

DFT studies on tautomeric preferences. Part 3: Proton transfer in 2-(8-acylquinolin-2-yl)-1,3-diones

Robert Dobosz · Borys Ośmiałowski ·
Ryszard Gawinecki

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Abstract 8-Acetyl- and 8-benzoyl-2-(quinolin-2-yl) derivatives of 1,3-diketones were studied from point of view of their tautomeric preferences. Effective electron delocalization and strong hydrogen bonds were found to be responsible for high stability of the enaminone form (the most stable tautomer). Density functional theory (DFT) calculations prove that enolimine and ketimine species are less favored. Contribution of the zwitterionic resonance structures to the enaminone form is most significant in 2-(quinolin-2(1*H*)-ylidene)-2*H*-indene-1,3-dione derivatives. Formation of the bifurcated hydrogen bonds was found to take place only in 8-acetyl derivatives. One of these bonds is of the RAHB (Resonance Assisted Hydrogen Bond) type. There is a steric interaction of the pyridine β -hydrogen and carbonyl oxygen atoms in the enaminone tautomers.

Keywords 1,3-Diketones · Quinolines · Tautomerism · Hydrogen bond · Electron delocalization

Introduction

1,3-Dicarbonyl compounds are usually in equilibrium with the respective ketoenol forms [1]. Their 2-(quinolin-2-yl) derivatives may also equilibrate with the enaminone and enolimine tautomers (Scheme 1) [2]. Some of these compounds, shortly called phthalones, reveal the complexing,

semiconductive, antiinflammatory, and anesthetic properties [3–7] and are widely used as yellow to red pigments [2, 8]. 8-Acyl derivatives of 2-(quinolin-2-yl)-1,3-diketones seem even more interesting. Carbonyl oxygen atom of the 8-acyl group may act as the hydrogen bond acceptor (such bond is expected to stabilize the respective tautomeric species). Basic properties of the said oxygen atom may finally enable formation of the new enolimine tautomer **O''** (Scheme 2). It would be interesting to see if the 8-acyl group in such compounds affects their properties significantly. This requires the results of Density functional theory (DFT) calculations for 2-(quinolin-2-yl)-1,3-diketones (Scheme 1) to be compared with these for their 8-acyl derivatives (Scheme 2). Such a procedure was found recently very efficient in studies on tautomeric preferences [9–11]. Substituents present in the considered tautomers are specified in Scheme 3 (only selected tautomer is shown). Numbering of hydrogens originates from this used for the attached heavy atoms.

Computational details

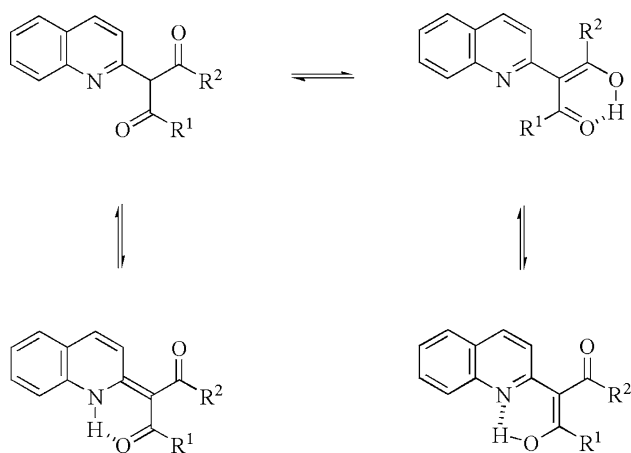
Full geometry optimizations have been carried out using Gaussian software package [12]. Computations for the isolated molecules (no intermolecular interactions were considered) were performed at the B3LYP/6-31 + G(2d,p) level of theory [13, 14]. Frequencies were calculated to make sure that geometry is in minimum (no imaginary frequencies).

