Available online at www.sciencedirect.com
ScienceDirect
Tetrahedron
Tetrahedron 63 (2007) 9172–9178

Tautomeric preferences of phthalones and related compounds

Robert Dobosz,[a] Erkki Kolehmainen,[b] Arto Valkonen,[b] Borys Ośmiałowski[a] and Ryszard Gawinecki[a,*]

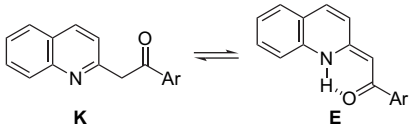
[a]*Department of Chemistry, University of Technology and Life Sciences, Seminaryjna 3, PL-85-326 Bydgoszcz, Poland*
[b]*Department of Chemistry, University of Jyväskylä, PO Box 35, FIN-40014 Jyväskylä, Finland*

Received 5 March 2007; revised 5 June 2007; accepted 21 June 2007
Available online 27 June 2007

Abstract—Multinuclear magnetic resonance and IR spectra prove that although 2-(diacylmethyl)pyridines and 2-(diacylmethyl)quinolines are β-diketones, their proton transfer product present in chloroform solution is not ketoenol but enaminone (earlier opinions were contradictory). Quinoline derivatives are less zwitterionic by character than the respective pyridyl congeners. The β-diketone form itself may also be rarely present in the solution. X-ray data show that 2-(2(1*H*)-pyridinylidene)-1*H*-indene-1,3(2*H*)-dione, i.e., enaminone tautomer of 2-(pyridin-2-yl)-2*H*-indene-1,3-dione, is also the only form present in crystal. Ab initio calculations show that the enaminone is usually more stable than other tautomeric forms. Values of geometry based aromaticity index HOMA (harmonic oscillator model of aromaticity) confirm that the zwitterionic structure really contributes to the enaminone forms detected.

1. Introduction

In chloroform solution, 2-phenacylquinolines (**K**) are in equilibrium with (*Z*)-1,2-dihydro-2-benzoylmethylenequinolines (**E**) (Scheme 1).[1] Since proton exchange between **K** and **E** is relatively slow, one may observe separate signals for each tautomer in the NMR spectra.[1,2]



K **E**

Scheme 1.

2-(Diacylmethyl)pyridines may be considered as 2-(pyridin-2-yl)-1,3-diketones. Although 1,3-dicarbonyl compounds (**K**) are usually in equilibrium with their ketoenol forms (**O**),[3] solutions of their pyridyl derivatives may also contain the enaminone tautomer **E** (Scheme 2).

Opinions about the structure of the condensation product of phthalic anhydride with 2-methylpyridine and 2-methylquinoline are quite divergent. Thus, in solution the former (**1** in Scheme 2) is believed to have a structure **O**,[4–8] **Z** (a resonance form of **1E**)[9–11] or **O** being in tautomeric equilibrium with **E**[12–14] (Scheme 2). On the other hand, X-ray data prove that only **1E**, **1Z** or even **1O** is present in the crystalline state.[10]

The principal aim of the present paper is to clarify which forms are present in solution and in the solid state (crystal) of phthalones and some related compounds, the widely used yellow to red pigments[15,16] that also have interesting biological activities.[15]

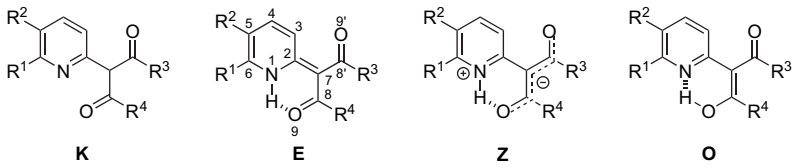
2. Results and discussion

Attempts to prepare the desired compound may result in formation of its more stable tautomer (species of comparable stability equilibrate with each other). The compounds listed in Scheme 2 were obtained by condensation of 2-methylpyridine or 2-methylquinoline with the respective anhydrides. Their melting points were generally in agreement with the literature values. Beckett et al.[17] found that compound **7** melted at 140 and 118 °C when crystallized from ethanol and from the hydrocarbon, respectively. Although these two crystal forms have different IR spectra, their solution UV–vis spectra are identical.[17] These two forms are present not only in the solid state but also in solution, where the preferred form depends upon the solvent.[17] Absorptions at 325 and 370 nm are ascribed to the enaminone (**7E**) and ketoenol (**7O′**) forms, respectively (Scheme 3), but no other data supporting the nature of these tautomers are available.[17]

Crystals of 2-methyl-2-quinolin-2-ylpropiophenones (**K** in Scheme 4), the fixed tautomers of 2-phenacyquinolines, are colorless.[18] On the other hand, (*Z*)-1,2-dihydro-2-

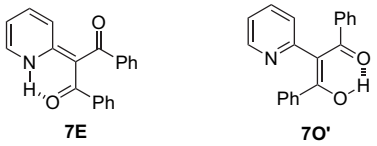
Keywords: Phthalones; Tautomerism; Enaminones; Molecular structure.
* Corresponding author. Tel.: +48 52 3749070; fax: +48 52 3749005; e-mail: gawiner@utp.edu.pl

