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Unexpected pyrylium to pyrylium domino transformation. Synthesis of pyrano[3,4-*c*]pyran-7-ium cation and its recyclization to 2,7-naphthyridine derivative

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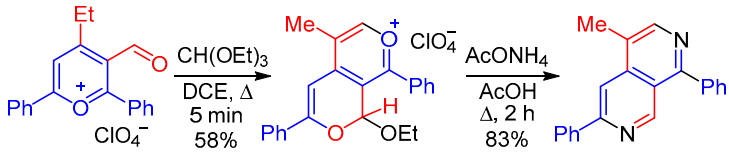


4-Ethyl-3-formyl-2,6-diphenylpyrylium perchlorate was obtained from 2,6-diphenylpyrylium perchlorate in three steps. Its reaction with triethyl orthoformate was accompanied by rearrangement of the initial pyrylium ring and led to pyrano[3,4-*c*]pyran-7-ium perchlorate system through a domino process involving ethanol addition-elimination. A plausible mechanism of the reaction is suggested on the basis of DFT quantum-chemical calculations. Reaction of the obtained pyrano[3,4-*c*]pyran-7-ium perchlorate with ammonium acetate led to a 2,7-naphthyridine derivative without a skeletal rearrangement.

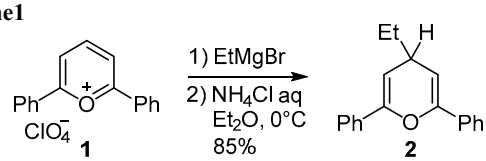
Keywords: naphthyridine, pyrylium salts, triethyl orthoformate, domino process, recyclization.

Pyrylium salts have been investigated quite extensively by many research groups. Being aromatic, they are easily produced from simple starting materials.[1] The reactivity of pyrylium salts toward nucleophiles makes them useful for obtaining other compounds with strong aromatic character. These cations react with nucleophiles at positions 2, 4, and 6, inducing ring-opening[2] and recyclization reactions affording pyridines, phosphinines,[3] new pyridinium[4] and thiopyrylium salts.[5] Reduction of pyrylium salts leads to hydrocarbons, hydrogenated pyridines, tetrahydropyrans, and thiopyrans.[6] There are many papers devoted to the conversion of pyrylium salts to furan derivatives.[7]

Pyrylium derivatives have been used as fluorescent biomarkers[8] and nonlinear optical chromophores.[9] Recently, pyrylium salts have been employed as ionic liquids[10] and in supramolecular chemistry studies, acting as guests in cucurbituril hosts.[11] Pyrylium salts bound with macrocyclic crown compounds have been used as reagents for the recognition of transition metal cations.[12] Despite the large number of publications on recyclization reactions of pyrylium cations, no information is yet available about transformations involving the reorganization of carbon skeleton and conversion of one pyrylium cation to another. Such a recyclization was surprisingly discovered during our study of 4-ethyl-3-formyl-2,6-diphenylpyrylium perchlorate reaction with triethyl orthoformate.

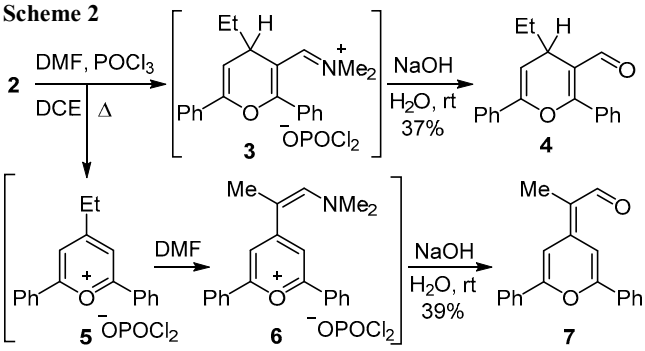
The initial purpose of our study was to obtain a pyrylium salt containing aldehyde and alkyl groups in vicinal positions and to investigate its reaction with triethyl orthoformate. We synthesized such a salt in three steps from 2,6-diphenylpyrylium perchlorate (**1**) according to the method developed in our earlier work.[13] First we obtained 4*H*-pyran **2** by reaction of perchlorate **1** with ethylmagnesium bromide (Scheme 1).

