

Role of intermolecular interactions and conformational changes in polymorphism and vitrification process of 2,2''-bis-substituted *para*-terphenyls

Supplementary

Table of contents

1. Packing diagrams and characteristic interactions in crystal lattice
2. Calculation of enrichment ratios
3. NMR data
4. IR and Raman data
5. Calorimetric studies 2,2''-bis(hydroxymethyl)-*para*-terphenyl
6. DFT studies of 2,2''-bis(acetyloxymethyl)-*para*-terphenyl

1. Packing diagrams and characteristic interactions in crystal lattice

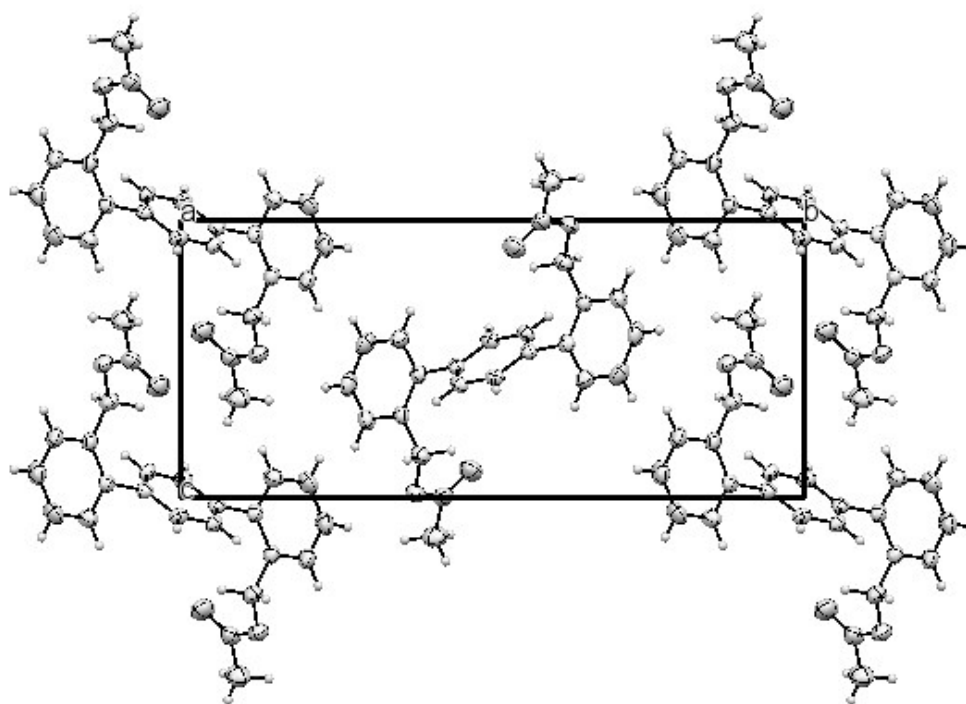


Fig. S1. Packing diagram for 2,2''-bis(acetyloxymethyl)-*para*-terphenyl (**1**). View along *a* axis.

