

Regioselective Nitration of 4'-R-Dibenzo-18-Crown-6 by Some Alkaline Metals Nitrates in Polyphosphoric Acid

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Abstract

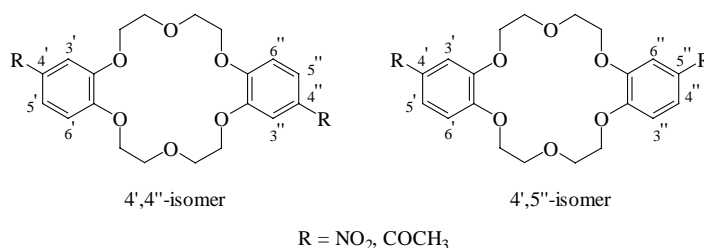
We have studied the effect of the substituent nature on nitration of 4'-R-dibenzo-18-crown-6 (DB18C6, where R is NO_2 , CH_3CO , or C_2H_5) in polyphosphoric acid (PPA). We also studied the influence of cations' nature on regioselectivity of nitration. It was found that electron withdrawing substituents direct the incoming NO_2 -group mainly to the 4''-position of the unsubstituted benzene ring in the reactions with lithium nitrates. If there are two substituents: electron releasing and electron withdrawing in one benzene ring, then the orientation effect of the latest one is stronger. The obtained results once more confirmed the existence of 'transannular transmission', which we first of all observed during the acetylation of DB18C6. Based on these observations preparative methods leading to 4',4''-dinitro-DB18C6, 4',5''-dinitro-DB18C6, 4'-acetyl-4''-nitro-DB18C6, 4'-acetyl-5''-nitro-DB18C6, 4'-ethyl-5',5''-dinitro-DB18C6, and 4'-ethyl-5',4''-dinitro-DB18C6 have been developed.

Introduction

Recently, we have found that the acetylation and nitration of dibenzo-18-crown-6 (DB18C6) are more regioselective, if instead of acetic and nitric acids, their potassium salts were used in polyphosphoric acid (PPA) [1, 2]. Acetylation with the use of potassium acetate proceeds more selectively with formation of only one

tivity of nitration and acetylation is responsible coordination of potassium cation by the starting material. The distribution of electron density on unsubstituted aromatic ring was affected by 'transannular transmission' of the first substituent introduced into DB18C6 molecule.

In connection with above observations it was of interest to study the influence of the nature of alkaline



low-melting 4',4''-isomer, whereas the nitration proceeds less selectively with formation of a mixture of 4',4''- and 4',5''-dinitro-DB18C6 isomers with predominance of low-melting 4',4''-isomer.

The prepared potassium nitrate complexes of DB18C6 and its 4'-nitroderivative upon treatment with PPA have given 4'-nitro-DB18C6 and 4',4''-dinitro-DB18C6, respectively. We showed that for regioselectivity of nitration and acetylation is responsible coordination of potassium cation by the starting material.

metal nitrates, and also the nature of the substituent on the nitration reaction of 4'-monosubstituted DB18C6.

Experimental

The ^1H -NMR-spectra were recorded in CDCl_3 on a 'UNITY 400+' spectrometer at 400 MHz working frequency, with HMDS as internal standard.

For chromatographic separation neutral aluminium oxide was used.

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The starting compounds: 4'-acetyl-DB18C6 and 4'-nitro-DB18C6 were prepared according to literature procedures [1, 2].

Preparation of 4'-ethyl-DB18C6: To 1.30 g (3.2 mmol) 4'-acetyl-DB18C6 dissolved in 40 mL 1,4-dioxane 1.88 g amalgamated zinc, 5 mL HCl and 5 mL water were added. The mixture was boiled for 15 h with adding 0.2 mL HCl every 0.5 h. After the reaction was completed the mixture was separated from zinc, and diluted with 100 mL of cold water. The sediment was collected and passed through Al₂O₃ column using chloroform as an eluent. After recrystallization from *n*-hexane 0.60 g (48%) of 4'-ethyl-DB18C6 was obtained. Mp 111–113 °C. ¹H-NMR-spectrum (δ, ppm.): 6.89 (2H, d, *J* = 2.0 Hz)—ArH (5',6'); 6.81 (1H, d, *J* = 2.0 Hz)—ArH (3'); 6.72 (4H, s)—ArH (3'',4'', 5'',6''); 4.14–4.19 (8H, m)—α-OCH₂; 4.03–4.06 (8H, m)—β-OCH₂; 2.58 (2H, q, *J* = 9.5 Hz)—CH₂; 1.20 (3H, t, *J* = 6.4 Hz)—CH₃.

