SYNTHESIS AND COMPLEXING PROPERTIES OF NEW POLYETHER MACROCYCLES CONTAINING THE ANTHRAQUINONIC SYSTEM

A. Nabil[1], H. Qerrich[2], Y. Kandri Rodi[2], E.M. El Hadrami[2], M. Pierrot[3], E.M. Essassi [1*]

[1]*Laboratoire de Chimie Organique Hétérocyclique, Faculté des Sciences, Université Mohamed V, Rabat, Maroc*
[2]*Laboratoire de Chimie Organique, Faculté des Sciences et Techniques Fès-Saïss Université Sidi Mohamed Ben Abdallah, Fès, Maroc*
[3]*Laboratoire de Bio-inorganique Structurale, UMR 6517, Université d'Aix-Marseille, 13397, Marseille Cedex 20, France*

*Corresponding author: E-mail: essassi@fsr.ac.ma

Abstract: We describe the synthesis of the new open system **3** and polyether macrocycles containing an anthraquinonic system **4** and **5**; their sulphur compounds **6** and **7** have also been prepared. X-Ray crystallographic study of compound **5** in the presence of calcium and barium perchlorates shows that the latter crystallizes into monoclinic and triclinic system respectively. The UV spectrometry shows that the macrocycle **5** presents complexing properties toward Ca^{2+}, Ba^{2+} and Pb^{2+} ions. By contrast macrocycle **4** selectively complexes Pb^{2+} ions; these complexes were observed by electrospray, IR and UV spectrophotometry.

Keywords: *1, 2 - diaminoanthraquinone, phase transfer catalysis, complexation, constant of stability, Lawesson reagent, X-ray study*

INTRODUCTION

Since Pedersen's [1] discovery of the first crown ether, many ligands have been synthesized [2-5] for the complexation of metallic ions [6-9]. Several physico-chemical methods were performed about these complexes to determine their constants of formation. The great interest of these complexes is their use in physiology for the transportation of some ions through an artificial or a natural membrane [10-14], in industry for the building of selective electrodes [15], in reactions of phase transfer catalysis [16], as well as in the field of biology by determining the concentration of potassium and sodium in the blood [17].

EXPERIMENTAL

Melting points were determined in capillary and are uncorrected. Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AC 250 spectrometer. Mass spectra were performed with a VARIAN MAT A311 by field of desorption (DIC, NH_3) and AE MS9 Electro spray techniques. The Infrared spectra (IR) were carried with Perkin-Elmer 1760x spectrometer. The UV spectra were monitored on a Perkin-Elmer Lambda 17 spectrophotometer coupled with an Epson PC-AX Elmer computer. Elemental analyses were carried out by "Service Commun de Microanalyse-Ecole de chimie" in Toulouse. X-ray determinations were performed on a Euraf Nonius CCD diffractometer.

Preparation of compounds 3-5

To a solution of 1H-anthra[1,2-d]imidazolin-2-one **1** ($3,8.10^{-3}$ mol) in dimethyl-formamide (60 mL), we added the sodium carbonate, the dichloro di(tri) or tetraethyleneglycol **2** ($3,8 \cdot 10^{-3}$ mol) and tetra n-butylammonium bromide ($3,8.10^{-4}$ mol). The reaction mass was stirred between 80-90°C during 24 h. After completion of the reaction, the salts were screened; the solvent was evaporated under diminished pressure. The residue extracted in column of silica gel (elected; chloroform/ ether: 9/1).

1,3-dichloroéthyléneglycol)anthra[1, 2-d]imidazolino-2-one : 3

92 % yield; m.p. = 135-137°C; ^{1}H NMR ($CDCl_3$) δ : 3.28 (2H, t, J = 5.4); 3.48-3.54 (4H, m); 3.63-3.69 (4H, m); 3.81 (2H, t, J = 5.1); 4.15 (2H, t, J = 5.1); 4.76 (2H, t, J = 5.4); 7.47-8.22 (6H, m); ^{13}C NMR ($CDCl_3$) δ : 41.92 (intense pick), 44.40; 69.40; 69.49; 70.66; 71.18 (CH_2); 113.08; 122.64; 126.84 ; 133.78 (=CHar); 119.11; 128.13; 128.98; 133.08; 134.88; 136.82 (C ar); 155.87(C=O lactame); 182.45; 184.05 (2C=O anthraquinon); IR cm^{-1} (KBr) : ν_{CH2} = 2800-3000; $\nu_{C=O}$ = 1658, 1719; SM (DIC / NH_3) : m/z = 477 $[MH]^+$; m/z = 494 $[MNH_4]^+$; Anal. calcd. for $C_{23}H_{22}N_2O_5Cl_2$: C, 57.87 ; H, 4.64 ; N, 5.86. Found: C, 58.01 ; H, 4.72 ; N : 5.72

