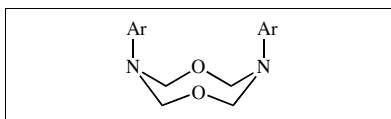


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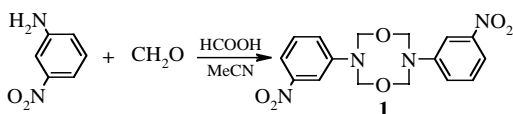
3,7-Di(3-nitrophenyl)-1,5-dioxa-3,7-diazacyclooctane was prepared from 3-nitroaniline and formaldehyde in acetonitrile. Conformational behavior of ring inversion of the molecule was studied so it prefers a crown conformation. The evaluated ΔG^\ddagger was approximately 58.0 ± 1.0 kJ/mole. The X-ray structure determination of the compound shows a crown conformation, in line with two-anomeric effect in N-C-O moiety.

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Replacement of CH_2 group in cyclooctane by heteroatoms such as O, S or N leads to different conformational structures [1,2]. In contrast to the parent compound, several cyclooctane derivatives and related compounds have different structures, which were determined by X-ray diffraction [3-6]. Some experimental data on heterocyclic eight-member rings that give more information about the barrier to interconversion of possible conformers have been published [7-10]. Compounds with special substitution patterns or with heteroatoms often exist partially or mainly in crown conformation [2]. Further experimental data and more investigation needs to show whether the conformational picture has real validity. So, in this work, in addition to a new synthesis approach we reported conformational analysis, X-ray structural determination and anomeric effect of 3,7-di(3-nitrophenyl)-1,5-dioxa-3,7-diazacyclooctane (**1**) [11].

Results and Discussion.

Compound **1** was prepared from 3-nitroaniline and formaldehyde in acetonitrile solvent. We studied the ^1H nmr spectrum of molecule **1** at various temperatures. At 40°C the spectrum of **1** displayed a broad singlet for CH_2 protons at 5.42 ppm.



Raising the temperature the ring proton signal sharpens, but lowering the temperature splits it into a closely packed AB quartet spectrum below 25°C (T_c). At -40°C the chemical-shift difference of the AB quartet was found to

remain constant at 187.7 Hz with $J_{\text{AB}}=13$ Hz while, the other signals remain unchanged. In addition, at both high and low temperatures, the signals corresponding to the CH_2 carbon atoms didn't change. The presence of only one AB quartet peak for CH_2 protons at low temperature indicates the existence of only one stable conformation. This is in accord with fairly well established evidence of a crown conformation in **1**. The free activation energy (ΔG^\ddagger) for ring inversion in the crown conformation [12,13] of **1** was approximately 58.0 ± 1.0 kJ/mole at 25°C . The ^1H nmr spectrum of **1** didn't show any additional dynamic nmr effect below -40°C . The ring inversion of **1** is similar to that which can be found for eight-member ring heterocyclics [14,15]. The structure of the compound **1** was established by X-ray crystallography (Figure 1). The atomic coordinates and thermal parameters are deposited in the supplementary pages. The torsion angles, $\text{C}_4\text{-O}_1\text{-C}_1\text{-N}_1 = -71.54(17)$, $\text{C}_{10}\text{-N}_1\text{-C}_1\text{-O}_1 = -64.23(18)$, $\text{C}_2\text{-N}_1\text{-C}_1\text{-O}_1 = 102.31(17)$, $\text{C}_3\text{-O}_2\text{-C}_2\text{-N}_1 = 70.4(2)$, $\text{C}_{10}\text{-N}_1\text{-C}_2\text{-O}_2 = 66.04(19)$, $\text{C}_1\text{-N}_1\text{-C}_2\text{-O}_2 = -100.50(18)$, $\text{C}_2\text{-O}_2\text{-C}_3\text{-N}_2 = -71.7(2)$, $\text{C}_4\text{-N}_2\text{-C}_3\text{-O}_2 = -61.0(2)$, $\text{C}_4\text{-N}_2\text{-C}_3\text{-O}_2 = 102.36(19)$, $\text{C}_1\text{-O}_1\text{-C}_4\text{-N}_2 = 69.45(19)$, $\text{C}_{11}\text{-N}_2\text{-C}_4\text{-O}_1 = 63.3(2)$, $\text{C}_3\text{-N}_2\text{-C}_4\text{-O}_1 = -100.03(18)$ in agreement with a crown family conformation. The monoclinic crystal of compound **1** showed a similar structure in the solid state as was expected in solution with the N-aryl in the axial position of the eight-member ring (similar to the other eight-member heterocyclic rings [2,6]). The two NO_2 groups of the aryl moieties are *syn*. There are some interesting structural features in this molecule; the C-N bonds are shorter than the usual values and bond angles around the N_1 or N_2 have sp^2 characteristics. The results show that the resonance of the aromatic rings with N atom reduces the N-pyramidalty. It also reduces the bond

length of N₁-C₁₀ (or N₂-C₁₁). Furthermore, experimental results and molecular mechanic calculations showed that the molecules having O-C-O, N-C-O and N-C-N units undergo anomeric interactions [16,17].

