Synthesis and molecular structure of 7*H*-12-oxa-3,7-diazapleiadene-substituted 1,3-tropolones

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An acid-catalyzed reaction of substituted 2-methyl-7*H*-12-oxa-3,7-diazapleiadenes with 1,2-benzoquinones leads to 7*H*-12-oxa-3,7-diazapleiadene-substituted 1,3-tropolones. Molecular structure of 5,7-di(*tert*-butyl)-2-[9,11-di(*tert*-butyl)-4-methyl-7*H*-12-oxa-3,7-diazapleiaden-2-yl]-4-nitro-1,3-tropolone was established by X-ray crystallography. Energy and structural characteristics of isomeric 5,7-di(*tert*-butyl)-2-[9,11-di(*tert*-butyl)-4-methyl-7*H*-12-oxa-3,7-diazapleiaden-2-yl]-4-nitro-1,3-tropolones in the gaseous phase and a polar solution were studied by the PBE0/6-31G** method.

Key words: pleiadenes, *o*-quinones, β-tropolones, intramolecular hydrogen bond, quantum chemical calculations, X-ray crystallography.

Direction of the processes leading to the formation of different heterocyclic systems in the reactions of sterically hindered *o*-quinones with 2-methyl-substituted nitrogen-containing heterocyclic compounds depends on both the nature of a heterocycle and the redox properties of *o*-quinone. For instance, the *o*-quinone ring expansion during the reaction with 2-methylquinolines[1,2] leads to 2-(quinolin-2-yl)-substituted 1,3-tropolones, however, when an amino group is present at position 5 of the quinoline ring **1**, the reaction with 3,5-di(*tert*-butyl)-1,2-benzoquinone **2** (Scheme 1) leads to the new heterocyclic system,[3] *viz.*, 7*H*-12-oxa-3,7-diazapleiadene **5**.

According to the suggested mechanism,[3] the first step of the reaction leads to *o*-quinonimines **3**, which, having highly pronounced oxidative properties, are easy involved into dehydrogenation reactions like *o*-quinones. The adduct **3** reacts with the corresponding 3,5-di(*tert*-butyl)-pyrocatechol to form aminophenol **4**, which gives 12-oxa-3,7-diazapleiadene **5** as a result of intramolecular cyclization. When a twofold excess of *o*-quinone **2** is used, the yields of compounds **5** do not exceed 20—30%, however, if 3,5-di(*tert*-butyl)pyrocatechol is introduced into the reaction, the yield of the final product **5** increases to 60%. The presence of the active methyl group at position 2 of 12-oxa-3,7-diazapleiadene **5** creates a possibility of functionalization of these system with the tropolone fragment. The present work is devoted to the reaction of the *o*-quinone ring expansion in 2-methyl-substituted 12-oxa-3,7-diazapleiadenes **5**.

We found that the reaction of 2-methyl-substituted 12-oxa-3,7-diazapleiadenes **5** with 1,2-benzoquinones **2a,b** in the melt or upon reflux in *o*-xylene results in the very low yields of the target product, however, when the reactants are maintained in acetic acid at 65—70 °C for 200 h, the 2-(7*H*-12-oxa-3,7-diazapleiaden-2-yl)-1,3-tropolone derivatives **6** (R^4 = H) are formed in low yields (10—15%) according to Scheme 2.

The mechanism of the formation of β-tropolones has been in detail studied earlier[1] taken the reactions of 3,5-di(*tert*-butyl)-1,2-benzoquinone with 2-methylquinoline derivatives as examples. The initial condensation of 2-methyl-substituted 12-oxa-3,7-diazapleiadenes **5** with 1,2-benzoquinones **2a,b** furnishes the intermediate adducts, *viz.*, 6-hydroxy-6-(12-oxa-3,7-diazapleiadenylmethylene)-2,4-cyclohexadien-1-ones (**7**). The intermediates **7** undergo cyclization with the formation of norcaradiene derivatives **8**, which further rearrange to dihydrotropolones **9**. Oxidation of dihydro-

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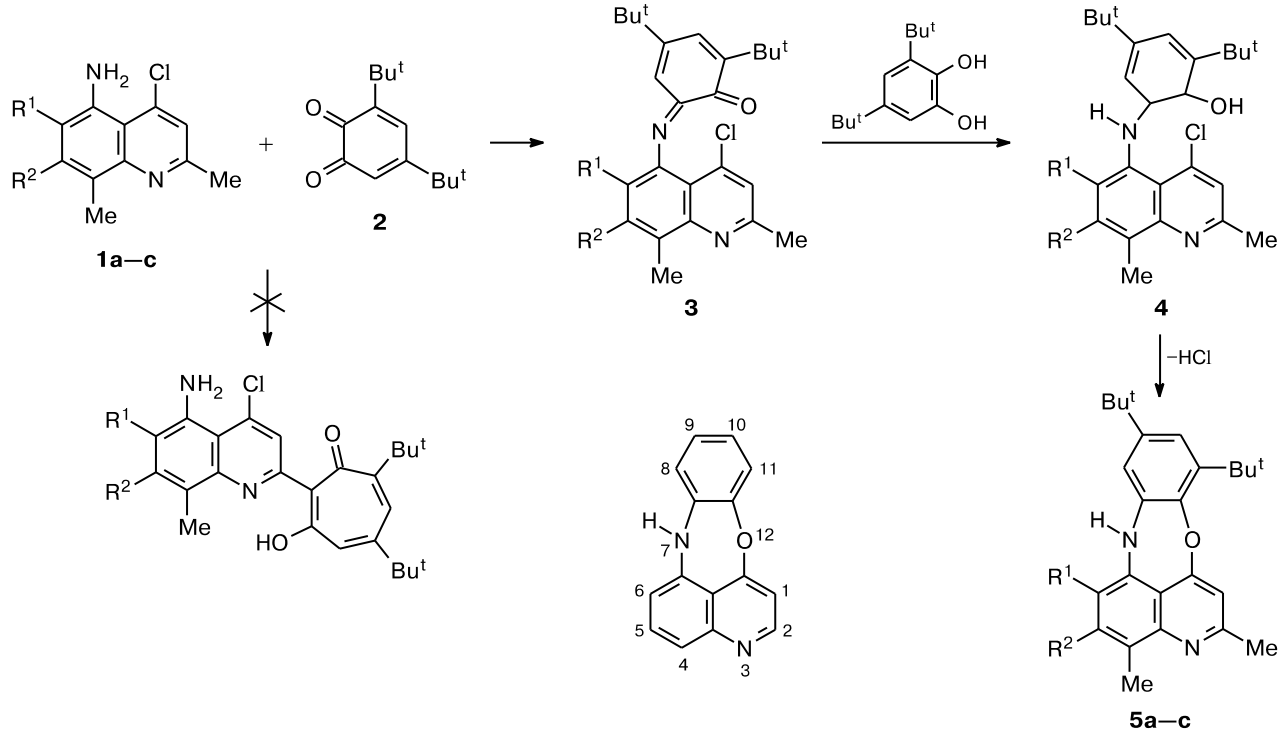
Scheme 1



$R^1 = R^2 = H$ (**a**); $R^1 = Me$, $R^2 = H$ (**b**); $R^1 = H$, $R^2 = Me$ (**c**)

tropolones **9** with excess of quinone **2** leads to 1,3-tropolones **6**.

