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Synthesis and structural and vibrational analysis of (5,7-dichloro-quinolin-8-yloxy) acetic acid

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ABSTRACT

We have prepared the (5,7-dichloro-quinolin-8-yloxy) acetic acid and characterized it by infrared and Raman spectroscopies in the solid phase and by nuclear magnetic resonance (NMR) spectroscopy in a $CDCl_3$ solution. The density functional theory (DFT) together with the 6-31G* and 6-311++G** basis sets were used to study its structure and vibrational properties. Two stable conformations of the compound were theoretically determined in the gas phase and probably these conformations are present in the solid phase. The harmonic vibrational wavenumbers for the optimized geometries were calculated at the same theory levels. For a complete assignment of all the observed bands in the vibrational spectra the DFT calculations were combined with Pulay's scaled quantum mechanical force field (SQMFF) methodology in order to fit the theoretical wavenumber values to the experimental ones. The force constants for the (5,7-dichloro-quinolin-8-yloxy) acetic acid were calculated and compared with those obtained for the (5-chloro-quinolin-8-yloxy) acetic acid and 2-(quinolin-8-yloxy)-acetic acid compounds. Furthermore, the characteristics of the electronic delocalization, the topological properties of the electronic charge density together with the highest occupied molecular orbital (HOMO)-lowest unoccupied molecular orbital (LUMO) energy gaps were studied.

1. Introduction

The syntheses of heterocyclic compounds containing the (quinolin-8-yloxy) moiety have been object of numerous studies for the last few years because they exhibit a wide range of biological properties [1–4]. Recently, a complete vibrational analysis of all observed bands in the vibrational spectra of 2-(quinolin-8-yloxy) [5] and (5-chloro-quinolin-8-yloxy) acetic acids [6] were studied by means of the DFT calculations combined with Pulay's scaled quantum mechanical force field (SQMFF) methodology [7–9]. In both studies, the normal mode calculations were accomplished by using a generalized valence force field (GVFF) [8,9] and by considering three different structures for each compound. The presence of the chloro atom in the structure of (5-chloro-quinolin-8-yloxy) acetic acid decreases the dipole moment value of the most stable structure in relation to the 2-(quinolin-8-yloxy)-acetic acid and, accordingly, their properties are slightly different. In this case, we carried out a structural, experimental and theoretical vibrational study of (5,7-dichloro-quinolin-8-yloxy) acetic acid (DQA) based on B3LYP theoretical calculations by using 6-31G* and 6-311++G** basis sets accomplished by means of the SQMFF methodology [7–9] in order to fit the theoretical wavenumber values to the experimental ones. In this work, the compound was synthesized and characterized by infrared and Raman spectroscopies in the solid phase and also by NMR spectroscopy for diluted solutions in $CDCl_3$. On the other hand, as the crystal and molecular structure of DQA were not previously determined and in order to carry out a complete assignment of all the observed bands in the vibrational spectra, the optimized geometries and the corresponding frequencies for the normal modes of vibration were calculated by taking into account two different stable structures of DQA. In order to obtain the corresponding force fields for those structures, Rauhut and Pulay [9] transferable scaling factors were used while the harmonic force constants were subsequently scaled to reproduce as much as possible the experimental frequencies. Thus, a complete assignment of the compound in terms of the potential energy distribution was performed and the force constants were calculated and compared with those corresponding to the (quinolin-8-yloxy) [5] and (5-chloro-quinolin-8-yloxy) acetic acids [6]. In addition, the nature of the different rings and bonds of the two studied structures of DQA were analyzed by means of NBO studies [10–12], while the topological properties of electronic charge density were determined by using Bader's atoms in molecule theory (AIM) [13,14].

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2. Experimental methods

2.1. Synthesis of methyl [(5,7-dichloroquinolin-8-yl)oxy]acetate

A mixture of 5,7-dichloro-8-hydroxyquinoline (2.14 g, 0.01 mol), potassium carbonate powder (2.76 g, 0.02 mol) and methyl bromoacetate (1.84 g, 0.012 mol) in acetone(100 mL) was heated at reflux monitored by TLC. After 4 h, the reaction was completed; the mixture was filtered and concentrated *in vacuo*. The residue (2.67 g) was crystallized from isopropyl ether (120 mL) to give (5,7-dichloroquinolin-8-yloxy) acetic acid methyl ester (2.08 g, 73%) m.p. 128.5–129 °C.