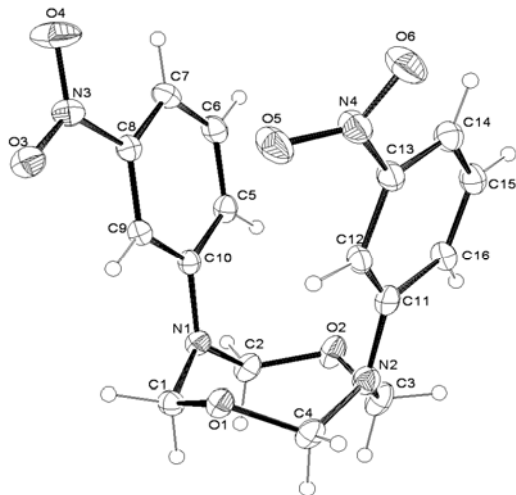


Figure 1. ORTEP plot of **1**, selected bond lengths (Å) and bond angles (°): O₁-C₁= 1.427(2), O₁-C₄=1.431(2), O₂-C₂=1.431(2), O₂-C₃=1.429(2), O₃-N₃=1.2238(19), N₁-C₁₀= 1.401(2), N₁-C₁=1.438(2), N₁-C₂=1.447(2), N₂-C₁₁=1.401(3), N₂-C₄=1.434(2), N₂-C₃=1.436(2), C₁-O₁-C₄=115.16(12), C₂-O₂-C₃=114.92(14), C₁-N₁-C₁₀=119.87(12), C₂-N₁-C₁₀=119.90(13), C₁-N₁-C₂=118.84(13), C₁₁-N₂-C₄=119.29(16), C₁₁-N₂-C₃=119.02(17), C₃-N₂-C₄=119.01(17), O₁-C₁-N₁=114.45(13), O₂-C₂-N₂=114.35(14), O₁-C₄-N₂=115.54(13).

Short C-N and C-O bonds in eight-member ring probably leads to an anomeric effect in N-C-O moiety due two cross hyperconjugation from n_N→σ*_{C-O} and n_O→σ*_{C-N}. Back donation of electron from N atom drastically has decreased N-pyramidal, which leading to an increase in p character of the 1p' s. This fact causes to produce unusual chemical shift of CH₂ protons and carbons.

EXPERIMENTAL

All commercially available chemical reagents were used without further purification. Melting points were determined with an Electrothermal 9200 apparatus and are uncorrected. Infrared spectrum was recorded on a Shimadzu 4300 spectrometer. The nmr spectrum was recorded on a Bruker DRX-500 AVANCE spectrometer. Mass data was obtained on a FISIONS TRIO 1000 GC-Mass instrument. Elemental analyses were carried out using a C,H,N,O Rapid-Heraeus apparatus.

3,7-Di(3-nitrophenyl)-1,5-dioxo-3,7-diazacyclooctane (**1**).

To a stirred solution of 3-nitroaniline (2.76 g, 20 mmole) and formic acid (0.05 g, of 98% aqueous solution, 1.1 mmole) in acetonitrile (100 ml) at 25 °C, formaldehyde (2.43 g, of 37% aqueous solution, 30 mmole) was added slowly. The solution was stirred at room temperature for 24 h until a yellow precipitate was formed. The mixture was filtered and the

precipitate washed with cold acetonitrile to give 3.05 g (84% yield) of **1**. Recrystallization from THF gave yellow crystals of **1**, mp 225.5-226 °C. ¹H nmr (DMSO-d₆, 25°C) ppm: 7.12-7.56 (m, 8H), 5.32 (s, 8H, CH₂), ¹H nmr (Acetone-d₆, 40°C) ppm: 7.14-7.69 (m, 8H), 5.42 (s, 8H, CH₂), ¹H nmr (Acetone-d₆, -40°C) ppm: 7.14-7.65 (m, 8H), 5.24, 5.27, 5.62, 5.64 (dd, 8H, CH₂, Δν=187.7 Hz, J=13Hz), ¹³C nmr (DMSO-d₆) ppm: 148.26, 145.58, 129.4, 121.5, 113.31, 109.59, 81.91. Ms: (70 eV, electron impact) m/z: 360 (molecular ion).

Anal. Calcd. for C₁₆H₁₆N₄O₆. C, 53.33; H, 4.44; N, 15.55. Found: C, 53.31; H, 4.43; N, 15.56.

X-Ray Diffraction

C₁₆H₁₆N₄O₆, FW=360.33 Monoclinic P 2₁/n Space group, a=6.6964(18) Å, b=12.369(3) Å, and c=19.003(5) Å, β=92.791(6)°, V=1572.8(7) Å³. Z=4, D (x-ray, calcd) =1.522 Mg/m³. μ=0.119 mm⁻¹, F (000)=752, T=120(2)°K. A yellow 0.32×0.28×0.18 mm³ crystal (recrystallized from THF) was used for data collection on a Bruker SMART 1000 CCD diffractometer with graphite monochromated Mo Kα (λ=0.71073 Å). The data collection range of hkl was -8 ≤ h ≤ 8, -16 ≤ k ≤ 16, -25 ≤ l ≤ 24. There were 3762 unique reflections, R_{int}=0.0424 from merging equivalent reflections, and 3022 were observed with I > 2σ (I). The structure was solved by direct methods (SHELXTL) [19] and refined by full-matrix least-squares (isotropic refinement of the molecule and location of remaining non-hydrogen atoms from a difference Fourier map and subsequent anisotropic refinement on all atoms; H atoms were found after high-angle refinement in a difference Fourier map and their positions included in the final stages of refinement), factors of R1=0.0551, Rw2=0.1201 for 3022 unique observed reflections (reflections with I < 2σ (I) are generally considered as unobserved). No significant features, only ripples from -0.285 to 0.299 e Å⁻³, were observed in the final Fourier difference map. The nonhydrogen atoms were refined anisotropically. Tables of atomic coordinates, bond distances and angles, and anisotropic thermal parameters are available as supplementary materials. Atomic coordinate, temperature factors, bond distances, bond angles and torsion have been deposited at the Cambridge Crystallographic Data Center, Number CCDC 280680. These data can be obtained free of charge via Cambridge Crystallographic Data Center (www.ccdc.cam.ac.uk/conts/retrieving).

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