

Crystal and Molecular Structure, and Spectral Characteristics of Sodium 3,5-Bis(Hydroxyimino)-1-Methyl-2,4,6-Trioxocyclohexanide

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Received September 26, 2012; revised November 1, 2012; accepted November 12, 2012

ABSTRACT

Sodium 3,5-bis(hydroxyimino)-1-methyl-2,4,6-trioxocyclohexanide $C_7H_5N_2NaO_5$ (I) has been isolated as the only product of the reaction of nitrosation of methylphloroglucinol. The structure of the titled compound has been determined from single crystal X-ray diffraction data. The hydrated $C_7H_5N_2NaO_5 \cdot 2.5H_2O$ crystallizes in the monoclinic space group C2/c, with $a(\text{\AA})$ 16.408(3); $b(\text{\AA})$ 12.446(3); $c(\text{\AA})$ 13.716(3); $\beta(^{\circ})$ 126.34(3). The planar organic anion exists in a triketo-dihydroxyimino form with the C–O and C–N distances from 1.220(2) to 1.271(2) Å and from 1.292(2) to 1.293 Å respectively. In the IR spectrum of I, the sharp absorption band occurred at 1681 cm^{-1} due to C=O stretching indicating the strong H-interactions. The correlations of theoretical (DFT-B3LYP/aug-cc-pVDZ) and experimental UV-vis absorption spectra in neutral and alkaline ethanolic solutions showed the existence of hydroxyimino-nitroso tautomerism while ionization of I.

Keywords: Sodium 3,5-Bis(Hydroxyimino)-1-Methyl-2,4,6-Trioxocyclohexanide; Crystal Structure; IR Spectra; Electronic Absorption Spectra; Quantum Chemical Modeling

1. Introduction

2,4,6-Trihydroxytoluene (methylphloroglucinol, MPG) possesses strong and attractive synthetic potential because of its specific structure. However, till recent years when the economically efficient method of synthesis of MPG on base of 2,4,6-trinitrotoluene [1,2] was developed, it practically has not been realized.

The reactions of electrophilic substitution of H-atoms in the benzene ring of methylphloroglucinol have been poorly studied till now. Except one paper concerning its bromination [3], a series of ancient publications on MPG acylation by HCN and nitriles [4-8], or ethanoil chloride [6] and anhydride [8] are known. And there is the only one example of MPG alkylation by formaldehyde in presence of sulfuric acid [9].

In frames of systematic investigations, some reactions of MPG electrophilic substitution (bromination, sulfation, Hoesch reaction, azo-coupling) were recently reported [10-13]. As it was shown, in all cases except azo-

coupling irrespectively of variations of reaction conditions mixtures of mono- and bis-substituted products were formed. In case of the reaction of MPG azo-coupling, non-standard conditions were found which allowed selective synthesis of mono- and bis azo-compounds based on MPG.

In the present paper, we report the crystal structure, tautomerism, and some spectral characteristics of the product of the reaction of MPG nitrosation.

2. Experimental

2.1. Synthesis of the Title Compound

The title compound was prepared by the reaction of methylphloroglucinol (MPG) with sodium nitrite. 5 g of MPG (0.0357 mole) were dissolved in 50 ml of water at 0°C. The solution containing 6.41 g of $NaNO_2$ (0.09 mole) in 25 ml of water was added with an intensive stirring. The solution was stored under 0°C for 40 min, and then 0.7 ml of H_2SO_4 in 28 ml of water were added drop

wise. After 30 min the formed precipitate was filtered off and dried over P_2O_5 . The product was finally purified by re-crystallization. Yield 82% M.p. 208°C (with decomposition). The authenticity of the compound has been established by microanalyses, UV and IR spectra, and single crystal X-ray diffraction analysis.

2.2. Materials and Physical Measurements

The melting point was determined on an Electrothermal Model 9200 apparatus and is uncorrected. The IR absorption spectrum was obtained in the region of 400 - 4000 cm^{-1} with a resolution of 4 cm^{-1} as KBr pellet using a Varian Excalibur HE 3100 IR spectrometer. Microanalysis was performed with a Carlo Erba Elemental Analyzer, model 1108. UV-vis spectrum was recorded in the range of 200 nm to 800 nm using a Varian Cary 50 Scan spectrophotometer. Calculations of ionization constants were performed according to the procedure described in [14].