Scheme1



The second step was a Vilsmeier formylation of pyran **2**. However, this reaction resulted in the formation of two products: the desired 3-formylpyran **4** and aldehyde **7**, which were separated by alumina column chromatography (Scheme 2). Obviously, two parallel processes occur: electrophilic attack at position 3 of pyran **2** to form a Vilsmeier intermediate **3** and an oxidation of pyran system

Scheme 2



to produce salt **5**. The ethyl-substituted salt **5** reacted with DMF to give the intermediate condensation product **6**. The formation of such products from alkyl-substituted pyrylium salts has been investigated earlier.[14] Treatment of the reaction mixture with alkali resulted in the formation of aldehydes **4** and **7**.

3-Formylpyran **4** was successfully oxidized to the desired 3-formylpyrylium perchlorate **8** by the action of trityl perchlorate (Scheme 3).

The reaction of pyrylium salt **8** with triethyl orthoformate gave a compound that was characterized by ^{1}H NMR spectroscopy, with a methyl group singlet at 2.68 ppm and ethyl group signals at 1.24 and 3.89–4.54 ppm. Initially, according to the data of our earlier work,[15] the reaction product was incorrectly assigned the structure **13** (Scheme 3). It was assumed that 4-ethylidene-4*H*-pyran **9** formed after the deprotonation, followed by a conventional acid-induced

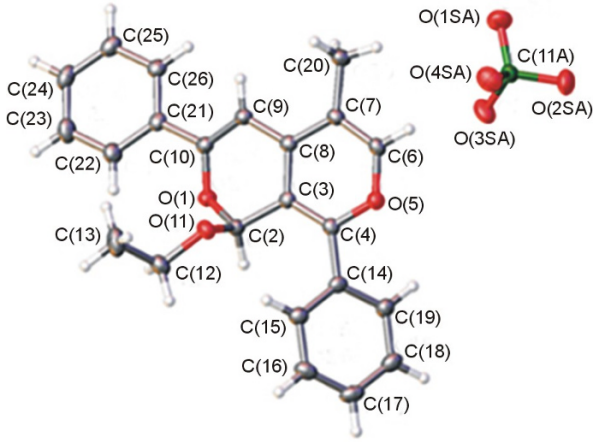


Figure 1. Molecular structure of product **19**.

addition of triethyl orthoformate to the double bond, gave the intermediate **10**. After ethanol elimination and cyclization through intermediates **11** and **12**, product **13** was expected to form. However, X-ray structural analysis showed that structure **13** was incorrect. Figure 1 demonstrates that the phenyl groups are located on different pyran rings. It means that structure **19** was actually formed. We have proposed a plausible reaction mechanism shown in Scheme 3 and have performed DFT calculations of the important stationary points (Table 1) on the potential energy surface (PES) of the reacting system (Scheme 3). Presumably, the initial salt **8** was deprotonated to ethylidenepyran **9**; the eliminated proton reacted with triethyl orthoformate to give a diethoxy carbenium cation, which then added to the double bond of

