Facile Regioselective Synthesis of 3-amino-2-(2′-arylindanedionyl)indenones from 2-aryl-2,2′-biindan-1,1′,3,3′-tetrones and Solvent-Dependent Keto-Enol Tautomerism in Enaminones

Suven Das[a,b], Roland Fröhlich[c] and Animesh Pramanik*[,a]

[a]*Department of Chemistry, University of Calcutta, 92, A. P. C. Road, Kolkata-700 009, India*

[b]*Department of Chemistry, Rishi Bankim Chandra College for Women, Naihati, North 24-parganas, Pin-743165, India*

[c]*Organisch-Chemisches Institut, Universität Münster, Corrensstraβe 40, D-48149, Münster, Germany*

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Abstract: Refluxing 2-Aryl-2,2′-biindan-1,1′,3,3′-tetrones in acetic acid with urea produces 3-amino-2-(2′-arylindanedionyl)indenones regioselectively within 2-3 h. in good yields. X-ray crystal structures of the products clearly indicate that in the solid state the compounds exist in the keto form. On the other hand NMR studies reveal that the enaminones exist in keto form in $CDCl_3$ and in enol form in DMSO-d_6 and acetone-d_6.

Keywords: Urea, 3-amino-2-(2′-arylindanedionyl)indenones, keto-enol tautomerism, iminoindenol.

INTRODUCTION

Enaminones are an important class of organosynthetic intermediates. They are very effective synthons for the synthesis of various heterocyclic as well as biologically active analogues [1] including anticonvulsant [2], anti-inflammatory [3] and antitumour agents [4]. The conventional method for the synthesis of enaminones is the azeotropic removal of water by refluxing an amine with 1,3-diketone in an aromatic solvent [5]. Various other methods for the synthesis of enaminones have been reported in the literature such as addition of metallic esters or amide enolates to nitriles [6], tosyl imines [7] or imidoyl halides [8]. Besides these, the enamination of 1,3-dicarbonyl compounds has been carried out using catalyst systems such as silica/microwave [9], clayK_{10}/ultrasound [10] and $NaAuCl_4$ [11]. Recently $Bi(TFA)_3$ [12], $Zn(ClO_4)_2.6H_2O$ [13], silica gel [14] and silica chloride [15] have also been reported as effective catalysts. An alternative access to enaminones from ynones and amines has been reported by Karpov and Müller [16]. However, only a few reports are found in the literature on the synthesis of 3-aminoindenones [17]. Johnson and co-workers synthesized a library of substituted 3-aminoindenones by reacting benzoate esters with alkyl- or phenylacetonitriles in the presence of excess LDA [17a,b]. In continuation with our research interest in the synthesis of various heterocyclic compounds from ninhydrin and in exploring the reactivity of the ninhydrin-based adducts towards different types of nucleophiles [18], we herein report the regioselective synthesis of 3-amino-2-(2′-arylindanedionyl)indenones from easily prepared 2-aryl-2,2′-biindan-1,1′,3,3′-tetrones.

*Address correspondence to this author at the Department of Chemistry, University of Calcutta, 92, A. P. C. Road, Kolkata-700 009, India; Tel: +91-33-2484 1647; Fax: +91-2351 9755; E-mail: animesh_in2001@yahoo.co.in

RESULTS AND DISCUSSION

Previously it has been observed that 2-hydroxy-2,2′-biindan-1,1′,3,3′-tetrone **1** undergoes condensation with various activated aromatic substrates in an acidic medium to afford 2-aryl-2,2′-biindan-1,1′,3,3′-tetrones **2a-n** (Scheme **1**) [18c]. To facilitate the condensation of **1** with less reactive aromatics such as benzene, halobenzenes *etc.* superacidic triflic acid was employed [18f]. The adducts **2** have the potential to undergo nucleophilic attack at the carbonyl carbons. It would be interesting to know which of the two types of carbonyl groups present in **2** is more reactive towards nucleophiles. To the end it was observed that refluxing **2** with urea in acetic acid produces only 3-amino-2-(2′-arylindanedionyl)indenones **3a-n** regioselectively within 2-3 h (Scheme **1**, Table **1**). The carbonyls of the indanedionyl group of **2** carrying aryl substituents are less reactive due to steric hindrance. Since urea is a weak nucleophile the effect is even more pronounced. Again the nucleophilic attack of urea at the 1,3-dicarbonyl part containing a hydrogen at the C-2 position is facilitated due to the possibility of subsequent dehydration. As a result the reaction gives selectively only one product **3**. The purification of the products was straightforward, requiring only filtration followed by crystallization from acetone. The product was isolated as an orange-red solid in modest to good yields (60-72 %). The structures of the compounds **3a-n** were characterized by IR, ^1H and ^{13}C NMR spectra. X-ray crystal structures [19] of **3d** and **3j** (Fig. **1** and **2**) clearly indicate that in the solid state the compounds exist in the keto form.

