New conformer of 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (CL-20). Crystal and molecular structures of the CL-20 solvate with glyceryl triacetate

S. M. Aldoshin,[a] Z. G. Aliev,[a] T. K. Goncharov,[a] D. V. Korchagin,[a] Yu. M. Milekhin,[b] and N. I. Shishov[b]*

[a]Institute of Problems of Chemical Physics, Russian Academy of Sciences,
1 prosp. Akad. Semenova, 142432 Chernogolovka, Moscow Region, Russian Federation.
E-mail: aliev@icp.ac.ru
[b]Soyuz Federal Center of Dual Technologies,
42 ul. Zhukova, 140090 Dzerzhinskii, Moscow Region, Russian Federation

Crystallization of CL-20 in different plasticizers (gyceryl triacetate and diethyleneglycol dinitrate) was studied. IR spectra of the crystals obtained under various conditions, as a rule, do not correspond to the spectra of known modifications. Crystal and molecular structures of the CL-20 solvate with glyceryl triacetate were studied. A new stable conformer of the CL-20 molecule was discovered.

Key words: 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane, polycyclic nitro amine, IR spectra, X-ray crystallography, crystal and molecular structures.

Polycyclic nitro amine, *viz.*, hexanitrohexaazaisowurtzitane (CL-20, HNIW), synthesized in 1987 at the Naval Air Wifave Center (USA) is of special interest among experts due to its high density and unique energy characteristics. Three stable conformational isomers of this product (β, γ, and ε) were found under normal conditions, as well as an α-modification, which is a hydrate of γ-conformer. A number of works were devoted to the study of these product structures by X-ray crystallography (including a low-temperature one)[1—5] and synchrotron radiation,[6] as well as by quantum chemical calculations.[7—10] A review[11] of the works on the CL-20 conformers studies was also published.

Nowadays, a plenty of attention is paid to the search for conditions of obtaining the most dense ε-modification.[11] Considerable disadvantage of all the conformers of this product is their high solubility in polar compounds (nitro ethers, acetates, nitro compounds, *etc.*). Some of the mentioned solvents are used as plasticizers in the preparation of mixed solid propellants. After a technological cycle of the product preparation is completed and the temperature returned to 20 °C, a dissolved portion of CL-20 can reprecipitate. The structure of CL-20, by all accounts, will depend on the nature of the solvent. There are virtually no works on crystallization of the dissolved portion of CL-20 in plasticizers.

We studied crystallization of CL-20 (**1**) in different plasticizers, such as glyceryl triacetate and diethyleneglycol dinitrate, ethyl acetate was used as a solvent for CL-20, chloroform served as a precipitant. The speed of crystallization was determined by the percentage of CL-20 in solutions (plasticizer + CL-20 in ethyl acetate) and different rate of the solvent pumping off. Plasticizers were washed off the crystals by the chloroform—ethyl acetate solvent mixture (3 : 1).

Figure 1 shows the IR spectrum of the sample **2**. The IR spectra of the CL-20 samples **3—10** obtained by crystallization under various conditions are given in the Experimental.

The work[11] dealt with the study on the preparation of different modifications of CL-20 and reported their virtually full IR and Raman spectra. Comparison of the recorded by us IR spectra and those reported in work[11] shows that only five out of ten samples can be assigned to a certain polymorphic conformation. The samples of crystals **1**, **3**, **4**, **7**, and **9** can definitely be assigned to ε-modification. The spectrum of the sample **2** corresponds to none of the reported spectra, it exhibits bands of the solvent (1745—1731 cm^{-1}) related to the stretching vibrations of the carbonyl group in glyceryl triacetate. In addition, the spectrum of the sample **2** has the least number of absorption bands among both the spectra of the samples obtained by us and the reported spectra. The spectrum is specifically characterized by the presence of only one maximum of asymmetric stretching vibrations of the nitro groups (see Fig. 1, *a*).