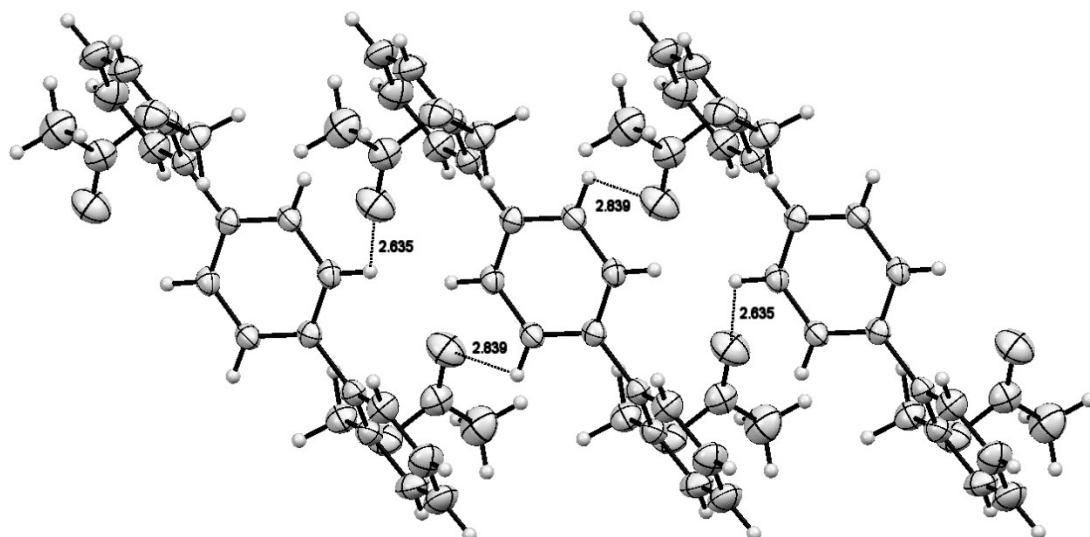


Fig. S2. Weak $C_{Ar}-H \cdots O$ (C1-H1 \cdots O2) interactions in crystal lattice of 2,2''-bis(acetyloxymethyl)-*para*-terphenyl (**1**) with marked $C_{Ar}-H \cdots O$ interactions.

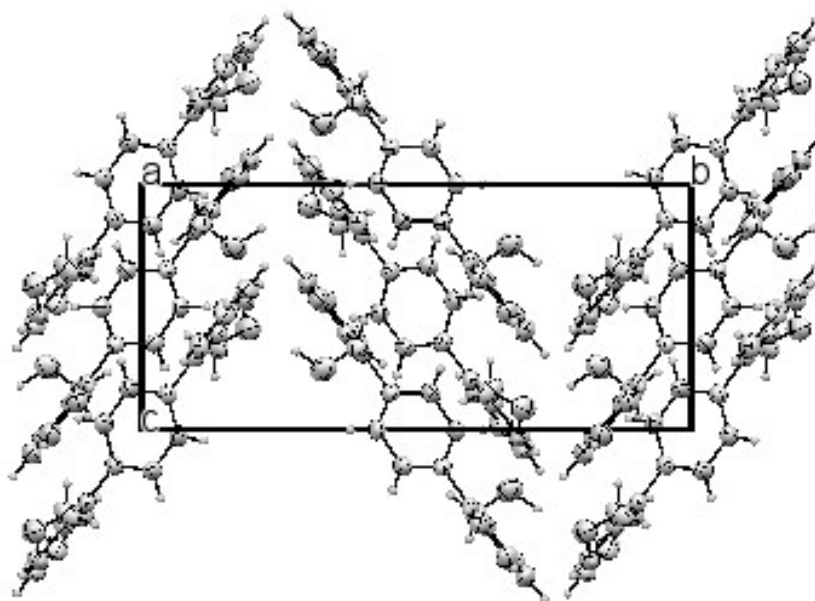


Fig. S3. Packing diagram for compound 2,2''-bis(hydroxymethyl)-*para*-terphenyl (**2**). View along *a* axis.

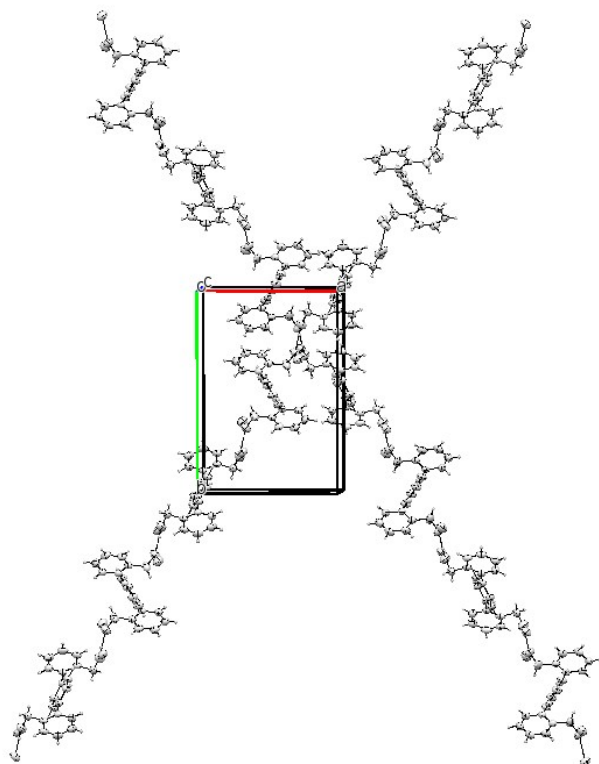


Fig. S4. Two ribbons of 2,2''-bis(hydroxymethyl)-*para*-terphenyl (**2**) molecules along the *c* axis.

