Molecular Structure Laboratory

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**Structural report on Gellman186\_sq**

May 14, 2019

Low Quality Structure

# Crystallographic Experimental Section

## Data Collection

A colorless crystal with approximate dimensions 0.10 x 0.10 x 0.08 mm3 was selected under oil under ambient conditions and attached to the tip of a MiTeGen MicroMount©. The crystal was mounted in a stream of cold nitrogen at 100(1) K and centered in the X-ray beam by using a video camera.

The crystal evaluation and data collection were performed on a Bruker Quazar SMART APEXII diffractometer with Mo Kα (λ = 0.71073 Å) radiation and the diffractometer to crystal distance of 4.96 cm [1].

The initial cell constants were obtained from three series of ω scans at different starting angles. Each series consisted of 12 frames collected at intervals of 0.5º in a 6º range about ω with the exposure time of 30 seconds per frame. The reflections were successfully indexed by an automated indexing routine built in the APEXII program suite. The final cell constants were calculated from a set of 4783 strong reflections from the actual data collection.

The data were collected by using the full sphere data collection routine to survey the reciprocal space to the extent of a full sphere to a resolution of 0.80 Å. A total of 36135 data were harvested by collecting 4 sets of frames with 0.6º scans in ω and φ with exposure times of 120 seconds per frame. These highly redundant datasets were corrected for Lorentz and polarization effects. The absorption correction was based on fitting a function to the empirical transmission surface as sampled by multiple equivalent measurements. [2]

### Structure Solution and Refinement

The systematic absences in the diffraction data were uniquely consistent for the space group *P*21/*c* that yielded chemically reasonable and computationally stable results of refinement [3-8].

A successful solution by the direct methods provided most non-hydrogen atoms from the *E*-map. The remaining non-hydrogen atoms were located in an alternating series of least-squares cycles and difference Fourier maps. All non-hydrogen atoms were refined with anisotropic displacement coefficients. All hydrogen atoms were included in the structure factor calculation at idealized positions and were allowed to ride on the neighboring atoms with relative isotropic displacement coefficients.

The only crystal large enough for the single-crystal X-ray diffraction experiment proved to be a non-merohedral twin with a 30.0(3) % second component contribution. The twin components are related by a 179.8° rotation about the reciprocal *a\** axis. Inclusion of the second component contributions to the observed data intensities yielded inferior results of refinement. Therefore, contributions from this minor domain are omitted from the final structural model.

There were several peaks of electron density in the structure that corresponded to solvent molecules of diethyl ether and methanol. It is likely that these solvent molecules are disordered over several positions and therefore have electron density that is diffuse. Option SQUEEZE of program PLATON [9] was used to correct the diffraction data for diffuse scattering effects and to identify the solvate molecule(s). PLATON calculated the upper limit of volume that can be occupied by the solvent to be 388.0 Å3, or 18.6% of the unit cell volume. The program calculated 93 electrons in the unit cell for the diffuse species. This corresponds to three molecules of methanol and one molecule of diethyl ether (96 electrons) in the unit cell. Please note that all derived results in the following tables are based on the known contents. No data are given for the diffusely scattering species.