It is usual to observe from two to four maxima for this absorption frequency in the IR spectra of CL-20. Thus, in work[11] three maxima were recorded for γ- and β-polymorphs, two for α-form, and four for ε-form. Symmetric

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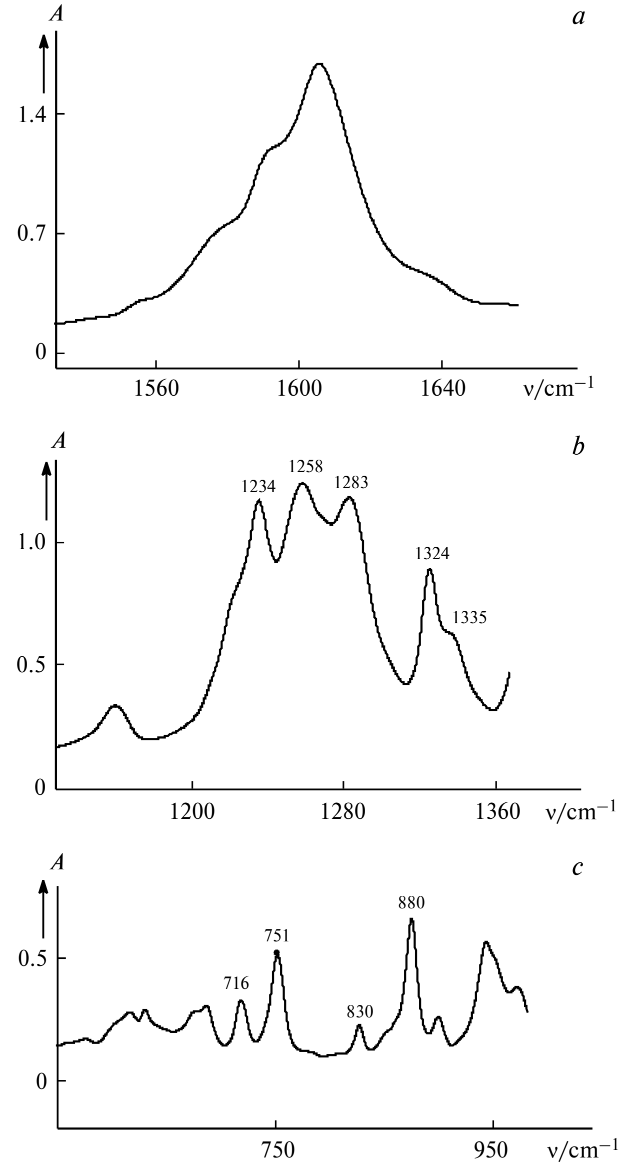

Fig. 1. The IR absorption spectrum of the sample **2**: asymmetric stretching vibrations with the maximum at 1605.8 cm^{-1} (*a*), symmetric (*b*), and bending vibrations (*c*).

vibrations of the nitro groups give four absorption maxima and a pronounced shoulder at 1335 cm^{-1} of the IR spectra. This region of the spectrum is characteristic of the symmetric vibrations of the nitro groups of different modifications of CL-20, but neither of five maxima coincide with the maxima of these vibrations in four modifications reported in the work.[11]

The IR spectrum of symmetric vibrations of the nitro group in the sample **2** is shown in Fig. 1, *b*. It is seen that the intensities of three absorption peaks are virtually the same, whereas the other two are somewhat less strong. The authors in the work[12] refer to the region of bending vibrations of the nitro group in the samples while determining the nature of modifications. They assign to ε-modification the samples, whose IR spectra exhibit a noticeable splitting of the absorption band in the region 780—740 cm^{-1} and a doublet instead of the normal singlet in other polymorphs in the region 840—820 cm^{-1}. The IR spectrum of the sample **2** in the region of bending vibrations of the nitro groups is shown in Fig. 1, *c*. It is seen that the spectrum has no bands at 854, 820, 757, and 737 cm^{-1}, whereas the bands at 716, 751, and 880 cm^{-1} are displaced by 1—2 cm^{-1} to either side in the spectra of all the polymorphic forms.

Analysis of the IR spectra of the sample **2** shows that the structure of this sample has higher symmetry as compared to the samples of CL-20 known polymorphic forms.

The IR spectrum of the sample **9** allows us to assign it to α-modification, since a whole number of bands in the spectrum of this sample, asymmetric, symmetric stretching and bending vibrations of the nitro groups, exactly correspond to those in the spectra of the samples of α-modification.

Comparison of the IR spectra of the samples **3** and **5** showed that a twofold increase in the concentration of CL-20 with respect to the glyceryl triacetate under the same conditions of crystallization produced rather considerable changes in the IR spectra of the crystals obtained. A total number of absorption bands decreased from 31 for the sample **3** to 23 for the sample **5**. Based on the IR spectra, the sample **5** can be assigned to none of the reported modifications. Maintaining of the sample (the sample **6**) in a drying oven at 50 °C for 72 h produced no changes in the spectra of the sample **5**. By all accounts, the rates of nucleation and crystal growth play a significant role in the formation of different polymorphic forms in the same solvent system. Crystallization of CL-20 from chloroform (the samples **9** and **10**) is a good example. As it was shown above, the sample **9** is related to α-modification. A twofold decrease in the concentration of CL-20 in chloroform leads to the increase in the number of absorption bands in the new IR spectrum from 23 to 28.