2.2. Synthesis of (5,7-dichloroquinolin-8-yloxy) acetic acid

A solution of *methyl [(5,7-dichloroquinolin-8-yl)oxy]acetate* (1.01 g, 3.5 mmol) and LiOH·H_2O (0.315 g, 7.5 mmol). in 10 mL of dimethylsulfoxide was stirred and heated at 50 °C for 12 h. The resulting white suspension was adjusted to pH 3 with 1 N HCl. The precipitate was filtered, washed with water and ethanol and dried to give (5,7-dichloroquinolin-8-yloxy) acetic acid (0.865 g, 91%) m.p. 221–222 °C.

^{1}H NMR (300 MHz, $CDCl_3$) δ: 4.77 (2H, s, O—CH_2); 7.64 (1H dd J = 4,28; J = 8,73 H_3); 7.67 (1H, s, H_6), 8,61 (1H dd J = 8,73; J = 1,28, H_4); 8.92 (1H dd J = 4,28; J = 1,28, H_2).

^{13}C NMR (75 MHz, $CDCl_3$) δ: 70.85 (CH_2); 123.42(C3); 125,24(C7); 125.24 (C5); 126.04 (C4a); 128.03 (C6); 133.67 (C4); 142.31 (C8a); 151.15(C2); 149.45(C8); 170.35 (CO_2H) (atom numbering according to naphthalene).

Nuclear magnetic resonance (NMR) spectra were recorded for dilute solutions in $CDCl_3$ by using a Bruker 300 FT spectrometer at 300 MHz for 1H and 75 MHz for 13C.

The infrared spectrum of the solid in KBr pellets from 4000 to 400 cm^{-1} was recorded with an FTIR GX1 spectrophotometer, equipped with a globar source and a DGTS detector at a resolution of 1 cm^{-1} and 64 scans. The Raman spectrum (resolution 4 cm^{-1}, 200 scans) was recorded between 4000 and 0 cm^{-1} with a Bruker RF100/S spectrometer equipped with a Nd: YAG laser source (excitation line 1064 nm, 150 mW power).

3. Computational details

The potential energy curves associated with rotation around the O17—C18 bond, described by the C10—O17—C18—C21 dihedral angle for the compound, were studied at the B3LYP/6-31G* and B3LYP/6-311++G** levels. The results show two stable conformations, namely, C_I and C_{II}, according to the OH group position in relation to the N atom of the quinoline ring. Besides, another plane structure was also considered (C_{III}) in accordance with the experimental structure of the 8-(Carboxymethoxy) quinolinium nitrate monohydrate compound [15]. The atom structures and labelling for all conformers of DQA can be seen in Fig. 1. The electronic charge density topological analysis for those structures and NBO calculations were performed by using the AIM200 program package [14] and the NBO 3.1 [16] program, as implemented in the GAUSSIAN 03 package [17]. The natural internal coordinates for the compound were defined as reported in the literature [5,6,18] and are listed in Table S1 (Supporting material). The resulting force fields were transformed to "natural" internal coordinates by using the MOLVIB program [19,20]. Then, following the SQMFF procedure [7–9,21], the harmonic force fields only for the C_I and C_{II} structures were evaluated at the B3LYP/6-31G* level because the C_{III} structure has an imaginary frequency. The potential energy distribution components (PED) higher than or equal to 10% were subsequently calculated with the resulting SQMFF. Vibrational modes were analyzed by using the *GaussView* program [22].