General method for nitration of monosubstituted DB18C6 by metals nitrates in PPA: 4'-R-DB18C6 (0.50 mmol) was added to vigorously stirred 4.00 g of PPA. After dissolution of the starting compound the appropriate metal nitrate (0.60 mmol) was added. In all cases the reaction occurs with self-warming and color change of the reaction mixture. The reaction progress was controlled by TLC (hexane:acetone = 2:1). When all starting material was consumed, the reaction mixture was poured into water. The precipitate was filtered off and washed until neutral. The oxidation products were removed by passing through a column with small amount of Al₂O₃ using chloroform as an eluent. The mixture of obtained structural isomers in all cases was separated by fractional crystallization from 2-methoxy-ethanol. The reagents, reaction conditions, yield, ratio of isomers and characteristics of the obtained products are listed in Table 1.

General method of preparation of 4'-R-DB18C6 complexes with lithium or potassium nitrates: A mixture of the appropriate metal nitrate (0.6 mmol) and 4'-R-DB18C6 (0.3 mmol) and 15 mL absolute 2-propanol was refluxed until complex compound was formed. The endpoint of reaction was determined by controlling the m.p. of the sediment. The complexes were purified by recrystallization from chloroform. Results of the experiments are summarized in Table 2.

General conditions for reaction of 4'-R-DB18C6 complexes with lithium and potassium nitrates in PPA: 0.06 g 4'-R-DB18C6 complex with metal nitrate was added to 1.25 g vigorously stirred PPA. In all cases there was exothermic reaction resulting in nitration products of 4'-R-DB18C6. The reaction conditions and obtained results are given in Table 3.

Results and discussion

The observed 'transannular transmission' is especially clearly shown when some monosubstituted DB18C6

were used. We have carried out series of reactions using 4'-nitro-, 4'-acetyl-, and 4'-ethyl-DB18C6 as substrates and lithium, sodium, and potassium nitrates in PPA.

The products obtained are shown in Figure 1.

The analysis of sample, taken in each case from reaction mixture every 5 min, has revealed the following sequence of nitrate activity:



The signals of the pair of protons 5'-H,5''-H (4',4''-isomer) and 5'-H,4''-H (4',5''-isomer) recorded on 'UNITY 400+' spectrometer were found to have the shape of doublet with different chemical shifts (contrary to spectra recorded at lower frequency [2]). The shifts of doublets of 3'-H,6''-H (4',4''-isomer) are also different from those for 3'-H,6''-H (4',5''-isomer). The above-mentioned signals of 4',5''-isomers are shifted to lower field comparing to the corresponding signals for 4',4''-isomers.

The NMR data obtained in [2] were carried by us on 4'-acetyl-4'' (5'')-nitro-DB18C6 and 4'-ethyl-5',5'' (4'')-dinitro-DB18C6. Signals for 4'', 6'' and 3'' protons of high-melting isomer of acetylnitroderivative are shifted to lower field as compared with the corresponding signals of 5'', 3'', and 6''-protons of the low-melting isomer. Based on the ¹H-NMR data in [2] we suggest that the high-melting isomer of acetyl-nitro-DB18C6 has the structure of 4'-acetyl-5''-nitro-DB18C6 and the low-melting one is 4'-acetyl-4''-nitro-DB18C6. The high-melting isomer of ethyl-dinitro-DB18C6 is proposed to have the structure of 4'-ethyl-5',4''-dinitro-DB18C6 and the low-melting one is 4'-ethyl-5',5''-dinitro-DB18C6 (Table 4).

