Supplementary Information (SI) for Journal of Materials Chemistry C.

Supporting Information

Polar-end 3,5-Diarylisoxazole Liquid Crystals with SmA and highly ordered CrE mesophases.

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Instrumentation, Spectral data and Equipments.

4-Hidroxybenzaldehyde, 1-bromooctane, potassium carbonate, 4-nitrobenzaldehyde, methyltriphenylphosphonium bromide, hydroxylamine hydrochloride, sodium acetate, sodium hypochlorite (5% in water), manganese (IV) oxide (activated, < 10 μm), tin(II) chloride dihydrate, acetonitrile, 1,4-dioxane, ethanol, dichloromethane and toluene were used without further purification from Sigma Aldrich Co. All other commercial solvents and reagents were used without further purification. The nuclear magnetic resonance spectra of hydrogen and carbon were recorded in a Bruker Ascend NMR with standard pulse sequences operating at 400 MHz for 1H nuclei and 100 MHz for 13C nuclei, using CDCl3 as a solvent. Chemical shifts were reported as values (ppm) relative to TMS (0.0 ppm). The NMR multiplicities brs, s, dd, t and m represent broad singlet, singlet, doublet of doublets, triplet and multiplet, respectively. The melting points and mesophase transition temperatures and textures of the samples were measured on a Mettler Toledo FP82HT Hot Stage FP90 Central Processor and DSC 2910 TA Instruments. CHN analyses were performed on a Perkin-Elmer 2400 CHN Elemental Analyzer. HRMS measurements were performed with a micro QTOF Q-III (Bruker Daltonics) mass spectrometer. The mass spectrometer was operated using ESI as ionization source. FT-IR spectra were obtained with a Shimadzu equipment operating in ATR mode.

Raman spectra were recorded with an Anton Paar-Cora 5001 with excitation source at 785 nm. Acquisition time and accumulations were adjusted accordingly to each sample. Offset and baseline corrections were applied when necessary. Theoretical calculations were performed using Gaussian package 09, basis set B3LYP, 6-31G(d,p) and applied the scalling factor 0.9722.

The X-Ray diffraction experiments were realized with the X`Pert-PRO (PANalytical) diffractometer system using the linear monochromatic CuKα1 beam ($\lambda = 1.5405$ Å), with an applied power of 1.2kVA. The scans were performed in continuous mode from 2° to 30° (2□ angle) and the diffracted radiation collected with the X'Celerator detector. Compounds **1**, **2** and **5** were placed on the TCU2000 - Temperature Control Unit (Anton Paar), which allows a precise control of the sample temperature during de measurement. The diffraction patterns were collected during the cooling from the isotropic phase.

Absorbance and emission spectra in solution were collected using an Ocean Optics spectrophotometer (Model USB4000) and a Hitachi fluorescence spectrophotometer (Model F-7000), respectively.

Electrical characterization was performed using a home-made cell consisting of two indium tin oxide (ITO) coated glass plates with sheet resistance of about 15 Ω/sq as electrodes separated by Mylar spacers of 8 μm and an active area of 1 μm^2. The *I/V* curves were collected at ambient atmosphere using a Keithley Series 2400 Source Measure Unit (SMU) equipped with a Mettler Toledo FP-82 hot stage to control the temperature. For ac impedance measurements, an Autolab Electrochemical Instruments was used over the frequency range of 0.1−106 Hz. The compounds were inserted by capillarity effect using the hot stage to heat the compounds until the isotropic phase.

X-ray photoelectron spectroscopy (XPS): Samples were analysed by XPS performed with a surface analysis station equipped with a hemispherical analyzer (SPHERA model). X-rays were produced with an aluminum anode (Al Kα radiation 1486.6 eV) operated at 15 kV and 15 mA (225 W). The survey spectrum was obtained with a 50 eV pass energy and 1 eV resolution. The base pressure in the analysis chamber was 1×10^{-9} mbar. Sample powders were put on a double-faced carbon adhesion tape for analysis.

