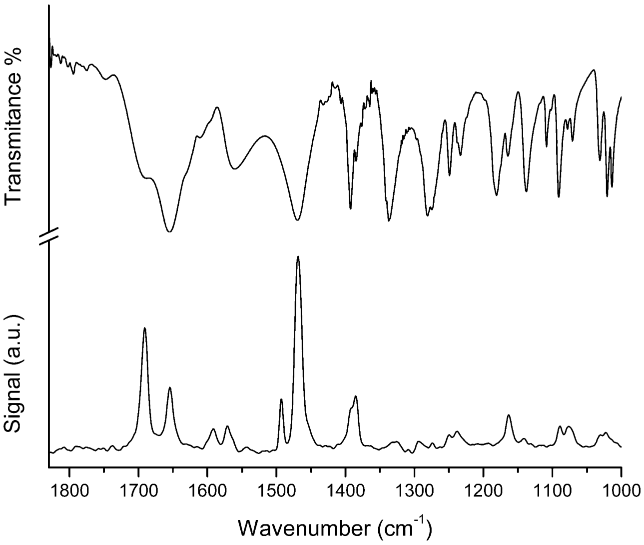


Figure 4. Selected region of the IR (in KBr pellet) and Raman spectra for the solid phase of the title species.

The following analysis is dedicated to the discussion of normal modes related to the central imide moiety. In the C═O stretching region of the infrared spectrum, an absorption with strong intensity is observed centered at 1665 cm^{-1}, while a shoulder is pronounced at higher wavenumbers (1691 cm^{-1}). These features are better defined in the Raman spectrum where a strong signal appearing at 1691 cm^{-1} is observed and a second, less intense signal is defined at 1664 cm^{-1}. Thus, the complementary analysis of both infrared and Raman spectra shows that the carbonyl oscillators are coupled, the symmetric motion being assigned to the higher frequency mode, in very good agreement with the computed carbonyl stretching normal modes.

The complex character of the νCN mode in imides and tertiary amides has already been mentioned.[27] From a potential energy distribution analysis, Desseyn et al.[23] suggested that the C–N stretching can be identified by an intense Raman signal and less intense infrared absorption in the 1530 cm^{-1} region. However, it should be noted that this mode is strongly coupled with methyl deformations modes and the potential energy distribution calculated considerable νCN contributions in 10 fundamentals in the 1650–600 cm^{-1} region for the compounds studied by these authors. In Figure 4, it is clearly observed that both the infrared and Raman spectra for the title species shows the presence of a series of signals, with strong bands at 1468 and 1469 cm^{-1}, respectively. However, it is well-known that the

Table 2. FTIR and FT-Raman Experimental Data for the Title Compound, Together with the Computed B3LYP/6-311++G** Values and Tentative Normal Mode Assignment