Nitration of 4'-nitro-DB18C6 by KNO₃ and LiNO₃ in PPA leads to formation of the mixtures of isomers with predominance of 4',4''-dinitro-DB18C6 (90/10) in the first case, and 4',5''-dinitro-DB18C6 (10/90), in second case. However, the nitration of 4'-nitro-DB18C6 by NaNO₃ in PPA leads to formation of only one low-melting isomer 4',4''-dinitro-DB18C6.

The acetyl group in 4'-acetyl-DB18C6 is weaker electron acceptor in comparison with nitro group. Thus, nitration of 4'-acetyl-DB18C6 by LiNO₃, NaNO₃, and KNO₃ results in formation of a mixture of two structural isomers 4'-acetyl-4'' (5'')-nitro-DB18C6. In the case of NaNO₃ and KNO₃ the low-melting 4'-acetyl-4''-nitro-DB18C6, and in a case LiNO₃—high-melting 4'-acetyl-5''-nitro-DB18C6 are predominant.

The observed high selectivity can be explained in a similar manner as in our previous paper [3], showing that the acetophenone fragment in PPA is able to exist in quinoid form. In this form, the positive charge is allocated on one catechol oxygen atom of the substituted benzene ring (Figure 2, Structure (a)).

Those results were based on the analysis of UV-spectra of 4'-acetyl-DB18C6, recorded in C₂H₅OH and

Table 1. Results of 4'-R-dibenzo-18-crown-6 nitration reactions (ratio of substrate: reagent: PPA = 1:1.2:15 (by mol))

R	Nitrate	Reaction time (min)	Yield of isomers (%)	Mp of isomers (°C)	Isomer	Compound obtained	Ratio of isomers	¹ H NMR data of the main isomer
			9	218–220	I	4',4''-Dinitro-DB18C6	I/II = 10/90	7.825 (2H, dd, $J_1 = 8.9$ Hz, $J_2 = 2.7$ Hz) –ArH (5',6''); 7.640 (2H, d, $J = 2.6$ Hz) –ArH (3',6''); 6.799 (2H, d, $J = 8.9$ Hz) –ArH (6',3''); 4.170 (8H, m) – α -OCH ₂ ; 3.970–3.959 (8H, m) – β -OCH ₂ .
4'-Nitro-	LiNO ₃	5	85	238–241	II	4',5''-Dinitro-DB18C6		
4'-Nitro-	NaNO ₃	10	79	218–219	I	4',4''-Dinitro-DB18C6	I/II = 100/0	7.820 (2H, dd, $J_1 = 8.9$ Hz, $J_2 = 2.7$ Hz) –ArH (5',5''); 7.643 (2H, d, $J = 2.6$ Hz) –ArH (3',3''); 6.794 (2H, d, $J = 9.0$ Hz) –ArH (6',6''); 4.169 (8H, m) – α -OCH ₂ ; 3.970 (8H, m) – β -OCH ₂ .
4'-Nitro-	KNO ₃	15	85	210–212	I	4',4''-Dinitro-DB18C6	I/II = 90/10	
			9	235–238	II	4',5''-Dinitro-DB18C6		
			8	160–164	III	4'-Acetyl-4''-Nitro-DB18C6	III/IV = 10/90	7.894 (1H, dd, $J_1 = 8.9$ Hz, $J_2 = 1.3$ Hz) –ArH (4''); 7.713 (1H, d, $J = 2.4$ Hz) –ArH (6''); 7.545 (1H, dd, $J_1 = 8.3$ Hz, $J_2 = 1.7$ Hz) –ArH (5''); 7.487 (1H, d, $J = 1.7$ Hz) –ArH (3''); 6.869 (1H, d, $J = 7.5$ Hz) –ArH (3''); 6.847 (1H, d, $J = 12.0$ Hz) –ArH (6''); 4.234 (8H, m) – α -OCH ₂ ; 4.028 (8H, m) – β -OCH ₂ ; 2.553 (3H, s) –COCH ₃ .
4'-Acetyl-	LiNO ₃	5	75	190–195	IV	4'-Acetyl-5''-Nitro-DB18C6		
			69	168–71	III	4'-Acetyl-4''-Nitro-DB18C6	III/IV = 80/20	
4'-Acetyl-	NaNO ₃	10	17	187–190	IV	4'-Acetyl-5''-Nitro-DB18C6		
			72	166–171	III	4'-Acetyl-4''-Nitro-DB18C6	III/IV = 95/5	7.890 (1H, dd, $J_1 = 8.9$ Hz, $J_2 = 1.3$ Hz) –ArH (5''); 7.709 (1H, d, $J = 2.4$ Hz) –ArH (3''); 7.548 (1H, dd, $J_1 = 8.3$ Hz, $J_2 = 1.7$ Hz) –ArH (5''); 7.490 (1H, d, $J = 1.7$ Hz) –ArH (3''); 6.866 (1H, d, $J = 7.5$ Hz) –ArH (6''); 6.849 (1H, d, $J = 12.0$ Hz) –ArH (6''); 4.240 (8H, m) – α -OCH ₂ ; 4.040 (8H, m) – β -OCH ₂ ; 2.556 (3H, s) –COCH ₃ .
'-Acetyl-	KNO ₃	15	3	187–190	IV	4'-Acetyl-5''-Nitro-DB18C6		
			6	122–125	V	4'-Ethyl-5',5''-Dinitro-DB18C6	V/VI = 15/85	7.900 (1H, dd, $J_1 = 8.7$ Hz, $J_2 = 2.4$ Hz) –ArH (5''); 7.713 (1H, d, $J = 2.5$ Hz) –ArH (6''); 7.561 (2H, s) –ArH (6',3''); 6.873 (1H, d, $J = 8.9$ Hz) –ArH (3''); 4.191 (8H, m) – α -OCH ₂ ; 4.027 (8H, m) – β -OCH ₂ ; 2.934 (2H, q, $J = 9.5$ Hz) –CH ₂ ; 1.256 (3H, t, $J = 6.4$ Hz) –CH ₃ .