0040–4020/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2007.06.064



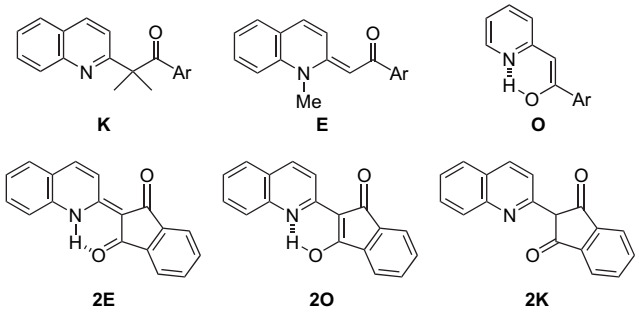
	R^1	R^2	R^3	R^4
1	H	H	1,2-phenylene	
2	benzo		1,2-phenylene	
3	H	H	1,8-naphthylene	
4	benzo		1,8-naphthylene	
5	H	H	2,2'-biphenylene	
6	benzo		2,2'-biphenylene	
7	H	H	Ph	Ph
8	benzo		Ph	Ph

Scheme 2.



Scheme 3.

benzoylmethylenequinolines (**E** in Scheme 1), (*Z*)-1-methyl-1,2-dihydro-2-benzoyl-methylenequinolines (**E** in Scheme 4), and (*Z*) 2-(2-hydroxy-2-phenyl vinyl)pyridines (**O** in Scheme 4) are brightly colored.[1,2,19] Since crystals of quinophthalone are yellow, this compound is expected to have the 2-(2(1*H*)-quinolidene)-1*H*-indene-1,3(2*H*)-dione (**2E**) or 3-hydroxy-2-(quinolin-2-yl)-1*H*-inden-1-one (**2O** in Scheme 4) structure (its tautomeric 2-(quinolin-2-yl)-2*H*-indene-1,3-dione (**2K** in Scheme 4) form is expected to be colorless).



Scheme 4.

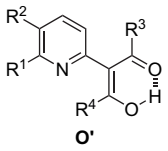
Numerous β-dicarbonyl compounds are susceptible to the proton transfer.[3] The NMR spectroscopy is very useful for identifying which species are present in the tautomeric mixture.[1,2,20–22] Six signals are expected to be present in the 180–210 ppm range of the ^{13}C NMR spectrum of the unsymmetric 1,3-diketone being in equilibrium with two different ketoenol forms. Two of them can be easily assigned to carbonyl C1 and C3 in the diketo form and four to the enol and carbonyl C1 and C3 in two ketoenol forms. Since proton exchange between diketo and ketoenol forms is relatively slow (on the NMR timescale), two signals of the former tautomer in an unsymmetric case are always visible in the spectrum.[23–25] Due to fast proton exchange between the ketoenol forms, only two average signals are seen in the spectrum of unsymmetric β-diketone.[24] It is obvious that only one 'diketo' and only two 'ketoenol' signals should be present in the spectrum of a symmetric β-diketone. One signal in 180–210 ppm range for a symmetric β-diketone proves that its solution contains practically one tautomer: diketo or ketoenol. Although cyclic β-diketones cannot be stabilized by the intramolecular hydrogen bond, four signals can still be seen in the spectrum of unsymmetric cyclic β-diketone: two of them can be assigned to the carbonyl carbon atoms in the diketo form and two to enol and carbonyl carbon atoms in two different ketoenol forms (fast proton exchange takes place between them).[24,26] Unique signal in 180–210 ppm range for symmetric cyclic β-diketone proves that solution contains practically only one tautomer: diketo or ketoenol.[26]

In addition to the C1 and C3 signals, C2 should also be considered when discussing the proton transfer phenomena in 1,3-diketones. Three signals of C2 are expected to be present in the ^{13}C NMR spectrum of unsymmetric β-diketone being in equilibrium with two different ketoenol forms: one for diketo form and two for two different ketoenol forms. Slow proton exchange between diketo form and the ketoenol forms is responsible for the presence of the C2 signal at 52–68 ppm for the diketo form.[23–25] On the other hand, proton exchange between two ketoenol forms is fast on the NMR timescale and this results in the presence of only one average C2 signal at 96–115 ppm in the spectrum of unsymmetric β-diketone.[24,25] One C2 signal for the diketo form[23,25] and one signal for C2 of the ketoenol form[25] are characteristic for the spectra of symmetric β-diketones. Unique signal for C2 in the spectrum of symmetric β-diketone proves that only one tautomeric form (diketo or ketoenol) is practically present in solution.[25] On the other hand, there are still two signals of C2 present in the spectrum of unsymmetric cyclic β-diketones: one for the diketo (at ca.59 ppm[24]) and one for two different ketoenol forms (at ca. 109 ppm[24,26]). If the solution of a symmetric cyclic β-diketone contains practically one tautomer, only one signal (either at 44–60 ppm for the diketo or at 107–112 ppm for the ketoenol form[26]) is present in the spectrum. One

should bear in mind that chemical shift of C7 (for numbering of the positions in the molecule, see Scheme 2) for the enolimine and enaminone tautomeric forms of 2-phenacylpyridines or 2-phenacylquinolines, respectively, vary in the range of 91–97 ppm[2] and 89–90 ppm,[1] respectively.