2-oxo-anthra [1, 2-d]imidazolino-11-crown-2 : 4

95 % yield; m.p. = 280-282°C; ^{1}H NMR ($CDCl_3$ + TFA) δ : 2.36-2.45 (1H, m); 2.88 - 2.98 (1H, m); 3.23-3.40 (3H, m); 3.65-3.71 (1H, m) ; 3.82-3.88 (1H, m) ; 3.97-4.08 (2H, m) ; 4.19-4.27 (1H, m) ; 4.63-4.87 (2H, m) ; 7.33-8.30 (6H, m); ^{13}C NMR ($CDCl_3$) δ :($CDCl_3$ + TFA) δ : 43.15; 47.64; 67.53; 69.01; 71.69; 72.80 (CH_2); 113.10 ; 123.72 ;

126.99 ; 127.09 ; 133.85 ; 133.94 (=CHar) ; 119.11 ; 127.62 ; 130.33 ; 133.26 ; 134.34 ; 140.48 (Car) ; 182.75 ; 182.46 (2 C=O anthraquinone) ; IR cm^{-1} (KBr) ν_{CH2} = 2800-3000; $\nu_{C=O}$ = 1660, 1721 ; SM (DIC / NH$_3$) : m/z = 379 [MH]$^+$, m/z = 396 [MNH$_4$]$^+$; Anal. calcd. for C$_{21}$H$_{18}$N$_2$O$_5$: C : 66.66; H : 4.79; N: 7.40. Found: C : 66.89; H : 4.81; N : 7.35

2-oxo-anthra[1,2-d]imidazolino-14- crown-3 : 5

97 % yield; m.p. = 221-223°C; ^{1}H NMR (CDCl$_3$) δ : 2.94-3.17 (3H, m); 3.42 -3.60 (4H, m); 3.79-4.00 (3H, m); 4.30-4.36 (1H, m) ; 4.71-4.92 (2H, m) ; 7.37-8.25 (6H, m).; ^{13}C NMR (CDCl$_3$) δ : 41.83; 44.83; 67.52; 68.12; 69.62; 69.79; 70.07; 70.49 (CH$_2$); 112.93; 122.65; 126.85 (=CHar); 118.65; 127.56; 133.25; 134.71; 137.85 (Car); 156.96 (C=O lactame); 182.51; 183.61 (2C=O anthraquinon); IR cm^{-1} (KBr) ν_{CH2} = 2800-3000; $\nu_{C=O}$ = 1663, 1713 ; Anal. calcd. for C$_{23}$H$_{22}$N$_2$O$_6$: C : 65.39; H : 5.24; N : 6.63. Found: C : 65.52; H : 5.22 ; N : 6.53

Preparation of macrocycle : 6-7

The mixture of macrocycle **4** or **5** (7.10^{-3} mol), Lawesson's reagent (21.10^{-3} mol) and toluene (50 mL) was heated with reflux during 20 h. Under diminished pressure we take out the toluene. The residue takes with hot water and extracts to chloroform. The organic phase was dried over anhydrous Na$_2$SO$_4$ and concentrated under diminished pressure. The residue extracted in column of silica gel (elected; chloroform/ether: 8/2).

2,6,11-trithioxo anthra[1,2-d]imidazolino-11- crown-2 : 6

85 % yield; m.p. = 122-124°C; ^{1}H NMR (DMSO-d$_6$) δ : 1.02-1.46 (4H, m); 2.36-2.68 (2H, m); 3.71-4.02 (6H, m); 7.14-8.74 (6H, m); ^{13}C NMR (DMSO d$_6$) δ : 61.85; 62.73; 62.97; 63.36; 64.03; 64.33 (CH$_2$); 118.01-147.40 (CHar, Car); IR cm^{-1} (KBr) ν_{CH2} = 2921-2851; $\nu_{C=O}$ = 1117, 1031; SM (ES$^+$): m/z = 379 [MH]$^+$, m/z = 458 [M + CH$_3$OH]$^+$; Anal. calcd. for C$_{21}$H$_{18}$N$_2$S$_3$O$_2$: C : 59.13; H : 4.25; N : 6.56. Found: C : 59.60; H : 4.42; N : 6.48.

