1,3-bis(2,4,6-trinitrophenylaminooxy)propane and its 4-cyano-2,6-dinitrophenyl Congener: Synthesis and Properties.

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Abstract: Starting from N-hydroxyphthalimide (5) and 1,3-dibromopropane (6) we obtained 1,3-bis(phthalimidooxy)propane (7) which led to 1,3-bis(aminooxy)propane dihydrochloride (8). From its reaction with picryl chloride or 4-cyano-2,6-dinitrochlorobenzene, the two title compounds (4b, 4a) were obtained.

¹H-NMR and ¹³C-NMR spectra are presented. For comparison with the analogous N-methoxy-2,6-dinitro-4-R-anilines 1a, 1b (R = CN or R = NO₂), we report the hydrophobic characteristics (by RPTLC), electronic spectra for the neutral compounds and their anions, pKₐ values, and the behavior towards oxidizers (DPPH, PbO₂, Pb(CH₃COO)₄, KMnO₄ and Ag₂O); DPPH converts compounds 1a, 1b and 4a, 4b into betainic structures 2a, 2b respectively.

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1 Introduction

It was shown in previous papers [1 - 10] that compounds of type 1 present interesting properties when substituents are strong electron acceptors (e.g. 1a, 1b). Among these properties, the generation of N-alkoxyaminyl free radicals on oxidation [4 - 8] allowed a
reaction with the free stable radical DPPH (2,2-diphenyl-1-picrylhydrazyl) leading to betainic structures 2a, 2b, which can be reduced reversibly to the corresponding hydrazines 3a, 3b [1,9,10]. Basic media lead to the formation of the corresponding anions with colors that depend on the substitution pattern [1,2].

Continuing our research, we investigated the possibility to obtain new compounds of Ar-NH-O-(CH$_2$)$_n$-O-NH-Ar type and to study their properties comparatively to their analogous compounds of type 1. For this purpose we synthesized the new compounds 1,3-bis(4-cyano-2,6-dinitrophenyloxy)propane (4a) and 1,3-bis(picramidooxy)propane or 1,3-bis(2,4,6-trinitrophenylaminooxy)propane (4b), and investigated their properties comparatively with those of compounds 1a, 1b [2].

2 Results and Discussion

2.1 Synthesis of compounds 4a, 4b

Compounds 4a, 4b were synthesized in three-steps [1,2,5,11,12]: (i) in the first step, N-hydroxyphthalimide 5 and 1,3-dibromopropane 6 led to 1,3-bis(phthalimidoxy)propane, 7 (yield 79%); (ii) in the second step, acid hydrolysis of compound 7 gave
1,3-bis(aminooxy)propane dihydrochloride, 8 (yield 40%); (iii) finally, compounds 4a, 4b were obtained from the reaction of compound 8 with 4-cyano-2,6-dinitrochlorobenzene, 9a, or with 2,4,6-trinitrochlorobenzene (picryl chloride) 9b (yields 88.5% and 72%, respectively).

![Synthesis of compounds 4a,b](image)

The structures of the new 4a,b compounds were confirmed by $^1$H- and $^{13}$C- NMR (Table 1), elemental analysis, and their physico-chemical properties.

| Comp. | $^1$H-NMR | $^{13}$C-NMR |
|-------|-----------|-------------|
| 4a    | 11.30 (b, N-H, deuterable); 8.67 (s, 2H, H-3-5); 3.88 (t, 4H, H-§,6.6); 1.93 (quintet, 2H, H-β, 6.6) | 138.50 (C-1); 136.18 (C-2-6); 133.82 (C-3 or C-5); 133.71 (C-5 or C-3); 116.31 (C-4); 99.02 (CN); 72.72 (C- α); 25.40 (C- β). |
| 4b    | 11.30 (b, N-H, deuterable); 8.81 (s, 2H, H-3-5); 3.94 (t, 4H, H-α, 6.7); 1.74 (quintet, 2H, H-β, 6.7). | 139.24(C-1); 134.58 (C-2-6); 133.46 (C-4); 125.49 (C-3-5); 72.77 (C- α); 25.75 (C- β). |
| 7     | 7.84 (b, 4H, H-3-6); 4.36 (t, 4H, H- α, 5.2); 2.09 (quintet, 2H, H- β, 5.2). | 163.41(CO); 134.80 (C-3-6); 128.60 (C-1-2); 123.25 (C-4-5); 74.42 (C- α); 27.11 (C- β). |
| 8     | 11.40 (s, N-H, deuterable); 4.08 (t, 4H, H-α, 5.4); 1.93 (quintet, 2H, H- β, 5.4). | 70.73 (C- α); 26.03 (C- β). |