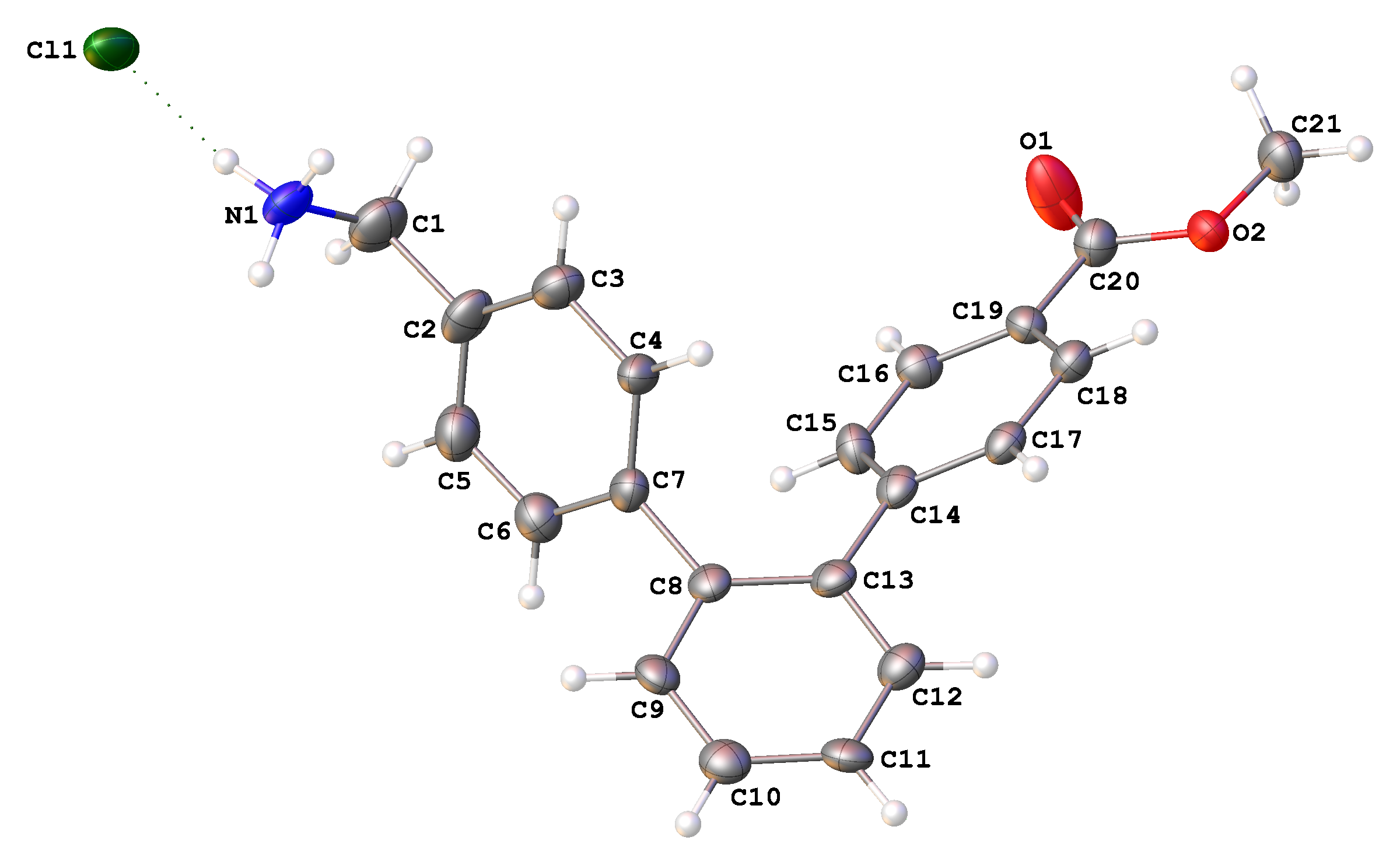
The final least-squares refinement of 229 parameters against 4828 data resulted in residuals *R* (based on *F*2 for *I*≥2*σ*) and *wR* (based on *F*2 for all data) of 0.0972 and 0.2745, respectively. The final difference Fourier map contains a peak (ca. 1.87 e-/Å3) 0.90 Å from atom Cl1 in a chemically unreasonable position and was considered noise.

### Summary

**Crystal Data** for C21H20ClNO2 (*M*=353.83 g/mol): monoclinic, space group P21/c (no. 14), *a* = 17.997(6) Å, *b* = 6.1519(18) Å, *c* = 19.636(6) Å, *β* = 106.549(11)°, *V*= 2083.9(11) Å3, *Z* = 4, *T* = 99.99 K, μ(Mo Kα) = 0.195 mm-1, *Dcalc* = 1.128 g/cm3, 36135 reflections measured (2.36° ≤ 2Θ ≤ 52.882°), 7579 unique (*R*int = 0.0784, Rsigma = 0.0582) of which 4282 were used for all calculations. The final *R*1 was 0.0972 (I > 2σ(I)) and *wR*2 was 0.2745 (all data).

### References

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**Figure 1**. A molecular drawing of Gellman186 shown with 50% probability ellipsoids.

