Solid Supramolecular Complexes of Potassium Salts of *N*-Methoxynitroaniline Derivatives and Methoxyamino-3,5-dinitropyridine with 18-Crown-6 Ether

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Reactions of substituted *N*-methoxynitroaniline derivatives (**1**) or 2-methoxyamino-3,5-dinitropyridine (**2**) with potassium hydroxide afford the corresponding potassium salts (K^+A^-) in high yield. After dissolution of these salts in dichloromethane in the presence of 18-crown-6 ether (18-C-6), the addition of petroleum ether led to the precipitation of the corresponding solid supramolecular complexes of the type $[18\text{-C-6}\cdots K]^+A^-$, having the stoichiometry 1:1:1. The UV/vis and ^1H NMR spectra are discussed. A barrier of $\Delta G^{\neq} = 15.3 \pm 0.2$ kcal/mol for rotation about the Ar–N bond has been determined for *N*-methoxy-2-cyano-4,6-dinitroaniline. The supramolecular complex $[18\text{-C-6}\cdots K]^+A^-$ derived from **2** has been *N*-methylated with methyl iodide to afford **3**, and *N*-arylated with 2-chloro-3,5-dinitropyridine to afford **4**. The conformations of compounds **3** and **4** have been calculated.

Introduction

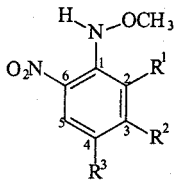
Supramolecular complexes of the type $[CE\cdots M]^+A^-$, where CE is a crown ether, M^+ is an organic or metallic cation, and A^- is an anion, are well-known.[1a–1f] Such compounds are able to promote cation transfer from the solid state or aqueous solution into an organic phase.[1a–1f] As a result, selective extractions[1c,1d,1e] and the generation of reagents for interphasic catalytic processes[1a,1b,1e,2] have been made possible. All these applications rely on the hydrophobicity of supramolecular complexes $[CE\cdots M]^+A^-$.[1a–1c,1e,2] The chromogenic character (i.e. the colour change in redox or acid-base processes) of the complex species is usually determined by the anion A^-.[1c,1d,1f] Such solid supramolecular complexes with 18-crown-6 ether and potassium cations, i.e. $[18\text{-C-6}\cdots K]^+A^-$, incorporating anions ($A^-$) obtained from compounds **1a**[3a] and **1b**[3b,3c] have been synthesized previously in our laboratories (Table 1).

In our previous papers, we also showed that the salts of compounds **1a–f** and **2** exhibit different colours (Table 1). It was further shown that the acidities of compounds **1a–f** and **2** (Table 1) determine the appearance of colours (red or blue, depending on the anion) in acid-base processes (Equation 1, where HA is compound **1** or **2**, A^- is the anion derived therefrom, and X^- is HO^- or NO_2^-).[3c] This process can be utilized in a preparative manner for nitrating the above compounds,[3d] or for the colourimetric determination of nitrite anions by monitoring the colour change.[3d,3e] The subscripts (s) and (o) denote solid and organic liquid phases, respectively.

$$M^+X^-_{(s)} + CE_{(o)} + HA_{(o)} \rightarrow [CE\cdots M]^+A^-_{(o)} + HX_{(o)} \quad (1)$$

The intensely coloured hydrophobic complexes $[CE\cdots M]^+A^-$ of compounds **1a–f** (Table 1) can be used as acid-base indicators in non-aqueous media since they turn yellow at the equivalent point depending on the pK_a values

Table 1. The pK_a values of compounds **1a–e** and **2** and the colours of the corresponding salts (see refs.[3a–3c])



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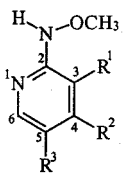

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Compound	R^1	R^2	R^3	pK_a	Colour of salt
1a	NO_2	H	NO_2	7.87	red
1b	NO_2	H	$COOCH_3$	5.00	red
1c	CN	H	NO_2	8.60	blue
1d	H	CN	NO_2	6.44	red
1e	NO_2	H	CN	6.19	red
1f	$COOCH_3$	H	NO_2	7.54	blue
2	NO_2	H	NO_2	6.54	red

