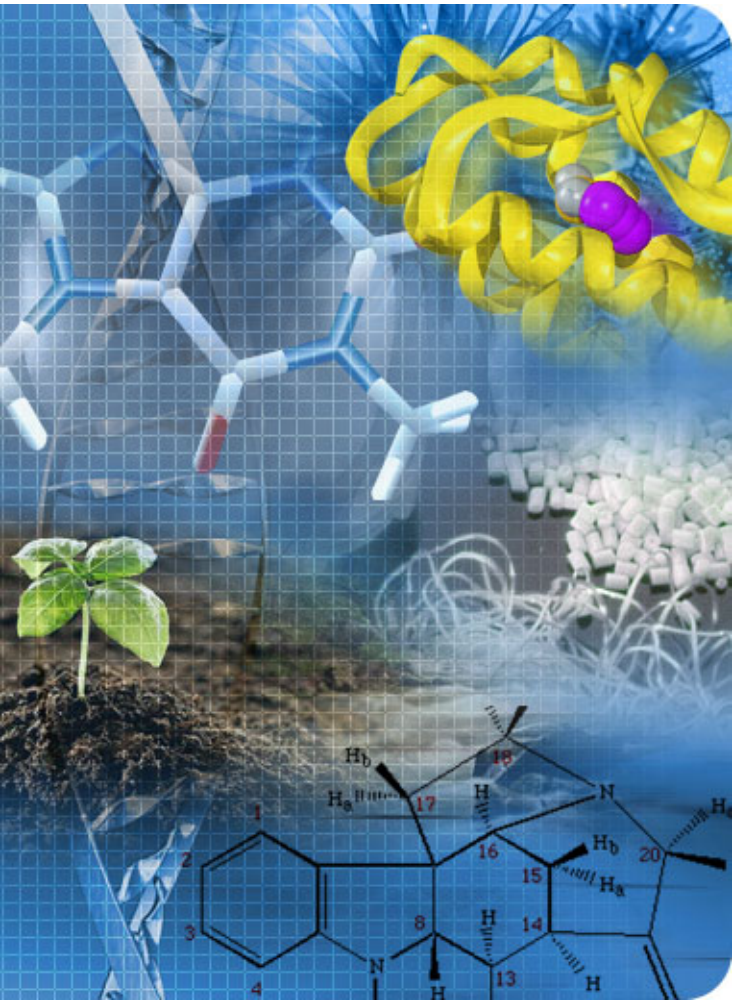


Tools for the Solution and Refinement of Problem Structures

Charles F. Campana, Ph.D.
Bruker AXS Inc.

Current Software Tools

Bruker Programs

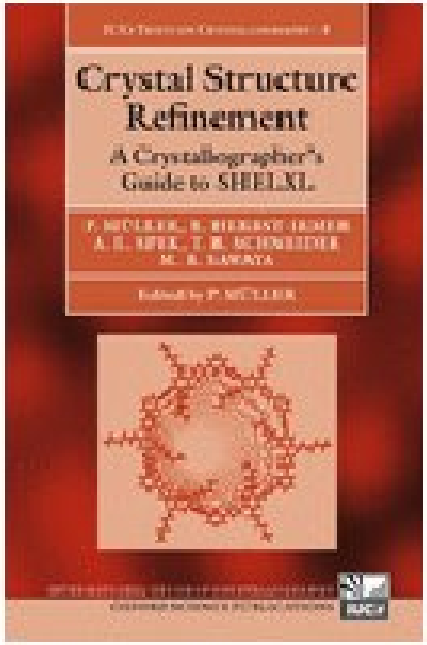
SMART (Chambers)
RLATT (Pressprich)
CELL_NOW (Sheldrick) [Version 2008/2]
XPREP (Sheldrick) [Version 2008/2]
SAINT (Chambers) [Version 7.53A]
SHELXTL (Sheldrick) [Version 2008/2]
SADABS & TWINABS (Sheldrick) [Version 2008/1]
APEX2 [Version 2008.2] (Kaercher et al.)

Other Programs

ROTAX (Parsons) [February 2006 Version]
PLATON (Spek) [August 2007 Version]
JANA2006 (Petricek & Dusek) [March 2008 Version]
Mercury (CCDC) [Version 1.4.2]

Recommended Reference for Problem Structures

Müller, P. *Crystal Structure Refinement*. 1st ed. New York, NY: Oxford University Press, 2006. ISBN: 0198570767



Application of Advanced Tools to Problem Structures

- **Non-Merohedral Twins**
  - Diagnosis – CELL_NOW, RLATT, ROTAX
  - Processing – SAINT (w/ multiple OM), TWINABS
  - Solution – XM or XS (HKLF 4 data)
  - Refinement – XL (BASF + HKLF 5)
- **Pseudo-Merohedral Twins**
  - Diagnosis – XPREP, ROTAX
  - Processing – SAINT, SADABS
  - Solution – XM or XS
  - Refinement – XL (BASF + TWIN)
- **Merohedral Twins**
  - Diagnosis – XPREP, ROTAX
  - Processing – SAINT, SADABS
  - Solution – XM or XS
  - Refinement – XL (BASF + TWIN)
- **Inversion (Racemic) Twins**
  - Diagnosis – XPREP, ROTAX
  - Processing – SAINT, SADABS
  - Solution – XM or XS
  - Refinement – XL (BASF + TWIN)
- **Modulated Structures**
  - Diagnosis – SMART, APEX2, RLATT
  - Processing – SAINT (w/ QVEC inst.), SADABS
  - Solution – XM or XS
  - Refinement – JANA 2000(Petricek & Dusek)

Introduction and Overview
Examples of Difficult Structures

Indexing, Unit Cell Determination Problems

- Split Crystals
- Non-Merohedral (Rotational) Twinning
- Modulated Structures

Structure Solution Problems

- Incorrect Space Group
- Pseudo-Merohedral Twinning
- Merohedral Twinning

Structure Refinement Problems

- Disordered Structures
- Pseudo-Merohedral Twinning
- Merohedral Twinning

Example 1 - Pseudo-Merohedral Twinning

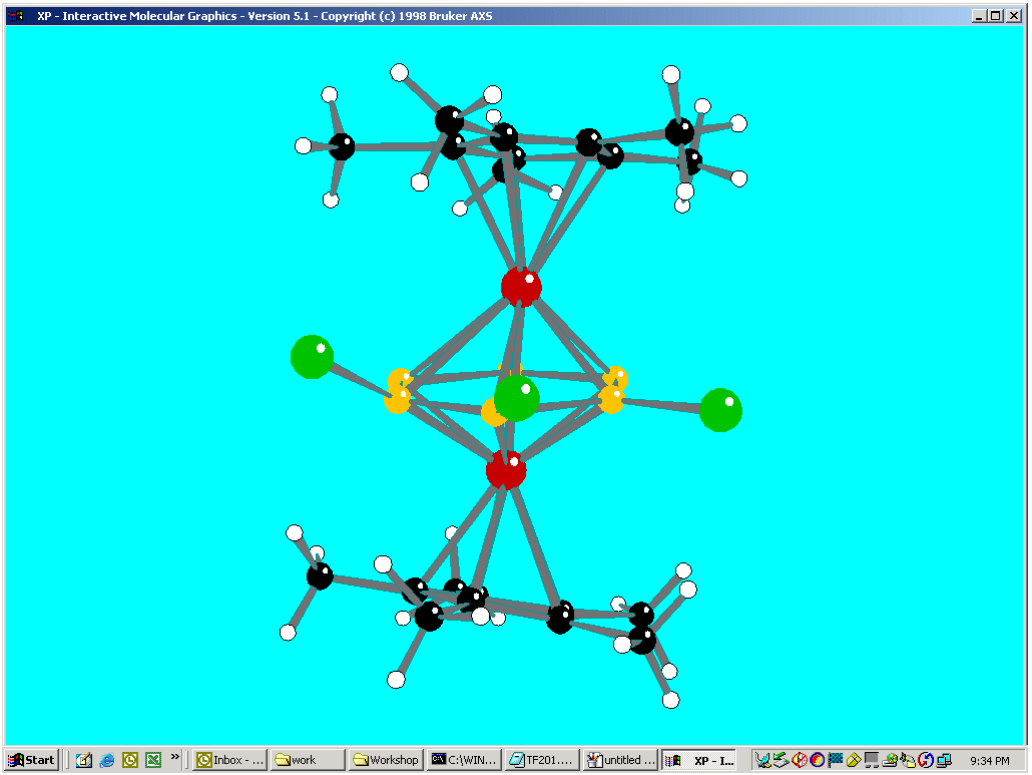
Background

- Organometallic Re complex ($C_{20}H_{34}B_6Cl_2Re_2$)
- Monoclinic – $P2_1/n$, Z = 4

Problems

- R1 = 20%
- Many atoms with NPD U-values
- Incorrect structure (3 Cl atoms per molecule)

Example 1 - Pseudo-Merohedral Twinning



Example 1 - Pseudo-Merohedral Twinning

Other important details

- 330 violations of systematic absence rules for $P2_1/n$
- 1679 Inconsistent equivalents
- R(int) = 0.2042 R(sigma) = 0.1212
- Many significant correlations in refinement
- Recommended weighting scheme: WGHT 0.0000 920.9722
- K 51.471 11.087 4.180 2.588
- Most Disagreeable Reflections

h	k	l	Fo^2	Fc^2	Delta(F^2)/esd	Fc/Fc(max)	Resolution(A)
-8	4	1	16585.63	7.47	6.25	0.004	1.25
-12	2	2	25248.76	151.15	6.16	0.017	0.87
8	6	4	20892.44	153.24	6.03	0.017	1.10
8	2	8	36143.16	635.95	6.03	0.035	1.01
-9	4	2	17985.62	302.20	5.99	0.024	1.12
-9	6	3	12074.38	93.03	5.94	0.013	1.07
12	2	2	18911.99	2.13	5.93	0.002	0.85
12	4	1	13717.04	11.69	5.91	0.005	0.85

Example 1 - Pseudo-Merohedral Twinning

Actual Unit Cell (Unconstrained)

```
    CELL     10.5146   16.7855   14.3817   89.9607   94.7430   90.0833   2529.575
    CELLSD    0.0011    0.0017    0.0014    0.0019    0.0017    0.0017      0.809
```

XPREP Output

```
    Option A: FOM = 0.089 deg.   MONOCLINIC   P-lattice   R(sym) = 0.224 [   5389]
    Cell:   10.515  16.785  14.382   89.96   94.74   90.08    Volume:      2529.57
    Matrix: 1.0000  0.0000  0.0000  0.0000  1.0000  0.0000  0.0000  0.0000  1.0000
-------------------------------------------------------------------------------
    Option B: FOM = 0.000 deg.   TRICLINIC    P-lattice   R(sym) = 0.000 [      0]
    Cell:   10.515  14.382  16.785   89.96   89.92   85.26    Volume:      2529.57
    Matrix:-1.0000  0.0000  0.0000  0.0000  0.0000  1.0000  0.0000  1.0000  0.0000
-------------------------------------------------------------------------------
    Option A selected (XPREP suggested Option B!!!)

    Systematic absence exceptions:
            -21-  -a-   -c-   -n-
    N        21   458   458   450
    N I>3s   11   377   358   337
    <I>     1.1  22.0  22.2   8.8
    <I/s>   6.9  13.3  12.4  10.0
```

True Space Group is TRICLINIC P-1

Example 1 - Pseudo-Merohedral Twinning

Refinement in P-1 Space Group

- **Unit Cell Parameters**
  CELL 0.71073 10.5146 14.3817 16.7855 89.961 89.917 85.257
  ZERR 4.00 0.0004 0.0006 0.0007 0.001 0.001 0.001
- 0 Inconsistent equivalents
- R(int) = 0.0267 R(sigma) = 0.0453
- R1 = 0.1342
- Correct structure, but many NPD U-values
- Recommended weighting scheme: WGHT 0.0000 649.6266

Most Disagreeable Reflections

h	k	l	Fo^2	Fc^2	Delta(F^2)/esd	Fc/Fc(max)	Resolution(A)
7	-7	1	11267.14	18.66	6.84	0.006	1.16
-5	4	4	8311.13	508.36	6.28	0.030	1.61
-2	5	3	3458.91	8.18	6.08	0.004	2.23
-5	3	3	8537.00	4.83	5.81	0.003	1.77
7	-8	3	13399.65	126.62	5.68	0.015	1.08
-3	8	4	6747.74	668.96	5.64	0.034	1.45
-5	-3	7	5815.16	320.09	5.63	0.024	1.53
7	-3	5	12077.00	413.54	5.57	0.027	1.29
0	4	2	3441.84	499.71	5.56	0.029	3.30

Insert LIST 4 instruction into .INS file and repeat refinement

Example 1 - Pseudo-Merohedral Twinning

Run ROTAX program from Command Prompt

ROTAX output

```
180.0 degree rotation about   0.  0.  1. direct lattice direction:
[  -1.000    0.000    0.002]
[   0.000   -1.000    0.001]
[   0.000    0.000    1.000]
Figure of merit =   0.77 ***********
No reflections omitted
```

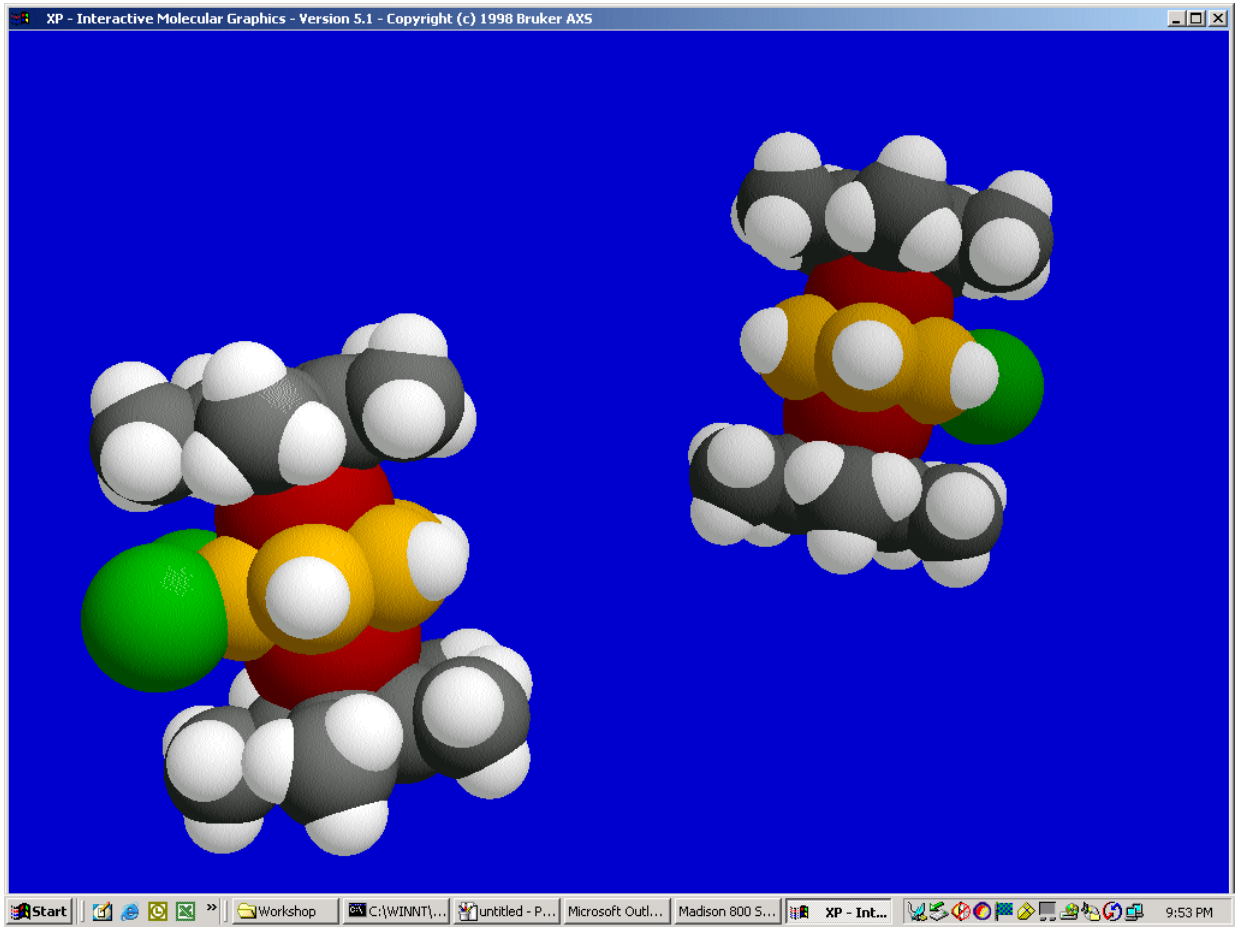
Insert TWIN and BASF instructions into .INS file and repeat refinement

```
PLAN 5
TWIN -1  0  0  0 -1  0  0  0  1
BASF 0.5
WGHT    0.040000
```

Results of twinned refinement

- BASF 0.23970
- R1 = 0.0329, wR2 = 0.0798, GooF = 1.066
- Correct structure, no NPD U-values, normal weighting scheme

Example 1 - Pseudo-Merohedral Twinning



Example 2 - Pseudo-Merohedral Twinning

Background

Form III of 2,2',4,4',6,6'-Hexanitroazobenzene (HNAB-III)

Two previous polymorphs (HNIABZ11 & HNIABZ20) characterized and published - E. J. Graeber & B. Morosin, Acta Cryst, B30, 310 (1974).

Beautiful orange plate-like crystals obtained (Sandia NL 1977)

X-Ray photographs indicated orthorhombic $C222_1$

Excellent data collected on Picker FACS-I diffractometer (Sandia NL) & later Syntex P3/F (UNM)

No solution after much effort (MULTAN etc.) – 30 years!

Hemisphere of data collected on SMART CCD system (Sandia NL 2003)

Example 2 - Pseudo-Merohedral Twinning

Standard XPREP run (accept default parameters)

```
-------------------------------------------------------------------------------

Search for higher metric symmetry
Identical indices and Friedel opposites combined before calculating R(sym)
-------------------------------------------------------------------------------
Option A: FOM = 0.008 deg.   ORTHORHOMBIC C-lattice   R(sym) = 0.046 [   3489]
Cell:   15.401  41.471   5.524   90.00   90.00   89.99    Volume:      3528.25
Matrix: 1.0000  0.0000  0.0000  1.0000  0.0000  2.0000  0.0000 -1.0000  0.0000

Option A selected

-------------------------------------------------------------------------------
```

Example 2 - Pseudo-Merohedral Twinning

Standard XPREP run (accept default parameters)

```
SPACE GROUP DETERMINATION
Lattice exceptions:  P      A      B      C      I      F     Obv    Rev    All

N (total) =          0   3801   3801      0   3844   3801   5050   5060   7586
N (int>3sigma) =     0   2826   2826      0   2903   2826   3754   3734   5596
Mean intensity =   0.0    9.1    9.1    0.0   21.4    9.1   18.4   18.0   18.3
Mean int/sigma =   0.0    9.8    9.8    0.0   11.2    9.8   10.5   10.5   10.6

Crystal system O and Lattice type C selected
Mean |E*E-1| = 0.616 [expected .968 centrosym and .736 non-centrosym]
Chiral flag NOT set

Systematic absence exceptions:
         c--   n--   -c-   -n-   --a   --b  --21
N        229   229    62    62   498   498     7
N I>3s   166   166    42    42   373   373     0
<I>     14.3  14.3  11.7  11.7   8.5   8.5   0.3
<I/s>   12.0  12.0  10.8  10.8   9.9   9.9   0.7

dentical indices and Friedel opposites combined before calculating R(sym)
Option  Space Group  No.  Type  Axes  CSD  R(sym) N(eq)  Syst. Abs.   CFOM
[A] C222(1)        # 20  chiral   1   155  0.046   3489  0.7 /  9.9   3.10
Option [A] chosen
```

Example 2 - Pseudo-Merohedral Twinning

Standard XPREP run (accept default parameters)

```
------------------------------------------------------------------------------
    --

File hnab.ins set up as follows:

TITL hnab in C222(1)
CELL 0.71073  15.4015  41.4709   5.5240  90.000  90.000  90.000
ZERR    8.00   0.0007   0.0023   0.0005   0.000   0.000   0.000
LATT -7
SYMM -X, -Y, 0.5+Z
SYMM -X, Y, 0.5-Z
SYMM X, -Y, -Z
SFAC C H N O
UNIT 96 32 64 96
TEMP 23
TREF
HKLF 4
END

    7586 Reflections written to new reflection file hnab.hkl

------------------------------------------------------------------------------
    --
```

Example 2 - Pseudo-Merohedral Twinning

XPREP run (change default parameters)

```
------------------------------------------------------------------------------

TOLERANCES CHANGED

Maximum deviation (deg.) in higher symmetry cell search =  1.000
Threshold (deg.) for terminating search =  0.000
R(int) maximum for terminating cell search =  0.600
R(int) maximum for space group determination =  0.300
Minimum number of data in group for syst. absence test =   5
Maximum mean I/sigma(I) for systematic absences =  2.554
Minimum I/sigma gap between absences and rest =  2.109
------------------------------------------------------------------------------
    --
```

Example 2 - Pseudo-Merohedral Twinning

XPREP run (change default parameters)

```
--------------------------------------------------------------------------------
Option A: FOM = 0.008 deg.   ORTHORHOMBIC C-lattice   R(sym) = 0.046 [   3489]
Cell:   15.401  41.471   5.524   90.00   90.00   89.99    Volume:      3528.25
Matrix: 1.0000  0.0000  0.0000  1.0000  0.0000  2.0000  0.0000 -1.0000  0.0000
--------------------------------------------------------------------------------
Option B: FOM = 0.000 deg.   MONOCLINIC   P-lattice   R(sym) = 0.032 [   2165]
Cell:   15.401   5.524  22.118   90.00  110.37   90.00    Volume:      1764.13
Matrix: 1.0000  0.0000  0.0000  0.0000  1.0000  0.0000  0.0000  0.0000  1.0000
--------------------------------------------------------------------------------
Option C: FOM = 0.008 deg.   MONOCLINIC   C-lattice   R(sym) = 0.042 [   2353]
Cell:   41.471  15.401   5.524   90.00   90.00   90.01    Volume:      3528.25
Matrix:-1.0000  0.0000 -2.0000  1.0000  0.0000  0.0000  0.0000 -1.0000  0.0000
--------------------------------------------------------------------------------
Option D: FOM = 0.008 deg.   MONOCLINIC   C-lattice   R(sym) = 0.042 [   2415]
Cell:   15.401  41.471   5.524   90.00   90.00   89.99    Volume:      3528.25
Matrix:-1.0000  0.0000  0.0000 -1.0000  0.0000 -2.0000  0.0000 -1.0000  0.0000
--------------------------------------------------------------------------------
Option E: FOM = 0.000 deg.   TRICLINIC    P-lattice   R(sym) = 0.000 [      0]
Cell:    5.524  15.401  22.118   69.63   90.00   90.00    Volume:      1764.13
Matrix: 0.0000  1.0000  0.0000 -1.0000  0.0000  0.0000  0.0000  0.0000  1.0000

Option B selected

--------------------------------------------------------------------------------
```

Example 2 - Pseudo-Merohedral Twinning

XPREP run (change default parameters)

```
SPACE GROUP DETERMINATION

Lattice exceptions:  P      A      B      C      I      F     Obv    Rev    All

N (total) =          0   3780   3791   3801   3777   5686   5054   5050   7586
N (int>3sigma) =     0   2767   2789   2826   2766   4191   3734   3750   5596
Mean intensity =   0.0   17.6   17.1    9.1   17.6   14.6   18.9   18.2   18.3
Mean int/sigma =   0.0   10.5   10.6    9.8   10.5   10.3   10.6   10.5   10.6

Crystal system M and Lattice type P selected
Mean |E*E-1| = 0.624 [expected .968 centrosym and .736 non-centrosym]
Chiral flag NOT set
Systematic absence exceptions:
        -21-   -a-   -c-   -n-
N         7   498   500   496
N I>3s    0   373   337   336
<I>     0.3   8.5  18.2  18.0
<I/s>   0.7   9.9  10.4  10.4

dentical indices and Friedel opposites combined before calculating R(sym)
Option  Space Group  No.  Type  Axes  CSD  R(sym) N(eq)  Syst. Abs.   CFOM

[A] P2(1)          #  4  chiral   1  3543  0.032   2165  0.7 /  9.9   2.29
[B] P2(1)/m        # 11  centro   1   402  0.032   2165  0.7 /  9.9  13.08
Option [A] chosen
```

Example 2 - Pseudo-Merohedral Twinning

XPREP run (change default parameters – M option)

```
------------------------------------------------------------------------------
File hnab3.ins set up as follows:

TITL hnab3 in P2(1)
CELL 0.71073  15.4015   5.5240  22.1182  90.000 110.367  90.000
ZERR    4.00   0.0007   0.0005   0.0011   0.000   0.001   0.000
LATT -1
SYMM -X, 0.5+Y, -Z
SFAC C H N O
UNIT 48 16 32 48
TEMP 32
FIND    33
PLOP    44    55    62
MIND 1.0 -0.1
NTRY 1000
HKLF 4
END

    7586 Reflections written to new reflection file hnab3.hkl
------------------------------------------------------------------------------
```

