

Use of Topotactic Phase Transformations to Obtain Solutions of the Crystal Structures of Highly Disordered Materials

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X-Ray data collection, solution, and refinement for 1_II. All operations were performed on a Bruker-Nonius Kappa Apex2 diffractometer, using graphite-monochromated MoK α radiation. All diffractometer manipulations, including data collection, integration, scaling, and absorption corrections were carried out using the Bruker Apex2 software.¹ Preliminary cell constants were obtained from three sets of 12 frames. Data collection was carried out at 135 K, using a frame time of 10 sec and a detector distance of 60 mm. The optimized strategy used for data collection consisted of one phi and two omega scan sets, with 0.5° steps in phi or omega; completeness was 97.6%. A total of 1041 frames were collected. Final cell constants were obtained from the xyz centroids of 4012 reflections after integration.

From the systematic absences, the observed metric constants and intensity statistics, space group $P2_1/a$ was chosen initially; subsequent solution and refinement confirmed the correctness of this choice. The structure was solved using *SIR-92*,² and refined (full-matrix-least squares) using the Oxford University *Crystals for Windows* program.³ The asymmetric unit contains three thiourea molecules and one twofold-disordered ferrocene molecule ($Z = 4$ (Fc); $Z = 12$ (thiourea)). The ferrocene disorder was modeled as a two-component disorder; occupancies of major/minor component atoms in each group were constrained to sum to 1.0. The components and their occupancies are: [C(201–204, 205–209)/C(101–104,106,108–110); 0.516/0.484(4)]. Atoms C(105) and C(107) were treated as ordered atoms, with fixed occupancies of 1.0: these two atoms are common to both components and remaining disorder could not be resolved. All non-hydrogen atoms were refined using anisotropic displacement parameters. Inspection of the individual frames of diffraction data, as well as observations during the course of solution and refinement of the structure, strongly suggested that the structure was twinned. During the refinement, processing of the data with *ROTAX*⁴ revealed that the crystal was a *trill*, i.e., it was

triply twinned. For twins, our general laboratory procedure involves (a) solution and refinement of the data with *ROTAX*, (b) reprocessing of the frames with *CELL_NOW*⁵ and *TWINABS*⁶ to produce a (b) hklf4 and (c) hklf5 file. Conventional refinement using these two files is then carried out, and the three models [(a) through (c)] are compared. Experience suggests that it is very difficult to predict which of the three models will be best in an individual case. In this case, the refinement using *ROTAX* was superior; on many occasions the ability to vary the twin overlap parameter in the *Crystals for Windows*³ software leads to substantive improvement. The crystal is a ($\approx 3:1:1$) TLQS⁷ conservative twin⁸ rotated about the 110 and -110 reciprocal directions. The twin laws and corresponding obliquities are $(-1\ 1\ 0)/[-3\ 1\ -1]$, 0.45° , $(0.507, -0.493, 0.501/-1.507, -0.507, -0.501/0,0,-1)$ and $(1\ 1\ 0)/[3\ 1\ 1]$, 0.45° , $(-0.507, -0.493, -0.501/1.507, -0.507, 0.501/0, 0, 1)$. Final refined values of each component were 0.602(4), 0.206(4) and 0.192(4). If conservative twinning,⁸ i.e., preservation of the trigonal symmetry of **1_I** in the resultant monoclinic **1_II** crystal by twinning, was fully achieved, one would expect an equal distribution of the three components. Such a distribution is most often seen in TLS²³ (merohedral or pseudo-merohedral) twins; kinetic factors may intervene to change the distribution. After location of H atoms on electron-density difference maps, the H atoms were initially refined with soft restraints on the bond lengths and angles to regularize their geometry (C---H in the range 0.93--0.98 Å and U_{iso} (H) in the range 1.2-1.5 times U_{eq} of the parent atom), after which the positions were refined with riding constraints.⁹ The final least-squares refinement converged to $R_1 = 0.0456$ ($I > 2\sigma(I)$, 3771 data) and $wR_2 = 0.1226$ (F^2 , 5357 data, 283 parameters). The final CIF is available as supporting material.