Results and discussion

It is known [15] that geometries of the extremely unstable species cannot be optimized by the Gaussian procedure

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R. Dobosz · B. Ośmiałowski · R. Gawinecki (✉)
Department of Chemistry, University of Technology and Life Sciences, Seminaryjna 3, 85-326 Bydgoszcz, Poland
e-mail: gawiner@utp.edu.pl

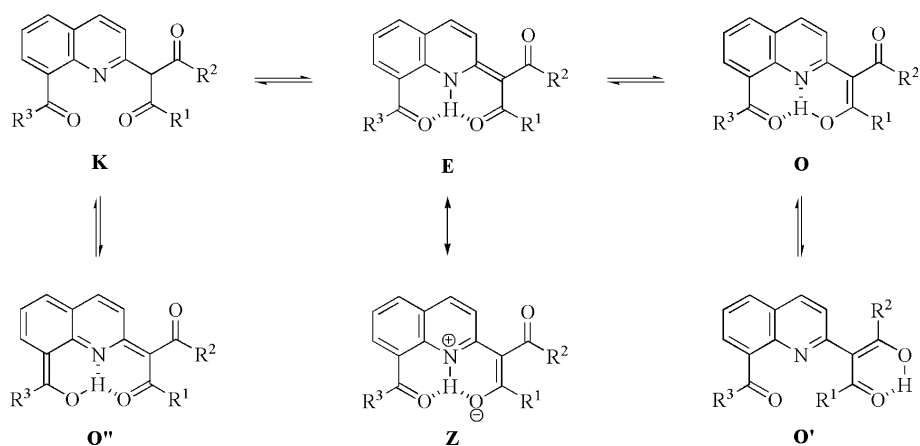


Scheme 1 Tautomeric equilibria between 2-quinolin-2-yl-1,3-diones and their tautomers

(during optimization such systems are automatically transformed into more stable ones). This was found to be the case for all **O''** tautomers (Scheme 2). The calculated energies (Table 1) show that of all tautomers, enaminone (**E**) is always most stable. Effective electron delocalization and double strong hydrogen bonds seem responsible for its stability. Although such effects are expected to be present in the enolinone (**O**) molecules as well, these species are energetically less favored than **E**. Electron delocalization in the **K** tautomers (Scheme 2) is less effective than in **E** and **O**. Moreover, the **K** form is not stabilized by the intramolecular hydrogen bonds. Preliminary calculations show that solvent (chloroform) has minor effect on tautomeric preferences.

The enaminone (**E**) tautomers are expected to be contributed with the zwitterionic (**Z**) resonance structures (Scheme 2) [2]. Extent of this phenomenon can be determined by analysis of the C2–C11 and C11–C12 bond lengths (Table 2). Keeping in mind that lengths of the typical $C(sp^2)–C(sp^2)$ and $C(sp^2)=C(sp^2)$ bonds are equal to 148 and 132 pm, respectively [16], one can see that

Scheme 2 Tautomeric equilibria between 2-(8-acylquinolin-2-yl)-1,3-diones and their tautomers



A

B

Series	Compound	R ¹	R ²	R ³ CO
A	1	1,2-phenylene		H
B	2	1,2-phenylene		acetyl
B	3	1,2-phenylene		benzoyl
A	4	1,8-naphthylene		H
B	5	1,8-naphthylene		acetyl
B	6	1,8-naphthylene		benzoyl
A	7	2,2'-biphenylene		H
B	8	2,2'-biphenylene		acetyl
B	9	2,2'-biphenylene		benzoyl
A	10	phenyl	phenyl	H
B	11	phenyl	phenyl	acetyl
B	12	phenyl	phenyl	benzoyl

Scheme 3 Formulas of the compounds studied

C2–C11 bonds in the compounds studied are considerably double by character (Table 2). It is significantly longer in phthalones (**1E–3E**). On the other hand, C11–C12 bonds in **1E–3E** are in general shorter than these in other compounds studied. Thus, contribution of the zwitterionic structure **Z** in **1E–3E** is higher than in **4E–12E**. The strain in the five membered ring of **1E–3E** is probably responsible for such a behavior. The 8-acyl group shortens and lengthens the C2–C11 and C11–C12 bonds, respectively. This results in lowering of contribution of the zwitterionic enaminone structure for **2E, 3E, 5E, 6E, 8E, 9E, 11E, and 12E**.

