Dicyano(7-methyl-6-oxo-6*H*-dibenzo[*b*,*d*]pyran-9-yl)methanide Salts *via* a Multicomponent Reaction

by **Mehdi Khoobi**[a]), **Ali Ramazani***[b]), **Alireza Foroumadi**[a]), **Ali Souldozi**[c]), **Katarzyna Ślepokura**[d]), **Tadeusz Lis**[d]), **Amir Mahyari**[b]), **Abbas Shafiee**[a]), and **Sang Woo Joo***[e])

[a]) Department of Medicinal Chemistry, Faculty of Pharmacy, and Pharmaceutical Sciences Research Center, Tehran University of Medical Sciences, Tehran 14176, Iran

[b]) Department of Chemistry, University of Zanjan, P.O. Box 45195-313, Zanjan, Iran (phone: +98 241 5152572; fax: +98 241 5152477; e-mail: aliramazani@yahoo.com)

[c]) Chemistry Department, Islamic Azad University, Urmia Branch, P.O. Box 969, Urmia, Iran

[d]) Faculty of Chemistry, University of Wrocław, 14 Joliot-Curie St., PL-50-383 Wrocław

[e]) School of Mechanical Engineering, Yeungnam University, Gyeongsan, 712-749, Korea (phone: +82 53 8102568; fax: +82 53 8102062; e-mail: swjoo@yu.ac.kr)

Dialkylammonium dicyano(7-methyl-6-oxo-6*H*-dibenzo[*b*,*d*]pyran-9-yl)methanides **4a**–**4j** are obtained in good yields *via* a simple reaction between 3-acetylcoumarins (= 3-acetyl-2*H*-1-benzopyran-2-ones) **1** and malononitrile (**2**) in EtOH (*Table 1*). In this reaction, a charge-separated zwitterionic salt is formed.

Introduction. – Dibenzopyranones are broadly found in biologically important natural products and synthetic pharmaceuticals including the structurally similar compounds autumnariol, autumnariniol, altenuisol, and alternariol (*Fig. 1*, **A**). As such, they are found in a number of natural antitumor and antibiotic agents such as gilvocarcins, ravidomycins, and chrysomycins (*Fig. 1*, **B**). Several natural products, including progesterone, androgen, glucocorticoid receptor agonists, and endothelial cell proliferation inhibitors, have been synthesized from these pharmacophores as intermediates [1].

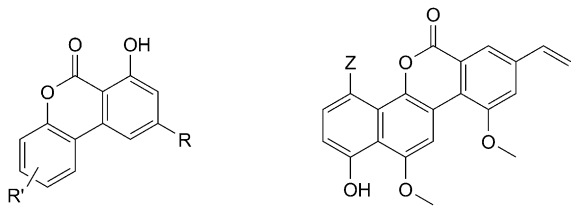


Fig. 1. *Biologically active compounds* **A** *and* **B** *based on coumarins (=2*H*-1-benzopyran-2-ones)*

A *Suzuki* cross-coupling reaction followed by metal or *Lewis* acid mediated lactonization is the most conventional approach for the synthesis of dibenzopyranones [2]. Cyclization of bromobenzyl fluorophenyl ethers in the presence of (*tert*-

butyl)lithium [3], condensation of resorcinol (= benzene-1,3-diol) with substituted 2-bromobenzoic acids in alkaline medium in the presence of copper sulfate catalyst (*Hurtley* reaction) [4], cyclotrimerization of aryldiynes in the presence of a ruthenium catalyst [5], $C–O_{carboxylic}$ coupling reaction catalyzed by copper(I) salts [6], and a *Diels–Alder* reaction between 4-cyanocoumarins (= 2-oxo-2*H*-1-benzopyran-4-carbonitriles) and 1-oxygenated dienes followed by elimination–aromatization with KO^{t}Bu [1] are also reported methods for the synthesis of dibenzopyranones. Such existing methods, however, require the use of Pd-catalysts, aryl fluorides and iodides, ionic liquids, or multistep reaction sequences and suffer from disadvantages including low yields, harsh conditions, and expensive reagents.

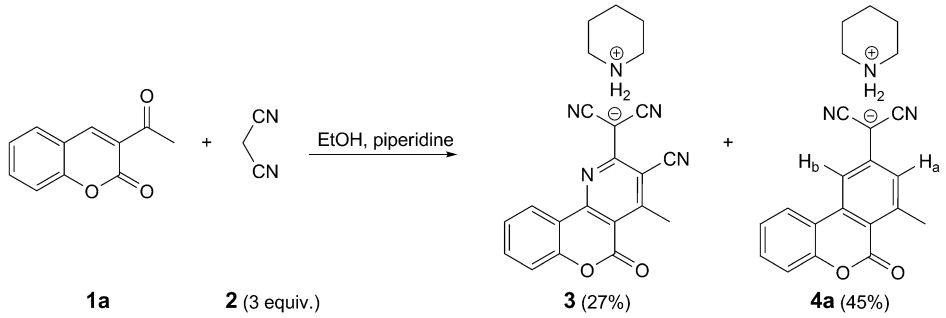
As part of our ongoing program on the search for efficient and robust synthetic methods [7], we found a convenient preparation of dialkylammonium dicyano(7-methyl-6-oxo-6*H*-dibenzo[*b*,*d*]pyran-9-yl)methanide salts **4**. Herein, we report our results on this new type of a multicomponent reaction with four molecules forming these new benzopyranones derivatives. Firstly, we examined the behavior of 3-acetylcoumarin (= 3-acetyl-2*H*-1-benzopyran-2-one; **1a**) and malononitrile (**2**) in the presence of secondary amines, thereby taking into account the discussed base-catalyzed *Thorpe* dimerization of malononitrile. The one-pot reaction between 3-acetylcoumarins **1** and an excess of **2** in the presence of a secondary amine in EtOH resulted in a novel reaction leading to the corresponding ammonium methanides **4a**–**4j** in good yields.

Malononitrile is an exceptionally versatile compound which is used in the synthesis of heterocyclic compounds, pharmaceuticals, pesticides, fungicides, and solvatochromic dyes [8]. The CH_2 group and either one or both cyano groups can take part in condensation reactions to give a variety of addition products and heterocyclic compounds. This specific property of malononitrile makes it an indispensable reactant in a whole number of multicomponent reactions, such as the one described herein.

