Supplementary Material

**Phase Transition Thermodynamics of 1,3,5-tris-(α-naphthyl)benzene: theory and experiment**

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*1 Materials*

**Table S1**

Provenance and purity of the materials.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Chemical Name | CASRN | Source | Sample purity | Purification method |
| TNB | 15546-43-7 | Hotspot Biotechnology | >0.98 a  >0.997 c | sublimation |
| biphenyl | 92-52-4 | Aldrich | 0.999 c | none |
| benzoic acid | 65-85-0 | Aldrich | 0.999 c | none |
| anthracene | 120-12-7 | Aldrich | 0.999 c | none |
| indium | 7440-74-6 | PerkinElmer | 0.99999a | none |
| zinc | 7440-66-6 | PerkinElmer | 0.99999a | none |
| sapphired | 1344-28-1 | PerkinElmer | not provided | none |

a Initial purity stated by supplier;

b Purity after fractional sublimation *in vacuo* determined by HPLC (mole fraction);

c Purity determined by GC (mass fraction);

d Sapphire disc provided by Perkin Elmer (USA) as a reference material for the heat capacity measurements.

*2 Differential scanning calorimetry*

**Table S2**

Enthalpies and temperatures of fusion of TNP measured in this work at 105 Pa.

|  |  |  |
| --- | --- | --- |
| Sample mass / mg | *T*m / K | / kJ mol-1 |
| 4.14 | 458.2 | 33.19 |
| 4.71 | 459.0 | 33.12 |
| 4.88 | 458.5 | 32.29 |
| **Average** | **458.6±0.4**a | **32.9±0.5**a |

a The uncertainties reported inside Table S2 include the expanded uncertainty of the mean *U* (0.95 level of confidence, coverage factor of 2.0) and reproducibility of calibration (0.1 K for temperature and 1 % for enthalpy); the standard uncertainty of pressure *u(p)* = 5·103 Pa.

**Table S3**

Isobaric heat capacities of crystalline and liquid TNB measured in this work using DSC at the pressure of 105 Pa.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| *T* / K | *C*p,m / J K-1 mol-1a | *u*(*C*p,m) / J K-1 mol-1 | *T* / K | *C*p,m / J K-1 mol-1a | *u*(*C*p,m) / J K-1 mol-1 |
| TNB (cr) | | | TNB (l) | | |
| 280 | 477.1 | 14.3 | 420 | 835.2 | 25.1 |
| 290 | 495.0 | 14.8 | 430 | 846.8 | 25.4 |
| 300 | 512.9 | 15.4 | 440 | 858.5 | 25.8 |
| 310 | 530.8 | 15.9 | 450 | 870.2 | 26.1 |
| 320 | 548.7 | 16.5 | 460 | 881.8 | 26.5 |
| 330 | 566.6 | 17.0 | 470 | 893.5 | 26.8 |
| 340 | 584.5 | 17.5 | 480 | 905.1 | 27.2 |
| 350 | 602.4 | 18.1 | 490 | 916.8 | 27.5 |
| 360 | 620.3 | 18.6 | 500 | 928.5 | 27.9 |
| 370 | 638.2 | 19.1 | 510 | 940.1 | 28.2 |
| 380 | 656.2 | 19.7 |  |  |  |
| 390 | 674.1 | 20.2 |  |  |  |
| 400 | 692.0 | 20.8 |  |  |  |
| 410 | 709.9 | 21.3 |  |  |  |
| 420 | 727.8 | 21.8 |  |  |  |
| 430 | 745.7 | 22.4 |  |  |  |

a The uncertainties include the expanded uncertainty of the mean *U* (0.95 level of confidence, coverage factor of 2.0) and the uncertainty of calibration; the standard uncertainty of pressure *u(p)* = 5·103 Pa. The expanded uncertainty of temperature is ±0.1 K (0.95 level of confidence, coverage factor of 2.0).