exptl[a]		calcd[b]	
FTIR (KBr pellets)	FT-Raman (solid)	B3LYP/6-311++G**	tentative assignment[c]
3150 w	3150 vvw	3146 (0.1)	ν C–H, Fur
		3145 (0.03)	ν C–H, Fur
3137 sh		3133 (1.4)	ν C–H, Fur
3131 w		3126 (0.6)	ν C–H, Fur
		3119 (1.2)	ν C–H, Fur
3123 m	3124 vvw	3116 (2.0)	ν C–H, Fur
3112 vw		3078(0.1)	ν C–H, Cl-Ph
		3077 (2.3)	ν C–H, Cl-Ph
3097 sh		3061 (3.0)	ν C–H, Cl-Ph
		3059 (5.0)	ν C–H, Cl-Ph
1691 sh	1691 s	1689 (227.0)	νs C=O
1665 vs	1664 m	1644 (389.3)	νas C=O
1630 sh		1567 (10.9)	ν C=C, Ph
1610 vw		1554 (0.4)	ν C=C, Ph
	1592 w	1541 (68.2)	ν C=C, Fur
1560 m, br	1572 w	1529 (26.8)	ν C=C, Fur
	1493 m	1460 (113.7)	ν C=C, Fur
1469 s	1469 vs	1436 (169.0)	ν C=C, Fur
1393 s	1393 sh	1431 (31.5)	ν C=C, Ph
1384 sh	1385 m	1376 (1.49)	ν C=C, Ph
		1363 (42.6)	ν C=C, Fur
		1359 (8.7)	ν C=C, Fur
1337 s	1332 br, w	1286 (343.8)	νs N–C(O)
	1326 w	1271 (2.6)	ν C=C, Ph
	1295 vw	1262 (1.3)	ν C=C, Ph
1281 s		1230 (234.0)	νas N–C(O)
1275 m	1273 vw	1208 (17.3)	ν N–C(Ph)
1249 m	1249 w	1203 (0.4)	δ(C–H)Fur
1238 sh	1238 w	1193 (20.1)	δ(C–H)Fur
1233 m		1150 (6.3)	δ(C–H)Ph
1181 s		1148 (84.6)	νas (C–O–C)Fur
1165 m	1165 m	1136 (51.3)	νas (C–O–C)Fur
1138 s	1141 vw	1107 (124.6)	νas N–C/δC–H Ph
		1084 (5.6)	δ(C–H)Ph
1109 m		1081 (50.8)	νs (C–O–C)Fur
		1066 (6.3)	νs (C–O–C)Fur
1091 s	1089 w	1057 (57.3)	δ(C–H)Fur
1078 w	1076 br	1051 (50.0)	δ(C–H)Fur
1071 w		1000 (29.7)	δ(C–H)Fur
1031 m, br		992 (27.0)	δ(C–H)Fur
	1031 w	990 (64.3)	δ(C–C)Ph
1021 s	1023 w	936 (2.4)	ρ(C–H)Ph
1014 s		933 (12.7)	ρ(C–H)Fur
957 m		915 (3.0)	ρ(C–H)Ph
943 m		907 (16.7)	ρ(C–H)Fur
929 s		874 (2.5)	ρ(C–H)Fur
900 m	901 vvw	869 (7.1)	ρ(C–H)Fur
883 m	882 w	868 (2.0)	δ(C–C)Fur
		867 (11.8)	δ(C–C)Fur
		836 (81.2)	δ(C–C)Fur
857 s	864 vw	827 (35.1)	δ(C–C)Fur
830 m	854 vw	822 (5.8)	δ C–N–C
819 sh	831 w	802 (57.3)	oop(C–H)Fur
810 vs	819 w	792 (0.01)	δ(C–C)Ph
782 m		787 (66.8)	oop(C–H)Ph
773 s	785 vvw	742 (27.1)	oop(C–H)Ph
769 s		740 (95.5)	oopC=O
753 w		736 (9.1)	oop(C–H)Fur
		729 (20.8)	oopC=O
745 s		689 (0.4)	oop(C=C)Ph
	676 vvw	655 (0.04)	νC–Cl
639 vw		629 (9.2)	oop(C=C)fur
627 sh	630 br, w	618 (3.3)	δ(C–C)Ph
622 w	623 w	605 (8.1)	oop(C=C)fur
594 w	597 vw	583 (6.3)	ρ(C–H)Fur
588 w	588 m	581 (6.2)	ρ(C–H)Fur
		566 (7.0)	δ(O=CNC=O)
513 m	516 vw	501 (21.1)	oop(C=C)Ph
500 vw		500 (4.1)	δCCC
454 w	446 br	450 (30.6)	oop N
	227 m		

[a] Band intensities and shape: vs = very strong; s = strong; m = medium; w = weak; vw = very weak, sh: shoulder, br: broad. [b] Scaled computed frequency and intensity values at the B3LYP/6-311++G** level of approximation. Computed IR intensities (km/mol) are given in parentheses. [c] ν: stretching (subscripts s and as refer to symmetric and antisymmetric modes, respectively). δ: deformation. ρ: rocking. oop: out of plane deformation modes.

furan[28,29] and benzyl groups also show intense features in this region, associated with the ν(C=C) stretching and δ(C–H) bending modes, respectively. Thus, on the basis of these reports and on the calculated displacement vectors calculated for the harmonic normal modes, we tentatively assign the intense band observed at 1337 cm^{-1} in the infrared spectrum to the symmetric motion of the stretching mode of the N–C(O) bonds, with the antisymmetric counterpart at 1281 cm^{-1}. The last absorption originates from a broad band in the infrared spectrum, with two clearly defined maxima; the second observed at 1275 cm^{-1} can be assigned with confidence to the ν(N–C(Ph)) fundamental.[13] These frequency values and the relative intensities are in very good agreement with the computed ones, as showed in Table 2. Such low frequency values for the ν(N–C(O)) fundamental, and the associated low force constants predicted for the amide-like C–N bonds, can be related with the relatively long carbon–nitrogen bond distances observed in the crystal (see previous section). It is postulated that the nonplanarity around the imide bonds causes these effects, mainly through a moderate disruption in the electronic conjugation. The electronic features associated with this aspect will be discussed in the next section.