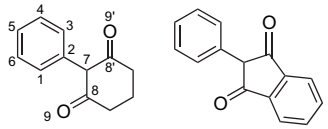
The chemical shift of the enol carbon atom (C1 or C3) in the ^{13}C NMR spectrum of unsymmetric cyclic β-diketone (6,7,8,9-tetrahydro-5*H*-benzocyclohept-5,7-dione) is at 163.70 ppm.[24] It is noteworthy, that a similar value was found for the enol carbon atom (ca. 162 ppm) for the enolimine tautomeric form of 2-phenacylpyridines.[2] The chemical shift of the enol carbon atom for acyclic ketoenol forms of β-diketones is >180 ppm,[24] which is very similar to those of the carbonyl carbon atoms in the spectra of enaminone tautomeric forms of 2-phenacylquinoline (ca. 183 ppm).[1]

The ketoenol form of acyclic 1,3-diketone such as **O′** in Scheme 5 may be stabilized by intramolecular hydrogen bond of the OH···O type. On the other hand, OH···N hydrogen bond can be present in 2-pyridyl substituted ketoenol forms of both cyclic and acyclic 1,3-diketones (see **O**, i.e., enolimine form in Scheme 2). Among the compounds studied in the present paper, only **7** and **8** can have the **O′** form. The presence of a broad singlet at ca. 18 ppm in the ^{1}H NMR spectrum of 4-(quinolin-2-yl)dimedone (R^1/R^2=benzo, R^3/R^4=$CH_2CMe_2CH_2$ in Scheme 2) detected by Yousif et al.[6] shows that **E** is the only form present in chloroform solution.



Scheme 5.

The literature[6] ^{1}H NMR spectrum of 2-phenyl-1,3-cyclohexanedione **9** (Scheme 6) shows that its chloroform solution contains practically only the ketoenol form. The presence of the H7 singlet at 4.34 ppm in the ^{1}H NMR spectrum and integration of the signals shows that solution of 2-phenylindanedione **10** (Scheme 6) in $CDCl_3$ contains only the diketo form.[27] Earlier studies[26] show that there are two important ^{13}C signals in the NMR spectrum of **10** in chloroform: 59.8 ppm (C7) and 198.1 ppm (C8 and C8′). Thus, there is no doubt that only diketo form **10** is present in solution. On the other hand, positions of C7, C8, and C8′ signals at 97.5 ppm, 194.0 ppm, and 190.2 ppm, respectively, present in ^{13}C NMR spectrum of **1** in the same solvent (Table 1) are comparable with those typical for (*Z*)-1,2-dihydro-2-benzoylmethylenequinolines (**E** in Scheme 1): $\delta(^{13}C7)$= 88.9–90.3 ppm, $\delta(^{13}C8)$=181.7–184.9 ppm.[1] Thus, one may conclude that only **1E** form (Scheme 2) is present in solution. It is noteworthy that the same tautomeric form is present in solution of the respective quinoline derivative **2** (99.0 ppm (C7), 194.3 ppm (C8), and 190.2 ppm (C8′) (Table 1)). Two carbonyl carbon signals in the ^{13}C NMR spectra of compounds **1** and **2** (Table 1) confirm that their molecules have the **E** character. Yavari et al.[29] reported that the ^{13}C NMR spectra of **2** recorded at various temperatures show an interesting behavior: some signals coalesce as a result of rotation around the C2–C7 'double' bond in **2E**. This phenomenon is possible due to increased contribution of the zwitterionic structure **2Z** (Scheme 2).[29] As a result of fast rotation and high contribution of the zwitterionic structure, the signals of carbonyl carbon atoms may not be observed in the ^{13}C NMR spectra of quinophthalone recorded at higher temperatures.[29] The presence of only one ^{13}C8′ signal in the NMR spectra of compounds **3**, **4**, and **7** (Table 1) proves that coalescence temperature for them is lower than 303 K (the spectra were recorded just at that temperature). Of course, there are no H7 signals in the ^{1}H NMR spectra of both **1** and **2**. As shown by the chemical shift of H1, **3** and **4** contain the strongest and **1** and **2** the weakest hydrogen bonds, respectively. One may see that ^{1}H1 and ^{15}N1 NMR signals in the spectra of pyridine derivatives **1**, **3**, and **7** are deshielded with respect to those in the spectra of quinoline derivatives **2**, **4**, **6**, and **8**. This suggests that electron density at N1 in **1**, **3**, and **7** is lower than that in **2**, **4**, and **8**, respectively. Thus, one may see that **1**, **3**, and **7** are more zwitterionic by character than **2**, **4**, and **8** (quantitative effect). It seems worthy to mention that benzo annulation of similar compounds may have a qualitative effect on the species present in solution: 2-phenacylpyridines and 2-phenacylquinolines equilibriate with (*Z*) 2-(2-hydroxy-2-phenyl vinyl)pyridines and (*Z*) 1,2-dihydro-2-benzoylmethylenequinolines, respectively.[1,2]



Scheme 6.

Only one or none C8′ signal is seen in the spectra of compounds **3**, **4**, **6**, and **7** (Table 1). One may suppose that increased contribution of the zwitterionic structure such as

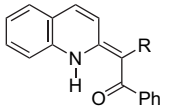
Table 1. Selected experimental NMR chemical shifts (δ) for 0.1–0.2 M solutions of **1–8** in $CDCl_3$ at 303 K

	N1	C2	C7	C8	C8′	C3	H1[b]
1	−221.6	151.3	97.5	194.0	190.2	120.8	14.72
2	−240.0	150.7	99.0	194.3	190.2	118.9	14.13
3	−184.9	155.9	104.4	[a]	182.1	124.6	19.80
4	−204.6	156.2	104.9	[a]	183.6	122.5	19.07
6	−220.0	152.8	112.9	[a]	[a]	120.1	18.10
7	−179.5, −67.0	[a]	105.7	[a]	193.4	120.7	18.04
8	−230.8	154.5	106.2	197.6	192.7	[a]	17.08

[a] Not observed.
[b] Singlet.