Results and Discussion. – Our research originated from an unexpected observation made during simple condensation of an excess amount (3 equiv.) of malononitrile (**2**) with 3-acetylcoumarin (**1a**). Surprisingly, when the reaction was performed in the presence of piperidine as base under reflux conditions, significant amounts of a polar solid identified as piperidinium dicyano(7-methyl-6-oxo-6*H*-dibenzo[*b*,*d*]pyran-9-yl)-methanide (**4a**) and piperidinium dicyano(3-cyano-4-methyl-5-oxo-5*H*-[1]benzopyrano[4,3-*b*]pyridin-2-yl)methanide (**3**), was isolated from the residue by flash chromatography after evaporation of the solvent (*Scheme 1*).

The products **3** and **4a** were fully characterized by IR, ^{1}H- and ^{13}C-NMR, and mass spectra and elemental analysis. The MS of **4a** displayed a molecular-ion signal at *m*/*z* 274 corresponding to the expected product generated by loss of piperidine and fragment at *m*/*z* 209 indicating the loss of the malononitrile group. In the ^{1}H-NMR spectrum of **4a**, in addition to the signal of the aromatic H-atoms of the 2-oxo-2*H*-1-benzopyran part (δ(H) 7–8) and those assigned to the piperidinium part (δ(H) 1.5–3), two sharp *s* due to two aromatic H-atoms of the benzo ring fused to the 2-oxo-2*H*-1-benzopyran moiety (δ(H) 6.72 (H_a) and 7.10 (H_b)) were observed. The assignments of H_a and H_b were established by a NOESY experiment which revealed the correlation between the Me group and H_a. The most important absorption bands of **4a** in the IR

Scheme 1. *Synthesis of Compounds* **3** *and* **4a** *from 3-Acetylcoumarin* (**1a**) *and Malononitrile* (**2**)



spectrum were found at 2174 and 2128 cm^{-1}, generated by $\tilde{\nu}_s$ and $\tilde{\nu}_a$ of the malononitrile part. Absorption bands at 1680 cm^{-1} were associated with the C=O group. The ^{1}H-decoupled ^{13}C-NMR spectrum of **4a** showed 19 distinct signals. In this spectrum, the Me group resonated at δ(C) 23.5, the carbanion at δ(C) 34.3 [9], the two nitrile groups at δ(C) 123.2, and the carbonyl group at δ(C) 159.4. In addition, signals of six methines and six quaternary C-atoms, all in the aromatic region, were in agreement with the proposed structure. Finally, the structure of **3** and **4i** (see below, *Table 1*) were confirmed by single-crystal X-ray diffraction (see *Fig. 2* and below *Table 2*).

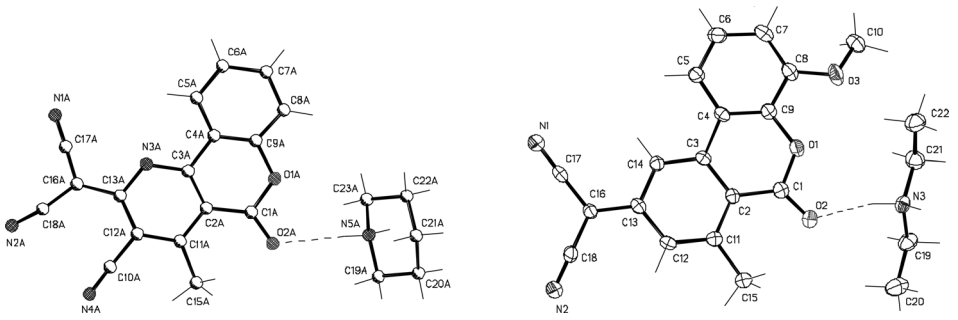
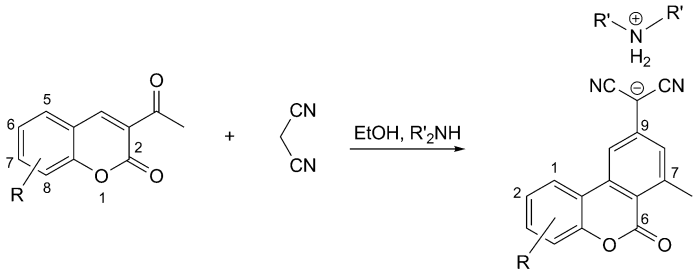


Fig. 2. *Molecular structure of compound* **3** (left) *and* **4i** (right) *showing the X-ray atom-numbering scheme and the symmetry-independent* N^+–$H\cdots O$ *H-bonds* (dashed lines). Only one position of disordered anion and cation of **3** is shown (only a model is presented; atoms shown as spheres of arbitrary radii). Displacement ellipsoids in **4i** represent the 50% probability level.

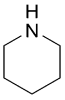
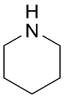
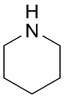
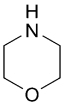
It seems that in this reaction, piperidine behaves both as base catalyst and as nucleophile. To optimize the reaction conditions for the synthesis of compounds **4**, the influences of solvent and amount of malononitrile (**2**) and piperidine were investigated in the reaction of 3-acetylcoumarin (**1a**) as a model reaction. Among the selected amount of malononitrile (**2**), 3.5 equiv. was the most promising one, and among several solvents (MeCN, H_2O, toluene, and EtOH), EtOH was selected as the best one for easy workup and good yield. Temperature and a decreased amount of amine (1 ml per 10 mmol of **1**) had no remarkable influence on the product yield.

Encouraged by the above results and inspired by our general interest in multi-component reactions [10], we utilized various 3-acetylcoumarins **1** with different

Table 1. *Synthesis of Substituted Dibenzopyranone-Derived Salts* **4a**–**4j**



1 **2** (3.5 equiv.) **4a** – **4j** (56 – 77%)

	R[a])	Amine	Time [h]	Yield [%][b])	M.p [°]
a	H		4	57	216–218
b	8-MeO		6	67	262–264
c	7-EtO		6	65	222–224
d	6-Br		4	58	274–276
e	8-MeO		4	60	263–265
f	H		3	56	217–220
g	H	Et_2NH	1	77	192–194
h	6-Br	Et_2NH	3	68	275–277
i	8-MeO	Et_2NH	1	75	262–264
j	H	Me_2NH	1	70	197–199