The presence of the free NH group in the oxazepine ring, which can enter a competing reaction with 1,2-benzoquinones, is the main reason that complicates this reaction.

In this connection, we obtained a series of 7-acyl-2-methyl-12-oxa-3,7-diazapleiadenes **5** (R^3 = Ac), which were further involved into the reaction with 1,2-benzoquinones **2a**,**b** at 60—70 °C, that furnished 2-(7-acyl-12-oxa-3,7-diazapleiaden-2-yl)-1,3-tropolone derivatives **6** (R^3 = Ac) in fairly high yields (40—60%).

The structures of the synthesized compounds **6** were confirmed by ^{1}H NMR and IR spectroscopy and mass spectrometry. According to the ^{1}H NMR spectroscopy, the signal for the proton of the hydroxy group of compounds **6** is observed in the low-field region δ 19.1—19.5 as a broad singlet, which indicates the presence of a strong hydrogen bond in the molecule between the hydroxy group and the quinoline nitrogen atom forming a six-membered chelate ring. In solutions, the **6**(OH)—**6**(NH) forms exist in the dynamic equilibrium (Scheme 3).

Molecular structure of β-tropolone **6c** was established by X-ray crystallography and is shown in Fig. 1, the principal interatomic distances and angles in the molecule are given in Table 1.

The hydrogen atom is certainly localized at the nitrogen atom N(1) at the distance 0.95(3) Å, the distanc-

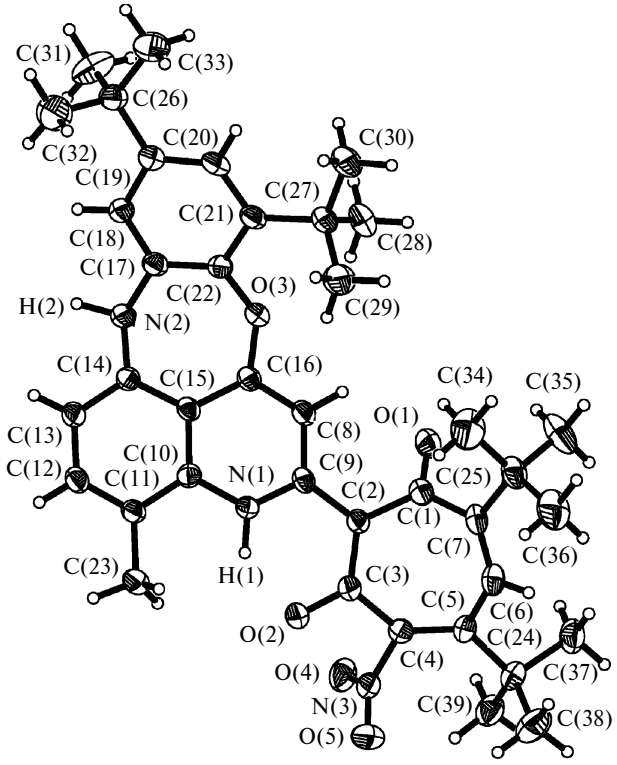
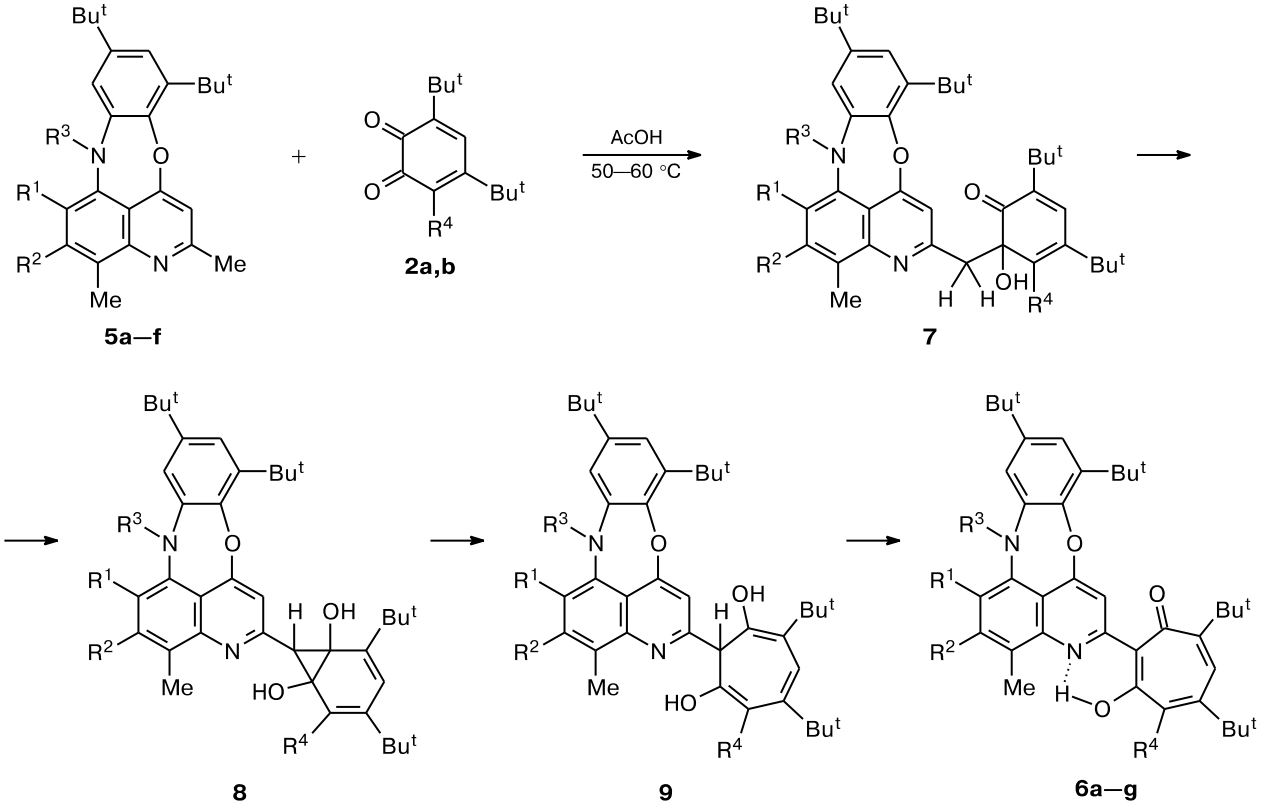


Fig. 1. Molecular structure of 5,7-di(*tert*-butyl)-2-[9,11-di(*tert*-butyl)-4-methyl-7*H*-12-oxa-3,7-diazapleiaden-2-yl]-4-nitro-1,3-tropolone (**6c**).

