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Synthesis and Characterization of Mono-, Di-, and Tetranitrated 7,8-Disubstituted Glycolurils

by William M. Sherrill, Eric C. Johnson, and Alexander J. Paraskos

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14. ABSTRACT

Three 7,8-disubstituted glycolurils were synthesized and subjected to various nitration conditions yielding the corresponding mono-, di-, and tetranitro derivatives. Prior to their synthesis, these nitrated compounds were evaluated computationally to determine their densities and heats of formation, from which explosive performance was predicted. Details on the methods used for the synthesis as well as the results from their computational analysis are discussed.

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Synthesis and Characterization of Mono-, Di-, and Tetranitrated 7,8-Disubstituted Glycolurils

William M. Sherrill,*[a] Eric C. Johnson,[b] and Alexander J. Paraskos[c]

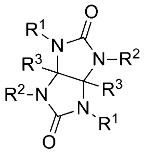
Abstract: Three 7,8-disubstitited glycolurils were synthesized and subjected to various nitration conditions yielding the corresponding mono-, di-, and tetranitro derivatives. Prior to their synthesis, these nitrated compounds were evaluated computationally to determine their densities and heats of formation, from which explosive performance was predicted. Details on the methods used for the synthesis as well as the results from their computational analysis are discussed.

Keywords: Substituted glycoluril · Tetranitroglycolurils · Nitration · Computational analysis

1 Introduction

Nitrated forms of glycolurils have been known to have explosive properties since the discovery of 1,4-dinitro-glycoluril (DINGU) (**1**) in the 1880's [1]. It was not until the 1970's that the 1,3,4,6-tetranitroglycoluril (sorguyl or TNGU) (**2**) form was announced by Boileau [2]. Since the discovery of **2**, very little research has been conducted to determine the energetic properties of glycoluril derivatives substituted at the 7,8-bridgehead positions despite widespread interest in using substituted glycolurils in cucurbituril type chemistry [3].

We have developed methodologies for the production of mono-, di-, and tetranitro-7,8-disubstituted glycolurils. To date, we have not been able to isolate or observe any trinitro-species analogous to those reported by Boileau 1985 [2]. We have found the strength of the nitration solution dictates the degree of nitration with few, if any, unwanted side products. While many substitution patterns exist in the literature for 7,8-disubsitituted glycolurils, herein we report only the nitration products for three of them: dimethyl **3**, dimethylester **4**, and diethylester **5** (Figure 1).



1 $R^1 = NO_2$, $R^2,R^3 = H$
2 $R^1,R^2 = NO_2$ $R^3 = H$
3 $R^1,R^2 = H$ $R^3 = Me$
4 $R^1,R^2 = H$ $R^3 = CO_2Me$
5 $R^1,R^2 = H$ $R^3 = CO_2Et$

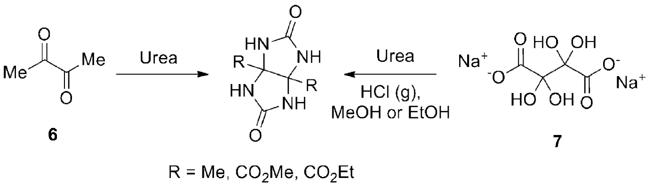
Figure 1. DINGU, TNGU, and substituted glycolurils.

2 Results and Discussion

2.1 Synthesis and Characterization

2.1.1 Preparation of Substituted Glycolurils

Substituted glycolurils are readily prepared by the reaction of urea with a substituted 1,2-dione **6** [4] or with a corresponding 1,2,-dione equivalent **7** [5]. Methyl and ethyl esters **4** and **5** were prepared according to the method outlined by Isaacs, in which tetrahydroxy tartaric acid **7** is reacted with urea in an acidified solution of the appropriate alcohol (Scheme 1) [5].



Scheme 1. Synthesis routes to glycolurils.