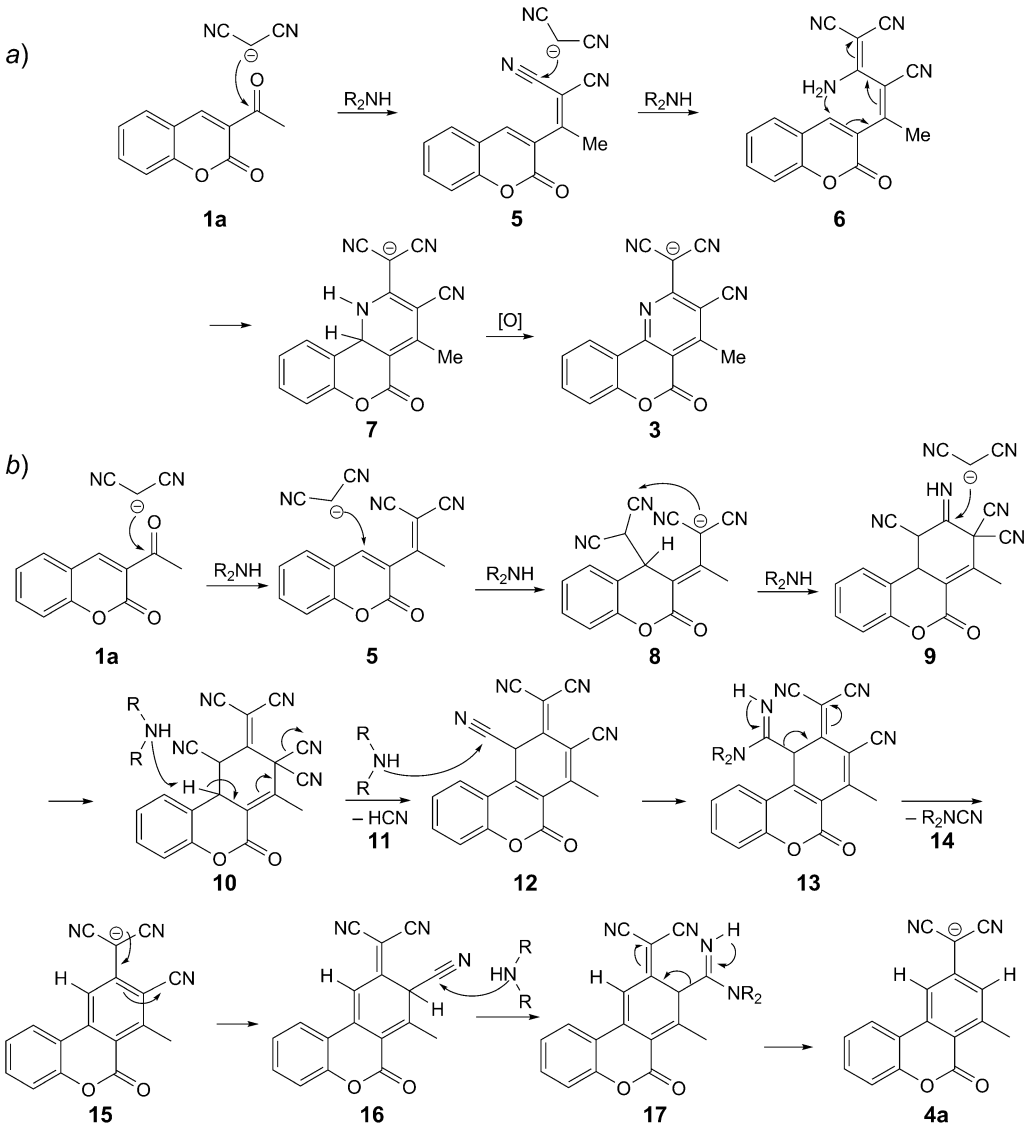
[a])Atom numbering of **1**. [b]) Yield of isolated ammonium salt. **4**.

secondary amines under the same reaction conditions. From the results shown in *Table 1*, we could see that all reactions afforded the corresponding salts **4** in moderate to good yields (56–77%); no predictable change in the yields was observed on changing of substituents in the coumarin derivatives **1**. But the type of amine had an obvious effect on the yield of this reaction, suggesting that the steric property of the amines may play an important role in the reaction. However, the structure of the

employed secondary amines had no significant influence on the yields of the compounds **4**.

To explain the mechanism of this one-pot, multicomponent reaction and the formation of the two products **3** and **4a**, we propose a plausible reaction mechanism, which is illustrated in *Scheme 2*. The reaction possibly can proceed in two different ways (*Paths a* and *b*) which result in the two different products, **3** or **4a**. Intermediate **5** can be obtained by nucleophilic attack of the anion of malononitrile (**2**) at the carbonyl

Scheme 2. *Possible Mechanisms for the Formation of Compounds* **3** *and* **4**



part of 3-acetylcoumarin (**1a**). The addition of another equiv. of malononitrile to the CN group of **5** results in compound **6** which can be converted *via* **7** to the desired fused (benzopyranopyridinyl)methanide **3** after aerial oxidation (*Path a*) [11]. For the production of compound **4a**, *Path b* can be postulated. From intermediate **5**, adduct **8** is obtained *via* a *Michael* addition of another equiv. of the anion of malononitrile (**2**). A fairly similar reaction pathway has been proposed previously [12]. In the next step, the nucleophilic C-center in **8** attacks the C-atom of a CN group in an intramolecular nucleophilic addition to afford compound **9**. The addition of another equiv. of malononitrile to compound **9** results in compound **10**. Elimination of hydrogen cyanide (**11**), assisted by the amine as base, produces **12**. In the next step, nucleophilic attack of the amine at the cyano substituent of **12** leads to compound **13**. This kind of nucleophilic attack and elimination of one hydrogen cyanide has been encountered in several reactions [11–13]. Intermediate **13** can produce compound **15** by elimination of *N*,*N*-dialkylcyanamide (**14**) followed by aromatization as the driving force. A fairly similar reaction pathway may then happen to produce compound **4a** *via* **16** and **17**. In the proposed reaction mechanism, the unique properties of the amine are a crucial factor, the amine acting as a nucleophile as well as a deprotonation agent. Moreover, it seems that also the presence of two cyano groups in malononitrile is an important factor in the reaction sequence, especially due to the stabilization of the carbanion intermediates **3**, **4a**, **7**, **8**, and **15**.

Negatively charged moieties of compounds **4** can be presented as a superposition of the two extreme mesomeric forms **C** and **D** (*Fig. 3*). This resonance and electron-withdrawing effect of the carbonyl group in the lactone moiety can be another important factor in the stabilization of these salts.