Scheme 2



2: R^4 = H (**a**), NO_2 (**b**)
5: R^1 = R^2 = R^3 = H (**a**); R^1 = Me, R^2 = R^3 = H (**b**); R^1 = R^3 = H, R^2 = Me (**c**); R^1 = R^2 = H, R^3 = Ac (**d**); R^1 = Me, R^2 = H, R^3 = Ac (**e**); R^1 = H, R^2 = Me, R^3 = Ac (**f**)
6: R^1 = R^2 = R^3 = R^4 = H (**a**); R^1 = Me, R^2 = R^3 = R^4 = H (**b**); R^1 = R^2 = R^3 = H, R^4 = NO_2 (**c**); R^1 = Me, R^2 = R^3 = H, R^4 = NO_2 (**d**); R^1 = R^2 = R^4 = H, R^3 = Ac (**e**); R^1 = Me, R^2 = R^4 = H, R^3 = Ac (**f**); R^1 = R^4 = H, R^2 = Me, R^3 = Ac (**g**)

es O(2)—C(3) and H(1)...O(2) are equal to 1.261(3) and 1.67(5) Å, respectively, the angle N(1)—H(1)—O(2) in the cycle formed by the intramolecular hydrogen bond is equal to 145(2)°, which indicate that β-tropolone **6c** exists in the crystal phase as an aminoenone form **6**(NH).

Scheme 3

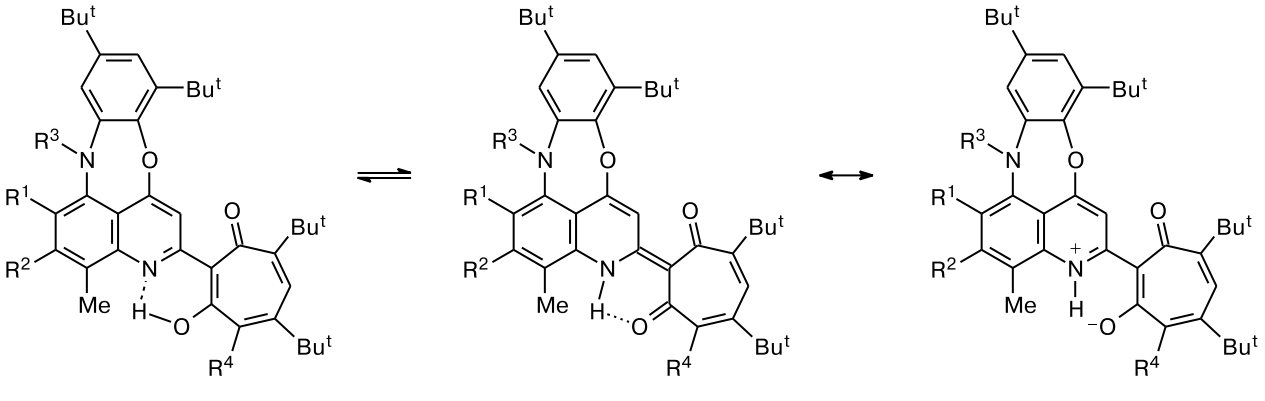


Table 1. The principal bond distances (*d*) and bond angles (ω) in the structure **6c**

Parameter	Value	Parameter	Value
Bond	*d*/Å	Bond	*d*/Å
O(1)—C(1)	1.227(4)	O(2)—C(3)	1.261(3)
O(3)—C(16)	1.364(3)	O(3)—C(22)	1.419(3)
O(4)—N(3)	1.223(4)	O(5)—N(3)	1.220(4)
N(1)—C(9)	1.351(3)	N(1)—C(10)	1.387(4)
N(1)—H(1)	0.95(3)	N(2)—C(14)	1.390(4)
N(2)—C(17)	1.420(3)	N(2)—H(2)	0.92(3)
N(3)—C(4)	1.486(4)	C(1)—C(2)	1.475(4)
C(1)—C(7)	1.483(4)	C(2)—C(3)	1.420(4)
C(2)—C(9)	1.431(4)	C(3)—C(4)	1.498(4)
C(4)—C(5)	1.349(4)	C(5)—C(6)	1.453(4)
C(5)—C(24)	1.549(4)	C(6)—C(7)	1.324(4)
C(7)—C(25)	1.544(4)	C(8)—C(16)	1.356(4)
C(8)—C(9)	1.417(4)	C(10)—C(11)	1.398(4)
C(10)—C(15)	1.415(4)	C(11)—C(12)	1.368(4)
C(11)—C(23)	1.513(4)	C(12)—C(13)	1.390(4)
C(13)—C(14)	1.384(4)	C(14)—C(15)	1.416(4)
C(15)—C(16)	1.426(4)	C(17)—C(18)	1.368(4)
C(17)—C(22)	1.382(4)	C(18)—C(19)	1.394(4)
C(19)—C(20)	1.381(4)	C(19)—C(26)	1.532(4)
C(20)—C(21)	1.404(4)		
Angle	ω/deg	Angle	ω/deg
C(16)—O(3)—C(22)	124.9(2)	C(9)—N(1)—C(10)	124.7(3)
C(9)—N(1)—H(1)	110 (2)	C(10)—N(1)—H(1)	121.4(17)
C(14)—N(2)—C(17)	123.2(2)	C(14)—N(2)—H(2)	114(2)
C(17)—N(2)—H(2)	104(2)	O(5)—N(3)—O(4)	124.8(3)
O(5)—N(3)—C(4)	118.2(3)	O(4)—N(3)—C(4)	116.9(3)
O(1)—C(1)—C(2)	121.8(3)	O(1)—C(1)—C(7)	120.4(3)
C(2)—C(1)—C(7)	117.4(3)	C(3)—C(2)—C(9)	119.3(2)
C(3)—C(2)—C(1)	121.4(3)	C(9)—C(2)—C(1)	119.2(3)
O(2)—C(3)—C(2)	124.0(3)	O(2)—C(3)—C(4)	114.8(3)
C(2)—C(3)—C(4)	120.6(3)	C(5)—C(4)—N(3)	120.3(3)
C(5)—C(4)—C(3)	132.3(3)	N(3)—C(4)—C(3)	107.2(2)
C(4)—C(5)—C(6)	117.7(3)	C(4)—C(5)—C(24)	127.1(3)
C(6)—C(5)—C(24)	115.2(2)	C(7)—C(6)—C(5)	129.9(3)
C(6)—C(7)—C(1)	120.9(3)	C(6)—C(7)—C(25)	122.9(3)
C(1)—C(7)—C(25)	116.2(3)	C(16)—C(8)—C(9)	121.2(3)
N(1)—C(9)—C(8)	116.3(3)	N(1)—C(9)—C(2)	118.3(3)
C(8)—C(9)—C(2)	125.4(2)	N(1)—C(10)—C(11)	118.3(3)
N(1)—C(10)—C(15)	118.9(2)	C(11)—C(10)—C(15)	122.8(3)
C(12)—C(11)—C(10)	117.1(3)	C(12)—C(11)—C(23)	121.5(3)
C(10)—C(11)—C(23)	121.5(3)	C(11)—C(12)—C(13)	122.2(3)
C(14)—C(13)—C(12)	121.1(3)	C(13)—C(14)—N(2)	119.2(3)
C(13)—C(14)—C(15)	118.9(3)	N(2)—C(14)—C(15)	121.5(3)
C(10)—C(15)—C(14)	117.7(2)	C(10)—C(15)—C(16)	116.3(3)
C(14)—C(15)—C(16)	125.8(3)	C(8)—C(16)—O(3)	113.8(2)
C(8)—C(16)—C(15)	121.9(3)	O(3)—C(16)—C(15)	124.1(3)
C(18)—C(17)—C(22)	119.9(3)	C(18)—C(17)—N(2)	119.5(3)
C(22)—C(17)—N(2)	120.5(3)	C(17)—C(18)—C(19)	121.3(3)
C(20)—C(19)—C(18)	116.9(3)	C(20)—C(19)—C(26)	123.0(3)
C(18)—C(19)—C(26)	120.1(3)	C(19)—C(20)—C(21)	124.5(3)
C(22)—C(21)—C(20)	115.0(3)	C(22)—C(21)—C(27)	123.2(3)
C(20)—C(21)—C(27)	121.8(3)	C(17)—C(22)—C(21)	122.2(3)
C(17)—C(22)—O(3)	119.9(2)	C(21)—C(22)—O(3)	117.2(3)

