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Accessory Publication

Novel Acentric Organic Solids with Nonlinear Optical and Ferroelectric Properties

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Experiment Section

X-ray Structure determinations: Single crystal X-ray diffraction measurements of **1-3** were carried out with a Bruker APEX II CCD diffractometer equipped with a graphite crystal monochromator. The lattice parameters were obtained by least-squares refinement of the diffraction data. All the measured independent reflections were used in the structural analysis, and semi-empirical absorption corrections were applied using the SADABS program. The program SAINT¹ was used for integration of the diffraction profiles. All the structures were solved by direct methods using the SHELXS program of the SHELX package and refined with SHELXL². All non-hydrogen atoms were located in successive difference Fourier syntheses. The final refinement was performed by full-matrix least-squares methods with anisotropic thermal parameters for all the non-hydrogen atoms based on F^2 . Except hydrogen atom bonded oxygen atom, the hydrogen atoms were first found in difference electron density maps, and then placed in the calculated sites and included in the final refinement in the riding model approximation with displacement parameters derived from the parent atoms to which they were bonded. Special computations for the crystal structure discussions were carried out with PLATON for Windows.³

Characterization of compounds of 1-3

Compound 1. m.p. 161–163 °C; ¹H NMR (400 MHz, CDCl₃): δ = 13.69 (br s, 1H), 8.78 (s, 1H), 8.47-8.45 (m, 1H), 7.93-7.91 (d, 1H), 7.80-7.68 (m, 3H), 7.41-7.15 (m, 4H), 5.14 (s, 1H), 3.35 (br s, 1H), 2.67 (br s, 1H), 2.14-1.71 (br m, 4H), 1.27-1.23 (br m, 4H); ¹³C NMR (100 MHz, CDCl₃): δ = 155.4, 150.3, 149.4, 136.3, 135.5, 132.0, 129.8, 128.9, 128.6, 126.6, 122.6, 120.5, 119.9, 115.2, 25.9, 24.0; IR (KBr): 3049 (w), 3029 (m), 2977 (m), 2956 (m), 2937 (m), 2917 (w), 2855 (br), 2545 (br), 1900 (w), 1803 (w), 1621 (s), 1598 (m), 1574 (s), 1514 (s), 1477 (s), 1464 (w), 1443 (s), 1422 (w), 1412 (s), 1364 (m), 1317 (s), 1299 (w), 1284 (w), 1270 (s), 1238 (s), 1207 (m), 1156 (s), 1141 (w), 1102 (m), 1089 (m), 1071 (m), 1057 (m), 1029 (s), 991 (m), 945 (s), 919 (m), 874 (m), 836 (m), 813 (m), 778 (w), 751 (m), 715 (m), 684 (m), 650 (m), 620 (m), 547 (m), 506 (m), 460 (m), 437 (m), 417 (m) cm⁻¹; MS (EI): m/z: 317; elemental analysis calcd (%) for C₂₁H₂₂N₂O (318.4): C 79.21; H 6.96; N 8.80; found: C 79.35; H 6.99; N 8.83.

Compound 2. m.p. 181–183 °C; ¹H NMR (400 MHz, CDCl₃): δ = 13.40 (s, 1H), 8.42 (d, 2H), 7.72 (d, 1H), 7.62 (dd, 2H), 7.43 (d, 2H), 7.37-7.27 (m, 1H), 7.17 (dd, 2H), 7.07 (d, 1H), 3.46-3.00 (m, 1H), 2.93-2.34 (m, 1H), 2.34-1.80 (m, 2H), 1.62 (d, 6H); ¹³C NMR (100 MHz, CDCl₃): δ = 155.5, 150.3, 148.5, 132.1, 129.9, 129.0, 128.7,

126.6, 123.7, 122.6, 120.4, 119.9, 114.7, 70.9, 25.9, 24.0; IR (KBr): 3083 (br), 2836 (br), 2722 (m), 1937 (w), 1626 (s), 1601 (s), 1557 (m), 1512 (m), 1464 (m), 1438 (s), 1411 (m), 1379 (m), 1363 (w), 1337 (m), 1290 (m), 1265 (s), 1219 (m), 1197 (m), 1169 (m), 1153 (m), 1098 (m), 1066 (m), 1025 (m), 1003 (s), 970 (s), 884 (m), 867 (m), 815 (s), 798 (m), 781 (w), 747 (s), 725 (m), 699 (m), 684 (w), 646 (m), 604 (m), 586 (m), 518 (m), 467 (m), 451 (w), 433 (w), 416 (m) cm^{-1} ; MS (EI): m/z: 317; elemental analysis calcd (%) for $\text{C}_{21}\text{H}_{22}\text{N}_2\text{O}$ (318.4): C 79.21; H 6.96; N 8.80; found: C 79.38; H 6.93; N 8.84.