The region of bending vibrations of the nitro group of the sample **10** in the IR spectrum is shown in Fig. 2. It is seen that the spectrum exhibits virtually all the bands characteristic of ε-modification. The incomplete resolution of the absorption bands at 740—780 cm^{-1} and 820—880 cm^{-1} put an uncertainty in the assignment of the sample **10** to ε-modification, but it is also difficult to assign it to the other three described[11] modifications. Similar picture is observed on the comparison of the IR spectra of the samples **7** and **8**. The sample **7** can be certainly assigned to ε-modification, whereas it is virtually difficult to make with the sample **8**, since its maxima are poorly resolved in the indicative regions of the spectrum. The most band maxima are considerably displaced, whereas some are absent at all.

The X-ray diffraction studies of the sample **2** showed that the CL-20 molecule crystallizes with the molecule of

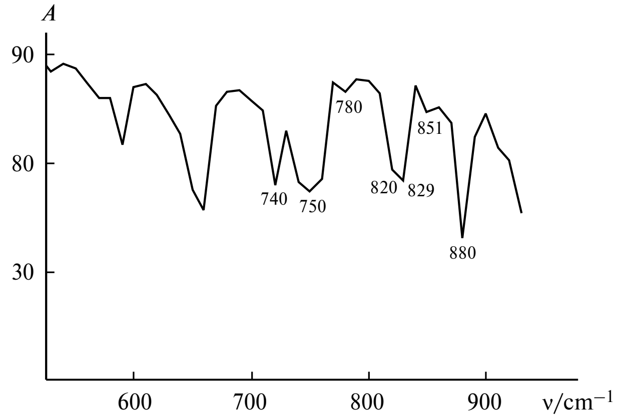

Fig. 2. The IR spectrum of bending vibrations of the nitro groups (the sample **10**) of CL-20.

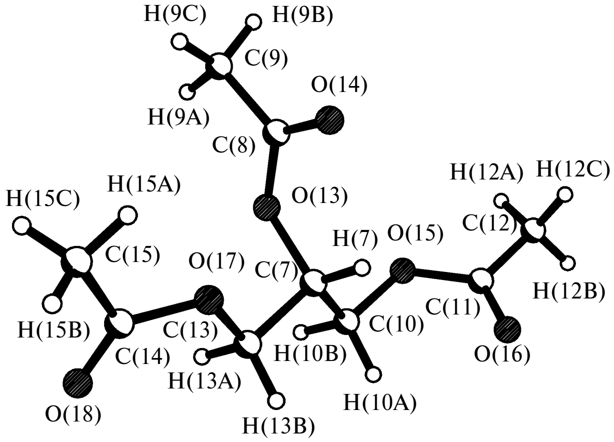

Fig. 4. The molecular structure of glyceryl triacetate.

glyceryl triacetate in equimolar ratio. The general views of the CL-20 and glyceryl triacetate molecules is shown in Figs 3 and 4, respectively. Being placed in the general crystallographic position, the CL-20 molecule has its own C_{2v} symmetry. This symmetry is confirmed not only by orientation of the nitro groups with respect to the central cage of the molecule, but also by equality of the corresponding bond distances within determination error limits. Thus, a new ξ-conformation was discovered. Earlier, existence of such a conformation at high pressures and low temperatures was postulated[13] and then theoretically predicted.[8] Figures 5 and 6 schematically show structures of all four conformers in the projection on the plane of carbon atoms of six- and five-membered rings, respectively, which demonstrates differences in their structures.

As it is seen in Figs 5 and 6, a significant difference in the conformer structures consists in the orientations of the nitro groups at the five-membered rings. The differences in the orientation of the nitro groups at the six-membered ring are not that pronounced. All of them are in equatorial positions with different torsional angles along the N—N bond. Only in ε-conformer, one of the amine nitrogen atoms has planar configuration, where the sum of bond angles is equal to 360°.

The character of distribution of bond distances in the central cage of the molecule under study coincides with that in the earlier studied conformers,[1—5] and they found to be the same within the error limits.

