# A Key *n→π\** Interaction in *N*-Acyl Homoserine Lactones

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## Contents

**General Experimental.** Commercial chemicals were of reagent grade or better, and were used without further purification. All chemicals were obtained from Sigma–Aldrich (St. Louis, MO). Anhydrous $CH_2Cl_2$ was obtained from CYCLE-TAINER® solvent delivery systems (J. T. Baker, Phillipsburg, NJ). Reactions were monitored by thin-layer chromatography with visualization by UV light or staining with $KMnO_4$. Flash chromatography was performed with columns of silica gel 60, 230–400 mesh (Silicycle, Québec City, Canada). The removal of solvents and other volatile materials "under reduced pressure" refers to the use of a rotary evaporator at water-aspirator pressure (<20 torr) and a water bath of <45 °C.

**Instrumentation.** NMR spectra were acquired at ambient temperature with a Bruker DMX 400 MHz spectrometer ($^1$H, 400 MHz; $^{13}$C, 100 MHz) in the National Magnetic Resonance Facility at Madison (NMRFAM). $^{13}$C spectra were proton-decoupled. Mass spectrometry was performed with a Micromass LCT (electrospray ionization, ESI) instrument in the Mass Spectrometry Facility of the Department of Chemistry at the University of Wisconsin–Madison. X-Ray diffraction data were collected in the Molecular Structure Laboratory of the Department of Chemistry at the University of Wisconsin–Madison on a Bruker Quazar SMART APEXII diffractometer.
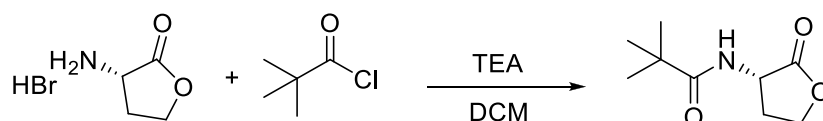


**Synthesis of *N*-trimethylacetyl homoserine lactone (1).** (*S*)-(-)-α-Amino-γ-butyrolactone hydrobromide (0.10 g, 0.55 mmol) was dissolved in 10 mL of anhydrous DCM with TEA (0.15 mL, 1.1 mmol). Trimethylacetylchloride (0.65 mL, 0.55 mmol) was added dropwise, and the resulting mixture was stirred at room temperature overnight. The mixture was then extracted with aqueous hydrochloric acid, followed by saturated aqueous sodium bicarbonate. The organic portion was then dried over anhydrous sodium sulfate, and solvent was removed under reduced pressure. Purification was achieved using silica gel chromatography with 4% v/v methanol in DCM. $^1$H NMR (CDCl$_3$) δ 6.21 (s, 1H), 4.47 (m, 2H), 4.28 (m, 1H), 2.84 (m, 1H), 2.11 (m, 1H), 1.22 (s, 9H); $^{13}$C NMR δ 179.1, 175.6, 66.0, 49.3, 38.6, 30.5, 27.4; ESI–MS: [M + H]$^+$ calculated 186.1125, found 186.1131.
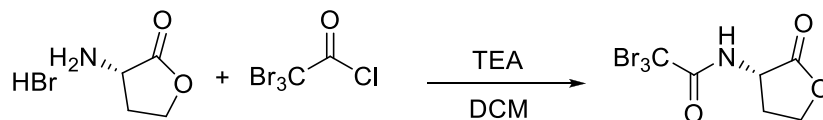


**Synthesis of *N*-tribromoacetyl homoserine lactone (2).** (*S*)-(-)-α-Amino-γ-butyrolactone hydrobromide (0.50 g, 2.8 mmol) was dissolved in 20 mL of anhydrous DCM containing TEA (1.15 mL, 8.25 mmol). Tribromoacetylchloride (0.53 mL, 2.75 mmol) was added dropwise, and the resulting mixture was stirred at room temperature overnight. The mixture was then extracted with aqueous hydrochloric acid, followed by saturated aqueous sodium bicarbonate. The organic portion was then dried over anhydrous sodium sulfate, and solvent was removed under reduced pressure. Purification was achieved using silica gel chromatography with 4% v/v methanol in DCM. $^1$H NMR (CDCl$_3$) δ 7.35 (s, 1H), 4.55 (m, 2H), 4.36 (m, 1H), 2.98 (m, 1H), 2.27 (m, 1H);

$^{13}C$ NMR $\delta$ 174.1, 163.1, 66.4, 51.2, 33.9, 29.8; ESI–MS: $[M + NH_4]^+$ calculated 394.8237, found 394.8229.