Interestingly, enaminones **3** show keto-enol tautomerism depending upon the polarity of the solvent. In ^1H NMR studies it has been observed that enaminones **3** exist exclusively in the keto form in $CDCl_3$, characterised by a 2H singlet (broad) corresponding to the -NH_2 at δ5.08 ppm in case of **3h** (Fig. **3**). But in more polar DMSO-d_6 two separate

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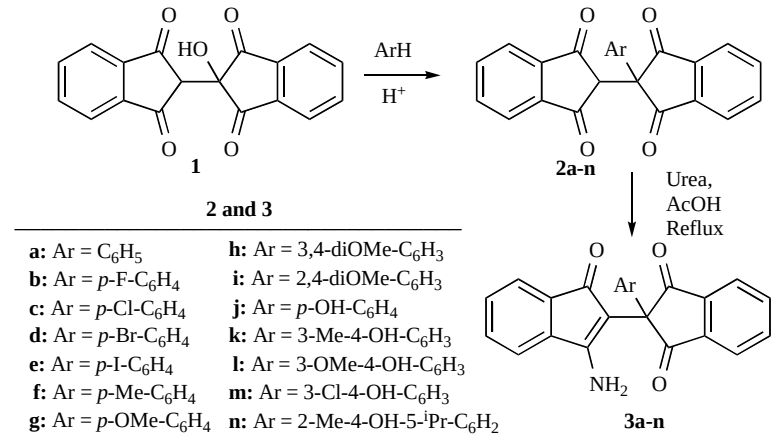


1 **2a-n** **3a-n**

2 and 3

a: Ar = C_6H_5 **h:** Ar = 3,4-diOMe-C_6H_3
b: Ar = *p*-F-C_6H_4 **i:** Ar = 2,4-diOMe-C_6H_3
c: Ar = *p*-Cl-C_6H_4 **j:** Ar = *p*-OH-C_6H_4
d: Ar = *p*-Br-C_6H_4 **k:** Ar = 3-Me-4-OH-C_6H_3
e: Ar = *p*-I-C_6H_4 **l:** Ar = 3-OMe-4-OH-C_6H_3
f: Ar = *p*-Me-C_6H_4 **m:** Ar = 3-Cl-4-OH-C_6H_3
g: Ar = *p*-OMe-C_6H_4 **n:** Ar = 2-Me-4-OH-5-^{i}Pr-C_6H_2

Scheme 1.

Table 1. Formation of 3-amino-2-(2′-arylindanedionyl)indenones 3a-n from 2a-n

Entry	Substrates	Products	Time (h)	Yield[a] (%)	Mp (˚C)[b]
1	**2a**	**3a**	2.0	64	276-278
2	**2b**	**3b**	2.0	70	270-271
3	**2c**	**3c**	2.5	72	261-262
4	**2d**	**3d**	2.5	72	275-276
5	**2e**	**3e**	2.5	68	278-279
6	**2f**	**3f**	2.5	70	248-249
7	**2g**	**3g**	2.0	70	225-226
8	**2h**	**3h**	2.5	65	242-243
9	**2i**	**3i**	2.5	60	>320
10	**2j**	**3j**	2.0	68	266-268
11	**2k**	**3k**	2.5	70	279-281
12	**2l**	**3l**	2.0	62	245-247
13	**2m**	**3m**	2.5	64	263-264
14	**2n**	**3n**	3.0	60	305-307

[a]Yields are for isolated products. [b]Mps are uncorrected.