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| Table 1 Crystal data and structure refinement for Gellman186\_sq. | |
| Identification code | Gellman186\_sq |
| Empirical formula | C21H20ClNO2 |
| Formula weight | 353.83 |
| Temperature/K | 99.99 |
| Crystal system | monoclinic |
| Space group | P21/c |
| a/Å | 17.997(6) |
| b/Å | 6.1519(18) |
| c/Å | 19.636(6) |
| α/° | 90 |
| β/° | 106.549(11) |
| γ/° | 90 |
| Volume/Å3 | 2083.9(11) |
| Z | 4 |
| ρcalcg/cm3 | 1.128 |
| μ/mm‑1 | 0.195 |
| F(000) | 744.0 |
| Crystal size/mm3 | 0.1 × 0.1 × 0.08 |
| Radiation | Mo Kα (λ = 0.71073) |
| 2Θ range for data collection/° | 2.36 to 52.882 |
| Index ranges | -22 ≤ h ≤ 21, 0 ≤ k ≤ 7, 0 ≤ l ≤ 24 |
| Reflections collected | 36135 |
| Independent reflections | 7579 [Rint = 0.0784, Rsigma = 0.0582] |
| Data/restraints/parameters | 4828/0/229 |
| Goodness-of-fit on F2 | 1.057 |
| Final R indexes [I>=2σ (I)] | R1 = 0.0972, wR2 = 0.2681 |
| Final R indexes [all data] | R1 = 0.1041, wR2 = 0.2745 |
| Largest diff. peak/hole / e Å-3 | 1.89/-0.60 |

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| **Atom** | ***x*** | ***y*** | ***z*** | **U(eq)** |
| Cl1 | 3983.6(7) | 4096(2) | 7195.4(10) | 47.8(4) |
| O1 | 7138(2) | 10609(8) | 3646(3) | 56.5(13) |
| O2 | 8312.3(19) | 12010(5) | 3814.6(18) | 29.0(7) |
| N1 | 5771(2) | 4112(8) | 7416(3) | 37.6(10) |
| C1 | 5764(3) | 4309(11) | 6655(4) | 47.9(14) |
| C2 | 6565(3) | 3969(10) | 6575(3) | 38.3(12) |
| C3 | 7117(3) | 5618(9) | 6745(3) | 36.9(11) |
| C4 | 7861(3) | 5252(8) | 6678(3) | 29.2(10) |
| C5 | 6769(3) | 1981(9) | 6343(3) | 40.2(12) |
| C6 | 7505(3) | 1650(9) | 6273(3) | 34.9(11) |
| C7 | 8063(3) | 3273(8) | 6443(2) | 28.0(9) |
| C8 | 8875(3) | 2863(7) | 6433(2) | 24.5(9) |
| C9 | 9273(3) | 1227(7) | 6869(3) | 28.3(9) |
| C10 | 10052(3) | 813(8) | 6937(3) | 33.0(11) |
| C11 | 10430(3) | 2078(7) | 6557(3) | 29.4(10) |
| C12 | 10043(3) | 3686(8) | 6107(3) | 31.1(10) |
| C13 | 9255(3) | 4114(7) | 6037(2) | 26.7(9) |
| C14 | 8866(3) | 5830(7) | 5525(2) | 26.1(9) |
| C15 | 8112(3) | 5551(8) | 5072(2) | 29.2(10) |
| C16 | 7774(3) | 7145(7) | 4580(2) | 27.9(10) |
| C17 | 9265(3) | 7714(7) | 5453(2) | 25.0(9) |
| C18 | 8935(3) | 9320(8) | 4953(2) | 27.1(9) |
| C19 | 8180(3) | 8990(7) | 4513(2) | 24.7(9) |
| C20 | 7814(3) | 10598(8) | 3947(3) | 31.6(10) |
| C21 | 7989(3) | 13538(9) | 3243(3) | 35.0(10) |