2.3. The X-Ray Crystallography

For the crystal structure determination, the single-crystal of the compound I was used for data collection on an Enraf-Nonius CAD-4 diffractometer. The β -filtered Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å) and an ω -2 θ scan were used for data collection. The lattice parameters were determined using reflections in the range $22 < 2\theta < 26^\circ$. The structure was solved with direct methods using SHELXS-93 [15]. The refinement of the structure was performed by the full-matrix least square method on F2 for all the data with anisotropic thermal parameters for non-hydrogen atoms. CCDC reference number 865,395. The supplementary crystallographic data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Molecular structure of the compound showing the atomic numbering scheme is shown in **Figure 1**. The crystallography details for the structures determination of the compound were presented in **Table 1**. Selected bond distances and bond angles are listed in **Table 2**.

2.4. Quantum-Chemical Modeling

The geometry optimization of isomers was performed by means of DFT-B3LYP/aug-cc-pVDZ approach. Electronic absorption spectra were predicted using TDDFT approach at the same theory level as geometry optimization. In TDDFT calculations, the bulk solvent effects were taken into account by means of polarizable continuum model (PCM). All calculations have been executed using the "SKIF-Chebyshev" supercomputer of the Moscow State University with FireFly package available free at <http://classic.chem.msu.su/gran/firefly/index.html>.

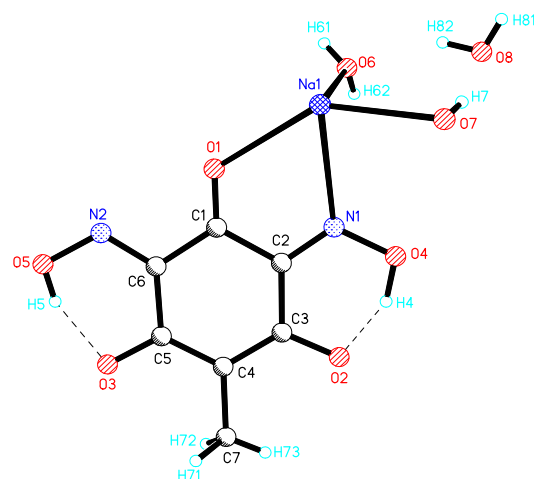


Figure 1. Molecular structure of I (O7-H7 represents 0.5 H_2O).

Table 1. Crystallographic data and structure refinement parameters.

| | |
|-----------------------------------|--|
| Empirical formula | $C_7H_{10}N_2NaO_{7.5}$ |
| Formula weight | 265.16 g/mol |
| Crystal color | Dark red |
| Temperature | 293(2) K |
| Wavelength | 0.71073 Å |
| Crystal system | Monoclinic |
| Space group | C2/c |
| Unit cell dimensions | $a = 16.408(3)$ Å, $b = 12.446(3)$ Å, $c = 13.716(3)$ Å, $\beta = 126.34(3)^\circ$ |
| Volume | $2256.1(8)$ Å ³ |
| Z, calculated density | 8, 1.561 Mg·m ⁻³ |
| Absorption coefficient | 0.172 mm ⁻¹ |
| $F(000)$ | 1096 |
| Crystal size | $0.50 \times 0.30 \times 0.20$ mm |
| Theta range for data collection | 2.25 to 25.47 deg. |
| Limiting indices | $-19 \leq h \leq 15$, $0 \leq k \leq 14$, $-16 \leq l \leq 15$ |
| Reflections collected/unique | 2191/2100 [R(int) = 0.0147] |
| Completeness to theta = 25.47 | 100% |
| Refinement method | Full-matrix least-squares on F2 |
| Data/restraints/parameters | 2100/0/200 |
| Goodness-of-fit on F2 | 1.056 |
| Final R indices [I > 2 sigma (I)] | R1 = 0.0280, wR2 = 0.0868 |
| R indices (all data) | R1 = 0.1160, wR2 = 0.1005 |
| Largest diff. peak and hole | $0.281 e^{-} \cdot \text{Å}^{-3}$ and $-0.294 e^{-} \cdot \text{Å}^{-3}$ |