*3 Solution calorimetry*

**Table S4**

Experimental enthalpies of solution of TNB in benzene measured in this work at 298.15 K and 0.1 MPa a.

|  |  |  |
| --- | --- | --- |
| Mass of sample / mg | Molality b / mmol·kg-1 | c / kJ mol-1 |
| 40.2 | 1.00 | 14.88 |
| 45.7 | 2.14 | 15.60 |
| 45.0 | 3.26 | 14.54 |
| 45.3 | 4.39 | 16.03 |
| 41.2 | 5.41 | 15.01 |
| 42.1 | 6.47 | 14.75 |
| Δ­soln*H*A/S = 15.13 ± 0.46 kJ·mol-1 d | | |

a Standard uncertainties u are u(T) = 0.01 K, u(p) = 5 kPa.

b Molality of the solute in solution after experiments. Standard uncertainty u is 0.01 mmol·kg-1.

c The experimental value obtained on each sample dissolution, assumed to correspond to the solution enthalpies at the infinite dilution.

d Average enthalpy of solution. Uncertainties reported inside Table S5 correspond to the combined expanded uncertainties of the mean U and the calibration reproducibilities (0.1 %), 0.95 level of confidence, coverage factor 2.0.

*4 Powder X-ray diffraction*

X-ray powder diffraction (XRPD) pattern of TNB was determined using a MiniFlex 600 diffractometer (Rigaku) equipped with a D/teX Ultra detector as reported previously [[2](#_ENREF_2)]. In this experiment, Cu Kα radiation (40 kV, 15 mA) was used and data were collected at room temperature in the range of 2θ from 3 to 50° with a step of 0.02° and exposure time at each point of 0.24 s without sample rotation.

PXRD pattern of TNB sample after fractional sublimation *in vacuo* and annealing at 443 K is provided below (Fig. S1). Analogous pattern was obtained for the commercial sample.

**Fig. S1.** PXRD pattern of TNB sample studied in this work.

*5 Quantum chemical calculations*

**Table S5**

Cartesian coordinates for TNB optimized with B3LYP/6-31+G(d,p).

| Atom | X | Y | Z |
| --- | --- | --- | --- |
| C | -3.548334 | -1.246553 | 0.196101 |
| C | -2.862686 | -0.497731 | -0.822091 |
| C | -3.586717 | 0.012054 | -1.888318 |
| C | -4.978585 | -0.206743 | -2.013862 |
| C | -5.650716 | -0.942957 | -1.065244 |
| C | -4.960712 | -1.474123 | 0.057952 |
| C | -2.899668 | -1.750605 | 1.359989 |
| C | -3.595427 | -2.460732 | 2.315663 |