**Structure determination by X-ray diffraction analysis.** Compounds were dissolved in hexane with a minimal amount of DCM. Slow evaporation afforded diffraction quality crystals in approximately three days. Crystals were 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. Crystal evaluation and data collection were performed on a Bruker SMART APEXII diffractometer with Cu $K_\alpha$ ($\lambda$ = 1.54178 Å) radiation for **1** and Mo $K_\alpha$ ($\lambda$ = 0.71073 Å) for **2**. Data were collected by using the full-sphere data collection routine to a resolution of 0.80 Å. The intensity data was then corrected for Lorentz and polarization effects. Absorption was corrected analytically. Structure solution by direct methods was carried out using SHELXTL V.6.10.[S1] Refinement was performed using the olex2.refine refinement package using Gauss-Newton minimization.[S2] All non-hydrogen atoms were refined anisotropically. The final difference Fourier maps were featureless.

**Computational methodology.** Preferred conformations were determined by optimizing the respective compounds at the B3LYP/6-311+G(2d,p) level of theory as implemented by Gaussian 09.[S3] Frequency calculations of optimized structures yielded no imaginary frequencies, indicating a true minimum on the potential energy surface. Energies were corrected by the zero-point vibrational energy. Optimized geometries were subjected to analysis by NBO 5.9 at the B3LYP/6-311+G(2d,p) level of theory implemented in Gaussian 09.[S4]

**References**

(S1) Sheldrick, G. M. *Acta Cryst.* **2008**, *A64*, 112-122.

(S2) Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *J. Appl. Cryst.* **2009**, *42*, 339-341.

(S3) Gaussian 09, Revision **A.1**, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2009.