Molecular structures of 5,7-di(*tert*-butyl)-2-(4-chloro-8-methylquinolin-2-yl)-1,3-tropolone **10** and 5,7-di(*tert*-butyl)-2-(8-methyl-4-morpholinoquinolin-2-yl)-1,3-tropolone **11** studied earlier[1] are shown in Fig. 2.

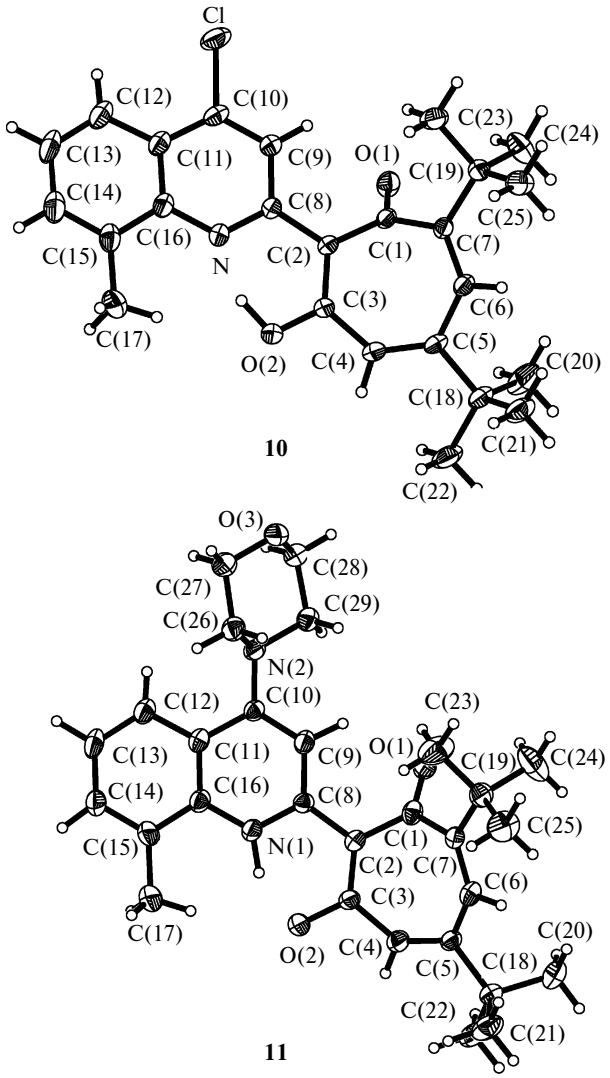


Fig. 2. The molecular structures of 1,3-tropolones **10** and **11**.

Figure 3 shows how the molecules of compounds **6c**, **10**, and **11** are superimposed when projected on the plane of the N(1)—C(9)—C(2) atoms.

Analysis of mutual arrangement of the quinoline rings shows that they coincide good enough in the earlier studied molecules **10** and **11**, whereas some deviation from their position for **6c** can be explained by the influence of the [1,4]oxazepine ring, which is bent along the line of N(2)—O(3) atoms so, that the angle between the planes of the atoms N(2)—O(3)—C(14)—C(15)—C(16) and N(2)—O(3)—C(17)—C(22) is 136° with the distances between the N(2)···O(3) atoms being equal to 2.82 Å. The structure of the tropolone ring of compound **6c** differs insignificantly from the analogs **10** and **11**, that is seen from the bend along the line of the C(3)—C(6) atoms to 138° (**6c**), while for compounds **10** and **11** they are equal to 145 and 144°, respectively. It is possible that this is due to the fact that the molecules in the monocrystal **6c** are

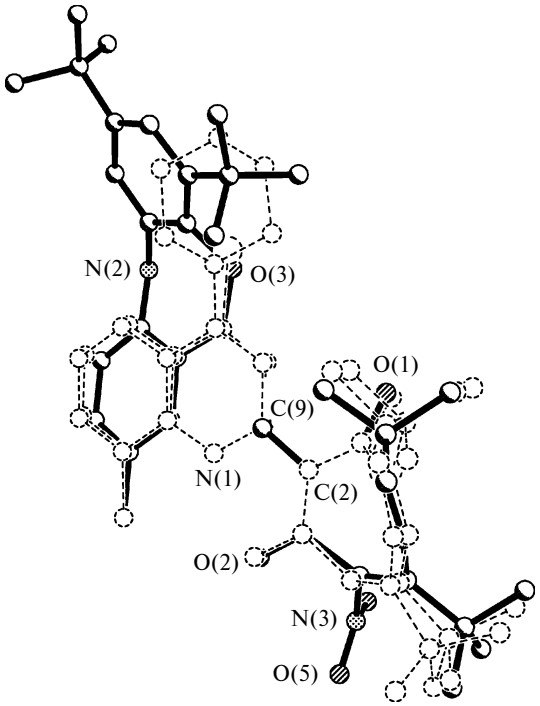


Fig. 3. The molecules of compounds **6c**, **10**, and **11** superimposed in the projections on the plane of the N(1)—C(9)—C(2) atoms.