Scheme 3

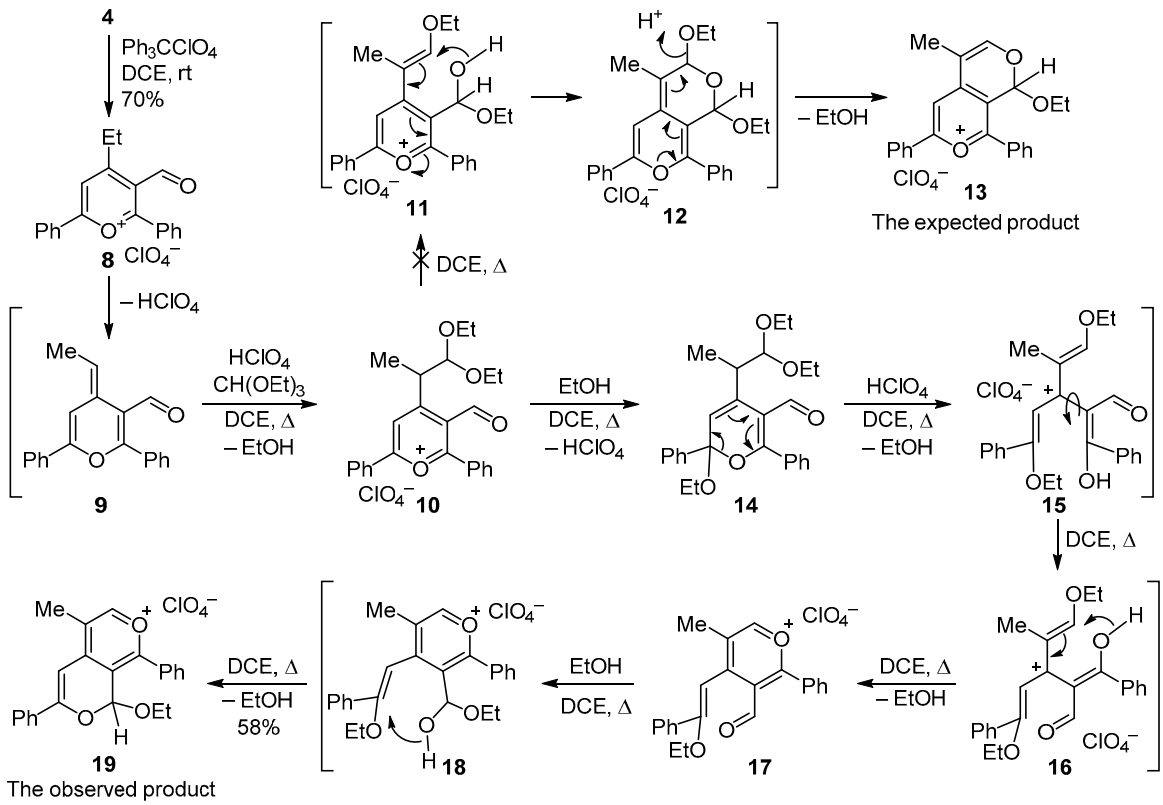


Table 1. Total (E) and relative (E_{rel}) energies of the stationary points on PES according to Scheme 3. B3LYP calculations by 6-31G** basis set in 1,2-dichloroethane

System	E, arb unit	E_{rel}*, kcal/mol
$CH(OEt)_3$	−502.06080	0.0
8	−922.66729	
EtOH	−155.05017	–
$HClO_4$	−761.30830	–
ClO_4^-	−760.8755	–
10	−1269.67139	4.1
11	−1114.59176	22.6
13	−1114.62488	1.8
14	−1424.27841	−10.6
19	−1114.63030	−1.6

*The total energy of isolated system comprised of compound **8** and triethyl orthoformate was set to zero. The calculations of E_{rel} took into account the reaction stoichiometry.

compound **9** to form pyrylium salt **10** and ethanol. The ethanol molecule liberated in this step reacted as a nucleophile and started the subsequent domino process. Salt **10** gave the addition product – 6*H*-pyran **14**, because according to our DFT quantum-chemical calculations with B3LYP functional and 6-31G** basis set, while assuming 1,2-dichloroethane as solvent, the largest positive charge (0.346 e^-) was located at position 6 of the pyrylium ring.