Compounds **1**, **2**, **3** and **4** were synthesized and data are reported reference 1, while compound **5** was prepared according to the reference 2.[1,2]

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Data for byproduct **6** (3,5-bis(4-(octyloxy)phenyl)-1,2,4-oxadiazole): Yield: 2% (byproduct isolated by silica column and *n*-hexane:ethyl acetate 95:5 as solvent); yellow solid; mp Cr 92.9 N 102.7 I; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.18 – 8.13 (m, 2H); 8.13 – 8.08 (m, 2H); 7.07 – 6.99 (m, 4H); 4.10 – 4.02 (m, 4H); 1.90 – 1.79 (m, 4H); 1.56 – 1.25 (m, 20H); 0.96 – 0.87 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 175.35; 168.54; 162.72; 161.46; 130.00; 129.05; 119.37; 116.71; 114.91; 114.70; 68.33; 68.16; 31.83; 31.82; 29.37; 29.34; 29.25; 29.24; 29.21; 29.12; 26.04; 26.00; 22.67; 14.11. Elem. anal. calc. for $C_{30}H_{42}N_2O_3$, 478.67 g/mol: C 75.28, H 8.84, N 5.85, O 10.03; found: C 75.79, H 8.86, N 5.84, O 9.51.

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[1] a) Itamar L. Gonçalves, Rafaela R. da Rosa, Vera L. Eifler-Lima and Aloir A. Merlo, *Beilstein J. Org. Chem.* **2020**, *16*, 175-184. https://doi.org/10.3762/bjoc.16.20
b) da Rosa, R. R.; Isoxazolinas e isoxazóis como reais candidatos na preparação de cristais líquidos polares. Tese de Doutorado em Química, Universidade Federal do Rio Grande do Sul, Brasil, **2018**. [https://lume.ufrgs.br/handle/10183/180639].

[2] Vilela GD, da Rosa RR, Schneider PH, et al. Expeditious preparation of isoxazoles from Δ^2-isoxazolines as advanced intermediates for functional materials. Tetrahedron Letters. **2011** 2011/12/07/;52(49):6569-6572. doi: https://doi.org/10.1016/j.tetlet.2011.09.122

X-ray diffraction data

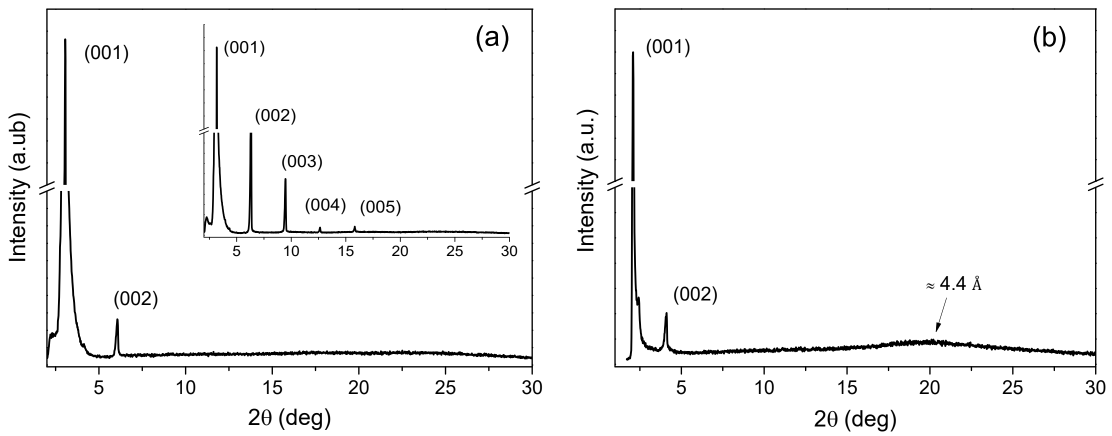


Figure S1. XRD patterns of (a) compound **1** in the SmA phase at 180 °C and CrE phase at 120 °C (inset); and (b) compound **2** in the SmA phase at 110 °C, illustrating the position related to the liquid-like order between the aliphatic chains in X-ray wide-angle region, and diffraction peaks in small-angle X-ray regions for structured layers smectic A and Crystal E mesophase.