2,6,11-trithioxo anthra[1, 2-d]imidazolino-14- crown-3 : 7

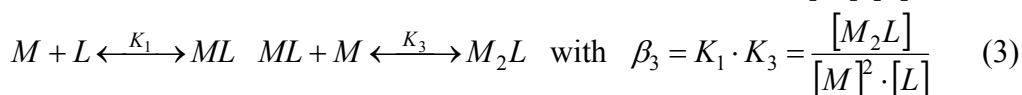82 % yield; m.p. = 212-214°C; ^{1}H NMR (C$_5$D$_5$N) δ : 1.10-1.31 (7H, m); 3.02-3.75 (9H, m); 7.19-8.69 (6H, m); ^{13}C NMR (CD$_3$CN) δ : 39.43; 39.14; 39.72; 61.90; 62.28; 69.41; 70.83 (CH$_2$); 126.74-145.75 (CHar, Car) ; IR cm^{-1} (KBr) ν_{CH2} = 2921-2851; $\nu_{C=O}$ = 1095, 1035; SM (ES$^+$): m/z = 470 [M]$^+$, m/z = 502 [M + CH$_3$OH]$^+$; Anal. calcd. for C$_{23}$H$_{22}$N$_2$S$_3$O$_3$: C : 58.70; H : 4.71; N : 5.95. Found: C : 58.40; H : 4.46 ; N : 6.01.

Determination of formation constants

The experimental etiquette used was that of J. Bellan et al [18]. The formation constants for cation-ligand complexes were determined by UV spectrophotometry in THF solutions following Smid [19]. The calculation method uses the STAR/FA and the STAR programs developed by J.L. Beltram [20]. The complexes equilibriums are of the type:

$$nM + mL \; \xrightleftharpoons{\qquad} \; M_nL_m \qquad \text{with } M : \text{metal and } L = \text{ligand}$$

For one M_nL_m complex associate one β_i constant, it is independent of complexe formation mechanism but, K_i stability constant, corresponding with equilibrium, depends on the formation mechanism. On the other hand, in the case of ML we have equality of constants ($K_i = \beta i$). In the order case, from the hypothesis on process of complex formation, the stability constants may be deducted from the formation constants. The most probable equilibrium, in our case, is (1), (2) and (3):

$$M + L \xleftrightarrow{K_1} ML \quad \text{with} \quad \beta_1 = K_1 = \frac{[ML]}{[M]\cdot[L]} \tag{1}$$

$$M + L \xleftrightarrow{K_1} ML \quad ML + L \xleftrightarrow{K_2} ML_2 \quad \text{with} \quad \beta_2 = K_1 \cdot K_2 = \frac{[ML_2]}{[M]\cdot[L]^2} \tag{2}$$

$$M + L \xleftrightarrow{K_1} ML \quad ML + M \xleftrightarrow{K_3} M_2L \quad \text{with} \quad \beta_3 = K_1 \cdot K_3 = \frac{[M_2L]}{[M]^2\cdot[L]} \tag{3}$$
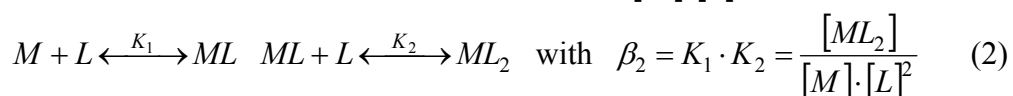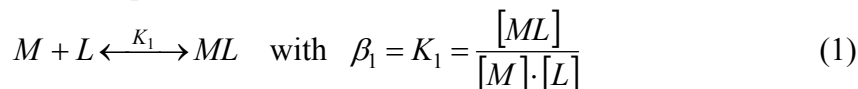
The formation constants (β_i) were determined by UV spectrophotometry (Tables 2 and 3).