X-Ray data collection, solution, and refinement for 1_I. All operations were performed on a Bruker-Nonius Kappa Apex2 diffractometer, using graphite-monochromated MoK α radiation.

All diffractometer manipulations, including data collection, integration, scaling, and absorption corrections were carried out using the Bruker Apex2 software.¹ Preliminary cell constants were obtained from three sets of 12 frames. Data collection was carried out at 260 K, using a frame time of 10 sec and a detector distance of 60 mm. The optimized strategy used for data collection consisted of one phi and two omega scan sets, with 0.5° steps in phi or omega; completeness was 99.8%. A total of 1041 frames were collected. Final cell constants were obtained from the xyz centroids of 2704 reflections after integration.

From the systematic absences, the observed metric constants and intensity statistics, space group $R\bar{3}c$ was chosen initially; subsequent solution and refinement confirmed the correctness of this choice. The structure was solved, in part, using *SIR-92*,² and refined after complete solution (see below) using the Oxford University *Crystals for Windows* program.³ The asymmetric unit contains one half-molecule ($Z' = 1/2$) of thiourea and one-sixth ($Z' = 1/6$) of a ferrocene molecule (Fe on a 32 position; thiourea on a 2 position ($Z = 6$ (Fc); $Z = 18$ (thiourea))). After a number of unsuccessful attempts at modelling a solution and using spherical density models (see main paper), we decided to explore whether a set of coordinates could be *generated* for **1_1** using the methods of topotaxy. In any crystal-to-crystal process, reaction or phase transition, one has the opportunity, if the process is observed during a single diffractometer session, to obtain the exact orientation relationship between the pair of unit cells observed.^{8,10,11} The procedure, using the current version (4.40) of our available program TOPO,¹¹ involves reading in a pair of *.p4p* or *.cif* files which contain the orientation matrices for Phase 1 and Phase 2, R_1 and R_2 , respectively. The product of the inverse of the orientation matrix for Phase 2 and the orientation matrix for Phase 1 gives the topotactic transformation matrix ϕ ; the ϕ matrix may be used to transform the direct space axial parameters of unit cell 1 to unit cell 2.^{8,10,11}

$$\varphi = R^{-T} R_I$$

The fractional coordinates associated with Phases 1 and 2 transform contravariantly to the unit cell parameters,¹² thus we can transform the coordinates as follows,

$$\begin{pmatrix} x_2 \\ y_2 \\ z_2 \end{pmatrix} = \overline{\varphi}^{-1} \begin{pmatrix} x_1 \\ y_1 \\ z_1 \end{pmatrix}$$

where the bar indicates the transform of matrix φ .

The coordinates of polymorph **1_II** were then multiplied by the transpose of the inverse topotactic transformation matrix, (-0.29240015, -1.02595031, 0.00465608/ -0.65292293, -0.07470173, -0.00103417/ 0.33493739, -0.00935831, -1.00324917). Conveniently, both φ and its inverse are part of the TOPO program output,¹³ and the Oxford University *Crystals for Windows* software provides an option for coordinate transformation.³ Once the new coordinate set was generated, redundant atoms, specifically those associated with 2½ of the original three thiourea moieties, had to be removed; these of course were symmetry-related to those of the half-molecule in the Wyckoff 18e position. The derived Fe atom position, (1/3, 2/3, -0.097) was displaced *ca.* 0.17 Å from the Wyckoff 6a position (1/3, 2/3, -0.0833) and therefore was assigned an occupancy of 0.5. Cyclopentadienyl C atoms, involved in a twofold disorder in **1_II**, were now initially set to occupancies of 0.0833 (= 0.5/6). When the parameter files were completely updated using the predicted new coordinates, and the occupancies adjusted, refinement was carried out using isotropic displacement parameters for the ring C atoms, and the refined occupancies of the two ferrocene orientations were constrained to sum to 1/6. The components and their occupancies are: [C(201–204, 205–209)/C(101–104,106,108–110); 0.0925/0.0741/(11), a ratio of \approx 55.5:44.5]. Atoms C(105) and C(107) were treated as ordered atoms, with fixed occupancies of 1/6: these two atoms are common to both components and