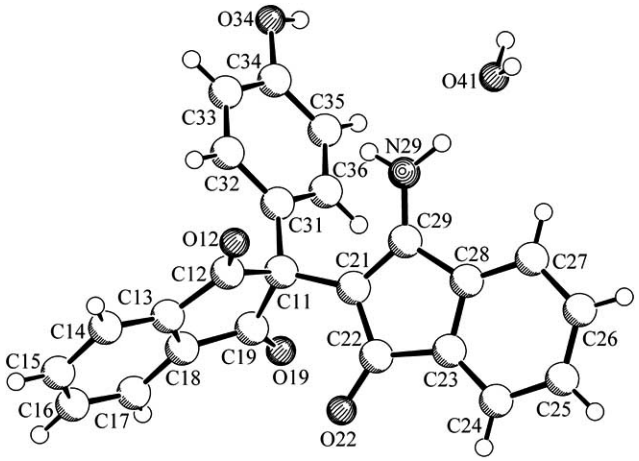


Fig. (1). X-ray crystal structure of **3d** with atom numbering scheme.

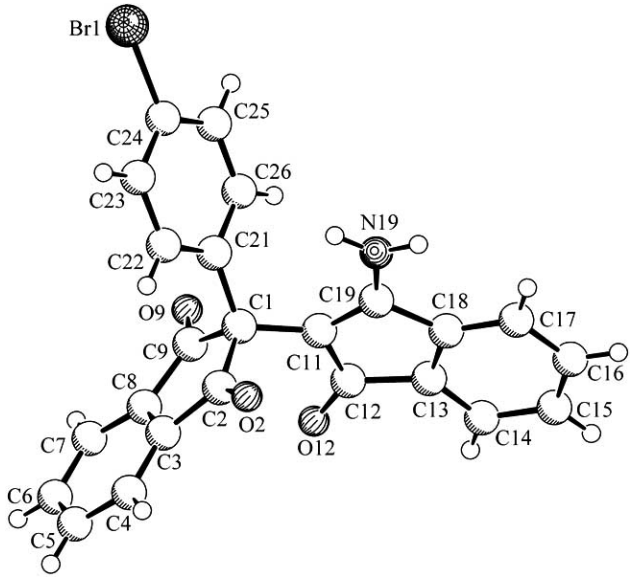
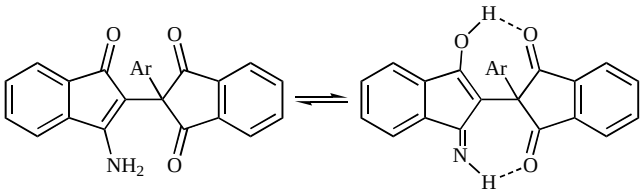


Fig. (2). X-ray crystal structure of **3j** with atom numbering scheme.

signals corresponding to –OH (at δ 8.14 ppm) and -NH (at δ 5.37 ppm) appear indicating the presence of the enol form (iminoindenol) **4h** which is stabilized by two intramolecular hydrogen bonds with the neighbouring 1,3-dicarbonyl moieties (Scheme **2**). Compounds **3h** and **3n** are also found to remain in enol form (**4h** and **4n**) in acetone-d_6. Previously it has been observed that 3-amino-2-aryl-1-indenones exist in their keto form in solution irrespective of the solvent polarity [17a]. The result clearly indicates that in the present case the intramolecular hydrogen bonding of –OH and –NH with the neighbouring carbonyl groups stabilises the iminoindenol **4**.



3a-n (in **$CDCl_3$**) **4a-n** (in **DMSO-d_6**)

Scheme 2.

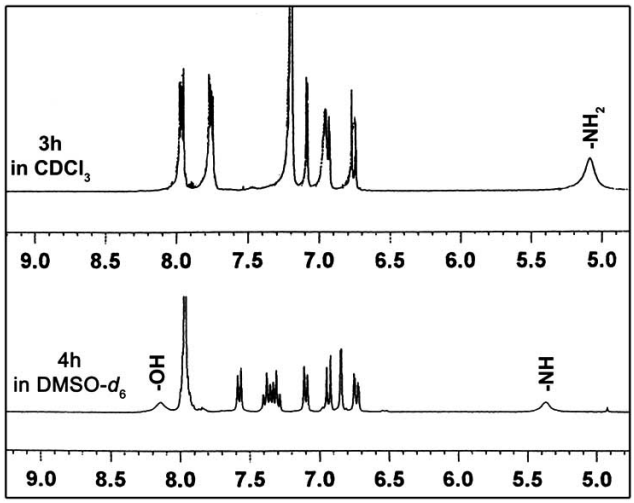


Fig. (3). ^{1}H NMR spectra of **3h** in $CDCl_3$ and DMSO-d_6.