Table 2. Selected bond lengths (Å) and angles (°).

| | | | |
|-----------|------------|----------------|------------|
| O(1)-C(1) | 1.220(2) | C(2)-N(1)-O(4) | 117.52(14) |
| O(2)-C(3) | 1.271(2) | C(6)-N(2)-O(5) | 118.20(15) |
| O(3)-C(5) | 1.265(2) | O(1)-C(1)-C(6) | 122.54(15) |
| O(4)-N(1) | 1.3583(19) | O(1)-C(1)-C(2) | 121.51(15) |
| O(5)-N(2) | 1.348(2) | C(6)-C(1)-C(2) | 115.95(13) |
| N(1)-C(2) | 1.293(2) | N(1)-C(2)-C(3) | 125.73(15) |
| N(2)-C(6) | 1.292(2) | N(1)-C(2)-C(1) | 113.70(14) |
| C(1)-C(6) | 1.471(2) | C(3)-C(2)-C(1) | 120.43(14) |
| C(1)-C(2) | 1.483(2) | O(2)-C(3)-C(4) | 123.67(15) |
| C(2)-C(3) | 1.481(2) | O(2)-C(3)-C(2) | 115.34(15) |
| C(3)-C(4) | 1.395(3) | C(4)-C(3)-C(2) | 120.98(15) |
| C(4)-C(5) | 1.398(3) | C(3)-C(4)-C(5) | 120.86(15) |
| C(4)-C(7) | 1.503(2) | C(3)-C(4)-C(7) | 119.62(18) |
| C(5)-C(6) | 1.482(2) | C(5)-C(4)-C(7) | 119.52(18) |
| | | O(3)-C(5)-C(4) | 123.19(16) |
| | | O(3)-C(5)-C(6) | 115.84(16) |
| | | C(4)-C(5)-C(6) | 120.97(15) |
| | | N(2)-C(6)-C(1) | 113.49(14) |
| | | N(2)-C(6)-C(5) | 125.84(15) |
| | | C(1)-C(6)-C(5) | 120.62(15) |

3. Results and Discussion

Dark-red plates of single crystals of the only product of MPG nitrosation were obtained by re-crystallization from ethanolic aqueous solution, and the crystal structure was determined by X-ray diffraction studies. The title compound crystallizes in a hydrated form of a sodium salt ($C_7H_5N_2NaO_5 \cdot 2.5H_2O$) in the monoclinic space group $C2/c$ with $Z = 1$.

As it is evident (**Figure 1**, **Table 2**), the isolated product of transformation of MPG exists in the anionic form of a triketo-dihydroxyimino tautomer. The negative charge of the anion is neutralized by Na^+ cations. The C–O distances in the planar organic anion (1.220(2); 1.271(2) and 1.265(2) Å for C1–O1, C3–O2 and C5–O3 respectively) as well as N1–C2 (1.293(2) Å) and N2–C6 (1.292(2) Å) are close to the corresponding double bonds. The C–C bonds of the ring are not equivalent: C1–C6, C1–C2, C2–C3, and C5–C6 bond lengths (1.471(2) – 1.483(2) Å) indicate a small degree of conjugation as well as C3–C4 (1.395(3) Å) and C4–C5 (1.398(3) Å) bonds are much shorter. Similar types of structures of polyketo-compounds of carbocyclic and heterocyclic series were reviewed in [16].

H4 and H5 atoms are located at O4 and O5 atoms of two hydroxyimino-groups of the anion and involved in the intramolecular H-bonds with the neighboring carbonyl O-atoms (**Table 3**).