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| Table 3 Anisotropic Displacement Parameters (Å2×103) for Gellman186\_sq. The Anisotropic displacement factor exponent takes the form: -2π2[h2a\*2U11+2hka\*b\*U12+…]. | | | | | | |
| **Atom** | **U11** | **U22** | **U33** | **U23** | **U13** | **U12** |
| Cl1 | 30.6(6) | 30.9(6) | 86.3(11) | 3.0(7) | 23.7(8) | 5.4(5) |
| O1 | 35(2) | 56(3) | 65(3) | 26(2) | -8(2) | -12.0(19) |
| O2 | 32.5(17) | 24.2(16) | 33.3(17) | 6.2(13) | 14.3(14) | 3.8(13) |
| N1 | 25.4(19) | 39(2) | 54(3) | -1(2) | 20(2) | 4.5(18) |
| C1 | 28(2) | 58(4) | 59(4) | 4(3) | 15(3) | 8(2) |
| C2 | 20(2) | 54(3) | 42(3) | 3(2) | 10(2) | 4(2) |
| C3 | 31(2) | 38(3) | 43(3) | 2(2) | 15(2) | 8(2) |
| C4 | 27(2) | 23(2) | 42(3) | -1.5(19) | 16(2) | -1.1(18) |
| C5 | 39(3) | 41(3) | 45(3) | 1(2) | 18(2) | -8(2) |
| C6 | 37(3) | 31(2) | 38(3) | 1(2) | 12(2) | -3(2) |
| C7 | 29(2) | 28(2) | 30(2) | 4.5(18) | 13.3(19) | 1.7(18) |
| C8 | 31(2) | 22(2) | 23(2) | -5.0(16) | 12.0(18) | 1.0(17) |
| C9 | 36(2) | 17(2) | 33(2) | -2.8(18) | 12(2) | -1.0(18) |
| C10 | 39(3) | 27(2) | 33(2) | -6.2(19) | 11(2) | 0(2) |
| C11 | 36(2) | 19(2) | 34(2) | -3.3(18) | 10(2) | 7.1(18) |
| C12 | 31(2) | 35(3) | 30(2) | -5(2) | 13(2) | 0.2(19) |
| C13 | 31(2) | 27(2) | 26(2) | -3.9(17) | 13.4(19) | 5.0(17) |
| C14 | 30(2) | 28(2) | 24(2) | -6.7(18) | 13.5(18) | -2.4(18) |
| C15 | 34(2) | 27(2) | 28(2) | 1.4(18) | 11.3(19) | -6.9(19) |
| C16 | 26(2) | 27(2) | 29(2) | -4.1(18) | 6.2(18) | -1.3(17) |
| C17 | 23(2) | 29(2) | 26(2) | -5.9(17) | 11.4(17) | -2.4(17) |
| C18 | 26(2) | 28(2) | 29(2) | -0.5(18) | 11.4(19) | 0.8(17) |
| C19 | 29(2) | 19(2) | 28(2) | 0.2(17) | 11.3(18) | 1.4(16) |
| C20 | 31(2) | 31(2) | 35(2) | 1(2) | 12(2) | -2.1(19) |
| C21 | 37(2) | 35(2) | 35(2) | 9(2) | 13(2) | 2(2) |

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| Table 4 Bond Lengths for Gellman186\_sq. | | | | | | |
| **Atom** | **Atom** | **Length/Å** |  | **Atom** | **Atom** | **Length/Å** |
| O1 | C20 | 1.192(7) |  | C8 | C13 | 1.403(6) |
| O2 | C20 | 1.326(6) |  | C9 | C10 | 1.393(7) |
| O2 | C21 | 1.452(6) |  | C10 | C11 | 1.383(7) |
| N1 | C1 | 1.495(8) |  | C11 | C12 | 1.377(7) |
| C1 | C2 | 1.509(7) |  | C12 | C13 | 1.409(6) |
| C2 | C3 | 1.392(8) |  | C13 | C14 | 1.488(7) |
| C2 | C5 | 1.391(8) |  | C14 | C15 | 1.405(7) |
| C3 | C4 | 1.399(7) |  | C14 | C17 | 1.392(6) |
| C4 | C7 | 1.387(7) |  | C15 | C16 | 1.389(7) |
| C5 | C6 | 1.385(8) |  | C16 | C19 | 1.376(6) |
| C6 | C7 | 1.387(7) |  | C17 | C18 | 1.400(7) |
| C7 | C8 | 1.490(6) |  | C18 | C19 | 1.402(6) |
| C8 | C9 | 1.382(7) |  | C19 | C20 | 1.493(7) |