Example 2 - Pseudo-Merohedral Twinning

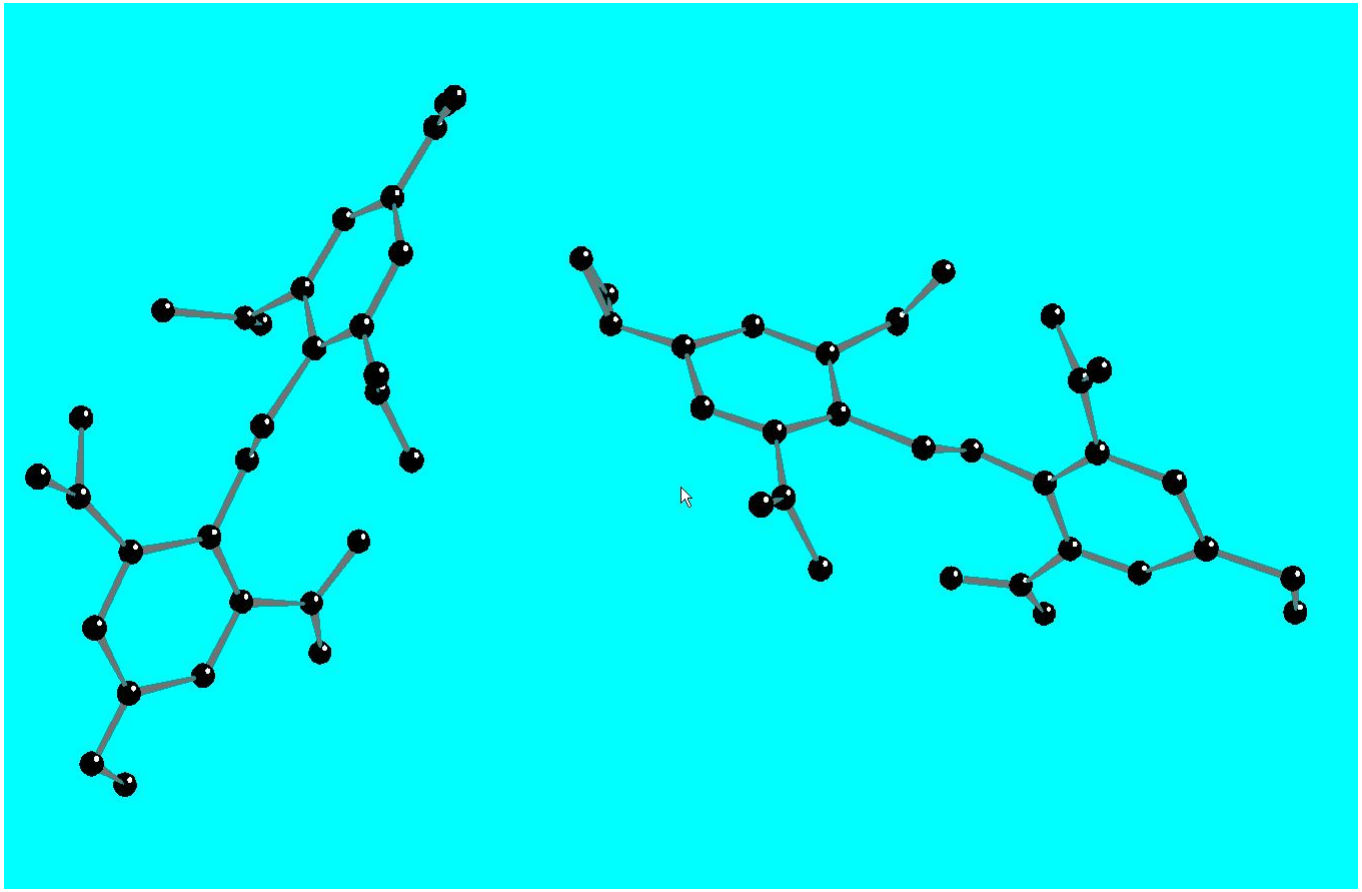
XM Results

```
------------------------------------------------------------------------------
REM TRY     49   FINAL CC 73.23   TIME      10 SECS
REM Fragments: 31 31
REM
TITL hnab3 in P2(1)
CELL 0.71073  15.4015   5.5240  22.1182  90.000 110.367  90.000
ZERR    4.00   0.0007   0.0005   0.0011   0.000   0.001   0.000
LATT -1
SYMM -X, 0.5+Y, -Z
SFAC C H N O
UNIT 48 16 32 48

------------------------------------------------------------------------------
```

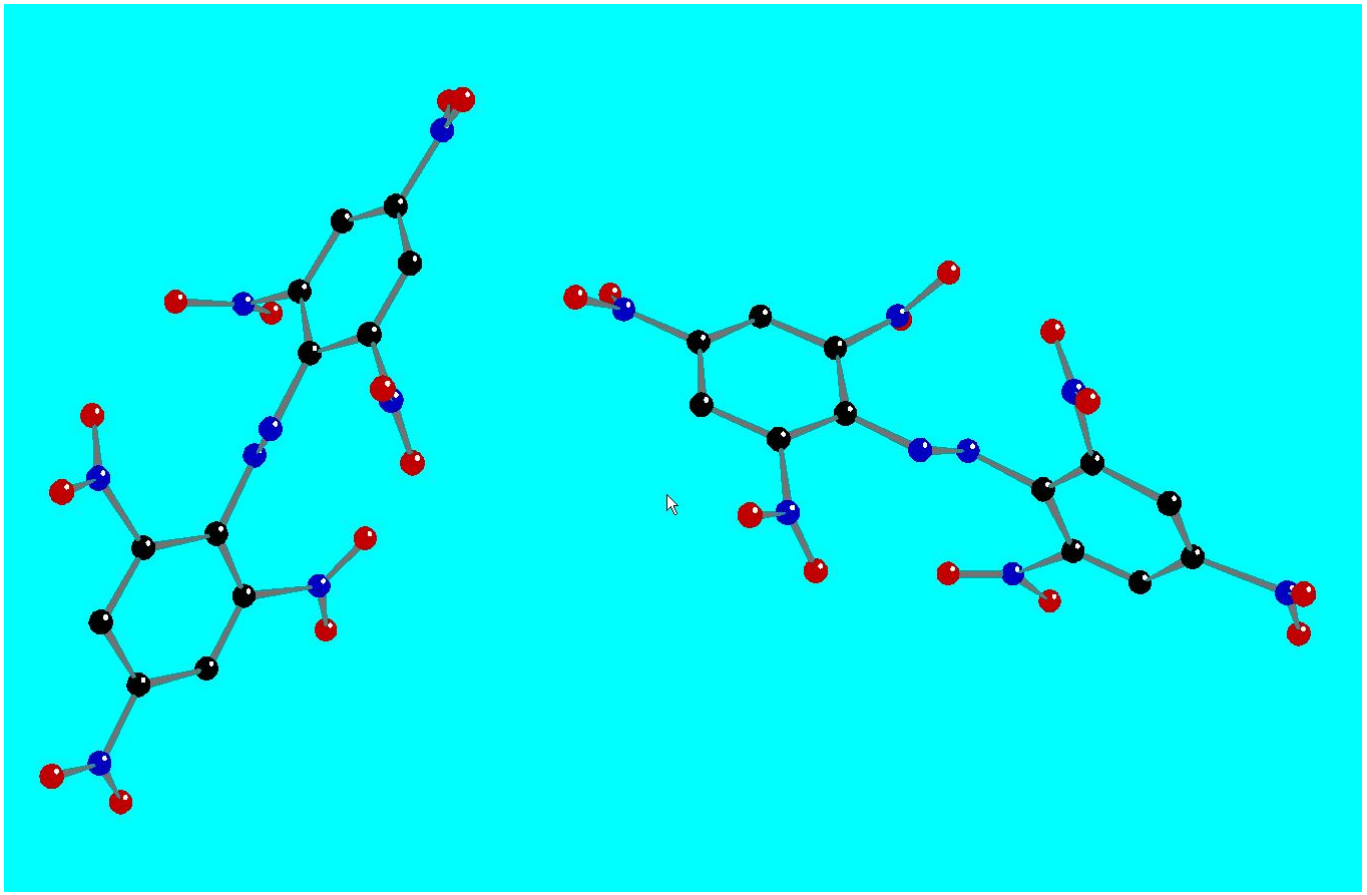
Example 2 - Pseudo-Merohedral Twinning

XM Results



Example 2 - Pseudo-Merohedral Twinning

XL Results – R1 = 17 %



Example 2 - Pseudo-Merohedral Twinning

XL Results – R1 = 17 %

Most Disagreeable Reflections (* if suppressed or used for Rfree)

h	k	l	Fo^2	Fc^2	Delta(F^2)/esd	Fc/Fc(max)	Resolution(A)
-2	1	12	555.54	17.30	7.18	0.025	1.74
-1	0	11	233.91	7.52	5.90	0.017	1.96
-2	-1	12	619.16	17.35	5.89	0.025	1.74
-13	0	11	403.33	28.87	5.54	0.032	1.15
5	0	2	1820.13	310.96	5.31	0.107	2.56
8	3	5	262.33	5.53	5.12	0.014	1.15
5	0	6	735.08	138.45	5.11	0.071	1.91
2	3	10	151.73	7.99	4.84	0.017	1.30
-9	0	11	269.03	7.10	4.77	0.016	1.51
-4	1	5	371.20	74.39	4.74	0.052	2.87
-11	0	12	265.56	28.40	4.74	0.032	1.28
2	-1	13	270.30	24.35	4.71	0.030	1.41
-1	0	19	419.68	61.03	4.70	0.047	1.12
-5	0	10	487.22	72.29	4.62	0.051	2.06
-1	0	21	241.18	7.45	4.59	0.016	1.01
4	3	3	163.01	20.78	4.59	0.028	1.54
-11	0	3	236.22	19.83	4.51	0.027	1.38
4	3	5	214.44	39.52	4.44	0.038	1.45
-4	3	6	185.38	9.78	4.43	0.019	1.58
2	1	13	253.70	24.36	4.40	0.030	1.41
-8	1	11	165.49	17.43	4.38	0.025	1.55
11	0	2	178.01	5.94	4.28	0.015	1.25
-2	1	16	210.01	14.64	4.24	0.023	1.32

Example 2 - Pseudo-Merohedral Twinning

ROTAX Results

```
180.0 degree rotation about   1.  0.  0. direct lattice direction:

[   1.000    0.000    0.000]
[   0.000   -1.000    0.000]
[  -0.999    0.000   -1.000]

Figure of merit =   0.11 ***********

No reflections omitted
```

Example 2 - Pseudo-Merohedral Twinning

Final XL Results – R1 = 3.17 %

```
TITL hnab3 in P2(1)
CELL 0.71073  15.4015   5.5240  22.1182  90.000 110.367  90.000
ZERR    4.00   0.0007   0.0005   0.0011   0.000   0.001   0.000
LATT -1
SYMM -X, 0.5+Y, -Z
SFAC C H N O
UNIT 48 16 32 48
TEMP 32
L.S. 4
ACTA
FMAP 2
PLAN 10
TWIN 1 0 0 0 -1 0 -1 0 -1
WGHT    0.029700
EXTI    0.003436
BASF   0.44866
FVAR       0.21356
```

Final Publication:

M. A. Rodriquez, C. F. Campana, A. D. Rae, E. Graeber and B. Morosin, Acta Cryst. C61, o127-o130 (2005)

Example 3 - Merohedral Twinning

Background

```
CELL 0.71073  16.5617  16.5617  15.4439  90.000  90.000 120.000
ZERR    6.00   0.0023   0.0023   0.0031   0.000   0.000   0.000
```

Hexagonal / Trigonal unit cell, Z = 6

Organometallic Ru complex ($C_{30}H_{24}N_6Ru$) -$Ru(bipy)_3$

Problems

Excellent quality data

R(int) = 0.0307 R(sigma) = 0.0179

Ambiguous space group, structure could not be solved

Example 3 - Merohedral Twinning

XPREP Output

```
------------------------------------------------------------------------------
Option A: FOM = 0.000 deg.   HEXAGONAL    P-lattice   R(sym) = 0.025 [   6448]
Cell:   16.562  16.562  15.443   90.00   90.00  120.00    Volume:      3668.43
Matrix: 1.0000  0.0000  0.0000  0.0000  1.0000  0.0000  0.0000  0.0000  1.0000
Option A selected
------------------------------------------------------------------------------
Systematic absence exceptions:

       61/65 62=31  63    -c-   --c

N        22    18    12   710   475
N I>3s    9     9     0     7   279
<I>   140.0 171.1   0.3   0.9  39.0
<I/s>  10.9  13.3   0.3   0.6   9.2

Option  Space Group  No.  Type  Axes  CSD  R(sym) N(eq)  Syst. Abs.   CFOM

[A] P-3c1          #165  centro   1    28  0.028   8263  0.6 /  9.2   8.91
[B] P3c1           #158  non-cen  1    11  0.028   8263  0.6 /  9.2  23.27
[C] P6(3)cm        #185  non-cen  1     2  0.031   9328  0.6 /  9.2  44.75
[D] P6(3)/mcm      #193  centro   1     1  0.031   9328  0.6 /  9.2  51.94
[E] P-6c2          #188  non-cen  1     0  0.031   9328  0.6 /  9.2 111.42

Option [A] chosen
```

True Space Group is TRIGONAL P-3c1 (No solution possible in any hexagonal space group)

Example 3 - Merohedral Twinning

Solution in P-3c1 Space Group with XS Program

- Two independent Ru(bipy)$_3$ molecules – one on D_3 site and one on C_3 site

Refinement in P-3c1 Space Group

- 0 Systematic absence violations
- 0 Inconsistent equivalents
- R(int) = 0.0305 R(sigma) = 0.0179
- R1 = 0.2542
- Correct structure, but some NPD U-values & very large residual peaks in map

Most Disagreeable Reflections

h	k	l	Fo^2	Fc^2	Delta(F^2)/esd	Fc/Fc(max)	Resolution(A)
-2	6	10	12249.62	7.38	4.69	0.006	1.34
-3	5	10	12390.42	8.50	4.55	0.007	1.40
-1	4	14	5660.73	13.56	4.45	0.009	1.06
-5	7	2	6912.71	25.24	4.37	0.012	2.20
-1	4	10	14770.25	301.41	4.33	0.041	1.44
0	5	10	11512.03	3.27	4.22	0.004	1.36
-6	11	10	4414.28	42.68	4.19	0.016	1.08
-8	9	10	11256.75	375.46	4.15	0.046	1.14

Insert LIST 4 instruction into .INS file and repeat refinement

Example 3 - Merohedral Twinning

Run ROTAX program from Command Prompt

ROTAX output

```
    180.0 degree rotation about  -1.  1.  0. direct lattice direction:

    [   0.000   -1.000    0.000]
    [  -1.000    0.000    0.000]
    [   0.000    0.000   -1.000]

    Figure of merit =   0.00 ***********
```

XPREP output - test for merohedral twinning

```
    [1] -3 / -31m: R(int) 0.028(9795)/0.017(1907), <|E^2-1|> 1.063/1.070
    TWIN  0 -1 0  -1 0 0  0 0 -1
    BASF  0.414 [C]  or  0.390 [NC]
```

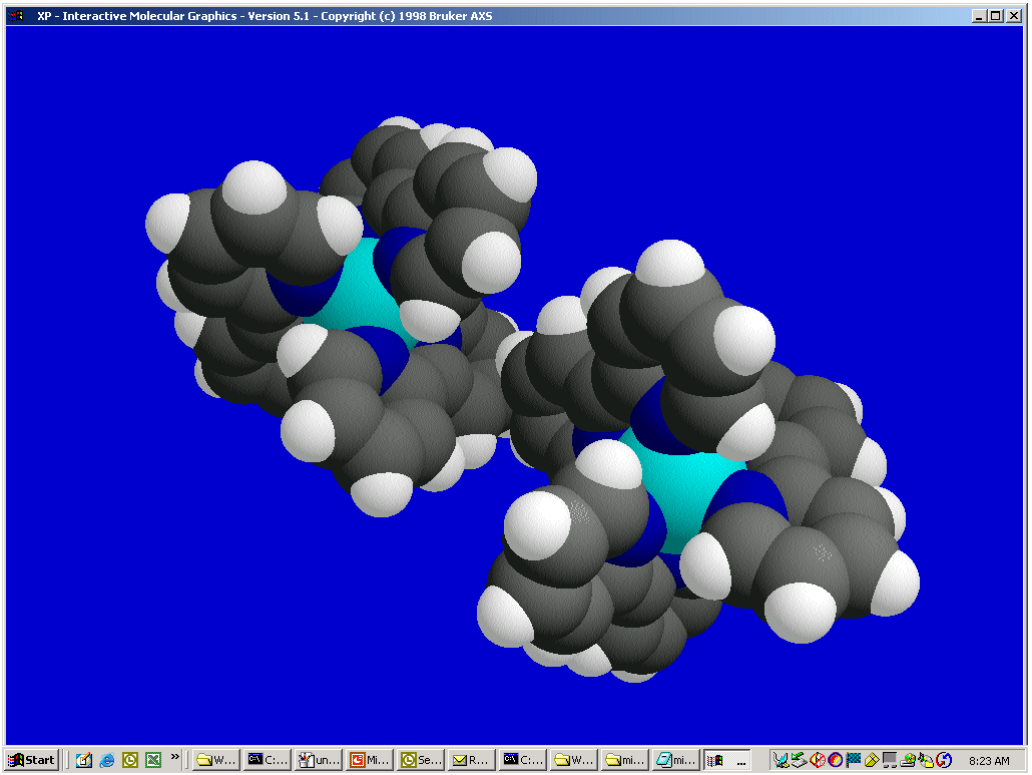
Insert TWIN and BASF instructions into .INS file and repeat refinement

```
    PLAN 5
    TWIN  0 -1 0  -1 0 0  0 0 -1
    BASF 0.5
    WGHT    0.040000
```

Results of twinned refinement

- BASF 0.49628 (perfect twinning)
- R1 = 0.0259, wR2 = 0.0725, GooF = 1.066
- Correct structure, no NPD U-values, normal weighting scheme, no large residual peaks

Example 3 - Merohedral Twinning

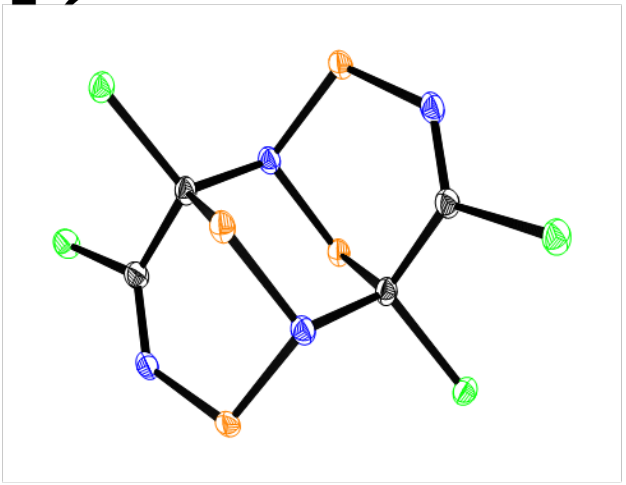


Example 4 – Non-Merohedral Twinning

Simple Monoclinic Structure

Formula – $C_4N_4S_4Cl_4$

Space Group – $P2_1/c$, Z = 2



Example 4 – Non-Merohedral Twinning

Refinement Output

0 Systematic absence violations
1611 Inconsistent equivalents
R(int) = 0.4518 R(sigma) = 0.1179
K 68.634 14.563 4.282 2.946 1.865 1.905
R1 = 0.2550, wR2 = 0.4532, GooF = 3.031
WGHT 0.1768 87.8417

Most Disagreeable Reflections (* if suppressed or used for Rfree)

h	k	l	Fo^2	Fc^2	Delta(F^2)/esd	Fc/Fc(max)	Resolution(A)
9	2	3	664.82	58.18	7.24	0.045	0.62
10	3	2	447.64	40.77	7.19	0.038	0.60
-7	17	3	251.81	0.62	5.95	0.005	0.62
9	1	2	123.93	20.71	5.33	0.027	0.66
8	0	2	540.63	161.71	4.29	0.076	0.73
-8	17	2	219.59	20.52	3.93	0.027	0.59
8	3	4	124.35	19.64	3.79	0.026	0.62
7	17	1	156.00	7.77	3.68	0.017	0.58
9	2	2	142.45	0.03	3.49	0.001	0.66
-6	4	2	1270.72	142.27	3.42	0.071	1.15
8	4	2	187.78	1.51	3.39	0.007	0.72

Example 4 – Non-Merohedral Twinning

ROTAX OUTPUT

180.0 degree rotation about 1. 0. 0. reciprocal lattice direction:
[1.000 0.000 0.955]
[0.000 -1.000 0.000]
[0.000 0.000 -1.000]
Figure of merit = 1.59 **********

Non-Integer Matrix Element – We cannot use a simple TWIN instruction- we must use **CELL_NOW**

Example 4 – Non-Merohedral Twinning

CELL_NOW Output

```
Cell for domain  1:    7.388   13.144    6.182    89.96   113.68    90.06


  1517 reflections within 0.250 of an integer index assigned to domain  1,
  1517 of them exclusively;    46 reflections not yet assigned to a domain

 ------------------------------------------------------------------------

 Cell for domain  2:    7.388   13.144    6.182    89.96   113.68    90.06


 Rotated from first domain by 179.2 degrees about
 reciprocal axis -0.484  0.006  1.000  and real axis -0.004  0.001  1.000

 Twin law to convert hkl from first to     -0.996   0.006  -0.967
 this domain (SHELXL TWIN matrix):         -0.028  -1.000  -0.001
                                           -0.007   0.002   0.996


  1350 reflections within 0.250 of an integer index assigned to domain  2,
    46 of them exclusively;     0 reflections not yet assigned to a domain
```

Example 4 – Non-Merohedral Twinning

.P4P File from CELL_NOW

```
FILEID SAINT        V7.06A        4.00        04/27/04 14:25:12 NSF2
SITEID Administrator                      ?
TITLE  Integration
CHEM   C4N4S4Cl4
CELL      7.3884   13.1436    6.1822   89.9643  113.6805   90.0630    549.797
CELLSD    0.0015    0.0026    0.0012    0.0300    0.0300    0.0300     0.275
ORT1        0.035939306    -0.056865178    -0.082636222
ORT2        0.017559534     0.049863208    -0.112305790
ORT3        0.142276525     0.008283437     0.108424976
ZEROS   0.0000000 -0.0178117 -0.0247456    0.0883    0.1712    0.3467
ADCOR       -6.3043     -0.1071     -0.0043      0.1575      0.1081     -0.0209
CELL2     7.3884   13.1436    6.1822   89.9643  113.6805   90.0630    549.797
CELLSD2   0.0015    0.0026    0.0012    0.0300    0.0300    0.0300     0.275
ORT12      -0.036804073     0.056372143    -0.118583880
ORT22      -0.015264848    -0.050249487    -0.127575904
ORT32      -0.142320156    -0.009261458    -0.029318471
ZEROS2  0.0000000 -0.0178117 -0.0247456    0.0883    0.1712    0.3467
ADCOR2      -6.3043     -0.1071     -0.0043      0.1575      0.1081     -0.0209
SOURCE MO     0.71073   0.70930   0.71359   2.00000    0.00    0.00
```

Read this .P4P file into SAINT Integration Program

Example 4 – Non-Merohedral Twinning

HKLF 5 format file from TWINABS

```
  0   9   3  801.97    7.43   1
  0  -9  -3  805.63    4.71   1
  3   9  -3  861.66    6.32  -2
  0  -9  -3  861.66    6.32   1
 -3   9   3  851.29    8.22  -2
  0  -9   3  851.29    8.22   1
 -3   9   3  796.70    7.03  -2
  0  -9   3  796.70    7.03   1
  3  -9  -3  779.89    7.47  -2
  0   9  -3  779.89    7.47   1
  3  -9  -3  841.68    7.58  -2
  0   9  -3  841.68    7.58   1
  3   9  -3  839.86    8.11  -2
  0  -9  -3  839.86    8.11   1
 -3  -9   3  862.09    6.34  -2
  0   9   3  862.09    6.34   1
  3   9  -3  872.52    8.36  -2
  0  -9  -3  872.52    8.36   1
  0  -9  -3  202.50    3.03   2
  0   9  -3  177.75    3.10   2
```