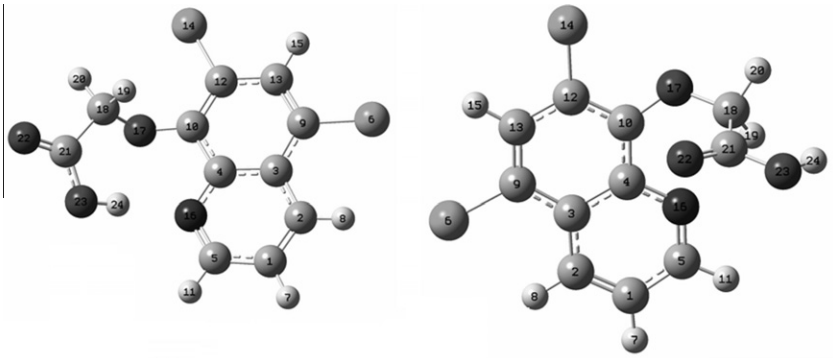
4. Results and discussion

4.1. Geometry

A comparison of the total energies together with the corresponding dipole moment values for all conformers of (5,7-dichloroquinolin-8-yloxy) acetic acid is shown in Table 1. The C_I energy is lower than that of the other two conformers, as was observed in the monochloro compound [6]. The potential energy difference between the C_I and C_{II} forms, by using the B3LYP/6-31G* and B3LYP/6-311++G** methods are 45.64 and 38.56 kJ/mol, respectively. These energy differences between both conformations are lower than the ones of (5-chloro-quinolin-8-yloxy) acetic acid [6]. In DQA, the presence of two Cl atoms probably indicates that the largest dipole moment value stabilizes the molecule, in accordance with the results obtained for other compounds [6,23,24]. Table 2 shows the geometrical parameters for the C_I and C_{II} structures of DQA. The stabilities of the two conformers of DQA were investigated by using natural atomic charges [25–28] and the results are given in *Table* S2. Notice that the natural charge values (NPA) corresponding to the C21 atoms have higher positive values in both structures, while the more negative values correspond to the O23 atoms. Bond orders, expressed by Wiberg's index for both conformers of DQA are given in *Table* S3. C9 and C12 atoms in both conformers have higher bond order values than the other ones because both atoms are linked to the Cl atoms.

4.2. NMR

Table 3 shows the ^{1}H NMR and ^{13}C NMR shifts of DQA in deuterated chloroform. Five signals corresponding to five different H



C_I C_{II}

Fig. 1. Theoretical structures and labelling of the atoms for the stable C_I and C_{II} conformers of (5,7-dichloro-quinolin-8-yloxy) acetic acid.

Table 1
Calculated total energy (E) and dipolar moments for the structures of (5,7-dichloro-quinolin-8-yloxy) acetic acid at different theory levels.

(5,7-dichloro-quinolin-8-yloxy) acetic acid							
Method	C_I		C_{II}			C_{III}	
	E_1 (Hartrees)	μ (D)	E_2 (Hartrees)	μ (D)	$\Delta E = E_1 - E_2$ (kJ/mol)	E_P (Hartrees)	μ (D)
B3LYP/6-31G*	−1624.2030	6.55	−1624.1856	4.50	45.64	−1624.1856	0.40
B3LYP/6-311++G**	−1624.4561	6.79	−1624.4414	4.79	38.56	−1624.4391	0.70

atoms can be seen in the spectrum. Peaks at 7.64, 8.61, and 8.92 ppm belong to three H atoms on 7, 8, and 11 positions of the hetero ring, respectively, while the peak at 7.67 belongs to H atom on position 15 of the carbocyclic ring. The peak belonging to H atoms of the CH_2 group appears at 4.77 ppm. These chemical shift values are in agreement with those reported in the literature [6]. A slight shift of these peaks towards lower fields implies the existence of some intermolecular interaction between nonbonding electrons. In the ^{13}C NMR spectrum the peak at 170.35 ppm belongs to the C21 atom of the carboxy group and the peak at 70.85 ppm corresponds to the C18 atom of the methylene group. The observed chemical shifts are in agreement with those reported in the literature for the ^{13}C NMR of (5-chloro-quinolin-8-yloxy) acetic acid [6].

4.3. NBO study

The stability of the C_I and C_{II} structures of DQA was also investigated by means of NBO calculations [10–12]. Tables S4 and S5 show the second order perturbation energies $E^{(2)}$ (donor → acceptor) that involve the most important delocalization for C_I and C_{II} conformers of DQA, respectively. In this work, the contributions of the stabilization energies for the $\delta ET_{\sigma\rightarrow\sigma*}$ charge transfers are similar to those obtained for all conformers of the (5-chloro-quinolin-8-yloxy) acetic acid [6], while the LP(3)Cl14 → σ^*C10—C12 delocalizations due to other Cl atom are observed for the two conformers of DQA. On the other hand, the LP(1)N16 → σ^*O23—H24 delocalization, possible only for the C_I conformer and that confers a high stability is calculated. The calculated total energy values favor the C_I conformer, whose structure, by using both basis sets, is the most stable in the gas phase. In this way, the stabilization energies justify the different stabilities between both conformers.

Table 2
Calculated geometrical parameters for the two stable conformers of (5,7-dichloro-quinolin-8-yloxy) acetic acid.