(S4) NBO 5.9. Glendening, E. D.; Badenhoop, J. k.; Reed, A. E.; Carpenter, J. E.; Bohmann, J. A.; Morales, C. M.; Weinhold, F. Theoretical Chemistry Institute, University of Wisconsin-Madison, Madison, WI, 2012.
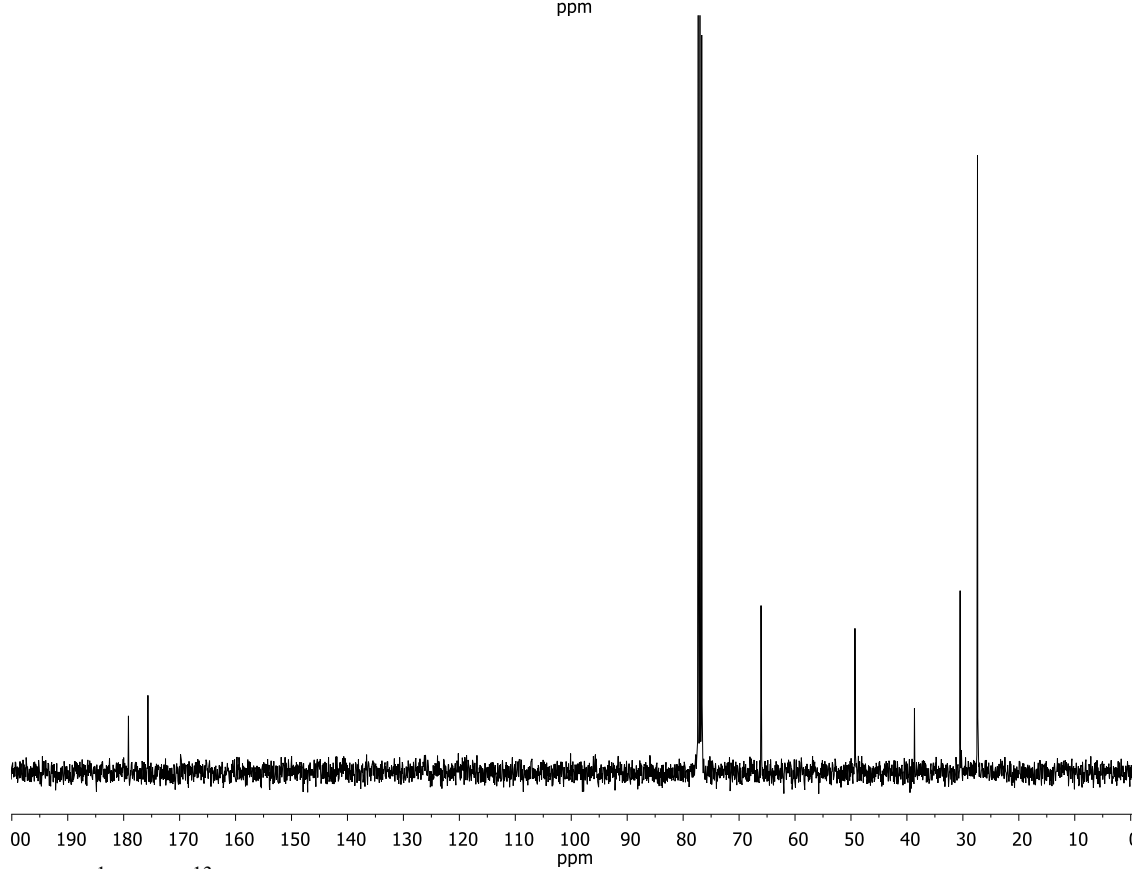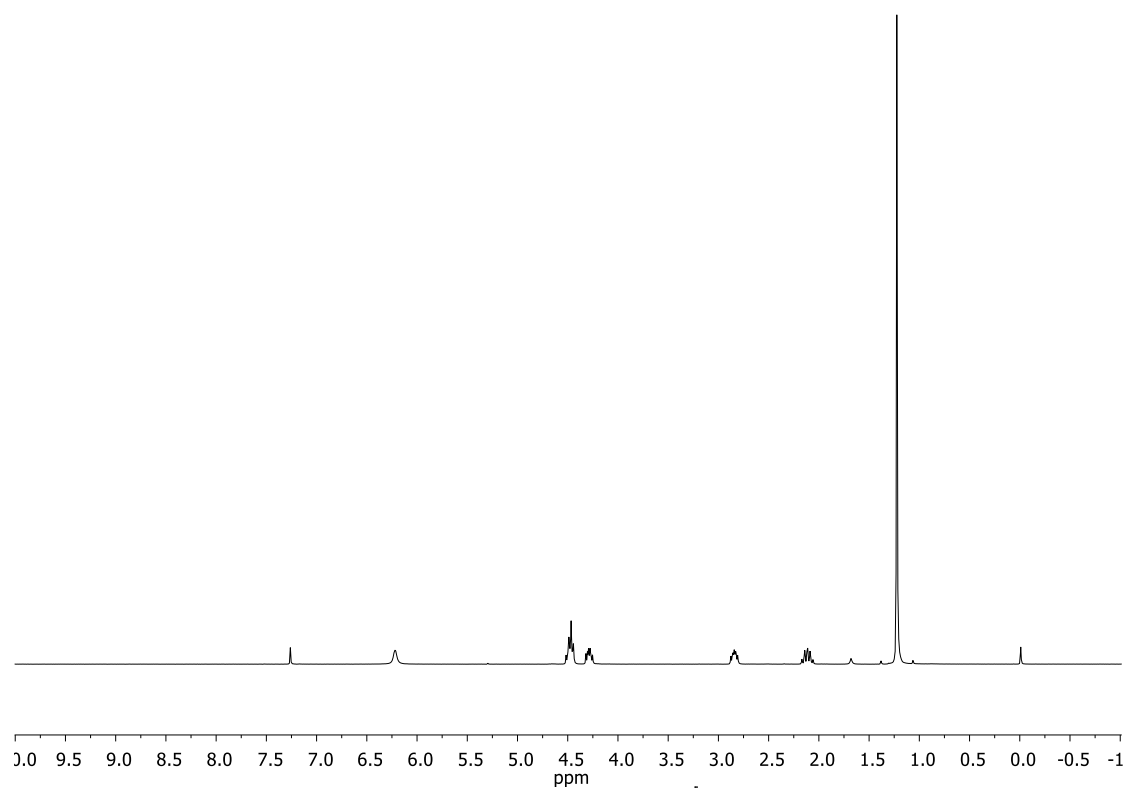
**Figure S1.** ¹H and ¹³C NMR spectra of *N*-trimethylacetyl homoserine lactone (**1**) in CDCl₃.
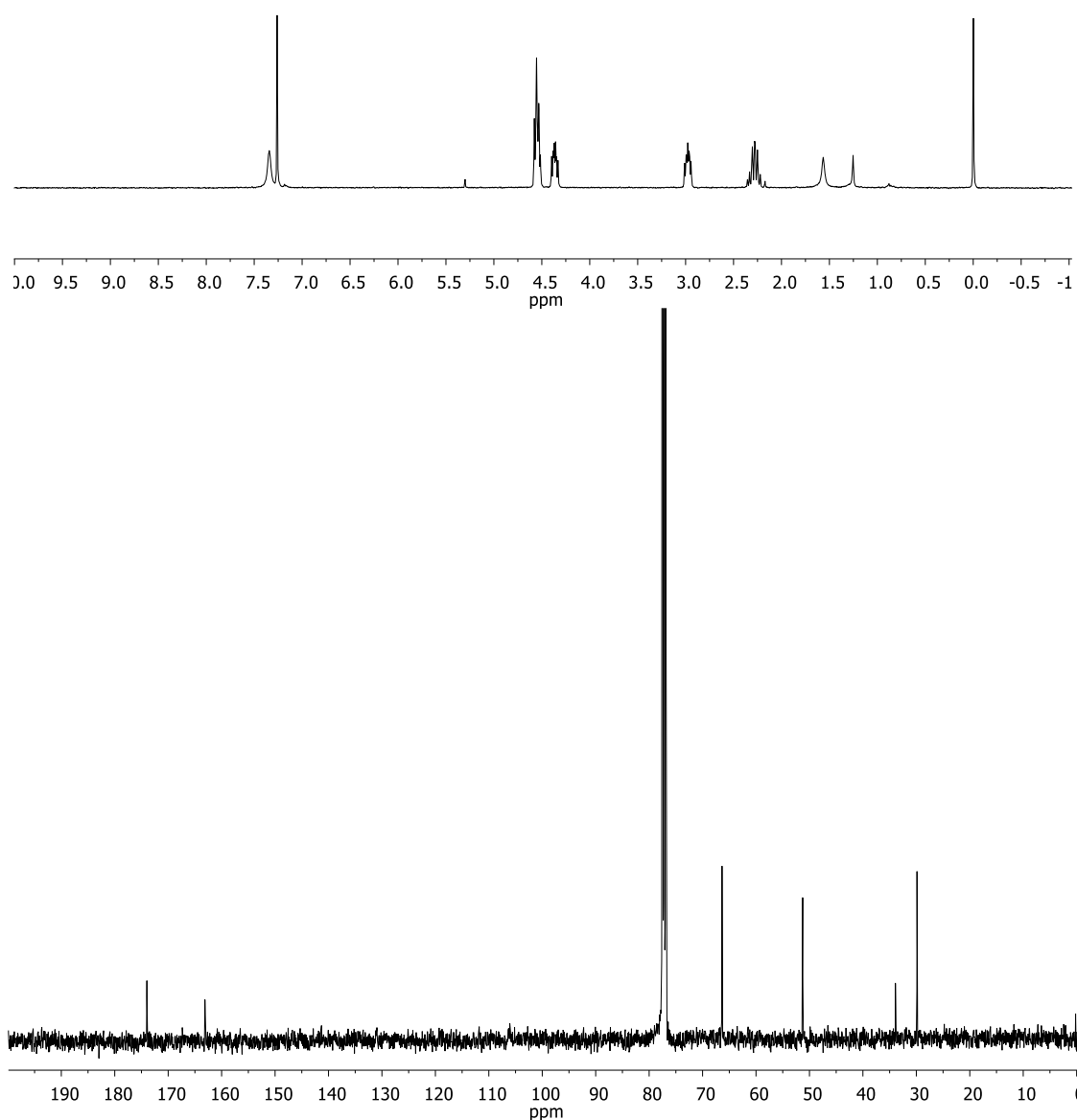
**Figure S2.** $^1H$ and $^{13}C$ NMR spectra of *N*-tribromoacetyl homoserine lactone (**2**) in CDCl$_3$/H$_2$O.