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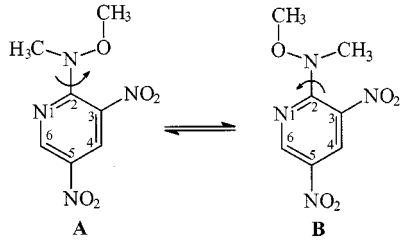
of compounds HA (Table 1). For these analytical applications, it is important to have standard complexes for obtaining standard curves. A further feature is that in the supramolecular complexes the anion A^- is activated for nucleophilic attack.[2]

In the present paper, we discuss the synthesis and characteristics (UV/vis and ^1H NMR spectra, as well as other physicochemical properties) of solid supramolecular complexes of the type [18-C-6···K]$^+A^-$, where A^- is an anion of compounds **1c−f** or **2**. We also report the syntheses of 2-(*N*-methyl-*N*-methoxyamino)-3,5-dinitropyridine (**3**) and *N*,*N*-bis(3,5-dinitro-2-pyridyl)methoxyamine (**4**) via this supramolecular complex, where A^- is the anion derived from compound **2**. For compounds **3** and **4**, the energies of the possible conformers have been calculated.



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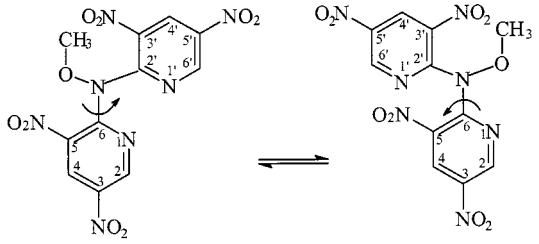

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Results and Discussion

The solid supramolecular complexes [18-C-6···K]$^+A^-$ (where A^- is an anion of compounds **1c−f** or **2**), with stoichiometric compositions 1:1:1, were obtained in two steps: (i) an initial acid-base process (Equation 2) yielded the solid salt K^+A^- by precipitation from methanol with dichloromethane (yield 82−99%); (ii) subsequent dissolution of the salt (K^+A^-) in dichloromethane in the presence of 18-C-6 (Equation 3) followed by the addition of petroleum ether led to the quantitative precipitation of the solid supramolecular complex.

$$HA + KOH \leftrightarrows K^+A^- + H_2O \quad (2)$$

$$K^+A^-_{(s)} + 18\text{-C-}6_{(o)} \leftrightarrows [18\text{-C-}6\cdots K]^+A^-_{(o)} \quad (3)$$

The characteristics of these supramolecular complexes (complexation ratio, λ_{max}, ε, colour) are summarized in Table 2.

Table 2. Characteristics of the 1:1:1 solid supramolecular complexes

[18-C-6···K]$^+A^-$	λ_{max} (CH_2Cl_2); nm (log ε)	Colour
1c	400 (4.17); 514 (3.41)	Red
1d	400 (4.10); 514 (3.42)	Red
1e	400 (3.94); 583 (3.73)	Blue
1f	540 (3.50)	Red
2	400 (4.18); 450 (3.36)	Red

Table 2. The colour of the supramolecular complex in solution depends, as expected, on the colour of the anion (A^-).[3c]

The stoichiometries of the supramolecular complexes were checked by the UV/vis spectral method[3b] and by scrutiny of the NMR integrals. The supramolecular complexes do not have definite melting points but rather melt over a temperature range.

^1H NMR Spectra of the Supramolecular Complexes

In Table 3, the ^1H NMR spectral data (chemical shifts and coupling constants) of compounds **1c−f** and **2** (HA), of their salts (K^+A^-), and of the supramolecular complexes ([18-C-6···K]$^+A^-$) in [D_6]acetone solution are compared. The methylene protons of 18-C-6 in the complexes appear at δ = 3.65.