Example 4 – Non-Merohedral Twinning

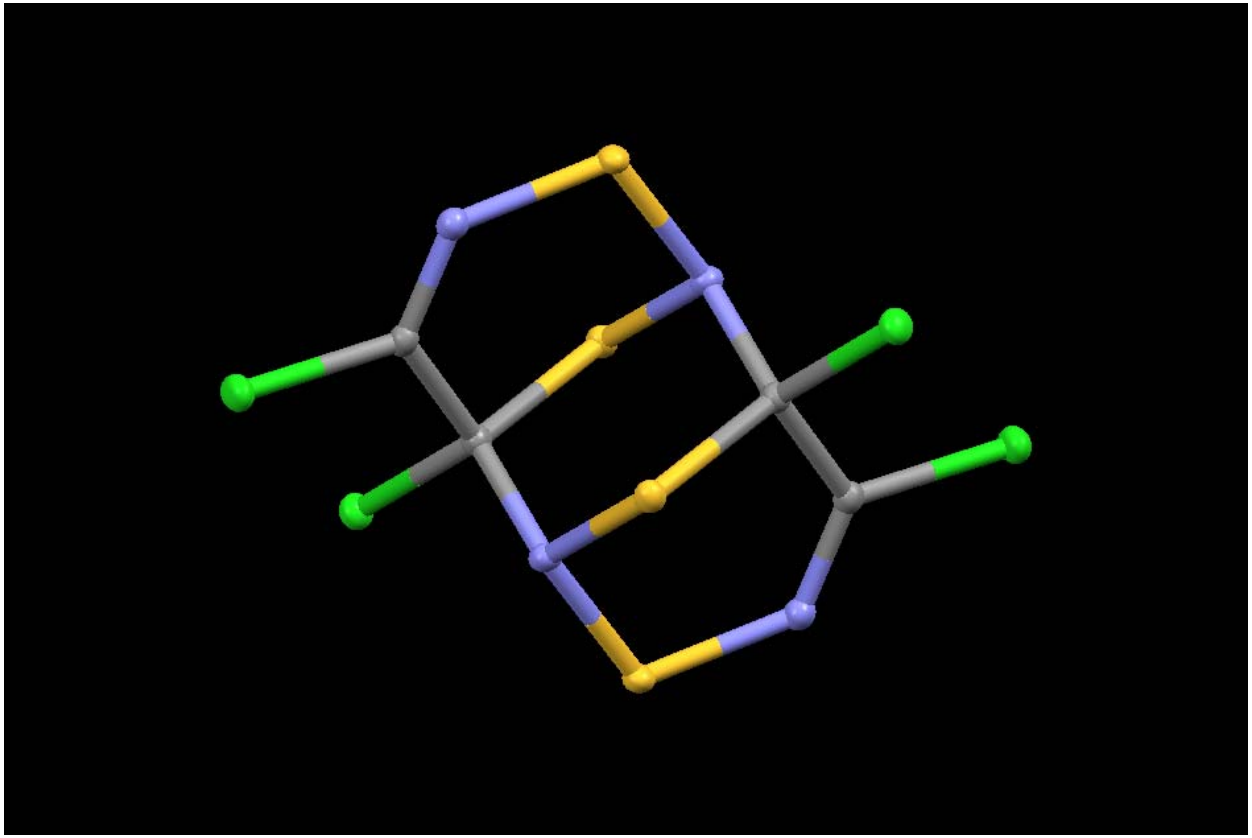
Final Refinement

```
FMAP 2
PLAN 5
WGHT    0.023000
EXTI    0.002298
BASF   0.18207
FVAR       0.65985
CL1   4    0.807182    0.420776    0.495285    11.00000    0.01294    0.01349 =
      0.01087    0.00096    0.00272    0.00102
C2    1    0.711815    0.368499    0.035413    11.00000    0.01049    0.00888 =
         0.01396    0.00045    0.00539    0.00048
 …..
HKLF 5

REM  NSF2 in P2(1)/c
REM R1 =  0.0241 for   9786 Fo > 4sig(Fo)  and  0.0302 for all  12385 data
REM     75 parameters refined using      0 restraints
```

Example 4 – Non-Merohedral Twinning

Final Structure



Example 5 – Whole Molecule Disorder

Background

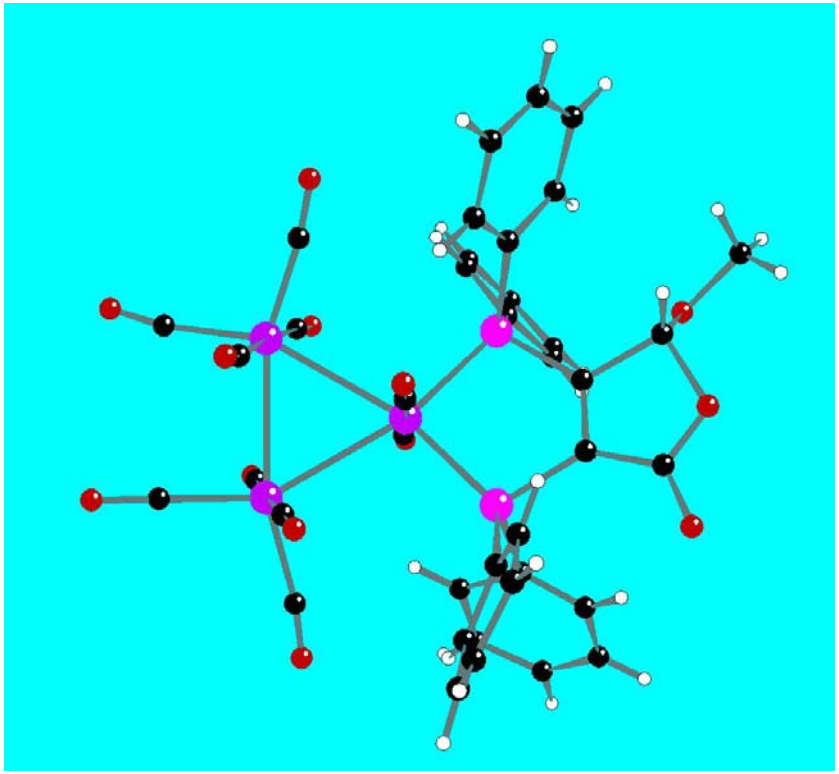
- Sample from UCSD Summer School
- Prof. Michael Richmond et al. (U. of North Texas)
- NMR indicated dynamic equilibrium between two isomers

Structure was easily ‘solved’, but could not be refined

- R1 = 16%
- Many NPD atoms
- Three very large difference peaks (‘Star of David’)

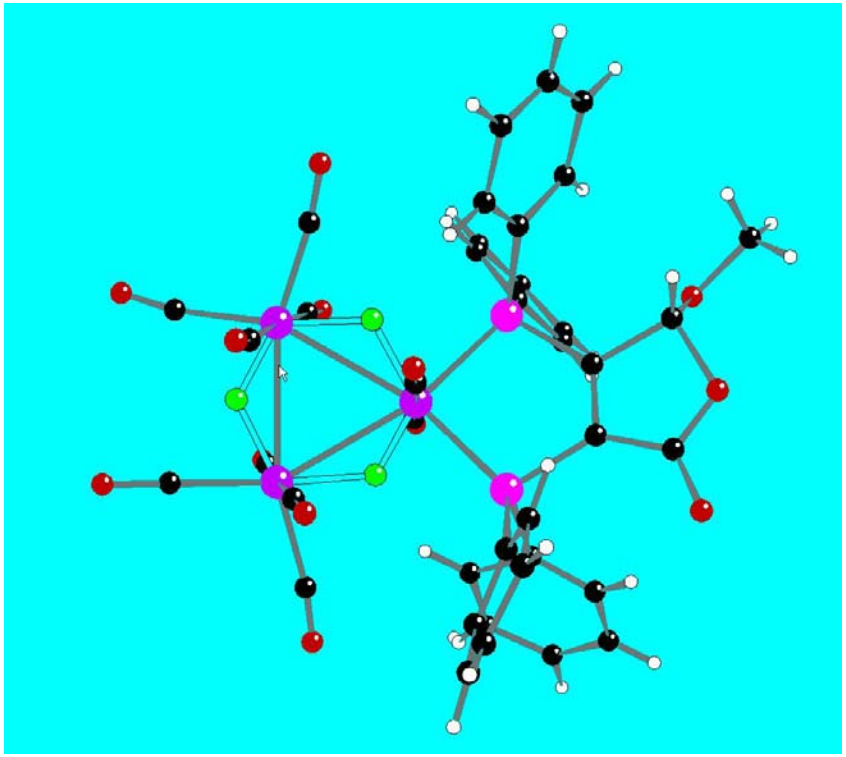
Example 5 – Whole Molecule Disorder

Preliminary structure – Chelating Phosphine Ligand



Example 5 – Whole Molecule Disorder

Three Large Difference Peaks



Example 5 – Whole Molecule Disorder

```
FVAR        0.15477   0.8500
OS1   5     1.38180   0.36327   0.23664   21.00000   0.01306
OS2   5     1.16037   0.44356   0.29321   21.00000   0.01737
OS3   5     1.22802   0.46498   0.16310   21.00000   0.01676
C1A   1     1.22737   0.29544   0.22637   21.00000   0.01424
O1A   3     1.14724   0.25371   0.21696   21.00000   0.01327
C2A   1     1.53166   0.43473   0.24515   21.00000   0.02705
O2A   3     1.61483   0.47245   0.24881   21.00000   0.01637
C3A   1     1.00907   0.38885   0.25481   21.00000   0.02644
O3A   3     0.91212   0.35992   0.23556   21.00000   0.03082
C4A   1     1.33420   0.49045   0.32785   21.00000   0.02520
O4A   3     1.42200   0.51620   0.35349   21.00000   0.02519
C5A   1     1.13429   0.40796   0.37402   21.00000   0.01968
O5A   3     1.11507   0.38537   0.42076   21.00000   0.04168
C6A   1     1.03019   0.51972   0.29063   21.00000   0.02206
O6A   3     0.94876   0.56097   0.28462   21.00000   0.04682
C7A   1     1.12667   0.38230   0.13189   21.00000   0.02768
O7A   3     1.06313   0.34129   0.11120   21.00000   0.02261
C8A   1     1.33629   0.53964   0.20167   21.00000   0.02088
O8A   3     1.39946   0.58535   0.21995   21.00000   0.02206
C9A   1     1.34144   0.46478   0.08771   21.00000   0.02607
O9A   3     1.39311   0.47459   0.04379   21.00000   0.02768
C10A  1     1.07098   0.52231   0.13931   21.00000   0.02470
O10A  3     0.98114   0.55458   0.12305   21.00000   0.04529
P1    4     1.49269   0.30401   0.31810   11.00000   0.01685
P2    4     1.51235   0.30162   0.16667   11.00000   0.02253
C1    1     1.64848   0.25992   0.21803   11.00000   0.02086
C2    1     1.64668   0.26068   0.28099   11.00000   0.02963
C3    1     1.77319   0.22528   0.30686   11.00000   0.03008
```

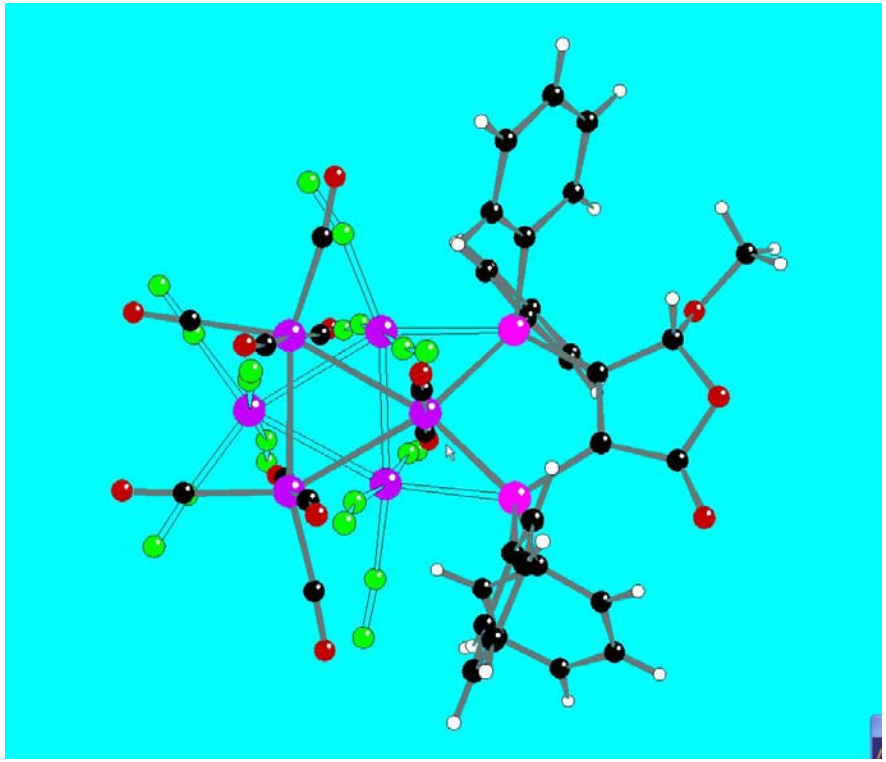
Example 5 – Whole Molecule Disorder

```
FVAR       0.14765   0.84986
PART  1
ANIS   3
OS1   5    1.381809    0.363269    0.236644    21.00000    0.01398
OS2   5    1.160375    0.443563    0.293216    21.00000    0.01832
OS3   5    1.228021    0.464972    0.163111    21.00000    0.01769
PART  2
ANIS   3
OS4   5    1.279201    0.372329    0.290337   -21.00000    0.01897
OS5   5    1.356916    0.404339    0.165486   -21.00000    0.01516
OS6   5    1.132255    0.478575    0.221611   -21.00000    0.02121
PART  1
C1A   1    1.227149    0.295498    0.226379    21.00000    0.01463
O1A   3    1.147208    0.253766    0.216857    21.00000    0.01437
C2A   1    1.531363    0.434503    0.245167    21.00000    0.02786
O2A   3    1.614757    0.472385    0.248824    21.00000    0.01766
...

C9A   1    1.341290    0.464934    0.087821    21.00000    0.02657
O9A   3    1.392650    0.474727    0.043766    21.00000    0.02908
C10A  1    1.071073    0.522226    0.139298    21.00000    0.02516
O10A  3    0.981357    0.554645    0.123065    21.00000    0.04658
PART  0
ANIS   2
P1    4    1.492683    0.304015    0.318087    11.00000    0.01777
P2    4    1.512382    0.301606    0.166718    11.00000    0.02357
C1    1    1.648401    0.259913    0.218106    11.00000    0.02206
C2    1    1.646876    0.260442    0.280954    11.00000    0.03039
```

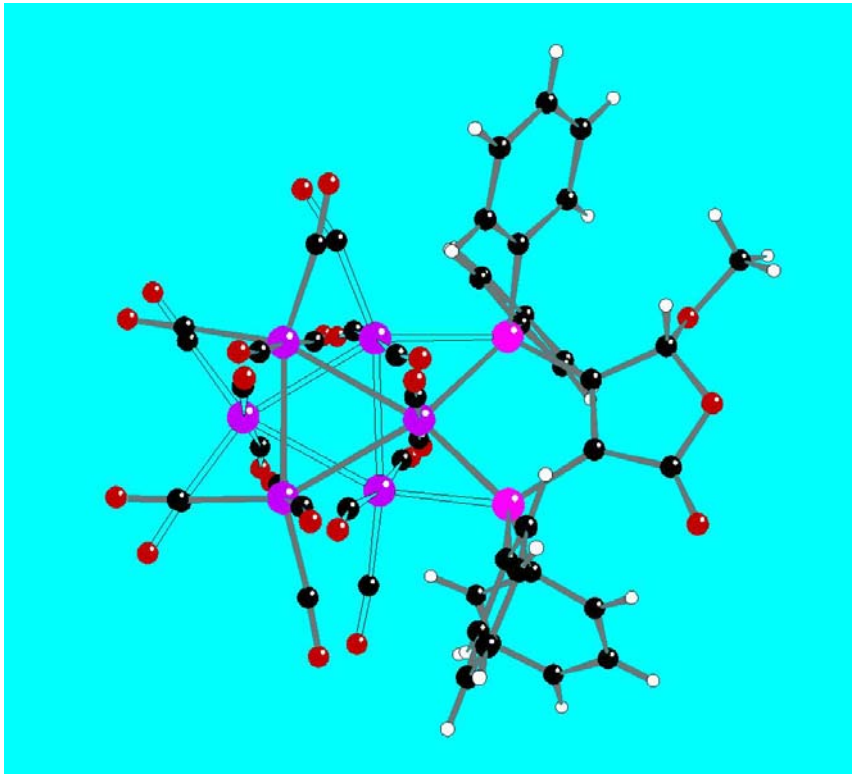
Example 5 – Whole Molecule Disorder

Remaining Carbonyl Atoms Revealed in Difference Map



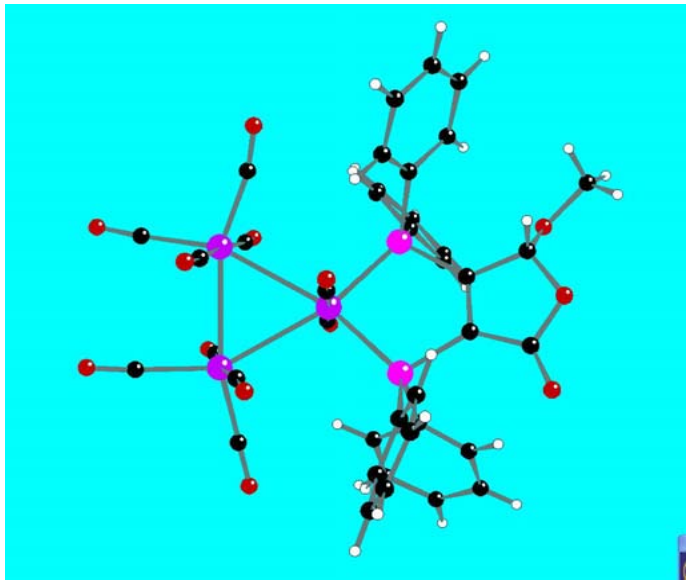
Example 5 – Whole Molecule Disorder

Superposition of both isomers

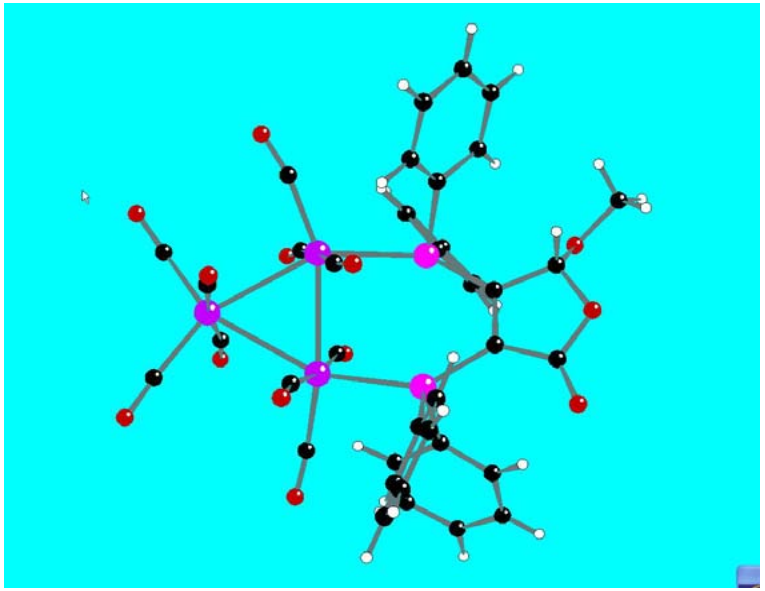


Example 5 – Whole Molecule Disorder

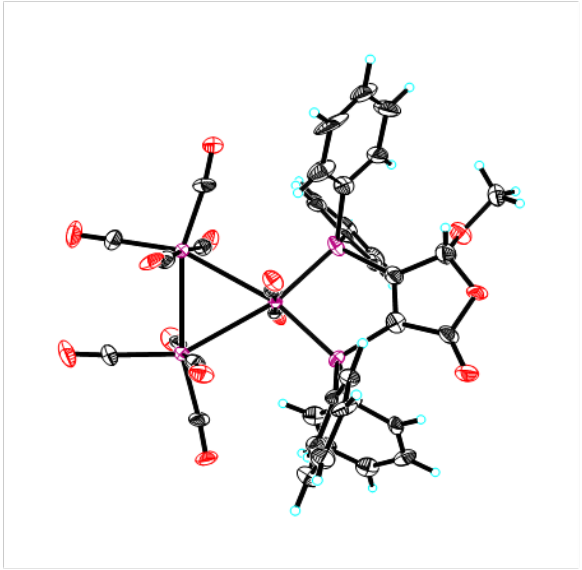
Chelating Phosphine Ligand (85%)

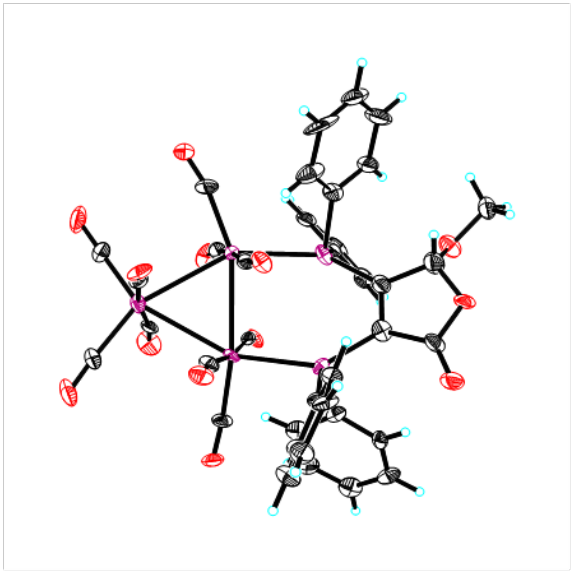


Bridging Phosphine Ligand (15%)



Example 5 – Whole Molecule Disorder





Crystallographic restraints (SADI, ISOR, SIMU, EADP) were used in initial refinement

Final refinement converged at R1 = 5.2%

Example 6 – Urea Host : Guest Complex

Background

- Prof. Mark Hollingsworth et al. (Kansas State U.)
- Urea host lattice with long-chain carboxylic acid in channels

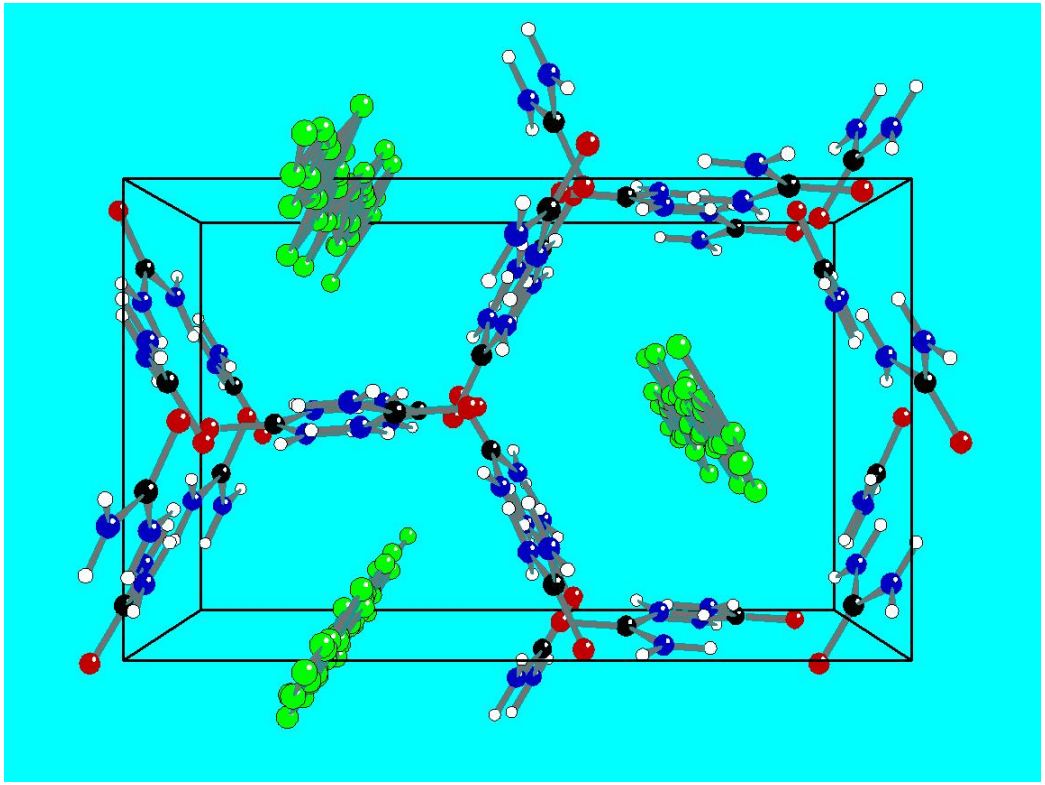
Structure of urea lattice was 'solved', but carboxylic acid molecules could not be located

Apparent unit cell

- Orthorhombic $P2_12_12_1$
- a = 8.3096 Å , b = 10.9591 Å , c = 13.6330 Å
- 12 Urea molecules, 4 carboxylic acid molecules per cell