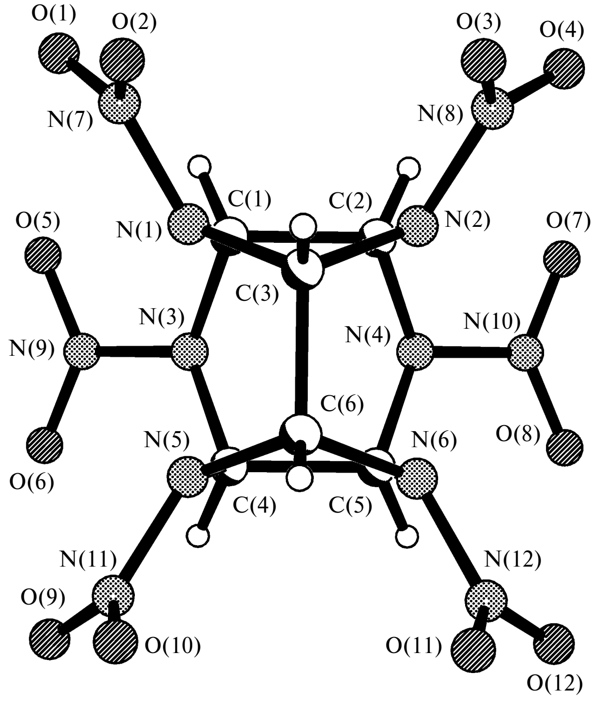

Fig. 3. The molecular structure of CL-20.

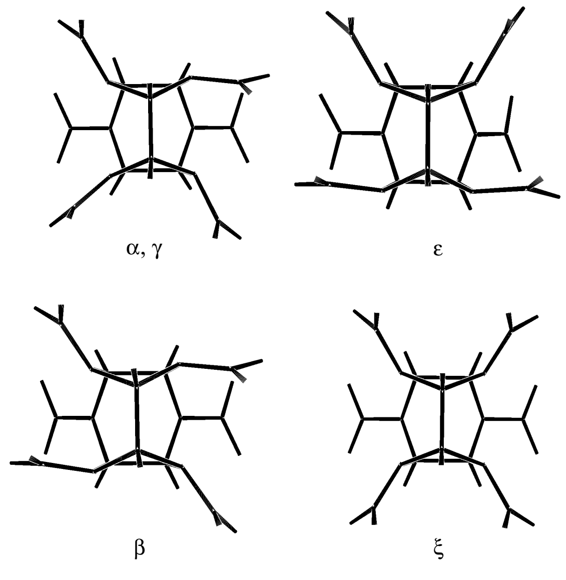

Fig. 5. Four conformers of CL-20 in the projection on the plane of the six-membered ring carbon atoms.

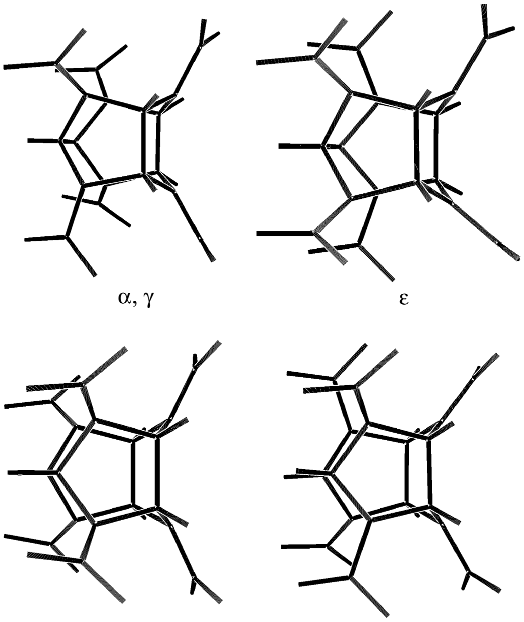
α, γ ε β ξ

Fig. 6. Four conformers of CL-20 in the projection on the plane of the five-membered ring carbon atoms.

In all the conformers, the amine nitrogen atoms in the six-membered rings have more planar configuration than in the five-membered rings. The sum of the bond angles of the amine nitrogen atoms in the six-membered rings on average is by 8—9° larger than in the five-membered ones (in our case 343 and 352°). The N—N bond distances lie within a wide enough range of values 1.397(4)—1.415(4) Å. The same spread of values (1.373—1.443 Å) is observed in γ-, ε-, and β-conformers.[1—3] However, no dependence of the N—N bond distances from the degree of pyramidality of the amine nitrogen atoms and conformation of the molecule is observed, with all the N—O bonds being the same and equal to 1.208±0.005 Å (with the same value of determination error). The latter allows us to suggest that the electron structure of the molecule, even if it changes from conformer to conformer, changes very insignificantly. This is also confirmed by the close values of the conformer total energies: −1791.1918582 (β), −1791.1902724 (γ), −1791.1892926 (ε), and −1791.1886287 au (ξ), which is in good agreement with the published data.[7—9] The difference in total energies between the conformers closest in energy does not exceed ~1 kcal mol^{-1}, with the ξ-conformer being the least stable in this row.