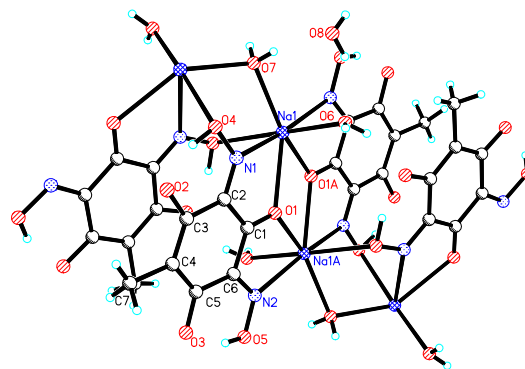
The organic anion chelates the Na^+ cations by the oxygen atoms of C=O groups and N-atoms of neighboring oxime fragments ($r_{O_1Na} -25,647(15)$ Å; $r_{N_1Na} -26,625(16)$ Å). The O(1), N(2) atoms as well as the O-atoms of both oxime groups are also involved in coordination with the Na^+ cations of the neighboring molecules. The coordination sphere of Na^+ also includes two water molecules, one of which is bridging. One of H_2O molecules is of the lattice nature. Thus, a 3D lattice is formed (**Figure 2**) which is linked by intermolecular H-bonds involving coordinated and lattice water molecules (**Table 3**).

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Table 3. Hydrogen bonds in I (Å and deg.).

| D-H...A | d(D-H) | d(H...A) | d(D...A) | <(DHA) |
|---------------------------------|---------|----------|----------|--------|
| O(4)-H(4)...O(2) ^{#1} | 1.06(3) | 1.46(3) | 2.442(2) | 151(3) |
| O(5)-H(5)...O(3) ^{#1} | 0.81(3) | 1.69(3) | 2.470(2) | 161(3) |
| O(7)-H(7)...O(8) ^{#1} | 0.83(3) | 1.98(3) | 2.797(2) | 165(3) |
| O(6)-H(61)...O(2) ^{#4} | 0.76(3) | 2.03(3) | 2.748(2) | 158(3) |
| O(6)-H(62)...O(8) ^{#5} | 0.88(5) | 1.86(5) | 2.732(2) | 169(4) |
| O(8)-H(81)...O(3) ^{#6} | 0.77(4) | 2.01(4) | 2.763(2) | 170(3) |
| O(8)-H(82)...O(6) ^{#1} | 0.82(4) | 2.01(4) | 2.737(2) | 147(4) |

Symmetry transformations used to generate equivalent atoms: ^{#1} x, y, z ^{#2} -x + 1, -y + 1, -z ^{#3} -x + 1, y, -z + 1/2 ^{#4} x, -y + 1, z - 1/2 ^{#5} -x + 1/2, -y + 1/2, -z ^{#6} x, y - 1, z.

**Figure 2. Fragment of the crystal structure of I.**

Elemental analyses of the compound I for carbon, hydrogen, and nitrogen are in good agreement with theoretical values. The theoretical and observed element percentages respectively are: %C: 32.07 and 31.71, %H: 3.65 and 3.80, %N: 10.24 and 10.56.

The IR spectrum of the title compound shows sharp characteristic absorption bands at 1681/1645 cm^{-1} due to C=O stretching mode of the keto-groups which are involved into strong H-interactions. The wide absorption band in the interval 3550 - 3300 cm^{-1} with two maxima at 3460 and 3380 cm^{-1} are $\nu(\text{CO})$ vibrations of OH groups of NOH fragments and water molecules [17]. The sharp skeleton bands observed at 1580 (w), 1520 (s) and 1510 (m) cm^{-1} characterize the C...C and C...N vibrations.

The electronic absorption spectrum of I (**Figure 3**) is characterized by two absorption bands at 273.42 nm ($\log \epsilon$ 4.03) and 380.55 nm ($\log \epsilon$ 3.83). The addition of HCl till pH 1 does not provoke any changes in the spectrum. This may indicate the stability of anionic form of the organic species in I. In alkaline solutions, the absorption bands collapse, and an intensive absorbance at 329.08 nm ($\log \epsilon$ 4.25) appears.