| C | -4.981786 | -2.705353 | 2.162555 |
| C | -5.645888 | -2.217166 | 1.059245 |
| C | -1.391354 | -0.249413 | -0.766400 |
| C | -0.474501 | -1.313580 | -0.764042 |
| C | 0.907929 | -1.083017 | -0.764172 |
| C | 1.370963 | 0.243110 | -0.765832 |
| C | 0.480122 | 1.325022 | -0.767676 |
| C | -0.899917 | 1.063059 | -0.768172 |
| C | 1.858694 | -2.232968 | -0.817805 |
| C | 1.773778 | -3.121663 | -1.878053 |
| C | 2.659830 | -4.217276 | -2.002341 |
| C | 3.639710 | -4.424076 | -1.058535 |
| C | 3.760596 | -3.553842 | 0.058537 |
| C | 2.856459 | -2.445019 | 0.195673 |
| C | 1.001090 | 2.723224 | -0.823307 |
| C | 1.808686 | 3.093992 | -1.886948 |
| C | 2.316357 | 4.408337 | -2.011690 |
| C | 2.012111 | 5.359421 | -1.064870 |
| C | 1.202118 | 5.029126 | 0.055259 |
| C | 0.691536 | 3.692670 | 0.192501 |
| C | 4.753321 | -3.768243 | 1.054898 |
| C | 4.849882 | -2.942272 | 2.152666 |
| C | 3.944050 | -1.864543 | 2.305086 |
| C | 2.974786 | -1.624260 | 1.354033 |
| C | 0.897671 | 5.995293 | 1.054241 |
| C | 0.137220 | 5.666133 | 2.154268 |
| C | -0.346136 | 4.343841 | 2.306327 |
| C | -0.075211 | 3.384930 | 1.353046 |
| H | -5.518921 | -3.269453 | 2.919495 |
| H | -3.076827 | -2.831889 | 3.194941 |
| H | -1.840759 | -1.563963 | 1.497669 |
| H | -6.712700 | -2.388406 | 0.939165 |
| H | -6.718305 | -1.124409 | -1.158765 |
| H | -5.508482 | 0.201156 | -2.869700 |
| H | -3.065659 | 0.574295 | -2.657909 |
| H | -0.841739 | -2.335469 | -0.769653 |
| H | 2.439529 | 0.436069 | -0.772902 |
| H | -1.601292 | 1.891991 | -0.777091 |
| H | 2.037374 | 2.360945 | -2.655215 |
| H | 2.937937 | 4.662195 | -2.865410 |
| H | 2.390357 | 6.374176 | -1.157655 |
| H | 1.284716 | 7.004156 | 0.934994 |
| H | -0.085652 | 6.414341 | 2.909377 |
| H | -0.931663 | 4.081797 | 3.182872 |
| H | -0.445401 | 2.375330 | 1.489960 |
| H | 1.021885 | -2.957201 | -2.644527 |
| H | 2.567146 | -4.885448 | -2.853572 |
| H | 4.330990 | -5.257704 | -1.151285 |
| H | 5.435303 | -4.606410 | 0.935718 |
| H | 5.612119 | -3.119665 | 2.905799 |
| H | 4.010664 | -1.224437 | 3.180104 |
| H | 2.283745 | -0.800449 | 1.491515 |

