SYNTHESIS AND STRUCTURES OF MOLECULAR COMPLEXES OF THE cis-anti-cis DIASTEREOMER OF DICYCLOHEXANO-18-CROWN-6 WITH o-NITROANILINES

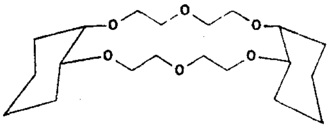
É. V. Ganin, V. F. Makarov,
S. A. Kotlyar, N. G. Luk'yanenko,
M. S. Fonar', A. A. Dvorkin, and Yu. A. Simonov

UDC 547.898'592.12'551.54:541.634:548.737

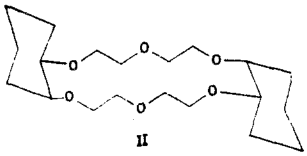
In the reaction of the cis-syn-cis and cis-anti-cis diastereomers of dicyclohexano-18-crown-6 with 2-nitro and 2,4-dinitroaniline crystalline complexes with a 1:2 stoichiometric composition were obtained only when the cis-anti-cis diastereomer was used. The three-dimensional structure of the complex of the cis-anti-cis diastereomer of dicyclohexano-18-crown-6 with 2,4-dinitroaniline was determined by an x-ray diffraction study. The complexing of o-nitroanilines with the cis-anti-cis diastereomer is explained by the topological conformity of the interacting compounds. The isolation of the individual cis diastereomers from the mixture of them formed as a result of the catalytic hydrogenation of dibenzo-18-crown-6 was accomplished by means of the selective formation of the crystalline complex of the cis-anti-cis diastereomer with 2-nitroaniline.

A study of the crystalline stoichiometric complexes of 18-crown-6 with a number of NH-acidic organic molecules has shown that their formation is determined by the development of a hydrogen bond between the oxygen atoms of the macrocyclic ring of 18-crown-6 and the hydrogen atom of the NH-acidic molecule [1-3]. An increase in the steric hindrance at the complexing H_2N center on passing from 4-nitroaniline to 2,4-dinitroaniline does not have a substantial effect on the formation of complexes with 18-crown-6, and, in conformity with the decrease in the basicity of the aniline, the stability of the latter complex increases [2].

From the point of view of ascertaining the selective interactions of the crown ethers and the organic molecules undergoing complexing [1] it seemed of interest to study the reaction of o-nitroanilines with the cis-syn-cis (I) and cis-anti-cis (II) diastereomers of dicyclohexano-18-crown-6, which are more sterically hindered and sterically nonequivalent.



I



II

It was observed that in the reaction of the cited diastereomers with 2,4-dinitroaniline and 2-nitroaniline in a molar ratio of 1:1 in methanol the corresponding complexes (III, IV) with a 1:2 composition are formed only when diastereomer II is used. The crystallization in unchanged form of 2,4-dinitroaniline from a methanol solution of diastereomer I indicates that the formation of the indicated complex does not occur at all and that, as one might have assumed, a readily soluble complex with a 1:1 composition is not formed. In order to ascertain the reasons for the observed difference in the ability of diastereomers I and II to form complexes we made an x-ray diffraction study of complex III formed by diastereomer II and two molecules of 2,4-dinitroaniline.

Institute of Applied Physics, Academy of Sciences of the Moldavian SSR, Kishinev 277028. A. V. Bogatskii Physicochemical Institute, Academy of Sciences of the Ukrainian SSR, Odessa 270080. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 9, pp. 1190-1195, September, 1988. Original article submitted March 26, 1987.

0009-3122/88/2409-0979$12.50

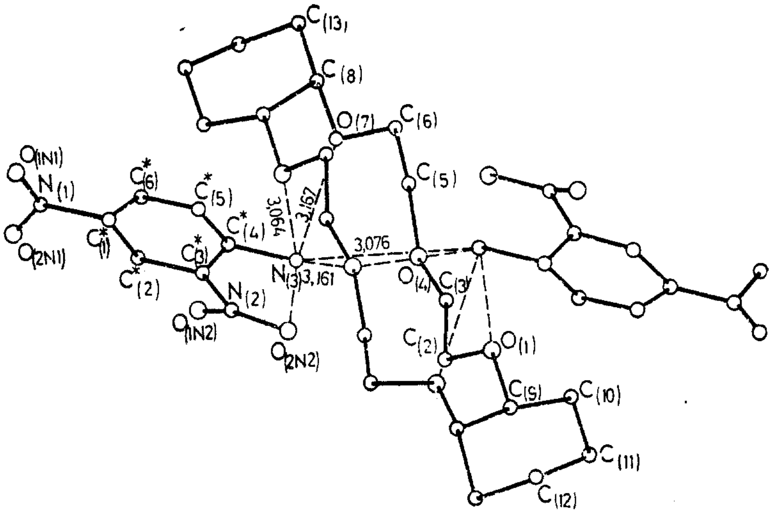


Fig. 1. Three-dimensional structure of complex III.