2-4. Natural Bond Orbital Analysis. The resonance model of the amide bond has been generally accepted by considering a conjugation of the nitrogen lone pair with the C=O double bond in terms of resonance between structures **I** and **II** (Scheme 3). On the basis of comparisons of the

Scheme 3. Main Resonance Structures for the Amide Moiety

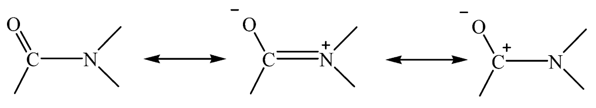

I II III

Table 3. Crystal Data and Structure Refinement for the Title Compound

emp formula	$C_{16}H_{10}ClNO_4$
formula wt	315.70
temp (K)	173(2)
wavelength (Å)	0.71073
crystal system	monoclinic
space group	$P2_1/c$
unit cell dimens (Å, deg)	a = 12.2575(5), α = 90 b = 7.7596(2), β = 92.771(4) c = 15.0234(7), γ = 90
volume (Å^3)	1427.25(10)
Z	4
density (calcd) (Mg/m^3)	1.469
absorption coeff (mm^{-1})	0.285
F(000)	648
crystal size (mm^3)	0.39 × 0.37 × 0.37
θ range for data collection (deg)	3.36 to 29.61
index ranges	$-16 \le h \le 16$, $-10 \le k \le 10$, $-20 \le l \le 20$
reflections collected	40234
independent reflections	3999 [R(int) = 0.0445]
completeness to θ = 25.00° (%)	99.7
absorption correction	semiempirical from equivalents
max and min transmission	0.9018 and 0.8969
refinement method	full-matrix least-squares on F^2
data/restraints/parameters	3999/0/200
goodness-of-fit on F^2	1.043
final R indices [$I > 2\sigma(I)$]	R1 = 0.0352, wR2 = 0.0907
R indices (all data)	R1 = 0.0378, wR2 = 0.0924
extinction coefficient	0.149(5)
largest diff peak and hole (e·Å^{-3})	0.290 and −0.404

calculated electron densities in amide bonds, Wiber and Breneman[30] suggested a third resonance structure **III**. These resonances also apply for the carbonyls in the imide group.

NBO analysis for the syn−anti conformer of the title molecule clearly indicates the presence of one lone pair orbital formally attached at the nitrogen atom. The nature of this orbital is a pure p-type [$lp_p(N)$], with a low electron occupancy of 1.76 **e**, indicating the electron-donating capacity for this orbital. Delocalizing interactions evaluated by a second-order perturbation approach reveals that the lone pair orbital contributes to a strong resonance interactions with both carbonyl bonds $lp_p(N) \rightarrow \pi^*(C{=}O)$, leading to the "amide resonance" (form **II** in Scheme 2). The computed $E^{(2)}$ interaction values are 32.3 and 44.4 kcal/mol for the C=O groups oriented in syn and anti conformations, respectively. This electron donation into the $\pi^*(C{=}O)$ antibonding orbitals is reflected also in its high electronic occupancy of ca. 0.16 **e**. For planar amide groups, however, much higher resonance interaction values are computed, reaching 59.8 kcal/mol for formamide.[31]

The lone pair orbital at the carbonyl oxygen atom donates electronic density mainly to the vacant C−N antibonding orbital via a negative hyperconjugation interaction; $lp_\pi(O) \rightarrow \sigma^*(N{-}C)$, with a $E^{(2)}$ value of 38.5 and 36.1 kcal/mol for the C=O groups in syn and anti conformations, respectively.

The atomic charges obtained using the natural population analysis (NPA) approach reveal that negative charges −0.67 and −0.62 are located at the both the nitrogen and the carbonyl oxygen atoms, while the carbon atoms in the C=O groups bear a strong positive charge (+0.81), denoting the contribution of the resonance structure **III** in the description of the imide bond of the title compound.

The most relevant donor−acceptor interactions have also been evaluated for the main conformers (showed in Table S2 in the Supporting Information). The same description for the imide bond is valid for the three forms here analyzed, remarkable differences being observed depending on the orientation of the furan ring with respect to the carbonyl double bonds. Thus, the mesomeric effect, reflected mainly by the $lp_p(N) \rightarrow \pi^*(C{=}O)$ interaction, is definite larger when the C=O double bond is oriented in anti position with respect to the furan ring. On the other hand, the $lp_\pi(O) \rightarrow \sigma^*(N{-}C)$ anomeric interaction is slightly higher for the syn conformation. The complex interplay between these and other interactions that depend on the conformation adopted around the central imide bond is responsible for the stabilities of the different conformers isolated in a vacuum.

3. CONCLUSION

N,*N*-Bis(furan-2-carbonyl)-4-chloroaniline was synthesized in a one-pot procedure by the reaction of 2-furoic acid with 4-chloroaniline using carbonyldiimidazole. The X-ray crystal structure revealed that the two carbonyls double bonds are twisted with respect to the plane around the tertiary nitrogen atom. The nonplanarity of the imide group seems to be related with steric hindrances of the 2-carbonyl furan rings. Intramolecular donor→ acceptor electronic interactions within the imide moiety were evaluated and the nonplanarity is mainly reflected in the computation of relatively low resonance interaction values. These results invite to synthesize related species with substituted furan and benzyl rings in order to analyze the effect of bulky substituent on the molecular structure, not only in the solid phase but also in solution.