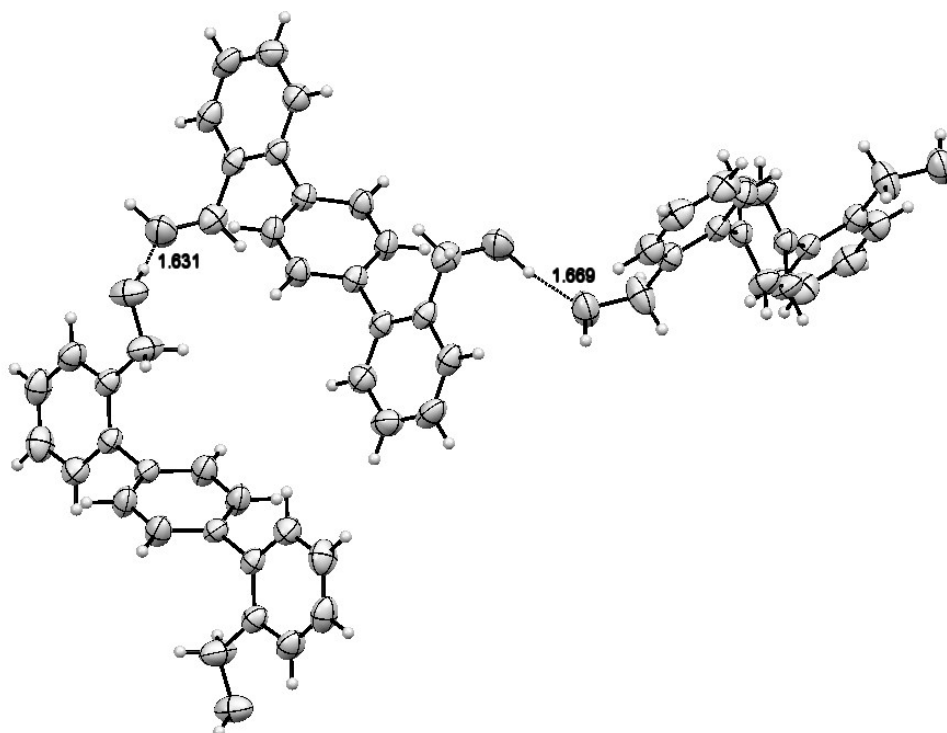


Fig. S5. Hydrogen bonds between molecules of 2,2''-bis(hydroxymethyl)-*para*-terphenyl (**2**) in ribbon part (1.631Å) and between molecules in crossing sections of ribbons (1.669Å).

2. Calculation of enrichment ratios

The contacts matrices for each analysed crystal structure were obtained by the fingerprints decomposition, derived in CrystalExplorer 17.5 programme. The so-called surface values, S_x ,

were calculated according to formula: $S_x = C_{XX} + 0.5 \sum_{Y \neq X} C_{XY}$, where C_{XY} is the actual percentage contributions of contacts between two selected atom types in the crystal. This quantity describe the an average percentage of Hirshfeld surface involved in the formation of intermolecular interactions between the X atom of the molecule being weighed and other atoms of neighbouring molecules. The random contact matrices describe the probabilities of each intermolecular contact in the crystal structure (on the assumption of equi-distribution of contacts XY between all chemical types). These quantities are calculated according to formulas: $R_{XX} = S_X S_X$ and $R_{XY} = 2S_X S_Y$. The enrichment ratios were calculated as proportions of actual percentage contributions of contacts between two selected atom types in the crystal, C_{XY} , and the theoretically calculated percentages of random contacts between those atoms, R_{XY} :

$$E_{XY} = C_{XY}/R_{XY}$$

Table S1. Values of each parameter for two symmetrically independent molecules (*I* and *II*) of 2,2''-bis(hydroxymethyl)-*para*-terphenyl (**2**).