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| Table 5 Bond Angles for Gellman186\_sq. | | | | | | | | |
| **Atom** | **Atom** | **Atom** | **Angle/˚** |  | **Atom** | **Atom** | **Atom** | **Angle/˚** |
| C20 | O2 | C21 | 115.6(4) |  | C11 | C12 | C13 | 120.6(5) |
| N1 | C1 | C2 | 110.9(5) |  | C8 | C13 | C12 | 118.6(4) |
| C3 | C2 | C1 | 120.8(5) |  | C8 | C13 | C14 | 123.6(4) |
| C5 | C2 | C1 | 120.4(5) |  | C12 | C13 | C14 | 117.7(4) |
| C5 | C2 | C3 | 118.8(5) |  | C15 | C14 | C13 | 121.7(4) |
| C2 | C3 | C4 | 119.8(5) |  | C17 | C14 | C13 | 120.1(4) |
| C7 | C4 | C3 | 121.4(5) |  | C17 | C14 | C15 | 118.1(4) |
| C6 | C5 | C2 | 120.8(5) |  | C16 | C15 | C14 | 120.4(4) |
| C5 | C6 | C7 | 121.1(5) |  | C19 | C16 | C15 | 120.6(4) |
| C4 | C7 | C8 | 120.3(4) |  | C14 | C17 | C18 | 122.1(4) |
| C6 | C7 | C4 | 118.2(4) |  | C17 | C18 | C19 | 118.2(4) |
| C6 | C7 | C8 | 121.3(4) |  | C16 | C19 | C18 | 120.6(4) |
| C9 | C8 | C7 | 116.9(4) |  | C16 | C19 | C20 | 118.9(4) |
| C9 | C8 | C13 | 119.7(4) |  | C18 | C19 | C20 | 120.4(4) |
| C13 | C8 | C7 | 123.4(4) |  | O1 | C20 | O2 | 123.4(5) |
| C8 | C9 | C10 | 121.4(4) |  | O1 | C20 | C19 | 122.9(5) |
| C11 | C10 | C9 | 118.8(5) |  | O2 | C20 | C19 | 113.6(4) |
| C12 | C11 | C10 | 120.8(5) |  |  |  |  |  |

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| Table 6 Hydrogen Bonds for Gellman186\_sq. | | | | | | |
| **D** | **H** | **A** | **d(D-H)/Å** | **d(H-A)/Å** | **d(D-A)/Å** | **D-H-A/°** |
| N1 | H1A | Cl11 | 0.91 | 2.37 | 3.179(5) | 148.4 |
| N1 | H1B | Cl1 | 0.91 | 2.24 | 3.121(4) | 164.2 |
| N1 | H1C | Cl12 | 0.91 | 2.35 | 3.160(5) | 147.6 |