remaining disorder was not resolved. Both Fe and remaining non-hydrogen atoms were refined using anisotropic displacement parameters. The atom numbering scheme is identical to that in the polymorph **1_II**. Bond length, vibration and angle restraints for the C- C and Fe-C distances were also included. The final least-squares refinement converged to $R_1 = 0.0425$ ($I > 2\sigma(I)$, 934 data) and $wR_2 = 0.1330$ (F^2 , 791 data, 104 parameters). The final CIF is available as supporting material.

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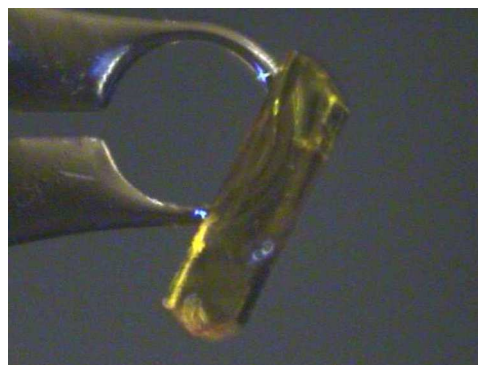


Figure S1. Prismatic crystals (*ca.* 2 mm on an edge (left), and acicular crystals (*ca.* $0.2 \times 0.2 \times 0.7$ mm) of compound **1** (right). Acicular crystals had well-developed (101), $(-1\ 0\ 1)$, $\pm(110)$, $\pm(-1\ 1\ 0)$, $\pm(010)$, $\pm(011)$, $\pm(1\ -1\ 1)$, $\pm(1\ -1\ 0)$, $\pm(100)$ and $\pm(001)$ faces.