Parameter	[a]B3LYP/6-31G*		[a]B3LYP/6-311++G**	
	C_I	C_{II}	C_I	C_{II}
Bond length (Å)				
C3—C4	1.430	1.434	1.429	1.431
C4—N16	1.359	1.359	1.358	1.362
C5—N16	1.440	1.414	1.439	1.417
C4—C10	1.535	1.529	1.534	1.526
C9—Cl6	1.755	1.759	1.755	1.759
C12—Cl14	1.745	1.746	1.745	1.744
C10—O17	1.210	1.201	1.205	1.195
C18—O17	1.332	1.360	1.329	1.362
C18—C21	1.430	1.434	1.429	1.431
C21—O22	1.359	1.359	1.358	1.362
C21—O23	1.440	1.414	1.439	1.417
Bond angle (°)				
C4—N16—C5	118.8	118.9	118.9	118.9
C4—C10—C12	118.7	118.4	118.6	118.5
C4—C10—O17	118.4	125.1	118.2	123.9
C12—C10—O17	122.8	116.3	123.0	117.3
C10—O17—C18	119.1	123.6	119.8	122.3
O17—C18—C21	111.8	113.3	112.5	113.5
C18—C21—O23	117.2	114.0	117.6	113.9
C18—C21—O22	119.5	124.9	119.3	125.3
O22—C21—O23	123.3	121.1	123.0	120.8
Dihedral angles (°)				
C21—C18—O17—C10	−121.3	−53.8	−117.2	−58.1
C4—C10—O17—C18	102.2	−35.5	104.6	−46.4
C12—C10—O17—C18	−81.9	149.6	−80.4	139.3

[a] This work.

4.4. AIM analysis

The two most stable structures of DQA were also analysed by means of Bader's charge electron density topological analysis [13]. The calculated electron density (ρ), and the *Laplacian* values, $\nabla^2\rho(r)$ in the bond critical points (BCPs) and in the ring critical points (RCPs) for those structures are shown in *Table* S6. The BCP has the typical properties of the closed–shell interaction and for this reason, the value of $\rho(r)$ is relatively low, the relationship between $|\lambda_1|/\lambda_3$ and <1 $\nabla^2\rho(r)$ is positive, indicating that the interaction is dominated by the charge contraction away from the interatomic surface toward each nucleus. Notice that the results are slightly dependent on the size basis set. Thus, the analysis shows the same BCPs for the C_I and C_{II} structures by using both basis sets. These results, together with the NBO analysis, justify the C_I structure stability due to the presence of a short intramolecular N16—H24 bond (1.872 Å by using 6-31G* basis set), as observed in Table S6. Also, the topological properties are more significant in this stable structure than C_{II}. This study reveals that the H bonds are different in both conformers. In C_I, the H bond is between N16—H24 while in C_{II} between N16—H19.

4.5. Vibrational analysis

In this study, in accordance with the NBO and AIM results, only the C_I and C_{II} structures of DQA in the gas phase were considered.

Table 3
Experimental chemical shifts (in ppm) for (5,7-chloro-quinolin-8-yloxy) acetic acid.

H atoms	δ (ppm)	Integ. multiplicity (JHz)
^1H NMR in $CDCl_3$		
11	8.92	1H dd (4,28; 1,28)
7	7.64	1H dd (4,28; 8,73)
8	8.61	1H dd (8,73; 1,28)
15	7.67	1H s
19, 20	4.77	2H s
C atoms		Multiplicity
^{13}C NMR in $CDCl_3$		
5	151.15	Doblete
1	123.42	Doblete
2	133.67	Doblete
3	126.04	Singlete
9	125.24	Singlete
13	128.03	Doblete
12	125.24	Singlete
10	149.45	Singlete
4	142.31	Singlete
21	170.35	Singlete
18	70.85	Triplete

The DQA structures have C_1 symmetries and 66 normal vibration modes, all active in the infrared and Raman spectra. Figs. 2 and 3 show the registered infrared and Raman spectra for the compound in the solid phase. The assignment of the experimental bands to the expected normal vibration modes were made on the basis of PED in terms of symmetry coordinates, and by taking into account the corresponding assignment of related molecules [5,29–37]. Tables 4, S7 and S8 shows the experimental and calculated frequencies, potential energy distribution based on the 6-31G* basis set, and assignment for the C_I and C_{II} structures of DQA. The observed broad band in the IR spectrum of the solid sample with several shoulders between 2800 and 1900 cm^{-1} are probably attributed to the N—H and O—H hydrogen bondings formed by the spatial arrangement of molecules in the lattice crystal, as observed in the molecular packing of the 2-(2′-furyl)-1*H*-imidazole [23], 2-(2′-furyl)-4,5-1*H*-dihydroimidazole [26] and tolazoline hydrochloride molecules [35,36]. Here, B3LYP/6-31G* calculations were considered because the used scale factors are defined for this basis set. The SQM force fields for this compound can be obtained upon request. Below, we discuss the assignment of the most important groups.