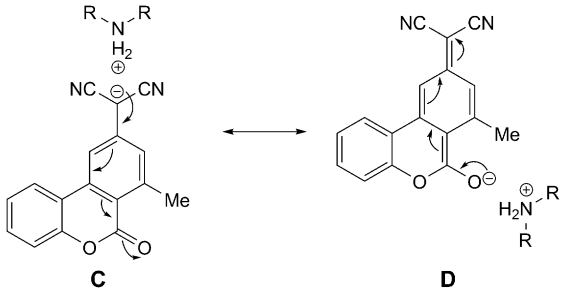


Fig. 3. *Two extreme mesomeric forms* **C** *and* **D** *of compound* **4**

X-Ray Analyses. – A summary of the conditions for the data collection and the structure refinement parameters for compounds **3** and **4i** are given in *Table 2*. Due to a large disorder of both the cation and the anion in the crystal of **3** (see *Exper. Part*), its structure is presented only as a model and, therefore, will not be discussed in detail. The selected geometrical parameters for **4i** are given in *Table 3*. The overall geometry of the anions in the crystals of **3** and **4i** (*Fig. 2*) is the planar arrangement of the atoms with the malononitrile group slightly twisted relative to the main plane (the distance of N(1) and N(2) from the plane is the range of 0.13–0.45 Å; see also the torsion angles in *Table 3*.) The Me group of MeO of **4i** is more displaced from the anion main plane,

Table 2. *Crystallographic Data of Compounds* **3** *and* **4i**

	3	**4i**
Crystallized from	acetone/AcOEt 1 : 1	acetonitrile
Empirical formula	$C_{22}H_{19}N_5O_2$	$C_{22}H_{23}N_3O_3$
M_r	385.42	377.43
Crystal color, habit	light yellow, needle	yellow, plate
Crystal dimensions [mm]	$0.22 \times 0.04 \times 0.02$	$0.36 \times 0.21 \times 0.05$
Radiation type, λ [Å]	MoK_α, 0.71073	MoK_α, 0.71073
Temperature [K]	90(2)	100(2)
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/n$
Z	2	4
θ Range [°]	4.87 – 25.00	2.61 – 35.01
a [Å]	6.753(4)	7.906(3)
b [Å]	11.807(6)	23.371(9)
c [Å]	13.158(7)	10.686(4)
α [°]	64.15(5)	
β [°]	86.64(5)	100.90(4)
γ [°]	81.38(5)	
V [Å^3]	933.5(9)	1938.8(13)
D_x (calc.) [g cm^{-3}]	1.371	1.293
μ [mm^{-1}]	0.09	0.09
$F(000)$ [e]	404	800
Scan type	ω and φ	ω and φ
Index range	$-8 \le h \le 8$	$-9 \le h \le 12$
	$-14 \le k \le 10$	$-34 \le k \le 34$
	$-15 \le l \le 15$	$-17 \le l \le 16$
Measured reflections	6788	21313
Independent reflections	3166	7606
Reflections with $I > 2\sigma(I)$	871	4039
R_{int}	0.121	0.044
Refinement on	F^2	F^2
Data, restraints, parameters	3166, 73, 231	7606, 0, 257
R ($F_o^2 > 2\sigma(F_o^2)$)	$R_1 = 0.060$[a]), $wR_2 = 0.062$[a])	$R_1 = 0.051$[a]), $wR_2 = 0.100$[a])
R (all data)	$R_1 = 0.235$, $wR_2 = 0.077$	$R_1 = 0.112$, $wR_2 = 0.110$
Goodness-of-fit = S	0.77	1.00
Weighting parameter a/b	0.0/0.0	0.0410/0.0
$\Delta\rho$ (max; min) [e Å^{-3}]	0.36; −0.25	0.41; −0.27

[a]) $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$; $wR_2 = \sqrt{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]}$. Weighting scheme: $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = (F_o^2 + 2F_c^2)/3$.

which is reflected by the torsion angle C(10)–O(3)–C(8)–C(9) of 154.99(11)°. The cations in both **3** and **4i** exist in typical conformations: chair (piperidinium in **3**) and extended (diethylammonium in **4i**).

In the crystal lattice of **4i**, the anions related by an inversion center are joined to each other by weak C–H$\cdots\pi$, C=O$\cdots\pi$, and $\pi\cdots\pi$ interactions (*Table 4*) to form stacks along the *a*-axis, as shown in *Fig. 4*. Connections between the adjacent stacks in the remaining directions are provided by the cation$\cdots$anion H-bonds of the N$^+$–H$\cdots$O and N$^+$–H$\cdots$N type (*Table 4*), which results in the packing diagram presented in *Fig. 5*.

Table 3. *Selected Interatomic Distances, Bond Angles, and Torsion Angles of* **4i**

	Bond length [Å]		Bond length [Å]
N(1)–C(17)	1.158(2)	C(16)–C(17)	1.417(2)
N(2)–C(18)	1.157(2)	C(16)–C(18)	1.406(2)
	Bond angle [°]		Torsion angle [°]
C(17)–C(16)–C(13)	121.92(10)	C(10)–O(3)–C(8)–C(9)	154.99(11)
C(17)–C(16)–C(18)	116.66(10)	C(12)–C(13)–C(16)–C(17)	173.78(10)
C(18)–C(16)–C(13)	121.39(11)	C(12)–C(13)–C(16)–C(18)	– 8.27(16)

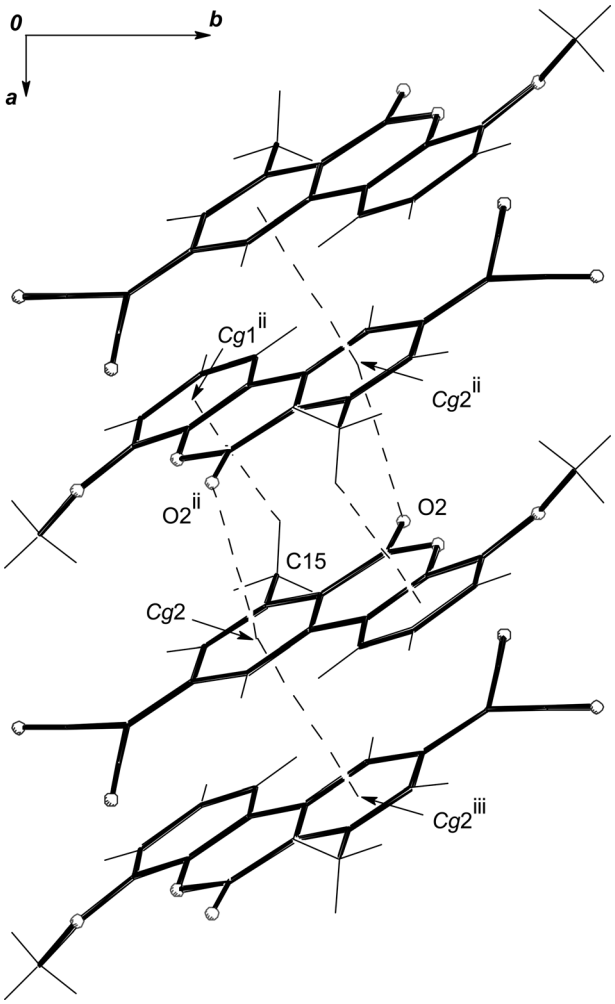


Fig. 4. *The anions of* **4i** *stacking down the* a-*axis.* C–H$\cdots\pi$, C=O$\cdots\pi$, and $\pi\cdots\pi$ interactions are shown with dashed lines. The symmetry codes are given in *Table 4.*