EXPERIMENTAL

General Procedures

Melting points were determined in an open capillary and were uncorrected. IR spectra were examined in KBr disc on a Perkin Elmer-782 spectrophotometer. Proton magnetic resonance (^{1}H NMR) and carbon magnetic resonance (^{13}C NMR) spectra were recorded on a Bruker Avance 300 (300 MHz for ^{1}H NMR and 75 MHz for ^{13}C NMR) spectrometer in the solvents indicated. Elemental analyses were performed on a Perkin Elmer 240C analyzer.

General Procedure for the Synthesis of 3-amino-2-(2′-arylindanedionyl)indenones 3a-n

The appropriate substrate **2a-n** (1.4 mmol) was added to acetic acid (10 ml) followed by the addition of urea (1 gm, 16.6 mmol). The reaction mixture was refluxed for the time indicated in Table **1**. The solution turned a red colour. The cold reaction mixture was then poured into 50-60 ml ice cold water. The solid product separated was filtered and washed thoroughly with water. The resulting solids were purified by crystallisation from acetone to afford orange-red crystals.

3-Amino-2-(2′-phenylindanedionyl)indenone, 3a (remains as 4a in DMSO-d_6)

Red crystals; IR (KBr): 3450, 3316, 3219, 1702, 1626, 1545 cm^{-1}. ^{1}H NMR (300 MHz, DMSO-d_6): δ8.23 (1H, bs, -OH), 8.01-7.93 (4H, m), 7.58 (1H, d, J = 6.9 Hz), 7.39-7.24 (7H, m), 7.11 (1H, d, J = 6.9 Hz), 5.49 (1H, bs, -NH). ^{13}C NMR (75 MHz, DMSO-d_6): δ198.7 (2C), 189.5, 163.7, 140.9 (2C), 138.0, 136.3 (2C), 133.8, 133.7, 131.3, 130.7, 129.0 (2C), 128.4 (2C), 128.1, 123.6 (2C), 119.5, 119.1, 100.1, 62.0. Anal. Calcd for $C_{24}H_{15}NO_3$: C, 78.89; H, 4.14; N, 3.83. Found: C, 78.80; H, 4.09; N, 3.78 %.

3-Amino-2-[2′-(4-fluorophenyl)indanedionyl]indenone, 3b (remains as 4b in DMSO-d_6)

Orange crystals; IR (KBr): 3469, 3323, 3217, 1704, 1627, 1554 cm^{-1}. ^{1}H NMR (300 MHz, DMSO-d_6): δ8.32 (1H, bs, -OH), 8.02-7.94 (4H, m), 7.63 (1H, d, J = 6.9 Hz), 7.40-7.07 (6H, m), 7.08 (1H, d, J = 6.3 Hz), 5.99 (1H, bs, -NH). ^{13}C NMR (75 MHz, DMSO-d_6): δ198.5 (2C), 189.1, 163.6 (2C), 161.8 (d, $J_{c\text{-}f}$ = 243.7 Hz), 140.9 (2C), 137.8, 136.3 (2C), 133.8, 131.3, 130.8, 130.6 (2C, d, $J_{c\text{-}f}$ = 8.5 Hz), 130.0 (d, $J_{c\text{-}f}$ = 3.4 Hz), 123.6 (2C), 119.5, 119.2, 115.8 (2C, d, $J_{c\text{-}f}$ = 21.7 Hz), 99.5, 61.4. Anal. Calcd for $C_{24}H_{14}FNO_3$: C, 75.19; H, 3.68; N, 3.65. Found: C, 75.12; H, 3.61; N, 3.58: %.

3-Amino-2-[2′-(4-chlorophenyl)indanedionyl]indenone, 3c (remains as 4c in DMSO-d_6)

Red crystals; IR (KBr): 3404, 3312, 1706, 1620, 1536 cm^{-1}. ^{1}H NMR (300 MHz, DMSO-d_6): δ8.40 (1H, bs, -OH), 8.06-7.99 (4H, m), 7.68 (1H, d, J = 7.2 Hz), 7.47-7.36 (4H, m), 7.25 (2H, d, J = 8.5 Hz), 7.15 (1H, d, J = 6.7 Hz), 6.21 (1H, bs, -NH). ^{13}C NMR (75 MHz, DMSO-d_6): δ198.5 (2C), 189.4, 164.0, 141.4 (2C), 138.2, 136.8 (2C), 134.2, 133.5, 133.1, 131.8, 131.2, 130.9 (2C), 129.3 (2C), 124.1 (2C), 119.9, 119.7, 99.4, 62.0. Anal. Calcd for $C_{24}H_{14}ClNO_3$: C, 72.10; H, 3.53; N, 3.50. Found: C, 72.02; H, 3.48; N, 3.43 %.