2Z (Scheme 2), that enables fast rotation around the C2–C7 bond in their molecules,[29] is responsible for the observed feature of their NMR spectra.

Unexpectedly, the position of the N1 signal in ^{15}N NMR spectrum of (*Z*)-1,2-dihydro-2-benzoylmethylenequinoline (Scheme 7, R=H, $\delta(^{15}N)=-228.7$ ppm[1]) is comparable with that of 1,3-diphenyl-2-(quinolin-2(1*H*)-ylidene)propane-1,3-dione (Scheme 7, R=COPh, $\delta(^{15}N)=-230.8$ ppm (Table 1.)). This shows that (i) no ketimine (**K**) or enolimine (**O**) forms are present in solutions of compounds **1** and **2** (see Scheme 2 to identify the tautomers) and (ii) enaminone (**E**) structure of the tautomer detected is unquestionable. On the other hand, ^{15}N1 signals of **3** and **4** are deshielded when compared with those of **1** and **2**, which shows that electron density at N1 in former compounds is low. Significant zwitterionic character of the former compounds is responsible for the disappearance of one signal of carbonyl carbon atom and shielding of the signal of another carbonyl carbon atom in their spectra (Table 1). The contribution of the zwitterionic structure is extremely high for **3**. When comparing the $\delta(^{15}N1)$ values, one may also see that contribution of the **E** structure in solutions of **2** and **4** is higher than that in solutions of **1** and **3**, respectively. $\delta(^{1}H1)$ values also prove high contribution of the **Z** structure in **3** and **4** ($\delta(^{1}H1)>18$ ppm shows that zwitterionic character of the molecule is significant: positive charge at N1 deshields this proton). $\delta(^{1}H1)<15$ ppm suggests that the molecule has the enaminone character (it is the case for **1** and **2**).

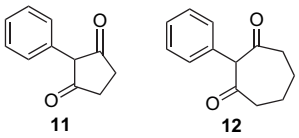


Scheme 7.

^{15}N1 chemical shifts (−179.5 ppm) and ^{13}C7 (−105.7 ppm) of **7** show that the **E** form is present in solution. On the other hand, signals at −67.0 ppm (^{15}N1) and 65.9 ppm (^{13}C7) prove that it contains also the **K** form.[1,2]

Exceptionally large deshielding of N1 in compounds **3** and **7** (see the respective ^{15}N NMR shifts in Table 1) suggests a very low electron density at the nitrogen atom. This significant deshielding of N1 signals in the spectra of **3** and **7** is indicative of a high contribution of the zwitterionic structure to the molecular character of these compounds.

The IR spectra may also help to distinguish the species present in the tautomeric mixture. The 1580–1800 cm^{-1} region seems to be very important in studies on keto–enol tautomerism of β-diketones.[30] Strong bands at 1639 and 1695 cm^{-1} and weak absorption at 1735 cm^{-1} in the IR spectrum of 2-phenyl-1,3-cyclopentanedione **11** (Scheme 8) in 1,2-dichloroethane (there are no other bands in the 1580–1800 cm^{-1} region) prove that ketoenol predominates in solution.[31] On the other hand, only ketoenol form is present in chloroform solution of this compound (it absorbs at 1607 cm^{-1} only).[27] The same tautomer is a major species present in 1,2-dichloroethane solution of 2-phenyl-1,3-cyclohexanedione **9** (Scheme 6) (proved by strong bands at 1630 and 1655 cm^{-1} in its IR spectrum).[31] Weak absorption at 1735 cm^{-1} shows that this solution also contains low amount of the diketo form.[31] On the other hand, Gren et al.[31] found that intensive bands at 1705 and 1732 cm^{-1} and weak absorption at 1609 cm^{-1} in the IR spectrum of 2-phenyl-1,3-cycloheptanedione **12** prove that its 1,2-dichloroethane solution contains the diketo form and an insignificant amount of ketoenol.



Scheme 8.

The presence of the bands at 1600, 1700, and 1720 cm^{-1} in the IR spectrum of chloroform solution of 2-phenylindanedione **10**[28] shows that only diketo form is present there. Chloroform solution of 4-(pyridin-2-yl)dimedone (R^1=H=R^2, $R^3/R^4=CH_2CMe_2CH_2$ in Scheme 2) absorbs at 1625, 1650, 1708, and 1741 cm^{-1}.[32] The presence of the two latter bands shows that the diketo form is present in solution.[32]

Irrespective of **O** (Scheme 2) or **O′** (Scheme 5) character of the ketoenol, similar bands can also be seen in the IR spectra of compounds **1**–**4** and **6**–**8** (Table 2). Conjugation of the ketone carbonyl group with the aromatic part of the molecule is responsible for the absorption at 1670 and 1677 cm^{-1} for **1** and **2**, respectively.[30] The bands at ca. 1710 cm^{-1} for **7** and **6**, and at 1740 cm^{-1} for **3** are the results of symmetric and antisymmetric stretching vibrations in dicarbonyl compounds.[33,34]