4.5.1. Assignments

4.5.1.1. OH modes. The bands in the IR spectra at 3952 and 3448 cm^{-1} are assigned to the O—H stretching vibrations of both conformers, in accordance with the values reported for similar molecules [30,32–34]. The width and shape of the latter band clearly shows the typical spectroscopic signature of an H-bond interaction. In accordance with the reported value for benzoic acid [33,34] and with theoretical calculations, the corresponding deformation modes of this group are assigned to the strong IR bands at 1455 and 1342 cm^{-1}, for the C_I and C_{II} conformers, respectively. The out-of-plane deformation mode (τOH or γOH) is assigned for the C_I conformer to the strong band in Raman spectrum at 75 cm^{-1} whereas, for the C_{II} conformer, it is assigned to the very weak band in the same spectrum at 419 cm^{-1}, as can be seen in the 4-hydroxybenzoic acid dimer [30].

4.5.1.2. CH modes. The C—H stretching modes can be clearly assigned, due to their positions, to the group of bands in the 3125–3041 cm^{-1} region of the IR and Raman spectra. The in-plane deformation modes of the quinoline ring are assigned to the bands at 1580, 1491, 1455, 1237 and 1214 cm^{-1}, as observed in similar compounds [30–32,36]. On the other hand, the four expected out-of-plane deformations of C—H group for the two conformers of DQA are assigned to the IR and Raman bands located at 1002, 949, 874 and 818 cm^{-1}, as observed in Table 5.

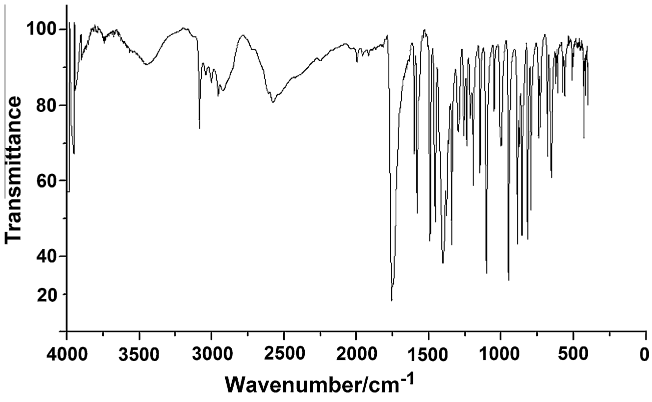


Fig. 2. Experimental infrared spectrum of the solid (5,7-dichloro-quinolin-8-yloxy) acetic acid in KBr pellets.

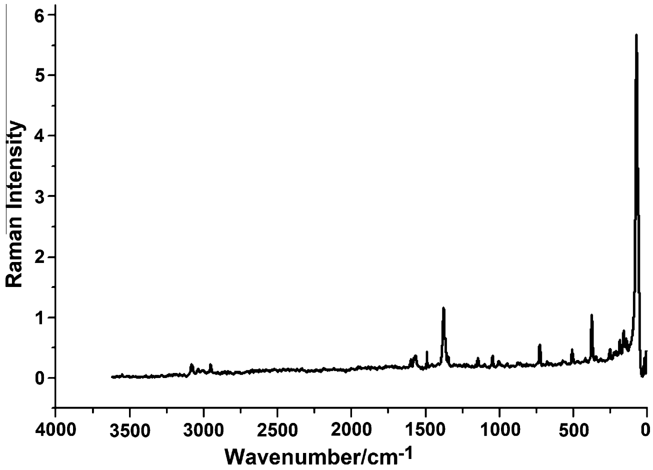


Fig. 3. Experimental Raman spectrum of the solid (5,7-dichloro-quinolin-8-yloxy) acetic acid in a glass capillary.