Table 1 NMR spectra of compounds 4a,b, 7 and 8 in DMSO-d$_6$: δ values, ppm; J (Hz)
2.2 Properties of compounds 4a, 4b

(a) Electronic absorption spectra

Electronic absorption maxima of the new compounds 4a,b are presented in Tables 2 and 3.

| Compound | 4a | 4b |
|----------|----|----|
| Solvent, $E_T(30)^*|$ $\lambda_{max}$ nm, (log $\varepsilon$) | $\lambda_{max}$ nm, (log $\varepsilon$) |
| CH$_2$Cl$_2$ (41.1) | 398 (3.48) | 338 (4.33) |
| Acetone (42.2) | 573 (2.94) | 450 (3.79) |
| DMSO-d$_6$(45.0) | 400 (3.96) and 579 (3.72) | 384 (3.96) and 498 (4.00) |
| H$_3$COH (55.5) | 396 (2.72) and 570 (2.95) | 356 (4.29) and 460 (4.31) |

Table 2 UV-VIS spectra of compounds 4a,b; Dimroth-Reichardt parameters [13]

The UV-Vis spectra (Table 2) provide the evidence of the influence of solvent polarity measured by the Dimroth-Reichardt parameters [13]; a slight bathocromic shift is observed as the $E_T(30)$ value increases (positive solvatochromic effect). The case of methanol is an exception because it is a protic solvent.

The electronic spectra of the anions of compounds 4a,b are presented in Table 3; these larger shifts account for the blue color of the anion of compound 4a ($\lambda_{max} = 580$ nm) and the red color for that of compound 4b ($\lambda_{max} = 530$ nm).

| Compound | $\lambda_{max}$, nm, (log $\varepsilon$) | Color |
|----------|---------------------------------|-------|
| 4a | 416 (3.52) and 580 (3.74) | blue |
| 4b | 384 (3.52) and 530 (3.74) | red |

Table 3 Visible absorption spectra of the anions of compounds 4a,b*
*In DMSO + KOH (the molar ratio compound : KOH =1 : 2)

The electronic spectra of the new compounds 4a,b (Table 3) are similar to those of their analogs 1a,b (Table 4) [2,14]. Some differences exist between the anion of compound 4b (table 4) and the anion of compound 1b (Table 4).

(b) Acidity

Our previous papers [1,2] showed that compounds of type 1 exhibit acidic characteristics depending on the nature and the position of the substituents [2]. Among the compounds 1 previously studied [1,2], the compounds two nitro groups and one carboxy group were the only ones with two ionizable protons due to the COOH group ($pK_{a1}$) and to the NH-OMe group ($pK_{a2}$). The compounds 4a,b were synthesized in order to investigate a different kind of bis-acidic species due to the two NH-OR groups contained in the molecule. Table 6 shows the $pK_a$ values (determined by
| Comp. | Neutral compound | Anion | Color |
|-------|------------------|-------|-------|
|       | $\lambda_{max}$,nm (log $\varepsilon$)<sup>a</sup> | $\lambda_{max}$,nm (log $\varepsilon$)<sup>b,c</sup> |       |
| 1a    | 270 (4.27); 399 (3.56) | 400 (3.94); 583 (3.73) | blue  |
| 1b    | 333 (4.32); 402 (shoulder) | 462 (4.21); 600 (shoulder) | red   |

**Table 4** Electronic absorption maxima of compounds 1a,b and their anions [2,14].

<sup>a</sup> In dichloromethane;
<sup>b</sup> in dichloromethane as supramolecular complex with the crown ether 18-crown-6 and KOH for 1a [2];
<sup>c</sup> in methanol-water with NaOH (1 : 1, v/v) molar ratio 1 : 1 compound : NaOH [14].

The data from Table 5 show that indeed compounds 4a,b exhibit two ionization steps, differing by 3-4 orders of magnitude. The higher acidity of compounds 4 relatively to compounds 1 may be due to a supplementary intramolecular hydrogen bonding between an oxygen atom and an NH group from the bis(aminooxypropane) group, thus depressing the electron density around that oxygen. The lower acidity of a-type compounds relatively to b-type compounds is due to the CN group from the para position, which has a lower electron-withdrawing effect than the NO$_2$ group.