| Molecule I | | | | Molecule II | | | |
|--------------------------------------|-------|-------|------|--------------------------------------|-------|-------|------|
| Matrix of contacts [%] | | | | Matrix of contacts [%] | | | |
| Atoms | C | H | O | Atoms | C | H | O |
| C | 0.9 | - | - | C | 0.0 | - | - |
| H | 29.5 | 59.0 | - | H | 29.0 | 60.3 | - |
| O | 0.3 | 10.3 | 0.0 | O | 0.4 | 10.3 | 0.0 |
| Surface [%] | 15.80 | 78.90 | 5.30 | Surface [%] | 14.7 | 79.95 | 5.35 |
| Matrix of random contacts [%] | | | | Matrix of random contacts [%] | | | |
| Atoms | C | H | O | Atoms | C | H | O |
| C | 2.50 | - | - | C | 2.16 | - | - |
| H | 24.93 | 62.25 | - | H | 23.51 | 63.92 | - |
| O | 1.68 | 8.36 | 0.28 | O | 1.57 | 8.55 | 0.29 |
| Matrix of enrichment ratios | | | | Matrix of enrichment ratios | | | |
| Atoms | C | H | O | Atoms | C | H | O |
| C | 0.36 | - | - | C | 0.00 | - | - |
| H | 1.18 | 0.95 | - | H | 1.23 | 0.94 | - |
| O | 0.18 | 1.23 | 0.00 | O | 0.25 | 1.20 | 0.00 |

Table S2. Values of each parameter for two symmetrically independent molecules (*I* and *II*) of 2,2''-bis(acetyloxymethyl)-*para*-terphenyl (**2**).

| Compound 2 | | | |
|-------------------------------|-------|-------|-------|
| Matrix of contacts [%] | | | |
| Atoms | C | H | O |
| C | 0.3 | - | - |
| H | 26.8 | 52.4 | - |
| O | 1.1 | 18.5 | 0.9 |
| Surface [%] | 14.25 | 75.05 | 10.70 |
| Matrix of random contacts [%] | | | |
| Atoms | C | H | O |
| C | 2.03 | - | - |
| H | 21.39 | 56.33 | - |
| O | 3.05 | 16.06 | 1.14 |
| Matrix of enrichment ratios | | | |
| Atoms | C | H | O |
| C | 0.15 | - | - |
| H | 1.25 | 0.93 | - |
| O | 0.36 | 1.11 | 0.79 |

3. NMR data

2,2''-bis(acetyloxymethyl)-*para*-terphenyl (**1**):

¹H NMR (400MHz, CDCl₃); δ (ppm): 7.56-7.53 (m, 2H, ArH), 7.45-7.38 (m, 10H, ArH), 5.14 (s, 4H, -CH₂-O), 2.10 (s, 6H, -OCH₃).

¹³C NMR (CDCl₃); δ (ppm): 170.8 (CO), 141.9, 139.5, 133.3, 130.4, 129.6, 129.1, 129.0, 128.9, 128.4, 127.7, 64.4 (CH₂), 21.0(CH₃).

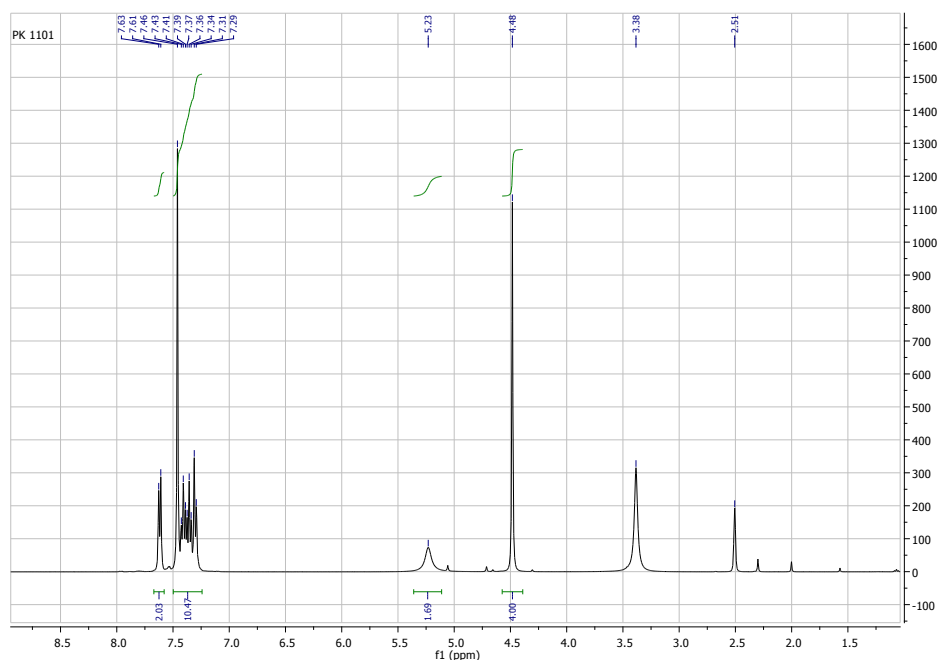


Fig. S6. ¹H NMR spectrum of 2,2''-bis(hydroxymethyl)-*para*-terphenyl (**1**).