**Table S6**

Computed fundamental vibrational wavenumbers of TNB used in the calculation of the ideal-gas heat capacities. The frequencies corresponding to the internal rotation were identified according to Ayala [[3](#_ENREF_3)] and excluded from the table and further calculations.

| ν / cm-1 | ν / cm-1 | ν / cm-1 | ν / cm-1 | ν / cm-1 |
| --- | --- | --- | --- | --- |
| 32.5 | 526.9 | 906.8 | 1212.8 | 1594.9 |
| 38.3 | 558.6 | 913.1 | 1213.1 | 1604.7 |
| 38.8 | 558.9 | 919.4 | 1213.6 | 1606.6 |
| 80.8 | 586.5 | 920.5 | 1238.8 | 1606.8 |
| 83.4 | 618.0 | 948.0 | 1239.3 | 1632.3 |
| 84.0 | 618.1 | 951.4 | 1252.3 | 1632.6 |
| 133.8 | 625.5 | 951.7 | 1263.8 | 1632.7 |
| 134.2 | 625.6 | 953.0 | 1269.8 | 3036.4 |
| 168.7 | 651.9 | 967.4 | 1270.2 | 3036.9 |
| 173.9 | 658.4 | 967.5 | 1313.6 | 3036.9 |
| 174.5 | 658.7 | 968.5 | 1331.1 | 3039.6 |
| 179.5 | 662.7 | 978.4 | 1337.1 | 3039.6 |
| 201.1 | 720.8 | 978.7 | 1337.2 | 3039.6 |
| 229.7 | 730.4 | 979.2 | 1344.3 | 3048.4 |
| 229.9 | 730.7 | 988.3 | 1370.6 | 3048.5 |
| 268.1 | 733.8 | 1009.0 | 1370.7 | 3048.8 |
| 268.5 | 733.8 | 1009.0 | 1371.3 | 3049.7 |
| 276.1 | 734.8 | 1026.4 | 1394.1 | 3049.9 |
| 329.3 | 776.0 | 1029.9 | 1394.5 | 3050.2 |
| 329.5 | 776.1 | 1030.2 | 1407.6 | 3057.3 |
| 359.7 | 776.6 | 1063.4 | 1422.5 | 3057.6 |
| 401.3 | 786.3 | 1069.5 | 1423.1 | 3058.8 |
| 401.7 | 787.9 | 1069.9 | 1443.3 | 3062.3 |
| 426.3 | 788.2 | 1123.1 | 1448.2 | 3062.6 |
| 431.3 | 797.4 | 1123.6 | 1448.4 | 3062.7 |
| 431.6 | 797.8 | 1125.0 | 1466.0 | 3063.8 |
| 459.3 | 798.6 | 1146.9 | 1466.1 | 3063.8 |
| 471.9 | 803.8 | 1147.1 | 1466.7 | 3064.0 |
| 471.9 | 860.0 | 1147.8 | 1519.1 | 3078.7 |
| 474.6 | 860.6 | 1162.0 | 1519.4 | 3078.8 |
| 502.4 | 863.5 | 1162.2 | 1519.7 | 3079.0 |
| 502.6 | 865.9 | 1163.2 | 1587.5 |  |
| 518.0 | 866.3 | 1177.4 | 1587.6 |  |
| 518.1 | 892.6 | 1177.7 | 1589.7 |  |
| 519.6 | 906.0 | 1191.5 | 1594.6 |  |