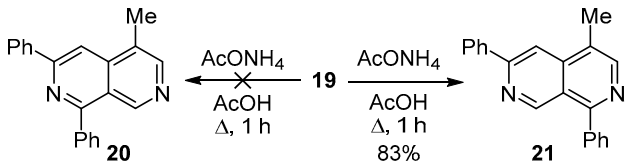
Ring opening, elimination of ethanol, and protonation gave cation **15**, which was stabilized by three vinyl groups (Scheme 3). Rotation around the single bond in cation **15** led to structure **16**, which cyclized to pyrylium perchlorate **17**. Perchlorate **17** rearranged to the observed product **19** through hemiacetal **18**.

In a recent DFT study of the complexes of some heterocyclic cations with Cl^-, NO_3^-, and BF_4^- anions it has been shown that the stabilization energies of the ionic pairs varied in the range from 1.2 to 2.0 kcal/mol, depending on the position of anions relative to the phenyl-substituted pyrylium cation. These values are certainly much smaller than the expected activation energies of the pyrylium system **8** toward the nucleophilic rearrangements under consideration.[16] Obviously, the same applies to the ClO_4^- anion, which is located not less than 3.0–3.5 Å from the plane of the heterocyclic cation, according to our X-ray structural analysis data. Moreover, the selected basis set provided accurate geometrical characteristics of these pyrylium salts, in particular cation **19** (Supplementary materials, Fig. S13). On one hand, it confirmed the suitability of the chosen computational method and on the other this indicated the practical independence of the cation structure rearrangements from the presence of counterion. Therefore, the sum of total energy values for cation **8** and triethyl orthoformate was adopted as the starting point for relative energy calculations.

Obviously, at the initial stage of the reaction, intermediate **10** was formed, which was less stable by 4.1 kcal/mol, compared to the system of reagents (Table 1). A stationary point of the PES corresponding to intermediate **10** was, in fact, the bifurcation point of the minimum energy pathways leading to products **13** and **19** (Supplementary materials, Table S2). According to our calculations, the formation of product **13** is unrealistic, since intermediate **11**, lying on the endothermic path to the expected product **13**, was substantially (22.6 kcal/mol) less stable. At the same time, the formation of the experimentally detected product **19** was predicted to be exothermic (Table 1).

In the reaction of pyrano[3,4-*c*]pyran-7-ium salt **19** with an excess of ammonium acetate, both rings underwent recyclization. Here it is appropriate to note that only a recyclization the pyrylium moiety occurred in pyrano[2,3,4-*de*]-chromen-4-ium system containing condensed pyran and pyrylium rings.[17] There was a methyl group singlet observed at 2.68 ppm and three aromatic CH singlets at 8.29, 8.63, 9.39 ppm in ^{1}H NMR spectrum of the product. These chemical shifts were in good agreement with the literature data for 2,7-naphthyridines.[18] However, the recyclization may produce predominantly one of the isomeric systems **20** or **21**, because both six-membered rings may be cleaved and recyclized (Scheme 4).

Scheme 4



In order to establish the exact naphthyridine structure resulting from this reaction, we performed X-ray structural analysis of the product, with the solved structure presented in Figure 2. It turned out that structure **21** represented the actual product obtained, proving the preferred formation of structures **19** and **21** with phenyl substituents in different rings.

2,7-Naphthyridines are a relatively unexplored class of N-heterocycles, and methods for their synthesis are insufficiently developed.[19] The most common route of synthesis involves a reaction of ammonia with *o*-ethynylpyridinecarbaldehydes.[20] However, the preparation of these starting materials requires a multistep functionalization of pyridine derivatives in the presence of palladium complexes. In our reaction sequence, an aldehyde group necessary for annulation of the second ring was introduced into the pyran

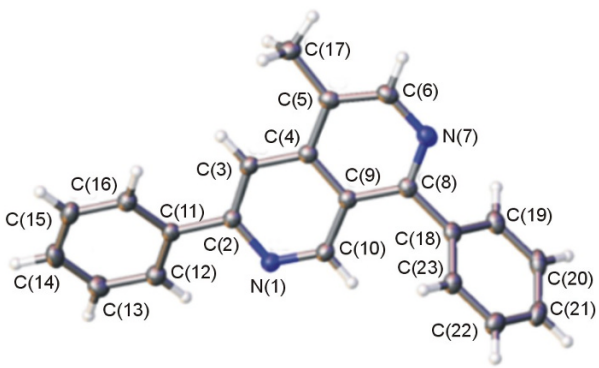


Figure 2. Molecular structure of 2,7-naphthyridine **21**.

ring by using the classic Vilsmeier reaction and did not require transition metal catalysis.