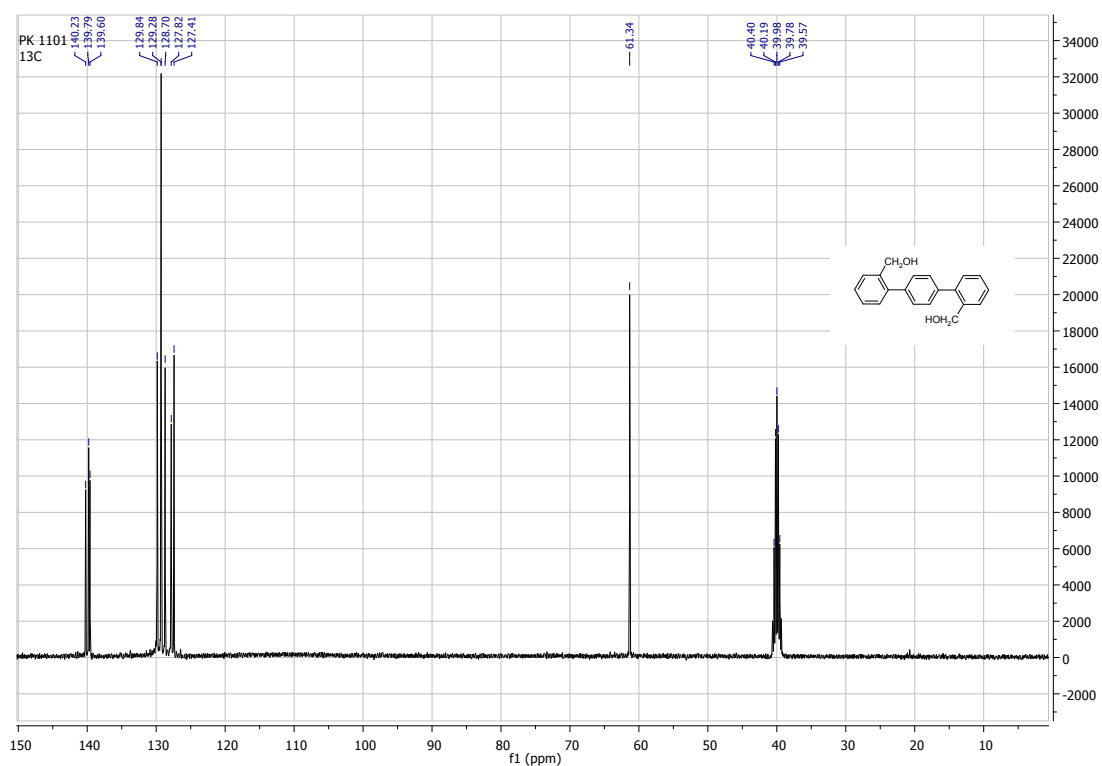


Fig. S7. ¹³C NMR spectrum of compound 2,2''-bis(hydroxymethyl)-*para*-terphenyl (1).