RESULTS AND DISCUSSION

Synthesis of compounds 3-7

The literature reports many papers concerning the synthesis of compound **1**. We planned to use the method of Kornet et al [21] by reacting at reflux, the 1,2-diaminoanthraquinone with the ethyl chloroformiate in pyridine during 24 hours. Under the conditions of solid-liquid phase transfer catalysis, in dimethylformamide and in the presence of potassium carbonate and using tetra-n-butyl ammonium bromide as a catalyst, the condensation of ether systems **2a-c** on the 1H-anthra [1,2-d]imidazolin-2-one: **1** leads to the open compound: 1,3-di(chloroethyleneglycol) anthra [1,2] imidazolin-2 one **3** and to the cyclic compounds of the from [1+1], the 2-oxo-anthra [1,2-d] imidazolino-11(14) diazacrown-2(3): **4** and **5** (Scheme 1).
The reaction of Lawesson's reagent [22, 23] with macrocycles **4**, **5** at reflux of toluene, leads to the sulfur compounds 2,6,11-trithiooxo anthra [1,2-d] imidazolin-11(14)-diazacrown-2(3) : **6** and **7** respectively (Scheme 2).
The structure of compounds **3-7** was determined by usual spectroscopic methods (^{1}H NMR, ^{13}C NMR and IR). The mass spectrometry of compounds **3** and **4** by chemical ionisation (DCI, NH$_3$) presents the protonated molecular ions MH$^+$ and MNH$_4^+$. The crystallographic analysis of compound **5** confirms that the macrocycle thus obtained is of the type [1+1] (scheme 3).
The crystallization of the complexed macrocycle **5** with calcium and barium perchlorates has been made. It appeared that the latter resulted crystallized both in monoclinic and triclinic systems [24, 25].
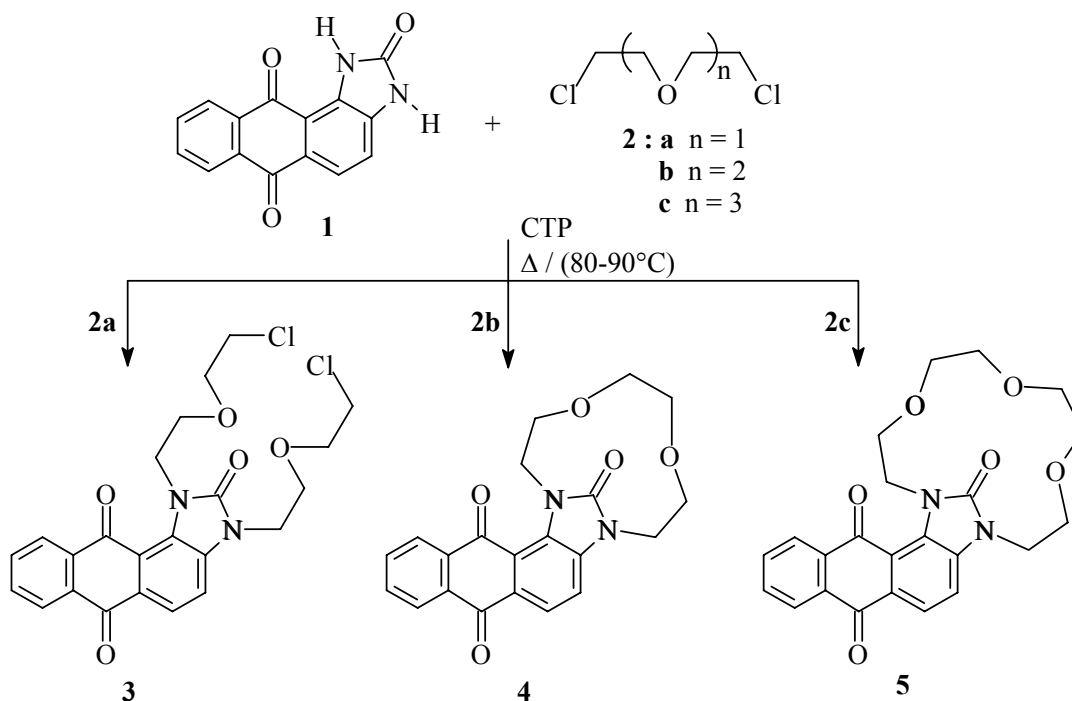
Scheme 1
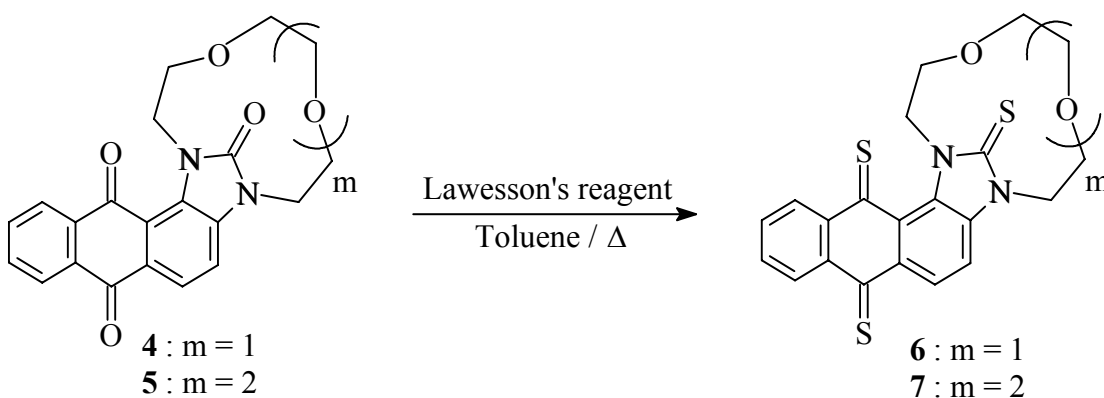
Scheme 2