Table 1. (Continued)

<i>R</i>	Nitrate	Reaction time (min)	Yield of isomers (%)	Mp of isomers (°C)	Isomer	Compound obtained	Ratio of isomers	¹ H NMR data of the main isomer
4'-Ethyl-	LiNO ₃	5	37	175-178	VI	4'-Ethyl-5',4''-Dinitro-DB18C6		.
4'-Ethyl-	NaNO ₃	10	35	121-124	V	4'-Ethyl-5',5''-Dinitro-DB18C6		
4'-Ethyl-	NaNO ₃	10	15	178-182	VI	4'-Ethyl-5',4''-Dinitro-DB18C6	V/VI = 70/30	
4'-Ethyl-	KNO ₃	15	45	122-124	V	4'-Ethyl-5',5''-Dinitro-DB18C6	V/VI = 100/0	7.882 (1H, dd, <i>J</i> ₁ = 8.8 Hz, <i>J</i> ₂ = 2.5 Hz) -ArH (4''); 7.704 (1H, d, <i>J</i> = 2.6 Hz) -ArH (3''); 7.561 (1H, s) -ArH (6'); 7.554 (1H, s) -ArH (3'); 6.864 (1H, d, <i>J</i> = 9.0 Hz) -ArH (6''); 4.186 (8H, m) -α-OCH ₂ ; 4.019 (8H, m) -β-OCH ₂ ; 2.926 (2H, q, <i>J</i> = 9.4 Hz) -CH ₂ ; 1.248 (3H, t, <i>J</i> = 6.4 Hz) -CH ₃ .

Table 2. Preparation of 4'-R-DB18C6 complexes with lithium and potassium nitrates

R	Salt	Reaction time (h)	Yield (%)	Mp (°C)
4'-Nitro-	LiNO ₃	3.5	92	170–173
4'-Nitro-	KNO ₃	3.5	92	186–188
4'-Acetyl-	LiNO ₃	1.5	98	140–143
4'-Acetyl-	KNO ₃	2	46	191–193
4'-Ethyl-	LiNO ₃	1	97	122–125
4'-Ethyl-	KNO ₃	1	51	124–127

PPA. It is necessary to note, that nitro group is also able to create quinoid form in PPA (see Structure (b)).