X-ray diffraction allows the determination of the molecular structure in the crystal state. The ORTEP plot (Fig. 1) shows that the **1E** tautomer is preferred not only in solution. The bond lengths as well as valence and dihedral angles of the molecule are listed in Table 3. One may see that our data, especially bond lengths, are more or less different from those

Table 2. Positions [cm^{-1}] of C=O stretching bands in the IR spectra of compounds **1**–**4** and **6**–**8** (solutions in chloroform)

1	1630, 1670
2	1627, 1677
3	1637, 1740, 1779
4	1636
6	1634, 1710
7	1620, 1695, 1789
8	1636

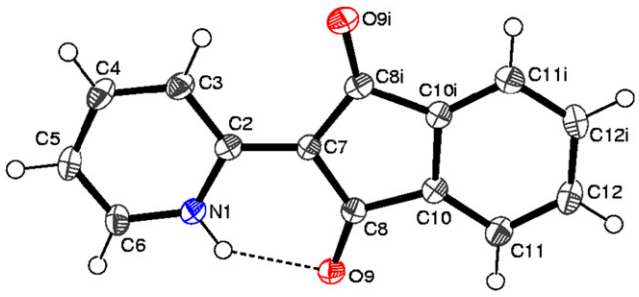


Figure 1. ORTEP-3 plot of the crystal structure of **1E**. The thermal ellipsoids are drawn by 50% probability level.

Table 3. Selected X-ray bond lengths, interatomic distances [pm] and valence and torsion angles [deg] in **1E**

N1–C2	136.4(2)	N1C2C3	116.09(18)	N1C2C3C4	2.2(3)
C2–C3	140.8(3)	C2C3C4	120.60(18)	N1C2C7C8	−1.1(3)
C3–C4	137.2(3)	C3C4C5	120.45(19)	N1C2C7C8′	−176.8(2)
C4–C5	139.9(3)	C4C5C6	118.32(19)	C3C2C7C8	177.4(2)
C5–C6	136.0(3)	C5C6N1	120.50(19)	C3C2C7C8′	1.8(3)
N1–C6	134.4(3)	C6N1C2	124.00(17)	C6N1C2C3	−1.9(3)
C2–C7	141.9(3)	N1C2C7	118.05(16)	C6N1C2C7	176.8(2)
C7–C8	143.3(3)	C3C2C7	125.85(16)	C2N1C6C5	0.3(3)
C7–C8′	144.4(3)	C2C7C8	123.96(16)	N1C6C5C4	1.0(3)
C8–O9	125.0(2)	C2C7C8′	126.97(17)	C7C2C3C4	−176.3(2)
C8′–O9′	123.6(2)	C7C8O9	127.85(18)	O9C8C7C2	3.9(3)
N1–H1	91.1(15)	C7C8′O9′	129.45(18)	O9′C8′C7C2	−0.9(3)
H1···O9	199.5(18)	C8C7C8′	108.96(17)	O9C8C7C8′	−179.8(2)
N1···O9	273.7(2)	N1H1O9	137.50(17)	O9′C8′C7C8	−177.1(2)

measured by Kemme.[10] As expected, the molecule is practically planar, the angle between the planes of the pyridine and indandione ring fragments being 5.75(9)°. C8′–O9′ bond is shorter (it has more double bond character) than C8–O9. The C7–C8 and C7–C8′ bonds are significantly shorter than typical C–C bonds. On the other hand, C2–C7 bond is much longer than typical C=C bonds. Thus, **Z** structure contributes considerably to enaminone form present in the crystal (it is stabilized by the strong intramolecular hydrogen bond).

Geometrical requirements of the five-membered ring in **1E**, rather than number of carbonyl groups in the molecule, are responsible for the length of intramolecular hydrogen bond: H1···O9 distance in **1E** is 5.5–33.5 pm longer than that in (*Z*)-1,2-dihydro-2-benzoylmethylenequinoline (**E** in Scheme 1).[1] The molecules in the dimer are attracted to each other by intermolecular NH···O=C hydrogen bonds.

The bond lengths of tautomeric forms can be used to estimate the geometry-based aromaticity index HOMA (harmonic oscillator model of aromaticity)[35] defined as in Eq. 1:

$$\mathrm{HOMA} = 1 - \frac{1}{n}\sum_{j=1}^{n} \alpha_i \left(R_{\mathrm{opt},i} - R_j\right)^2 \qquad (1)$$

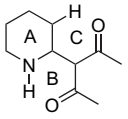
where n represents the total number of bonds in the molecule, α_i is a normalization constant (for CC, CO, and CN bonds α_{CC}=257.7, α_{CO}=157.38, and α_{CN}=93.52, respectively). It is fixed to give HOMA=0 for a model non-aromatic system, e.g., Kekulé structure of benzene and HOMA=1 for the system with all bonds equal to the optimal value $R_{\mathrm{opt},i}$, assumed to be realized for fully aromatic systems. For C–C bonds, $R_{\mathrm{opt,C-C}}$=138.8 pm, for CN bonds $R_{\mathrm{opt,C-N}}$=133.4 and for C–O is $R_{\mathrm{opt,C-O}}$=126.5 pm. The higher the HOMA value, the more aromatic is the ring in question, and hence, more delocalized the π electrons of the system.