**Table S1.** Crystal data and structure refinement for **1**.

| | |
|---|---|
| Identification code | raines66 |
| Empirical formula | $C_9H_{10}NO_3$ |
| Formula weight | 185.22 |
| Temperature/K | 100.01 |
| Crystal system | monoclinic |
| Space group | $P2_1$ |
| $a$/Å | 5.9595(4) |
| $b$/Å | 9.2235(10) |
| $c$/Å | 9.2066(6) |
| $\alpha$/° | 90 |
| $\beta$/° | 102.719(4) |
| $\gamma$/° | 90 |
| Volume/Å$^3$ | 493.65(7) |
| $Z$ | 2 |
| $\rho_{calc}$ (mg/mm$^3$) | 1.2460 |
| m/mm$^{-1}$ | 0.771 |
| $F_{000}$ | 200.7 |
| Crystal size/mm$^3$ | 1.942 × 0.371 × 0.348 |
| $2\Theta$ range for data collection | 9.84 to 145.38° |
| Index ranges | $-7 \leq h \leq 7$, $-8 \leq k \leq 10$, $-11 \leq l \leq 11$ |
| Reflections collected | 10374 |
| Independent reflections | 1721[$R_{int}$ = 0.0277] |
| Data/restraints/parameters | 1721/0/120 |
| Goodness-of-fit on $F^2$ | 1.613 |
| Final $R$ indexes [$I \geq 2\sigma_I$] | $R_1$ = 0.0583 |
| Final $R$ indexes [all data] | $R_1$ = 0.0584, w$R_2$ = 0.1605 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.35/–0.67 |
| Flack parameter | –0.0(2) |