TABLE 1. Coordinates of the Basis Atoms with the Standard Deviations ($\times 10^4$) in the Structure of Complex III

Atom*	x	y	z	Atom*	x	y	z
O_1	12057(21)	589(23)	10881(25)	O_{1N_1}	2909(30)	1776(44)	4135(41)
O_4	10613(20)	2299(23)	8450(24)	O_{2N_1}	2907(33)	4247(49)	3281(56)
O_7	9009(20)	1933(25)	6940(24)	O_{1N_2}	6502(28)	5898(29)	550(37)
C_2	11199(34)	2071(38)	10729(42)	O_{2N_2}	8198(29)	4310(34)	50(41)
C_3	11097(33)	3063(36)	8999(41)	N_1	3409(32)	2865(48)	3435(44)
C_5	10414(35)	3216(41)	6806(39)	N_2	7100(29)	4587(35)	577(36)
C_6	10182(35)	2221(43)	6195(39)	N_3	8264(31)	1396(35)	567(36)
C_8	8663(32)	1010(37)	6339(37)	C_1*	4696(34)	2503(47)	2709(42)
C_9	7618(33)	419(38)	7539(39)	C_2*	5296(34)	3662(42)	1995(42)
C_{10}	6491(33)	1734(43)	7693(42)	C_3*	6504(32)	3318(38)	1291(37)
C_{11}	6071(38)	2835(46)	6038(49)	C_4*	7122(32)	1819(39)	1234(36)
C_{12}	7069(40)	3530(44)	4851(42)	C_5*	6425(38)	673(42)	2001(47)
C_{13}	8199(39)	2199(44)	4713(40)	C_6*	5253(38)	988(46)	2701(45)

---

*The numbering of the atoms is presented in Figs. 1 and 2.

A three-dimensional model of complex III with designation of the atoms is presented in Fig. 1; the coordinates of the atoms and the bond lengths and bond angles are presented in Tables 1-3.

The crystal is constructed from molecular complexes formed by the centrosymmetric molecule of diastereomer II and two molecules of 2,4-dinitroaniline. With respect to the character of the interaction the complex can be assigned to the "host—guest" type, where the "guest" has the proton-donor H_2N group [1-3]. The presence of four N...O contacts that are of close magnitude (Table 4) made it possible to place data on proton—acceptor group distances at the foundation in the interpretation of the hydrogen bonds. It is apparent from the data in Table 4 that the following two bifurcated (forked) systems of hydrogen bonds are formed in complex III: one with the participation of the H_1 proton with the O_4 and O_1 atoms of the crown ether, and the second with the participation of the H_2 proton with the O_4 atom and the O_{2N_2} atom of the o-nitro group of 2,4-dinitroaniline. The $O_7...N_3$ distance, which is equal to 3.164 Å ($H_1...O_7$ = 2.959 Å), is determined by the mutual orientation of the components of complex III, which is dictated by the presence of the indicated hydrogen bonds. Thus, according to our data, as in [2], the interaction between crown ether II and 2,4-dinitroaniline is realized through hydrogen bonds of the NH...O type. The bonds between the molecular complexes have van der Waals character. A similar structure of the complexes of nitroanilines with 18-crown-6 was previously noted in [1-4].