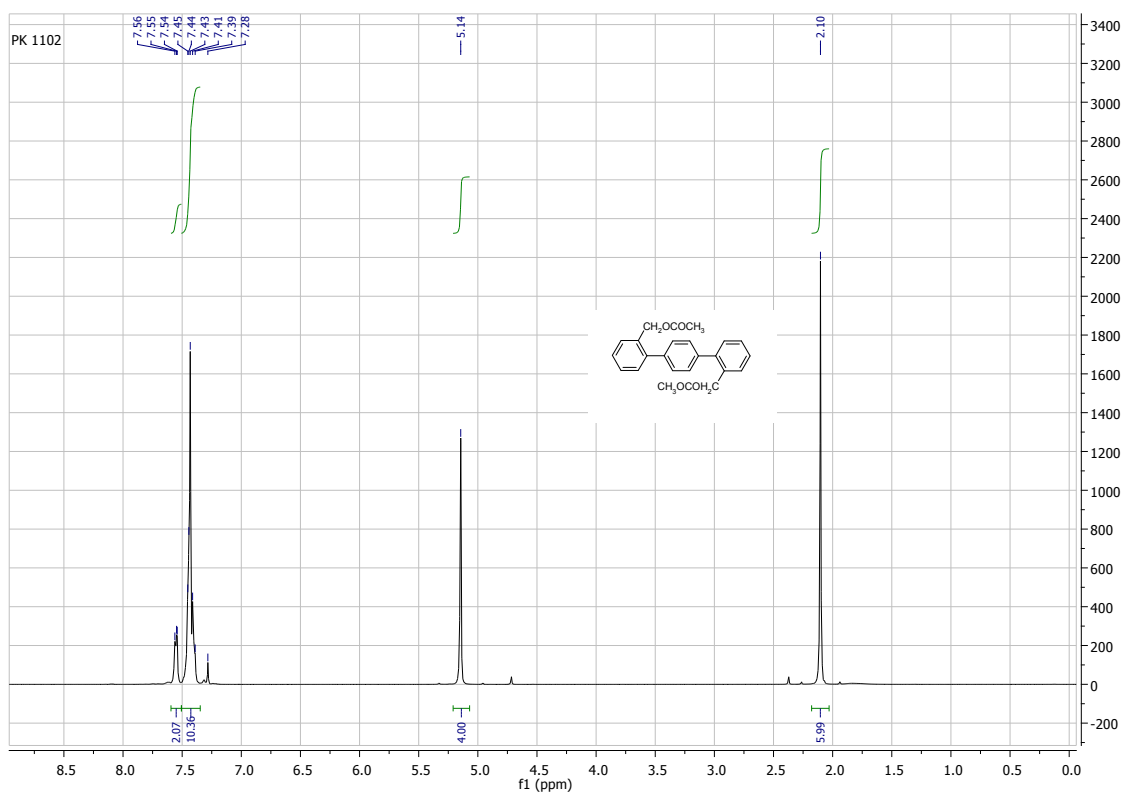


Fig. S8. ¹H NMR spectrum of compound 2,2''-bis(acetyloxymethyl)-*para*-terphenyl (2).

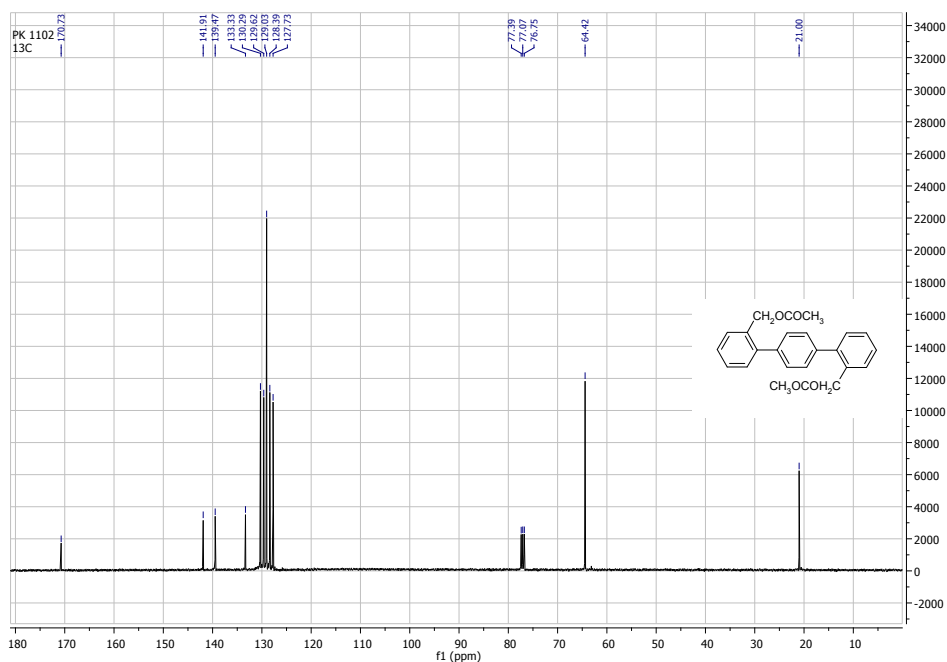


Fig. S9. ^{13}C NMR spectrum of compound 2,2''-bis(acetyloxymethyl)-*para*-terphenyl (**2**).

2,2''-Bis(hydroxymethyl)-*para*-terphenyl (**2**):

^1H NMR (400MHz, DMSO- d_6); δ (ppm): 7.60 (d, 2H, $J = 8\text{Hz}$, ArH), 7.46 (s, 4H, ArH), 7.41 (t, 2H, $J = 8\text{Hz}$, ArH), 7.36 (t, 2H, $J = 8\text{Hz}$, ArH), 7.30 (d, 2H, $J = 2\text{Hz}$, ArH), 5.25 (bs, 2H, OH), 4.47 (s, 4H, $-\text{CH}_2\text{-O}$).