To correlate the formation of quinoid structure of 4'-nitro-DB18C6 molecule on selectivity of nitration the UV spectra of this compound in PPA were recorded. The formation of quinoid structure is proved by the appearance of absorption band at 505 nm. However, the

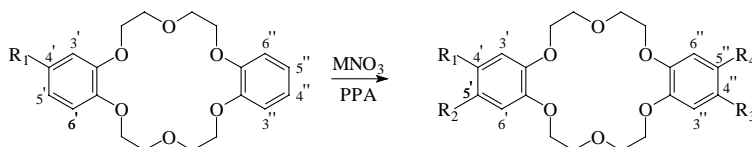
comparison of the ratio of intensity of $n \rightarrow \pi^*$ transition bands of electronic system of an aromatic nucleus to intensity of the absorption band of quinoid structure in 4'-nitro-DB18C6 and 4'-acetyl-DB18C6 indicates that 4'-acetyl-DB18C6 exists in quinoid form, whereas the quinoid form of nitroderivative is present in PPA solution along with not ionized 4'-nitro-DB18C6.

On nitration of 4'-ethyl-DB18C6 by metals nitrates in PPA the first nitro group enters the substituted ring in *o*-position to ethyl group, as expected. The second nitro group enters the second aromatic ring.

The reaction of 4'-ethyl-DB18C6 with NaNO₃ and LiNO₃ in PPA leads to a mixture of structural isomers: 4'-ethyl-5',5'' (4'')-dinitro-DB18C6, in which 4',5',5''-isomer in the first case, and 4',5',4''-isomer, in the second case are predominant. The reaction of 4'-ethyl-DB18C6 with KNO₃ in PPA results in formation of only one 4'-ethyl-5',5''-dinitro-DB18C6.

Table 3. Results of interaction of lithium and potassium nitrate complexes of 4'-R-DB18C6 with PPA (ratio of complex: PPA = 1:20)

R	Nitrate	Reaction time (min)	Yield (%)	Mp (°C)	Isomer	Compound obtained	Ratio of isomers
4'-Nitro-	LiNO ₃	<5	81	238–241	II	4',5''-Dinitro-DB18C6	I/II = 0/100
4'-Nitro-	KNO ₃	10	90	218–222	I	4',4''-Dinitro-DB18C6	I/II = 100/0
4'-Acetyl-	LiNO ₃	<5	78	190–195	IV	4'-Acetyl-5''-Nitro-DB18C6	III/IV = 0/100
4'-Acetyl-	KNO ₃	10	71	163–165	III	4'-Acetyl-4''-Nitro-DB18C6	III/IV = 100/0
			10	124–125	V	4'-Ethyl-5',5''-Dinitro-DB18C6	V/VI = 15/85
4'-Ethyl-	LiNO ₃	<5	50	173–175	VI	4'-Ethyl-5',4''-Dinitro-DB18C6	
4'-Ethyl-	KNO ₃	10	69	123–125	V	4'-Ethyl-5',5''-Dinitro-DB18C6	V/VI = 100/0



- M = Li, Na, K
 I. R₁, R₃ = NO₂; R₂, R₄ = H;
 II. R₁, R₄ = NO₂; R₂, R₃ = H;
 III. R₁ = COCH₃; R₃ = NO₂; R₂, R₄ = H;
 IV. R₁ = COCH₃; R₄ = NO₂; R₂, R₃ = H;
 V. R₁ = C₂H₅; R₂, R₄ = NO₂; R₃ = H;
 VI. R₁ = C₂H₅; R₂, R₃ = NO₂, R₄ = H.

Figure 1. Products of nitration of 4'-R-DB18C6 by lithium, sodium, and potassium nitrates in PPA.