Electrical Measurements

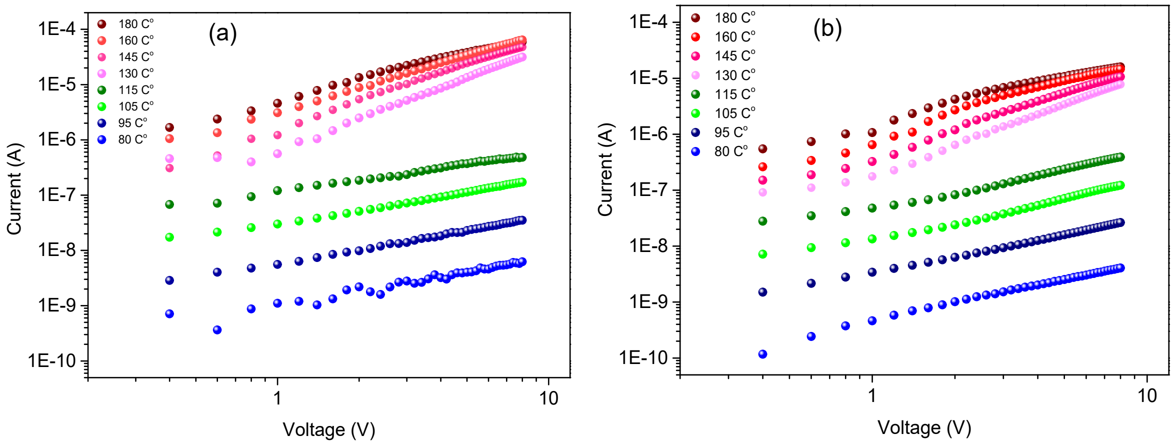


Figure S2. Log-log current × voltage measurements for **1** (left) and **3** (right) derivatives as a function of temperature.