^{13}C NMR (DMSO- d_6); δ (ppm): 140.2, 139.8, 139.6, 129.8, 129.3, 128.7, 127.8, 127.4, 61.32 (CH_2).

4. IR and Raman data

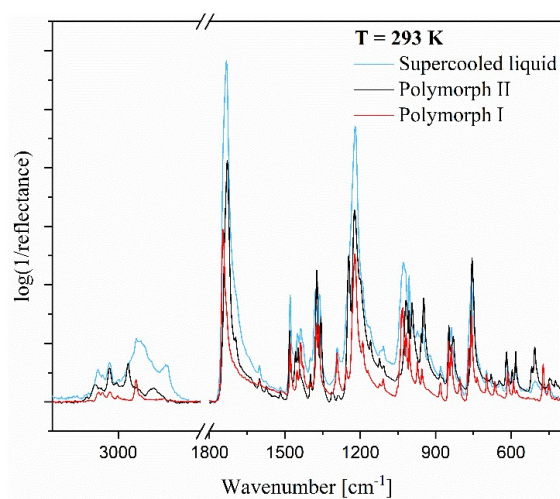


Fig. S10. IR spectra of polymorphs I and II and supercooled liquid of 2,2''-bis(acetyloxymethyl)-*para*-terphenyl (**2**) measured at 293 K.

IR selected vibrations:

2,2''-Bis(acetyloxymethyl)-para-terphenyl (1) – polymorph I:

IR $\nu_{\max}/\text{cm}^{-1}$: 3058, 3047, 3021, 3001, 2944, 1728, 1598, 1577, 1480, 1457, 1446, 1399, 1372, 1353, 1245, 1222, 1151, 1124, 1036, 1030, 1016, 1004, 972, 955, 880, 849, 837, 803, 769, 757, 732, 696, 663, 612, 591, 577, 472, 447.

2,2''-Bis(acetyloxymethyl)-para-terphenyl (1) – polymorph II:

IR $\nu_{\max}/\text{cm}^{-1}$: 3065, 3052, 3022, 3002, 2968, 2891, 1744, 1598, 1477, 1449, 1437, 1375, 1360, 1291, 1256, 1221, 1188, 1109, 1017, 1005, 993, 958, 947, 882, 846, 829, 754, 679, 646, 617, 595, 580, 518, 504, 447, 422.

2,2''-Bis(acetyloxymethyl)-para-terphenyl (1) – supercooled liquid:

IR $\nu_{\max}/\text{cm}^{-1}$: 3068, 3026, 2944, 2931, 2856, 1731, 1598, 1477, 1448, 1434, 1396, 1377, 1360, 1292, 1217, 1028, 1006, 972, 952, 921, 879, 849, 837, 804, 757, 697, 663, 641, 613, 577, 502, 472, 447.

2,2''-Bis(hydroxymethyl)-para-terphenyl (2):

IR $\nu_{\max}/\text{cm}^{-1}$: 3271, 3026, 2989, 2928, 2878, 1476, 1448, 1395, 1367, 1265, 1235, 1195, 1118, 1102, 1053, 1006, 954, 885, 845, 823, 756, 729, 696, 681, 644, 613, 583, 540, 518, 496, 449.

Raman vibrations:

2,2''-Bis(acetyloxymethyl)-para-terphenyl (1) – mixture of polymorphs:

Raman $\nu_{\max}/\text{cm}^{-1}$: 3059, 2941, 1609, 1580, 1492, 1450, 1279, 1203, 1189, 1162, 1050, 1006, 925, 843, 768, 752, 641, 622, 591, 560, 542, 523, 474, 441, 352.

2,2''-Bis(hydroxymethyl)-para-terphenyl (2):

Raman $\nu_{\max}/\text{cm}^{-1}$: 3059, 1609, 1577, 1489, 1457, 1373, 1311, 1280, 1265, 1188, 1051, 1005, 851, 832, 777, 764, 728, 640, 622, 560, 511, 452, 364, 342.