3-Amino-2-[2′-(4-bromophenyl)indanedionyl]indenone, 3d (remains as 4d in DMSO-d_6)

Orange-red crystals; IR (KBr): 3385, 3308, 3217, 1705, 1622, 1543 cm^{-1}. ^{1}H NMR (300 MHz, DMSO-d_6): δ8.41 (1H, bs, -OH), 8.07-7.99 (4H, m), 7.69 (1H, d, J = 6.9 Hz), 7.59 (2H, d, J = 8.4 Hz), 7.44-7.33 (2H, m), 7.21-7.14 (3H, m), 6.21 (1H, bs, -NH). ^{13}C NMR (75 MHz, DMSO-d_6): δ198.5 (2C), 189.4, 164.1, 141.4 (2C), 138.1, 136.7 (2C), 134.2, 133.9, 132.2 (2C), 131.7, 131.2 (3C), 124.1 (2C), 121.8, 119.9, 119.7, 99.4, 62.1. Anal. Calcd for $C_{24}H_{14}BrNO_3$: C, 64.88; H, 3.18; N, 3.15. Found: C, 64.83; H, 3.12; N, 3.08 %.

3-Amino-2-[2′-(4-iodophenyl)indanedionyl]indenone, 3e (remains as 4e in DMSO-d_6)

Orange crystals; IR (KBr): 3394, 3305, 3205, 1704, 1619, 1540 cm^{-1}. ^{1}H NMR (300 MHz, DMSO-d_6): δ8.34 (1H, bs, -OH), 8.01-7.94 (4H, m), 7.71 (2H, d, J = 8.4 Hz),

7.62 (1H, d, *J* = 6.9 Hz), 7.40-7.29 (2H, m), 7.10 (1H, d, *J* = 6.6 Hz), 6.99 (2H, d, *J* = 8.4 Hz), 6.11 (1H, bs, -NH). ^{13}C NMR (75 MHz, DMSO-d_6): δ198.0 (2C), 188.9, 163.6, 141.0 (2C), 137.7, 136.7 (2C), 136.3 (2C), 133.9, 133.8, 131.3, 130.8 (2C), 123.6 (2C), 119.5, 119.2, 98.9, 94.5, 61.8. Anal. Calcd for $C_{24}H_{14}INO_3$: C, 58.68; H, 2.87; N, 2.85. Found: C, 58.61; H, 2.82; N, 2.80 %.

3-Amino-2-[2'-(4-methylphenyl)indanedionyl]indenone, 3f (remains as 4f in DMSO-d_6)

Orange crystals; IR (KBr): 3408, 3303, 3222, 1706, 1619, 1542 cm^{-1}. ^{1}H NMR (300 MHz, DMSO-d_6): δ8.21 (1H, bs, -OH), 8.00-7.90 (4H, m), 7.84-7.81 (2H, m), 7.58 (1H, d, *J* = 6.9 Hz), 7.40-7.28 (2H, m), 7.17-7.12 (3H, m), 5.42 (1H, bs, -NH), 2.25 (3H, s). Anal. Calcd for $C_{25}H_{17}NO_3$: C, 79.14; H, 4.52; N, 3.69. Found: C, 79.08; H, 4.47; N, 3.63 %.

3-Amino-2-[2'-(4-methoxyphenyl)indanedionyl]indenone, 3g

Orange-red crystals; IR (KBr): 3401, 3307, 3222, 1704, 1621, 1542 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ8.07-8.04 (2H, m), 7.90-7.84 (2H, m), 7.46 (2H, d, *J* = 8.9 Hz), 7.33-7.31(4H, m), 6.93 (2H, d, *J* = 8.9 Hz), 5.14 (2H, bs, -NH_2), 3.80 (3H, s). ^{13}C NMR (75 MHz, $CDCl_3$): δ 199.6 (2C), 191.0, 162.8, 159.5, 141.4 (2C), 138.2, 135.6 (2C), 133.4, 131.1, 130.7, 129.9 (2C), 128.8, 125.4, 123.8 (2C), 120.8, 116.4, 114.5 (2C), 61.1, 55.3. Anal. Calcd for $C_{25}H_{17}NO_4$: C, 75.94; H, 4.33; N, 3.54. Found: C, 75.87; H, 4.29; N, 3.48 %.