In summary, we have synthesized 4-ethyl-3-formyl-2,6-diphenylpyrylium perchlorate, a new representative of pyrylium salts bearing alkyl and formyl functional groups, which can be further modified. An unexpected reaction of this perchlorate, including a rearrangement of the initial pyrylium ring leading to 1-ethoxy-5-methyl-3,8-diphenyl-1*H*-pyrano[3,4-*c*]pyran-7-ium perchlorate, has been discovered. Both rings of the bicyclic pyrano[3,4-*c*]pyran-7-ium perchlorate underwent recyclization to form 4-methyl-1,6-diphenyl-2,7-naphthyridine without a skeletal rearrangement. This reaction can be used for further developing the synthesis of 2,7-naphthyridines.

Experimental

^{1}H and ^{13}C NMR spectra were acquired on a Bruker DPX-250 spectrometer (250 and 63 MHz, respectively). The internal standard was TMS. Elemental analysis was performed on an Elementar varioMICROcube CHNS-analyzer. The content of halogens was determined separately by the Schöniger method. Melting points were determined in open capillaries on a Khimlaborpribor PTP apparatus.

All commercially available compounds were used without further purification. The starting 2,6-diphenylpyrylium perchlorate (**1**) was obtained by a previously published procedure.[21]

4-Ethyl-2,6-diphenyl-4*H*-pyran (2). Ethyl bromide (14.17 g, 9.4 ml, 0.13 mol) was added to a suspension of magnesium (3.0 g, 0.13 mol) with few iodine crystals in anhydrous diethyl ether (40 ml). After the interaction of the reagents, pyrylium salt **1** (16.62 g, 0.050 mol) was added to the reaction mixture, while cooling with ice water. Then it was treated with 20% aqueous solution of ammonium chloride. The organic phase was dried over anhydrous calcium chloride, and the solvent was removed by distillation using a water bath, providing a yellow solid. The residue was recrystallized from EtOH. Yield 11.2 g (85%), colorless crystals, mp 57–59°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 1.00 (3H, t, *J* = 7.4, 4-$CH_2C\underline{H}_3$); 1.46–1.68 (2H, m, 4-$C\underline{H}_2CH_3$); 2.97–3.24 (1H, m, H-4); 5.38 (2H, d, *J* = 3.8, H-3,5); 7.26–7.47 (6H, m, H Ph); 7.70 (4H, d, *J* = 6.9, H Ph). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 10.2; 31.1; 33.1; 100.8 (2C); 124.5 (4C); 128.2 (2C); 128.3 (4C); 134.8 (2C); 148.9 (2C). Found, %: C 86.80; H 6.75. $C_{19}H_{18}O$. Calculated, %: C 86.99; H 6.92.

Synthesis of 4-ethyl-2,6-diphenyl-4*H*-pyran-3-carbaldehyde (4) and 2-(2,6-diphenyl-4*H*-pyran-4-ylidene)-propanal (7). $POCl_3$ (8.28 g, 5.0 ml, 54 mmol) was added to a solution of DMF (3.95 g, 3.8 ml, 54 mmol) in anhydrous 1,2-dichloroethane (25 ml). The reaction mixture was kept at room temperature for 1 h and then 4*H*-pyran **2** (7.07 g, 27 mmol) was added. The reaction mixture was refluxed for 2 h, cooled, kept at room temperature for 24 h, and then treated with a solution of NaOH (2.16 g, 54 mmol) in water (10 ml). The organic phase was dried over anhydrous calcium chloride, and the solvent was removed by distillation using a water bath. The crude residue was purified by alumina column chromatography (eluent $CHCl_3$). Product **4** was eluted as a part of the red fraction with R_f 0.9 and purified by crystallization from 2-propanol. Product **7** was eluted as a part of the yellow fraction with R_f 0.7 and purified by crystallization from 2-propanol.