Table 4. The ¹H-NMR data of aromatic protons of 4',4''-dinitro-DB18C6, 4',5''-dinitro-DB18C6, 4'-acetyl-4''-nitro-DB18C6, 4'-acetyl-5''-nitro-DB18C6, 4'-ethyl-5',5''-dinitro-DB18C6, 4'-ethyl-5',4''-dinitro-DB18C6, δ (ppm)

4',4''-Dinitro-DB18C6 (I)	4',5''-Dinitro-DB18C6 (II)	4'-Acetyl-4''-nitro-DB18C6 (III)	4'-Acetyl-5''-nitro-DB18C6 (IV)	4'-Ethyl-5',5''-dinitro-DB18C6 (V)	4'-Ethyl-5',4''-dinitro-DB18C6 (VI)
7.823	7.827	7.894	7.898	7.877	7.897
7.817	7.820	7.886	7.890	7.886	7.903
(5',5'')	(5',4'')	(5'')	(4'')	(4'')	(5'')
7.643	7.640	7.709	7.713	7.704	7.713
(3',3'')	(3',6'')	(3'')	(6'')	(3'')	(6'')
6.794	6.799	6.866	6.869	6.864	6.873
(6',6'')	(6',3'')	(6'')	(3'')	(6'')	(3'')

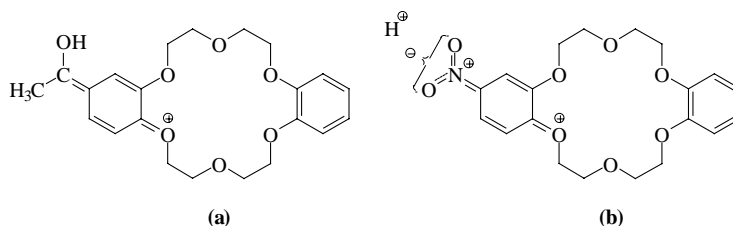


Figure 2. The quinoid structures of protonated 4'-acetyl- and 4'-nitro-DB18C6.

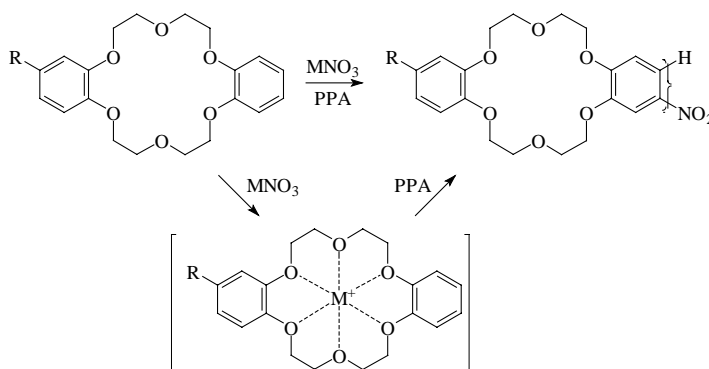


Figure 3. Two ways of nitration of 4'-R-DB18C6 by metal nitrates in PPA.

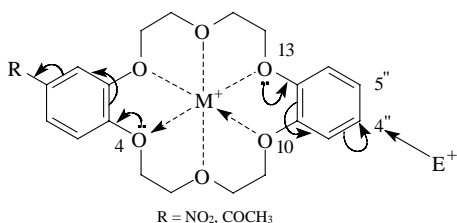


Figure 4. The assumed mechanism of 'transannular transmission' in the nitration of 4'-R-DB18C6 by metal's nitrates in PPA.

The selectivity, shown in the investigated reactions, can be explained by assuming parallel processes shown in Figure 3.

For more detailed study on the way of reaction, and also on the mechanism of cation participation in this process we carried out reactions of PPA with the formerly prepared complexes of 4'-R-DB18C6 with LiNO_3 and KNO_3 .

Treatment of 4'-nitro- and 4'-acetyl-DB18C6 KNO_3 complexes with PPA gave exclusively 4',4''-isomers as the appropriate nitration products. The reaction of

LiNO_3 complexes with PPA has resulted in exclusive formation of 4',5''-isomers.