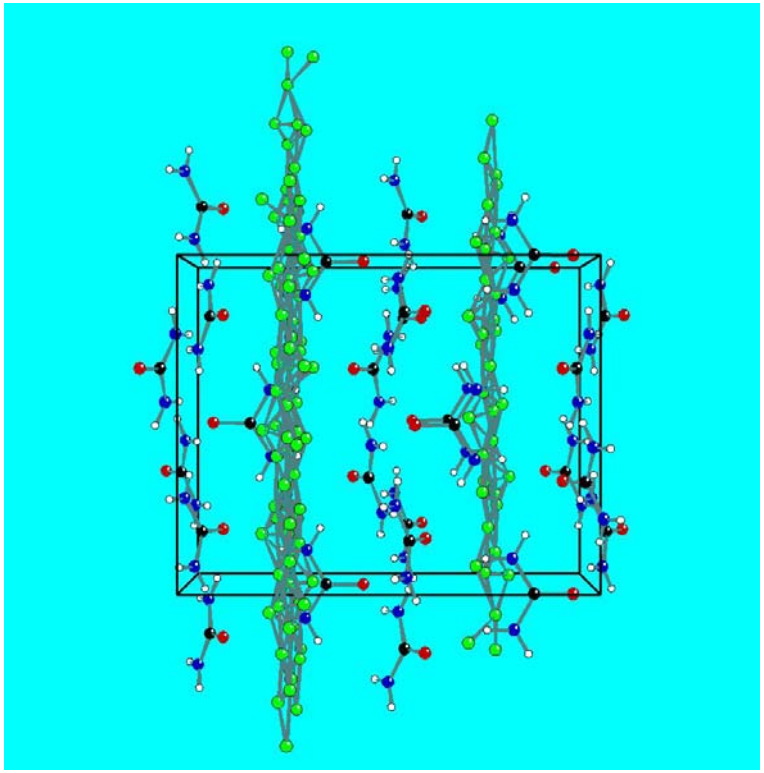
Example 6 – Urea Host : Guest Complex

Projection down b-axis



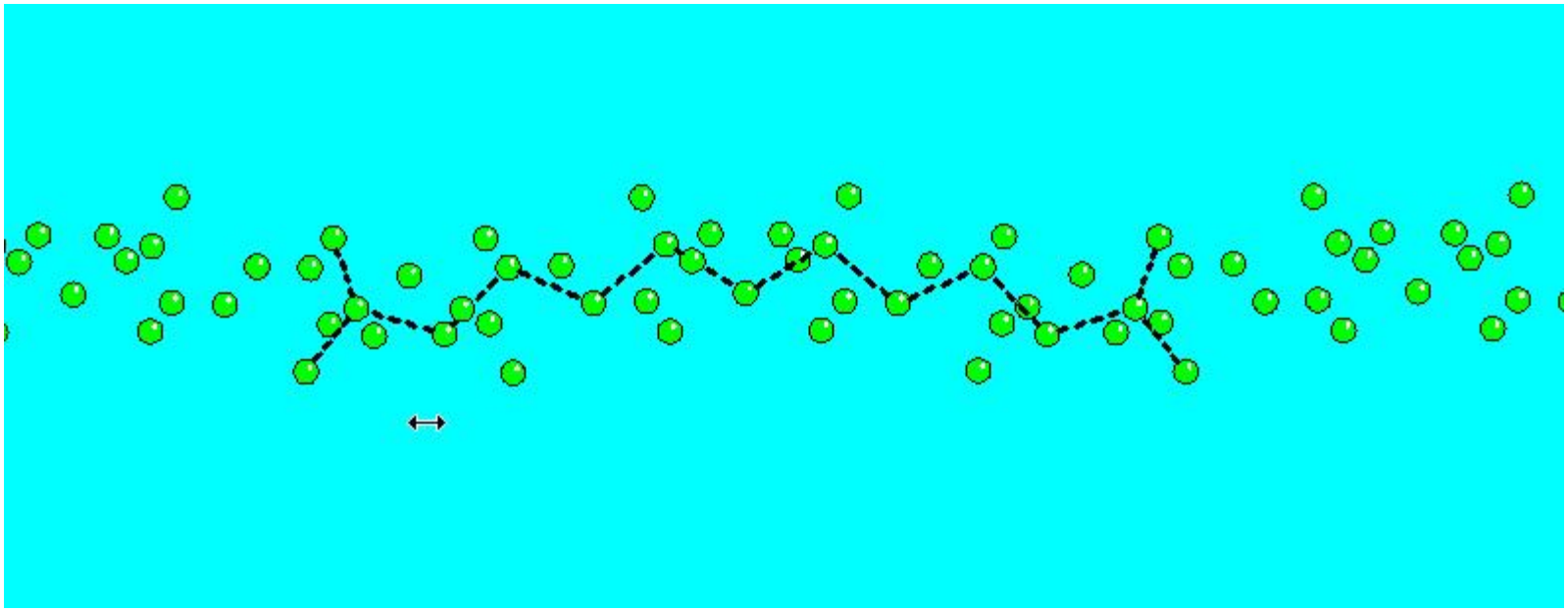
Example 6 – Urea Host : Guest Complex

Projection down a-axis



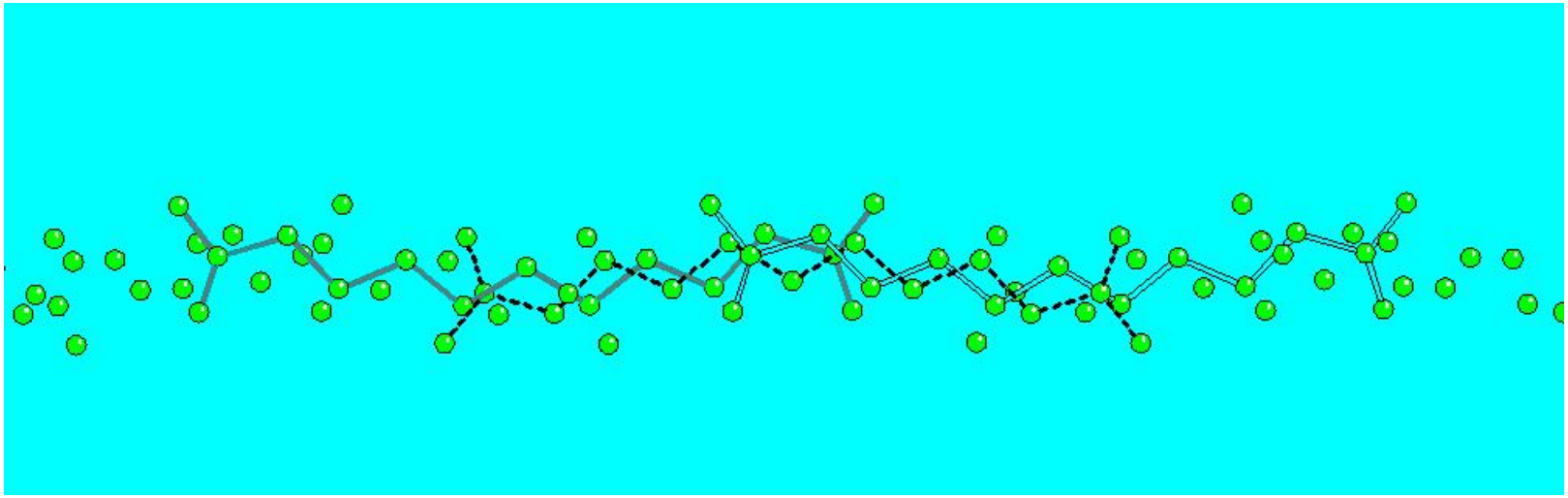
Example 6 – Urea Host : Guest Complex

Analysis of Q-peaks



Example 6 – Urea Host : Guest Complex

Analysis of Q-peaks



Example 6 – Urea Host : Guest Complex

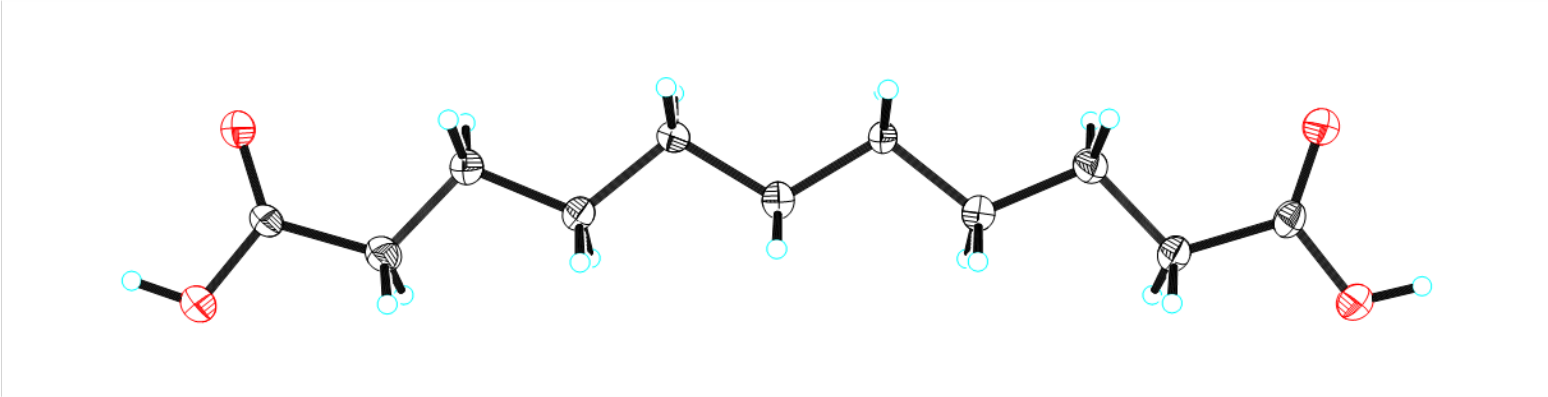
```
N2C   3    0.662814    0.937759    0.024542    11.00000    0.02028
AFIX  93
H2CA  2    0.626060    1.006875    0.048581    11.00000    0.05118
H2CB  2    0.753628    0.936746   -0.008654    11.00000    0.05692
AFIX   0
PART  -1
C1S   1    0.047758    0.093743    0.256429    10.33333    0.02221
O1S   4   -0.065938    0.059457    0.208123    10.33333    0.03123
O2S   4    0.147213    0.019479    0.303494    10.33333    0.03285
AFIX   3
H2S   2    0.117603   -0.055411    0.292184    10.33333    0.05883
AFIX   0
C2S   1    0.090446    0.226023    0.271096    10.33333    0.02369
AFIX  23
H2SA  2    0.196427    0.240424    0.240008    10.33333    0.03582
H2SB  2    0.103898    0.240028    0.342366    10.33333    0.05245
AFIX   0

....

C10S  1    0.080032    1.122110    0.284898    10.33333    0.02266
AFIX  23
H10A  2    0.095393    1.108073    0.356020    10.33333    0.03019
H10B  2    0.185537    1.108980    0.252859    10.33333    0.07844
AFIX   0
C11S  1    0.034726    1.252421    0.270929    10.33333    0.02477
O3S   4   -0.087391    1.287204    0.233376    10.33333    0.03143
O4S   4    0.147522    1.327757    0.305089    10.33333    0.03101
AFIX   3
H4S   2    0.123082    1.402847    0.301909    10.33333    0.66676
PART   0
```

Example 6 – Urea Host : Guest Complex

Anisotropic refinement of dicarboxylic acid



Example 6 – Urea Host : Guest Complex

Final refinement

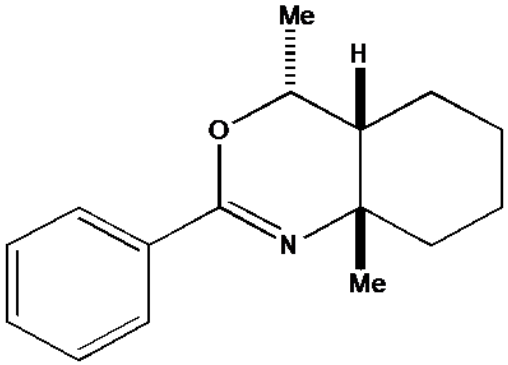
- R1 = 3.83%
- Temperature factors on hydrogen atoms refined

Example 7 – An organic compound exhibiting two types of enantiomeric disorder

4,8a-dimethyl-2-phenyl-
4a,5,6,7,8,8a-hexahydro
-4*H*-benzo[d] [1,3]oxazine

$C_{16}H_{21}NO$

Hemant Yennawar et al.
(Pennsylvania State U.)



Example 7 – An organic compound exhibiting two types of enantiomeric disorder

Triclinic P-1, Z = 8

a = 10.1195(5) Å

b = 14.1443(7) Å

c = 19.3863(10) Å

α = 82.979(3)°

β = 84.235(3)°

γ = 88.777(3)°

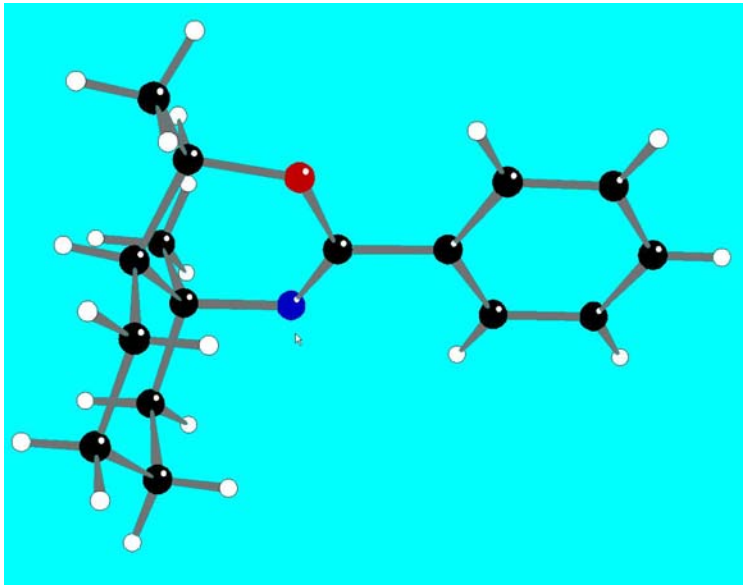
Example 7 – An organic compound exhibiting two types of enantiomeric disorder

Problems

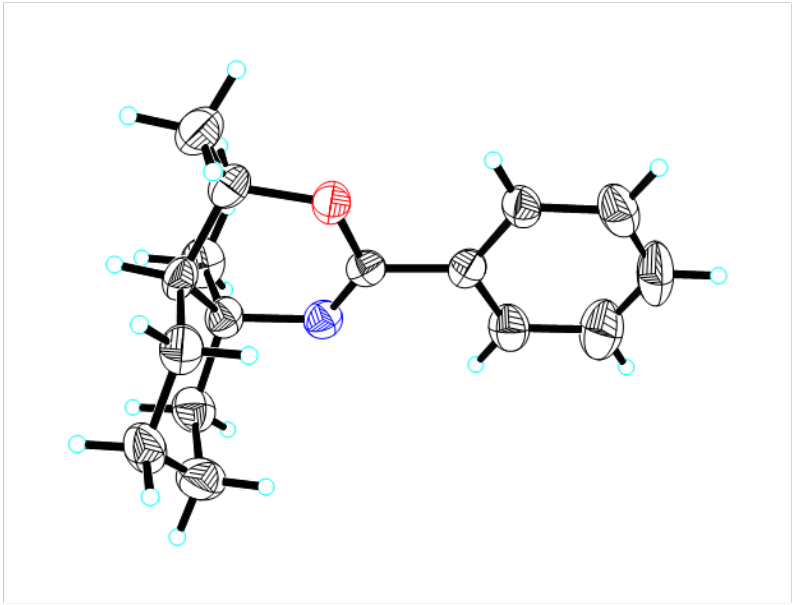
- **R1 = 18%**
- **Many atoms with large U-values & strange thermal ellipsoids**
- **Two well-behaved molecules, two abnormal molecules**

Example 7 – An organic compound exhibiting two types of enantiomeric disorder

Initial Structure – Molecule A

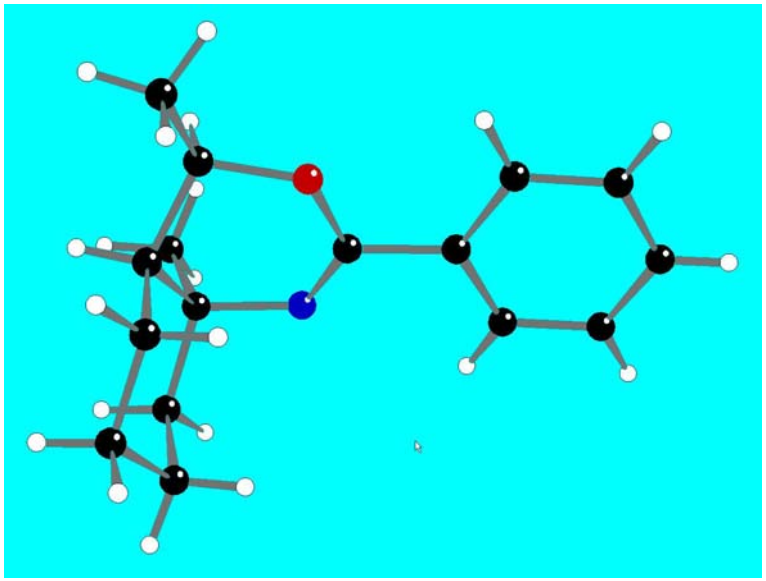


50% Thermal Ellipsoids

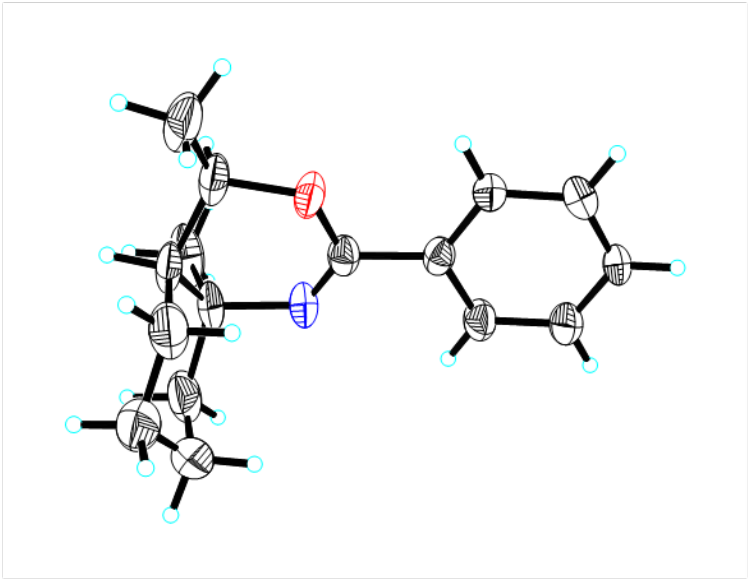


Example 7 – An organic compound exhibiting two types of enantiomeric disorder

Initial Structure – Molecule B

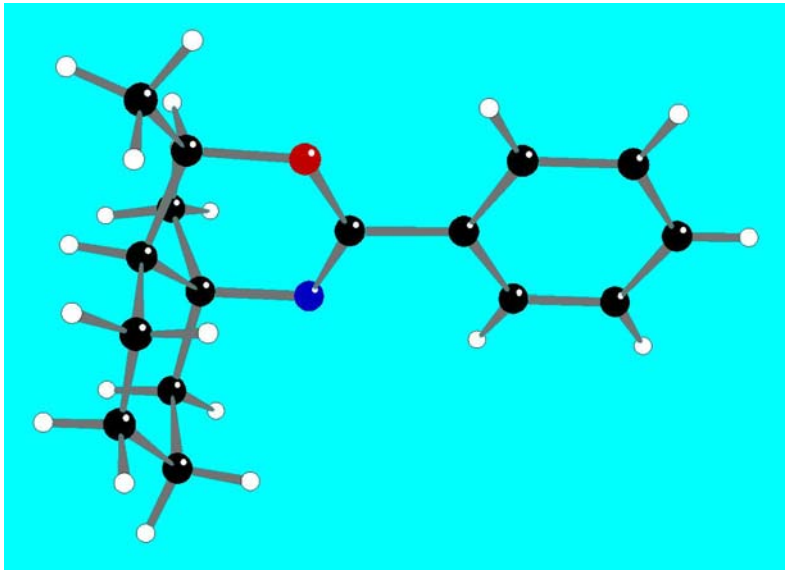


50% Thermal Ellipsoids

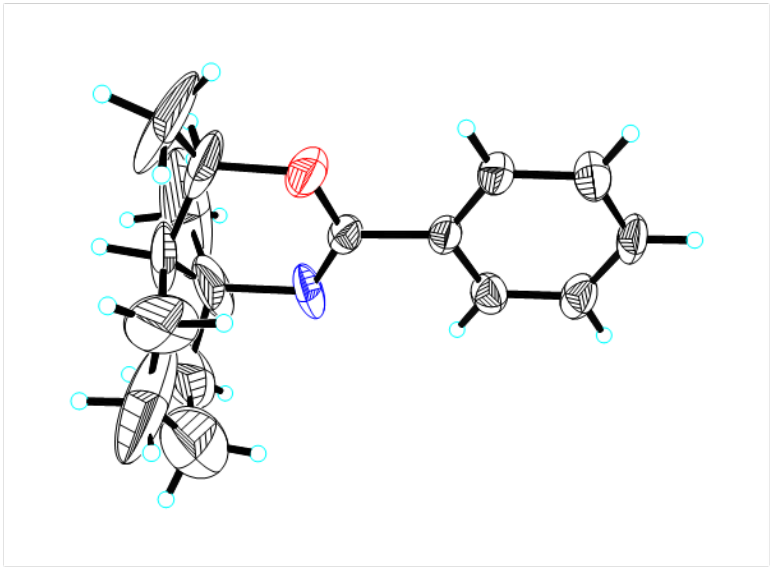


Example 7 – An organic compound exhibiting two types of enantiomeric disorder

Initial Structure – Molecule C

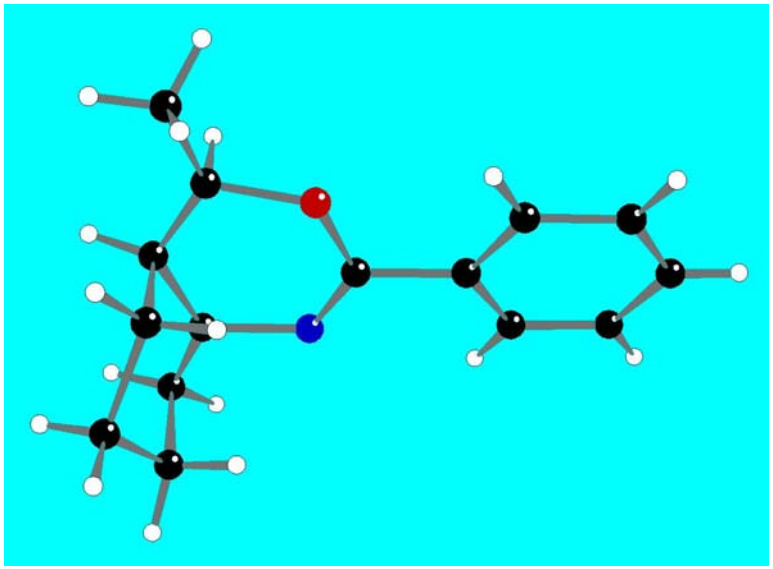


50% Thermal Ellipsoids

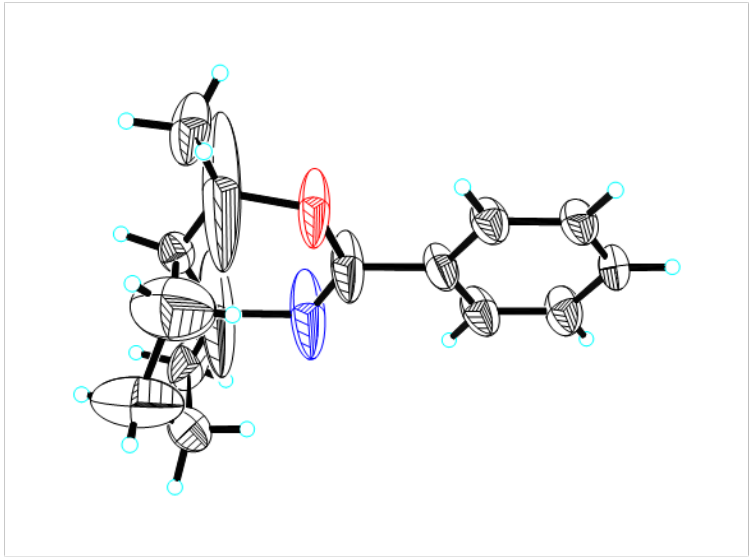


Example 7 – An organic compound exhibiting two types of enantiomeric disorder

Initial Structure – Molecule E

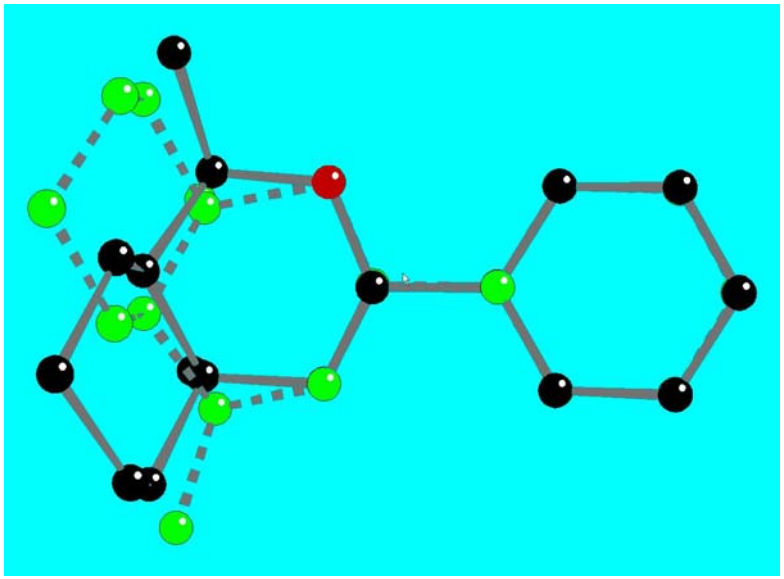


50% Thermal Ellipsoids



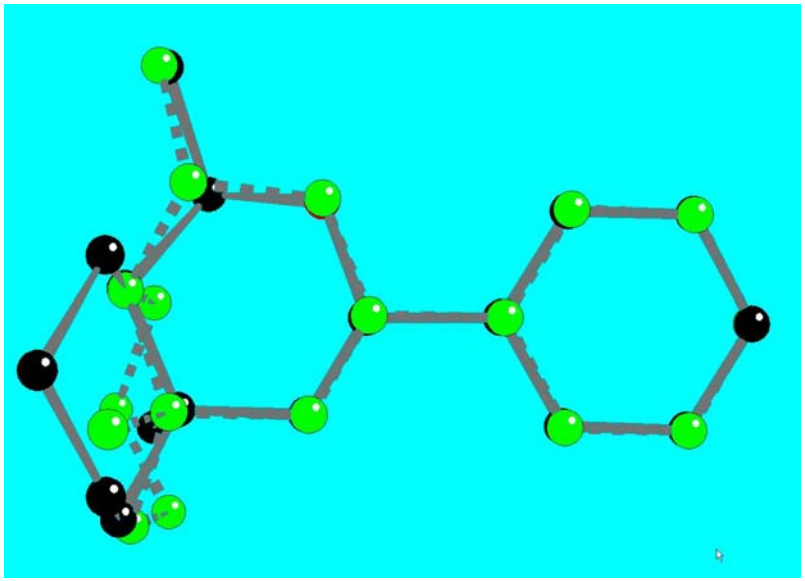
Example 7 – An organic compound exhibiting two types of enantiomeric disorder