Table 4. *Geometry of Proposed H-Bonds and Close Contacts for* **4i**

D–H···A[a])	D–H [Å]	H···A [Å]	D···A [Å]	D–H···A [°]
N(3)–H(3*B*)···O(2)	0.92	2.00	2.789(2)	143
N(3)–H(3*A*)···N(2)[b])	0.92	2.02	2.901(2)	159
C(20)–H(20*C*)···O(2)	0.98	2.59	3.262(2)	126
C(15)–H(15*C*)···*Cg*(1)[c])	0.98	2.70	3.508(2)	140
C=O···π or π···π[a])	C=O [Å]	O···π [Å]	C···π or π···π [Å]	C=O···π [°]
C(1)=O(2)···*Cg*(2) [d])	1.217(2)	3.808(2)	3.685(2)	74.9(1)
Cg(2) ···*Cg*(2)[c])			3.432(2)	

[a]) *Cg*(1) and *Cg*(2) are the centroids of the C(4) to C(9) and C(2) to C(11) rings, respectively. [b]) Symmetry code: $-x+3/2$, $y+1/2$, $-z+½$. [c]) Symmetry code: $-x+1$, $-y+1$, $-z+1$. [d]) Symmetry code: $-x+2$, $-y+1$, $-z+1$.

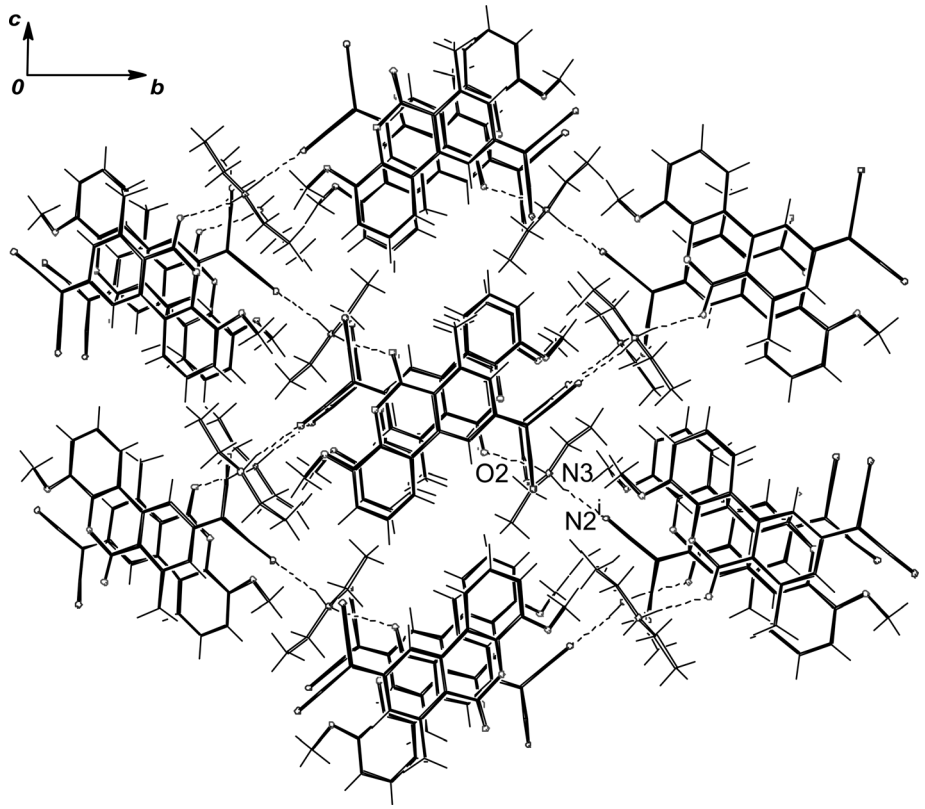


Fig. 5. *The anionic stacks joined to each other by the N⁺–H···O and N⁺–H···N cation···anion H-bonds* (dashed lines) *in the crystal lattice of* **4i**. Anions are drawn with solid lines, cations with open lines. The symmetry code is given in *Table 4*.

Conclusions. – The described method presents an easy way for the preparation of novel stable zwitterionic salts. A series of new charge-separated secondary ami-

nium–dicyanomethanide zwitterionic salts were thus prepared in good yields in a convenient manner. The most attractive features of the discussed reactions are the novelty, the operational simplicity, good yields, the one-pot multicomponent-reaction procedure, as well as commercially available starting materials. All the reactions performed well on a large scale, hence establishing the applicability of the presented method to large-scale processes.

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Experimental Part

General. All chemicals and reagents were obtained from *Merck Chemical Company* (Darmstadt, Germany). The 3-acetylcoumarins **1** were prepared by reported methods [14]. Anal. TLC: *Merck* silica gel *60 F_{254}* plates. IR Spectra: *Nicolet-FT-IR-Magna-550* spectrographs (*Nicolet*, Madison, WI, USA); KBr disks; $\tilde{\nu}$ in cm^{-1}. ^{1}H- and ^{13}C-NMR Spectra: *Bruker-500* spectrometer (*Bruker*, Rheinstetten, Germany); δ in ppm rel. to Me_4Si as internal standard, *J* in Hz. MS: *Finnigan-MAT-TSQ-70* spectrometer (*Finnigan Mat*, Bremen, Germany); at 70 eV; in m/z (rel. %). Elemental analyses (C, H, N): within $\pm$ 0.4% of the theoretical values for C, H, and N.