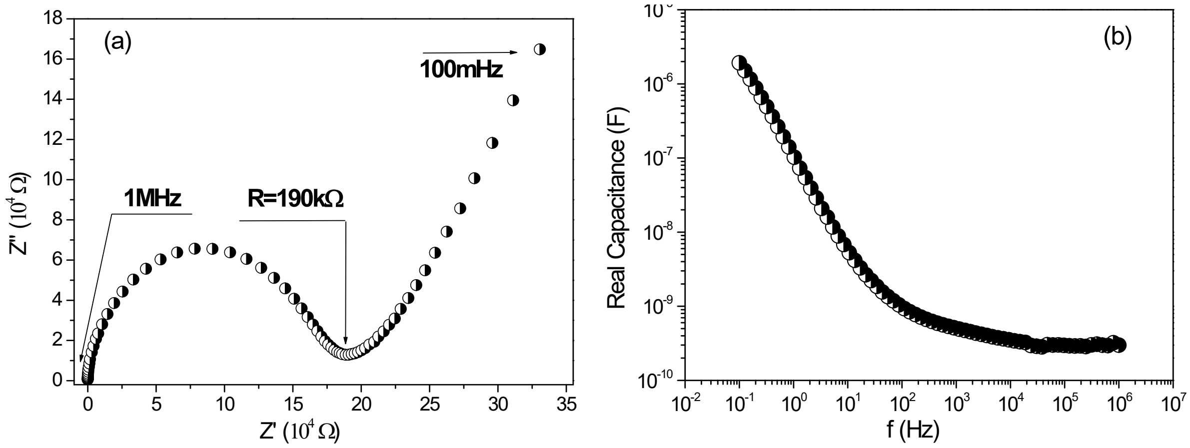
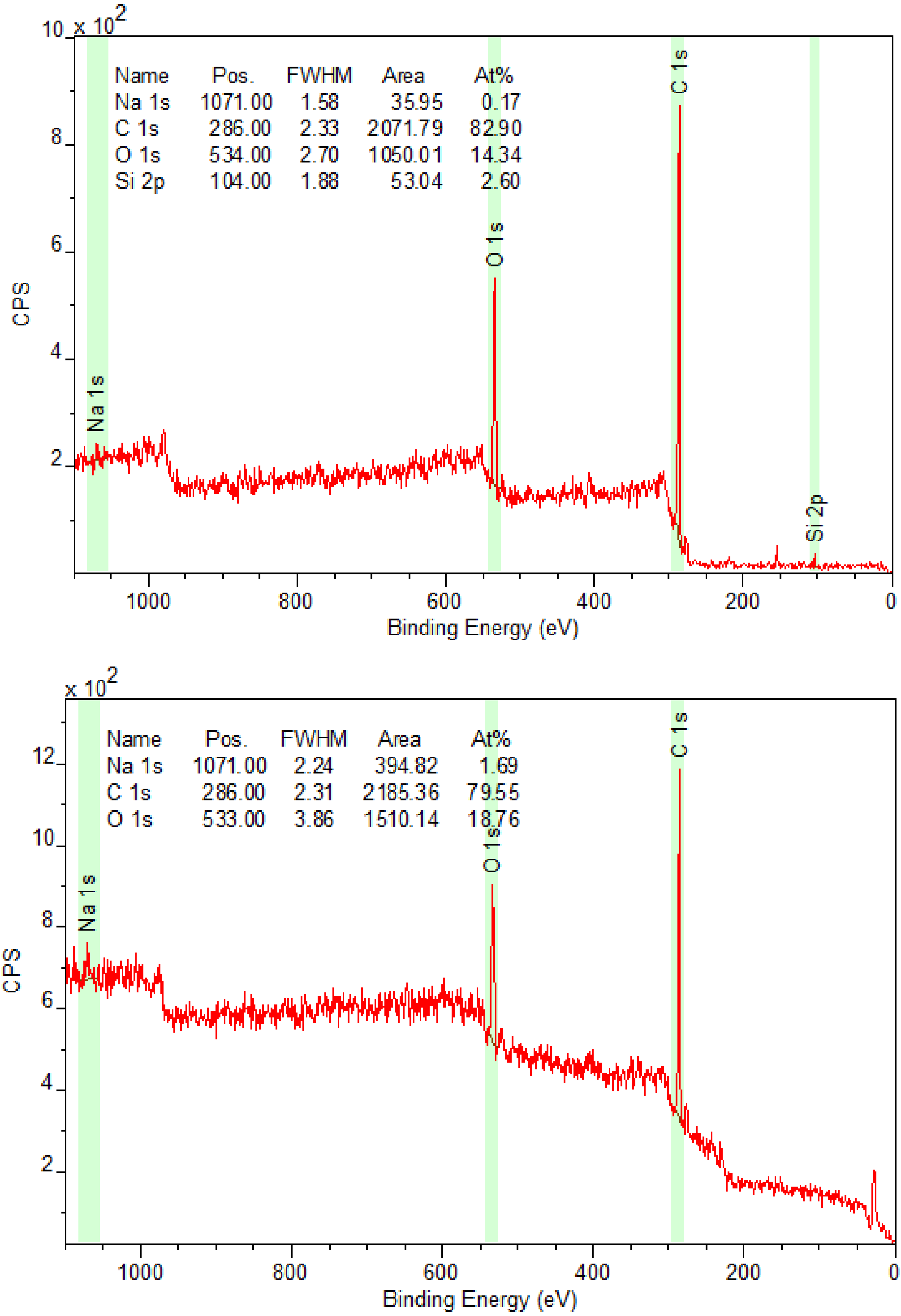


Figure S3. The complex impedance graph - Nyquist plot (Z″ vs Z′) and the capacitance as a function of the frequency in the CrE phase at 120ºC for compound **5** (bromine).

X-ray photoelectron spectroscopy (XPS)



Name	Pos.	FWHM	Area	At%
Na 1s	1071.00	1.58	35.95	0.17
C 1s	286.00	2.33	2071.79	82.90
O 1s	534.00	2.70	1050.01	14.34
Si 2p	104.00	1.88	53.04	2.60

Name	Pos.	FWHM	Area	At%
Na 1s	1071.00	2.24	394.82	1.69
C 1s	286.00	2.31	2185.36	79.55
O 1s	533.00	3.86	1510.14	18.76

Figure S4. X-ray photoelectron spectroscopy (XPS) spectra of a) Isoxazole liquid crystal **1** and b) isoxazole liquid crystal **2**. Very low content of sodium was found in **1** (0.17 %) and **2** (1.69 %). Silicon was detected in 2.60 % for **1**.