Length of the C11–C12 bond (Table 2) is only slightly affected by R¹, R² and R³. On the other hand, the C12–O14

Table 1 Calculated (B3LYP/6-31 + G(2d,p)) relative (with respect to the E form) energies [kJ/mol] of different tautomers

	O (O')	K
1	30.34	66.11
2	34.39	68.54
3	29.93	65.03
4	10.40	74.28
5	11.22	68.75
6	7.99	69.55
7	9.40	56.15
8	13.07	51.43
9	8.76	50.61
10	10.91 (20.68)	22.03
11	16.12 (20.85)	30.69
12	10.52 (19.32)	20.01

Absolute energies of all tautomeric forms are available in the supporting informations

bond in phthalones (**1E**–**3E**) is considerably shorter than in other enaminones. Geometry of the five membered ring in **1E**–**3E** is probably responsible for this unique character. For the same reason, the H1...O14 hydrogen bond in phthalones (**1E**–**3E**) is considerably longer (more weak) than in other enaminone tautomers. In **1E**, **4E**, **7E**, and **10E** it is much stronger (shorter) than in the respective 8-acyl derivatives. Formation of the H1...O17 hydrogen bond in 8-acetyl derivatives **2E**, **5E**, **8E**, and **11E** results in a decrease of C9N1H1 valence angle as compared to this in **1E**, **4E**, **7E**, and **10E** (Table 2). In most of 8-benzoyl-substituted enaminones it is higher than in 8-acetyl

derivatives (Table 2). Moreover, the N1H1O17C16 dihedral angle in the former compounds (Table 2) show this moiety to be nonplanar. Thus, bifurcated O17...H1...O14 hydrogen bond seems to be present only in the molecules of 8-acetyl derivatives.

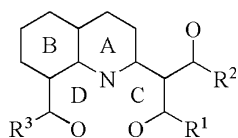
Geometry optimization shows that the C2C11C12O14 moiety in the molecules of **1E**–**6E** is practically planar (see C2C11C12O14 dihedral angle in Table 2). It is not the case for the other enaminones studied. The C9C8C16O17 moiety in the molecules of **2E**, **5E**, **8E**, and **11E** (acetyl derivatives) is more or less planar (see C9C8C16O17 dihedral angle in Table 2). On the other hand, steric interaction of the *ortho* hydrogen atom in the benzoyl moiety with H7 seems to be responsible for its considerably twisting around the C8–C16 bond in **3E**, **6E**, **9E**, and **12E**. Values of the N1H1O14C12 dihedral angle (Table 2) show that the N1H1O14C12 fragment in numerous enaminones (**E**) studied is not planar.

C2C11C13O15 and C3H3O15C13 moieties in the molecules of **1E**–**6E** are planar or almost planar (see the C2C11C13O15 and C3H3O15C13 dihedral angles in Table 2). On the other hand, significant twist around the C11–C13 bond can be seen in **7E**–**12E**. The H3...O15 distances (Table 2) show that these two atoms may sterically interact with each other [2] in all compounds studied. This effect seems to be less significant in **1**, **4**, **7**, and **10**.

Proton transfer affects delocalization of π electrons in the molecule. Aromaticity measures are known to be helpful to show how effective these changes are [9–11]. The HOMA index (harmonic oscillator model of aromaticity) is based on the bond lengths in the molecule

Table 2 Selected calculated (B3LYP/6-31 + G(2d,p)) bond lengths and interatomic distances [pm] as well as valence and torsion angles [deg] in the enaminone tautomers

	1E	2E	3E	4E	5E	6E	7E	8E	9E	10E	11E	12E
N1–H1	103.1	103.2	102.9	105.2	104.4	104.9	104.7	103.9	104.2	104.1	103.4	103.6
C2–C11	140.2	139.6	139.7	143.9	143.2	143.5	143.3	142.2	142.7	142.3	141.0	141.6
C11–C12	145.0	146.1	145.8	144.9	145.9	145.4	144.5	145.6	145.2	144.8	146.2	145.6
C11–C13	146.4	147.0	146.7	146.7	147.3	146.9	147.8	148.1	147.8	148.9	149.2	149.0
C12–O14	124.0	122.9	123.1	126.0	124.5	125.3	125.8	124.1	124.8	125.6	124.0	124.7
C13–O15	122.5	122.6	122.6	123.7	123.7	123.7	122.8	122.7	122.8	122.9	122.9	122.9
H1...O14	183.4	201.9	196.1	156.6	168.8	160.4	158.9	173.8	165.0	164.1	181.8	171.1
H1...O17	–	191.9	207.5	–	200.5	234.1	–	197.8	227.4	–	195.5	222.4
H3...O15	232.5	220.4	223.7	203.0	195.8	200.6	210.1	205.2	205.8	219.1	215.6	216.0
C9N1H1	121.2	117.8	116.1	122.7	120.2	122.3	122.6	119.5	121.7	122.1	118.6	121.1
C2C11C12O14	0.0	0.0	–0.7	0.0	0.0	–1.8	7.0	–9.7	–10.7	13.1	18.1	–16.1
C9C8C16O17	–	0.0	29.0	–	0.0	41.6	–	1.2	39.2	–	–4.7	37.1
C2C11C13O15	0.0	0.0	1.3	0.0	0.0	2.2	35.1	–35.7	–32.9	45.5	46.5	–45.3
N1H1O14C12	0.0	0.0	9.8	–0.1	0.0	–2.8	–3.3	2.8	12.6	1.7	6.9	5.6
N1H1O17C16	–	0.0	38.6	–	0.0	–53.8	–	2.8	53.8	–	–4.8	48.8
C3H3O15C13	0.0	0.0	0.8	0.0	0.0	8.1	30.6	–30.4	–24.5	40.3	43.1	–38.9