Complexation

Sites of complexation

In order to determine the sites of complexation [26], the best method was the comparison by IR of free and complexed ligands with metallic cations. The IR spectra of compounds **4** and **5** were recorded in acetonitrile-tetrahydrofurane solutions (50-50), in the presence of an increasing quantity of metallic perchlorates.

A typical study of free and complexed ligands by IR spectra shows a perturbation of the vibration frequency associated to groups CH_2, C-O-C and C=O (lactame) whereas the vibrators CH, C=C(aromatic) and C=O(anthraquinon) don't display any significant change The results obtained are shown in Table 1.

Scheme 3. ORTEP diagram of compound 5 with numbering scheme

Table 1. Spectral data IR (as solution) of ligand 4 and 5 in free and complexed forms with calcium perchlorates

Compound	Vibration	Ligand	Complex	Δν*
4	ν CH2	2860	2846	- 14
	ν C-O-C	952	940	- 12
	ν C=O (lactame)	1721	1698	- 23
5	ν CH2	2842	2830	- 12
	ν C-O-C	970	959	- 11
	ν C=O.(lactame)	1713	1691	- 22

* Δν = ν complex − ν ligand

During the complexation a significant shift towards weaker wave numbers [23 and 22 cm^{-1}] was observed for complexes **4**/Pb (ClO$_4$)$_2$, 3H$_2$O and **4**/Ca (ClO$_4$)$_2$, 6H$_2$O. This phenomenon may be explained by the decrease of the double bond character of C=O due to the coordination of the oxygen of the lactame function; these results are in good agreement with those observed for alkaline-earth complexes with acyclic [27] and cyclic amides [28].

Stability constants

The UV spectrometry is the best method to determine the stability constants of the complexes formed by ligands and cations. This technique needs very small quantities of product and is particularly suitable for the measurement of stability constants ranging from $10^2 < K < 10^5$ [29]. Thus, this method has been chosen to study the complexing properties of compounds **4** and **5**. However, significant modifications in the absorption

spectra resulting from the complexation phenomenon must occur to be observed. In the attempts of complexation of ligand **5** with various alkaline metal, alkaline-earth and transition elements in addition of calcium perchlorates, barium and lead, we have observed a bathochromic shift and a hypsochromic effect for the amidic band of absorption; as well as the presence of isobestic points at 400 nm for Ca^{2+}, 407 nm for Ba^{2+} and 405 nm for Pb^{2+}. Thus, it must be noticed that the complexation is in agreement with the well known macrocyclic effect. Moreover, an informatic treatment (START program) evaluates the equilibrium formation constants of complexes. The VOIRDO program evidences the likely type of complexes between ligand and metal. An additional program determines the number of absorbents species in solution from which we deduct the number of complexes.

For Ca^{2+}, one break for $\rho = 2$ so one complex of type M_2L.
For Ba^{2+}, one break for $\rho = 0, 5$ so one complex of type ML_2.
For Pb^{2+}, one break for $\rho = 1$ so one complex of type ML.
The constants of theses complexes were calculated by the START program with satisfactory statistic tests.

Table 2. Complexes formation constants

Complex	Log β_{ML}	Log β_{ML2}	Log β_{M2L}
5 / Ca^{2+}	-	-	$8,44 \pm 0,03$
5 / Ba^{2+}	-	$3,86 \pm 0,1$	-
5 / Pb^{2+}	$3,68 \pm 0,1$	-	-

Attempts of complexation of the same macrocycle **4** by various alkali metal, alkaline-earth and transition metal did not lead to any variation of optical density except in the case of lead perchlorates in acetonitrile where a bathochromic shift and an hypsochromic effect of the bands of absorption, as well as one isobestic point at 406 nm were observed proving the formation of only one complexe ML. The formation constant $Log\beta_{ML}$ calculated by the STAR program is reported in Table 3.