From the presented data, the following points emerge: (i) The neutral forms of compounds **1c−f** and **2** give rise to different ^1H NMR spectra compared to their K^+A^- salts and the supramolecular complexes [CE···K]$^+A^-$; the neutral forms show an HN resonance, and the chemical shifts of their aromatic and OCH_3 protons are more deshielded. (ii) The complexation of the K^+A^- salt with 18-C-6 does not lead to significant differences in the ^1H NMR data. (iii) The Ar−N bond in both the complexed and non-complexed anions has partial double-bond character, leading to a broadening of the aromatic proton signals and an increase in the barrier to rotation.

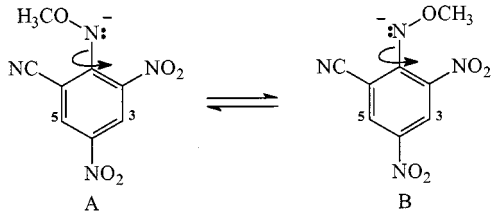
Energy Barrier for Rotation About the Ar−N Bond in Compound 1c

Compound **1c** represents a favourable structure for studying the barrier to rotation about the Ar−N bond by variable-temperature ^1H NMR spectroscopy. Due to the presence of the CN and NO_2 groups, the 3-H and 5-H protons in the two possible rotamers **A** and **B** (Scheme 1) have different chemical shifts. We recorded ^1H NMR spectra of the corresponding K^+A^- salt of compound **1c** in [D_6]acetone at various temperatures and, using Eyring's relationship,[4] we estimated the barrier associated with rotation about the Ar−N bond to be $\Delta G^{\neq} = 15.3 \pm 0.2$ kcal/mol, as shown below. From the signal of the 5-H proton, little information could be obtained; at low temperatures its signal seems to be a doublet with $J = 2.4$ Hz. For the 3-H proton, however, one observes a clear temperature dependence: in the high temperature region (spectra recorded at 25, 30, 35, 40, 45,

Table 3. Chemical shifts (δ, ppm) and coupling constants (*J*, Hz) in the ^{1}H NMR spectra (300 MHz, in [D_6]acetone) of compounds **1** and **2** at 303 K

Compound	N−H	N−OMe	3-H	4-H	5-H	6-H	COOMe
HA **1c**	11.69 br. s	4.01 s	9.11 d	–	8.79 d	–	–
K^+A^- of **1c**	–	3.72 s	8.18 br. s	–	7.81 br. s	–	–
[18-C-6···K]$^+$A	–	3.73 s	8.24 br. s; 8.12 br. s	–	7.81 br. d	–	–
HA **1d**	11.47 br. s	3.99 s	9.06 s	–	–	8.03 s	–
K^+A^- of **1d**	–	3.82 s	8.70 s	–	–	7.30 s	–
[18-C-6···K]$^+$A	–	3.82 s	8.71 s	–	–	7.30 s	–
HA **1e**	11.02 br. s	3.76 s	8.58 s	–	–	–	–
K^+A^- of **1e**	–	3.67 s	7.68 br. s	–	–	–	–
[18-C-6···K]$^+$A	–	3.64 s	7.64 br. s	–	–	–	–
HA **1f**	10.97 br. s	3.96 s	8.77 d	–	8.67 d	–	3.77 s
K^+A^- of **1f**	–	3.68 s	8.45 br. s	–	7.75 br. s	–	3.69 s
[18-C-6···K]$^+$A	–	3.65 s	8.56 s	–	7.60 s	–	3.65 s
HA **2**	11.60 br. s	3.92 s	-	9.26 d; 2.3	–	9.05 d; 2.3	–
K^+A^- of **2**	–	3.76 s	-	8.59 d; 2.4	–	8.36 d; 2.4	–
[18-C-6···K]$^+$A	–	3.73 s	-	8.58 d; 2.4	–	8.38 br. s	–

and 50 °C), one observes coalescence of the two signals at T_C = 35 °C.