4.5.1.3. CH_2 modes. The IR bands at 3002 and 2956 cm^{-1} are assigned to the antisymmetric and symmetric stretching modes of this group in agreement with similar compounds [25,32]. The scissoring modes for both conformers of DQA can be assigned to the strong IR band at 1491 cm^{-1}. The IR bands at 1342 and 1256 cm^{-1} are assigned to the wagging modes of this group, as predicted by calculation, while the strong bands and the shoulder at 1455 and 1362 cm^{-1} are respectively assigned to the rocking modes. The twisting mode for both conformers are associated with the weak IR band at 1048 cm^{-1} as observed in similar compounds [5,6].

4.5.1.4. COO modes. As predicted by calculations, the expected C═O stretching modes for both conformers are assigned at 1754 cm^{-1} [5,6] while the C—O stretching modes are clearly assigned to the IR bands at 1342 and 1144 cm^{-1} for the C_I and C_{II} conformers, respectively. Theoretical calculations for 4-hidroxybenzoic acid dimer predict [30] the two γ(COO) modes at 772 cm^{-1}, whereas the two δ(COO) modes are predicted at 771 and 620 cm^{-1}. Here, the modes for the C_I and C_{II} conformers are predicted at different wavenumbers, hence the IR bands at 655 and 610 cm^{-1} are associated with the δ(COO) modes, while the IR band at 562 cm^{-1} is assigned to the γ(COO) modes, as observed in Table 5. The rocking modes of COO groups for the C_I and C_{II} conformers are predicted at 470 and 264 cm^{-1}, as in similar compounds [30,33,34]; hence, they are assigned respectively to the IR and Raman bands at 475 and 254 cm^{-1}. The SQM clearly predicts the twisting modes between 121 and 38 cm^{-1}, for this reason, only the first mode was assigned to the Raman band at 121 cm^{-1}.

4.5.1.5. Skeletal modes. In this compound, the skeletal stretching modes are predicted to be strongly mixed (Tables 4, S7 and S8). In accordance with the values reported for similar molecules [30,32,36] and at our theoretical results, the strong IR bands at 1754, 1600 and 1580 cm^{-1} are mainly associated with the C═C stretching modes, while the IR bands at 1402, 1375, 1256, 1237, 1101, 857 and 681 cm^{-1} are associated with the C—C stretching modes, as observed in Table 4. The strong IR band at 1455, 1362, 1342 and 1296 cm^{-1} are associated with the C—N stretching modes, while the IR bands at 742 and 403 cm^{-1} and the Raman band at 378 cm^{-1} are assigned to the C—Cl stretching modes for both conformers, as observed in (5-Chloro-quinolin-8-yloxy) acetic acid [6]. On the other hand, the six quinoline ring deformations and torsions are assigned to the expected regions, as observed in similar molecules [5,6,32–34]. Finally, the butterfly modes are

Table 4
Observed and calculated wavenumbers (cm^{-1}) and assignment for the (5,7-dichloro-quinolin-8-yloxy) acetic acid.