arranged so, that they are combined in dimers (Fig. 4) because of intermolecular hydrogen bonds between the hydrogen atom of the NH group of one molecule (for example, H(2B)) and the oxygen atom of the NO_2 group of the other molecule (in this case, O(4A)). The parameters of intermolecular hydrogen bond are as follows: the distances N(2B)—H(2B), H(2B)...O(4A), and N(2B)...O(4A) are 0.931(0.028), 2.267(0.029), and 3.182(0.003) Å, respectively, the angle N(2B)—H(2B)—O(4A) is equal to 168(2)°.

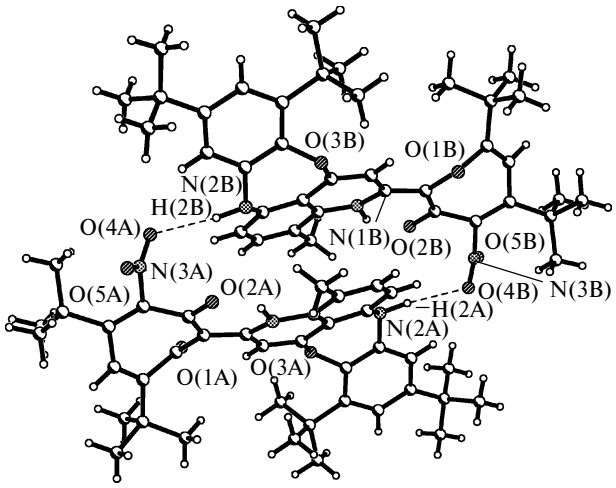


Fig. 4. The molecules of **6c** combined by hydrogen bonds.

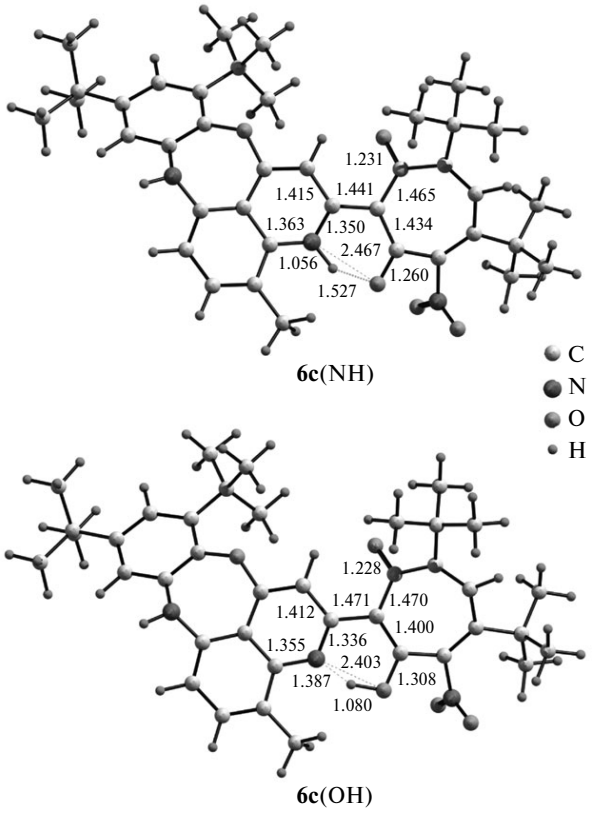


Fig. 5. The structural characteristics of the tautomeric forms of compounds **6c** in the gaseous phase according to the data calculated by the PBE0/6-31G** method. The picture shows the bond distances (Å).

To determine relative thermodynamic stabilities of the NH- and OH-isomers of **6c**, we calculated relative stabilities of these forms using the PBE0/6-31G** method. The calculation results are shown in Table 2 and in Fig. 5.

It was found that the NH-form is the most thermodynamically stable form of compound **6c** in both the gaseous phase and in the polar solvent, that agrees with the experimental data.

The bond distances calculated for compound **6c**(NH) in the gaseous phase are close to the X-ray crystallographic data. The noticeable differences of the experimental and theoretical results (~0.1 Å) are observed only in the localization of the proton involving into the intramolecular hydrogen bond. According to the calculations, the N(1)—H bond distance in the gaseous phase is by 0.106 Å longer than the corresponding distance in the crystal. In other cases discrepancies do not exceed 0.03 Å.

Table 2. The total energies calculated by the PBE0/6-31G** method in the gaseous phase (gas) and in DMSO (sol) with allowance for the energy of zero vibrations (E_{tot}+ZPE, at. units) and relative energies (ΔE/kcal mol^{-1}) of the NH and OH isomers of compound **6c**

Structure	E_{tot} + ZPE (gas)	ΔE_{gas}	E_{tot} + ZPE (sol)	ΔE_{sol}
6c(OH)	−2051.657049	0.7	−2051.669198	1.0
6c(NH)	−2051.658189	0	−2051.670735	0

Experimental

^{1}H NMR spectra were recorded on a Varian Unity-300 spectrometer. Chemical shifts are given relatively to the signal for Me_4Si (an internal standard). Mass spectra were recorded on a Finnigan MAT INCOS 50 instrument. IR spectra were recorded on a Varian 3100FT-IR Excalibur Series spectrometer using the frustrated total internal reflection method (FTIR). Chromatography was performed on columns with Al_2O_3 (II—III degree of Brockmann activity). Melting points were measured in glass capillaries on a PTP apparatus and were not corrected. The synthesis of substituted 2-methyl-7*H*-12-oxa-3,7-diazapleiadenes **5a—c** is described in the work.[3]

7-Acetyl-9,11-di(*tert*-butyl)-2,4-dimethyl-7*H*-12-oxa-3,7-diazapleiadene (5d). A solution of 9,11-di(*tert*-butyl)-2,4-dimethyl-7*H*-12-oxa-3,7-diazapleiadene (**5a**) (1.87 g, 5 mmol) in acetic anhydride (15 mL) was refluxed for 3 h, cooled, diluted with water, and extracted with chloroform. The extract was concentrated and compound **5d** (1.5 g, 72%) was obtained after recrystallization from propan-2-ol, light yellow crystals, m.p. 159—161 °C (propan-2-ol). IR, ν/cm^{-1}: 1678, 1604, 1504, 1473, 1444, 1425, 1385, 1369, 1344, 1318, 1260, 1232, 1206, 1162, 1138, 1057, 1019, 984. ^{1}H NMR ($CDCl_3$), δ: 1.31 (s, 9 H, Bu^t(9)); 1.49 (s, 9 H, Bu^t(11)); 2.00 (s, 3 H, COMe); 2.73 (s, 6 H, Me(2), Me(4)); 7.16—7.53 (m, 5 H, H arom.). MS (EI, 70 eV), *m/z* (I_{rel} (%)): 416 [M]$^+$ (10), 374 (35), 359 (4), 343 (2), 329 (2), 315 (3), 301 (5), 287 (4), 273 (5), 259 (5), 245 (3), 233 (4), 115 (3), 91 (2), 77 (3), 57 (15), 43 (70). Found (%): C, 77.72; H, 7.58; N, 6.56. $C_{27}H_{32}N_2O_2$. Calculated (%): C, 77.85; H, 7.74; N, 6.72.