Taking into account the colors of these anions that facilitate the visualization of the acid-base reaction (similarly to compounds of type 1) [15], the new compounds 4 can be used analytically for the extraction of alkaline cations or amino acids in the presence of a crown ether [16].

(c) **Solubility and hydrophobicity**

Compounds 4a,b have low solubility in water. Compound 4a is also less soluble in most organic solvents, whereas compound 4b is highly soluble in organic solvents. This leads to a slight difference from compound 1a which is less soluble in water but highly soluble in organic solvents [1,2]. The retention factors $R_f$ of compounds 4a,b and 1a, b in a liquid/liquid system depend on the acidity of the aqueous phase. Table 6 shows the results obtained using reverse phase thin layer chromatographs (RPTLC). There is a linear correlation between log $R_f$ and the pH of the aqueous phase, as indicated by the correlation coefficient ($r \geq 0.90$) for the equation indicated under Table 6.

As the concentration of the acidic phase decreases, the compounds will begin to be found as the corresponding anions that are soluble in aqueous phase, therefore the $R_f$ values will increase. A supplementary argument is that at hydrochloric acid
The use of RPTLC for the measurement of hydrophobicity is based on the relationship [17,18]: \( R_M = R_{M0} + bC \), where \( R_M = \log\left(1/R_f\right) \); \( R_{M0} \) is the \( R_M \) value extrapolated for zero organic solvent in the mobile phase and \( b \) is the decrease of \( R_M \) for 1% volume of organic component in mobile phase and \( C \) is molar hydrochloric acid concentration.

It is also well known that the measurement of hydrophobicity of ionizable compounds implies experimental conditions in which the compounds should be maintained in the non-ionized form [19,20]. For this reason, in order to evaluate with accuracy the hydrophobicity of compounds 1a,b and 4a,b we have chosen the value of 1 M for the concentration of the hydrochloric acid, keeping thus these compounds in the non-ionized form. Table 7 shows the results.

| Comp. | \( R_{M0} \) | \( b \) | \( r \) | log P* |
|-------|--------------|--------|--------|--------|
| 1a    | 1.108        | -0.0214| 0.96   | -0.25  |
| 1b    | 1.662        | -0.0259| 0.95   | -0.02  |
| 4a    | 1.675        | -0.0265| 0.95   | 0.74   |
| 4b    | 2.222        | -0.0314| 0.91   | 1.2    |

Table 7 \( R_{M0} \), \( b \) and \( r \) values obtained for 1a,b and 4a,b*  
* Hansch hydrophobicity parameter calculated by fragment method [19]

From the data shown in Table 7 one can notice that the hydrophobicity \( R_{M0} \) is dependent on the para-substituents (NO\(_2\) > CN), increasing further for the compounds of type 4, due to the presence of the bis(aminoxypropane) moiety. The \( r \) values show a fair correlation (correlation coefficient 0.886) of the experimental data, and the \( R_{M0} \) values fit with log P values calculated by fragment method [19].

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Table 6 \( R_f \) values of compounds 1a,b and 4a, b at various acidities *

"RPTLC plates Merck RP-18 F\(_{254}\), mobile phases ethanol / hydrochloric aqueous acid (1M...0.001M) 1/1 v/v; \( r \# \) means correlation coefficient from the equation \( \log R_f = a + b \log C \), where \( C \) is the concentration of the acid from the aqueous phase.

| Comp. | 1 M | 0.1 M | 0.01 M | 0.001 M | 0.0001 M | \( r \# \) |
|-------|-----|-------|--------|---------|----------|--------|
| 1a    | 0.48| 0.48  | 0.50   | 0.60    | 0.61     | 0.90   |
| 1b    | 0.30| 0.31  | 0.54   | 0.73    | 0.77     | 0.95   |
| 4a    | 0.30| 0.34  | 0.34   | 0.45    | 0.47     | 0.95   |
| 4b    | 0.16| 0.17  | 0.20   | 0.68    | 0.73     | 0.91   |

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ing into account the acidic and hydrophobic properties of compounds 4a,b we can assume that there exist possible applications of these compounds as indicators for non-aqueous media, similarly with compounds 1 [1,2].