In order to explain the changes in the UV-Vis spectra recorded at different pH values, quantum chemical calculations of electronic absorption spectra of ethanolic solutions of the most stable neutral dihydroxyimino- and dinitroso-tautomers as well as their anionic forms (**Figure 4**) were performed by the TDDFT method.

The calculated UV spectrum of the neutral dihydroxyimino-form is characterized by an absorption band at 354.79 nm (f 0.056) and an intensive doublet 280.89 (f 0.383), and 265.62 (f 0.284) nm (**Figure 5(a)**). In a dihydroxyimino monoanionic form the bands are increased in intensity and shifted to 369.36 (f 0.130) and 271.48 (f 0.513) nm (**Figure 5(c)**). The shape of the spectrum and relative intensities of the absorption bands are in a good accordance of the experimental spectrum of I in neutral solutions.

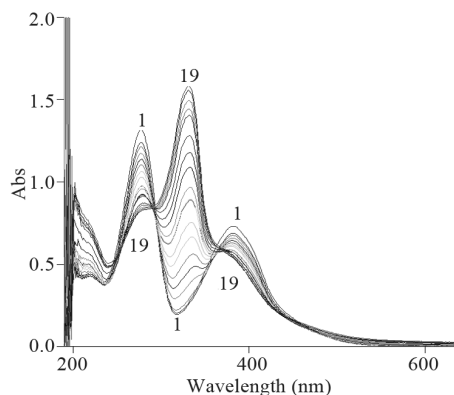


Figure 3. Experimental electronic absorption spectra of ethanol solutions of I in the pH range between 6.0 (curve 1) and 11.0 (curve 19).

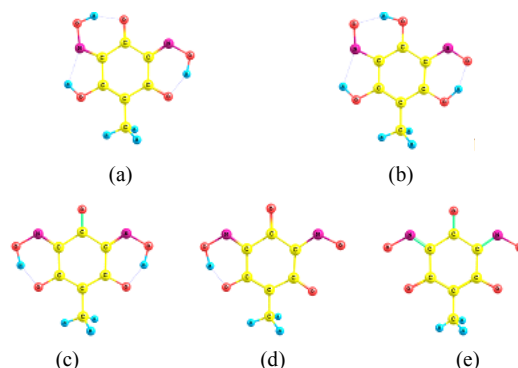


Figure 4. Optimized geometries of the neutral dihydroxyimino (a), dinitroso (b) tautomers of I and its mono- (c), di- (d) and trianionic (e) forms.

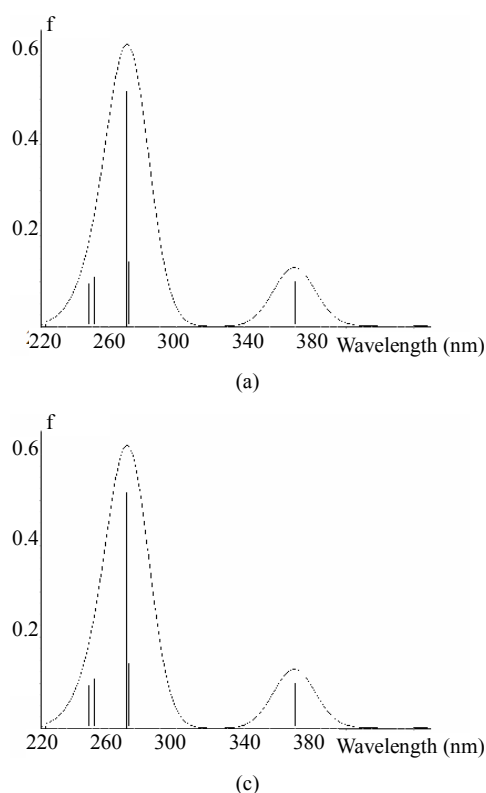


Figure 5. Calculated UV-Vis spectra of the dihydroxyimino tautomer of I in a neutral (a) and monoanionic (c) forms.