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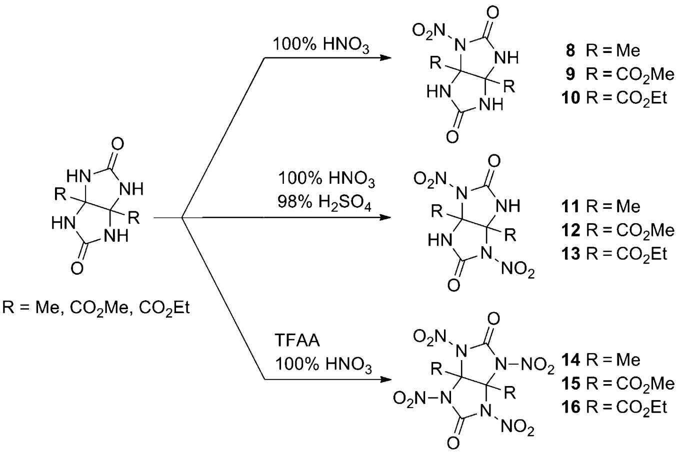
2.1.2 Nitration of Substituted Glycolurils

Mono-, di-, and tetranitro variations of the substituted glycoluril framework can be achieved directly from the parent compounds by simply varying the nitration strength of the solution used (Scheme 2). Nitration of **3–5** with 100% nitric acid results in the exclusive formation of the parent compound mononitro derivative. By employing a mixed acid nitration solution of 100% HNO_3 and $>98\%$ H_2SO_4, the dinitrated products can be isolated. Finally, more aggressive conditions using a mixture of trifluoroacetic anhydride and 100% HNO_3 result in formation of the tetranitro derivative.



Scheme 2. Nitration methods for substitutued glycolurils.

2.1.3 Explosive and Sensitivity Properties of Nitrated Substituted Glycolurils

The materials' properties were calculated by estimating the heat of formation and density using the computational methods developed by Betsy Rice [6]. In addition to the calculations, the density of each of the synthesized materials was experimentally determined using gas pycnometry with N_2 as the analysis gas. The results of these studies can be found in Table 1. In all cases, the computationally determined densities were in reasonable agreement ($<10\%$ disparity) with the experimental measurements, with the calculated values tending to be slightly higher. Using the calculated heat of formation values together with the experimental density measurements, detonation pressure, shock velocity, and heat of detonation were estimated using Cheetah 7.0 [7]. All of the compounds **8–13** are predicted to have performance values less than TNT with **15** and **16** approaching the performance of TNT. Compound **14**, with a measured density of 1.922 $g\,mL^{-1}$, is predicted to be similar in performance to RDX (Table 1).

Many of the materials examined were determined to be insensitive and recorded maximum values for both impact and friction tests. In all cases, the materials tested met or exceeded the ESD shock values determined for class 1 RDX using our testing equipment. The tetranitro derivatives **14–16** did exhibit varying degrees of impact sensitivity with **14** being more than twice the sensitivity of RDX using the same test equipment.

The major issue that has precluded TNGU (**2**) from finding widespread use in the energetic community is the inherent hydrolytic instability of the dinitrourea moiety. While **2** is stable when stored under anhydrous conditions, it rapidly hydrolyzes in the presence of moisture. In investigating 7,8-disubstituted glycolurils, it was believed that by varying the electronic nature of the substituents in the bridgehead positions, it might be possible to return some hydrolytic stability to the tetranitro derivatives. However, during the course of the study, it was observed that all of the tetranitro compounds **14–16** were still extremely sensitive to moisture, while in solution, but like **2**, could be stored un-

Table 1. Yield and performance data.