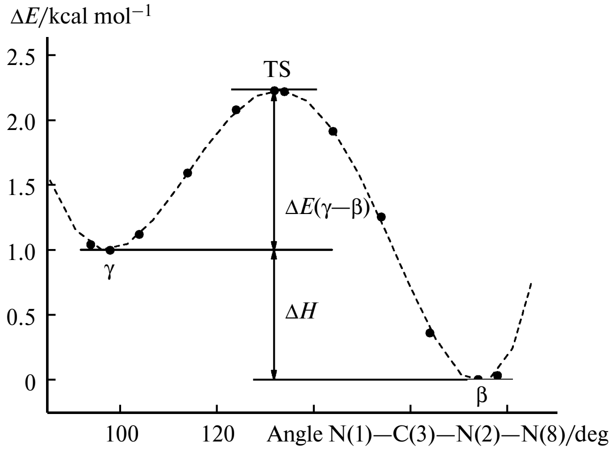

Fig. 7. A cross-section of the PES for the transition γ ↔ β.

For evaluation of energy barriers of transition from one conformation to another, we scanned a potential energy surface (PES) by the B3LYP/6-31G** density functional method. A dihedral angle N(1)—C(3)—N(2)—N(8) of γ-conformer, changing the most during transition to β-conformer, was chosen as a coordinate of the process. Figure 7 shows the PES of the conformational transition γ ↔ β, where the two minima for the N(1)—C(3)—N(2)—N(8) angle values 98.5 and 174.05° correspond to γ- and β-conformers, respectively. β-Conformer is lower in energy by ΔH ~1 kcal mol^{-1} and thermodynamically is more stable than γ-conformer. The energy barrier of transition from γ- to β-conformer is $\Delta E(\gamma\text{—}\beta) \approx 1.2$, whereas from β- to γ-conformer $\Delta E(\beta\text{—}\gamma) = \Delta E(\gamma\text{—}\beta) + \Delta H \approx 2.2$ kcal mol^{-1} (see Fig. 7 and Table 1).

Thus, transitions from one conformer to another have rather low energy barriers.

To sum up, the close total energies of conformers together with low energy barriers of conformational transitions indicate easy interconversion of conformers in liquid media.

In the crystal cell, molecules of CL-20 and glyceryl triacetate are placed in the alternating *ab* planes, whereas molecules themselves alternate in the direction *c* (Fig. 8). Similar crystal packing is also observed in the solvate of CL-20 γ-conformer with DMF.[14]

In the crystal, molecules of CL-20 and glyceryl triacetate are bound by intermolecular hydrogen bonds. They

Table 1. Dependence of the total energy of the CL-20 molecule from the N—C—N—N dihedral angle (φ)

φ/deg	−*E*/au	Δ*E*/kcal mol^{-1}
178.0500	1791.191807220	0.032
174.0537^{β}	1791.191858220	0.000
164.0536	1791.191286920	0.359
154.0536	1791.189862070	1.253
144.0535	1791.188810470	1.913
134.0533	1791.188325040	2.217
131.9890^{TS}	1791.188311300	2.226
124.0537	1791.188547330	2.078
114.0539	1791.189322380	1.591
104.0536	1791.190077670	1.117
98.50000^{γ}	1791.190272400	0.995
94.05360	1791.190201450	1.040