Disorder - Molecules C & D

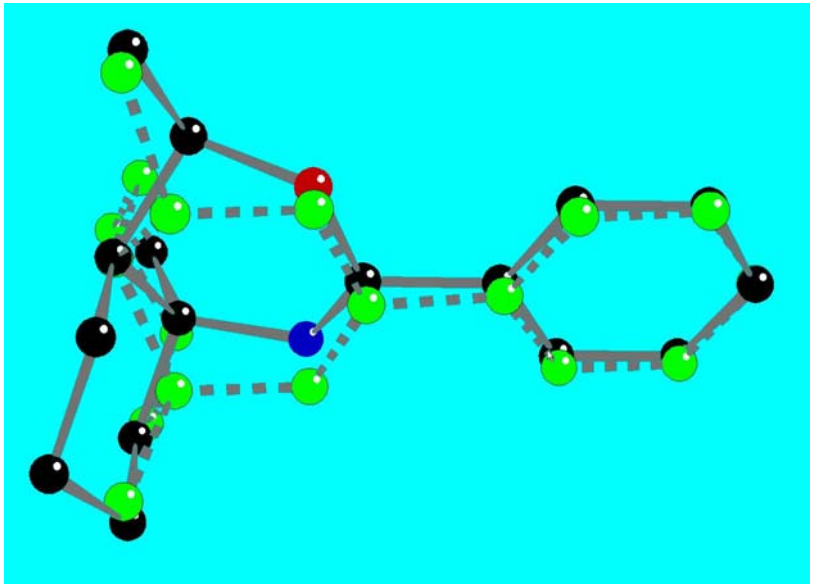


Example 7 – An organic compound exhibiting two types of enantiomeric disorder

Disorder - Molecules E & F



Disorder - Molecules E & F



Example 7 – An organic compound exhibiting two types of enantiomeric disorder

Refinement Strategy

- Use XP to sort out disorder (PRUN, JOIN, LINK)
- Use restraints (SADI, SAME, EXYZ, EADP, etc.) in XL to refine

Final refinement

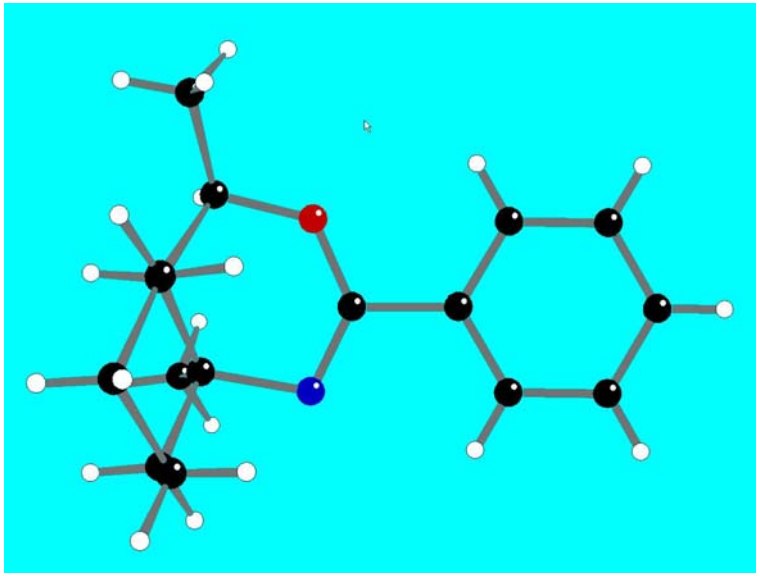
- R1 = 0.0526 , wR2 = 0.1274, GooF = 1.077

Results

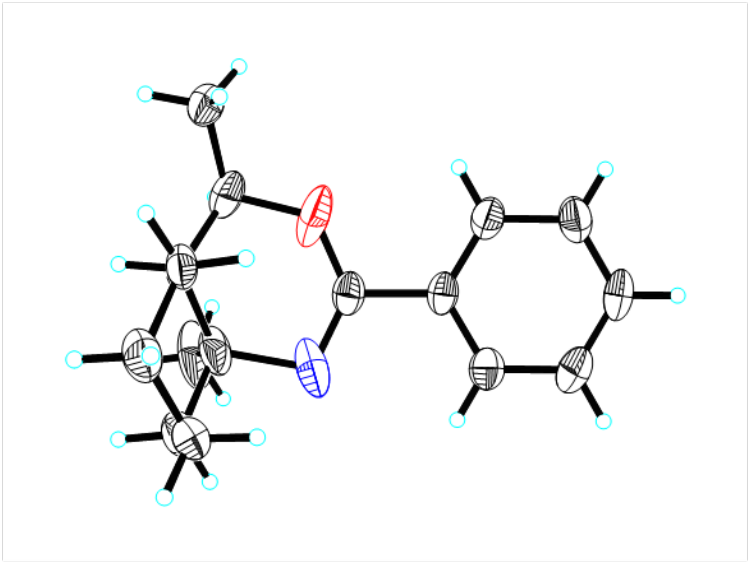
- Correct structure, normal U-values, normal weighting scheme, no large residual peaks

Example 7 – An organic compound exhibiting two types of enantiomeric disorder

Final Structure – Molecule C

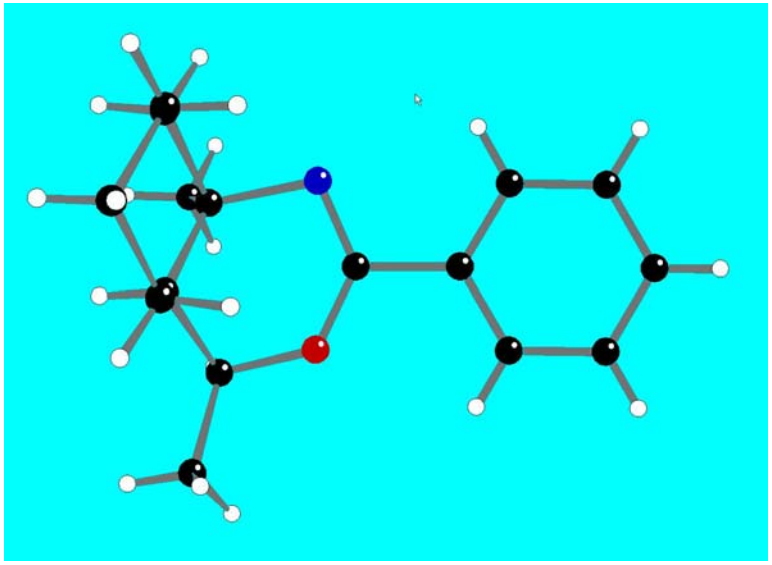


50% Thermal Ellipsoids

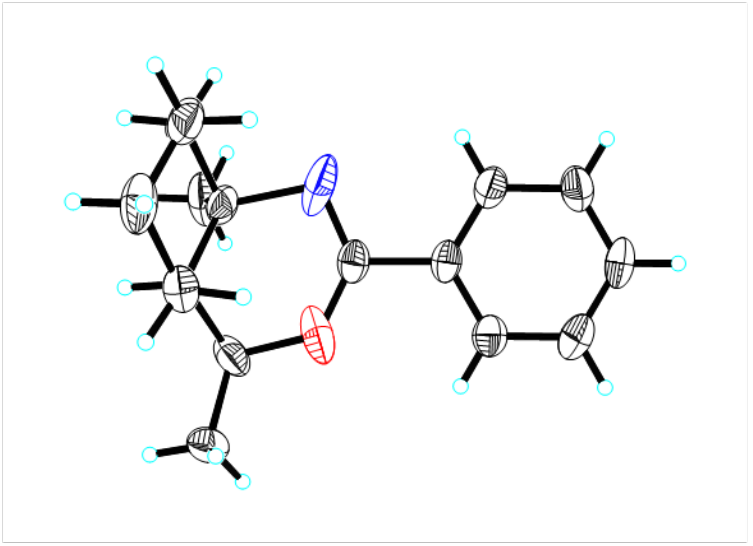


Example 7 – An organic compound exhibiting two types of enantiomeric disorder

Final Structure – Molecule D

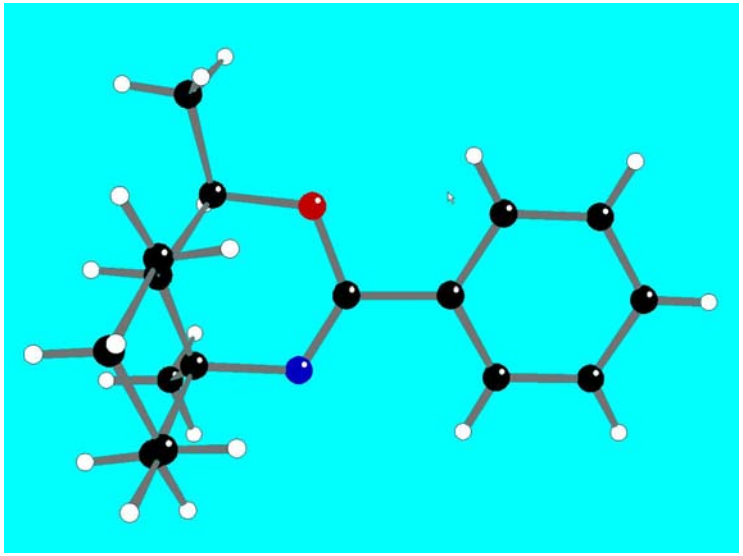


50% Thermal Ellipsoids

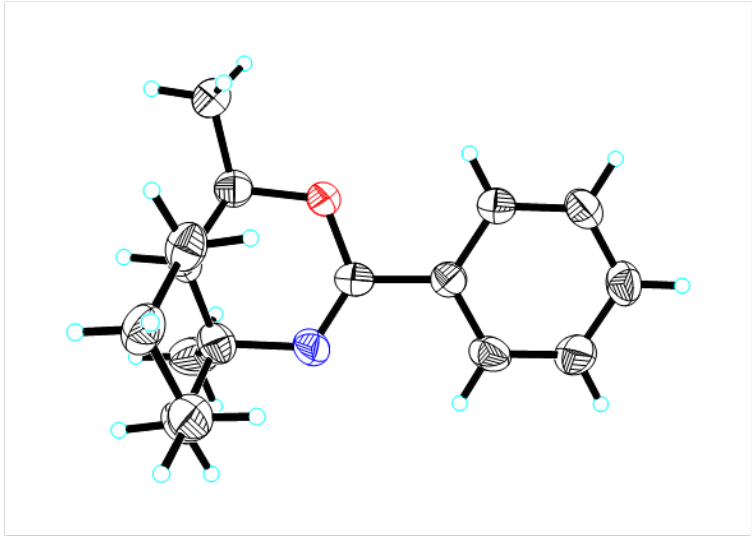


Example 7 – An organic compound exhibiting two types of enantiomeric disorder

Final Structure – Molecule E

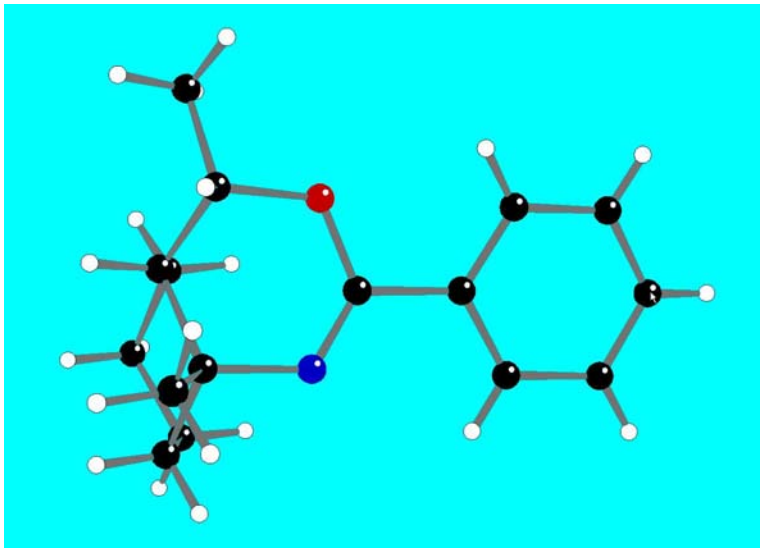


50% Thermal Ellipsoids

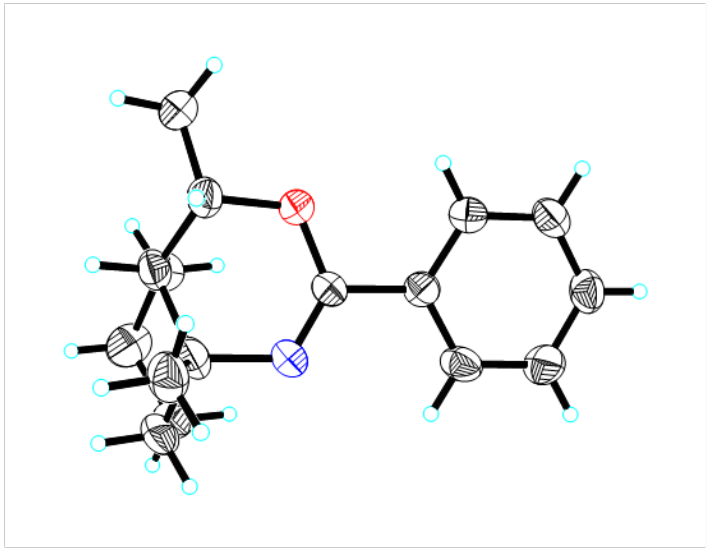


Example 7 – An organic compound exhibiting two types of enantiomeric disorder

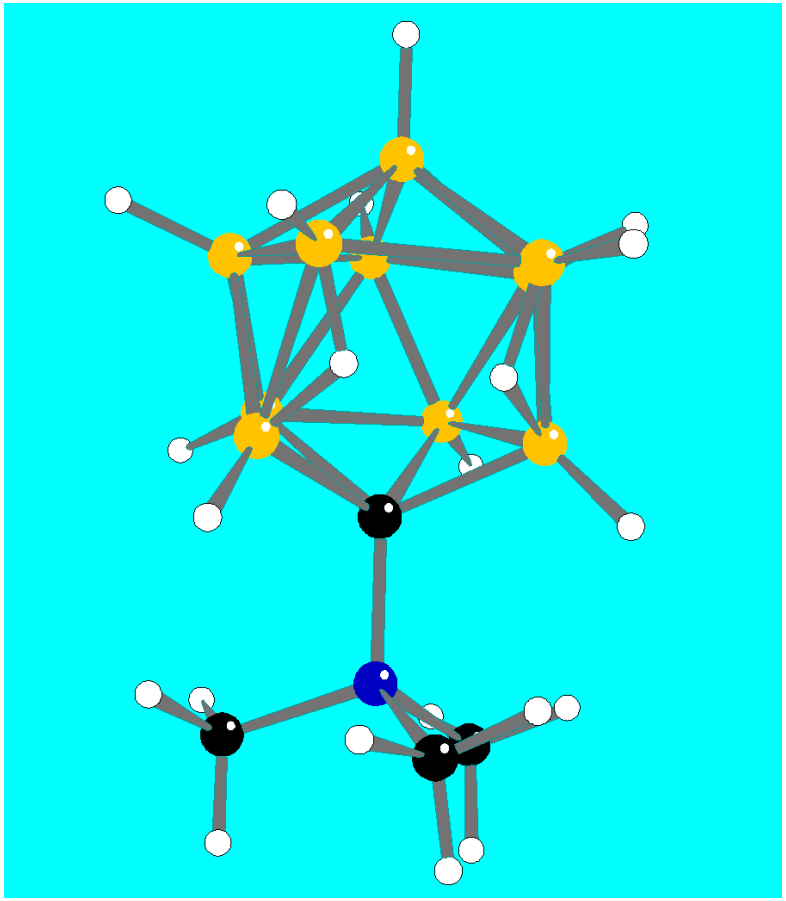
Final Structure – Molecule F



50% Thermal Ellipsoids



Example 8 – A Commensurately Modulated Carborane Compound



$(CH_3)_3N\text{-}CB_{10}H_{12}$

Compound prepared by D.E. Hyatt – Lee Todd's first graduate student at Indiana U. – 1966. No Structure published.

Hyatt, D. E., Owen, D. A., and Todd, L. J., Inorg. Chem., 5, 1749-51 (1966).

Recent paper from Durham U. with synthesis, spectroscopy, etc. No structure published.

Batsanov , A.S., Fox, M. A., Goeta, A. E., Howard, J. A. K., Hughes, A. K. and Malget, J. M., J. Chem. Soc. , Dalton Trans., 2624-2631 (2002).

Example 8 – A Commensurately Modulated Carborane Compound

Empirical formula	$C_4H_{21}B_{10}N$
Chemical formula	$(CH_3)_3N\text{-}CB_{10}H_{12}$
Formula weight	191.32
Crystal size	0.364 x 0.624 x 0.720 mm
Crystal habit	clear, colorless prism
Density (calculated)	1.077 Mg/m3
Absorption coefficient	0.05 mm-1

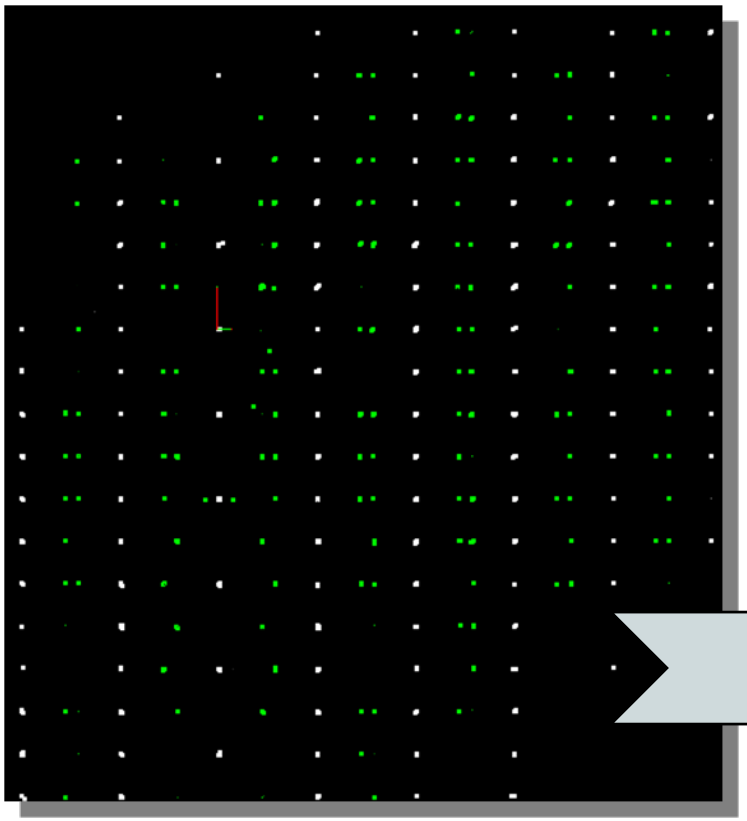
Example 8 – A Commensurately Modulated Carborane Compound

Early attempts with film and / or scintillation counter methods gave ambiguous unit cells

- **Small cell – Orthorhombic P, Z = 4, 16 Å × 10 Å × 7 Å**
- **Intermediate cell - Orthorhombic P, Z = 8, 16 Å × 10 Å × 14 Å**
- **Large cell - Orthorhombic P, Z = 28, 16 Å × 10 Å × 49 Å**

Example 8 – A Commensurately Modulated Carborane Compound

Reciprocal Lattice Viewer



Very strong main reflections (white color)

Weak satellite reflections in between (green color)

h = *0 1 2 3 4 5 6 7*

Example 8 – A Commensurately Modulated Carborane Compound

Correct Unit Cell – Small Cell

Crystal system	**Orthorhombic**
Space group	**Pnma**
Unit cell dimensions	**a = 16.1370(8) Å**
	b = 10.5017(5) Å
	c = 6.9605(3) Å
Volume	**1179.57(10) Å^3**
Z	**4**
F(000)	**408**
Q-vector	**0, 0, 3/7 (0.0000, 0.0000, 0.42857)**

Example 8 – A Commensurately Modulated Carborane Compound

CCD Data Collection

Instrument Used	**Bruker SMART APEXII**
Crystal to Detector Distance	**8.926 cm.**
Image Width (ω or ϕ)	**0.5°**
Maximum 2θ angle	**68.80°**
Maximum Resolution	**0.63 Å**
Total Images Collected	**6523**
Exposure Time / Image	**10.0 sec.**
Total Data Collection Time	**21.74 hours**
Temperature	**100(2) K**
Total Reflections Measured	**21978**
Independent Reflections	**2492**
R(int)	**4.81%**
R(sig)	**2.54%**
Reflections > 2sigma(I)	**1965**

Example 8 – A Commensurately Modulated Carborane Compound

Integration of satellite reflections with SAINT

New features of SAINT (Version 7.53A)

allows the input and refinement of up to three QVEC instructions for up to 6-dimensional modulated structures. The following input .P4P file was used for this integration:

```
FILEID SAINT        V7.09A        4.00        07/08/04 14:25:34 carborane
SITEID Administrator                        ?
TITLE  Integration
CHEM   (Ch3)3N-CB10H12
CELL     16.1418   10.5087    6.9644   90.0000   90.0000   90.0000   1181.365
CELLSD    0.0011    0.0007    0.0005    0.0000    0.0000    0.0000      0.131
ORT1    -9.6469503e-003  6.6842519e-002 -9.9723525e-002
ORT2    -5.8215410e-002  1.0598534e-002  4.6428315e-002
ORT3     1.8862667e-002  6.6895336e-002  9.2288941e-002
ZEROS   0.0000000 -0.0264180  0.0316215   -0.5332   -0.8447   -0.9388
QVEC     0.00000   0.00000   0.43194
SOURCE MO     0.71073   0.70930   0.71359   2.00000    0.00    0.00
LIMITS    0.00    0.00    0.00    0.00    0.00    0.00    0.00    0.00    0.00
    0.00
MORPH  Prism
DNSMET ?
CCOLOR clear
```

Example 8 – A Commensurately Modulated Carborane Compound

Integration of satellite reflections with SAINT

When the SAINT program encounters a QVEC instruction in the .P4P file, it automatically produces output files with the .ram extension, instead of the normal .raw extension.