*Piperidinium Dicyano(3-cyano-4-methyl-5-oxo-5*H-[1]*benzopyrano[4,3-*b*]pyridin-2-yl)methanide* (**3**). To a soln. of 3-acetylcoumarin **1a** (10 mmol) and malononitrile (**2**; 1.7 g, 25 mmol, 3.5 equiv.) in EtOH (20 ml), piperidine (1 ml) was added. The mixture was stirred under reflux condition for 2 h. After completion of the reaction and cooling, the org. phase was concentrated and the resulting crude product purified by CC (silica gel, $CHCl_3$/MeOH 8:2): **3** (27%). Single crystals of **3** were obtained by slow evaporation of its EtOH soln. at 20–25°. The single crystals were filtered, washed with cold EtOH, and dried at r.t. Yellow solid. M.p. 274–276°. UV (95% EtOH): 211 (4.59), 278 (4.37), 318 (4.20), 315 (4.19), 369 (4.62). ^{1}H-NMR ($CDCl_3$): 1.54–1.55 (*m*, CH_2 pip.); 1.61–1.62 (*m*, 4 H, CH_2 pip.); 2.75 (*s*, Me); 3.00 (*t*, *J* = 5.3, CH_2NCH_2 pip.); 7.30 (*d*, *J* = 8.2, 1 arom. H); 7.45 (*t*, *J* = 7.5, 1 arom. H); 7.61 (*t*, *J* = 7.2, 1 arom. H); 8.30 (br. *s*, NH_2^+), 8.31(*d*, *J* = 7.6, 1 arom. H). ^{13}C-NMR ($CDCl_3$): 20.2 (Me); 21.5 (CH_2 pip.); 22.2 (2 CH_2 pip.); 43.7 (CH_2NCH_2 pip.); 46.2 (C^-); 95.3 (C(3)); 97.3 (CN); 105.1 (2 CN); 115.5; 116.3 (arom. CH); 118.4; 124.1 (arom. CH); 125.3 (arom. CH); 132.8 (arom. CH); 152.7; 152.9; 158.0; 158.5; 162.3 (C=O). (4.62) EI-MS: 301 (57, $[M+1]^+$), 300 (100, M^+), 273 (20), 164 (20), 84 (82). Anal. calc. for $C_{22}H_{19}N_5O_2$: C 68.56, H 4.97, N 18.17; found: C 68.34, H 4.71, N 18.31.

*Dialkylammonium Dicyano(7-methyl-6-oxo-6*H-*dibenzo[*b,d*]pyran-9-yl)methanide Salts: General Procedure*. To a soln. of 3-acetylcoumarin (10 mmol) and malononitrile (**2**; 2.3 g, 35 mmol, 3.5 equiv.) in EtOH (20 ml), the secondary amine (1 ml) was added. The mixture was stirred under reflux for the appropriate time (*cf. Table 1*). After completion of the reaction and cooling, the solid was filtered off, washed with cooled EtOH, and dried; pure **4a**–**4j**. Further purification was done by recrystallization from EtOH. Single crystals of **4i** were obtained by slow evaporation of its acetone/AcOEt 1:1 soln. at 20–25° for 4 d. The single crystals were filtered, washed with a cold mixture of acetone/AcOEt 1:1, and dried at r.t.

*Piperidinium Dicyano(7-methyl-6-oxo-6*H-*dibenzo[*b,d*]pyran-9-yl)methanide* (**4a**): Yellow pale solid. M.p. 216–218°. IR: 2174 (CN), 2128 (CN), 1680 (CO). ^{1}H-NMR ($CDCl_3$): 1.49 (br. *s*, CH_2 pip.); 1.66 (br. *s*, 2 CH_2 pip.); 2.69 (*s*, Me); 3.10 (br. *s*, CH_2NCH_2 pip.); 6.72 (*s*, H_a); 7.27–7.30 (*m*, 2 arom. H, H_b); 7.49 (*t*, *J* = 7.5, 1 arom. H); 7.86 (*d*, *J* = 7.5, 1 arom. H); 8.22 (br. *s*, NH_2^+). ^{13}C-NMR ($CDCl_3$): 21.4 (CH_2 pip.); 22.2 (2 CH_2 pip.); 23.5 (Me); 34.3 (C^-); 43.6 (CH_2NCH_2 pip.); 106.7 (arom. CH); 107.6; 116.6 (CH_a); 118.0; 121.8 (arom. CH); 122.8 (CH_b); 123.2 (2 CN); 124.0 (arom. CH); 129.9 (arom. CH); 135.6; 142.8; 149.1; 151.1; 159.4 (C=O). EI-MS: 275 (21, $[M+1]^+$), 274 (100, M^+), 209 (5), 165 (10), 85 (25). Anal. calc. for $C_{22}H_{21}N_3O_2$: C 73.52, H 5.89, N 11.69; found: C 73.31, H 5.71, N 11.38.

*Piperidinium Dicyano(4-methoxy-7-methyl-6-oxo-6*H*-dibenzo[*b,d*]pyran-9-yl)methanide* (**4b**): Yellow pale solid. M.p. 262–264°. IR: 2174 (CN), 2128 (CN), 1685 (CO). ^{1}H-NMR ((D$_6$)DMSO): 1.55 (br. *s*, CH$_2$ pip.); 1.64 (br. *s*, 2 CH$_2$ pip.); 2.62 (*s*, Me); 3.01 (br. *s*, CH$_2$NCH$_2$ pip.); 3.89 (*s*, MeO); 6.78 (*s*, H$_a$); 7.14 (*d*, *J* = 7.8, 1 arom. H); 7.22–7.25 (*m*, 1 arom. H, and H$_b$); 7.50 (*d*, *J* = 7.8, 1 arom. H); 8.20 (br. *s*, NH_2^+). ^{13}C-NMR ((D$_6$)DMSO): 21.5 (CH$_2$ pip.); 22.1 (2 CH$_2$ pip.); 23.6 (Me); 34.1(C$^-$); 43.7 (CH$_2$NCH$_2$ pip.); 55.8 (MeO); 107.1 (arom. CH); 107.5; 111.9 (CH$_a$); 113.9 (arom. CH); 118.6; 121.8 (CH$_b$); 123.0 (2 CN); 123.6 (arom. CH); 135.8; 140.7; 142.8; 147.1; 149.1; 158.9 (C=O). Anal. calc. for $C_{23}H_{23}N_3O_3$: C 70.93, H 5.95, N 10.79; found: C 70.75, H 5.69, N 10.52.

*Piperidinium Dicyano(3-ethoxy-7-methyl-6-oxo-6*H*-dibenzo[*b,d*]pyran-9-yl)methanide* (**4c**): Green pale solid. M.p. 222–224°. IR: 2186 (CN), 2143 (CN), 1681 (CO). ^{1}H-NMR ((D$_6$)DMSO): 1.35 (*t*, *J* = 6.6, *Me*CH$_2$O); 1.55 (br. *s*, CH$_2$ pip.); 1.64 (br. *s*, 2 CH$_2$ pip.); 2.59 (*s*, Me); 3.00 (br. *s*, CH$_2$NCH$_2$ pip.); 4.09 (*q*, *J* = 6.6, MeC*H*$_2$O); 6.70 (*s*, H$_a$); 6.81 (*s*, H$_b$); 6.89 (*d*, *J* = 8.4, 1 arom. H); 7.14 (*s*, 1 arom. H); 7.82 (*d*, *J* = 8.4, 1 arom. H); 8.17 (br. *s*, NH_2^+). ^{13}C-NMR ((D$_6$)DMSO): 14.4 (*Me*CH$_2$O); 21.5 (CH$_2$ pip.); 22.2 (2 CH$_2$ pip.); 23.6 (Me); 34.0 (C$^-$); 43.7 (CH$_2$NCH$_2$ pip.); 63.5 (Me*C*H$_2$O); 101.1 (CH$_a$); 106.0 (CH$_b$); 106.5; 110.9; 112.0 (arom. CH); 121.0 (arom. CH); 123.2 (2 CN); 123.8 (arom. CH); 136.0; 142.7; 149.0; 152.4; 159.5; 159.9 (C=O). Anal. calc. for $C_{24}H_{25}N_3O_3$: C 71.44, H 6.25, N 10.41; found: C 71.64, H 6.51, N 10.13.