5. Calorimetric studies 2,2''-bis(hydroxymethyl)-*para*-terphenyl

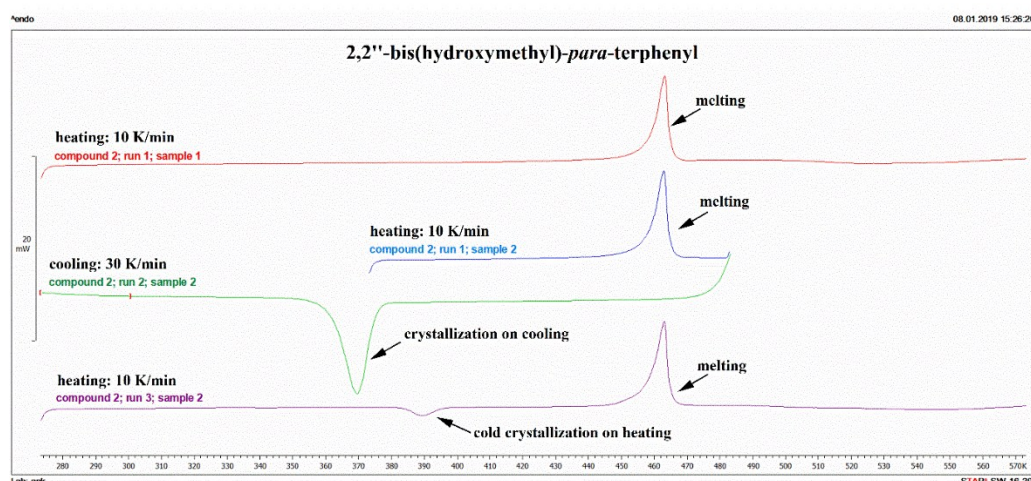


Fig. S11. DSC thermograms of 2,2''-bis(hydroxymethyl)-*para*-terphenyl (**2**).

During cooling with a rate of 30 K/min crystallization process occurred at 373 K (see Fig.S12, run 2 sample 2), however not the whole amount of compound **2** became crystalline. Cold crystallization process is visible in the subsequent heating scan (Fig.S12, run 3 sample 2). This indicates, that it is possible to vitrify this compound by rapid quenching, *e.g.* by the use of a cuprite plate cooled previously in liquid nitrogen (providing huge gradient of temperatures). However such the procedure could not be implemented during DSC scans due to technical reasons. The glass transition was not registered in the calorimetric studies because the thermal effect was below the detection threshold.

6. DFT studies of 2,2''-bis(acetyloxymethyl)-*para*-terphenyl

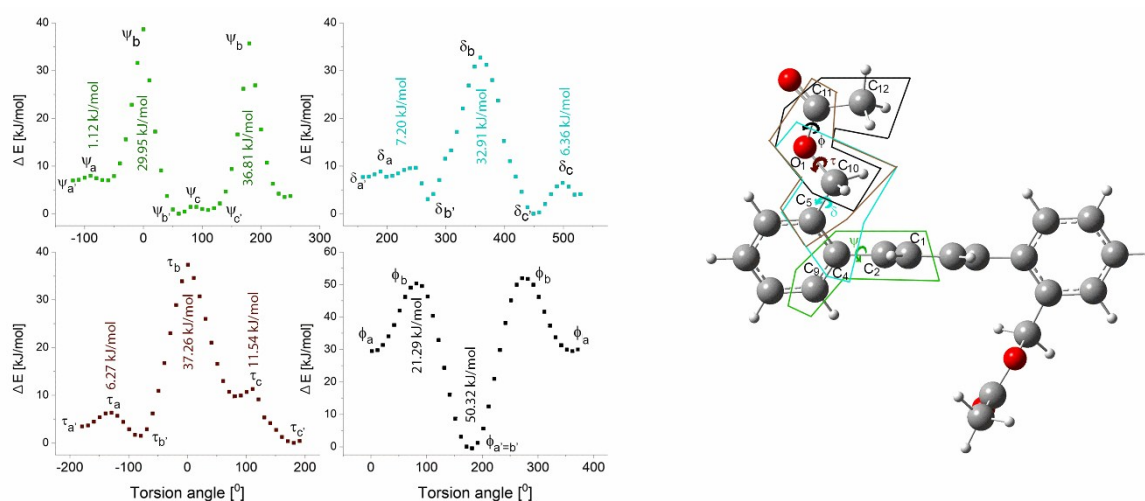


Fig. S12. Theoretically calculated rotational surface for 2,2''-bis(acetyloxymethyl)-*para*-terphenyl (**1**).