**Table S7**

Energy levels of hindered rotation of naphthyl substituents in TNB (all three naphthyl rotating tops are equivalent, therefore they have equal energy levels of hindered rotation).

| ν / cm-1 | ν / cm-1 | ν / cm-1 | ν / cm-1 | ν / cm-1 |
| --- | --- | --- | --- | --- |
| 15.2 | 481.9 | 1075.3 | 1813.5 | 2690.3 |
| 20.7 | 483.8 | 1081.4 | 1828.1 | 2704.4 |
| 37.8 | 492.0 | 1089.2 | 1830.1 | 2721.2 |
| 38.7 | 494.7 | 1094.9 | 1843.0 | 2739.6 |
| 54.2 | 502.3 | 1103.1 | 1846.7 | 2754.1 |
| 56.6 | 505.7 | 1108.4 | 1858.1 | 2771.5 |
| 70.2 | 512.6 | 1117.1 | 1863.4 | 2798.2 |
| 74.1 | 516.7 | 1122.0 | 1873.2 | 2820.3 |
| 85.9 | 523.1 | 1131.2 | 1880.1 | 2823.7 |
| 90.6 | 527.8 | 1135.6 | 1888.2 | 2825.4 |
| 101.3 | 533.6 | 1145.3 | 1896.8 | 2859.3 |
| 106.7 | 539.0 | 1149.3 | 1903.4 | 2878.0 |
| 116.6 | 544.3 | 1159.5 | 1913.6 | 2889.1 |
| 121.1 | 550.3 | 1162.9 | 1918.5 | 2922.9 |
| 122.6 | 555.0 | 1173.9 | 1930.5 | 2933.2 |
| 131.6 | 561.6 | 1176.7 | 1933.5 | 2934.2 |
| 137.9 | 565.8 | 1188.2 | 1947.3 | 2960.2 |
| 140.4 | 572.9 | 1190.5 | 1948.8 | 2988.7 |
| 146.2 | 576.7 | 1202.7 | 1964.0 | 2992.2 |
| 153.1 | 584.3 | 1204.3 | 1964.2 | 3033.5 |
| 158.6 | 587.6 | 1217.2 | 1979.1 | 3052.2 |
| 160.4 | 595.8 | 1218.1 | 1981.2 | 3056.6 |
| 167.8 | 598.7 | 1231.8 | 1994.4 | 3067.1 |
| 174.1 | 607.3 | 1232.1 | 1998.1 | 3108.9 |
| 175.9 | 609.8 | 1246.0 | 2009.6 | 3114.4 |
| 182.2 | 618.8 | 1246.5 | 2015.1 | 3126.5 |
| 187.2 | 621.0 | 1260.0 | 2024.8 | 3178.7 |
| 192.2 | 630.2 | 1261.2 | 2032.2 | 3186.1 |
| 196.3 | 632.3 | 1274.0 | 2040.3 | 3198.1 |
| 199.5 | 641.7 | 1276.0 | 2049.3 | 3245.2 |
| 199.8 | 643.7 | 1288.0 | 2055.5 | 3261.9 |
| 207.2 | 653.0 | 1290.9 | 2066.5 | 3264.7 |
| 209.8 | 655.1 | 1302.1 | 2070.8 | 3271.2 |
| 210.9 | 664.1 | 1305.8 | 2083.6 | 3314.2 |
| 215.0 | 666.6 | 1316.2 | 2086.3 | 3344.2 |
| 219.7 | 674.7 | 1320.8 | 2100.8 | 3345.4 |
| 221.3 | 678.2 | 1330.4 | 2101.5 | 3385.6 |
| 222.7 | 684.6 | 1335.9 | 2116.9 | 3419.8 |
| 228.2 | 689.8 | 1344.6 | 2118.1 | 3423.9 |
| 228.6 | 694.1 | 1351.0 | 2132.6 | 3459.5 |
| 233.1 | 701.6 | 1358.8 | 2135.4 | 3479.2 |
| 234.5 | 704.0 | 1366.2 | 2147.8 | 3493.9 |
| 239.3 | 713.4 | 1373.1 | 2152.8 | 3502.8 |
| 239.4 | 714.5 | 1381.5 | 2163.3 | 3536.0 |
| 243.7 | 725.2 | 1387.4 | 2170.2 | 3566.0 |
| 245.8 | 725.4 | 1396.8 | 2179.1 | 3579.0 |
| 247.2 | 736.4 | 1401.7 | 2187.6 | 3615.1 |