Note: The SAINT.INI file must be edited to include a MAXSATIND = 2 parameter to the INTEGRATE section (to integrate both first and second-order satellite reflections):

```
VOLTARGET=1.00000
BGQSCALE=6
MAXSATIND=2
IBATNO=1
ESD_SCALE=1.00000
PARNAME=C:\Frames\guest\carborane\work\carborane_0m.p4p
```

Example 8 – A Commensurately Modulated Carborane Compound

SADABS output formats

.hkl file – SHELX-compatible files for normal solution and refinement (main reflections only)

```
-1  -6   0    0.19    0.40
-1  -6   0   -0.02    0.35
 1  -6   0    0.12    0.32
-2  -6   0  218.05    7.44
-2   6   0  222.14    8.67
-2  -6   0  222.34    8.49
 2  -6   0  215.54    7.41
-2  -6   0  221.98   10.43
 2   6   0  211.25    8.64
 2  -6   0  203.46   10.39
-3  -6   0    0.17    0.36
-3  -6   0   -0.03    0.39
 3   6   0   -0.03    0.50
```

Example 8 – A Commensurately Modulated Carborane Compound

SADABS output formats

.hk6 file – **JANA2006**-compatible files for modulated structure refinement with **JANA2006**

```
-2  -5  -8   0   0   0    8.98    0.66   7
-2  -6   0   0   0   0  215.66    7.41   7
-2  -6   0   2   0   0   20.74    7.31   7
-2  -6   0  -1   0   0    0.76    7.29   7
-2  -6   0   1   0   0    1.66    7.29   7
-2  -6   0  -2   0   0    8.67    7.29   7
 2  -6   0   0   0   0  218.17    7.44   7
 2  -6   0   1   0   0    2.09    7.30   7
 2  -6   0  -1   0   0    0.79    7.29   7
 2  -6   0  -2   0   0    6.14    7.29   7
 2  -6   0   2   0   0   18.14    7.31   7
-2  -6  -1   2   0   0   29.00    3.36   7
-2  -6  -1   1   0   0   95.42    3.42   7
-2  -6  -1   0   0   0  104.30    3.41   7
-2  -6  -1  -1   0   0    0.60    3.31   7
```

Example 8 – A Commensurately Modulated Carborane Compound

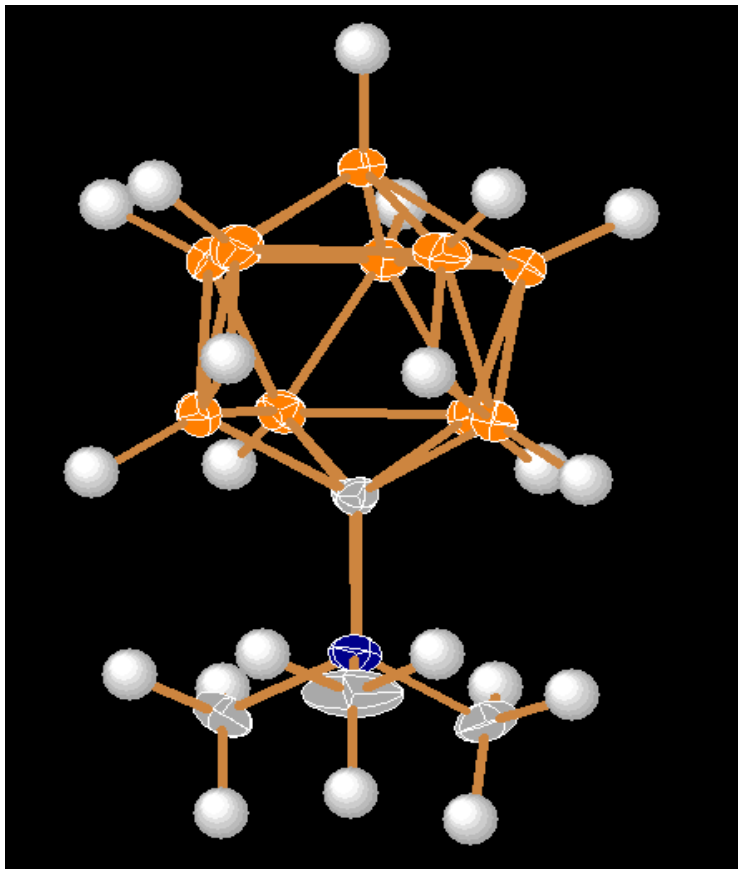
Absorption correction for modulated structure data with SADABS

The SADABS (Version 2008/2) scaling and absorption program has been modified to include the following new features:

When files with the .ram extension are read into SADABS, the program uses the main reflections to optimize the absorption correction model in the normal manner. The correction is then applied to all reflections, including satellite reflections.

Example 8 – A Commensurately Modulated Carborane Compound

Solution and refinement - small cell



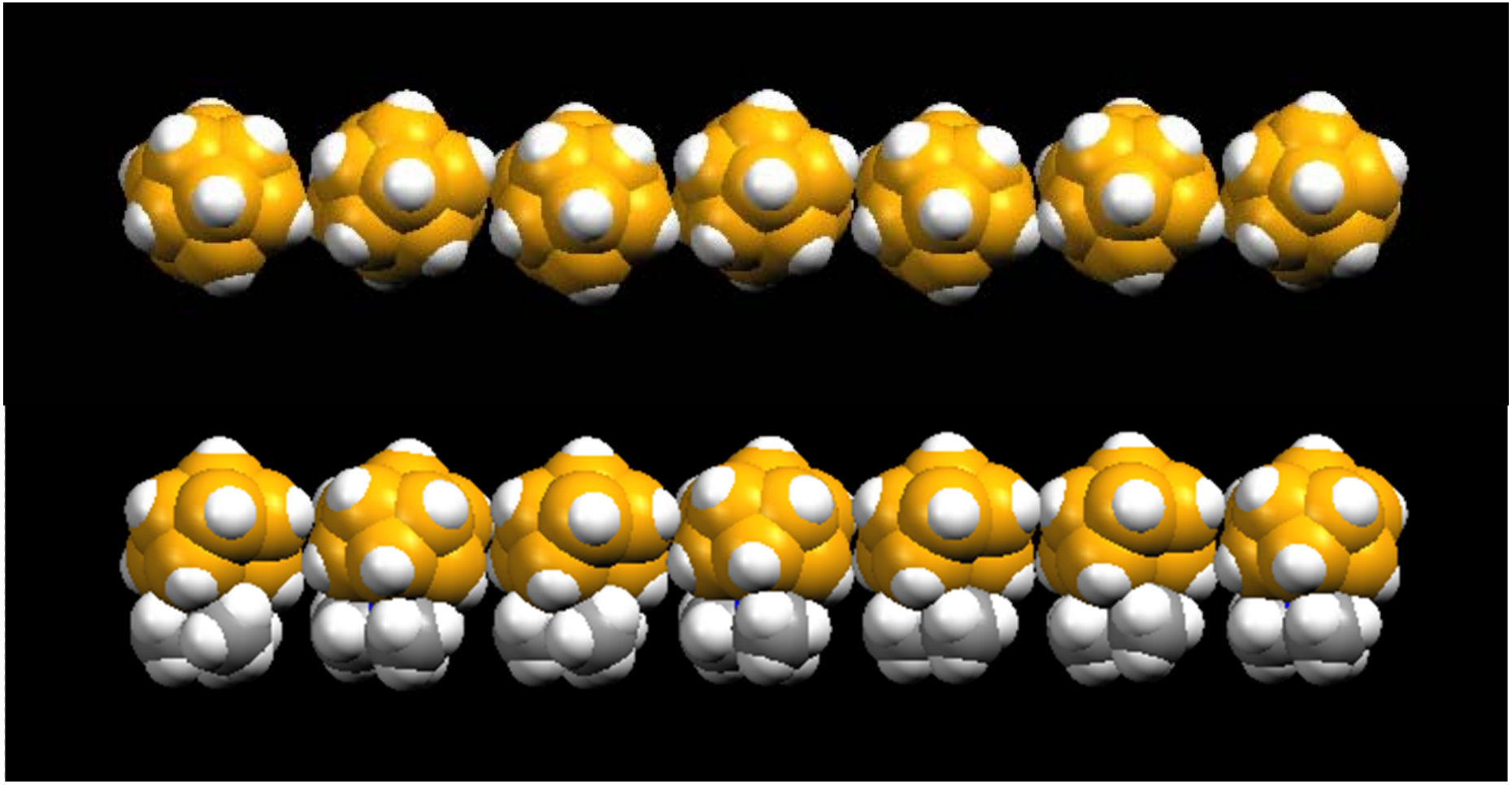
Small Cell Refinement (.hkl file main reflections only)

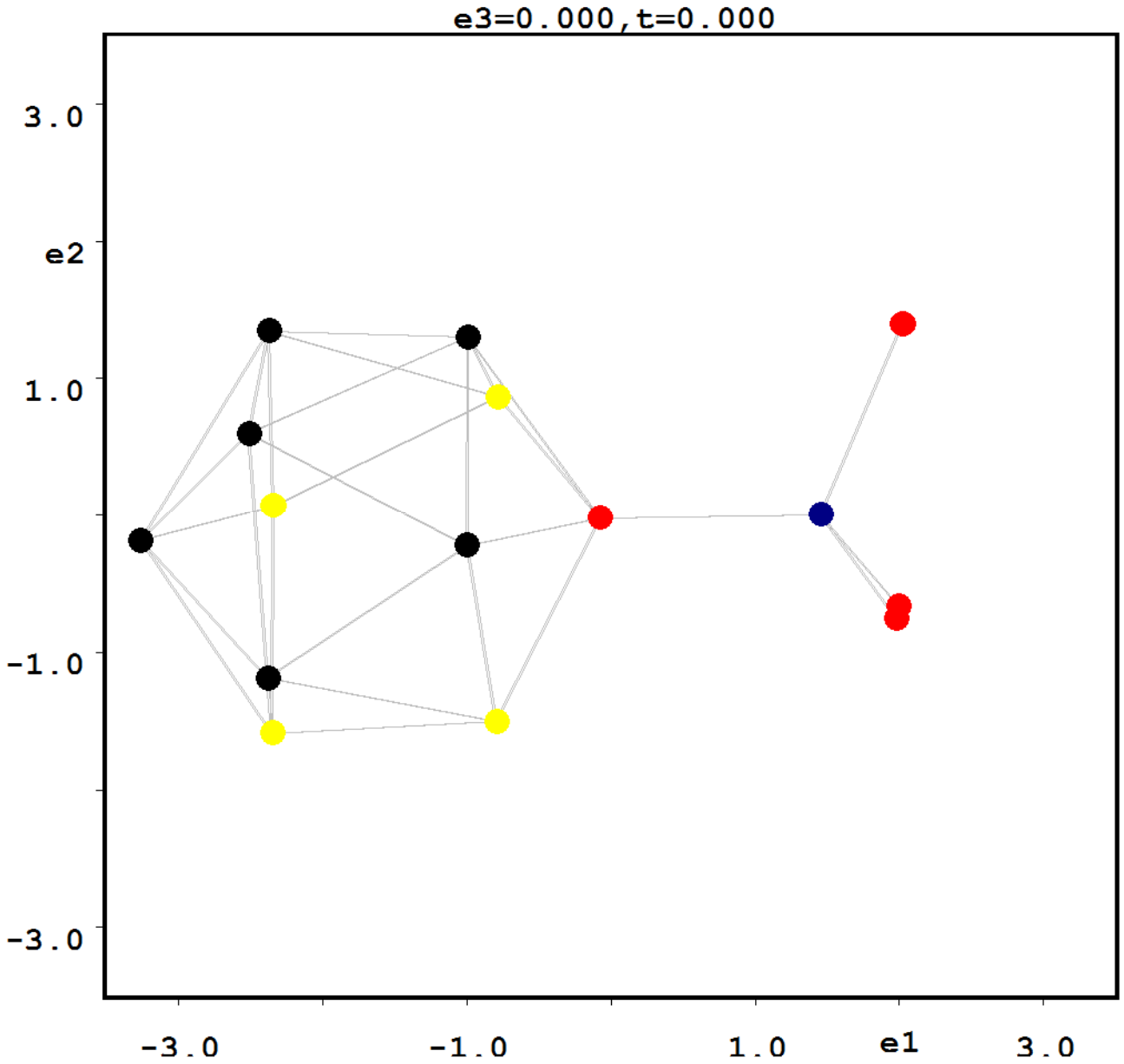
Space Group – Pnma, Z = 4

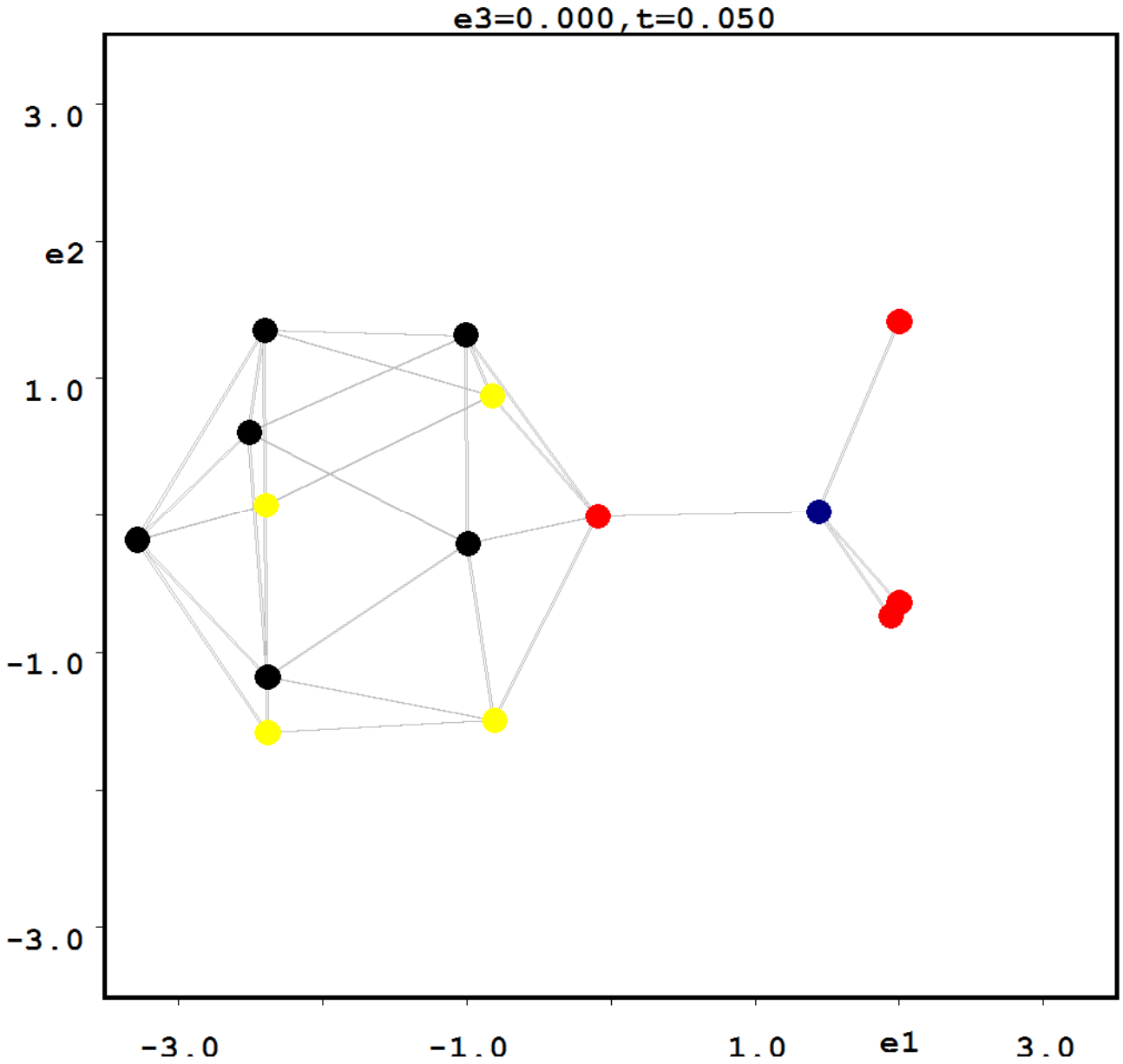
Modeled as 2-fold disorder with Ratio 4:3 (PART –1, PART –2)

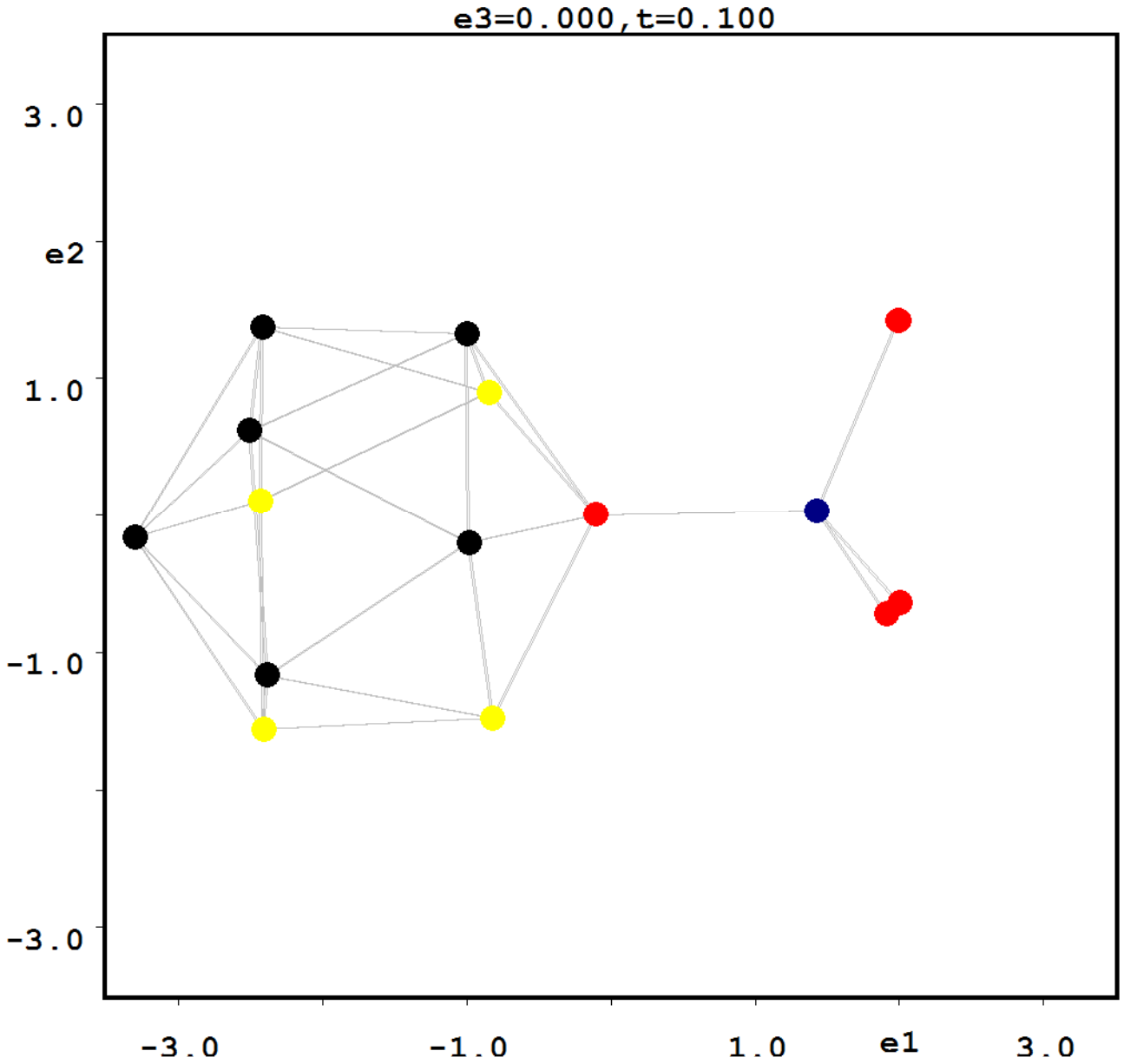
R1 = 7.9%

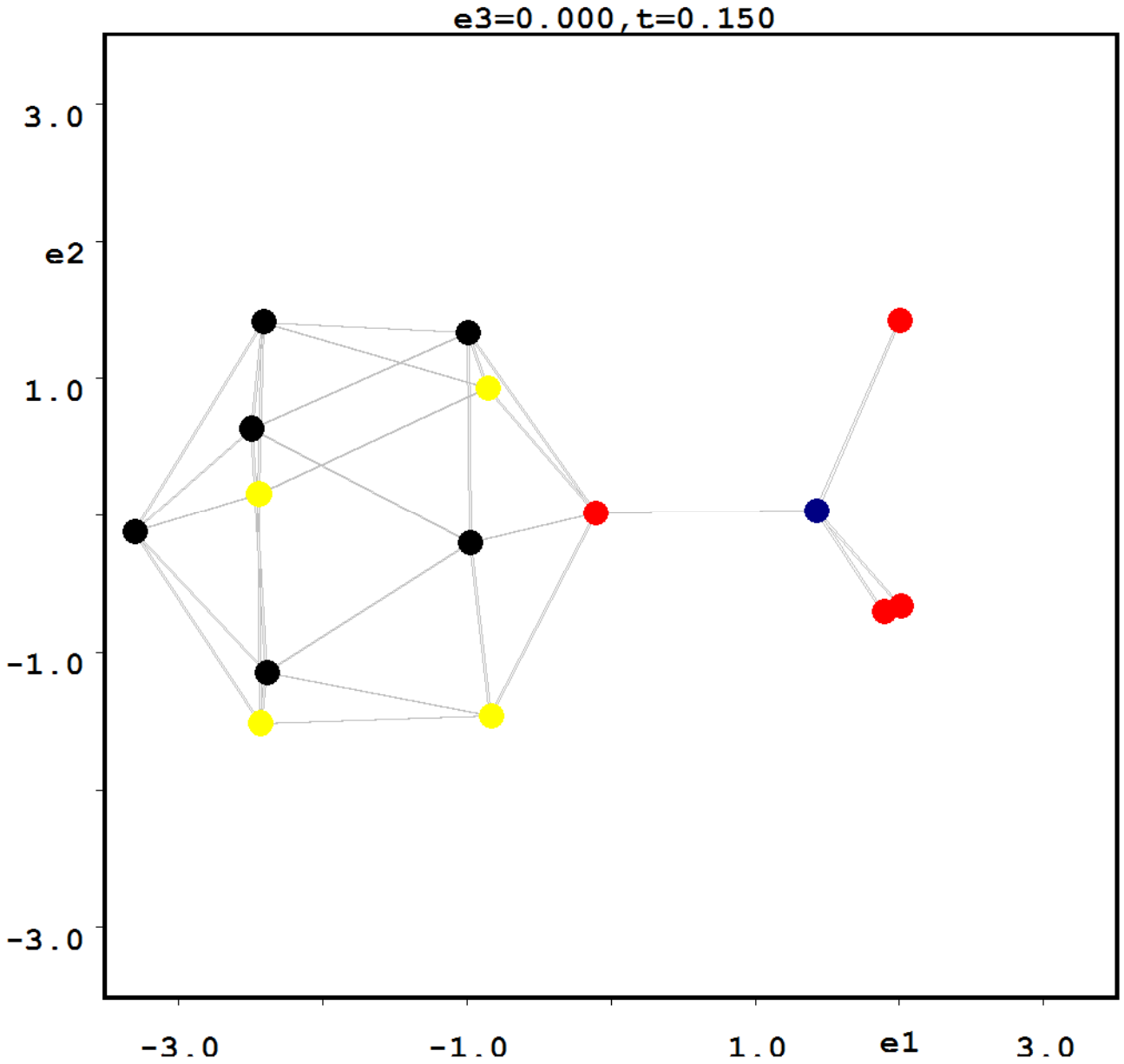
Example 8 – A Commensurately Modulated Carborane Compound- Supercell Structure