Compound 3. m.p. 184–186 °C; ^1H NMR (400 MHz, CDCl_3): δ = 13.64 (br s, 1H), 8.42 (d, 8.6 Hz, 1H), 8.10-8.07 (d, 1H), 7.96 (s, 1H), 7.81-7.79 (d, 1H), 7.74–7.70 (m, 2H), 7.47-7.17 (m, 4H), 5.21 (s, 1H), 3.37 (br s, 1H), 2.64 (br s, 1H), 2.15-1.72 (br m, 4H), 1.30-1.26 (br m, 4H); ^{13}C NMR (100 MHz, CDCl_3): δ = 155.4, 142.0, 134.9, 131.9, 130.0, 129.1, 128.6, 126.8, 123.9, 123.0, 122.7, 120.4, 120.1, 115.0, 25.9, 23.9. IR (KBr): 3091 (w), 3068 (m), 2954 (m), 2857 (br), 2811 (w), 2670 (w), 1921 (w), 1813 (w), 1620 (s), 1598 (m), 1579 (s), 1533 (s), 1474 (s), 1441 (s), 1414 (s), 1343 (m), 1313 (s), 1271 (w), 1259 (s), 1237, 1156 (s), 1107 (w), 1084 (m), 1034 (s), 1002, 988 (m), 961 (s), 942, 908, 866 (m), 831 (m), 817 (m), 804 (w), 784 (m), 762 (w), 749 (s), 734 (m), 691 (m), 665 (m), 647 (w), 620 (w), 548 (w), 531 (w), 509 (w), 487 (w), 460 (w), 438 (m), 417 (m) cm^{-1} ; MS (EI): m/z: 361; elemental analysis calcd (%) for $\text{C}_{22}\text{H}_{22}\text{N}_2\text{O}_3$ (362.4): C 72.91; H 6.12; N 7.73; found: C 72.71; H 6.14; N 7.70.

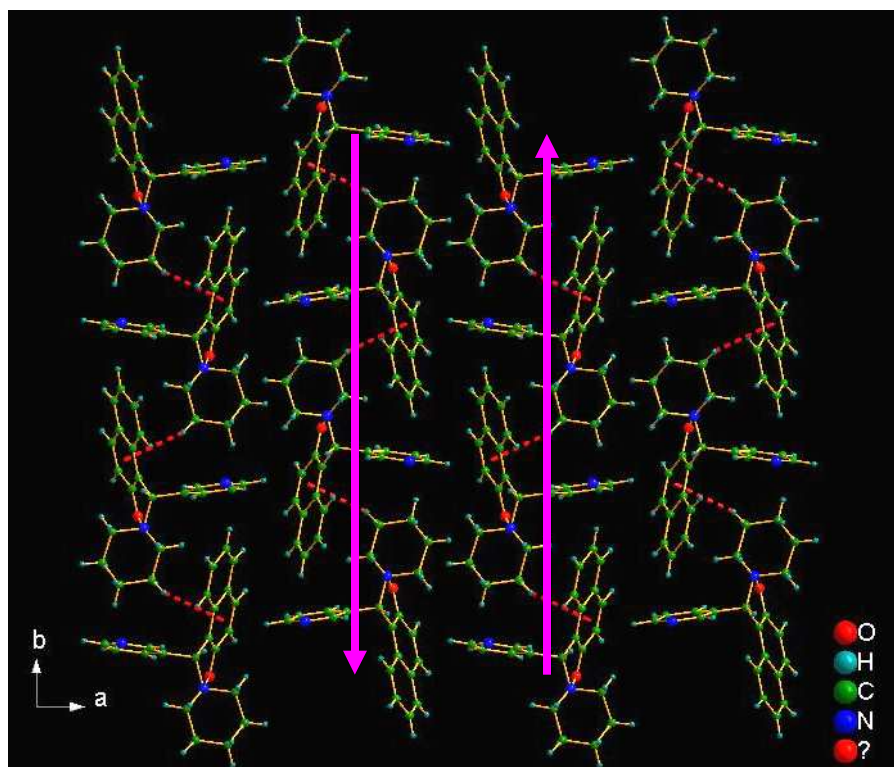


Fig. S1 A portion of the crystal structure of **1** showing the antiparallel packing along the *c* axis. The red dashed-lines stand for C-H... π packing interactions.

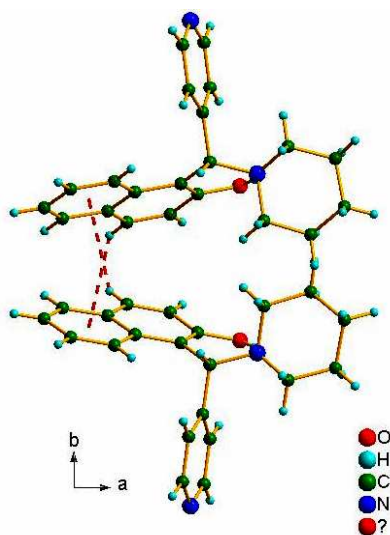


Fig. S2 View point of 1D chain extending along the *c* axis in **2**. The red dashed-lines stand for C-H... π packing interactions.