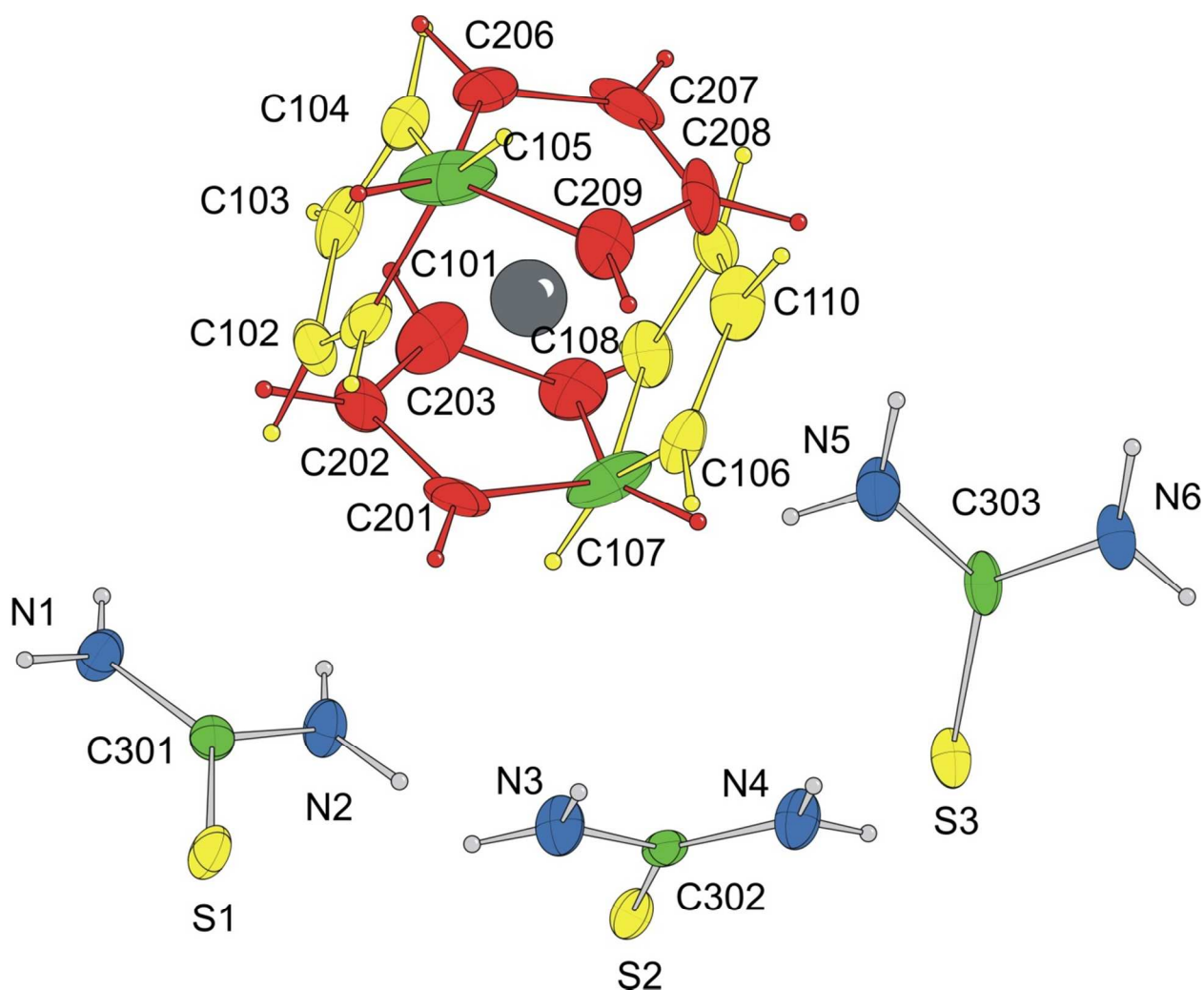


Figure S2. View of the asymmetric unit of polymorph **1_II**, with labels. C atoms in green are associated with both disordered ring sets and have fixed occupancies of 1.0; atom C(105) is in the upper left and C(107) at lower right. For clarity, atoms C(204) and C(109) have not been labelled; C(204, yellow) bonds to C(203, red) and C(107, green), while C(109, yellow) bonds to C(108, yellow) and C(110, yellow).