**Table S2.** Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for **1**. $U_{eq}$ is defined as $^1/_3$ of the trace of the orthogonalized $U_{IJ}$ tensor.

| Atom | $x$ | $y$ | $z$ | $U_{eq}$ |
|---|---|---|---|---|
| O1 | 1617(2) | 5131.8(17) | 8378.8(15) | 22.9(4) |
| O2 | 4374(2) | 4238.6(17) | 11934.2(14) | 19.6(4) |
| O3 | 679(2) | 4873.8(17) | 11438.7(15) | 20.9(4) |
| N1 | 243(3) | 2940(2) | 8815.7(16) | 17.2(4) |
| C1 | 2178(3) | 4079(2) | 11210.1(18) | 14.5(4) |
| C6 | -1304(3) | 4122(2) | 6399(2) | 17.8(4) |
| C4 | 5810(3) | 3099(3) | 11505(2) | 22.5(5) |
| C2 | 1936(3) | 2756(2) | 10196.3(19) | 16.4(4) |
| C5 | 319(3) | 4115(2) | 7953(2) | 16.2(4) |
| C3 | 4404(3) | 2486(2) | 10051(2) | 24.2(5) |
| C7 | -2932(4) | 2842(3) | 6089(2) | 32.0(6) |
| C8 | 239(5) | 4154(5) | 5288(2) | 58.8(12) |
| C9 | -2765(7) | 5496(4) | 6285(4) | 70.4(15) |

**Table S3.** Anisotropic displacement parameters ($\text{Å}^2 \times 10^3$) for **1**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+...+2hka{\times}b{\times}U_{12}]$.

| Atom | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|---|---|---|---|---|---|---|
| O1 | 26.0(7) | 20.1(9) | 19.9(6) | -8.5(6) | -0.6(5) | 0.5(6) |
| O2 | 16.1(6) | 19.3(8) | 21.5(6) | 0.2(5) | -0.2(5) | -3.6(6) |
| O3 | 18.6(6) | 20.0(9) | 24.9(7) | 2.0(6) | 6.6(5) | -1.5(6) |
| N1 | 17.2(7) | 15.4(9) | 16.5(7) | -2.7(6) | -1.7(6) | 0.9(6) |
| C1 | 14.9(8) | 11.7(11) | 16.1(8) | -2.8(7) | 1.9(6) | 1.9(7) |
| C6 | 18.3(8) | 16.1(10) | 17.1(8) | 1.4(8) | -0.1(7) | 0.8(7) |
| C4 | 17.5(8) | 28.1(13) | 20.5(9) | 4.0(8) | 1.5(7) | -3.0(8) |
| C2 | 16.9(8) | 15.1(11) | 15.4(8) | 0.6(7) | -0.3(6) | 1.0(7) |
| C5 | 13.4(7) | 16.8(11) | 17.1(8) | 1.0(7) | 0.7(6) | -0.2(7) |
| C3 | 23.3(9) | 27.2(13) | 19.9(9) | 12.8(9) | 0.2(7) | -5.8(9) |
| C7 | 32.3(9) | 38.4(15) | 19.8(9) | -16.5(11) | -6.3(7) | 4.6(9) |
| C8 | 37.9(12) | 121(4) | 17.6(10) | -37.3(19) | 6.9(9) | -5.7(15) |
| C9 | 88(2) | 34.8(19) | 58(2) | 35.2(19) | -50.1(19) | -21.9(15) |

**Table S4.** Bond lengths for **1.**

| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|------|------|----------|------|------|----------|
| O1 | C5 | 1.224(3) | C6 | C5 | 1.541(2) |
| O2 | C1 | 1.340(2) | C6 | C7 | 1.515(3) |
| O2 | C4 | 1.464(3) | C6 | C8 | 1.518(3) |
| O3 | C1 | 1.209(2) | C6 | C9 | 1.528(3) |
| N1 | C2 | 1.448(2) | C4 | C3 | 1.523(3) |
| N1 | C5 | 1.350(3) | C2 | C3 | 1.526(2) |
| C1 | C2 | 1.524(3) |    |    |          |