Raman spectroscopy data

Raman spectroscopy was conducted to the 3,5-diarylisoxazoles **1**, **2** and **5** to illustrate their molecular vibrational modes, being dominated by peaks arising from the aromatic rings and aliphatic polar groups, (Table 1 and Figure S4). The most intense peak originated from contributions of C-C stretching and C-H bending are slightly shifted for each compound arising at 1618, 1612 and 1613 cm^{-1}, for **1**, **2** and **5** respectively. The C-H in plane bending mode deformations related to the peak at 1455 cm^{-1} for 1 is shifted to 1452 cm^{-1} for **2** and **5**. On the other hand, no displacement was observed for the peak at 951 cm^{-1} assigned to out-of-plane C-H bending ring of the compounds according to the Figure S4. Also, it was observed less intense common peak at 819 cm^{-1} (C-H out-of-plane bending). In **1** the nitrobenzene signal can be seen at 1109 and 1347 cm^{-1}, assigned to C-N stretching plus ring breathing and NO_2 symmetric stretching, and in a modest peak at 1523 cm^{-1} (NO_2 antisymmetric stretching).[3,4] Also, the 853 cm^{-1} peak is attributed to NO_2 bending scissoring.[5] In **2** the NH_2 stretching modes (symmetric and antisymmetric) usually arise around ~3300 cm^{-1} are not seen in the **2**. On the other hand, NH_2 in-plane bending can be identify at 1573 cm^{-1} (usually expected at ~1620 cm^{-1}) and NH_2 out-of-plane bending at 729 cm^{-1} and 613 cm^{-1}.[6] The assignments of C–Br vibrations for compound **5** appear in the lower range of frequencies i.e. 650 – 200 cm^{-1} and with low intensity. The peak centered at 221 cm^{-1} was assigned to C-Br bending[7] and the pair at 1064 and 1071 cm^{-1} are 7 cm^{-1} shifted in relation to bromobenzene neat, which is related to the deformation bending in plane of C-H bond. In addition, can be noticed the increase in the intensity of 718 cm^{-1} peak which can be related to the crystallinity.

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[4] A. M. McCullagh, E. K. Gibson, S. F. Parker, K. Refson and D. Lennon, Physical Chemistry Chemical Physics, **2023**, 25, 25993-26005.

[5] D. Lin-Vien, N. B. Colthup, W. G. Fateley and J. G. Grasselli, in The Handbook of Infrared and Raman Characteristic Frequencies of Organic Molecules, eds. D. Lin-Vien, N.B. Colthup, W.G. Fateley and J.G. Grasselli, Academic Press, San Diego, **1991**, DOI: https://doi.org/10.1016/B978-0-08-057116-4.50017-1, 179-189.

[6] G. Ćirić-Marjanović, M. Trchová and J. Stejskal, Journal of Raman Spectroscopy, **2008**, 39, 1375-1387.

[7] S. Jeyavijayan, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, **2015**, 136, 890-899.

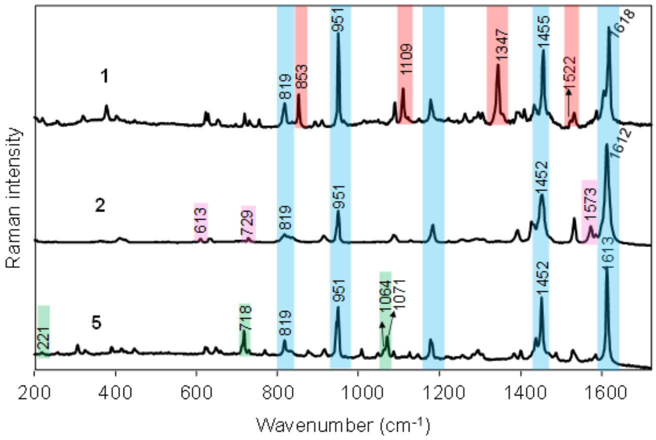

Figure S5. Raman spectra of compounds **1**, **2** and **5** in powder.

Table 1. Experimental and theoretical vibrational assignments for compound 5 obtained in powder.