(d) Reactions with oxidizing species:

**Reaction with DPPH**

Compounds 4a,b react with DPPH leading to the same betainic compounds as compounds 1a,b, namely 1-picryl-2-phenyl-2-(4-cyano-2,6-dinitrophenyl)-diazenium betaine 2a (R = CN) and 1-picryl-2-phenyl-2-(para-picramidophenyl)-diazenium betaine 2b (R = NO₂) (Fig. 2). In both cases, alkoxy groups are eliminated after the N-alkoxy-arylamino free radical (intermediately formed when a molecule of DPPH had abstracted a hydrogen atom from 4) attacked the para-position of a phenyl group in a second molecule of DPPH.¹,⁹,¹⁰

![Fig. 2 Formation of betainic compounds 2a,b and the corresponding hydrazines 3a,b](image)

Our previous papers [9,10] showed that the betainic compounds 2a,b can be reduced reversibly to the corresponding hydrazines 3a,b. The identity of compounds 2a,b and 3a,b was confirmed by TLC and NMR by comparison with authentic samples.

**Attempted reaction with other oxidizing species**

The stability of N-aryl-N-alkoxyaminals that can be obtained from compounds 1 is due to the ‘push-pull [21 - 23], merocyaninic [24], or capto-dative effect [25 - 27]. Unexpectedly, no stable free radicals could be detected by ESR spectroscopy in the reaction of compounds 4a,b with several oxidizing species in solid state suspended in dichloromethane: Ag₂O, PbO₂, KMnO₄ or Pb(OAc)₄. TLC Analysis shows the presence of several spots, as in strongly oxidative reactions; the number of these spots decreases in the order: Pb(OAc)₄ >> Ag₂O ≥ PbO₂ > KMnO₄. The more powerful oxidative effect of Pb(OAc)₄ probably is due to its solubility in the reaction mixture, whereas the other oxidants are insoluble. On the other hand, through TLC one can notice a higher stability of compounds 1a,b (appreciated through the number of detected spots). A possible explanation for this difference of compounds 4 from 1 is that compounds 4 may undergo intramolecular cyclization with formation of an N-N bond, similarly to the synthesis of 1,4,2,3-dioxadiazines from 1,2-bis(aminoxy)ethane derivatives [28].
3 Conclusions

New analogs 4a,b of compounds 1a,b were synthesized. In comparison with compounds 1a,b studied previously, the new compounds 4a,b have slightly different electronic absorption maxima, hydrophobicity and acidic properties; no stable radicals generated by oxidation of the new compounds could be detected by ESR. However, both classes of compounds afford the same betainic compounds 2a,b and their corresponding hydrazinic reduction products 3a,b in the reaction with DPPH. Plausible explanations for these differences have been provided.

4 Experimental

UV-VIS Spectra were recorded using a spectrophotometer Specord M-400 Carl Zeiss Jena; $^1$H- and $^{13}$C- NMR spectra were recorded on a Varian Gemini 300 MHz instrument; internal TMS was used as reference. Potentiometric titrations were performed with an MV Digital pH-meter. Solvents were commercial grade with analytical purity.

Compounds 1a,b, 2a,b and 3a,b were synthesized previously [1,4,9,10]. N-Hydroxyphthalimide (5) and 1,3-dibromopropane (6) were Merck products. 4-Cyano-2,6-dinitrochlorobenzene (9a) was a Lancaster product, and 2,4,6-trinitrochlorobenzene (9b) was prepared by the known method [29]. The pre-coated plates were from Merck. The other reagents used were high grade commercial chemicals.

4.1 Synthesis of compounds 4a,b. General procedure.

The procedure involves three steps, 5 $\rightarrow$ 7 $\rightarrow$ 8 $\rightarrow$ 4a,b, as follows:

4.1.1 1,3-Bis(phthalimidoxy)propane, 7

Compounds 5 and 6 (molar ratio 5: 6 =3:1) were dissolved in dimethylformamide (7 mL of solvent/g mixture of compounds 5 + 6) and triethylamine was added (1 mL/g mixture of compounds 5 + 6). The mixture was heated at 60°C for 5 days. The reaction mixture was then filtered through a glass filter, and the precipitate was washed with 10% aqueous sodium hydrogen carbonate till the filtrate was colorless. Then the precipitate was washed with 10% aqueous hydrochloric acid till the filtrate became acidic (pH ~ 2) and with distilled water till a neutral pH was reached. The precipitate was dried in a dessicator with calcium chloride, yielding compound 7 (yield 79%, m.p.= 175°C).