Scheme 1. Rotation about the Ar−N bond of compound **1c** yielding rotamers **A** and **B**

Calculation of the rotational energy barrier for the anion of **1c** from T_C = 308 K for the 3-H proton signal:

δ(H-3A) = 8.25 ppm (ν_A = 2475.206 Hz)

δ(H-3B) = 8.12 ppm (ν_B = 2436.609 Hz)

$\Delta\delta$ = 2475.206 – 2436.610 = 38.596 Hz

$\Delta G^{\neq}$ = 4.575 T(10.319 + logT/k_C) [cal/mol]

$\Delta\nu$ = (ν_A – ν_B) = (2475.2 – 2436.6) = 38.6 Hz;

$$k_C = \frac{\pi \times \Delta\nu}{\sqrt{2}} = 2.22\ \Delta\nu;\ k_C = 2.22 \times 38.6 = 85.7\ s^{-1}$$

log(T_C/k_C) = log(308/85.7) = log(3.59) = 0.5556

$\Delta G^{\neq}$ = 4.575T_C (10.319 + 0.56) = 4.575 T_C × 10.879 = 49.77

T_C = 49.77 × 308 = 15330 cal/mol =15.3 ± 0.2 kcal/mol

Some Properties of the Supramolecular Complexes

In the presence of nitrous acid generated in the biphasic system dichloromethane/water (containing sodium nitrite and hydrochloric acid), the anions (A^-) of compounds **1c**−**f** involved in the synthesis of the supramolecular complexes [18-C-6···K]$^+A^-$ do not give (through *ipso*-substitution) the picramide **1a**. This behaviour is similar to that observed for the neutral compounds **1c**−**f**.[3d]

Compound **2** is of special interest in that it contains a pyridine ring. Its supramolecular complex [18-C-6···K]$^+A^-$ reacts with methyl iodide in dichloromethane to afford the *N*-methylated compound **3** (94% yield); with 2-chloro-3,5-dinitropyridine this complex gives the *N*-arylated compound **4** in moderate yield (53%), the lower yield probably reflecting the greater steric hindrance. These results prove that the presence of a negative charge on the naked anion A^- of the supramolecular complex [18-C-6···K]$^+A^-$ activates it for nucleophilic attack. Compounds **3** and **4** could not be obtained through the usual method using the same reagents (methyl iodide or 2-chloro-3,5-dinitropyridine) with potassium hydroxide in dimethyl sulfoxide.[3b]

Compounds **3** and **4** were also synthesized in a one-pot reaction from the supramolecular complex [18-C-6···K]$^+A^-$ (where A^- is the anion of compound **2**) generated in situ in dichloromethane according to the reactions described by Equations 2 and 3.

Compounds **3** and **4** do not have an acidic proton but exhibit Lewis acid character: they produce colours in the presence of strong bases, probably through generation of the corresponding Meisenheimer complexes. They react with π-bases (e.g. anthracene, or even dibenzo-18-crown-6) to give red colorations.

Compound **3** is complexed by the Dragendorff reagent ($KBiI_4$) leading to a red coloration; this reaction proves the basic character of the amino nitrogen atom due to the electron-donating effect of the methyl group (compound **4** does not give this reaction, while compound **2** leads to a transient coloration, these compounds being weaker bases). Compound **4** does not give a red coloration with Fe^{2+} ions either.

The R_f values for compounds **2**, **3**, and **4**, which were found to be 0.14, 0.32, and 0.60, respectively, using silica gel as the stationary phase and toluene as the mobile phase, offer supplementary data concerning the properties of these compounds: (i) compound **2** has a low R_f value because it is strongly associated with SiOH through hydrogen bonds; (ii) compound **3** is more basic than compound **2** and is associated with SiOH by protonation; (iii) compound **4** has the highest R_f value because it is neither acidic nor basic.