| 252.2 | 737.1 | 1412.2 | 2194.2 | 3631.6 |
| 252.6 | 747.5 | 1416.1 | 2205.2 | 3649.3 |
| 257.4 | 749.1 | 1427.6 | 2209.9 | 3689.4 |
| 259.7 | 758.8 | 1430.5 | 2222.8 | 3696.5 |
| 263.2 | 761.2 | 1443.1 | 2225.7 | 3701.4 |
| 267.1 | 770.2 | 1444.9 | 2240.3 | 3721.4 |
| 269.3 | 773.3 | 1458.7 | 2240.7 | 3762.0 |
| 274.8 | 781.7 | 1459.3 | 2256.8 | 3780.2 |
| 275.7 | 785.5 | 1473.8 | 2257.7 | 3803.6 |
| 282.3 | 793.3 | 1474.3 | 2272.5 | 3849.2 |
| 282.6 | 797.8 | 1488.3 | 2275.7 | 3865.7 |
| 289.2 | 805.1 | 1489.9 | 2287.3 | 3896.6 |
| 290.7 | 810.1 | 1502.9 | 2293.8 | 3917.6 |
| 296.3 | 817.0 | 1505.7 | 2303.9 | 3947.9 |
| 299.0 | 822.4 | 1517.4 | 2310.7 | 3952.8 |
| 303.6 | 829.0 | 1521.4 | 2319.4 | 4001.0 |
| 307.4 | 834.9 | 1532.0 | 2328.5 | 4040.6 |
| 311.1 | 841.1 | 1537.3 | 2333.6 | 4058.8 |
| 316.0 | 847.3 | 1546.6 | 2347.9 | 4116.7 |
| 318.8 | 853.3 | 1553.2 | 2351.4 | 4118.7 |
| 324.8 | 859.9 | 1561.3 | 2364.2 | 4128.4 |
| 326.7 | 865.6 | 1569.1 | 2366.4 | 4184.3 |
| 333.8 | 872.5 | 1575.9 | 2379.4 | 4214.1 |
| 334.8 | 878.0 | 1585.1 | 2380.1 | 4252.5 |
| 342.9 | 885.2 | 1590.6 | 2399.5 | 4277.5 |
| 343.0 | 890.5 | 1601.1 | 2400.4 | 4297.5 |
| 351.3 | 897.9 | 1605.3 | 2413.8 | 4328.2 |
| 352.1 | 903.2 | 1617.2 | 2423.5 | 4361.2 |
| 359.8 | 910.6 | 1620.0 | 2425.4 | 4407.1 |
| 361.5 | 915.9 | 1633.3 | 2433.3 | 4413.5 |
| 368.5 | 923.5 | 1634.7 | 2448.6 | 4474.6 |
| 371.1 | 928.7 | 1649.5 | 2449.7 | 4496.2 |
| 377.3 | 936.3 | 1649.5 | 2462.9 | 4544.3 |
| 380.7 | 941.6 | 1664.3 | 2473.6 | 4590.1 |
| 386.2 | 949.3 | 1665.7 | 2481.1 | 4618.3 |
| 390.5 | 954.6 | 1679.1 | 2497.7 | 4698.0 |
| 395.2 | 962.3 | 1681.9 | 2499.3 | 4700.8 |
| 400.5 | 967.6 | 1693.9 | 2510.6 | 4788.5 |
| 404.4 | 975.3 | 1698.2 | 2515.2 | 4813.1 |
| 410.5 | 980.8 | 1708.7 | 2526.3 | 4887.4 |
| 413.7 | 988.4 | 1714.6 | 2532.1 | 4948.7 |
| 420.7 | 994.0 | 1723.6 | 2548.7 | 4992.9 |
| 423.1 | 1001.5 | 1731.0 | 2570.7 | 5095.6 |
| 430.9 | 1007.4 | 1738.5 | 2575.9 | 5114.4 |
| 432.6 | 1014.7 | 1747.4 | 2582.5 | 5245.6 |
| 441.3 | 1020.8 | 1753.3 | 2587.3 | 5278.2 |
| 442.3 | 1028.0 | 1763.9 | 2603.2 | 5401.6 |
| 451.8 | 1034.3 | 1768.2 | 2612.7 | 5483.4 |
| 452.0 | 1041.3 | 1780.4 | 2628.9 | 5573.0 |
| 461.9 | 1047.9 | 1783.2 | 2630.4 | 5787.6 |
| 462.4 | 1054.6 | 1796.9 | 2631.3 | 5818.5 |
| 471.8 | 1061.6 | 1798.1 | 2673.5 | 6033.5 |
| 473.1 | 1068.0 | 1813.1 | 2683.6 | 6427.8 |