**Table S5.** Bond angles for **1.**

| Atom | Atom | Atom | Angle/° | Atom | Atom | Atom | Angle/° |
|------|------|------|---------|------|------|------|---------|
| C4 | O2 | C1 | 110.61(15) | C9 | C6 | C8 | 111.0(3) |
| C5 | N1 | C2 | 120.19(16) | C3 | C4 | O2 | 105.21(14) |
| O3 | C1 | O2 | 121.68(17) | C1 | C2 | N1 | 113.43(16) |
| C2 | C1 | O2 | 110.06(15) | C3 | C2 | N1 | 116.16(14) |
| C2 | C1 | O3 | 128.17(15) | C3 | C2 | C1 | 102.78(15) |
| C7 | C6 | C5 | 114.62(17) | N1 | C5 | O1 | 121.84(16) |
| C8 | C6 | C5 | 106.04(15) | C6 | C5 | O1 | 121.16(18) |
| C8 | C6 | C7 | 110.2(2) | C6 | C5 | N1 | 117.01(17) |
| C9 | C6 | C5 | 107.40(16) | C2 | C3 | C4 | 102.55(15) |
| C9 | C6 | C7 | 107.6(2) |    |    |    |          |

**Table S6.** Hydrogen atom coordinates ($Å \times 10^4$) and isotropic displacement parameters ($Å^2 \times 10^3$) for **1.**

| Atom | $x$ | $y$ | $z$ | $U_{eq}$ |
|---|---|---|---|---|
| H1 | -838(3) | 2284(2) | 8538.1(16) | 20.6(5) |
| H4a | 7282(3) | 3505(3) | 11358(2) | 26.9(6) |
| H4b | 6146(3) | 2336(3) | 12278(2) | 26.9(6) |
| H2 | 1450(3) | 1918(2) | 10743.6(19) | 19.7(5) |
| H3a | 4739(3) | 3003(2) | 9181(2) | 29.0(6) |
| H3b | 4704(3) | 1438(2) | 9959(2) | 29.0(6) |
| H7a | -2052(5) | 1939(3) | 6290(20) | 48.0(8) |
| H7b | -4040(20) | 2898(12) | 6733(17) | 48.0(8) |
| H7c | -3760(30) | 2861(13) | 5044(7) | 48.0(8) |
| H8a | 1280(50) | 4980(20) | 5500(30) | 88.2(18) |
| H8c | 1140(50) | 3256(19) | 5370(30) | 88.2(18) |
| H8b | -709(6) | 4240(40) | 4277(4) | 88.2(18) |
| H9a | -3510(50) | 5544(19) | 7130(20) | 106(2) |
| H9b | -1780(12) | 6348(4) | 6290(40) | 106(2) |
| H9c | -3940(40) | 5477(17) | 5356(18) | 106(2) |

**Table S7.** Crystal data and structure refinement for **2**.

| | |
|---|---|
| Identification code | Raines67 |
| Empirical formula | $C_6H_6NO_3Br_3$ |
| Formula weight | 379.83 |
| Temperature/K | 100.01 |
| Crystal system | orthorhombic |
| Space group | $P2_12_12_1$ |
| $a$/Å | 9.559(4) |
| $b$/Å | 9.933(4) |
| $c$/Å | 10.094(4) |
| $\alpha$/° | 90 |
| $\beta$/° | 90 |
| $\gamma$/° | 90 |
| Volume/Å$^3$ | 958.4(6) |
| $Z$ | 4 |
| $\rho_{calc}$ (mg/mm$^3$) | 2.6321 |
| m/mm$^{-1}$ | 12.598 |
| $F_{000}$ | 709.4 |
| Crystal size/mm$^3$ | 0.463 × 0.37 × 0.048 |
| Radiation | MoKα ($\lambda$ = 0.71073) |
| $2\Theta$ range for data collection | 5.76 to 61.04° |
| Index ranges | $-13 \le h \le 13, -14 \le k \le 14, -14 \le l \le 14$ |
| Reflections collected | 22866 |
| Independent reflections | 2931[$R_{int}$ = 0.0611] |
| Data/restraints/parameters | 2931/0/117 |
| Goodness-of-fit on $F^2$ | 0.602 |
| Final $R$ indexes [$I \ge 2\sigma_I$] | $R_1$ = 0.0229 |
| Final $R$ indexes [all data] | $R_1$ = 0.0280, $wR_2$ = 0.0494 |
| Largest diff. peak/hole / e Å$^{-3}$ | 1.44/−0.78 |
| Flack parameter | 0.033(15) |

**Table S8.** Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for **2**. $U_{eq}$ is defined as $^1/_3$ of the trace of the orthogonalized $U_{IJ}$ tensor.