Energies of Rotameric Forms of Compounds 3 and 4

Molecular mechanics (MM2) calculations were carried out for the two possible rotamers of compound **3** and for

Table 4. Energies (kcal/mol) of the rotamers of compounds **3** and **4**

Energy	Rotamer **3A**	Rotamer **3B**	Rotamer **4A**	Rotamer **4B**	Rotamer **4C**
Stretch	1.2986	1.3485	3.4876	5.3021	4.0599
Bend	5.2436	7.6848	11.2337	8.0957	10.3081
Stretch-bend	0.0943	0.2644	0.1315	−3.6609	−0.8245
Torsion	3.4353	5.6522	8.0224	8.4270	10.6812
Non-1,4 VdW	−0.3639	0.3725	10.3700	2.4117	1.6382
1,4 VdW	9.7602	8.7194	14.4480	13.2562	12.4416
Charge/charge	1.6504	1.6808	−2.7570	2.5317	3.0369
Charge/dipole	−1.2203	0.3076	−12.1486	−3.4095	0.3438
Dipole/dipole	2.5312	5.2576	9.0959	10.5804	13.9831
Total	**22.4194**	**31.2877**	**41.8834**	**43.5344**	**55.6624**

the three possible rotamers of compound **4** using the CambridgeSoft Corporation program Chem3D Pro. The results are presented in Table 4, while stereoviews of the rotamers are depicted in Figure 1 and Figure 2. It can be seen that the lower-energy conformer **3A** has cisoid methoxy and nitro groups. Among the three rotamers of **4**, the lowest-energy rotamer **4A** has the methoxy group between the two nitrogen heteroatoms in *cisoid* conformation: the medium-energy rotamer **4B** has the methoxy group *cisoid* to a nitro group and a nitrogen heteroatom; and th highest-energy rotamer **4C** has the methoxy group *cisoid* to two bulky nitro groups.

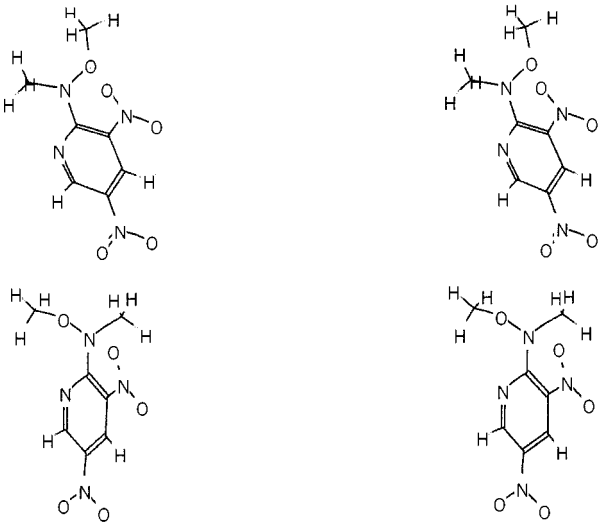


Figure 1. Stereoviews of the rotamers: compound **3A** (top) and **3B** (bottom)