HOMA values based on optimized geometries for the ring A (Table 4) in the pyridine and quinoline derivatives of the **E** type are equal to 0.86–0.90 and 0.72–0.76, respectively. Significant contribution of the zwitterionic structure probably results in the relatively high aromaticity of the ring A. Presence of the benzene ring in the quinoline derivatives **2**, **4**, and **8** results in low contribution of the **Z** structure as compared to this in the pyridine derivatives **1**, **3**, and **7**. Effective delocalization of π electrons in the quasiring B in the pyridine and quinoline tautomers **E** (HOMA=0.62–0.73 and 0.61–0.70, respectively) prove that intramolecular hydrogen bond, which stabilizes this form, is of RAHB type (resonance assisted hydrogen bond).[35–39] As proved by the HOMA values, π electrons are also effectively delocalized in the quasiring C of the same tautomers. One may see that HOMA values for rings A, B, and C in **1E** based on X-ray geometries are higher than those based on optimized geometries (Table 4). Thus, the intramolecular interactions in crystal increase the aromatic character of **1E** molecule.

HOMA values for the **K** tautomers based on optimized geometries are also listed in Table 4. The ring A in respective pyridine derivatives is fully aromatic (HOMA=1.00) and this in quinoline derivatives has HOMA=0.84. Quasirings B and C are, of course, non-aromatic both in pyridine and quinoline derivatives **K**.

The calculations show that **5O** and **7O** are slightly more stable than **5E** and **7E**, respectively, and **3O** is only slightly less stable than **3E** (Table 5). The NMR spectral data (Table 1) show, however, that no **O** forms are present in solutions of

Table 4. HOMA values (B3LYP/6-311G(2d,p)) based on optimized geometries for compounds **1–8**



		Ring A	Ring B	Ring C
1	E	0.86 (0.92)[a]	0.73 (0.78)[a]	0.52 (0.67)[a]
	K	1.00	−1.70	−1.69
2	E	0.72	0.70	0.42
	K	0.84	−1.79	−1.75
3	E	0.90	0.62	0.38
	K	1.00	−1.54	−1.54
4	E	0.76	0.61	0.28
	K	0.84	−1.71	−1.75
5	E	0.88	0.64	0.26
	K	1.00	−1.72	−1.75
6	E	0.74	0.66	0.17
	K	0.84	−1.73	−1.82
7	E	0.86	0.68	0.19
	K	1.00	−1.76	−1.77
8	E	0.72	0.68	0.08
	K	0.83	−1.78	−1.86

[a] Values based on X-ray geometries.

Table 5. Calculated (B3LYP/6-311g(2d,p)) relative energies [kJ/mol] in vacuum for different tautomers **1**–**8** (with respect to the **E** form)

	O	K
1	15.82	54.83
2	29.34	70.94
3	0.93	74.58
4	9.78	78.59
5	−0.25	48.47
6	8.83	59.64
7	−0.97	5.12
8	10.27	18.75

3 and **7**. Presence of the low field signal at −67.0 ppm in the ^{15}N NMR spectrum of **7** is not unexpected: since **7K** is only 5.12 kJ/mol less stable than **7E** (Table 5), the former tautomer is present in low amount in chloroform solution.

3. Conclusions

2-(2(1*H*)-Pyridinylidene)-1*H*-indene-1,3(2*H*)-dione with zwitterionic character is the only species present in chloroform solution (it is not contaminated by 2-(pyridin-2-yl)-2*H*-indene-1,3-dione and 3-hydroxy-2-(pyridin-2-yl)-1*H*-inden-1-one). The enaminone form is also the only tautomer found in solutions of the related condensation products of 2-methylpyridine and 2-methylquinoline with 1,8-naphthalic, 2,2′-diphenic and benzoic anhydrides (low amount of 1,3-diphenyl-2-(pyridin-2-yl)propane-1,3-dione was detected only in solution of 1,3-diphenyl-2-(pyridin-2(1*H*)-ylidene)-propane-1,3-dione). The contribution of the zwitterionic structure in 2-(2(1*H*)-pyridinylidene)-1,3(2*H*)-diones is more distinct than the respective quinoline derivatives. 2-(2(1*H*)-Pyridinylidene)-1*H*-indene-1,3(2*H*)-dione is the only tautomer present also in the crystal state. Values of the geometry-based aromaticity index HOMA show that the zwitterionic structure contributes significantly to the character of the enaminone form.

4. Experimental

Anhydrous zinc chloride (0.2 g) was added to a solution of 2-methylpyridine or 2-methylquinoline (0.02 mol) and phthalic, 1,8-naphthalic, diphenic or benzoic anhydride (0.02 mol) in nitrobenzene (25 mL) and the obtained mixture was refluxed for 4–6 h. The contents of the flask were cooled down and the precipitated product recrystallized from ethanol (yield: 36–39%). Melting points are as follows [°C]—**1**: 325–326 (lit. 290–292,[4] 295–296,[40] 286–288[41]), **2**: 241–242 (lit. 242–243,[40] 239–241,[41] 241–242,[42] 238–239[43]), **3**: 262–265 (lit. 268–269[44]), **4**: 254–255 (lit. 254–255,[44] 265–266[42]), **6**: 233–235 (lit. 228–229[47]), **7**: 135–137 (lit. 140,[17] 141.5[45]), **8**: 189–191 (lit. 189–190[46]).