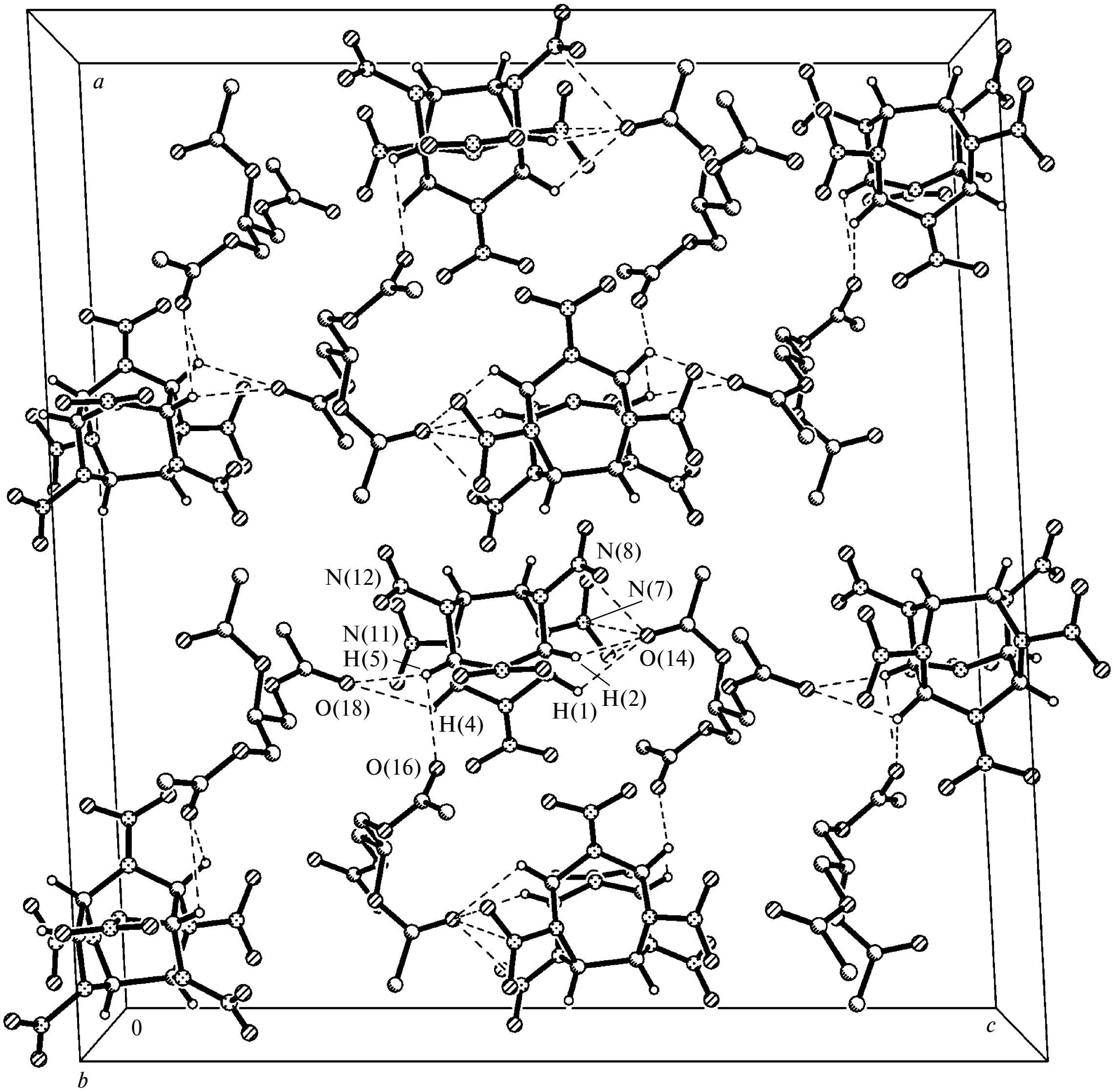

Fig. 8. The projection of the structure on the plane *ac*. The dashed lines represent the shortened intermolecular contacts.

involve the oxygen atoms of three carbonyl groups of glyceryl triacetate and four atoms of the CL-20 six-membered ring. Parameters of these hydrogen bonds are given in Table 2. The hydrogen atoms H(4) and H(5) are simultaneously bound with the oxygen atoms O(16) and O(18) and form a bifurcated bond. The angles at the hydrogen atoms H(4) and H(5) are equal to 89.2 and 87.1°, respectively. The carbon atoms C(3) and C(6) of the CL-20 molecules are not involved into hydrogen bonds.

In addition, the O(14) oxygen atom of glyceryl triacetate has intermolecular contacts on the bounds of the sum of Van der Waals radii with the nitrogen atoms of nitro groups at the atoms N(7) (2.877 Å) and N(8) (2.866 Å), and these contacts are orthogonal to the corresponding planes of the nitro groups. Thus, as it can be seen in Fig. 8, molecules of CL-20 and glyceryl triacetate in crystal are bound by intermolecular contacts into the infinite double bands along direction *c* of the crystal.