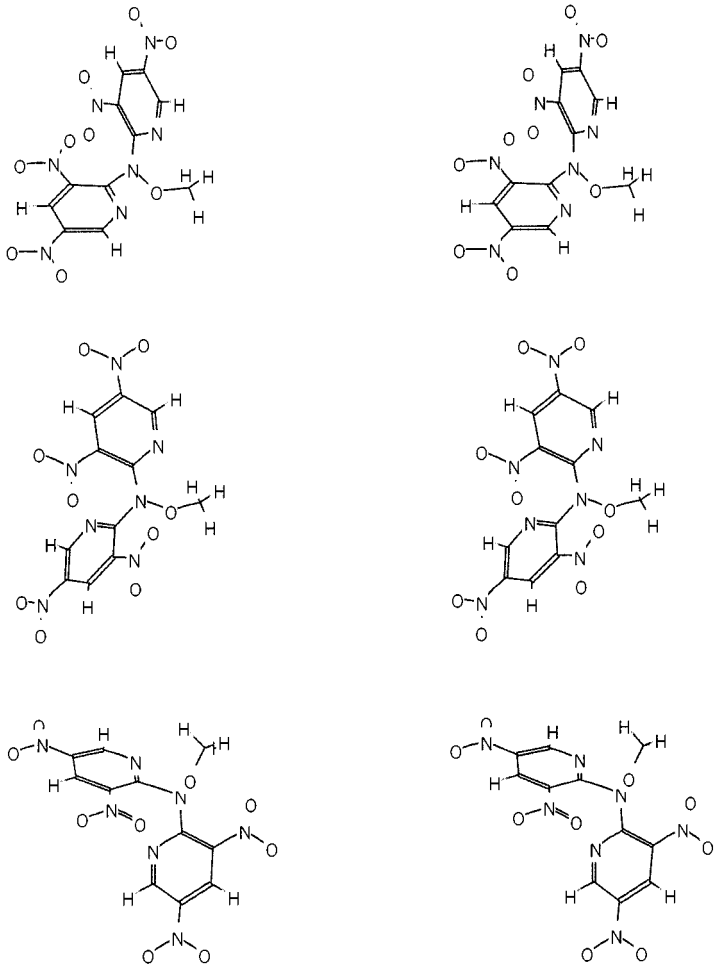


Figure 2. Stereoviews of the rotamers: compound **4A** (top), **4B** (middle), and **4C** (bottom)

Conclusions

Starting from the neutral (HA) compounds **1c−f** or **2**, potassium hydroxide, and the crown ether 18-C-6, we have obtained in a two-step process the 1:1:1 stoichiometric supramolecular complexes [18-C-6···K]$^+$A$^-$. Their colours and spectral characteristics (UV/vis and ^{1}H NMR) have been shown to depend on the nature of the anion A$^-$. When A$^-$ is the anion of compound **2**, the supramolecular complex [18-C-6···K]$^+$A$^-$ reacts with methyl iodide to give the *N*-methylated compound **3** in good yield, and with 2-chloro-3,5-dinitropyridine to give the *N*-arylated compound **4** in moderate yield.

Experimental Section

General Remarks: UV/vis spectra were recorded on a Specord m 400 spectrophotometer from Carl Zeiss Jena. − ^{1}H and ^{13}C NMR spectra were recorded with samples in [D$_6$]acetone solution on a Varian Gemini 300 BB MHz instrument; internal TMS was used as reference for both the ^{1}H and ^{13}C NMR spectra. − The syntheses of the starting compounds **1c−f** and **2** have been described in our previous papers;[3b,3c] the crown ether 18-C-6 was purchased from Merck, 2-chloro-3,5-dinitropyridine from Aldrich; the other reagents were analytical grade.

Synthesis of the Supramolecular Complexes [18-C-6···K]$^+$A$^-$ − General Two-Step Method: Step (i): The salts K$^+$A$^-$ were obtained by dissolving equimolar amounts of potassium hydroxide (at room temperature) and the appropriate compound **1c−f** or **2** in methanol (minimum volume), diluting with dichloromethane, and stirring the resulting solution at 5 °C for 1 h. The solid salt thus obtained was collected by filtration, washed with dichloromethane, and dried. Step (ii): The supramolecular complexes [18-C-6···K]$^+$A$^-$ were obtained by dissolving the K$^+$A$^-$ salts in the minimum volume of dichloromethane containing an equimolar amount of 18-C-6, followed by precipitation with petroleum ether (boiling range 30−60 °C). The mixture was cooled (5 °C) and the solid deposited was collected by filtration, washed with petroleum ether, and dried. The stoichiometries of the salts (1:1) and complexes (1:1:1) were established by UV/vis spectrophotometry after hydrolysis to the corresponding parent compounds (HA) **1c−f**, as in previous cases,[3b] and by analysis of the ^{1}H NMR integrals. The yields of the K$^+$A$^-$ salts were found to depend on the nature of the anion A$^-$ from compounds **1c−f** and **2** (83%, 82%, 91%, 98%, and 99%, respectively). The yields of the supramolecular complexes [18-C-6···K]$^+$A$^-$ were quantitative (>99%), irrespective of the nature of the anion A$^-$. The relevant λ_{max} and ε values are presented in Table 2, while the ^{1}H NMR data are presented in Table 3.