NMR spectra were recorded for 0.1–0.2 M $CDCl_3$ solutions at 303 K with Bruker Avance DRX 500 FT NMR spectrometer equipped with an inverse detection dual 5 mm probehead and a z-gradient accessory working at 500.13 MHz for ^{1}H, 125.77 MHz for ^{13}C, and 50.70 MHz for ^{15}N. ^{1}H and ^{13}C NMR chemical shifts are referenced to internal TMS (δ=0.00 ppm) and ^{15}N NMR chemical shifts to the resonance of an external neat CH_3NO_2 (δ=0.00 ppm) in a 1 mm diameter capillary inserted coaxially inside the 5 mm NMR tube. All NMR acquisition and processing parameters are available from E.K. on request.

IR spectra were recorded on a Bruker Vector 22 FTIR spectrophotometer with samples at room temperature as solutions in chloroform using KBr cell of 0.25 mm thickness. The concentration of solutions was chosen to give absorption in the 75–85% range.

Crystals of compound **1** were obtained by slow evaporation of $CDCl_3$ from NMR tube. The X-ray crystallographic data were collected with Nonius Kappa CCD diffractometer, using graphite monochromatised Mo Kα radiation (λ= 71.073 pm) and temperature of 173±0.1 K. The CCD data were processed with DENZO-SMN v0.93.0[48] and all structures were solved by direct methods, using SHELXS-97,[49] and refined on F^2 by full-matrix least-squares techniques with SHELXL-97.[50] The hydrogen atoms, except N–*H*, were calculated to their idealized positions with isotropic temperature factors, U_{iso}(H)=1.2U_{eq}(C), and refined as riding atoms. H bonded to N was found from the difference Fourier map and fixed to its ideal distance from the parent atom (0.91 Å at 173 K), with isotropic temperature factor U_{iso}(H)=1.2U_{eq}(N). Absorption correction was not used. The figure was drawn with ORTEP-3[51] and MERCURY.[52] Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC-638269. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK [fax: +44 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk].

Full geometry optimizations have been carried out using the GAUSSIAN software package.[53] Structural computations were performed using the B3LYP theory. The 6-311G(2d,p) basis set was used. The frequency calculations were performed to make sure that geometry is in the global minimum.

Acknowledgements

The authors are grateful to Spec. Lab. technician Reijo Kauppinen for his help in running the NMR spectra. We are very much indebted to the Academic Computer Centre, CI TASK, Gdańsk, for supply of computer time and providing programs.

References and notes

1. Kolehmainen, E.; Ośmiałowski, B.; Krygowski, T. M.; Kauppinen, R.; Nissinen, M.; Gawinecki, R. *J. Chem. Soc., Perkin Trans. 2* **2000**, 1259–1266.
2. Kolehmainen, E.; Ośmiałowski, B.; Nissinen, M.; Kauppinen, R.; Gawinecki, R. *J. Chem. Soc., Perkin Trans. 2* **2000**, 2185–2191.
3. Gilli, G.; Bertolasi, V. Structural Chemistry. In *The Chemistry of Enols*; Rappoport, Z., Ed.; Wiley: Chichester, UK, 1990; pp 713–764.
4. Manly, D. G.; Richardson, A.; Stock, A. M.; Tilford, C. H.; Amstutz, E. D. *J. Org. Chem.* **1958**, *23*, 373–380.