Experimental	Theoretical	Assignment[a]
718	740	C-C Oop bending ring
818	851	C-H Oop bending
946	984	C-H Oop bending ring
950	988	C-H Oop bending ring
1177	1211	C-H ip bending ring
1181	1225	C-H ip bending
1437	1495	C-H ip bending, C=N stretching
1452	1511	C-H ip bending
1613	1678	C-C stretching, C-H ip bending

[a] Out-of-plane (Oop) and in plane (ip) vibrational modes.

Table 2. Data from theoretical calculations

Atomic Coordinates of 1

C	0.830656000	-4.303821000	0.000000000
C	0.341786000	-5.744754000	0.000000000
C	1.495116000	-6.755591000	0.000000000
C	1.017583000	-8.213177000	0.000000000
C	2.164250000	-9.231274000	0.000000000
C	1.688707000	-10.689124000	0.000000000
C	2.834392000	-11.708618000	0.000000000
C	2.350917000	-13.161886000	0.000000000
H	3.191037000	-13.863828000	0.000000000
H	1.739038000	-13.376017000	0.883623000
H	1.739038000	-13.376017000	-0.883623000
H	3.472481000	-11.535023000	-0.877160000
H	3.472481000	-11.535023000	0.877160000
H	1.049740000	-10.863017000	0.877645000
H	1.049740000	-10.863017000	-0.877645000
H	2.803122000	-9.058146000	-0.877749000
H	2.803122000	-9.058146000	0.877749000
H	0.378776000	-8.384490000	0.877717000
H	0.378776000	-8.384490000	-0.877717000
H	2.133522000	-6.584339000	-0.878208000
H	2.133522000	-6.584339000	0.878208000
H	-0.294940000	-5.898497000	0.879666000
H	-0.294940000	-5.898497000	-0.879666000
O	-0.318793000	-3.453226000	0.000000000
C	-0.141898000	-2.105281000	0.000000000
C	-1.314907000	-1.334996000	0.000000000
C	-1.240728000	0.049580000	0.000000000
C	0.000000000	0.709827000	0.000000000
C	1.164494000	-0.070742000	0.000000000
C	1.104195000	-1.461594000	0.000000000
H	2.025322000	-2.031210000	0.000000000
H	2.129838000	0.423726000	0.000000000
C	0.081443000	2.178010000	0.000000000
C	-0.984941000	3.128558000	0.000000000
C	-0.361622000	4.344690000	0.000000000
O	0.979333000	4.154208000	0.000000000
N	1.255099000	2.789770000	0.000000000
C	-0.840396000	5.723829000	0.000000000
C	0.072111000	6.794726000	0.000000000
C	-0.381021000	8.107958000	0.000000000
C	-1.753814000	8.347144000	0.000000000
C	-2.682492000	7.307068000	0.000000000
C	-2.220382000	5.998274000	0.000000000
H	-2.935852000	5.183114000	0.000000000
H	-3.740139000	7.537238000	0.000000000

N	-2.238264000	9.734655000	0.000000000
O	-3.456437000	9.914023000	0.000000000
O	-1.397263000	10.633429000	0.000000000
H	0.305552000	8.944858000	0.000000000
H	1.135832000	6.588482000	0.000000000
H	-2.045006000	2.933171000	0.000000000
H	-2.163405000	0.621488000	0.000000000
H	-2.271015000	-1.847218000	0.000000000
H	1.445549000	-4.101021000	-0.888482000
H	1.445549000	-4.101021000	0.888482000