| Atom | $x$ | $y$ | $z$ | $U_{eq}$ |
|---|---|---|---|---|
| Br1 | -583.9(3) | -967.5(3) | -3272.6(4) | 11.56(7) |
| Br2 | -2246.3(4) | -1198.7(4) | -5951.1(4) | 13.19(7) |
| Br3 | -3792.9(3) | -1710.5(3) | -3241.8(4) | 12.12(7) |
| O1 | -1277(3) | -3972(2) | -3136(2) | 11.7(4) |
| O2 | -3692(3) | -5885(3) | -3465(3) | 19.3(6) |
| N1 | -2065(3) | -4169(3) | -5233(3) | 10.3(5) |
| O3 | -2004(3) | -7403(3) | -3748(3) | 15.5(5) |
| C3 | -1975(4) | -5613(3) | -5262(3) | 9.8(6) |
| C5 | -514(4) | -6238(3) | -5248(4) | 11.4(6) |
| C1 | -2039(4) | -1947(3) | -4195(3) | 8.4(6) |
| C2 | -1731(3) | -3466(3) | -4154(4) | 8.5(6) |
| C4 | -794(4) | -7602(3) | -4606(4) | 14.1(7) |
| C6 | -2679(4) | -6267(4) | -4052(4) | 13.3(6) |

**Table S9.** Anisotropic displacement parameters ($\text{Å}^2 \times 10^3$) for **2**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a*^2U_{11}+...+2hka \times b \times U_{12}]$.

| Atom | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|---|---|---|---|---|---|---|
| Br1 | 11.58(14) | 9.94(14) | 13.15(16) | -1.59(11) | -2.62(14) | 0.08(13) |
| Br2 | 19.54(17) | 11.21(14) | 8.82(15) | 2.69(13) | -1.42(13) | 2.63(13) |
| Br3 | 9.75(14) | 13.06(14) | 13.54(16) | 2.52(12) | 1.67(14) | 1.22(14) |
| O1 | 15.5(11) | 11.7(10) | 8.0(11) | 1.3(10) | -3.8(10) | -0.9(10) |
| O2 | 15.6(12) | 22.4(13) | 19.9(15) | -3.6(11) | 7.2(12) | -0.7(11) |
| N1 | 15.4(14) | 7.1(12) | 8.4(13) | -1.1(10) | -2.3(11) | 0.6(10) |
| O3 | 18.6(14) | 14.3(12) | 13.7(13) | -1.8(10) | 3.2(10) | 3.6(10) |
| C3 | 13.5(15) | 7.8(13) | 8.2(15) | -3.3(12) | -1.4(13) | -0.1(12) |
| C5 | 13.1(14) | 8.6(13) | 12.6(16) | 0.3(13) | 3.8(13) | 0.7(12) |
| C1 | 11.5(14) | 8.8(13) | 4.9(14) | 1.0(11) | -0.6(11) | 0.3(11) |
| C2 | 8.0(13) | 5.6(13) | 11.8(16) | 1.8(11) | 1.4(12) | 2.6(12) |
| C4 | 18.0(17) | 8.4(14) | 15.8(18) | -0.1(13) | 2.9(14) | 1.5(13) |
| C6 | 10.9(14) | 15.3(14) | 13.7(15) | -5.2(12) | -3.5(14) | 2.2(14) |

**Table S10.** Bond lengths for **2.**

| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|------|------|----------|------|------|----------|
| Br1 | C1 | 1.936(3) | O3 | C4 | 1.458(5) |
| Br2 | C1 | 1.932(3) | O3 | C6 | 1.336(4) |
| Br3 | C1 | 1.947(3) | C3 | C5 | 1.528(5) |
| O1 | C2 | 1.223(4) | C3 | C6 | 1.539(5) |
| O2 | C6 | 1.197(5) | C5 | C4 | 1.526(5) |
| N1 | C3 | 1.438(4) | C1 | C2 | 1.538(4) |
| N1 | C2 | 1.332(5) | | | |

**Table S11.** Bond angles for **2.**

| Atom | Atom | Atom | Angle/° | Atom | Atom | Atom | Angle/° |
|------|------|------|---------|------|------|------|---------|
| C2 | N1 | C3 | 121.6(3) | C2 | C1 | Br2 | 115.0(2) |
| C6 | O3 | C4 | 111.2(3) | C2 | C1 | Br3 | 105.7(2) |
| C5 | C3 | N1 | 117.4(3) | N1 | C2 | O1 | 123.8(3) |
| C6 | C3 | N1 | 112.3(3) | C1 | C2 | O1 | 119.6(3) |
| C6 | C3 | C5 | 102.8(3) | C1 | C2 | N1 | 116.5(3) |
| C4 | C5 | C3 | 101.8(3) | C5 | C4 | O3 | 105.7(3) |
| Br2 | C1 | Br1 | 108.75(16) | O3 | C6 | O2 | 123.0(3) |
| Br3 | C1 | Br1 | 108.65(16) | C3 | C6 | O2 | 127.8(3) |
| Br3 | C1 | Br2 | 108.57(16) | C3 | C6 | O3 | 109.1(3) |
| C2 | C1 | Br1 | 110.0(2) | | | | |