Of independent interest is the question of the conformational restructuring of the crown ether in an interaction of the "host—guest" type with proton-donor neutral molecules [3]. The molecule of diastereomer II (Fig. 2) in our case is characterized by a series

TABLE 2. Bond Lengths d (Å) in Complex III (the standard deviations are given in parentheses)

Bond	*d*	Bond	*d*
O_1—C_2	1,422(5)	C_1^*—N_1	1,474(6)
C_2—C_3	1,492(5)	N_1—O_{1N_1}	1,225(6)
C_3—O_4	1,430(5)	N_1—O_{2N_1}	1,234(7)
O_4—C_5	1,442(4)	C_1^*—C_2^*	1,358(6)
C_5—C_6	1,492(6)	C_1^*—C_6^*	1,408(6)
C_6—O_7	1,428(5)	C_2^*—C_3^*	1,391(6)
O_7—C_8	1,418(5)	C_3^*—C_4^*	1,420(5)
O_1—C_9	1,441(4)	C_4^*—C_5^*	1,425(6)
C_8—C_9	1,533(5)	C_4^*—N_3	1,329(5)
C_9—C_{10}	1,524(6)	C_5^*—C_6^*	1,352(7)
C_{10}—C_{11}	1,546(6)	C_3^*—N_2	1,442(5)
C_{11}—C_{12}	1,492(6)	N_2—O_{1N_2}	1,228(5)
C_{12}—C_{13}	1,532(6)	N_2—O_{2N_2}	1,233(5)
C_{13}—C_8	1,545(5)		

TABLE 3. Bond Angles ω in the Structure of Complex III (the standard deviations are given in parentheses)

Angle	ω (°)	Angle	ω (°)
O_1—C_2—C_3	107,8(3)	C_1^*—C_2^*—C_3^*	118,8(4)
C_2—C_3—O_4	108,7(3)	C_2^*—C_3^*—C_4^*	122,5(4)
C_3—O_4—C_5	112,9(3)	C_3^*—C_4^*—C_5^*	115,0(3)
O_4—C_5—C_6	110,3(3)	C_4^*—C_5^*—C_6^*	122,9(4)
C_5—C_6—O_7	108,6(3)	C_1^*—C_6^*—C_5^*	118,9(4)
C_6—O_7—C_8	112,8(3)	C_2^*—C_1^*—C_6^*	121,5(4)
O_7—C_8—C'_9	107,7(3)	C_2^*—C_1^*—N_1	119,2(4)
O_7—C_8—C_{13}	112,1(3)	C_6^*—C_1^*—N_1	119,1(4)
C_2—O_1—C_9	113,7(5)	C_1^*—N_1—O_{1N_1}	117,6(4)
C_9—C_8—C_{13}	108,0(3)	C_1^*—N_1—O_{2N_1}	117,7(4)
O_1—C_9—C'_8	112,5(3)	O_{1N_1}—N_1—O_{2N_1}	124,6(5)
O_1—C_9—C_{10}	106,7(3)	C_3^*—N_2—O_{1N_2}	118,7(3)
C_8—C_9—C_{10}	111,6(3)	C_3^*—N_2—O_{2N_2}	119,0(3)
C_9—C_{10}—C_{11}	109,3(3)	O_{1N_2}—N_2—O_{2N_2}	122,2(4)
C_{10}—C_{11}—C_{12}	110,9(4)	C_3^*—C_4^*—N_3	126,5(4)
C_{11}—C_{12}—C_{13}	110,1(4)	C_5^*—C_4^*—N_3	118,4(4)
C_8—C_{13}—C_{12}	111,1(3)	C_2^*—C_3^*—N_2	116,3(3)
		C_4^*—C_3^*—N_2	121,1(3)

of six gauche rotamers with respect to the C—C bonds and 10 trans and two gauche conformations with respect to the C—O bonds. The latter two are energically unfavorable [5], and their development is dictated by the presence of interactions of the NH...O type between the "host" and "guest" molecules. A comparison of the conformation of free diastereomer II [6] in [Pb·dicyclohexano-18-crown-6•$(NO_3)_2$]•$CHCl_3$ [7] and in the complex III under consideration (Fig. 2) reveals appreciable conformational restructuring of this crown ether. Whereas in the free II molecule the conformation is determined by 1,5-CH...O transannular interactions, in the complexes with lead [7] and III the change in the conformation of crown ether II with respect to the C—O bonds is due to the peculiarities of its interaction with the cation or neutral organic molecule. In complex III the six ether oxygen atoms of diastereomer II are coplanar with an accuracy of 0.167 Å; the O_4 and O'_4* atoms have the maximum deviation, the average C—C distance is 1.506 Å, the average C—O distance is 1.430 Å, the angles at the carbon atoms are 109.6°, and the angles at the oxygen atoms are 113.1°. According to the data in [8], the crown ether can be described as biangular, where, as applied to II, two gauche bonds of the same type converge at the C_9 and C'_9 atoms. This leads to the development of 1,4-CH...CH repulsive interactions [5], which deforms the bond angle at C_9, increasing it to 112.5°. In the cyclohexane substituents, which have a chair conformation, the interatomic distances and bond angles are the usual ones [9] with average values of 1.527 Å and 110.2°, respectively.