	8	9	10	11	12	13	14	15	16	RDX
Yield [g, %]	0.99, 52	1.03, 58	1.29, 74	1.14, 50	1.42, 70	0.79, 35	1.57, 76	0.99, 58	1.29, 79	–
ρ ^a)^ [$g\,mL^{-1}$]	1.732 [1.617]	1.575 [1.730]	1.533 [1.627]	1.666 [1.738]	1.754 [1.812]	1.584 [1.706]	1.922 [1.901]	1.816 [1.940]	1.837 [1.834]	[1.816]
ΔH_f [$kJ\,mol^{-1}$]	−429.15	−1062.48	−1158.36	−351.69	−995.62	−1092.17	−98.81	−721.64	−835.31	70.05
D_v b) [$km\,s^{-1}$]	7.255	6.446	6.362	7.161	7.193	6.736	8.819	8.067	7.948	8.862
P_{CJ} b) [GPa]	16.34	12.88	12.218	20.03	19.32	14.85	35.43	27.69	26.05	33.46
ΔH_d b) [$kJ\,mL^{-1}$]	3.33	3.10	3.26	5.83	5.33	4.19	9.92	7.96	7.65	10.4
OB [%]	−92.95	−65.97	−89.36	−61.50	−45.95	−68.04	−22.85	−18.26	−37.75	−21.61
Decomp. c) [°C]	226	253	243	223	204	205	168	159	145	240
Impact d) [cm]	<152.4	<152.4	<152.4	<152.4	<152.4	<152.4	10.7	24.6	63.2	25.2
Friction e) [N]	<360	<360	<360	<360	<360	<360	282	282	282	125
ESD [J]	0.625	0.625	0.625	0.25	1.25	3.125	0.625	0.25	1.25	0.25

a) Calculated values in brackets. b) Calculated using Cheetah 7.0. c) Peak decomposition temperature at 10 $K\,min^{-1}$ in a pinhole pan. d) Explosive Research Laboratory (ERL) type impact test 2.5 kg weight from a maximum height of 152.4 cm using the Langlie one shot H_{50} method [8]. e) BAM friction apparatus.

changed under anhydrous conditions. When **14–16** were dissolved in wet solvents, they were observed to decompose in minutes, while the same compounds dissolved in dry solvents were sufficiently stable to allow the collection of NMR spectroscopic data. It should be noted that more than 50 % decomposition is observed upon compound exposure to solvent overnight at room temperature, even in dry solvents in an inert atmosphere. From this, it was concluded that the substituents examined exhibited little influence on the hydrolytic stability of tetranitroglycolurils.

3 Experimental Section

Note: While these compounds were prepared without incident according the following procedures, these materials are energetic and should be prepared and handled cautiously by trained personnel.

3.1 General Considerations

NMR spectra were recorded with an Anasazi Instruments 90-MHz or a Bruker 600 MHz NMR spectrometer as noted. All NMR chemical shifts are reported in ppm relative to TMSCl. FTIR spectra were recorded with a Bruker Alpha-T instrument fitted with a diamond ATR (DATR) cell. Density was measured with a gas pycnometry with a Micromeritics AccuPyc 1330 instrument using nitrogen as the analysis gas. Elemental analysis was conducted with a PerkinElmer 2400 Series II CHNS/O combustion elemental analyzer using helium as the carrier gas. DSC was performed with a TA instruments Q10 or Q20 calorimeter calibrated to the melting point of indium. All deuterated solvents were obtained from Cambridge Isotope Laboratories, Andover, MA, USA. All other materials used were obtained from Sigma Aldrich Corp. St. Louis, MO, USA and were used as received unless otherwise noted.

3.2 Synthetic Procedures

3.2.1 Compound 8

Compound **3** (1.5 g, 8.81 mmol) was added slowly in three portions to HNO_3 (1.8 mL, 100 %) chilled to 0 °C. Once the addition was completed, the solution was allowed to stir at 0 °C for 1 h. Afterwards, it was removed from the ice bath and allowed to stir for an additional hour at room temperature. The solution was precipitated by pouring it into ice cold Et_2O (20 mL), filtered, and vacuum dried to constant mass. The total mass recovered was 0.9916 g (4.61 mmol, 52 %) of a pale yellow powder, which decomposed at 226 °C. ^{1}H NMR (90.420 MHz, DMSO-d_6): $\delta = 9.10$, 8.14, 7.82 (s, 1 H), 1.72 (s, 3 H), 1.43 (s, 3 H). ^{13}C NMR (22.736 MHz, DMSO-d_6): $\delta = 158.4$, 147.8, 81.1, 72.1, 21.6, 18.5. FT-IR (DATR): $\tilde{\nu} = 3383$, 3198, 1808, 1776, 1705, 1556, 1258, 1145, 710 cm^{-1}. $C_6H_9N_5O_4$: calcd. C 33.49; H 4.22; N 32.55 %; found: C 33.75; H 3.88; N 32.11 %.