7-Acetyl-9,11-di(*tert*-butyl)-2,4,6-trimethyl-7*H*-12-oxa-3,7-diazapleiadene (5e) was obtained from compound **5b** (5 mmol) similarly to compound **5d**. The yield was 58%, light yellow crystals, m.p. 171—173 °C (propan-2-ol). IR, ν/cm^{-1}: 1678, 1606, 1567, 1475, 1423, 1392, 1365, 1339, 1325, 1307, 1256, 1241, 1225, 1208, 1176, 1155, 1057, 1033, 1003, 982. ^{1}H NMR ($CDCl_3$), δ: 1.31 (s, 9 H, Bu^t(9)); 1.47 (s, 9 H, Bu^t(11)); 2.00 (s, 3 H, COMe); 2.48 (s, 3 H, Me(4)); 2.69 (s, 3 H, Me(6)); 2.73 (s, 3 H, Me(2)); 7.12—7.41 (m, 4 H, H arom.). MS (EI, 70 eV), *m/z* (I_{rel} (%)): 430 [M]$^+$ (4), 388 (7), 371 (2), 357 (2), 315 (2), 299 (2), 287 (3), 273 (3), 257 (2), 247 (3), 231 (2), 115 (3), 91 (2), 77 (3), 57 (7), 43 (50). Found (%): C, 77.94; H, 7.82; N, 6.42. $C_{28}H_{34}N_2O_2$. Calculated (%): C, 78.10; H, 7.96; N, 6.51.

7-Acetyl-9,11-di(*tert*-butyl)-2,4,5-trimethyl-7*H*-12-oxa-3,7-diazapleiadene (5f) was obtained from compound **5c** (5 mmol) similarly to compound **5d**. The yield was 51%, light yellow crystals, m.p. 193—195 °C (propan-2-ol). IR, ν/cm^{-1}: 1683, 1608, 1556, 1510, 1471, 1442, 1424, 1376, 1365, 1332, 1318, 1298, 1227, 1211, 1178, 1159, 1129, 1100, 1051, 1031, 1009, 984. ^{1}H NMR ($CDCl_3$), δ: 1.31 (s, 9 H, Bu^t(9)); 1.48 (s, 9 H, Bu^t(11)); 2.00 (s, 3 H, COMe); 2.49 (s, 3 H, Me(5)); 2.67 (s, 3 H, Me(4)); 2.70 (s, 3 H, Me(2)); 7.09—7.37 (m, 4 H, H arom.). MS (EI, 70 eV), *m/z* (I_{rel} (%)): 430 [M]$^+$ (5), 388 (10), 373 (2), 357 (3), 315 (2), 301 (3), 287 (2), 273 (3), 259 (2), 247 (2), 232 (2),

115 (3), 91 (3), 77 (2), 57 (5), 43 (60). Found (%): C, 77.98; H, 7.80; N, 6.38. $C_{28}H_{34}N_2O_2$. Calculated (%): C, 78.10; H, 7.96; N, 6.51.

5,7-Di(*tert*-butyl)-2-[9,11-di(*tert*-butyl)-4-methyl-7*H*-12-oxa-3,7-diazapleiaden-2-yl]-1,3-tropolone (6a). A solution of 3,5-di(*tert*-butyl)-1,2-benzoquinone (**2a**) (1.1 g, 5 mmol) and compound **5a** (0.94 g, 2.5 mmol) in AcOH (10 mL) was heated for 200 h at 65—70 °C. After cooling, the solution was diluted with water and a precipitate formed was filtered off, dried, and dissolved in the hexane—$CHCl_3$ solvent mixture. The solution was subjected to column chromatography with Al_2O_3 (eluent: hexane—$CHCl_3$ (1 : 1)) to collect a bright yellow fraction. The solvent was evaporated, the residue was recrystallized from propan-2-ol to obtain compound **6a** (0.21 g, 14%), light yellow crystals, m.p. 296—298 °C (propan-2-ol). ^{1}H NMR ($CDCl_3$), δ: 1.25 (s, 9 H, Bu^t(5)); 1.31 (s, 9 H, Bu^t(9′)); 1.40 (s, 9 H, Bu^t(7)); 1.56 (s, 9 H, Bu^t(11′)); 2.62 (s, 3 H, Me(4′)); 6,66 (s, 1 H, NH); 6.72 (s, 1 H, H arom.); 6.87 (d, 1 H, H(4), J = 2.08 Hz); 7.12 (d, 1 H, H(6), J = 2.08 Hz); 7.59 (s, 1 H, H arom.); 8.01 (s, 1 H, H arom.); 9.91 (s, 1 H, H arom.); 11.58 (s, 1 H, H arom.); 18.89 (s, 1 H, OH). Found (%): C, 78.84; H, 8.02; N, 4.66. $C_{39}H_{48}N_2O_3$. Calculated (%): C, 79.02; H, 8.16; N, 4.73.

5,7-Di(*tert*-butyl)-2-[9,11-di(*tert*-butyl)-4,6-dimethyl-7*H*-12-oxa-3,7-diazapleiaden-2-yl]-1,3-tropolone (6b) was obtained from compound **5b** (5 mmol) similarly to compound **6a**. The yield was 16%, orange crystals, m.p. 239—241 °C (propan-2-ol). ^{1}H NMR ($CDCl_3$), δ: 1.27 (s, 9 H, Bu^t(5)); 1.31 (s, 9 H, Bu^t(9′)); 1.41 (s, 9 H, Bu^t(7)); 1.53 (s, 9 H, Bu^t(11′)); 2.53 (s, 3 H, Me(4′)); 2.64 (s, 3 H, Me(6′)); 5.93 (s, 1 H, NH); 6.79 (br.s, 1 H, H(4)); 6.85 (br.s, 1 H, H(6)); 6.97 (s, 1 H, H arom.); 7.13 (s, 1 H, H arom.); 7.40 (s, 1 H, H arom.); 8.08 (s, 1 H, H arom.); 18.14 (br.s, 1 H, OH). MS (EI, 70 eV), m/z (I_{rel} (%)): 605 [M^+ – H] (7), 459 (2), 302 (10), 287 (8), 273 (5), 259 (3), 207 (4), 149 (4), 57 (100), 41 (63). Found (%): C, 78.96; H, 8.14; N, 4.54. $C_{40}H_{50}N_2O_3$. Calculated (%): C, 79.17; H, 8.30; N, 4.62.