---

*The atoms linked to the basis center of symmetry are denoted by a prime sign.

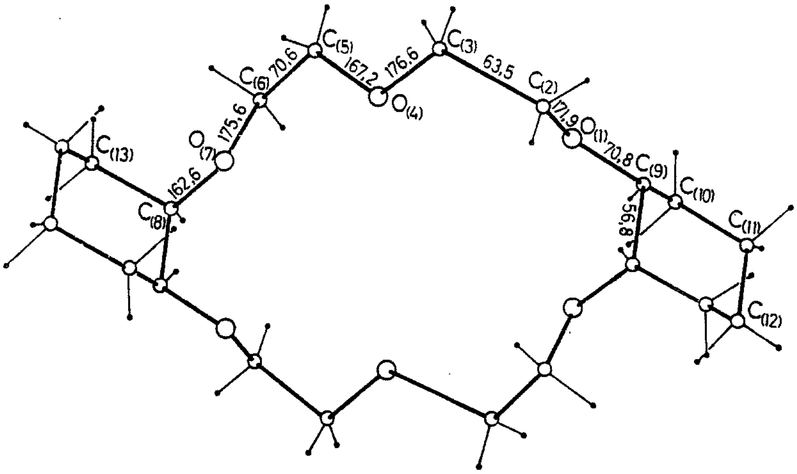


Fig. 2. Three-dimensional structure of diastereomer II entering into the composition of complex III.

TABLE 4. Geometrical Parameters of the Hydrogen Bonds in Complex III

D–H···A*	D–H, Å	D···A, Å	H···A, Å	Angle D–H...A, deg
N_3—H_1···O_7	0,71	3,17	2,96	100,2**
N_3—H_2···O_4	0,59	3,08	2,61	137,5
N_3—H_2···O_{2N2}	0,59	2,66	2,32	119,5
N_3—H_1···O_1	0,71	3,06	2,43	149,6***
N_3—H_1···O_4	0,71	3,16	2,57	142,3

---

*Symbols: D is a proton donor, and A is an acceptor.

**Symmetry transformation for the 2,4-dinitroaniline molecule: x, y, z.

***Symmetry transformation for the 2,4-dinitroaniline molecule: 2–x, –y, –z.

The 2,4-dinitroaniline molecules that enter into the composition of complex III have a planar aromatic ring. An analysis of the interatomic distances (average value 1.392 Å) and bond angles (average value 119.9°) in the aromatic ring of 2,4-dinitroaniline demonstrates their substantial deviation; this is determined by the donor characteristic of the amino group and the acceptor character of the nitro group and corresponds to the data in [10].

The steric and packing conditions in the crystal due to interaction of diastereomer II and 2,4-dinitroaniline in complex III do not lead to significant distortions in the "guest" molecules. Thus the dihedral angles between the benzene ring in the II molecule and each of the nitro groups are identical and are equal to 5.9°. The intramolecular hydrogen bond (Table 4) that is characteristic for 2-nitroanilines [4, 11] promotes stabilization of the planar structure of the o-nitro groups.

The plane of the aromatic ring of 2,4-dinitroaniline forms an angle of 78° with the average plane of the six oxygen atoms of diastereomer II. The aromatic ring deviated from the cyclohexane substituent of diastereomer II that was closest to it, and the shortest distances between them were as follows: $C_{12}...N_2$ = 3.725 Å, $C_{10}...C^*_4$ = 3.728 Å, $C_{10}...C^*_5$ = 3.74 Å, and $C_{12}...C^*_3$ = 3.79 Å. The absence of substantial mutual steric and packing [3] hindrance of the "guest" and "host" molecules in complex III (which evidently arises when one uses diastereomer I, the cyclohexane substituents of which are located on the same side of the macrocyclic ring) may evidently be the reason for the selective formation of crystalline complexes of 2-nitro- and 2,4-dinitroaniline with diastereomer II.

The reaction of 2,4,6-trinitroaniline with both diastereomers I and II and with the sterically unhindered 18-crown-6 under the described conditions does not lead to the formation of complexes. This result is explained not only by an increase in steric hindrance but also by the realization in 2,4,6-trinitroaniline of two intramolecular hydrogen bonds, which significantly decreases the ability of this molecule to form intermolecular hydrogen bonds with the ether oxygen atoms of the crown ether.