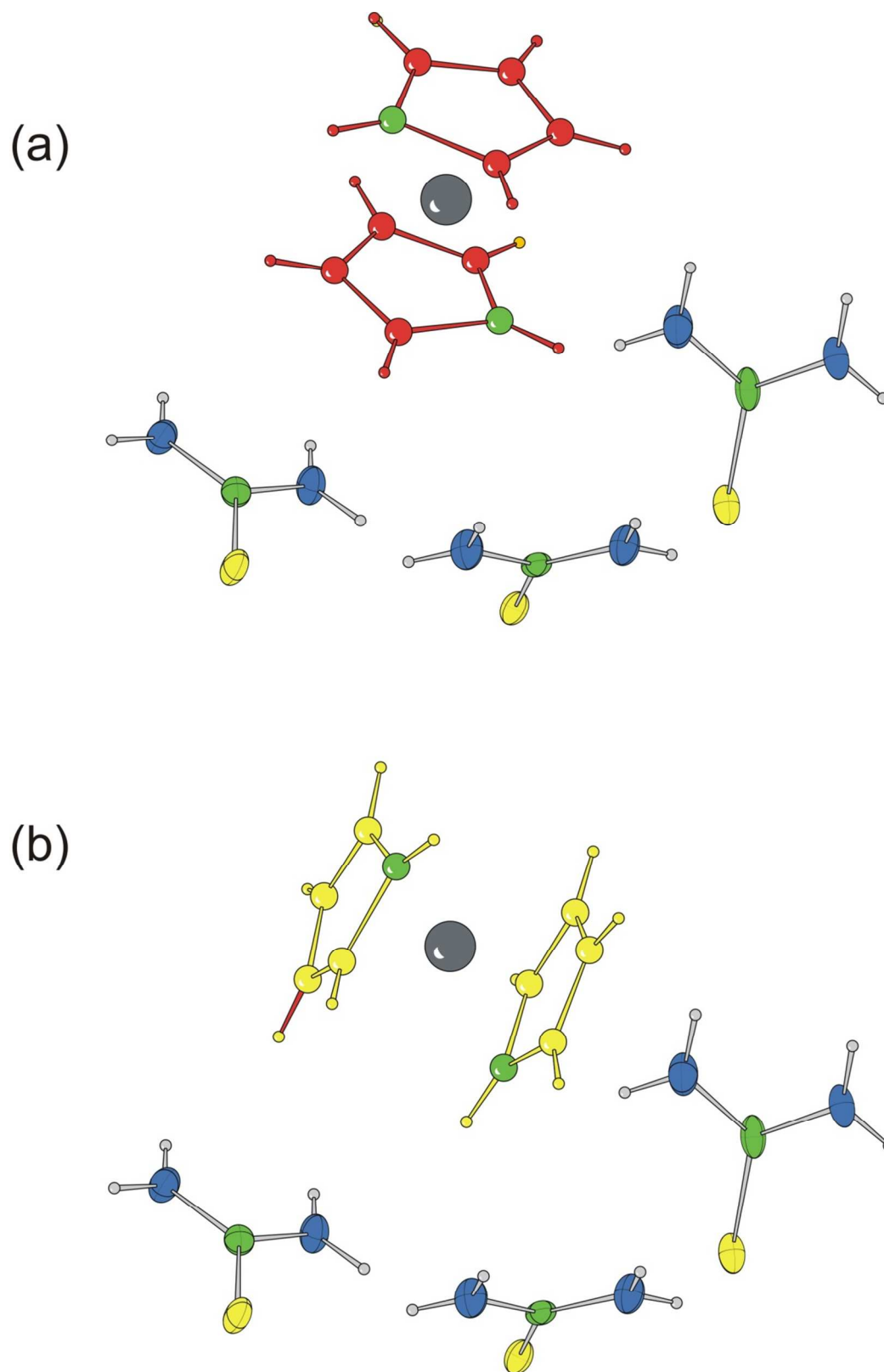


Figure S3. View of the two separate disordered ferrocene molecules in Figures 1 and S2.

I. Diffractometer files (*.p4p) for calculations using program TOPO. Only the beginning of each file is shown, but these may be cut, pasted into an editor, and saved as text .p4p files for further calculations in TOPO.

Compound 1_I, 260K

```

FILEID APEX2          2014.11-0      4.00      09/08/17 11:08:42 fctu_11
SITEID ?
TITLE ?
CHEM ?
CELL      16.3194    16.3194    12.3630    90.0000    90.0000    120.0000    2851.445
CELLSD    0.0005      0.0000      0.0004      0.0000      0.0000      0.0000      0.234
ORT1      -3.0994322e-002    1.6973387e-002    -5.8737345e-002
ORT2       5.8696888e-002    2.4880277e-002    -4.4780970e-002
ORT3      -2.4504134e-002    -6.4025789e-002    -3.2973193e-002
ZEROS     0.0000000    -0.0498614    0.0073687    -0.0820      0.2598     -0.3366
SOURCE MO      0.71073    0.70930    0.71359    2.00000      50.00     30.00
LIMITS      0.00      0.00      0.00      0.00      0.00      0.00      0.00      0.00      0.00      0.00
MORPH ?
DNSMET ?
CCOLOR ?
CSIZE      0.194      0.204      0.712      ?      -153.150
ADPAR       268.0800    260.4000      6.0000      512
ADCOR       1.6242     -0.2337      0.0045     -0.1349      0.0576      0.2240
BRAVAIS Hexagonal R
MOSAIC      0.41 1.09
FACE       -1.00 -1.00  0.00      0.084
FACE        1.00  1.00  0.00      0.097
FACE        1.00 -1.00 -1.00      0.274
FACE       -1.00  1.00  1.00      0.289
FACE        0.00  1.00  0.00      0.101
FACE        0.00 -1.00  0.00      0.100
FACE        0.00 -1.00 -1.00      0.284
FACE        0.00  1.00  1.00      0.300
FACE        1.00 -1.00  1.00      0.291
FACE       -1.00  1.00 -1.00      0.321
FACE        1.00  0.00  1.00      0.291
FACE       -1.00  1.00  0.00      0.097
FACE        1.00 -1.00  0.00      0.102
FACE       -1.00  0.00  0.00      0.061
FACE        1.00  0.00  0.00      0.103
FACE       -1.00  0.00  1.00      0.283
FACE        0.00  0.00  1.00      0.332
FACE        0.00  0.00 -1.00      0.356