Table 3. Complex formation constant

Complex	ρ	type	Log β_{ML}
4/Pb^{2+}	1	ML	$7,44 \pm 0,03$

Characterization of complexes by mass spectrometry (electrospray ionisation)

The compounds of coordination forming the ionic edifices of the type $[(ML)^{n+}, nX^-]$ can be characterized by mass spectroscopy in FAB^+ [30, 31] mode (FAST ATOM BOMBARDEMENT) or (ES positive mode) [32-34]. This technique is the best method for the structural determination of supramolecular edifices because it involves an ionisation which leads to a little fragmentation. We used samples which were equimolar solution of ligand and metallic salt (10^{-5} M). The main peaks observed for an equimolar solution of **4(5)** by means of ES^+ in acetonitrile and the type of complexes are reported below (Table 4).

Table 4. *Complex observed by ES$^+$ with metal and ligand*

Complex	Type of complex	m/z observed
5 / Ca(ClO$_4$)$_2$,6H$_2$O	M$_2$L	502,2
5 / Ba(ClO$_4$)$_2$,3H$_2$O	ML$_2$	981,3
5 / Pb(ClO$_4$)$_2$,3H$_2$O	ML	629,2
4 / Pb(ClO$_4$)$_2$,3H$_2$O	ML	585,2

The first attempts of complexation of compounds **6** and **7** are not encouraging due to the insolubility of their by product in the solvent used for the UV, IR spectrophotometry and mass electrospray.

CONCLUSION

We have demonstrated that, under phase transfer catalysis, the condensation of ether systems **2a-c** with 1H-anthra [1,2-d]imidazolino-2-one **1** leads to open system **3** and macrocycles **4** and **5** in the form [1+1]. The compound **5** resulting from complexation with calcium and barium perchlorate crystallizes in the lead free form in both monoclinic and triclinic systems in presence of the calcium perchlorate and lead perchlorate. The IR spectra highlights the intervention of the C=O group of the lactame function. Formation constants of complexes of types ML, ML$_2$ and M$_2$L were found by UV spectrometry.

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24. Crystal data for compound **5**: ($C_{23}H_{22}N_2O_6$) obtained by crystallisation in the presence of calcium perchlorate; chemical formula weight: 422.431; experimental crystal description: needle, crystal size max: 0.35 mm, crystal size mid: 0.15 mm crystal size min: 0.10 mm; symmetry cell setting: triclinic, symmetry space group name h-m: P -1. Cell length a: 6.9501(3) A°, cell length b: 9.2501 (6) A°, cell length c: 15.5980 (10) A°, cell length α : 81.440 (3), cell length β : 82.756 (4), cell length δ: 83.173 (4), cell volume: 978.6 (1) A$^{\circ 3}$, cell formula units z : 2. Diffraction ration type Mo-Kα, radiation wavelength: 0.71073 A° Cell measurement device: Enraf Nonius CCD Experimental absorption correction: none. Reflections number total: 6928, reflections number observed 3569. Refinement data: refine is structure factor coefficients: F2. Refine is R factor observed: 0.042, refine is wR factor observed : 0.054, refine is number reflections 2814, refine is number parameters : 280. Atom type scattering source: Waasmaier, D and Kirfel, A. (1995). *Acta cryst. A*, **51**, 416-431.

25. Crystal data for compound **5**: ($C_{23}H_{22}N_2O_6$) obtained by crystallisation in the presence of barium perchlorate; chemical formula weight: 422.431; experimental crystal description: needle, crystal Size max: 0.35 mm, crystal size mid: 0.15 mm, crystal size min: 0.10 mm; symmetry cell setting: monoclinic symmetry

space group name h-m: P2$_1$/c. Cell length a: 16.5509 (6) A°, cell length b: 8.6858 (4) A°, cell length c: 14.1895 (7) A°, cell length β: 104.955 (3) A°, cell volume: 1870.8 (2) A$^{°3}$,cell formula units z: 4. Diffraction radiation type: Mo-Ka, radiation wavelength: 0.71073 A°. Cell measurement device: Enraf Nonius CCD. Experimental absorption correction: none. Reflections number total 13992, reflections number observed 3939. Refinement data: refine is structure factor coefficients: F2. Refine is R factor observed: 0.052, refine is wR factor observed: 0.058, refine is number reflections: 2930, refine is number parameters: 280. Atom type scattering source: Waasmaier, D and Kirfel, A. (1995) *Acta Cryst. A*, **51**, 416-431.

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