The reaction of 4'-ethyl-DB18C6 complexes with LiNO_3 and KNO_3 has led to the same results. In the case of KNO_3 complex the 4'-ethyl-5',5''-dinitro-DB18C6 was formed. The complex of 4'-ethyl-DB18C6 with LiNO_3 in reaction with PPA has given a mixture of structural isomers ethyl-dinitroderivative with predominance of 4'-ethyl-5',4''-dinitro-DB18C6.

Thus, the reaction of 4'-R-DB18C6 metal nitrate complexes with PPA has resulted in substantial increase of nitration selectivity. Hence, formation of complexes is crucial and responsible for selectivity. The regioselectivity also depends on the cation nature.

Considering the above statements it could be assumed that the metal cation serves as conductor of 'transannular transmission' of electron density from O^4 to O^{10} and O^{13} macrocycle atoms, which become to a different degree conjugated with aromatic system of the unsubstituted aromatic ring of monosubstituted derivative (Figure 4). The conjugation of O^{10} atom allows to increase electron density on $\text{C}^{4''}$ atom of aromatic

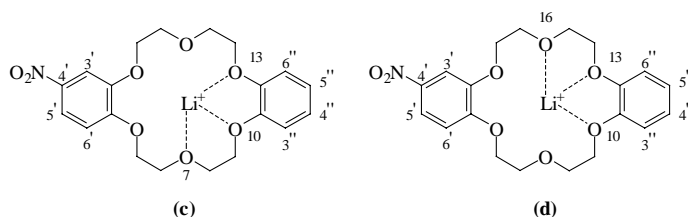


Figure 5. The assumed structures of 4'-nitro-DB18C6 complex with LiNO_3 .

Table 5. Results of calculation (method PM3) of electron density distribution in a lithium complex of 4'-nitro-DB18C6

Structure (c)		Structure (d)	
Atom	Charge	Atom	Charge
O ¹⁰	-0.189	O ¹⁰	-0.170
O ¹³	-0.171	O ¹³	-0.186
C ^{4''}	-0.123	C ^{4''}	-0.075
C ^{5''}	-0.084	C ^{5''}	-0.125

system. Therefore, the most preferable in this case is the formation of 4',4''-isomer, as it is observed for nitration of 4'-nitro- and 4'-acetyl-DB18C6 by KNO₃ and NaNO₃ in PPA.

The reversed selectivity of 4'-R-DB18C6 nitration with LiNO₃ was found yielding high-melting 4',5''-isomer. It can be explained, as calculations based on MM method [4] demonstrate, that lithium cation in complexes occupies nonsymmetrical position and coordinates only 3 from 6 oxygen atoms: two catechol and one ether oxygen. Distortion of macrocyclic cavity proceeds here more significantly, whereas in the case of sodium and potassium ions distortions are insignificant. The above-stated data allow assuming two ways of coordination of lithium ion:

The MM calculations of geometry of these complexes showed that the conformation of macrocyclic cavity undergoes essential reorganization: in the structure (c) (Figure 5), as well as in the structure (d) the angles between catechol oxygen atoms of the unsubstituted aromatic ring are different and, hence, to a different degree are conjugated with aromatic system. The last conclusion was confirmed by calculation of charge distribution by semi-empirical PM3 method (Table 5).

The calculated charge distribution in complex of structure (d), suggests the most probable electrophilic attack at C^{5''}-atom, as is observed in experiment.

Conclusions

The nitration of 4'-R-dibenzo-18-crown-6 with electron withdrawing (R = NO₂ or CH₃CO) and electron releasing (C₂H₅) groups by alkali metal nitrates in PPA occurs regioselectively with formation of mixture of isomers, where one of 4',4''- or 4',5''-isomers predominate.

The structure of the formed isomers depends on the nature of reagent cation.

If there are two substituents, an electron releasing and electron withdrawing in benzene ring, the orientation effect of the last one is stronger.

Alternative method for nitration has been developed consisting in reaction of alkali metal nitrate complexes of 4'-R-DB18C6 with PPA. This method allowed increasing the selectivity of nitration leading to only one isomer.

The complex formation has been found to be crucial for transfer of substituent effect from substituted benzene ring to unsubstituted one.

The structure of reaction product depends on the structure of the intermediate complex.

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