*Piperidinium (2-Bromo-7-methyl-6-oxo-6*H*-dibenzo[*b,d*]pyran-9-yl)dicyanomethanide* (**4d**): Yellow solid. M.p. 274–276°. IR: 2178 (CN), 2143 (CN), 1673 (CO). ^{1}H-NMR ((D$_6$)DMSO): 1.55 (br. *s*, CH$_2$ pip.); 1.64 (br. *s*, 2 CH$_2$ pip.); 2.51 (*s*, Me); 3.01 (br. *s*, CH$_2$NCH$_2$ pip.); 6.80 (*s*, H$_a$); 7.17 (*s*, H$_b$); 7.25 (*d*, *J* = 8.3, 1 arom. H); 7.62 (*d*, *J* = 8.3, 1 arom. H); 8.01 (*s*, 1 arom. H); 8.22 (br. *s*, NH_2^+). ^{13}C-NMR ((D$_6$)DMSO): 21.5 (CH$_2$ pip.); 22.1 (2 CH$_2$ pip.); 23.6 (Me); 34.6 (C$^-$); 43.7 (CH$_2$NCH$_2$ pip.); 106.9 (CH$_a$); 107.3; 111.5; 119.0 (CH$_b$); 120.2; 122.3 (arom. CH); 122.8 (2 CN); 125.0 (arom. CH); 132.4 (arom. CH); 134.2; 143.0; 149.3; 150.3; 158.7 (C=O). Anal. calc. for $C_{22}H_{20}BrN_3O_2$: C 60.28, H 4.60, N 9.59; found: C 60.54, H 4.32, N 9.38.

*Morpholin-4-ium Dicyano(4-methoxy-7-methyl-6-oxo-6*H*-dibenzo[*b,d*]pyran-9-yl)methanide* (**4e**): Yellow pale solid. M.p. 263–265°. IR: 2178 (CN), 2151 (CN), 1693 (CO). ^{1}H-NMR ((D$_6$)DMSO): 2.61 (*s*, Me); 3.10 (br. *s*, CH$_2$NCH$_2$ morph.); 3.75 (br. *s*, CH$_2$OCH$_2$ morph.); 3.89 (*s*, MeO); 6.78 (*s*, H$_a$); 7.13 (*d*, *J* = 7.4, 1 arom. H); 7.24–7.26 (*m*, 1 arom. H, and H$_b$); 7.49 (*d*, *J* = 7.8, 1 arom. H); 8.20 (br. *s*, NH_2^+). ^{13}C-NMR ((D$_6$)DMSO): 23.6 (Me); 34.1(C$^-$); 42.8 (CH$_2$NCH$_2$ morph.); 55.8 (MeO); 63.2 (CH$_2$OCH$_2$ morph.); 107.2 (arom. CH); 107.5; 111.9 (CH$_a$); 113.9 (arom. CH); 118.6; 121.8 (CH$_b$); 123.1 (2 CN); 123.6 (arom. CH); 135.8; 140.7; 142.8; 147.1; 149.1; 158.9 (C=O). EI-MS: 305 (25, $[M+1]^+$), 3004 (100, M^+), 261 (52), 218 (39), 57 (82). Anal. calc. for $C_{22}H_{21}N_3O_4$: C 67.51, H 5.41, N 10.74; found: C 67.34, H 5.23, N 10.56.

*Pyrrolidinium Dicyano(7-methyl-6-oxo-6*H*-dibenzo[*b,d*]pyran-9-yl)methanide* (**4f**): Yellow pale solid. M.p. 217–220°. IR: 2170 (CN), 2139 (CN), 1681 (CO). ^{1}H-NMR (CDCl$_3$): 1.83 (br. *s*, 2 CH$_2$ pyr.), 2.61 (*s*, Me), 3.09 (br. *s*, CH$_2$NCH$_2$ pyr.); 6.64 (*s*, H$_a$); 7.26–7.33 (*m*, 2 arom. H, H$_b$); 7.47 (*t*, *J* = 7.5, 1 arom. H); 7.96 (*d*, *J* = 7.5, 1 arom. H); 8.20 (br. *s*, NH_2^+). ^{13}C-NMR (CDCl$_3$): 23.5 (Me); 23.6 (CH$_2$ pyr.); 34.2 (CH$_2$NCH$_2$ pyr.); 44.9 (C$^-$); 106.7 (arom. CH); 107.6; 116.6 (CH$_a$); 118.0; 121.8 (arom. CH); 122.8 (CH$_b$); 123.0 (2 CN); 124.0 (arom. CH); 129.9 (arom. CH); 135.6; 142.8; 149.1; 151.1; 159.2 (C=O). EI-MS: 275 (22 $[M+1]^+$), 274 (100, M^+), 245 (8), 209 (5), 165 (8), 71 (21), 43 (42). Anal. calc. for $C_{21}H_{19}N_3O_2$: C 73.03, H 5.54, N 12.17; found: C 73.23, H 5.24, N 12.37.

*Diethylammonium Dicyano(7-methyl-6-oxo-6*H*-dibenzo[*b,d*]pyran-9-yl)methanide* (**4g**): Yellow pale solid. M.p. 192–194°. ^{1}H-NMR (CDCl$_3$): 1.06 (br. *s*, 2, *Me*CH$_2$N); 2.51 (*s*, Me); 2.62 (br. *s*, 2, MeC*H*$_2$N); 6.78 (*s*, H$_a$); 7.28–7.32 (*m*, 2 arom. H, H$_b$); 7.47 (*t*, *J* = 7.2, 1 arom. H); 7.67 (*d*, *J* = 7.2, 1 arom. H); 8.16 (br. *s*, NH_2^+). ^{13}C-NMR (CDCl$_3$): 10.9 (*Me*CH$_2$N); 23.6 (Me); 34.1 (C$^-$); 41.3 (Me*C*H$_2$N); 106.7 (arom. CH); 107.6; 116.6 (CH$_a$); 118.0; 121.8 (arom. CH); 122.8 (CH$_b$); 123.0; 124.0 (arom. CH); 129.9 (arom. CH); 135.6; 142.8; 149.1; 151.1; 159.2 (C=O). Anal. calc. for $C_{21}H_{21}N_3O_2$: C 72.60, H 6.09, N 12.10; found: C 72.34, H 6.23, N 12.32.