4-Ethyl-2,6-diphenyl-4*H*-pyran-3-carbaldehyde (4). Yield 2.90 g (37%), colorless crystals, mp 155–156°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 0.95 (3H, t, *J* = 7.5, 4-$CH_2C\underline{H}_3$); 1.46–1.88 (2H, m, 4-$C\underline{H}_2CH_3$); 3.52 (1H, td, *J* = 5.9, *J* = 4.5, H-4); 5.73 (1H, d, *J* = 5.5, H-5); 7.12–7.95 (10H, m, H Ph); 9.63 (1H, s, 3-CHO). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 9.5; 29.0; 30.5; 103.8; 116.3; 124.4 (2C); 128.5 (4C); 128.7; 130.2 (2C); 131.0; 131.8; 133.0; 148.8; 168.4; 191.6. Found, %: C 82.60; H 6.14. $C_{20}H_{18}O_2$. Calculated, %: C 82.73; H 6.25.

2-(2,6-Diphenyl-4*H*-pyran-4-ylidene)propanal (7). Yield 3.03 g (39%), yellow crystals, mp 188–189°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 1.89 (3H, s, 4-C(C$\underline{H}_3$)CHO); 6.98 (1H, d, *J* = 1.9, H-5); 7.35–7.68 (6H, m, H Ph); 7.91 (1H, d, *J* = 1.8, H-3); 7.93–8.11 (4H, m, H Ph); 10.29 (1H, s, 4-C(CH_3)C$\underline{H}$O). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 9.4; 101.1; 104.0; 117.6; 125.3 (2C); 125.5 (2C); 128.9 (4C); 130.1; 130.5; 132.3; 132.5; 142.2; 153.4; 155.6; 187.2. Found, %: C 83.18; H 5.73. $C_{20}H_{16}O_2$. Calculated, %: C 83.31; H 5.59.

4-Ethyl-3-formyl-2,6-diphenylpyrylium perchlorate (8). Trityl perchlorate (3.42 g, 0.01 mol) was added to a solution of 3-formylpyran **4** (2.88 g, 0.01 mol) in anhydrous 1,2-dichloroethane (4 ml). The obtained yellow crystalline precipitate was filtered off, washed with diethyl ether, and air-dried. Yield 2.70 g (70%), mp 187–189°C. ^{1}H NMR spectrum (CF_3COOD), δ, ppm (*J*, Hz): 1.81 (3H, t, 4-$CH_2C\underline{H}_3$); 3.64–3.89 (2H, m, 4-$C\underline{H}_2CH_3$); 7.81–8.36 (8H, m, H Ph); 8.62 (2H, d, *J* = 7.8, H Ph); 8.79 (1H, s, H-5); 10.33 (1H, s, 3-C$\underline{H}$O). ^{13}C NMR spectrum (CF_3COOD), δ, ppm: 11.7; 29.1; 119.1; 125.7; 126.8; 126.9; 129.2; 129.9; 130.3; 131.4; 135.7; 137.7; 174.1; 177.2; 179.9; 190.2. Found, %: C 61.61; H 4.25; N 8.91. $C_{20}H_{17}ClO_6$. Calculated, %: C 61.78; H 4.41; N 9.12.