Experimental[a]		C$_{I}$		C$_{II}$	
IR solid	Raman solid	SQM[b]	Assignment	SQM[b]	Assignment
3952 m				3715	ν(O23—H24)
3938 w					
3448 w, br		3309	ν(O23—H24)		
3125		3243	ν(C13—H15)	3244	ν(C13—H15)
		3235	ν(C2—H8)	3233	ν (C2—H8)
3084 w	3081 vw	3220	ν(C1—H7)	3214	ν(C1—H7)
3041 vw	3038 vvw	3190	ν(C5—H11)	3169	ν(C5—H11)
3002 vw	3005 vvw	3152	ν_aCH$_2$	3126	ν_aCH$_2$
2956 w	2958 vw	3075	ν_sCH$_2$	3069	ν_sCH$_2$
1754 vs		1865	ν(C21—O22)	1898	ν(C21—O22)
1754 vs		1657	ν(C1—C2); ν(C2—C3)	1658	ν (C1—C2); ν(C2—C3)
1600 s	1601 vw	1629	ν(C13—C9)	1630	ν(C13—C9)
1580 s	1581 vw	1613	ν(C12—C10)	1608	ν(C12—C10)
1580 s	1570 vw	1537	βC1—H7	1540	βC1—H7
1491 s		1507	δCH$_2$	1500	δ CH$_2$
1491 s	1492 vw	1491	βC5—H11	1483	βC5—H11
1455 s		1440	δOH	1437	ρCH$_2$
1455 s		1431	βC13—H15	1435	ν(C5—N16)
1402 s	1415 vw	1419	ν(C10—C4)	1413	ν(C10—C4)
1402 s		1392	ν(C3—C4)		
1375 s	1380 m			1380	ν(C3—C9)
1362 w	1369 w	1370	ρCH$_2$		
1362 w	1346 vw			1332	ν(C4—N16)
1342 s		1329	ν(C4—N16)	1320	δOH
1342 s		1310	ν(C21—O23)	1310	wag CH$_2$
1296 w		1273	ν(C5—N16)	1277	ν(C10—O17)
1256 w		1266	wag CH$_2$	1260	ν(C13—C12)
1237 m		1243	ν(C13—C12)		
1237 m		1231	ν(C3—C9)	1233	βC13—H15
1214 w		1175	βC2—H8	1177	βC2—H8
1144 m	1148 vw			1168	ν(C21—O23)
1101 s		1128	ν(C10—O17)	1139	ν(C18—O17)
1101 s		1076	ν(C1—C5)	1078	ν(C1—C5)
1048 w				1060	βR$_1$ (A2)
1048 w	1049 vw	1032	τwCH$_2$	1032	τw CH$_2$
1002 m		1016	ν(C18—O17)		
1002 m	1009 vw	1004	γC2—H8	1000	γC2—H8
949 s		977	γC5—H11	968	γC5—H11
949 s	951 vw	960	βR$_1$(A1)	959	βR$_1$ (A1)
884 s		896	βR$_1$(A2)	894	βR$_1$ (A2); ν(C12—Cl14); βR$_3$ (A2); βR$_3$ (A1)
874 m	877 vw	885	γC13—H15	887	γ C13—H15
857 s	861 vw	879	ν (C18—C21)	870	ν(C18—C21)
818 s		827	τR$_1$ (A2)	823	γC2—H8
818 s		811	γC1—H7		
795 m		796	γC10—O17	789	τR$_1$ (A2)
742 w		746	ν(C9—Cl6)	747	βR$_2$ (A1)
730 w	729 w	740	βR$_2$ (A2); βR$_3$ (A2); βR$_2$ (A1)		
681 m	678 vw	694	γC12—Cl14	712	ν(C3—C4)
681 m				700	δCCO
655 m		659	δCOO	662	τR$_1$ (A1)
623 vw		632	βR$_3$ (A2)		
610 w		619	τR$_1$ (A1)	618	δCOO
610 w				609	γC9—Cl6
575 w	575 vw	584	βR$_2$ (A2)	587	βR$_2$ (A2)
562 w		560	γCOO	567	γCOO
533 vw	511 w	518	τR$_2$ (A1)	516	γC12—Cl14
508 vw		513	βR$_3$ (A1)		
502 vw				501	βR$_3$ (A2)
489 vw				485	βR$_3$ (A1)
475 vw		470	ρ COO		
429 m		438	τR$_3$ (A2)	434	τR$_3$ (A2)
417 w	419 vw	422	γC9—Cl6	426	τOH
403 w				399	ν(C9—Cl6)
	378 m	374	ν (C12—Cl14)		
	378 m			369	ν(C12—Cl14)
	349 vw	346	βR$_2$ (A1)	349	γC10—O17
		309	ρC10—O17	291	δCOC
	254 w	252	δCCO	264	ρCOO
	254 w	240	Butt	244	ρC10—O17
	227 vw	220	βC9—Cl6	234	Butt
	212 vw			211	βC9—Cl6
	188 w	203	δCOC	193	βC12—Cl14

(continued on next page)

Table 4 (*continued*)

Experimental[a]		C_I		C_{II}	
IR solid	Raman solid	SQM[b]	Assignment	SQM[b]	Assignment
	162 w	182	βC12—Cl14		
	145 w	143	τR_2 (A2)	143	τCCOC
	121 w	121	τwCOO	124	τR_2 (A2)
	75 vs	99	τ OH	75	τR_2 (A1)
	75 vs	77	τCCOC		
		51	τR_3 (A1)	53	τR_3 (A1)
				38	τwCOO
	20 vw	28	τwRing	10	τw Ring

Abbreviations: ν, stretching; β, deformation in the plane; γ, deformation out of plane; wag, wagging; τ, torsion; $β_R$, deformation ring τR, torsion ring; ρ, rocking; $τ_w$, twisting; δ, deformation; Butt, butterfly; a, antisymmetric; s, symmetric; A1, Ring 1; A2, Ring 2.

[a] This work.

[b] B3LYP/6-31G*.