Atomic Coordinates of 2

C	2.403155000	2.721530000	0.000000000
C	3.837642000	3.230286000	0.000000000
C	3.919122000	4.761572000	0.000000000
C	5.359863000	5.287617000	0.000000000
C	5.451871000	6.818258000	0.000000000
C	6.891951000	7.345090000	0.000000000
C	6.986138000	8.875812000	0.000000000
C	8.427600000	9.393320000	0.000000000
H	8.460805000	10.487619000	0.000000000
H	8.974011000	9.044347000	0.883594000
H	8.974011000	9.044347000	-0.883594000
H	6.455434000	9.270474000	-0.877107000
H	6.455434000	9.270474000	0.877107000
H	7.423506000	6.949973000	0.877591000
H	7.423506000	6.949973000	-0.877591000
H	4.920939000	7.213705000	-0.877695000
H	4.920939000	7.213705000	0.877695000
H	5.889583000	4.891332000	0.877640000
H	5.889583000	4.891332000	-0.877640000
H	3.389684000	5.157556000	-0.878124000
H	3.389684000	5.157556000	0.878124000
H	4.352654000	2.825023000	0.879517000
H	4.352654000	2.825023000	-0.879517000
O	2.447418000	1.294506000	0.000000000
C	1.275217000	0.599164000	0.000000000
C	1.393737000	-0.798221000	0.000000000
C	0.258123000	-1.595366000	0.000000000
C	-1.027711000	-1.028867000	0.000000000
C	-1.131499000	0.368970000	0.000000000
C	0.000000000	1.181327000	0.000000000
H	-0.121182000	2.257734000	0.000000000
H	-2.117374000	0.821121000	0.000000000
C	-2.234250000	-1.872672000	0.000000000
C	-2.321816000	-3.296513000	0.000000000
C	-3.665363000	-3.561087000	0.000000000
O	-4.340917000	-2.385709000	0.000000000
N	-3.436056000	-1.320895000	0.000000000
C	-4.452789000	-4.786415000	0.000000000

C	-5.858612000	-4.747717000	0.000000000
C	-6.609205000	-5.913383000	0.000000000
C	-5.981572000	-7.175138000	0.000000000
C	-4.572315000	-7.217695000	0.000000000
C	-3.830351000	-6.046898000	0.000000000
H	-2.746557000	-6.113453000	0.000000000
H	-4.065779000	-8.179301000	0.000000000
N	-6.721669000	-8.331866000	0.000000000
H	-6.276434000	-9.232428000	0.000000000
H	-7.725932000	-8.303654000	0.000000000
H	-7.694611000	-5.856402000	0.000000000
H	-6.361953000	-3.787151000	0.000000000
H	-1.513826000	-4.009953000	0.000000000
H	0.376493000	-2.674371000	0.000000000
H	2.387201000	-1.234047000	0.000000000
H	1.862977000	3.080291000	-0.888138000
H	1.862977000	3.080291000	0.888138000

Atomic Coordinates of 5

C	-5.482353000	0.007811000	-0.000031000
O	-4.429532000	-0.958380000	-0.000713000
C	-3.138680000	-0.527285000	-0.000685000
C	-2.159153000	-1.531657000	-0.001413000
C	-0.813739000	-1.194717000	-0.001441000
C	-0.401640000	0.148793000	-0.000739000
C	1.024938000	0.508680000	-0.000773000
N	1.399175000	1.777416000	-0.001304000
O	2.793403000	1.765338000	-0.001057000
C	3.236478000	0.485499000	-0.000491000
C	4.682520000	0.278376000	-0.000183000
C	5.562639000	1.373358000	-0.000297000
C	6.940700000	1.178136000	0.000006000
C	7.446528000	-0.120536000	0.000431000
C	6.594261000	-1.224385000	0.000550000
C	5.218431000	-1.020035000	0.000240000
H	4.557625000	-1.880895000	0.000320000
H	7.002424000	-2.228367000	0.000876000
Br	9.336271000	-0.394744000	0.000853000
H	7.615927000	2.025930000	-0.000082000
H	5.161555000	2.380482000	-0.000622000
C	2.160565000	-0.357412000	-0.000288000
H	2.170863000	-1.435283000	0.000255000
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C	-2.744458000	0.818401000	0.000011000
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C	-8.016570000	0.192714000	0.000418000

C	-9.356198000	-0.554220000	0.000178000
C	-10.574766000	0.376333000	0.000844000
C	-11.915037000	-0.369101000	0.000648000
C	-13.127403000	0.566732000	0.001260000
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H	-13.127987000	1.215354000	-0.882108000
H	-14.067023000	0.004974000	0.001152000
H	-11.961649000	-1.028294000	-0.876804000
H	-11.961427000	-1.029155000	0.877464000
H	-10.528018000	1.036378000	0.878909000
H	-10.528270000	1.037300000	-0.876541000
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H	-7.970245000	0.851677000	0.878943000
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H	-5.400470000	0.650956000	-0.888033000