Table 3 HOMA values (B3LYP/6-31 + G(2d,p)) for studied systems

	(Quasi)ring			
	A	B	C	D
1E	0.71	0.91	0.69	–
1O	0.79	0.82	0.71	–
1K	0.83	0.79	–1.77	–
2E	0.67	0.85	0.56	0.11
2O	0.77	0.73	0.75	–0.06
2K	0.82	0.76	–1.80	–0.21
3E	0.68	0.87	0.60	0.05
3O	0.78	0.78	0.73	–0.07
3K	0.82	0.79	–1.77	–0.18
4E	0.75	0.90	0.58	–
4O	0.80	0.83	0.40	–
4K	0.81	0.81	–1.82	–
5E	0.70	0.83	0.51	0.04
5O	0.77	0.74	0.44	–0.09
5K	0.81	0.77	–1.81	–0.18
6E	0.73	0.87	0.56	–0.06
6O	0.79	0.80	0.41	–0.10
6K	0.81	0.80	–1.82	–0.21
7E	0.73	0.91	0.65	–
7O	0.79	0.84	0.39	–
7K	0.82	0.80	–1.85	–
8E	0.67	0.85	0.57	0.07
8O	0.77	0.76	0.47	–0.08
8K	0.81	0.77	–1.76	–0.22
9E	0.70	0.88	0.60	–0.03
9O	0.78	0.81	0.43	–0.11
9K	0.81	0.79	–1.74	–0.20
10E	0.70	0.92	0.67	–
10O	0.78	0.84	0.44	–
10K	0.82	0.81	–1.85	–
11E	0.64	0.86	0.55	0.10
11O	0.76	0.76	0.53	–0.08
11K	0.81	0.78	–1.82	–0.25
12E	0.67	0.88	0.61	0.00
12O	0.77	0.81	0.48	–0.11
12K	0.82	0.80	–1.88	–0.19

[17, 18]. It is equal to *zero* for a model non-aromatic system, e.g., Kekulé benzene, and to *one* for the system with all bonds equal to the optimal value assumed to be realized for fully aromatic systems (the higher HOMA

value, the more aromatic is the ring in question, and hence, more delocalized the π electrons of the system). The HOMA values for the ring A in the enaminone molecules are equal to 0.64–0.75 (Table 3). This parameter was found to be higher for the ketimino and enolimino tautomers (~ 0.78 and ~ 0.80 , respectively). The HOMA values show ring A in the **K** and **O** forms to be highly aromatic. On the other hand, significant contribution of the zwitterionic structure is probably responsible for the relatively high aromaticity of this ring in the enaminone (**E**) tautomers. Relatively high aromaticity of the quasi-ring C in these compounds (Table 3) prove intramolecular hydrogen bond H1...O14 in their molecules to be of RAHB (Resonance Assisted Hydrogen Bond) type [19–22]. On the other hand, the H1...O17 interaction in these tautomers has quite different character. Geometry optimization (see the respective HOMA values in Table 3) shows that electrons in the quasi-ring D are not delocalized.

Conclusions

DFT calculations show that among numerous tautomers of 8-acyl-2-(quinolin-2-yl)-1,3-diketones, enaminone is the most stable form. The acyl group was found to decrease contribution of its zwitterionic resonance structure. This effect is also dependent on steric requirements in the ring dione moiety. Bifurcated C=O...H...O=C hydrogen motif is expected to appear only in the molecules of 8-acetyl derivatives. Calculated aromaticity indexes prove that two intramolecular hydrogen bonds in the compounds studied differ from the point of view of their character: only one of them is of RAHB (Resonance Assisted Hydrogen Bond) type.

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