Table 2. Geometric characteristics of intermolecular hydrogen bonds

Bond	*d*/Å		Angle D—H—A /deg
	D...A	H...A	
C(1)—H(1)...O(14)	2.966	2.52	107.9
C(2)—H(2)...O(14)	2.950	2.48	109.2
C(4)—H(4)...O(16)	2.845	2.40	107.1
C(5)—H(5)...O(16)	2.927	2.53	103.7
C(4)—H(4)...O(18)	3.083	2.54	115.2
C(5)—H(5)...O(18)	3.059	2.50	116.2

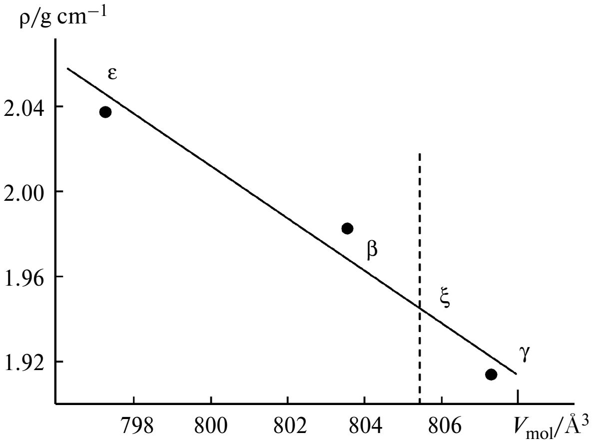

Fig. 9. The dependence of the compound density (ρ) from the size of free molecule (V_{mol}).

For evaluation of probable density of crystals of the ξ-conformer molecules, we compared sizes of free molecules of conformers, β-, γ-, and ε-conformers with their densities. As it is seen from Fig. 9, the indicated dependence is linear. Based on this, it can be suggested that the density of crystals of ξ-conformer is between the values of density of β- and γ-conformers. The energies of crystal lattice are equal to –38.2 (β), –35.9 (γ), –35.1 kcal mol^{-1} (ε) and are adequate to the energies of free molecule: $E(\beta) < E(\gamma) < E(\varepsilon) < E(\xi)$, whereas the crystal densities form another order: $d(\gamma) < d(\xi) < d(\beta) < d(\varepsilon)$.

In conclusion, this work results in the discovery of new, forth in order, stable ξ-conformer of the CL-20 molecule. Total energies of all four conformers are close to each other. Transitions from one conformer to another have low energy barriers (1—2 kcal mol^{-1}). Density of the crystal modification is inversely proportional to the size of the conformer free molecule.

Experimental

Preparation of complex **2**. A mixture of CL-20 (2 g) and glyceryl triacetate (2 cm^3) was heated in a thermostat at 60 °C for 24 h. In 2 h after the temperature was reduced to 20 °C, a solution of CL-20 in glyceryl triacetate was separated from the undissolved portion of CL-20. Maintaining the solution at 20 °C for 20 days showed that no crystallization occurred. Cooling the solution to –20 °C and maintaining at this temperature for 10 days did not lead to the nucleation either. Only after heating and cooling of the solution were repeated three times, nucleation of crystals began at ~20 °C. The crystals were grown during 30 days to obtain clear rectangular crystals of different sizes, the length of some of them reached 3 mm, the width, 2 mm. Crystals of the sample **2** were filtered off from glyceryl triacetate and washed with chloroform.

The samples **3**—**10** were prepared as follows: CL-20 was dissolved in ethyl acetate in the amount necessary to reach a desired concentration, then it was mixed with a given volume of the second solvent. Ethyl acetate was pumped off under the same conditions until crystallization began, and after a certain time the pumping off was stopped. The samples of crystals were filtered off from the solvent. The crystals were always washed with chloroform and dried, followed by recording their IR spectra.

IR spectra were recorded in KBr pellets on a Specord-75 spectrometer or using FTIR spectroscopy.

Starting compound **1**, ν/cm^{-1}: 3049, 3020—1630, 1605, 1587, 1571—1379, 1325, 1284, 1264—1190, 1180, 1134, 1124—1085, 1020—980, 939, 910—882, 854, 830, 820—760, 745, 724—659, 650, 624.

Sample **2**: monocrystals from 30% solution of ε-modification of CL-20 in glyceryl triacetate at –20 °C, ν/cm^{-1}: 3078, 3069, 3050—1745, 1731—1605—1369, 1342, 1283, 1259—1034—981—881, 829—749, 715—684, 672, 634.

Sample **3**: from 30% solution in glyceryl triacetate at 20 °C for 2 days, ν/cm^{-1}: 3045, 3035, 3017—1633, 16061, 591, 1566—1383, 1329, 1295, 1265, 1217—1184, 1139, 1125—1088, 1052, 1045, 1022—981, 945, 938—883, 854, 832, 820—758, 751, 744, 739, 723—659, 648, 625.