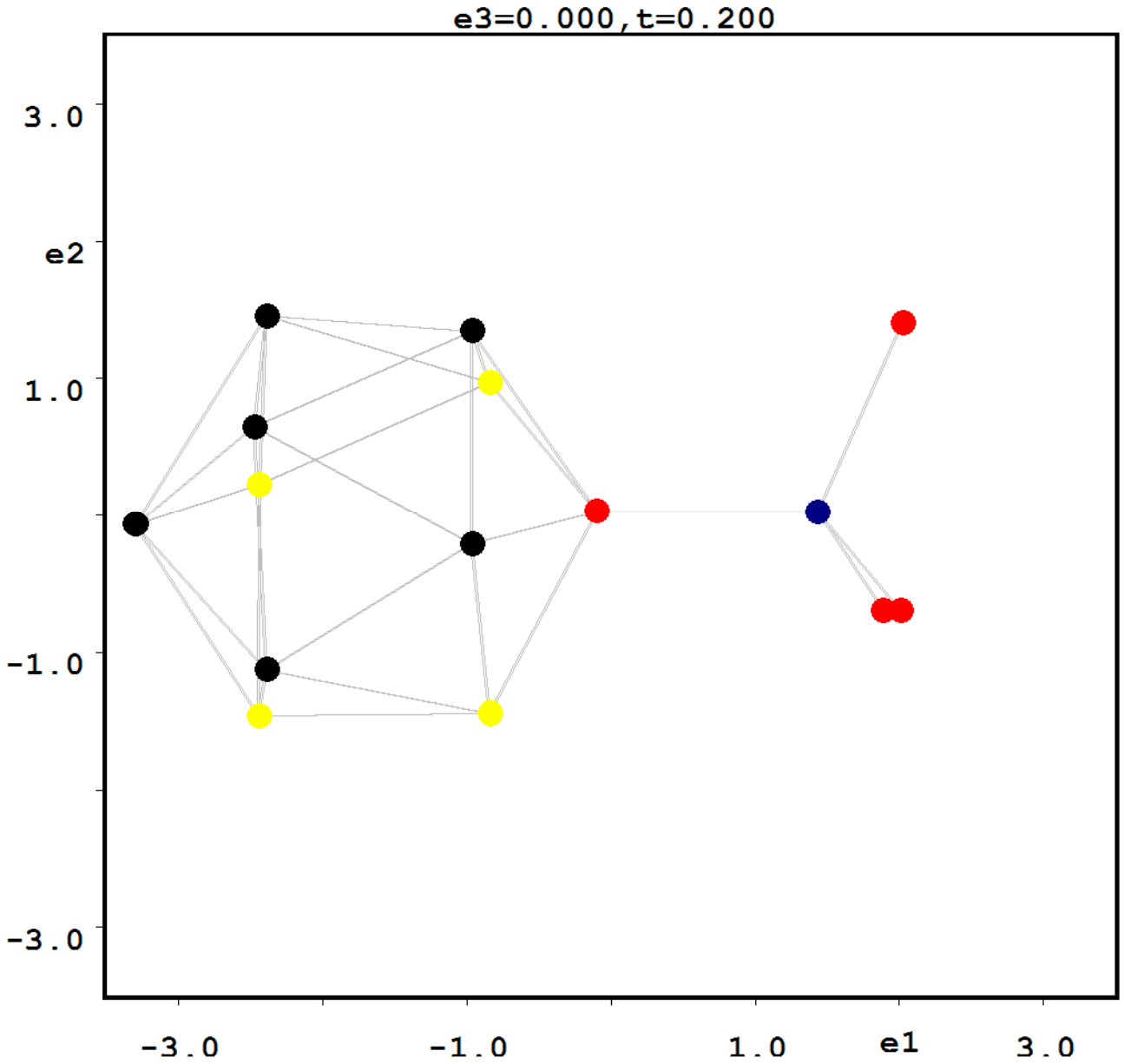


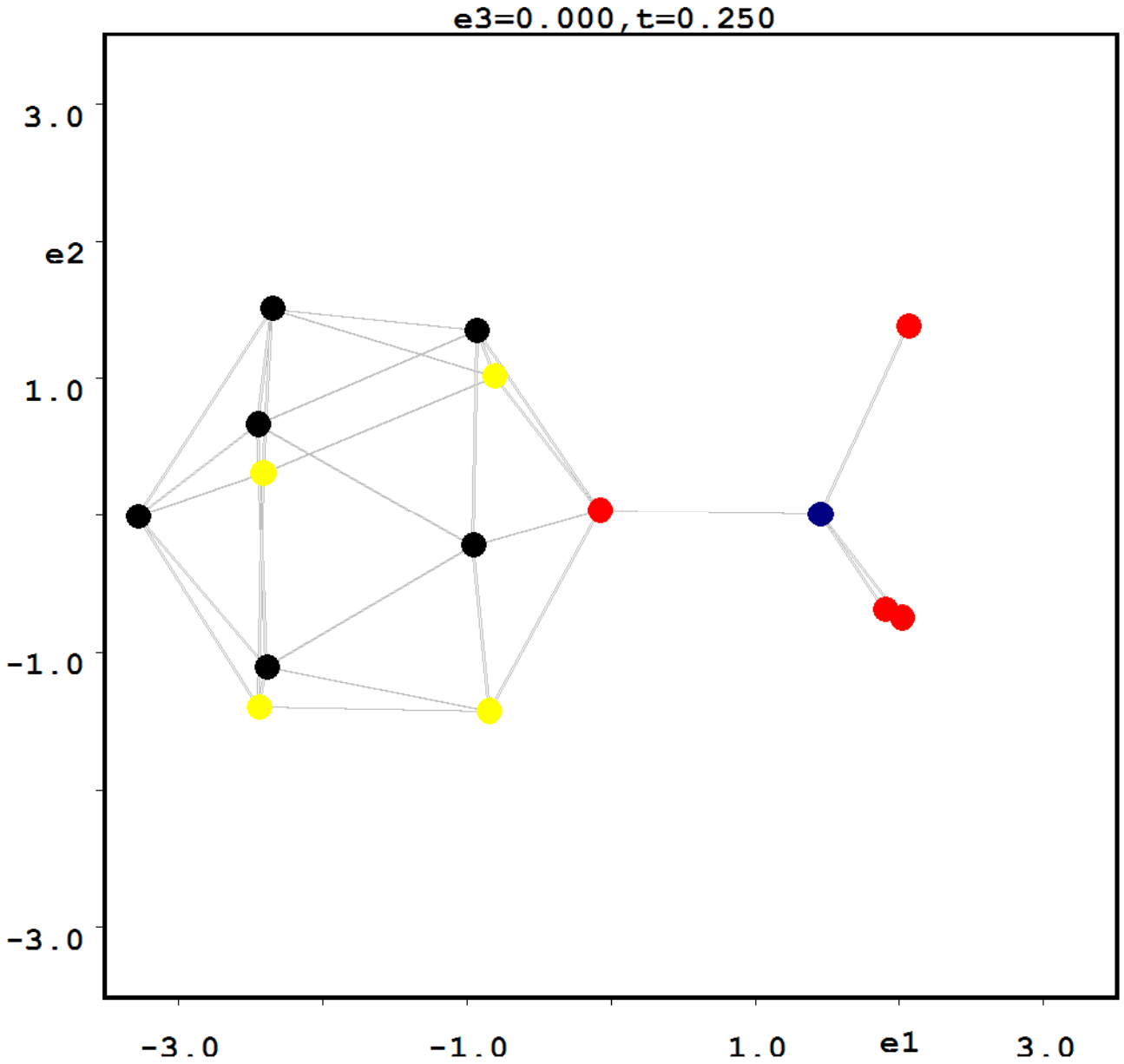

e3=0.000,t=0.000
3.0
e2
1.0
-1.0
-3.0
-3.0
-1.0
1.0
e1
3.0


e3=0.000,t=0.050
3.0
e2
1.0
-1.0
-3.0
-3.0
-1.0
1.0
e1
3.0


e3=0.000,t=0.100
3.0
e2
1.0
-1.0
-3.0
-3.0
-1.0
1.0
e1
3.0


e3=0.000,t=0.150
3.0
e2
1.0
-1.0
-3.0
-3.0
-1.0
1.0
e1
3.0


e3=0.000,t=0.200
3.0
e2
1.0
-1.0
-3.0
-3.0
-1.0
1.0
e1
3.0


e3=0.000,t=0.250
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e2
1.0
-1.0
-3.0
-3.0
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1.0
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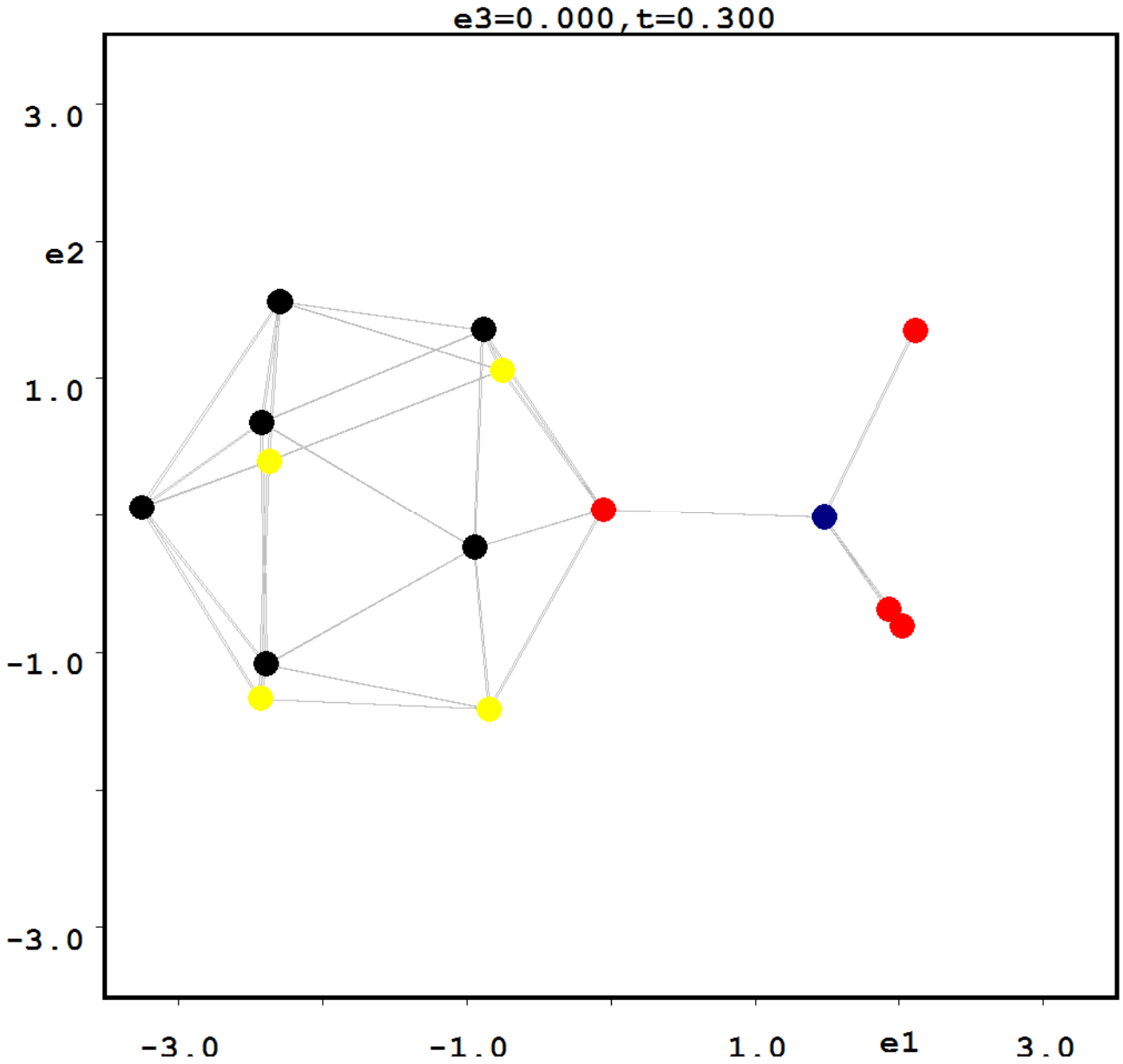
3.0


e3=0.000,t=0.300
3.0
e2
1.0
-1.0
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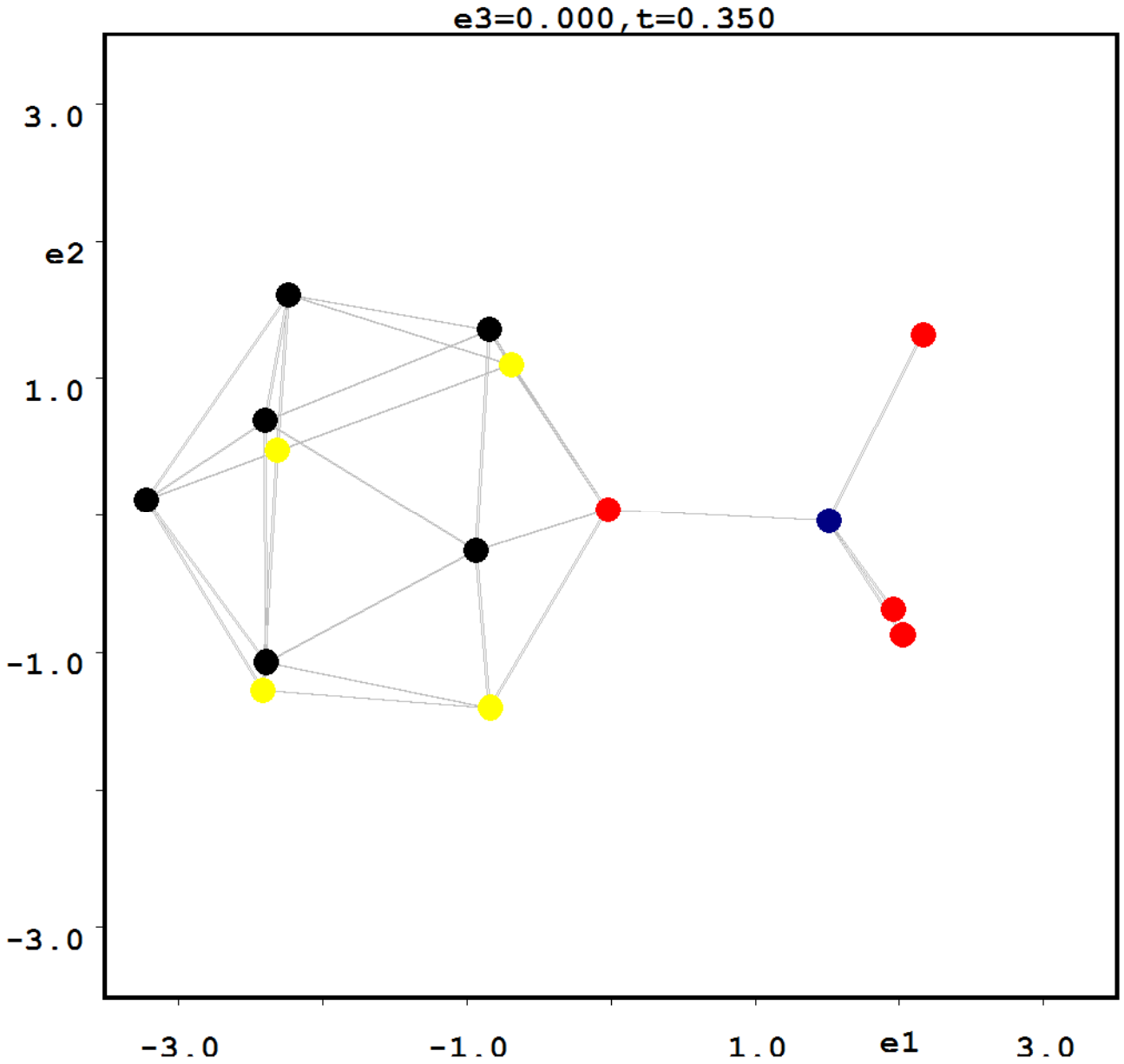
-3.0
-1.0
1.0
e1
3.0


e3=0.000,t=0.350
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e2
1.0
-1.0
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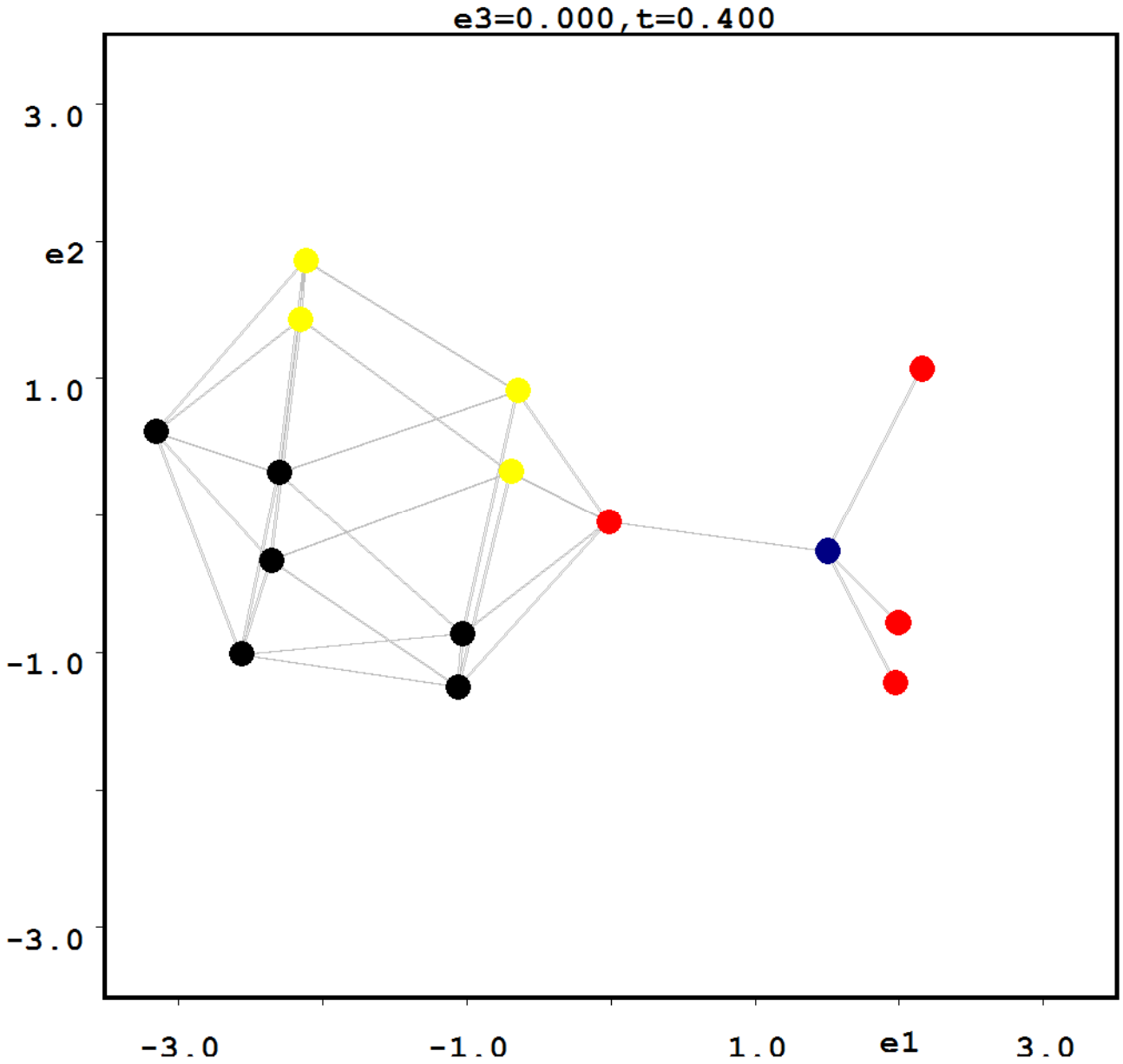
-3.0
-1.0
1.0
e1
3.0


e3=0.000,t=0.400
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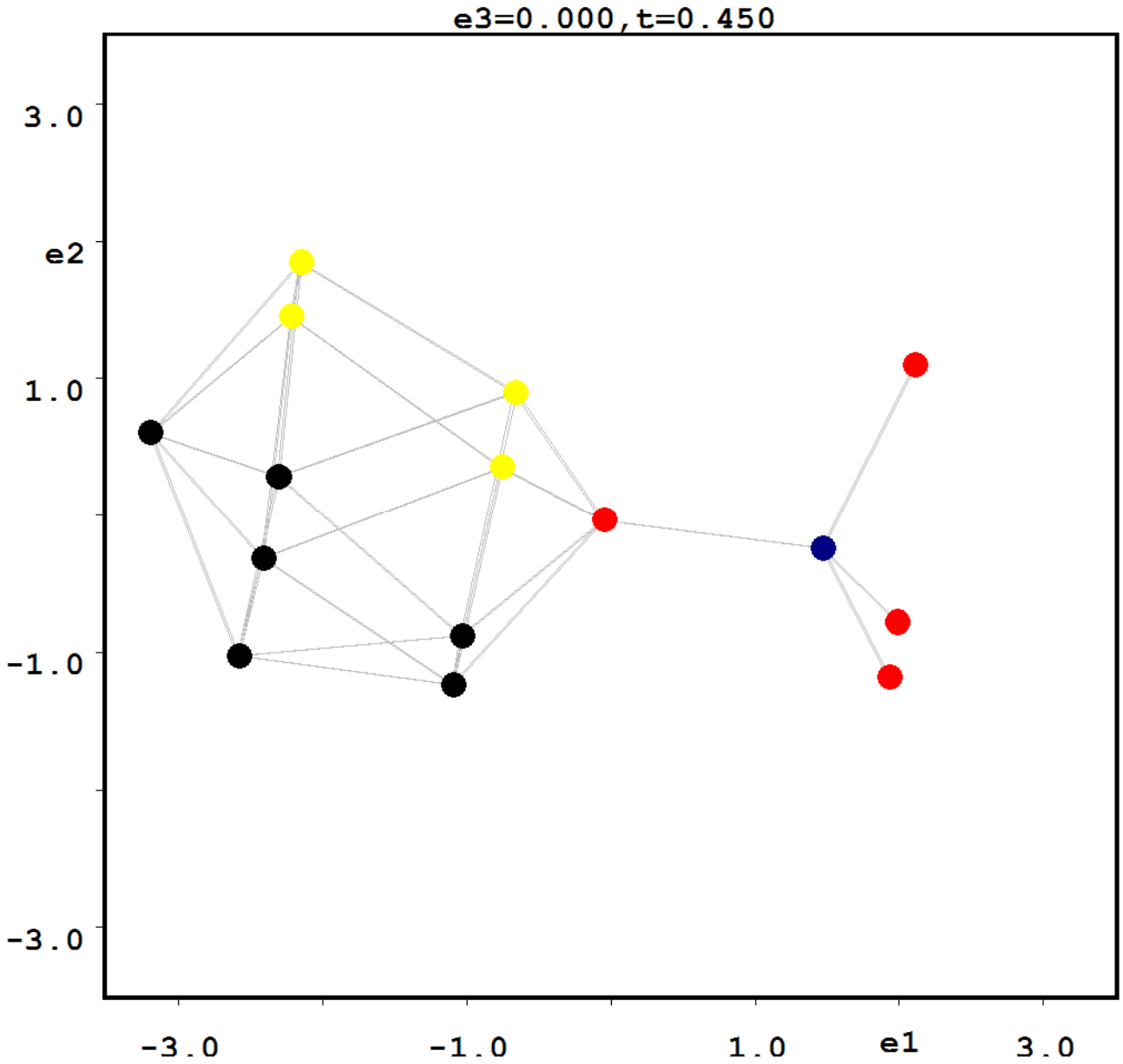
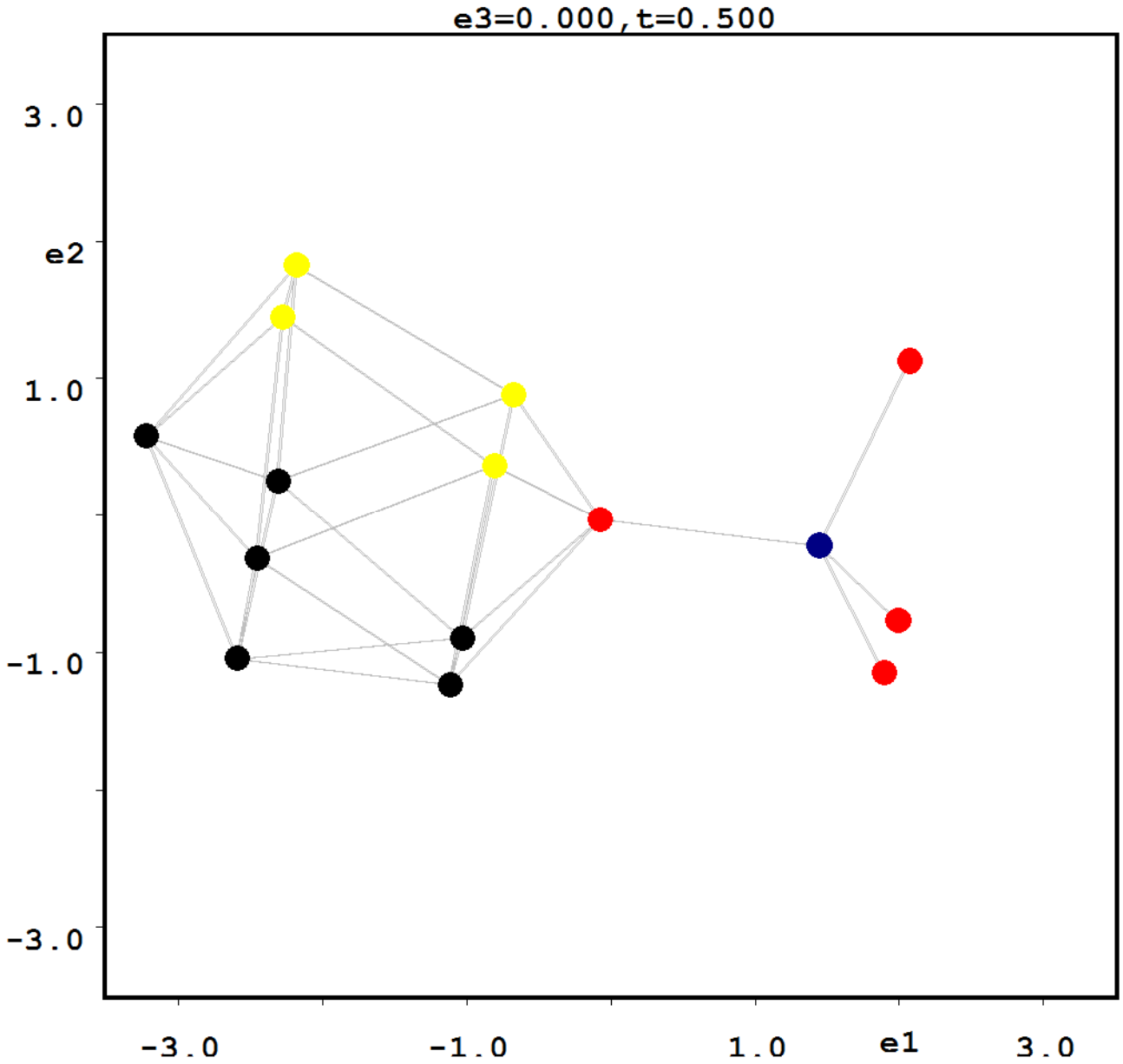
e2
1.0
-1.0
-3.0
-3.0
-1.0
1.0
e1
3.0