```

Compound 1_II, 135K

```

FILEID C_NOW          2008/4          4.00      08/30/17 09:26:09 FCTU_LL
SITEID ?
TITLE ?
CHEM      C13 H22 Fe N6 S3
CELL      10.1077    16.2085    12.4068    89.9105    114.0199    89.8810    1856.584
CELLSD    0.0020      0.0032      0.0025      0.0300      0.0300      0.0300      0.928
ORT1      -0.030734396      0.038954463      0.047956225
ORT2      -0.032633148     -0.047689125      0.034178820

```

```

ORT3      0.098602526   -0.003842198    0.065717474
ZEROS    0.0000000    0.0000000    0.0000000    0.0000    0.0000    0.0000
ADCOR     0.2194     -0.1354     -0.0002     -0.1304     0.1000     0.2395
CELL2    10.1077    16.2085    12.4068    89.9105    114.0199    89.8810    1856.584
CELLSD2   0.0020     0.0032     0.0025     0.0300     0.0300     0.0300     0.928
ORT12     -0.074197136   -0.004922336   -0.082943983
ORT22     0.055647928     0.040024608   -0.026735747
ORT32     0.055947088   -0.046693325   -0.013866247
ZEROS2    0.0000000    0.0000000    0.0000000    0.0000    0.0000    0.0000
ADCOR2     0.2194     -0.1354     -0.0002     -0.1304     0.1000     0.2395
CELL3    10.1077    16.2085    12.4068    89.9105    114.0199    89.8810    1856.584
CELLSD3   0.0020     0.0032     0.0025     0.0300     0.0300     0.0300     0.928
ORT13     -0.045702171   -0.034178864    0.042681538
ORT23     0.087384835     0.007916741    0.075406939
ORT33     -0.044801623    0.050750330    0.016699020
ZEROS3    0.0000000    0.0000000    0.0000000    0.0000    0.0000    0.0000
ADCOR3     0.2194     -0.1354     -0.0002     -0.1304     0.1000     0.2395
SOURCE MO  0.71073    0.70930    0.71359    2.00000    50.00    30.00
LIMITS    0.00    0.00    0.00    0.00    0.00    0.00    0.00    0.00    0.00    0.00
MORPH ACICULAR FRAGMENT
DNSMET ?
CCOLOR orange
CSIZE ? ? ? ? -138.640
ADPAR      266.1700    260.0300    6.0000    512
BRAVAIS Monoclinic(b-unique) P
MOSAIC 0.42 1.47

```

Topotactic matrices from output of program (Starting phase = 135K)

TOPOTACTIC TRANSFORMATION MATRIX (PHI)

GOUGOUTAS, J. Z. ISR. J. CHEM. 1972, 10, 395-407

```

0.11517220   -1.00731349    0.04784676
-1.58204138    0.44847247   -0.53235203
0.00216531   -0.00513724   -0.99599057

```

DETERMINANT OF TOPOTACTIC TRANSFORMATION MATRIX: 1.537

THIS SHOULD EQUAL V(DAUGHTER)/V(MOTHER)

INVERSE TOPOTACTIC TRANSFORMATION MATRIX (PHI)^-1

GOUGOUTAS, J. Z. ISR. J. CHEM. 1972, 10, 395-407

```

-0.29240015   -0.65292293    0.33493739
-1.02595031   -0.07470173   -0.00935831
0.00465608   -0.00103417   -1.00324917

```