We have used the observed selective formation of a crystalline complex of diastereomer II with 2-nitroaniline for the preparative separation of diastereomers I and II, a mixture of which is formed in the catalytic hydrogenation of dibenzo-18-crown-6 [12].

EXPERIMENTAL

The IR spectra of KBr pellets of the compounds were recorded with an IKS-29 spectrometer. Thin-layer chromatography was carried out on Silufol UV-254 plates in methanol–chloroform (1:8-1:10) with development in UV light and with ninhydrin.

A bright-yellow single crystal with a prismatic habitus and linear dimensions 0.3 × 0.4 × 1.0 mm was selected for the x-ray diffraction study. The crystal was triclinic and had the following unit cell parameters: a = 11.844(8), b = 9.895(6), c = 9.621(4) Å, α = 61.61(3)°, β = 73.21(3)°, γ = 69.06(4)°, symmetry space group $P\bar{1}$, Z = 1, composition $C_{32}H_{46}N_6O_{14}$, d_{calc} = 1.338 g/cm^3. An RÉD-4 diffractometer with an M-6000 regulating computer and Mo Kα emission was used. For the calculations and the refinement we used 1901 reflections with $I \geq 2\sigma(I)$. The structure was solved by the direct method. A model of the structure was found by means of the MULTAN program [13] with a decrease in the symmetry to the acentric P1 group. The refinement was carried out within the framework of the SHELXTL-CM complex [14] with an SM-4 computer using an experimental weight scheme. The final R_W factor was 0.061.

Complexes (III, IV) of the cis-anti-cis Diastereomer of Dicyclohexano-18-crown-6 with o-Nitroanilines. A 1-mmole sample of diastereomer I or II and 1 mmole of 2,4-dinitroaniline, 2-nitroaniline, or 2,4,6-trinitroaniline were dissolved at 64°C in 20, 3, or 25 ml of methanol, respectively. The crystals that precipitated on cooling to −10 to −15°C were removed by filtration. The following complexes III and IV were obtained.

The cis-anti-cis diastereomer (III) of the 1:2 complex of dicyclohexano-18-crown-6 and 2,4-dinitroaniline was obtained in 92% yield and had mp 147-149°C. IR spectrum: 3460, 3300 (N–H), 2900 (C–H), 1100 cm^{-1} (C–O–C). Found, %: N 11.3. $C_{32}H_{46}N_6O_{14}$. Calculated, %: N 11.4.

The cis-anti-cis diastereomer (IV) of the 1:2 complex of dicyclohexano-18-crown-6 and 2-nitroaniline was obtained in 85% yield and had mp 94-96°C. IR spectrum: 3480, 3350 (N–H), 2930 (C–H), 1100 cm^{-1} (C–O–C). Found, %: N 8.7. $C_{32}H_{48}N_4O_{10}$. Calculated, %: N 8.6.

Complexes were not formed in the remaining cases.

cis-syn-cis and cis-anti-cis Diastereomers (I, II) of Dicyclohexano-18-crown-6. A 14.9-g (0.04 mole) sample of a mixture of diastereomers I and II, which was obtained as a result of the catalytic hydrogenation of dibenzo-18-crown-6 [12], and 8.3 g (0.06 mole) of 2-nitroaniline were dissolved at 64°C in 50 ml of methanol. The crystals of complex IV that precipitated when the solution was cooled were removed by filtration. The filtrate was evaporated, the residue was dissolved in 100 ml of 36% hydrochloric acid, and the solution was extracted with 100 ml of chloroform. The chloroform extract was washed with 36% hydrochloric acid (two 50-ml portions) and water (two 100-ml portions) and evaporated, and the residue was recrystallized from diethyl ether to give 3.7 g (25%) of cis-syn-cis diastereomer I with mp 60-61°C. The crystals of complex IV were washed with methanol and dissolved in 100 ml of 36% hydrochloric acid, and the solution was then treated in the same way as the filtrate to give 4.7 g (32%) of cis-anti-cis diastereomer II with mp 69-70°C (from hexane). The constants of diastereomers I and II were in agreement with the values presented in [12].