3-Amino-2-[2'-(3,4-dimethoxyphenyl)indanedionyl]indenone, 3h

Orange crystals; IR (KBr): 3448, 3357, 1707, 1630, 1514 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ7.94-7.89 (2H, m), 7.78-7.74 (2H, m), 7.21-7.17 (3H, m), 7.09 (1H, d, *J* = 2.1 Hz), 6.96-6.92 (2H, m), 6.76 (1H, d, *J* = 8.4 Hz), 5.08 (2H, bs, -NH_2), 3.78 (6H, s). ^{13}C NMR (75 MHz, $CDCl_3$): δ199.6 (2C), 191.5, 163.0, 149.6, 149.2, 141.2 (2C), 138.3, 135.6 (2C), 133.3, 131.1, 130.7, 125.6, 123.8 (2C), 120.7, 120.6, 116.6, 111.9, 111.2, 103.5, 61.1, 56.1, 55.9. Anal. Calcd for $C_{26}H_{19}NO_5$: C, 73.40; H, 4.50; N, 3.29. Found: C, 73.34; H, 4.58; N, 3.24 %.

3-Amino-2-[2'-(3,4-dimethoxyphenyl)indanedionyl]indenone, 3h (remains as 4h in DMSO-d_6)

^{1}H NMR (300 MHz, DMSO-d_6): δ8.14 (1H, bs, -OH), 8.00-7.90 (4H, m), 7.58 (1H, d, *J* = 6.9 Hz), 7.40-7.28 (2H, m), 7.10 (1H, d, *J* = 6.9 Hz), 6.93 (1H, d, *J* = 8.4 Hz), 6.85 (1H, d, *J* = 2.1 Hz), 6.74 (1H, dd, *J* = 8.4, 2.1 Hz), 5.37 (1H, bs, -NH), 3.70 (3H, s), 3.63 (3H, s). ^{13}C NMR (75 MHz, DMSO-d_6): δ199.2 (2C), 189.9, 163.8, 149.2, 149.0, 140.7 (2C), 138.4, 136.3 (2C), 133.6, 131.4, 130.7, 125.3, 123.6 (2C), 120.7, 119.5, 119.1, 112.2, 112.0, 100.8, 61.5, 55.7, 55.6.

3-Amino-2-[2'-(3,4-dimethoxyphenyl)indanedionyl]indenone, 3h (remains as 4h in Acetone-d_6)

^{1}H NMR (300 MHz, Acetone-d_6): δ8.00-7.95 (5H, m), 7.50 (1H, d, *J* = 6.3 Hz), 7.42-7.31 (2H, m), 7.20 (1H, dd, *J* = 6.3, 1.8 Hz), 7.13 (1H, d, *J* = 1.8 Hz), 6.97-6.93 (2H, m), 5.26 (1H, bs, -NH), 3.78 (3H, s), 3.75 (3H, s).

3-Amino-2-[2'-(2,4-dimethoxyphenyl)indanedionyl]indenone, 3i (remains as 4i in DMSO-d_6)

Orange crystals; IR (KBr): 3403, 3312, 3237, 1706, 1620, 1537 cm^{-1}. ^{1}H NMR (300 MHz, DMSO-d_6): δ8.68 (1H, bs, -OH), 7.92-7.83 (4H, m), 7.65 (1H, d, *J* = 6.9 Hz), 7.37-7.31 (2H, m), 7.09 (1H, d, *J* = 6.9 Hz), 7.01 (1H, d, *J* = 8.1 Hz), 6.65 (1H, bs, -NH), 6.57-6.51 (2H, m), 3.73 (3H, s), 3.27 (3H, s). Anal. Calcd for $C_{26}H_{19}NO_5$: C, 73.40; H, 4.50; N, 3.29. Found: C, 73.35; H, 4.57; N, 3.25 %.