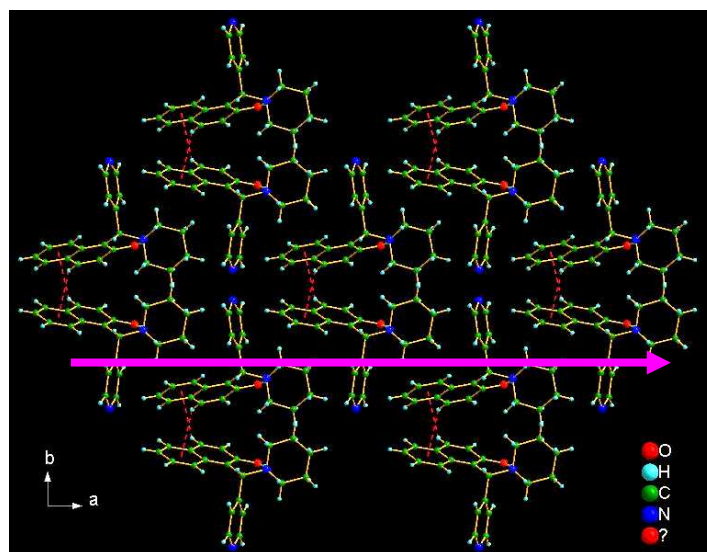


Fig. S3 A portion of the crystal structure of **2** showing the parallel packing along the *c* axis. The red dashed-lines stand for C-H... π packing interactions.

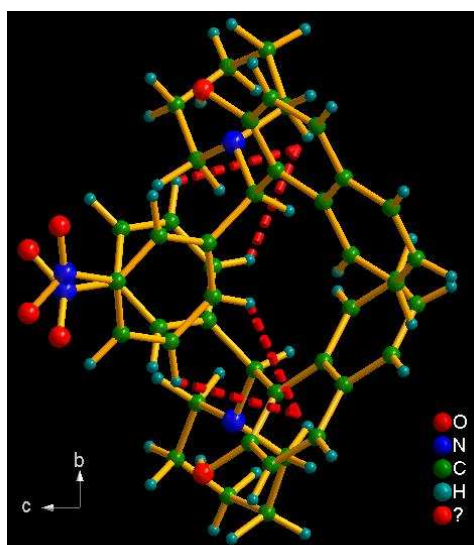


Fig. S4 View point of 1D chain extending along the *a* axis in **3**. The red dashed-lines stand for C-H... π packing interactions.

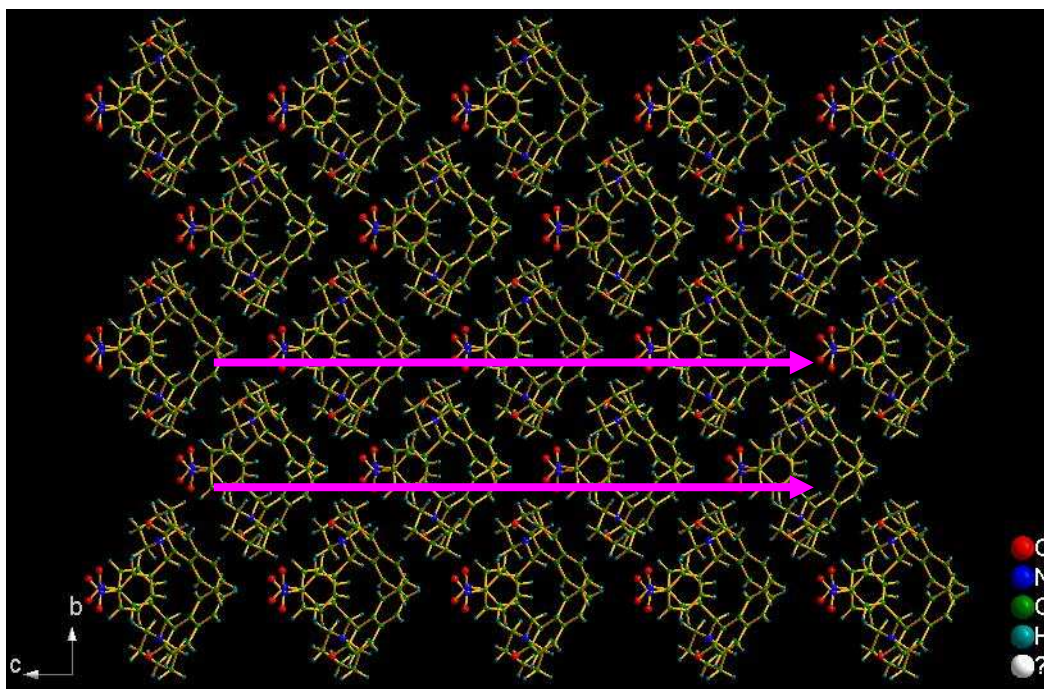


Fig. S5 A portion of the crystal structure of **3** showing the parallel packing along the *a* axis.

Table S1. Comparison of ferroelectric properties for three samples (at $f = 5$ Hz and $E = 1.5$ kV/cm)

Sample	P_r ($\mu\text{C}/\text{cm}^2$)	E_c (kV/cm)	P_s ($\mu\text{C}/\text{cm}^2$)
1	0.0159	0.513	0.04
2	0.0435	0.522	0.11
3	0.006	0.13	0.02

References:

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3. A.L. Spek, *J. Appl. Cryst.*, 2003, **36**, 7.