11-X,-1/2+Y,3/2-Z; 21-X,1/2+Y,3/2-Z

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| Table 7 Torsion Angles for Gellman186\_sq. | | | | | | | | | | |
| **A** | **B** | **C** | **D** | **Angle/˚** |  | **A** | **B** | **C** | **D** | **Angle/˚** |
| N1 | C1 | C2 | C3 | -78.1(7) |  | C9 | C10 | C11 | C12 | -1.6(7) |
| N1 | C1 | C2 | C5 | 100.6(7) |  | C10 | C11 | C12 | C13 | 1.7(7) |
| C1 | C2 | C3 | C4 | 178.8(5) |  | C11 | C12 | C13 | C8 | -0.3(7) |
| C1 | C2 | C5 | C6 | -179.5(6) |  | C11 | C12 | C13 | C14 | -178.3(4) |
| C2 | C3 | C4 | C7 | 0.2(8) |  | C12 | C13 | C14 | C15 | 137.7(5) |
| C2 | C5 | C6 | C7 | 1.2(8) |  | C12 | C13 | C14 | C17 | -38.2(6) |
| C3 | C2 | C5 | C6 | -0.8(9) |  | C13 | C8 | C9 | C10 | 1.3(7) |
| C3 | C4 | C7 | C6 | 0.1(7) |  | C13 | C14 | C15 | C16 | -177.5(4) |
| C3 | C4 | C7 | C8 | -175.0(5) |  | C13 | C14 | C17 | C18 | 176.7(4) |
| C4 | C7 | C8 | C9 | 116.5(5) |  | C14 | C15 | C16 | C19 | 2.0(7) |
| C4 | C7 | C8 | C13 | -60.1(6) |  | C14 | C17 | C18 | C19 | -0.3(6) |
| C5 | C2 | C3 | C4 | 0.1(8) |  | C15 | C14 | C17 | C18 | 0.7(6) |
| C5 | C6 | C7 | C4 | -0.8(8) |  | C15 | C16 | C19 | C18 | -1.6(7) |
| C5 | C6 | C7 | C8 | 174.3(5) |  | C15 | C16 | C19 | C20 | 176.1(4) |
| C6 | C7 | C8 | C9 | -58.5(6) |  | C16 | C19 | C20 | O1 | 16.0(8) |
| C6 | C7 | C8 | C13 | 124.9(5) |  | C16 | C19 | C20 | O2 | -164.3(4) |
| C7 | C8 | C9 | C10 | -175.5(4) |  | C17 | C14 | C15 | C16 | -1.6(6) |
| C7 | C8 | C13 | C12 | 175.4(4) |  | C17 | C18 | C19 | C16 | 0.7(6) |
| C7 | C8 | C13 | C14 | -6.8(7) |  | C17 | C18 | C19 | C20 | -177.0(4) |
| C8 | C9 | C10 | C11 | 0.1(7) |  | C18 | C19 | C20 | O1 | -166.2(5) |
| C8 | C13 | C14 | C15 | -40.1(6) |  | C18 | C19 | C20 | O2 | 13.5(6) |
| C8 | C13 | C14 | C17 | 144.0(4) |  | C21 | O2 | C20 | O1 | -3.2(7) |
| C9 | C8 | C13 | C12 | -1.1(6) |  | C21 | O2 | C20 | C19 | 177.1(4) |
| C9 | C8 | C13 | C14 | 176.7(4) |  |  |  |  |  |  |

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| Table 8 Hydrogen Atom Coordinates (Å×104) and Isotropic Displacement Parameters (Å2×103) for Gellman186\_sq. | | | | |
| **Atom** | ***x*** | ***y*** | ***z*** | **U(eq)** |
| H1A | 6033.79 | 2890.2 | 7606.8 | 45 |
| H1B | 5275.21 | 4029.41 | 7443.2 | 45 |
| H1C | 6007.9 | 5296.7 | 7661.43 | 45 |
| H1D | 5572.79 | 5768.33 | 6475.35 | 57 |
| H1E | 5405.41 | 3214.44 | 6367.91 | 57 |
| H3 | 6989.57 | 6986.91 | 6904.97 | 44 |
| H4 | 8234.74 | 6383.26 | 6796.53 | 35 |
| H5 | 6399.98 | 836.42 | 6231.32 | 48 |
| H6 | 7630.51 | 288.28 | 6105.03 | 42 |
| H9 | 9009.61 | 365.62 | 7128.49 | 34 |
| H10 | 10318.22 | -317.72 | 7238.06 | 40 |
| H11 | 10964.86 | 1835.01 | 6608.54 | 35 |
| H12 | 10308.08 | 4513.2 | 5840.58 | 37 |
| H15 | 7831.5 | 4263.14 | 5101.63 | 35 |
| H16 | 7257.95 | 6959.66 | 4286.88 | 33 |
| H17 | 9777.43 | 7916.42 | 5752.12 | 30 |
| H18 | 9215.57 | 10599.06 | 4912.48 | 32 |
| H21A | 7804.79 | 12747.57 | 2793.4 | 53 |
| H21B | 8389.83 | 14580.49 | 3211.25 | 53 |
| H21C | 7555.38 | 14318.3 | 3339.89 | 53 |