3-Amino-2-[2'-(4-hydroxyphenyl)indanedionyl]indenone, 3j (remains as 4j in DMSO-d_6)

Red crystals; IR (KBr): 3592, 3527, 3427, 3129, 1704, 1628, 1542 cm^{-1}. ^{1}H NMR (300 MHz, DMSO-d_6): δ9.68 (1H, s, phenolic-OH), 8.17 (1H, bs, -OH), 8.03-7.96 (4H, m), 7.60 (1H, d, *J* = 7.1 Hz), 7.44-7.32 (2H, m), 7.15-7.13 (3H, m), 6.81 (2H, d, *J* = 8.7 Hz), 5.24 (1H, bs, -NH). ^{13}C NMR (75 MHz, DMSO-d_6): δ199.8 (2C), 190.2, 164.1, 157.8, 141.1 (2C), 138.8, 136.6 (2C), 133.9, 131.8, 131.1, 129.9 (2C), 123.9 (2C), 123.6, 119.8, 119.3, 116.5 (2C), 101.5, 61.6. Anal. Calcd for $C_{24}H_{15}NO_4$: C, 75.58; H, 3.96; N, 3.67. Found: C, 75.63; H, 3.91; N, 3.60 %.

3-Amino-2-[2'-(3-methyl-4-hydroxyphenyl)indanedionyl] indenone, 3k (remains as 4k in DMSO-d_6)

Orange-red crystals; IR (KBr): 3509, 3382, 3310, 3209, 1703, 1623, 1543 cm^{-1}. ^{1}H NMR (300 MHz, DMSO-d_6): δ9.62 (1H, s, phenolic-OH), 8.15 (1H, bs, -OH), 8.00 (4H, m), 7.59 (1H, d, *J* = 7.0 Hz), 7.44-7.32 (2H, m), 7.14 (1H, d, *J* = 6.8 Hz), 7.02-6.96 (2H, m), 6.81 (1H, d, *J* = 8.3 Hz), 5.20 (1H, bs, -NH), 2.09 (3H, s). ^{13}C NMR (75 MHz, DMSO-d_6): δ199.9 (2C), 190.3, 164.1, 156.0, 141.1 (2C), 138.8, 136.6 (2C), 133.9, 132.0, 131.0, 129.2, 127.2, 125.3, 123.8 (2C), 123.3, 119.8, 119.3, 115.6, 101.5, 61.6, 19.3. Anal. Calcd for $C_{25}H_{17}NO_4$: C, 75.94; H, 4.33; N, 3.54. Found: C, 75.86; H, 4.28; N, 3.48 %.

3-Amino-2-[2'-(3-methoxy-4-hydroxyphenyl)indanedionyl] indenone, 3l (remains as 4l in DMSO-d_6)

Orange crystals; IR (KBr): 3440, 3376, 3311, 3211, 1701, 1624, 1541 cm^{-1}. ^{1}H NMR (300 MHz, DMSO-d_6): δ 9.27 (1H, s, phenolic-OH), 8.09 (1H, bs, -OH), 7.99-7.93 (4H, m), 7.56 (1H, d, *J* = 6.9 Hz), 7.40-7.28 (2H, m), 7.09 (1H, d, *J* = 6.9 Hz), 6.84 (1H, d, *J* = 2.1 Hz), 6.76 (1H, d, *J* = 8.4 Hz), 6.64 (1H, dd, *J* = 8.4, 2.1 Hz), 5.17 (1H, bs, -NH), 3.65 (3H, s). Anal. Calcd for $C_{25}H_{17}NO_5$: C, 72.99; H, 4.16; N, 3.40. Found: C, 72.93; H, 4.12; N, 3.35 %.

3-Amino-2-[2'-(3-chloro-4-hydroxyphenyl)indanedionyl] indenone, 3m (remains as 4m in DMSO-d_6)

Red crystals; IR (KBr): 3373, 3221, 1702, 1623, 1542 cm^{-1}. ^{1}H NMR (300 MHz, DMSO-d_6): δ10.40 (1H, s, phenolic-OH), 8.33 (1H, bs, -OH), 8.05-7.98 (4H, m), 7.67 (1H, d, *J* = 7.0 Hz), 7.45-7.33 (2H, m), 7.15-7.14 (2H, m), 7.05-6.97 (2H, m), 6.00 (1H, bs, -NH). ^{13}C NMR (75 MHz, DMSO-d_6): δ199.1 (2C), 189.6, 164.1, 153.4, 141.2 (2C), 138.4, 136.7 (2C), 134.1, 131.8, 131.2, 130.0, 128.7, 125.5, 124.0 (2C), 120.5, 119.9, 119.6, 117.5, 100.1, 61.4. Anal. Calcd for $C_{24}H_{14}ClNO_4$: C, 69.32; H, 3.39; N, 3.37. Found: C, 69.26; H, 3.34; N, 3.31 %.