3.2.2 Compound 9

Dimethylester **4** (1.5 g, 5.81 mmol) was added in three portions to HNO_3 (4.5 mL, 100 %) at 0 °C. Once all of the material had dissolved, the solution was warmed to 50 °C and stirred for 2 h. The material was poured onto approximately 5 g of crushed ice and a white precipitate formed. After approximately 10 min, the material was filtered, washed with cold water until neutral (ca. 20 mL) and dried in a vacuum oven (0 Pa, 60 °C) until constant mass was achieved. The yield was 1.03 g (3.39 mmol, 58 %) of a white powder with an observed decomposition temperature of 253 °C. ^{1}H NMR (90.420 MHz, DMSO-d_6): $\delta = 10.21$, 9.21, 8.71 (s, 1 H), 3.77 (s, 3 H), 3.76 (s, 3 H). ^{13}C NMR (22.736 MHz, DMSO-d_6): $\delta =$ 165.9, 164.5, 158.8, 147.1, 80.6, 73.4, 54.6, 54.3. FT-IR (DATR): $\tilde{\nu} = 3262$, 3096, 2956, 2852, 1806, 1767, 1722, 1581, 1252, 1219, 1182, 1143, 1022, 771 cm^{-1}. $C_8H_9O_5O_8$: calcd. C 31.69; H 2.99; N 23.10 %; found: C 31.81; 2.69; 22.95 %.

3.2.3 Compound 10

Diethylester **5** (1.5 g, 5.24 mmol) of was added in three portions to HNO_3 (4.5 mL, 100 %) at 0 °C. Once all of the material had dissolved, the solution was allowed to stir at 0 °C for 1 h at which point it was warmed to 55 °C. After 1 h at 55 °C, the material was poured onto approximately 10 g of crushed ice and a white precipitate formed. After approximately 10 min, the material was filtered, washed with cold water (20 mL) and dried in a vacuum oven (0 Pa, 60 °C) until constant mass was achieved. The yield on the process was 1.29 g (71 %, 3.89 mmol, 74 %) of a white powder, which decomposed with melting at 243 °C. ^{1}H NMR (90.420 MHz, DMSO-d_6): $\delta = 10.18$, 9.20, 8.67 (s, 1 H), 4.20 (q, 2 H, $J = 7.1$ Hz), 4.13 (q, 2 H, $J = 7.1$ Hz), 1.21 (t, 3 H, $J =$ 7.1 Hz), 1.19 (t, 3 H, $J = 7.1$ Hz) ^{13}C NMR (22.736 MHz, DMSO-d_6): $\delta = 165.5$, 163.9, 159.2, 147.6, 80.9, 73.5, 64.2, 64.0, 14.0, 13.9. FT-IR (DATR): $\tilde{\nu} = 3373$, 3109, 2987, 1791, 1770, 1573, 1257, 1217, 1146, 1024, 761 cm^{-1}. $C_{10}H_{13}N_5O_8$: calcd. C 36.26; H 3.96; N 21.14 %; found: C 36.32; H 3.74; N 20.36 %.

3.2.4 Compound 11

Compound **3** (1.5 g, 8.81 mmol) of was added slowly in three portions to HNO_3 (3.75 mL, 100 %) and H_2SO_4 (2.25 mL, 98 %) chilled to 0 °C. Once the addition was completed, the solution was allowed to stir at 35 °C for 2 h. Afterwards, it was poured over ca. 10 g of crushed ice and no immediate precipitate was observed. The solution was extracted twice with EtOAc (20 mL). The combined organic layers were washed with saturated $NaHCO_3$ (20 mL) followed by saturated NaCl (20 mL). The organic layer was dried with Mg_2SO_4, filtered, and concentrated in vacuo. **11** was isolated as a pale yellow solid, 1.14 g (4.38 mmol, 50 %) decomposing at 223 °C. ^{1}H NMR (90.420 MHz, DMSO-d_6): $\delta = 9.93$ (s, 2 H), 1.81 (s, 6 H). ^{13}C NMR (22.736 MHz, DMSO-d_6): $\delta = 146.6$, 77.0, 17.8, FT-IR (DATR): $\tilde{\nu} = 3314$, 3205, 3109, 2922, 2252, 1763, 1580, 1546, 1273, 1152, 1075, 734 cm^{-1}. $C_6H_8N_6O_6$: calcd. C 27.70; H 3.10; N 32.30 %; found: C 27.87; 2.91; 32.0 %.