**Fig. S2.** Potential energy surface for internal rotation of naphthyl substituents in TNB. A dihedral angle of 0 degrees corresponds to the optimal configuration.

**Table S8**

Contributions of vibration and internal rotation to the heat capacities of TNB, as well as isochoric and isobaric heat capacities calculated in this work.

| *T /* K | *C*v.vib(*T*)/ J K-1 mol-1 a | *∑C*v.ir(*T*)/ J K-1 mol-1 b | *C*v.m(*T*)/ J K-1 mol-1 | *C*p.m(*T*)/ J K-1 mol-1 |
| --- | --- | --- | --- | --- |
| 200 | 254.5 | 24.0 | 303.4 | 311.7 |
| 220 | 287.6 | 22.9 | 335.4 | 343.7 |
| 240 | 321.5 | 22.1 | 368.6 | 376.9 |
| 260 | 356.0 | 21.5 | 402.4 | 410.7 |
| 280 | 390.6 | 20.9 | 436.5 | 444.8 |
| 298.15 | 421.9 | 20.5 | 467.3 | 475.7 |
| 300 | 425.0 | 20.5 | 470.5 | 478.8 |
| 320 | 459.1 | 20.1 | 504.2 | 512.5 |
| 340 | 492.4 | 19.9 | 537.2 | 545.5 |
| 360 | 525.0 | 19.6 | 569.5 | 577.8 |
| 380 | 556.5 | 19.4 | 600.9 | 609.2 |
| 400 | 587.0 | 19.2 | 631.1 | 639.5 |
| 420 | 616.4 | 19.0 | 660.3 | 668.6 |
| 440 | 644.6 | 18.9 | 688.4 | 696.7 |
| 460 | 671.6 | 18.7 | 715.2 | 723.5 |
| 480 | 697.4 | 18.6 | 740.9 | 749.3 |
| 500 | 722.1 | 18.4 | 765.5 | 773.8 |
| 520 | 745.7 | 18.3 | 789.0 | 797.3 |
| 540 | 768.3 | 18.2 | 811.4 | 819.7 |
| 560 | 789.8 | 18.0 | 832.8 | 841.1 |
| 580 | 810.4 | 17.9 | 853.2 | 861.5 |
| 600 | 830.0 | 17.8 | 872.7 | 881.0 |
| 620 | 848.7 | 17.7 | 891.3 | 899.7 |
| 640 | 866.7 | 17.5 | 909.1 | 917.5 |
| 660 | 883.8 | 17.4 | 926.2 | 934.5 |
| 680 | 900.2 | 17.3 | 942.4 | 950.8 |
| 700 | 916.0 | 17.1 | 958.0 | 966.3 |
| 720 | 931.0 | 17.0 | 972.9 | 981.3 |
| 740 | 945.5 | 16.8 | 987.3 | 995.6 |
| 760 | 959.4 | 16.7 | 1001.0 | 1009.3 |
| 780 | 972.7 | 16.5 | 1014.1 | 1022.4 |
| 800 | 985.5 | 16.4 | 1026.8 | 1035.1 |

a Vibrational contribution to the heat capacity. Calculated based on the set of frequencies listed in Table S7 using Eq. (S1).

b Sum of the internal rotation contributions for all rotating tops of the molecule.

*The procedure of ideal gas phase heat capacities calculation*

According to the rigid rotor − harmonic oscillator model, the vibrational contribution to the molar heat capacity in the ideal gas phase can be calculated by Eq. (S1) with the set of frequencies from Table S6:

 (S1)

where *Θi* is the *i­*-th fundamental vibrational frequency of the molecule.

The contribution of hindered rotation from each rotating top is calculated by Eq. (S2) [[4](#_ENREF_4)] using the energy levels listed in Table S7:

 (S2)

where *εj* is the frequency of the *j*-th energy level.

The molar isobaric heat capacity in the ideal gas phase can be found by summing the contributions of vibration (*C*v,vib), internal rotation of all rotating tops (*∑C*v,ir), translation (3/2 *R*), overall rotation (3/2 *R*), and the difference between isobaric and isochoric heat capacity (*R*):

 (S3)

*6 Molecular refractivity determination*

**Table S9**

Molar refractions of TNB derived according to Eq. (10) of the manuscript and experimentally measured densities and refractive indices of TNB solutions in benzene at 298.15 K required for its calculation (uncertainties are expressed as standard deviation).

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Compound | Mole fraction ×103 a | Density b / g∙cm-3 | Refractive index c | *MR* / cm3·mol-1 |
| TNB | 1.026 | 0.875156 | 1.49872 | 154.8 |
| 1.700 | 0.876125 | 1.49931 | 152.5 |
| 2.652 | 0.877482 | 1.50043 | 156.2 |
| Density (benzene) = 0.873666 g∙cm-3  Refractive index (benzene) = 1.49768  ***MR* =** **154.5 ± 3.2 cm3·mol-1 d** | | | | |

a Mole fraction of TNB in benzene solutions. Standard uncertainty *u* is 0.002.

b Density of TNB solution in benzene at a given molality (accuracy stated by the device manufacturer is ±0.000007 g·cm-³).

c Refractive index of TNB solution in benzene at a given molality (accuracy stated by the device manufacturer is ±0.00010).

d The standard uncertainty of the mean *MR* value is the propagated error, including the reproducibility of experimental *MR* and uncertainties of the refractive index and density.

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