5,7-Di(*tert*-butyl)-2-[9,11-di(*tert*-butyl)-4-methyl-7*H*-12-oxa-3,7-diazapleiaden-2-yl]-4-nitro-1,3-tropolone (6c) was obtained from compound **5a** (5 mmol) and 4,6-di(*tert*-butyl)-3-nitro-1,2-benzoquinone (**2b**) (10 mmol) similarly to compound **6a**. The yield was 11%, orange crystals, m.p. 293—295 °C (propan-2-ol). ^{1}H NMR ($CDCl_3$), δ: 1.25 (s, 9 H, Bu^t(5)); 1.30 (s, 9 H, Bu^t(9′)); 1.39 (s, 9 H, Bu^t(7)); 1.57 (s, 9 H, Bu^t(11′)); 2.38 (s, 3 H, Me(4′)); 6.06 (s, 1 H, NH); 6.34 (s, 1 H, H(6)); 6.71 (d, 1 H, H(6′), J = 7.91 Hz); 6.95 (d, 1 H, H(10′), J = 1.98 Hz); 7.10 (d, 1 H, H(8′), J = 1,98 Hz); 7.21 (d, 1 H, H(5′), J = 7.91 Hz); 8.02 (s, 1 H, H(1′)); 16.98 (br.s, 1 H, OH). Found (%): C, 73.32; H, 7.30; N, 6.48. $C_{39}H_{47}N_3O_5$. Calculated (%): C, 73.44; H, 7.43; N, 6.59.

5,7-Di(*tert*-butyl)-2-[9,11-di(*tert*-butyl)-4,6-dimethyl-7*H*-12-oxa-3,7-diazapleiaden-2-yl]-4-nitro-1,3-tropolone (6d) was obtained from compound **5b** (5 mmol) and compound **2b** (10 mmol) similarly to compound **6a**. The yield was 14%, orange crystals, m.p. 280—282 °C (propan-2-ol). ^{1}H NMR ($CDCl_3$), δ: 1.27 (s, 9 H, Bu^t(5)); 1.32 (s, 9 H, Bu^t(9′)); 1.39 (s, 9 H, Bu^t(7)); 1.54 (s, 9 H, Bu^t(11′)); 2.50 (s, 3 H, Me(4′)); 2.55 (s, 3 H, Me(6′)); 5.92 (s, 1 H, NH); 6.34 (s, 1 H, H(6)); 6.85 (d, 1 H, H(10′), J = 2.06 Hz); 7.13 (d, 1 H, H(8′), J = 2.06 Hz); 7.34 (s, 1 H, H(5′)); 8.09 (s, 1 H, H(1′)); 17.35 (s, 1 H, OH). Found (%): C, 73.64; H, 7.42; N, 6.30. $C_{40}H_{49}N_3O_5$. Calculated (%): C, 73.70; H, 7.58; N, 6.45.

2-[7-Acetyl-9,11-di(*tert*-butyl)-4-methyl-7*H*-12-oxa-3,7-diazapleiaden-2-yl]-5,7-di(*tert*-butyl)-1,3-tropolone (6e). A solution of compound **2a** (0.44 g, 2 mmol) and compound **5d** (0.42 g, 1 mmol) in AcOH (5 mL) was heated for 10 h at 65—70 °C. After cooling, the solution was diluted with water and a precipitate formed was filtered off, dried, and dissolved in the hexane—$CHCl_3$ solvent mixture. The solution was subjected to column chromatography with Al_2O_3 (eluent: hexane—$CHCl_3$ (1 : 1)) to collect a bright yellow fraction. The solvents were evaporated, the residue was recrystallized from methanol to obtain compound **6e** (0.25 g, 41%), bright yellow crystals, m.p. 251—253 °C (methanol). ^{1}H NMR ($CDCl_3$), δ: 1.25 (s, 9 H, Bu^t(5)); 1.31 (s, 9 H, Bu^t(9′)); 1.43 (s, 9 H, Bu^t(7)); 1.59 (s, 9 H, Bu^t(11′)); 1.97 (s, 3 H, COMe); 2.68 (s, 3 H, Me(4′)); 6.66 (d, 1 H, H(4), J = 1.80 Hz); 6.76 (d, 1 H, H(6), J = 1.80 Hz); 7.26—7.58 (m, 4 H, H arom.); 8.07 (s, 1 H, H(1′)); 19.16 (s, 1 H, OH). MS (EI, 70 eV), m/z (I_{rel} (%)): 607 [M + H – CO] (2), 592 [M + H – $COCH_3$] (2), 550 (2), 532 (2), 501 (2), 57 (13), 43 (41). Found (%): C, 77.42; H, 7.78; N, 4.26. $C_{41}H_{50}N_2O_4$. Calculated (%): C, 77.57; H, 7.94; N, 4.41.

2-[7-Acetyl-9,11-di(*tert*-butyl)-4,6-dimethyl-7*H*-12-oxa-3,7-diazapleiaden-2-yl]-5,7-di(*tert*-butyl)-1,3-tropolone (6f) was obtained from compound **5e** (2 mmol) similarly to compound **6e**. The yield was 46%, orange crystals, m.p. 297—299 °C (methanol). ^{1}H NMR ($CDCl_3$), δ: 1.27 (s, 9 H, Bu^t(5)); 1.32 (s, 9 H, Bu^t(9′)); 1.43 (s, 9 H, Bu^t(7)); 1.59 (s, 9 H, Bu^t(11′)); 2.02 (s, 3 H, COMe); 2.50 (s, 3 H, Me(6)); 2.64 (s, 3 H, Me(4)); 6.66 (d, 1 H, H(4), J = 1.80 Hz); 6.76 (d, 1 H, H(6), J = 1.80 Hz); 7.41 (s, 1 H, H arom.); 7.42 (s, 1 H, H arom.); 7.46 (s, 1 H, H arom.); 8.05 (s, 1 H, H(1′)); 19.18 (s, 1 H, OH). MS (EI, 70 eV), m/z (I_{rel} (%)): 621 [M + H – CO] (2), 606 [M + H – $COCH_3$] (1), 588 (2), 562 (2), 388 (3), 57 (7), 43 (45). Found (%): C, 77.60; H, 7.98; N, 4.26. $C_{42}H_{52}N_2O_4$. Calculated (%): C, 77.74; H, 8.08; N, 4.32.