Elemental analysis: Calc. for C$_{22}$H$_{14}$N$_2$O$_6$: C, 65.57; H, 3.50; N, 6.96%. Found: C, 65.52; H, 3.61; N, 7.00%.

4.1.2 1,3-Bis(aminooxy)propane dihydrochloride, 8

Compound 7 was suspended in a mixture (7.5/15 v/v) of ethanol and 37% hydrochloric acid (22.5 mL/g of 7) and refluxed for 5 days. After cooling, the mixture was alkanilized at pH ~ 8 with sodium hydrogen carbonate and the resulting solution was extracted with
dichloromethane. The extract was treated with dry gaseous hydrogen chloride, yielding 8 as crystals (yield 40%, m.p. 165-168 °). Elemental analysis: Calc. for C₃H₁₂Cl₂N₂O₂: C, 20.12; H, 6.75; Cl, 39.60 N, 15.65% Found: C, 20.46; H, 7.05; Cl, 39.81; N, 15.51 %.

4.1.3 1,3-Bis(4-cyano-2,6-dinitrophenyloxy)propane (4a) and 1,3-bis(picramidooxy)propane (4b)

A solution of compounds 9a,b and 8 in ethanol was refluxed under stirring for 24h in the presence of solid sodium hydrogen carbonate (molar ratio between 9, 8 and NaHCO₃ = 2 : 1: 10). Aqueous hydrochloric acid (10%) was then added till pH ~ 1. In the case of compound 4a, a precipitate was obtained, which was purified by dissolving in warm acetone, cooling to 5 °, filtering on a glass filter and then washing with cold acetone. Pure 1,3-bis(picramidooxy)propane (4a) was obtained as yellow powder, as attested by TLC (silica gel GF 254 Merck, dichloromethane three times, or toluene twice) with yield 37% and m.p. 187.5 °. For 4b, which does not precipitate after the addition of HCl, the acidic solution was extracted with dichloromethane, dried over anhydrous sodium sulfate, and concentrated in a rotavapor under vacuum. Compound 4b resulted as yellow powder, yield 48% and m.p. 136 °.

Elemental analysis: Calc. for 4a, C₁₇H₁₂N₈O₁₀: C, 41.81; H, 2.47; N, 22.94% Found: C, 41.68; H, 2.55; N, 22.80 %.
Calc. for 4b, C₁₅H₁₂N₈O₁₄: C, 33.28; H, 2.21; N, 20.53.
Found: C, 33.50; H, 2.15; N, 20.33 %.

4.2 The pKₐ values of compounds 4a,b

These values were determined by potentiometry in MeOH:water 1:1 v/v by titration with a solution of potassium hydroxide (in MeOH:water 1:1 v/v); a correction of 0.65 pH units was applied due to the mixture of solvents. Values are presented in Table 5.

4.3 The hydrophobicity of compounds 4a,b

The hydrophobicity was determined by using RPTLC plates Merck RP-18 F₂₅₄ with the mobile phase a mixture of ethanol-aqueous hydrochloric acid 1 M. The results are shown in Tables 6 and 7.

4.4 Synthesis of the compounds 2a,b and 3a,b

The betainic compounds 2a,b were obtained in dichloromethane from the reaction of 4a,b with DPPH, as described previously [1,9,10] for a ratio of compound 2:DPPH = 1:2. The corresponding hydrazines 3a,b were obtained by the reduction of 2a,b in dichloromethane with solid ascorbic acid [1,9,10]. The identity of compounds 2a,b and 3a,b was established by TLC standards and by NMR.
4.5 Attempted oxidation of compounds 4a,b

Compounds 4a,b dissolved in dichloromethane or benzene were stirred with solid Ag₂O, PbO₂, KMnO₄ or Pb(CH₃COO)₄. The reaction mixtures were monitored by ESR as soon as possible, and then from time to time; no ESR signals could be observed. Time monitoring (1h, 2h and 24h) of the processes by TLC (silica gel GF 254, dichloromethane) evidenced advanced oxidative processes, dependent on the oxidant used. Similar oxidative reactions were performed for compounds 1a,b, when free radicals were evidenced by ESR, and TLC (in the same conditions) showed a higher resistance against oxidants, as mentioned above.

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