The calculated spectrum of the neutral dinitroso-tautomer of I can be characterized by a strong absorption due to imposing of two transitions at 296.76 (f 0.220) and 288.38 (f 0.522) nm (**Figure 6(b)**). In the spectrum of the trianionic form only one strong absorbance occurs at 297.21 nm (f 0.518) (**Figure 6(e)**). The calculated spectrum of the dianionic form is much more complicated and consists of transitions at 376.31 (f 0.043), 310.74 (f 0.285), 303.23 (f 0.138), 277.32 (f 0.153), and 266.73 (f 0.032) nm (**Figure 7**). The imposing of these transitions should lead to the appearance of a wide absorption band or a set of absorption bands. This fact

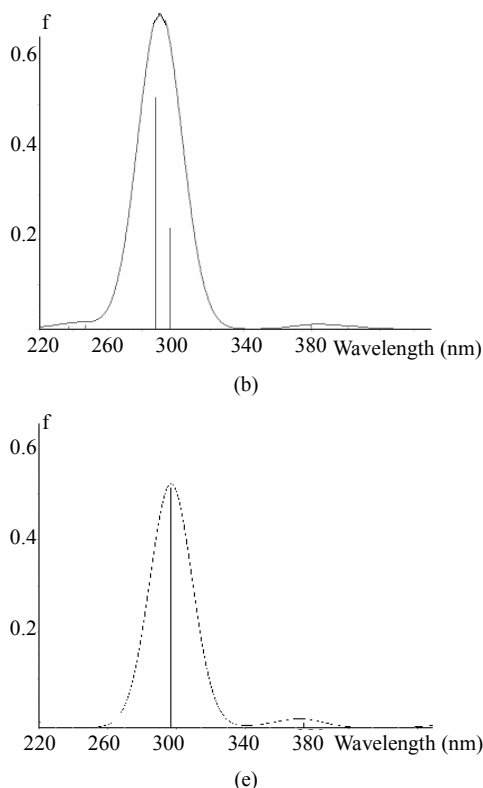


Figure 6. Calculated UV-Vis spectra of the dinitrozo neutral tautomer of I (b) and its trianionic (e) form.

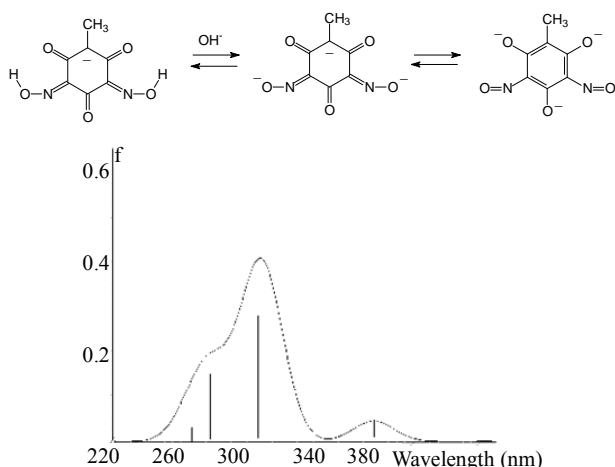


Figure 7. Calculated UV-Vis spectrum of the dianionic form of I.

contradicts with the shape of the experimental spectrum of I in alkaline solutions where a sharp intensive absorption occurs at 329.08 nm ($\log \epsilon$ 4.25).

Thus, it is possible to conclude that the dihydroxy-imino-isomer is more preferable in the crystalline form and neutral solutions. The process of ionization is accompanied by its tautomeric transformation into the dinitroso-form:

Basing on the results of the spectrophotometric titration of I, the ionization constant of the oxime groups was calculated to be pK 7.55 ± 0.42 . The calculated value correlates with the corresponding literature data for other cyclic oximes [18].

4. Conclusion

Consequently, the novel compound is obtained by the reaction of nitrosation of methylphloroglucinol. According to the single crystal X-ray diffraction data, it exists in the anionic form as sodium 3,5-bis(hydroxyl-imino)-1-methyl-2,4,6-trioxocyclohexanide. In the alkaline solutions, the further dissociation takes place which is accompanied by the transformation of the organic anion into the dinitroso-tautomer.

5. Acknowledgements

The research has been executed under financial support of the Russian Foundation for Basic Researches (project 10-03-00003-a).

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