1-Ethoxy-5-methyl-3,8-diphenyl-1*H*-pyrano[3,4-*c*]pyran-7-ium perchlorate (19). An excess of triethyl orthoformate (4 ml, 20 mol) was added to a boiling solution of 3-formylpyrylium salt **8** (2.40 g, 7 mmol) in anhydrous dichloromethane (4 ml). After cooling, the formed orange crystalline precipitate was filtered off, washed with diethyl ether, and air-dried. Yield 1.65 g (58%), mp 233–234°C. ^{1}H NMR spectrum (acetone-d_6), δ, ppm (*J*, Hz): 1.24 (3H, t, *J* = 7.1, $OCH_2C\underline{H}_3$); 2.68 (3H, s, CH_3); 3.89–4.54 (2H, m, $OC\underline{H}_2CH_3$); 6.80 (1H, s, H Ar); 7.57 (1H, s, H Ar); 7.60–8.41 (10H, m, H Ar); 9.20 (1H, s, H Ar). ^{13}C NMR spectrum (CD_3CN), δ, ppm: 13.8; 15.6; 66.4; 97.0; 98.7; 117.7; 126.8; 129.8 (2C); 129.9; 130.9 (4C); 131.0 (2C); 132.3; 134.9; 136.1; 155.4; 159.7; 169.0; 171.1. Found, %: C 61.91; H 4.59; Cl 7.79. $C_{23}H_{21}ClO_7$. Calculated, %: C 62.10; H 4.76; Cl 7.97.

4-Methyl-1,6-diphenyl-2,7-naphthyridine (21). Perchlorate **19** (0.30 g, 0.67 mmol) was added to a mixture of glacial acetic acid (5.25 g, 5 ml, 87 mmol) with an excess of ammonium acetate (0.30 g, 3.89 mmol). The reaction

mixture was refluxed for 1 h, cooled, treated with solid Na_2CO_3 (4.63 g, 44 mmol) until alkaline reaction, and extracted with chloroform (2×20 ml). The organic fraction was dried over anhydrous calcium chloride, and the solvent was removed by distillation using a water bath. The residue was recrystallized from EtOH. Yield 0.165 g (83%), light-green crystals, mp 164–165°C. ^{1}H NMR spectrum (acetone-d_6), δ, ppm: 2.68 (3H, s, CH_3); 7.25–7.59 (6H, m, H Ar); 7.63–7.85 (2H, m, H Ar); 8.16–8.30 (2H, m, H Ar); 8.35 (1H, s, H Ar); 8.56 (1H, s, H Ar); 9.41 (1H, s, H Ar). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 15.5; 111.8; 120.2; 125.6; 127.4 (2C); 128.6 (2C); 129.0 (2C); 129.2; 129.4; 130.2 (2C); 138.1; 138.9; 141.0; 145.9; 153.2; 154.4; 160.1. Found, %: C 84.92; H 5.29; N 9.29. $C_{21}H_{16}N_2$. Calculated, %: C 85.11; H 5.44; N 9.45.

X-ray structural study of compounds 19 and 21 was performed on a Bruker SMART APEX II CCD diffractometer (λ(MoKα) 0.71072 Å, ω-scans, 2θ<56°). For compound **19**, the intensities of 31372 reflections were recorded and 10656 independent reflections (R_{int} 0.0435) were used in further refinement. For compound **21**, the intensities of 15515 reflections were recorded and 3986 independent reflections (R_{int} 0.0351) were used in further refinement. The structures were solved by direct method and refined by the full-matrix least-squares technique against F^2 in isotropic-anisotropic approximation. The positions of hydrogen atoms were calculated geometrically and refined with the riding model. All calculations were performed using the SHELXTL PLUS 5.0 software suite.[22] The X-ray structural analysis datasets for compounds **19** and **21** were deposited at the Cambridge Crystallographic Data Center (deposits CCDC 1494063 and CCDC 1494064, respectively).

Supplementary information file (NMR spectra, X-ray data of compounds and quantum-chemical calculations obtained) associated with this article are available from the journal website at http://link.springer.com/journal/10593.

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