The Effect of Nitrous Acid on the Supramolecular Complexes: The effect of nitrous acid on the supramolecular complexes was monitored in the liquid/liquid biphasic system dichloromethane/water (containing sodium nitrite and 1 N hydrochloric acid) through qualitative TLC analysis aimed at detecting picramide **1a** in the organic phase (Merck silica gel GF 254 DC plates, twofold elution with toluene, UV detection at 254 nm, and exposure to ammonia vapour). No picramide formation was detected.

Syntheses of 2-(*N*-Methyl-*N*-methoxyamino)-3,5-dinitropyridine (3) and *N*,*N*-Bis(3,5-dinitro-2-pyridyl)methoxyamine (4) − Method A: To a solution of the supramolecular complex derived from compound **2** in dichloromethane, methyl iodide or 2-chloro-3,5-dinitropyridine was added (the molar ratio of **2** to the alkylating or arylating reagent was 1:8 in the former and 1:2.5 in the latter case). The resulting solution was stirred at room temperature for five days. It was then washed five times with 1 M hydrochloric acid and the organic phase was dried over sodium sulfate, concentrated, and then purified by preparative TLC (Merck silica gel GF 254, threefold elution with toluene). Yield: 93% of compound **3**; 53% of compound **4**.

Analysis for compound **3**: $C_7H_8N_4O_5$ (228.2): calcd. C 36.85, H 3.53, N 24.56; found C 36.63, H 3.34, N 24.28. − M.p. 143 °C. − ^{1}H NMR ($CDCl_3$): δ = 8.47 (d, *J* = 2.2 Hz, 1 H, 4-H), 8.07 (d, *J* = 2.2 Hz, 1 H, 6-H), 3.85 (s, 3 H, OCH_3), 3.63 (s, 3 H, NCH_3). − ^{13}C NMR ($CDCl_3$): δ = 144.02 (CH, C-6), 140.26 (C-q, C-3 or C-5), 133.22 (C-q), 126.71 (CH, C-4), 124.00 (C-q, C-5 or C-3), 63.01 (OCH_3), 42.01 (NCH_3).

Analysis for compound **4**: $C_{11}H_7N_7O_9$ (381.2): calcd. C 34.66, H 1.85, N 25.72; found C 34.48, H 1.70, N 25.48. − M.p. 192 °C. − ^{1}H NMR ($CDCl_3$): δ = 9.29 (d, *J* = 2.3 Hz, 1 H, 4-H), 9.03 (d, *J* = 2.3 Hz, 1 H, 6-H), 3.99 (s, 3 H, OCH_3). − ^{13}C NMR ($CDCl_3$): δ = 148.72 (C-q), 146.42 (CH, C-4 or C-6), 140.92 (C-q), 130.23 (CH, C-6 or C-4), 128.65 (C-q, C-5 or C-3), 64.22 (OCH_3).

Method B: Under stirring, potassium hydroxide was dissolved in dichloromethane containing 18-C-6 (molar ratio KOH/18-C-6 = 1:1.5). Compound **2** was then added (molar ratio KOH/**2** ≈ 1.5:1) and the resulting mixture was was stirred for about 10 min. at room temperature; the N-derivatization agent was then added in the molar ratio **2**/methyl iodide = 1:8 or **2**/2-chloro-3,5-dinitropyridine = 1:2.5. After five days, work-up was carried out as in Method A. That the compounds **3** and **4** obtained by the two methods were identical was verified by TLC.

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