LITERATURE CITED

1. F. Vögtle, Zh. Vses. Khim. Obshch. im. D. I. Mendeleeva, 36, 500 (1985).
2. F. Vögtle, H. Sieger, and W. M. Müller, Host–Guest Complex Chemistry, Vol. 1, edited by F. Vögtle, Berlin (1981), p. 107.
3. A. Elbasyouny, H. J. Brügge, K. Deuten, M. Dickel, A. Knöchel, K. U. Koch, J. Kopf, D. Melzer, and G. Rudolph, J. Am. Chem. Soc., 105, 6568 (1983).

4. G. Weber and G. M. Sheldrick, Acta Cryst., B37, 2108 (1981).
5. Yu. G. Ganin, Yu. A. Simonov, and T. I. Malinovskii, Izv. Akad. Nauk Moldavsk. SSR, Ser. Fiz.-Tekh. Mat. Nauk, No. 1, 18 (1985).
6. N. K. Dalley, D. E. Smith, and S. B. Larson, J. Chem. Soc., Chem. Commun., No. 1, 43 (1975).
7. N. F. Krasnova, Yu. A. Simonov, V. V. Yakshin, and M. B. Korshunov, Kristallografiya, 32, No. 2, 499 (1987).
8. J. Dale, Acta Chem. Scand., 27, 1115 (1973).
9. Yu. A. Simonov, N. F. Krasnova, N. A. Tsarenko, V. K. Bel'skii, V. V. Yakshin, and B. N. Laskorin, Dokl. Akad. Nauk SSSR, 285, 892 (1985).
10. A. Domenicano and P. Murrey-Rust, Tetrahedron Lett., No. 24, 2283 (1979).
11. J. R. Holden, Ch. Dichinson, and Ch. M. Boch, J. Phys. Chem., 76, 3597 (1972).
12. M. Hiraoka, Crown Compounds: Properties and Application [Russian translation], Mir, Moscow (1986).
13. P. Main, S. E. Hull, L. Lessinger, G. Germain, J.-P. Declerco, and M. M. Woolfson, MULTAN 78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-Ray Diffraction Data, University of York, England and University of Louvain, Belgium (1978).
14. V. K. Pechorskii, P. Yu. Zavalii, and L. G. Aksel'rud, Vestn. L'vov. Univ., No. 25, 9 (1984).

FREE RADICALS AND RADICAL ANIONS IN A SERIES OF TELLUROXANTHENE DERIVATIVES

A. A. Bumber, E. P. Ivakhnenko,
A. A. Ladatko, A. A. Arutyunyants,
I. D. Sadekov, and O. Yu. Okhlobystin

UDC 547.818.9:542.941:543.422.27

In the one-electron reduction of telluroxanthyl or telluroxanthone perchlorates, stable 9-aryltelluroxanthyl radicals and telluroxanthone radical anion are formed. An EPR study of the distribution of spin density in such radicals gives evidence that the nature of the heteroatoms in the xanthyl fragments has an insignificant influence on the distribution of the spin density.

Stable 9-aryltelluroxanthyl radicals [1], radical cations obtained in the electrochemical oxidation of 3,4-benzo-1-tellurocyclopentane [2] and phenoxatellurine [3], and radical anions obtained generated in the electrochemical reduction of 2-nitro and 2,8-dinitrophenoxatellurines [4], have been described among the series of heterocyclic, tellurium-containing systems. However, the electrochemical characteristics and the distribution of spin density in such systems have hardly been studied at all. Besides this, they are of definite interest both for the study of the spectral characteristics of radicals with a single type of structure and for understanding the differences in reactivity of the heterocyclic compounds leading to these radicals.

The present report deals with an investigation of the reducibility of telluroxanthyl [5] and telluroxanthone systems [5, 6] by means of cyclic voltammetry and the EPR spectroscopy of the resultant radical and radical anion systems.

We obtained voltammograms of the reduction of telluroxanthyl Ib in acetonitrile. On the addition of water to the supporting electrolyte, the characteristic pair of cathodic and anodic peaks decreased to zero (Fig. 1b, c). The subsequent addition of the acid CF_3COOH to the system leads to the appearance of oxidation-reduction peaks, and the solution

---

Scientific Research Institute of Physical and Organic Chemistry, M. S. Suslov State University, Rostov-on-Don, 334071. Scientific Research Institute of Free Radical Chemistry, K. L. Khetagurov Severo-Osetinskaya State University, Ordzhonikidze, 362000. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 9, pp. 1196-1100, September, 1988. Original article submitted March 26, 1987.

0009-3122/88/2409-0984$12.50