**Table S12.** Hydrogen atom coordinates ($Å\times10^4$) and isotropic displacement parameters ($Å^2\times10^3$) for **2.**

| Atom | $x$ | $y$ | $z$ | U(eq) |
|------|-----|-----|-----|-------|
| H1 | -2348(3) | -3738(3) | -5946(3) | 12.3(7) |
| H3 | -2469(4) | -5936(3) | -6075(3) | 11.8(7) |
| H5a | -138(4) | -6341(3) | -6156(4) | 13.7(7) |
| H5b | 146(4) | -5694(3) | -4714(4) | 13.7(7) |
| H4a | 26(4) | -7899(3) | -4083(4) | 16.9(8) |
| H4b | -997(4) | -8290(3) | -5289(4) | 16.9(8) |

**Table S13.** Cartesian coordinates of the optimized geometry of **1**. SCF Energy = –632.406154 Hartree.

| | | | |
|---|---|---|---|
| C | 2.79423600 | -1.14882200 | -0.51359800 |
| O | 2.89150600 | 0.27287300 | -0.76694000 |
| C | 1.38142100 | 0.06156300 | 1.04915900 |
| C | 2.03953700 | -1.30904900 | 0.81607500 |
| H | 2.24967500 | -1.58991700 | -1.34622100 |
| H | 3.81187600 | -1.53417600 | -0.48382100 |
| H | 1.68747100 | 0.48143200 | 2.00746500 |
| H | 2.73176200 | -1.53321900 | 1.62871700 |
| H | 1.30495200 | -2.10911800 | 0.76306200 |
| C | 2.00200000 | 0.96798100 | -0.03554900 |
| O | 1.78333200 | 2.13550500 | -0.18948300 |
| N | -0.07116000 | 0.10099100 | 1.03970900 |
| H | -0.52222200 | 0.63291800 | 1.76403000 |
| C | -0.78126300 | -0.22349000 | -0.07885300 |
| O | -0.21585200 | -0.69179800 | -1.05756100 |
| C | -2.30827900 | -0.01345200 | -0.06037200 |
| C | -2.95621700 | -1.40087900 | -0.23860700 |
| H | -2.73763100 | -2.05383400 | 0.61066900 |
| H | -4.04152100 | -1.29843500 | -0.31446500 |
| H | -2.58701000 | -1.88136400 | -1.14444200 |
| C | -2.65291700 | 0.88029300 | -1.26815400 |
| H | -3.73635000 | 1.00262000 | -1.34199000 |
| H | -2.20395000 | 1.87147900 | -1.16873400 |
| H | -2.28624500 | 0.43373100 | -2.19181300 |
| C | -2.83248300 | 0.63873200 | 1.22864600 |
| H | -3.91684400 | 0.75165400 | 1.16524300 |
| H | -2.62602800 | 0.02983400 | 2.11325800 |
| H | -2.41791100 | 1.63955600 | 1.38046500 |

**Table S14.** Cartesian coordinates of the optimized geometry of **2**. SCF Energy = 8235.128938 Hartree

| | | | |
|---|---|---|---|
| C | -4.07961800 | 1.20396900 | -0.52940700 |
| O | -4.24591900 | -0.21388400 | -0.76574000 |
| C | -2.70239000 | -0.05585800 | 1.02546300 |
| C | -3.29298900 | 1.34297800 | 0.78496000 |
| H | -3.53505000 | 1.61339600 | -1.37831300 |
| H | -5.07746000 | 1.63584500 | -0.48342600 |
| H | -3.00122700 | -0.44928700 | 1.99634900 |
| H | -3.95736400 | 1.60992200 | 1.60709300 |
| H | -2.52166400 | 2.10658800 | 0.71176000 |
| C | -3.38754700 | -0.94747200 | -0.03558700 |
| O | -3.23097500 | -2.12522500 | -0.17243000 |
| N | -1.25230700 | -0.16602400 | 0.98515100 |
| H | -0.78562500 | -0.66657100 | 1.72523500 |
| C | -0.55841700 | 0.15330100 | -0.12561400 |
| O | -1.06452400 | 0.60228500 | -1.13191900 |
| C | 0.99219000 | 0.00892500 | -0.04486300 |
| Br | 1.68377000 | 1.80645200 | 0.40784500 |
| Br | 1.60972100 | -1.27280000 | 1.33948900 |
| Br | 1.68218100 | -0.56302900 | -1.77486900 |