5. Lombardino, J. G. *J. Org. Chem.* **1967**, *32*, 1988–1992.
6. Yousif, M. M.; Saeki, S.; Hamana, M. *Chem. Pharm. Bull.* **1982**, *30*, 2326–2332.
7. Manukian, B. K.; Niklaus, P.; Ehrsam, H. *Helv. Chim. Acta* **1969**, *52*, 1259–1273.
8. Bontchev, P. R.; Mitewa, M.; Minchev, S.; Kashchieva, M.; Mechandjiev, D. *J. Prakt. Chem. Soc.* **1983**, *325*, 803–810.
9. Kacen, Ya. Ya.; Neiland, O. Ya.; Laberg, Ya. Ya. *Latv. PSR. Zinat. Akad. Vestis, Kim. Ser.* **1972**, 576–583.
10. Kemme, A. A.; Bundule, M. F.; Bleidelis, Ya. Ya.; Liepinsh, E. E.; Lavrinovich, E. S.; Fridmanis, Yu. E. *Khim. Geterotsykl. Soed.* **1978**, 1076–1080.
11. Brooker, L. G. S.; Keyes, G. H. *J. Am. Chem. Soc.* **1951**, *73*, 5356–5358.
12. Kuhn, R.; Bär, F. *Liebigs Ann. Chem.* **1935**, *516*, 155–161.
13. Amiel, J.; Ploquin, J.; Sparfel, L.; Le Baut, G.; Floc'h, R. *Bull. Soc. Chim. Fr.* **1974**, 2154–2160.
14. Kuramoto, N.; Kitao, T. *J. Chem. Soc., Perkin Trans. 2* **1980**, 1569–1572.
15. Neiland, O. Ya.; Kacen, Ya. Ya. *Chem. Heterocycl. Compounds* **1975**, *11*, 381–395; *(Khim. Geterotsykl. Soed.*, **1975**, 435–451).
16. Radtke, V. *Quinophthalone Pigments in High Performance Pigments*; Smith, H. M., Ed.; Wiley-VCH: Weinheim, 2002; pp 307–316.
17. Beckett, A. H.; Branch, R. F.; Cowell, D. B. *Tetrahedron* **1963**, *19*, 413–418.
18. Gawinecki, R.; Kolehmainen, E.; Ośmiałowski, B.; Palkovič, P.; Nissinen, M. *Heterocycl. Commun.* **1999**, *5*, 549–554.
19. Gawinecki, R.; Ośmiałowski, B.; Kolehmainen, E.; Nissinen, M. *J. Mol. Struct.* **2000**, *525*, 233–239.
20. Stefaniak, L. *Org. Magn. Reson.* **1979**, *12*, 379–382.
21. Stefaniak, L.; Witanowski, M.; Webb, G. A. *Pol. J. Chem.* **1981**, *55*, 1441–1444.
22. Llor, J.; Lopez-Mayorga, O.; Munoz, L. *Magn. Reson. Chem.* **1993**, *31*, 552–556.
23. Lloris, M. E.; Abramovitch, R. A.; Marquet, J.; Moreno-Mañas, M. *Tetrahedron* **1992**, *48*, 6909–6916.
24. Facchetti, A.; Streitwieser, A. *J. Org. Chem.* **2004**, *69*, 8345–8355.
25. Olah, G. A.; Grant, J. L.; Westerman, P. W. *J. Org. Chem.* **1975**, *40*, 2102–2108.
26. Sammes, M. P.; Maini, P. N. *Magn. Reson. Chem.* **1987**, *25*, 372–374.
27. Wheeler, Th. N. *J. Org. Chem.* **1979**, *44*, 4906–4912.
28. Crabb, T. A.; Patel, A.; Newton, R. F.; Price, B. J.; Tucker, M. J. *J. Chem. Soc., Perkin Trans. 1* **1982**, 2783–2786.
29. Yavari, I.; Adib, M.; Bijanzadeh, H. R.; Sadegi, M. M. M.; Loghmani-Khouzani, H.; Safari, J. *Monatsh. Chem.* **2002**, *133*, 1109–1114.
30. Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. *Spectrophotometric Identification of Organic Compounds*, 5th ed.; Wiley: New York, NY, 1991; pp 113–115.
31. Gren, E. Ya.; Grinvalde, A. K.; Vanag, G. Ya. *Zh. Obshch. Khim.* **1966**, *36*, 17–22.
32. Grens, E.; Grinvalde, A.; Stradinš, J. *Spectrochim. Acta* **1975**, *31A*, 555–564.
33. Alpert, N. A.; Keiser, W. E.; Szymansky, H. A. *IR. Theory and Practice of Infrared Spectroscopy*; Plenum: New York, NY, 1970; (Polish translation: *Spektroskopia w podczerwieni. Teoria i praktyka*, PWN, Warsaw, 1974, pp 254–261).
34. Perjéssy, A.; Hrnčiar, P. *Tetrahedron* **1971**, *27*, 6159–6169.
35. Krygowski, T. M. *J. Chem. Inf. Comput. Sci.* **1993**, *33*, 70–78.
36. Gilli, G.; Bellucci, F.; Ferretti, V.; Bertolasi, V. *J. Am. Chem. Soc.* **1989**, *111*, 1023–1028.
37. Bertolasi, V.; Gilli, P.; Ferretti, V.; Gilli, G. *J. Am. Chem. Soc.* **1991**, *113*, 4917–4925.
38. Gilli, P.; Bertolasi, V.; Ferretti, V.; Gilli, G. *J. Am. Chem. Soc.* **1994**, *116*, 909–915.
39. Bertolasi, V.; Gilli, P.; Ferretti, V.; Gilli, G. *Chem.—Eur. J.* **1996**, *2*, 925–934.
40. Wolfe, J. F.; Portlock, D. E.; Feuerbach, D. J. *J. Org. Chem.* **1974**, *39*, 2006–2010.
41. Cook, J. R.; Martin, D. F. *J. Inorg. Nucl. Chem.* **1964**, *26*, 571–577.
42. Kehrer, F.; Niklaus, P.; Manukian, B. K. *Helv. Chim. Acta* **1967**, *50*, 2200–2211.
43. Hamana, M.; Yamazaki, M. *Chem. Pharm. Bull.* **1963**, *11*, 415–421.
44. Awad, W. I.; Aly, O. M. *J. Org. Chem.* **1960**, *25*, 1872–1874.
45. Beckett, A. H.; Kerridge, K. A. *J. Chem. Soc.* **1954**, 2948–2951.
46. Tschitschibabin, A. E. *Ber.* **1927**, *60*, 1607–1617.
47. Aleksiev, B.; Milošev, M. *Pharmazie* **1969**, *24*, 291–292.
48. Otwinowski, Z.; Minor, W. *Methods in Enzymology, Macromolecular Crystallography, Part A*; Carter, C. W., Sweet, R. M., Eds.; Academic: New York, NY, 1997; pp 307–326.
49. Sheldrick, G. M. *Acta Crystallogr* **1990**, *A46*, 467–473.
50. Sheldrick, G. M. *SHELXL-97*; University of Göttingen: Göttingen, Germany, 1997.
51. Farrugia, L. J. *J. Appl. Crystallogr* **1997**, *30*, 565.
52. Macrae, C. F.; Edgington, P. R.; McCabe, P.; Pidcock, E.; Shields, G. P.; Taylor, R.; Towler, M.; van de Streek, J. *J. Appl. Crystallogr.* **2006**, *39*, 453–457.
53. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03, Revision D.01*; Gaussian: Pittsburgh, PA, 2003.