3-Amino-2-[2′-(2-methyl-4-hydroxy-5-isopropylphenyl)indanedionyl]indenone, 3n (remains as 4n in Acetone-d_6):

Orange crystals; IR (KBr): 3505, 3414, 3314, 3252, 1694, 1622, 1542 cm^{-1}. ^1H NMR (300 MHz, Acetone-d_6): δ 8.18 (1H, s, phenolic-OH), 8.06 (1H, d, J = 6.9 Hz), 7.97-7.87 (3H, m), 7.76 (1H, bs, -OH), 7.60 (1H, d, J = 6.6 Hz), 7.43-7.34 (2H, m), 7.20 (1H, d, J = 6.3 Hz), 7.11 (1H, s), 6.67 (1H, s), 6.30 (1H, bs, -NH), 3.21 (1H, septet, J = 6.9 Hz), 1.84 (3H, s), 1.14 (3H, d, J = 6.9 Hz), 1.07 (3H, d, J = 6.9 Hz). Anal. Calcd for $C_{28}H_{23}NO_4$: C, 76.87; H, 5.30; N, 3.20. Found: C, 76.80; H, 5.24; N, 3.15 %.

X-Ray Crystal Structure Analysis

3d. formula $C_{24}H_{14}BrNO_3$, M = 444.27, yellow-orange crystal 0.25 x 0.15 x 0.15 mm, a = 10.937(1), b = 13.229(3), c = 27.429(8)Å, β = 91.14(2)º, V = 3967.8(15) $Å^3$, ρ_{calc} = 1.487 g cm^{-3}, μ= 3.035 mm^{-1}, empirical absorption correction ($0.518 \le T \le 0.659$), Z = 8, monoclinic, space group $P2_1/n$ (No. 14), λ= 1.54178 Å, T = 293(2) K, ω/2θ scans, 8537 reflections collected (+h, -k, ±l), [(sinθ)/λ] = 0.62 $Å^{-1}$, 8100 independent (R_{int} = 0.044) and 4213 observed reflections [$I \ge 2\ \sigma(I)$], 539 refined parameters, R = 0.052, wR^2 = 0.158, max. (min.) residual electron density 0.39 (-0.61) e $Å^{-3}$, two almost identical molecules in the asymmetric unit, hydrogen atoms at nitrogen from difference fourier calculations, others calculated and refined as riding atoms.

3j. formula $C_{24}H_{15}NO_4$ * H_2O, M = 399.39, red crystal 0.20 x 0.10 x 0.05 mm, a = 8.066(1), b = 15.317(2), c = 15.702(2) Å, β = 92.39(1)º, V = 1938.2(4) $Å^3$, ρ_{calc} = 1.369 g cm^{-3}, μ= 0.797 mm^{-1}, empirical absorption correction (0.857 $\le T \le$ 0.961), Z = 4, monoclinic, space group $P2_1/n$ (No. 14), λ= 1.54178 Å, T = 293(2) K, ω/2θ scans, 4234 reflections collected (-h, +k, ±l), [(sinθ)/λ] = 0.62 $Å^{-1}$, 3949 independent (R_{int} = 0.071) and 2410 observed reflections [$I \ge 2\ \sigma(I)$], 288 refined parameters, R = 0.062, wR^2 = 0.197, max. (min.) residual electron density 0.29 (-0.33) e $Å^{-3}$, hydrogen atoms at nitrogen and water from difference fourier calculations, others calculated and refined as riding atoms.

Data sets were collected with a Enraf Nonius CAD4 diffractometer. Programs used: data collection Express [19a], data reduction MolEN [19b], structure solution SHELXS-97 [19c], structure refinement SHELXL-97 [19d], graphics SCHAKAL [19e]. CCDC 701844 & 701843 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44(1223)336-033, E-mail: deposit@ccdc.cam.ac.uk].

CONCLUSIONS

In summary, we have shown that 2-aryl-2,2′-biindan-1,1′,3,3′-tetrones **2** can regioselectively produce enaminones **3** upon refluxing with urea in acetic acid. NMR studies reveal that enaminones **3** can exhibit keto-enol tautomerism depending upon the polarity of the solvent. While the keto forms exist exclusively in $CDCl_3$, the enol forms predominate in more polar aprotic DMSO-d_6 and acetone-d_6. To the best of our knowledge, this is the first observation of keto-enol tautomerism in aminoindenone systems.

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