2-[7-Acetyl-9,11-di(*tert*-butyl)-4,5-dimethyl-7*H*-12-oxa-3,7-diazapleiaden-2-yl]-5,7-di(*tert*-butyl)-1,3-tropolone (6g) was obtained from compound **5f** (2 mmol) similarly to compound **6e**. The yield was 60%, orange crystals, m.p. 262—264 °C (methanol). ^{1}H NMR ($CDCl_3$), δ: 1.27 (s, 9 H, Bu^t(5)); 1.32 (s, 9 H, Bu^t(9′)); 1.43 (s, 9 H, Bu^t(7)); 1.58 (s, 9 H, Bu^t(11′)); 2.03 (s, 3 H, COMe); 2.53 (s, 3 H, Me(5′)); 2.59 (s, 3 H, Me(4′)); 6.65 (d, 1 H, H(4), J = 1.80 Hz); 6.72 (d, 1 H, H(6), J = 1.80 Hz); 7.26—7.40 (m, 3 H, H arom.); 8.01 (s, 1 H, H(1′)); 19.26 (s, 1 H, OH). MS (EI, 70 eV), m/z (I_{rel} (%)): 621 [M + H – CO] (2), 606 [M + H – $COCH_3$] (2), 577 (2), 563 (1), 388 (3), 57 (10), 43 (40). Found (%): C, 77.58; H, 7.92; N, 4.18. $C_{42}H_{52}N_2O_4$. Calculated (%): C, 77.74; H, 8.08; N, 4.32.

X-ray diffraction studies. Parameters of the crystal unit cell and three-dimensional set of intensities were obtained on a Bruker P-4 autodiffractometer (Mo-Kα radiation, graphite monochromator). Yellow clear crystals of **6c** are monoclinic, $C_{39}H_{43}N_3O_5 \cdot H_2O \cdot CH_3OH$, M = 687.85, a = 11.506(3) Å, b = 24.838(7) Å, c = 14.920(5) Å, β = 107.09(3)°, V = 4075(2) Å^3, Z = 4, d_{calc} = 1.121 g cm^{-3}, μ(Mo-Kα) = 0.76 mm^{-1}, the space group is $P2_1/n$. Intensities of 8307 reflections were measured in the quadrant of the reciprocal space (2θ ≤ 52°) using the ω/2θ scanning from the monocrystal of 0.43×0.40×0.35 mm in size. After the systematically extinct reflections were excluded and intensities of equivalent reflections were averaged, the operating massif of measured F^2_{hkl} and σ(F^2) contained 7999 independent reflections, from which 3227 were with $F^2 > 4\sigma(F^2)$. The struc-

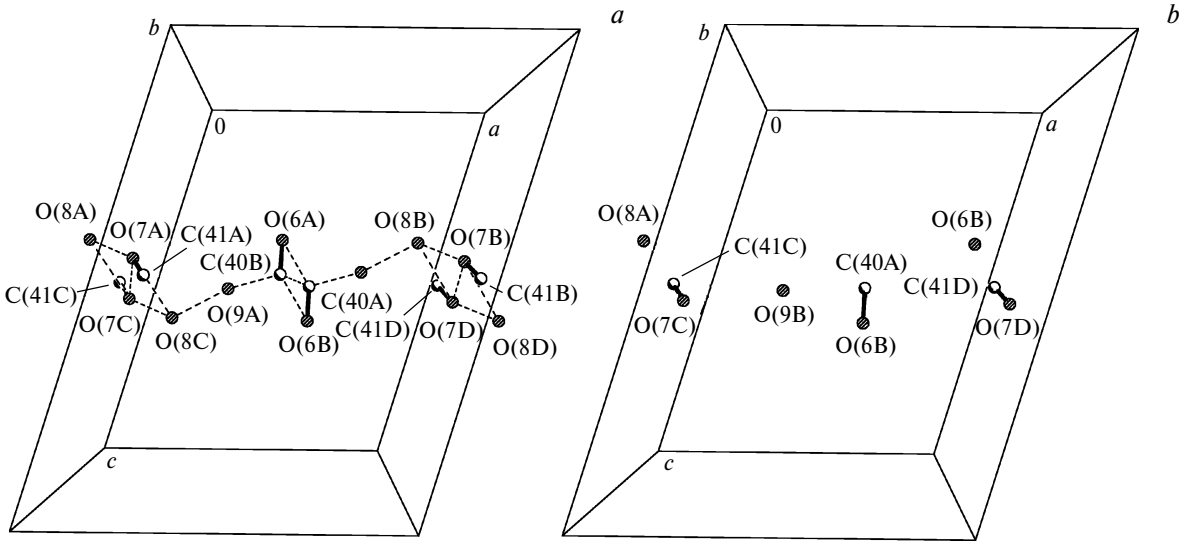


Fig. 6. The cavities between the molecules of **6c** filled with the statistically placed molecules of water and methanol (*a*) and their independent chain (*b*).

ture was solved by the direct method using the SHELXTL program (see Ref. 4) and refined by the full-matrix least squares method (LSM) relatively to F^2 using the SHELXT program (see Ref. 4) in anisotropic approximation for nonhydrogen atoms. In the crystal structure of **6c**, all the H atoms of the molecule are localized in the Fourier synthesis of the differential electron density, further the coordinates and isotropic thermal parameters of all the H atoms (except H(1) and H(2), whose positional parameters were refined) were calculated using the LSM procedure on the riding model.[4] In the last cycle of the full-matrix refinement, the absolute shifts of all the 490 variating parameters of the structure **6c** were less than 0.001σ. The final refinement parameters were as follows: $R_1 = 0.054$, $wR_2 = 0.142$ on 3209 of used reflections with $I \geq 2\sigma(I)$, GOF = 0.843. After the refinement was finished, the maximum and the minimum values of the differential electron density were 0.281 and −0.204 e Å^{-3}, respectively. Single crystals of compound **6c** were obtained from the solution in methanol. The crystal lattice has the low maxima in the cavities between the associates on the syntheses of differential electron density, which we identified as molecules of water and methanol statistically filling alternative positions with the probability 0.5, hydrogen atoms in them are not localized. The placement of the atom chains in the statistically distributed positions is shown in Fig. 6, *a*, while Fig. 6, *b* shows atoms of the independent chain possibly bound between each other by the system of hydrogen bonds, which is permitted by their mutual arrangement.

Calculation methods. Calculations were performed by the PBE0 hybrid functional,[5] in the 6-31G** basis using the GAUSSIAN 03 program package.[6] Calculation in solution was performed using the CPCM model (see Ref. 7) with the solvent parameters for DMSO (ε = 46.7).

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