3.2.5 Compound 12

Dimethylester **4** (1.5 g, 5.81 mmol) was added in three portions to a mixture of HNO_3 (3.75 mL, 100 %) and H_2SO_4 (2.25 mL, 98 %) cooled to 0 °C. Once all of the ester had dissolved, the solution was heated to 35 °C for 2 h, at which point the solution was poured over ca. 5 g of crushed ice. The small amount of precipitate formed was filtered and discarded. The filtrate was stored overnight and dinitrodiethylester **12** precipitated as white crystals. The crystals were filtered and dried in a vacuum oven (0 Pa, 60 °C) to constant mass for a total yield of 1.42 g (4.08 mmol, 70 %) of white crystals, which decomposed at 204 °C. ^{1}H NMR (90.420 MHz, DMSO-d_6): $\delta = 11.22$ (s, 2 H), 3.85 (s, 6 H). ^{13}C NMR (22.736 MHz, DMSO-d_6): $\delta = 162.5$, 146.9, 75.2, 55.7. FT-IR (DATR): $\tilde{\nu} = 2968$, 1831, 1793, 1761, 1652, 1636, 1624, 1271, 1218, 1182, 1143, 871, 829, 785, 774, 763, 738 cm^{-1}. $C_8H_8N_6O_{10}$: calcd. C 27.60; H 2.32; N 24.14 %; found: C 27.38; 2.15; 25.25 %.

3.2.6 Compound 13

Diethylester **5** (1.5 g, 5.24 mmol) was added in three portions to a 0 °C mixture of HNO_3 (3.75 mL, 100 %) and H_2SO_4 (2.25 mL, 98 %). Once all of the ester had dissolved, the solution was heated to 35 °C for 2 h, at which point the solution was poured over ca. 5 g of crushed ice. The small amount of precipitate formed was filtered and discarded. The filtrate was stored overnight and dinitrodiethylester **13** precipitated as white crystals. The crystals were filtered and dried in a vacuum oven (0 Pa, 60 °C) to constant mass. The total amount of material recovered was 0.79 g (1.86 mmol, 35 %) of white crystals, which decomposed on melting at 205 °C. ^{1}H NMR (90.420 MHz, DMSO-d_6): $\delta = 11.17$ (s, 2 H), 4.25 (q, 4 H, $J = 7.2$ Hz), 1.20 (t, 6 H, $J = 7.5$ Hz) ^{13}C NMR (22.736 MHz, DMSO-d_6): $\delta = 161.6$, 146.9, 75.0, 65.1, 13.6. FT-IR (DATR): $\tilde{\nu} = 3302$, 2990, 2838, 1801, 1748, 1606, 1586, 1264, 1179, 794 cm^{-1}. $C_{10}H_{12}N_6O_{10}$: calcd. C 31.92; H 3.21; N 22.34 %; found: C 31.20; H 2.95; N 22.54 %.