*Diethylammonium (2-Bromo-7-methyl-6-oxo-6*H*-dibenzo[*b,d*]pyran-9-yl)dicyanomethanide* (**4h**): Yellow solid. M.p. 275–277°. IR: 2178 (CN), 2135 (CN), 1693 (CO). ^{1}H-NMR ((D$_6$)DMSO): 1.16 (*t*, *J* = 7.0, 2, *Me*CH$_2$N); 2.60 (*s*, Me); 2.92 (*q*, *J* = 7.0, 2, MeC*H*$_2$N); 6.80 (*s*, H$_a$); 7.18 (*s*, H$_b$); 7.25 (*d*, *J* = 8.3, 1 arom. H); 7.62 (*d*, *J* = 8.3, 1 arom. H); 8.01 (*s*, 1 arom. H); 8.16 (br. *s*, NH_2^+). ^{13}C-NMR ((D$_6$)DMSO): 11.0

(*Me*CH_2N); 23.6 (Me); 34.6 (C^-); 41.3 (MeCH_2N); 106.9 (CH_a); 107.3; 115.8; 119.0 (CH_b); 120.2; 122.3 (arom. CH); 122.8 (2 CN); 125.0 (arom. CH); 132.4 (arom. CH); 134.2; 143.0; 149.3; 150.3; 158.7 (C=O). Anal. calc. for $C_{21}H_{20}BrN_3O_2$: C 59.17, H 4.73, N 9.86; found: C 59.32, H 4.58, N 9.61.

*Diethylammonium Dicyano(4-methoxy-7-methyl-6-oxo-6*H*-dibenzo[*b,d*]pyran-9-yl)methanide* (**4i**). Yellow pale solid. M.p. 262–264°. IR: 2175 (CN), 2133 (CN), 1687 (CO). ^{1}H-NMR ((D_6)DMSO): 1.56 (*t*, *J* = 7.0, 2, *Me*CH_2N); 2.50 (*s*, Me); 2.92 (*q*, *J* = 7.0, 2, MeCH_2N); 6.77 (*s*, H_a); 7.14 (*d*, *J* = 7.8, 1 arom. H); 7.23–7.25 (*m*, 1 arom. H, H_b); 7.49 (*d*, *J* = 7.8, 1 arom. H); 8.16 (br. *s*, NH_2^+). ^{13}C-NMR ((D_6)DMSO): 11.0 (*Me*CH_2N); 23.6 (Me); 34.1 (C^-); 41.3 (MeCH_2N); 55.8 (MeO); 107.1 (arom. CH); 107.5; 111.9 (CH_a); 113.9 (arom. CH); 118.6; 121.8 (CH_b); 123.0 (2 CN); 123.6 (arom. CH); 135.8; 140.7; 142.8; 147.1; 149.1; 158.9 (C=O). Anal. calc. for $C_{22}H_{23}N_3O_3$: C 70.01, H 6.14, N 11.13; found: C 70.32, H 6.01, N 11.35.

*Dimethylammonium Dicyano(7-methyl-6-oxo-6*H*-dibenzo[*b,d*]pyran-9-yl)methanide* (**4j**): Yellow pale solid. M.p. 197–199°. IR: 2171 (CN), 2136 (CN), 1672 (CO). UV (95% EtOH): 221 (4.59), 258 (4.18), 268 (4.23), 299 (4.19), 312 (4.27), 380 (4.49). ^{1}H-NMR ($CDCl_3$): 2.49 (*s*, Me); 2.60 (*s*, 2 MeN); 6.77 (*s*, H_a); 7.25–7.27 (*m*, 1 arom. H, H_b); 7.30 (*t*, *J* = 7.7, 1 arom. H); 7.46 (*d*, *J* = 7.4, 1 arom. H); 7.95 (*d*, *J* = 7.7, 1 arom. H); 8.13 (br. *s*, NH_2^+). ^{13}C-NMR ($CDCl_3$): 23.7 (Me); 34.2 (MeN); 34.3 (C^-); 106.8 (arom. CH); 107.6; 116.6 (CH_a); 118.0; 121.9 (arom. CH); 122.8 (CH_b); 123.1; 124.0 (arom. CH); 129.9 (arom. CH); 135.6; 142.9; 149.1; 151.1; 159.2 (C=O). Anal. calc. for $C_{19}H_{17}N_3O_2$: C 71.46, H 5.37, N 13.16; found: C 71.24, H 5.61, N 13.32.

X-Ray Crystal-Structure Determination of **3** *and* **4i** (*Table 2* and *Fig. 4*)[1]). Light yellow stable single crystals of **3** were obtained from its MeCN soln. by slow evaporation at r.t. over several days. Yellow single crystals of **4i** were grown in a similar way from its acetone/AcOEt 1:1 soln. by slow evaporation over 4 d. The crystallographic measurements were performed on a *Xcalibur-PX* automated four-circle diffractometer with graphite-monochromatized MoK_α radiation at 90(2) and 100(2) K for **3** and **4i**, resp. Data were corrected for *Lorentz* and polarization effects. Data collection, cell refinement, data reduction, and analysis were carried out with *Xcalibur-PX* software: Crysalis CCD and Crysalis RED [15]. The structures were solved by direct methods with the SHELXS-97 [16] program and refined by a full-matrix least-squares technique with SHELXL-97 [16] and anisotropic thermal parameters for all non-H atoms in **4i**. Data obtained for **3** were of poor quality (the crystal was highly disordered and thus gave a weak diffraction pattern). Therefore, its crystal structure is presented only as a model. All atoms in **3** were refined isotropically due to disorder of both the anion and cation (s.o.f. = 0.502(7) and 0.498(7) for two anion positions, and 0.549(8) and 0.451(8) for the cation positions). Geometrical restraints (SAME instructions) were applied to the disordered ions. The two positions of the C(3) atom (C3A and C3B) were constrained (with EXYZ and EADP) to have the same positional and displacement parameters. All H-atoms in **3** and **4i** were included from geometry and were treated as riding atoms, with N–H distances of 0.92 Å and C–H distances of 0.95–0.99 Å, and with U_{iso} values of 1.2 U_{eq} (for NH_2, CH, CH_2) or 1.5 U_{eq} (for Me). The figures were generated with the XP program [17].

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[1]) CCDC-808352 (**3**) and 808353 (**4i**) contain the supplementary crystallographic data for this article. These data can be obtained free of charge *via* http://www.ccdc.cam.ac.uk.

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