Table 5

Comparison of scaled internal force constants for the two conformers of (5,7-dichloro-quinolin-8-yloxy) acetic acid.

B3LYP/6-31G*							
Force constant	(5,7-Dichloro-quinolin-8-yloxy) acetic acid[a]		(5-Chloro-quinolin-8-yloxy) acetic acid[b]			2-(Quinolin-8-yloxy) acetic acid[c]	
	C_I	C_{II}	C_I	C_{II}	C_{III}	C_I	C_{II}
f(C=O)	13.65	14.22	13.62	14.16	14.10	12.53	13.07
f(C—O)	6.36	6.08	6.33	5.93	6.15	6.73	5.50
f(O—H)	6.10	7.73	6.11	7.71	7.65	5.55	7.10
f(C—H2)	5.34	5.29	5.31	5.23	5.10	4.87	4.80
f(C—H)	5.69	5.67	5.68	5.67	5.66	5.17	5.16
f(C—Cl)	3.65	3.61	3.51	3.49	3.42		
f(C—N)	7.89	7.76	7.90	7.77	7.84	7.26	7.12
f(C—C)	6.65	6.61	6.65	6.59	6.61	6.22	6.17
f(O=C=O)	1.34	1.23	1.33	1.24	1.26	1.33	1.23
f(H—C—H)	0.91	0.83	0.91	0.87	0.88	0.84	0.80
f(C—O—H)	1.06	0.79	1.01	0.79	0.77	0.91	0.70
f(C—O—C)	0.94	1.60	0.99	1.16	1.46	0.98	1.18

Units are mdyn $Å^{-1}$ for stretching and stretching/stretching interaction and mdyn Å rad^{-2} for angle deformations.

[a] This work.

[b] Anhydrous from Ref. [6].

[c] Anhydrous from Ref. [5].

assigned to the weak Raman bands at 254 and 227 cm^{-1}, as observed in Table 4.

4.6. Force field

The calculated force constants for the two DQA's conformers were calculated by means of Pulay et al. [7–9] scaling procedure together with the MOLVIB program [19,20] and they can be seen in Table 5 compared with the corresponding values for the (5-chloro-quinolin-8-yloxy) acetic acid [6] and 2-(quinolin-8-yloxy) acetic acid [5]. The analyses show that in both chloro compounds all values are approximately the same with the exception of the *f*(C—Cl) force constant that is higher in DQA than in (5-chloro-quinolin-8-yloxy) acetic acid [6]. The lower C—Cl distance in DQA justifies a higher value in the *f*(C—Cl) of this compound related to (5-chloro-quinolin-8-yloxy) acetic acid [6]. On the other hand, the presence of the Cl atoms slightly increases the force constant values as compared with the 2-(quinolin-8-yloxy) acetic acid [5] in relation to the other ones.

4.7. HOMO–LUMO energy gap

The frontier molecular HOMO and LUMO orbitals play an important role in the reactivity of the compounds and in many properties [37]. Here, those orbitales were calculated for DQA and compared with the corresponding values for the (5-chloro-quinolin-8-yloxy) acetic acid, as observed in Table S9. The results show that both orbitals are mainly localized on the rings, indicating that the HOMO–LUMO are mostly the π-antibonding-type orbitals and that the values of the energy separation between those orbitals are higher in the (5-chloro-quinolin-8-yloxy) acetic acid than in DQA. This large HOMO–LUMO gap for the (5-chloro-quinolin-8-yloxy) acetic acid automatically means high excitation energies for many excited states, good stability and high chemical hardness. For these reasons, the presence of other Cl atom in DQA increases the reactivity as compared with the (5-chloro-quinolin-8-yloxy) acetic acid.

5. Conclusions

The (5,7-dichloro-quinolin-8-yloxy) acetic acid was synthesized and characterized by infrared, Raman and NMR spectroscopic techniques. The presence of C_I and C_{II} conformers was detected in both spectra, and a complete assignment of the vibrational modes was accomplished. Two stable conformers for the DQA in the gas phase were determined by B3LYP/6-31G* and B3LYP/6-311++G** calculations. The SQM/B3LYP/6-31G* force fields were obtained for both structures of DQA and also for the force constants for the stretching and deformation modes. The NBO and AIM analyses confirm the presence of H bonds in the C_I conformer of DQA. The presence of two Cl atoms in the quinoline ring increases the molecule reactivity as compared to the (5-chloro-quinolin-8-yloxy) acetic acid.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.molstruc.2012.03.013.

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