Sample **4** was kept at 50 °C for 72 h, that produced no changes in positions of each wavelength maxima.

Sample **5**: from 60% solution of glyceryl triacetate at 20 °C, ν/cm^{-1}: 3052, 3039, 3024—1617, 1607, 1570, 1556—1330, 1291, 1273, 1228—1168, 1094—1051—991, 954, 945, 905—881, 834—765, 750, 719—656, 622.

To obtain sample **6**, the sample **5** was kept at 50 °C for 72 h, ν/cm^{-1}:

3052, 3039, 3024—1617, 1606, 1570, 1556—1330, 1291, 1273, 1228—1168, 1094—1051—991, 953, 945, 905—881, 834—765, 748, 738, 718—668, 655, 634.

Sample **7**: from 30% solution in diethyleneglycol dinitrate at 20 °C, ν/cm^{-1}: 3047, 3020—1628, 1605, 1587, 1565—1382, 1326, 1283, 1262—1136, 1124—1084, 1048, 1022—980, 938—882, 856, 830, 820—757, 746, 724—659, 651, 624.

Sample **8**: from 50% solution in diethyleneglycol dinitrate at 20 °C, ν/cm^{-1}: 3050, 3020—1632, 1598, 1561, 1510—1379, 1330, 1289, 1255—1187, 1139, 1120—1082, 1045, 1019—938—880, 849, (827, 820)—(780, 760, 740), 719—659, 590.

Sample **9**: from 40% solution in chloroform at 20 °C, ν/cm^{-1}: 3052, 3041, 3026—1618, 1606, 1571, 1556—1330, 1269, 1227—1167—1095, 1052—991, 944, 905—880, 834, 825—764, 750, 717—657.

Sample **10**: from 20% solution in chloroform at 20 °C, ν/cm^{-1}: 3048, 3020—1629, 1609, 1600, 1588, 1570—1379, 1330, 1280, 1257—1179, 1139, 1119—1083, 1049, 1019—980, 940—880, 849, (829, 820)—(760, 750, 740), 719—659, 590.

X-ray diffraction study. A crystal sized 0.3×0.3×0.08 mm was chosen for the study. The crystals $C_6H_6N_{12}O_{12} \cdot C_9H_{14}O_6$ belong to the monoclinic crystal system: a = 26.425(5) Å, b = 8.237(2) Å, c = 24.313(5) Å, β = 92.88(3)°, V = 5285.3(18) Å^3, M = 656.43, d_{calc} = 1.650 g cm^{-3}, Z = 8, the $C2/c$ space group. A set of experimental reflections was obtained on a KM-4 (Kuma Diffraction) automatic four-circle diffractometer with the χ-geometry by the ω/2θ-scanning method on a monochromatized Mo-Kα-radiation in the range of angles 1.54° ≤ θ ≤ 25.99°, that constitutes 98.5% of the reverse space. The total number of measured reflections was 5231, from which 5101 were independent [R(int) = 0.022]. No allowance for absorption was made (μ = 0.152 mm^{-1}). The structure was solved by the direct method using the SIR92 program (see Ref. 15) with subsequent series of calculations of the electron density maps. Hydrogen atoms were given geometrically. The full-matrix anisotropic (of non-hydrogen atoms) refining by the least squares method using the SHELXL-97 program (see Ref. 16) was completed at $R_1 = 0.0533$ $wR_2 = 0.1395$ on 2113 reflections with $I \geq 2\sigma(I)$ and $R_1 = 0.2011$, $wR_2 = 0.1681$ on all the 5101 reflections. GOOF = 0.861. The maximum peak on the differential synthesis of electron density is equal to 0.470 Å^3.

All the quantum chemical calculations were performed using the GAUSSIAN03 program.[17] Optimization of geometry of the CL-20 ground and transition states, scanning the PES of the $\gamma \leftrightarrow \beta$ conformational transition, and calculation of vibration frequencies were performed in the B3LYP/6-31G** approximation. All the vibration frequencies obtained for the ground states of CL-20 (α, β, γ, ε, ζ), are positive, *i.e.*, all the ground states correspond to the local minima on the PES. The optimized intermediate state of the conformational transition $\gamma \leftrightarrow \beta$, corresponding to the maximum on the PES, is characterized by the only imaginary vibration frequency. This indicates that this state is a transition one (TS).

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