4. EXPERIMENTAL SECTION

4.1. Synthesis and Characterization. Carbonyldiimidazole (CDI) (10 mmol) was dissolved in 30 mL of dry THF with stirring at room temperature under nitrogen atmosphere, and 2-furoic acid (10 mmol) (**1**) was added carefully. The reaction mixture was further stirred for 15 min, and then after the evolution of CO_2 ceased, 4-chloroaniline (5 mmol) (**2**) was added slowly. The stirring was continued for additional 10 min at room temperature and then refluxed for 10 h. After completion of the reaction, monitored by TLC, reaction mixture was concentrated to obtain crude product (**3**) purified by column chromatography using 20% EtOAc in hexane. Commercial carbonyldiimidazole (CDI) was used without further purification. THF was distilled from sodium/benzophenone prior to use. The melting points were recorded using conventional apparatus. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ at 300 and 75 MHz, respectively. Standard IR spectra were recorded as KBr pellets, and elemental analyses were conducted using a standard analyzer.

4.2. Vibrational Spectroscopy. Solid-phase IR spectra were recorded with a resolution of 2 cm^{-1} in the 4000−400 cm^{-1} range, whereas the FT-Raman spectra were recorded in the region 4000−100 cm^{-1} using a Nd:YAG laser source operating at 1.064 μm line with 200 mW power of spectral width 2 cm^{-1}.

4.3. Quantum Chemical Calculations. All quantum chemical calculations were performed with the GAUSSIAN 03 program package.[32] The molecular geometries were optimized to standard convergence criteria by using B3LYP DFT hybrid methods employing the

Pople-type[33] extended valence triple-ξ basis set augmented with diffuse and polarization functions in both the hydrogen and weighty atoms [6-311++G**]. The calculated vibrational properties corresponded in all cases to potential energy minima for which no imaginary frequency was found. Scott and Radom derived the scaling factors for the theoretical harmonic vibrational frequencies at 19 levels utilizing a total of 1066 individual vibrations for small molecules.[34] Zhou and co-workers[35] demonstrated that scaled B3LYP calculations are powerful approaches for understanding the vibrational spectra of medium-sized organic compounds and the recommended factors of 0.96 was used to scale the theoretical frequencies (1.0013 for frequencies lower than 500 cm^{-1}). Natural population analysis and second-order Donor→ acceptor interaction energies were estimated at the HF/6-311++G** level by using the NBO analysis[36] as implemented in the GAUSSIAN 03 program.

4.5. X-ray Data Collection, Structure Solution, and Refinement. An alcohol solution of compound **3** was stood at room temperature, and upon slowly evaporating alcohol from the solution, yellow crystals suitable for X-ray diffraction analysis were isolated one week later.

A two-circle diffractometer equipped with an image plate area detector was used. Pertinent crystal and refinement data for **3** are given in Table 3. The structure was solved by direct methods, full-matrix least-squares refinement based on F^2. All but H atoms were refined anisotropically. Hydrogen atoms were located from difference Fourier maps and refined at idealized positions riding on the relevant carbon with C−H = 0.95 Å and with isotropic displacement parameters $U_{iso}(H) = 1.2U_{eq}(C)$. Crystallographic data (excluding structure factors) for the structure in this paper has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (fax: +44-(0)1223-336033 or e-mail: deposit@ccdc.cam.ac.uk. Any request for this material should quote the full literature citation and the reference number CCDC 852552.

4.6. GC−MS Determination. The GC−MS measurements were recorded using gaseous helium as the mobile phase with the pressure in the column head equal to 100 kPa. A 1 μL volume of the compound dissolved in $CHCl_3$ was chromatographed under the following conditions: injector temperature was 210 °C, the initial column temperature (100 °C) was held for 3 min, then increased to 200 at 20 °C/min and held for 2 min after elevated to 300 at 35 °C/min and held for 2 min. In the spectrometer the source was kept at 200 °C.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Analytical data for the title compound (Table S1). NBO stabilization energies values (kcal/mol) for the main orbital interactions around the imide group for relevant conformers (Table S2). The whole geometrical parameters derived from the X-ray analysis together with atomic coordinates, equivalent isotropic displacement coefficients, and anisotropic displacement parameters (Tables S2−S6). Atom coordinates for optimized (B3LYP/6-311++G**) structures (Tables S7−S11). UV−vis spectrum (Figure S1) and ^1H and ^{13}C NMR spectra (Figures S2 and S3) for the title compound. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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