3.2.7 Compound 14

Compound **3** (1 g, 5.87 mmol) was added to trifluoroacetic anhydride (20 mL) that had been cooled to 0 °C. To this suspension was added HNO_3 (8 mL, 100 %) dropwise. The resulting suspension was equipped with a $CaCl_2$ drying tube and stirred in a nitrogen atmosphere. When the solution became homogeneous, it was heated to 35 °C with stirring for 1.5 h during which time a suspension of **14** appeared. The solution was filtered, washed with anhydrous DCM (20 mL) and vacuum dried (0 Pa, 25 °C) to constant mass. A total mass of 1.57 g (4.48 mmol, 76 %) of an off-white powder decomposing at 168 °C was recovered from this reaction. ^{1}H NMR (600.182 MHz, acetone-d_6): $\delta = 2.62$ (s, 6 H). ^{13}C NMR (150.046 MHz, acetone-d_6): $\delta = 139.50$, 78.20, 17.82. FT-IR (DATR): $\tilde{\nu} = 1794$, 1594, 1266, 1192, 1155, 1080, 1039, 702 cm^{-1}. $C_6H_6N_8O_{10}$: calcd. C 20.58; H 1.73; N 32.00; found: C 20.61; H 1.65; N 31.52 %.

3.2.8 Compound 15

Dimethylester **4** (1 g, 3.87 mmol) was added to trifluoroacetic anhydride (10 mL), which had been cooled to 0 °C in a nitrogen atmosphere. To the resulting suspension was added HNO_3 (4 mL, 100 %) dropwise. Once the addition was complete, the flask was fitted with a $CaCl_2$ drying tube and was allowed to stir at 0 °C for 1.5 h. Afterwards the precipitant was filtered, washed with anhydrous MeCN and vacuum dried (0 Pa, 25 °C) to constant mass of 0.99 g (2.25 mmol, 58 %) of a white powder decomposing at 159 °C. ^{1}H NMR (600.182 MHz, acetone-d_6): $\delta = 4.10$ (s, 6 H). ^{13}C NMR (150.046 MHz, acetone-d_6): $\delta = 159.73$, 140.07, 76.51, 57.31. FT-IR (DATR): $\tilde{\nu} = 1831$, 1794, 1761, 1652, 1636, 1624, 1440, 1219, 1182, 1143, 830, 764 cm^{-1}. $C_8H_6N_8O_{14}$: calcd. C 21.93; H 1.38; N 25.57 %; found: C 22.43; H 1.23; N 25.72 %.

3.2.9 Compound 16

5 (1 g, 3.49 mmol) was added to trifluoroacetic anhydride (10 mL) at 0 °C in an inert atmosphere. HNO_3 (4 mL, 100 %) was slowly added to the suspension dropwise. Once the addition was completed, and all of **5** was dissolved, the solution was stirred at 0 °C for 2 h during which time a precipitate of **16** formed in the solution. After 2 h, the suspension was filtered, and the crude **16** was washed with 50 mL of anhydrous DCM. Finally the material was dried under vacuum resulting in 1.29 g (2.76 mmol, 79 %) of **16** isolated as a white fluffy powder decomposing at 145 °C. ^{1}H NMR (600.182 MHz, acetone-d_6): $\delta = 4.58$ (q, 4 H, $J = 7.3$ Hz) 1.39 (t, 6 H, $J = 7.3$ Hz). ^{13}C NMR (150.046 MHz, acetone-d_6): $\delta = 158.92$, 140.17, 76.40, 67.99, 13.51. FT-IR (DATR): $\tilde{\nu} = 1826$, 1790, 1754, 1650, 1636, 1625, 1270, 1212, 1186, 1145, 1012, 851, 840, 823, 787 cm^{-1}. $C_{10}H_{10}N_8O_{14}$: calcd. C 25.76; H 2.16; N 24.03 %; found: C 25.81; H 1.81; N 23.92 %.

4 Conclusions

Three nitration methods for producing mono-, di-, and tetranitrated-7,8-substituted glycolurils were developed in our laboratories. By treating the starting materials with 100 % HNO_3, it is possible to isolate only mononitrated products in yields in excess of 50 %. By employing a mixed acid nitration solution, the dinitriated species can be generated selectively, while a mixture of trifluoroacetic anhydride and 100% HNO_3 results in the formation of the tetranitrated species. The experimentally determined density of the materials synthesized in this effort exhibit good agreement with the density as predicted through quantum mechanical methods. Using the calculated heat of formation and the experimental density, it was found that compounds **8–13**, **15**, and **16** are expected to have detonation properties most similar to TNT, whereas the tetranitrated compound **14** is expected to behave similarly to RDX.

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