e3=0.000,t=0.450
3.0
e2
1.0
-1.0
-3.0
-3.0
-1.0
1.0
e1
3.0


e3=0.000,t=0.500
3.0
e2
1.0
-1.0
-3.0
-3.0
-1.0
1.0
e1
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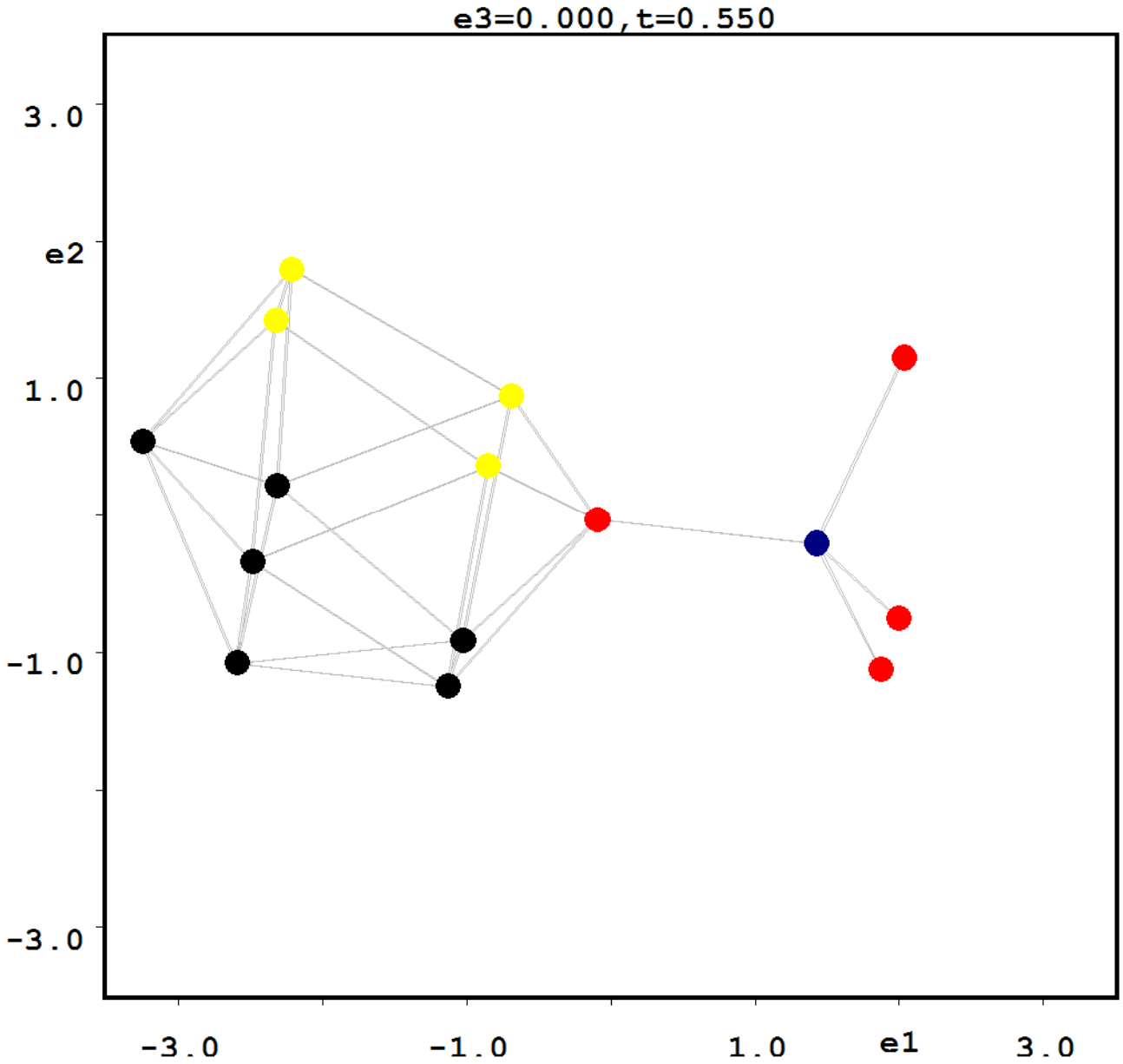
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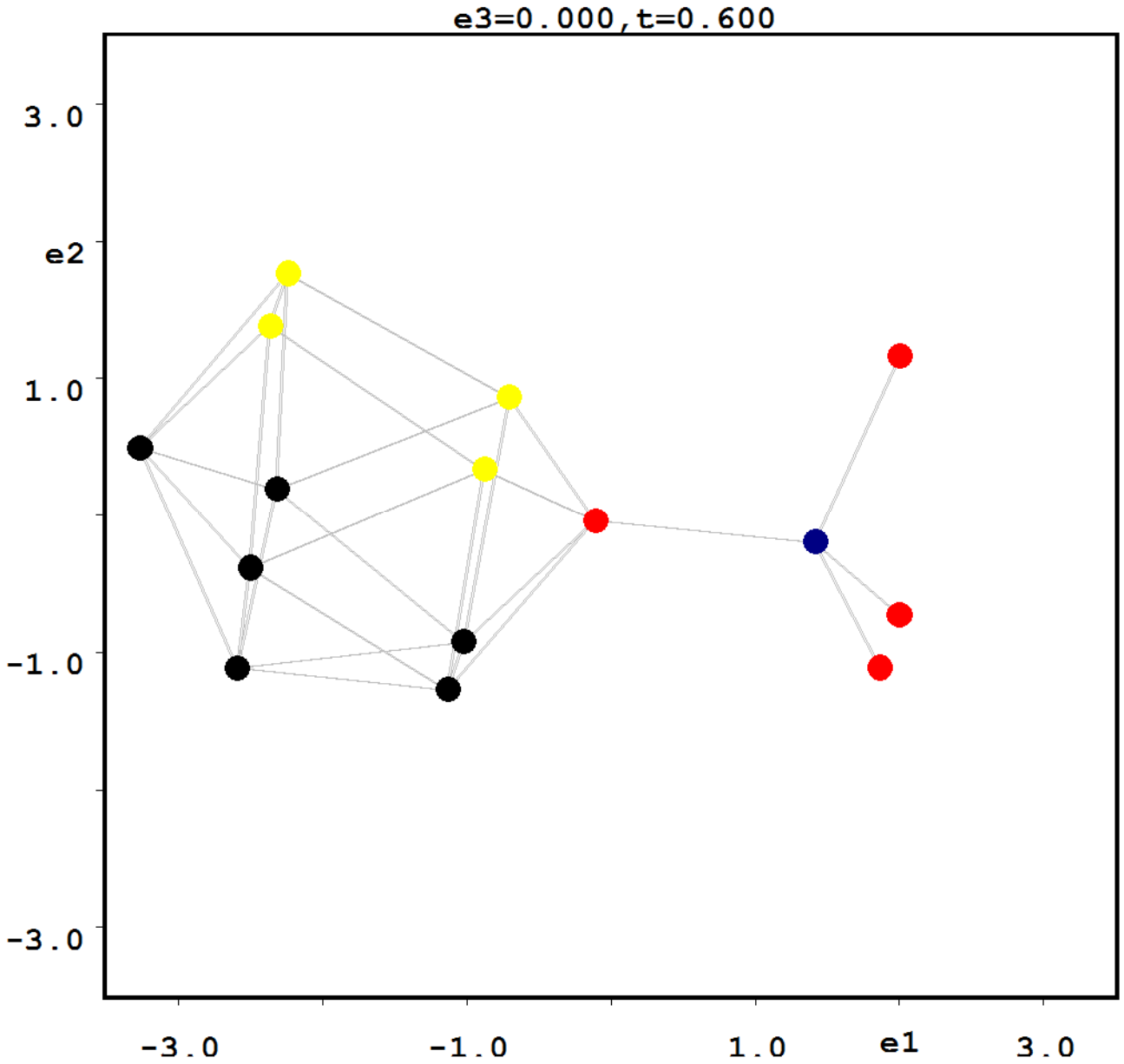
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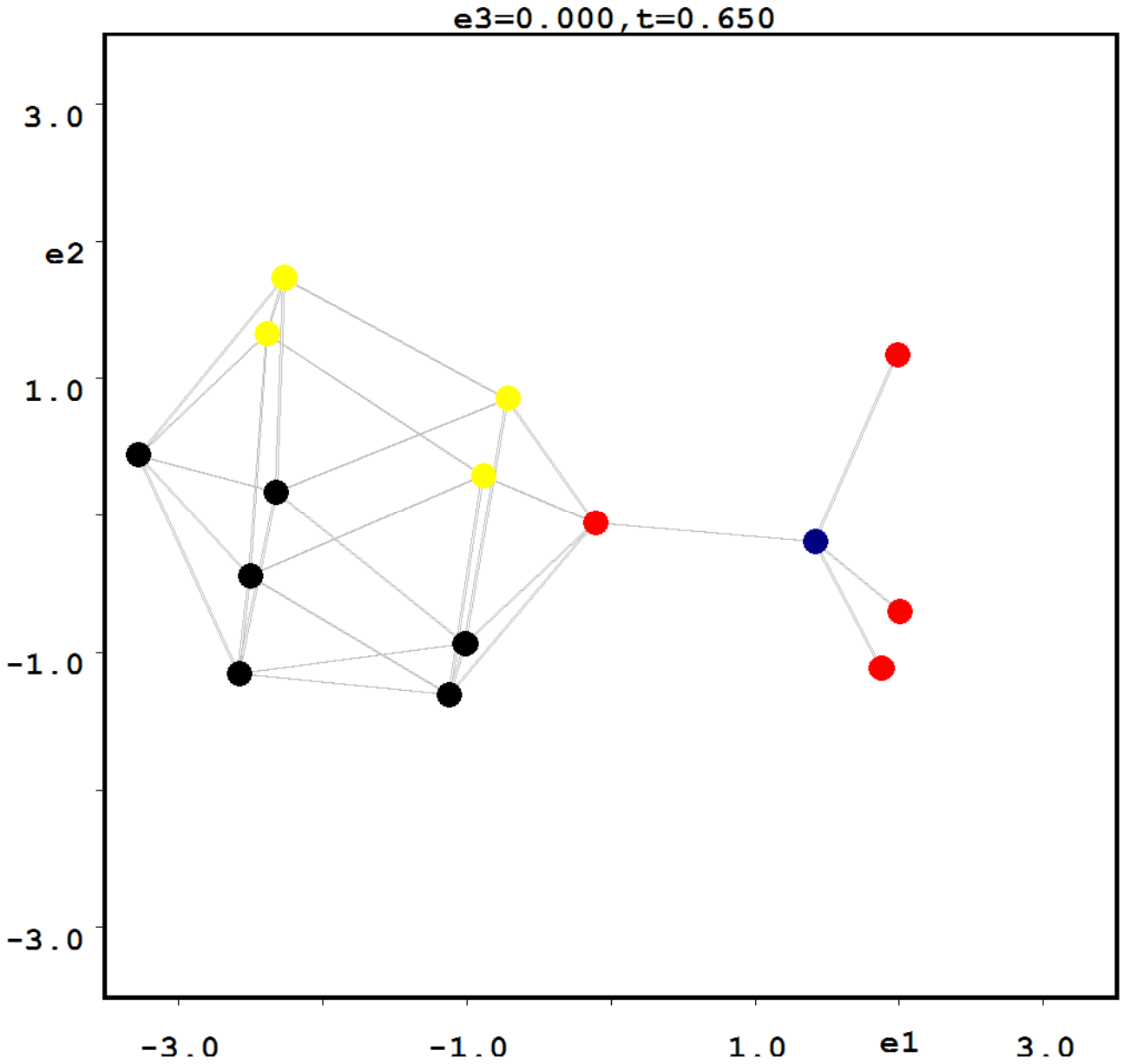
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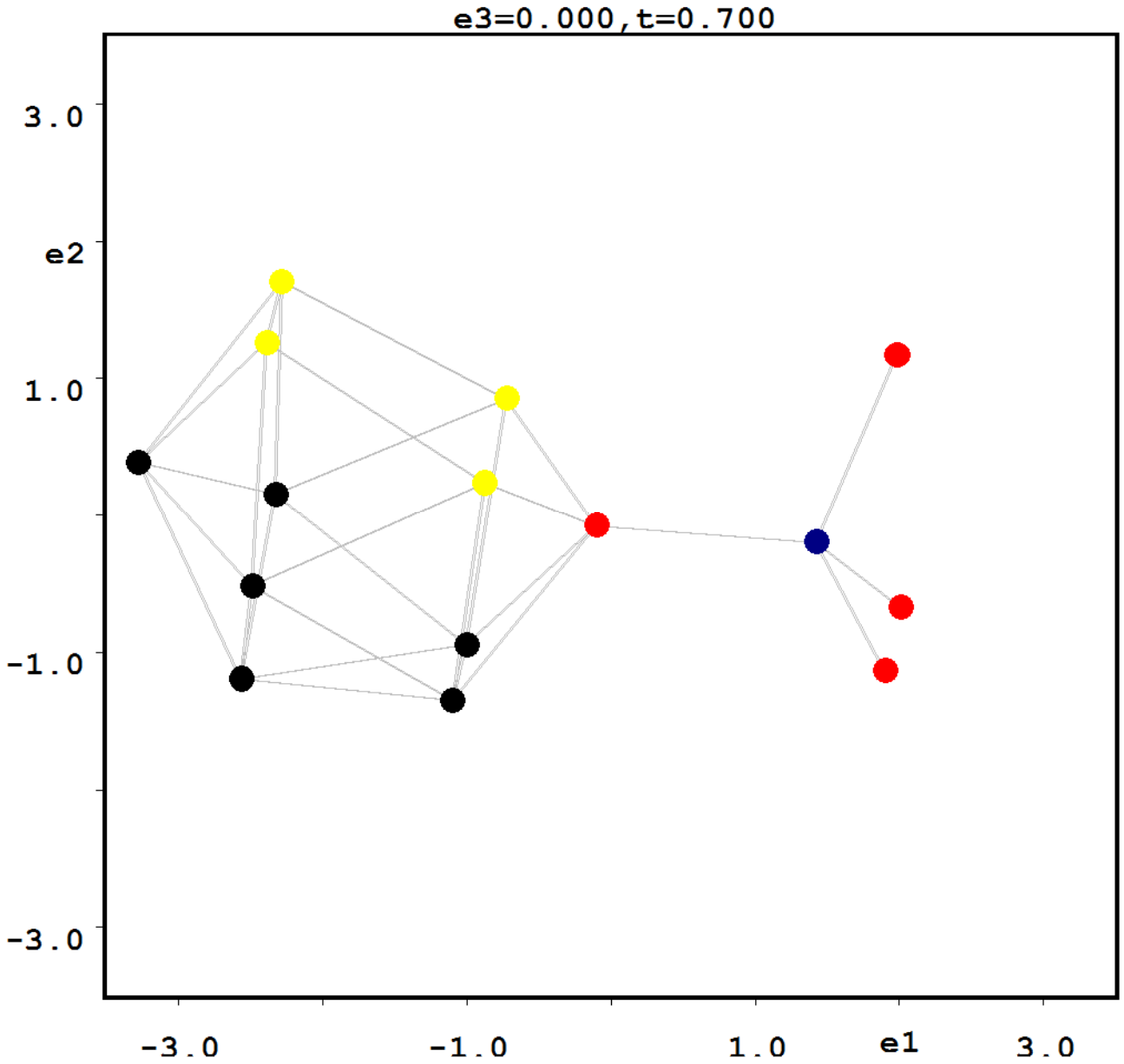
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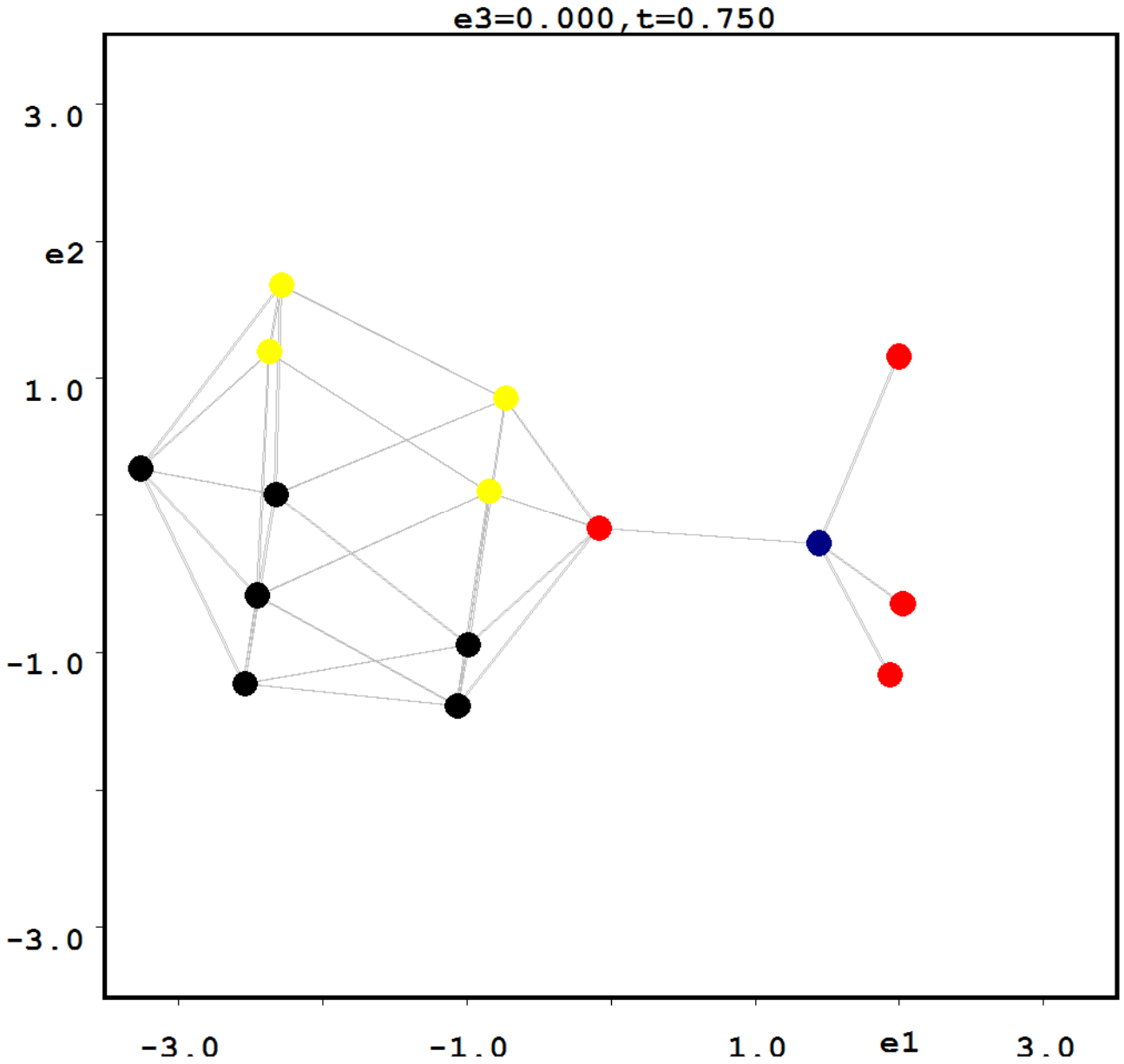
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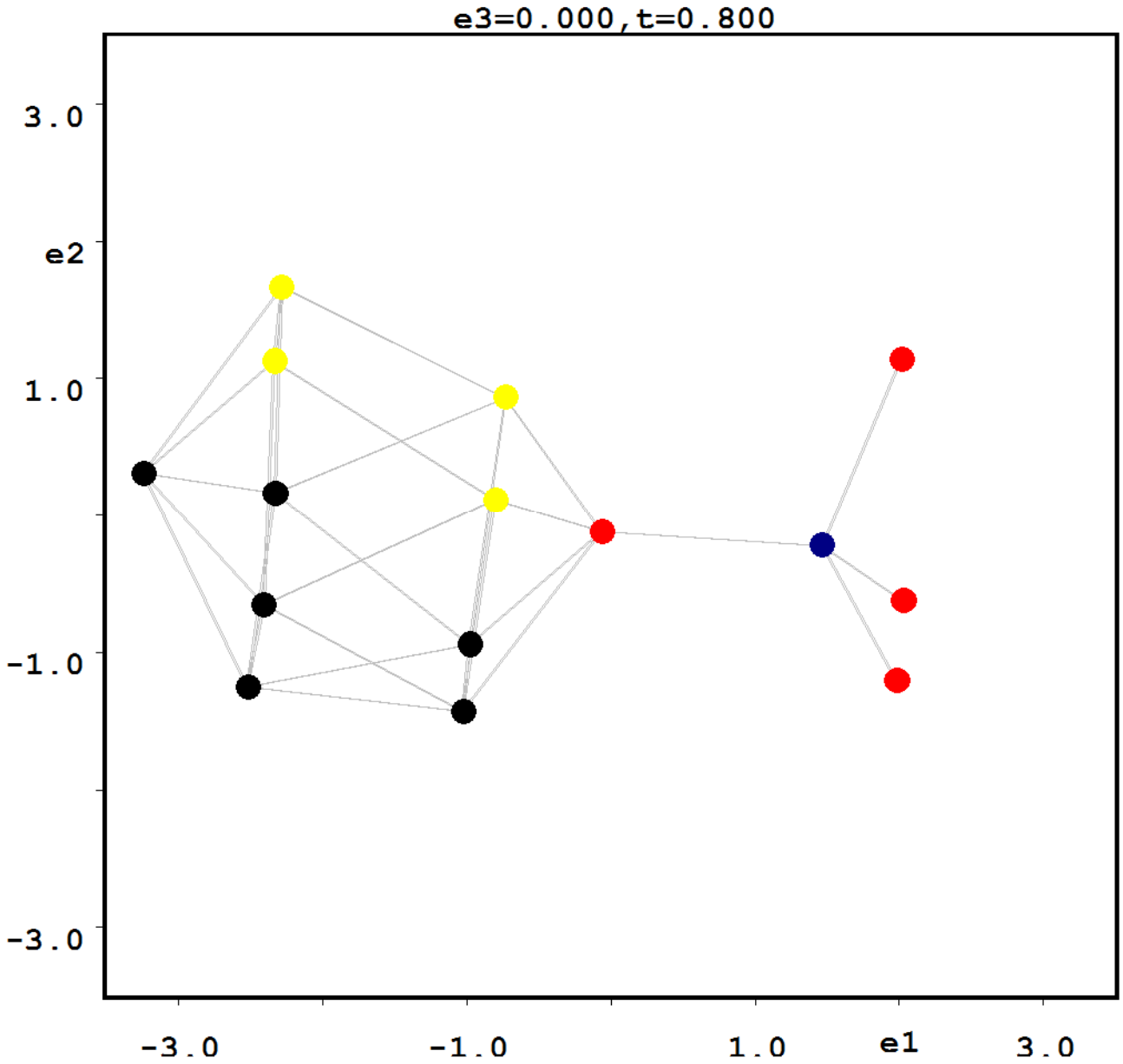
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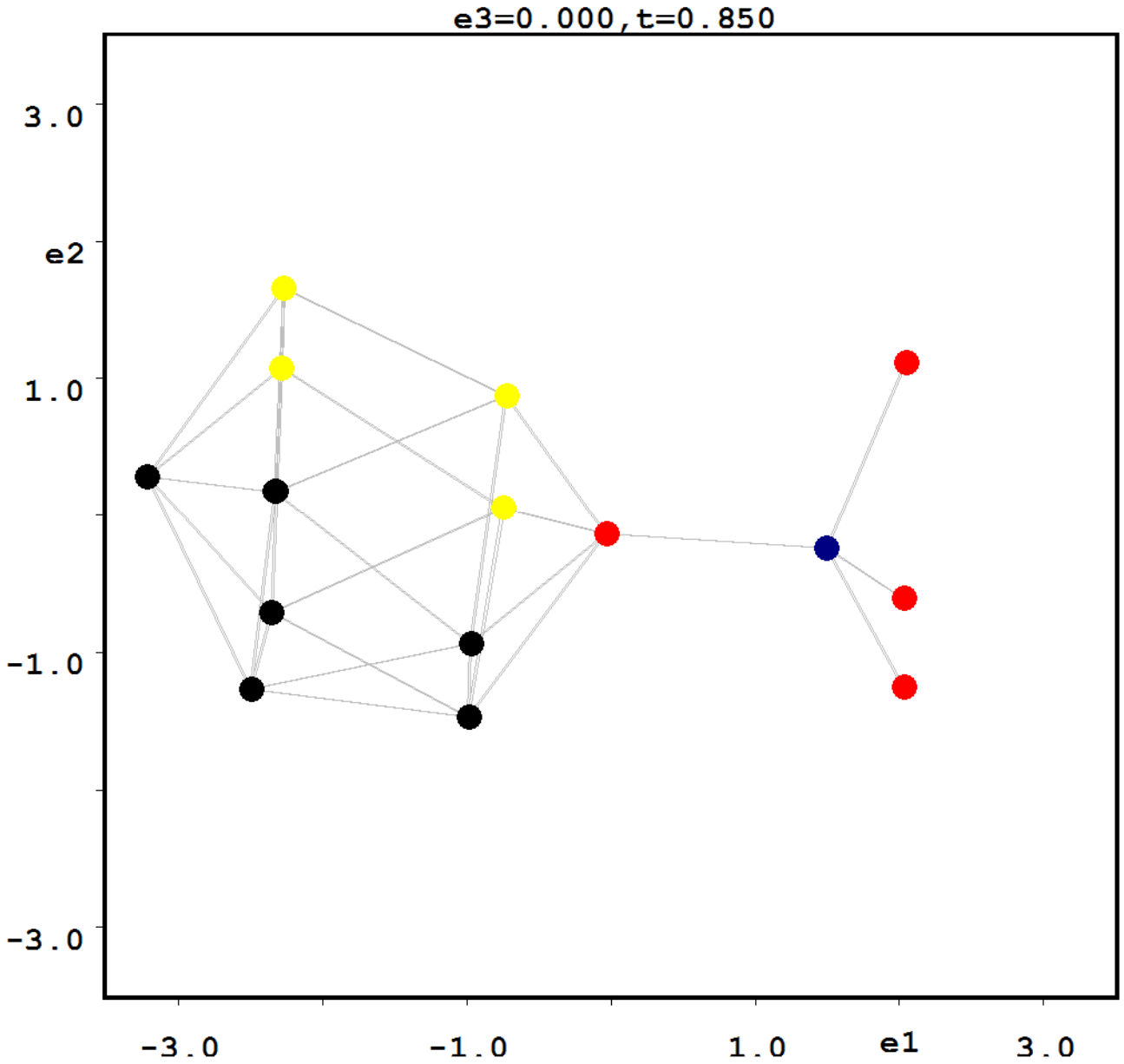
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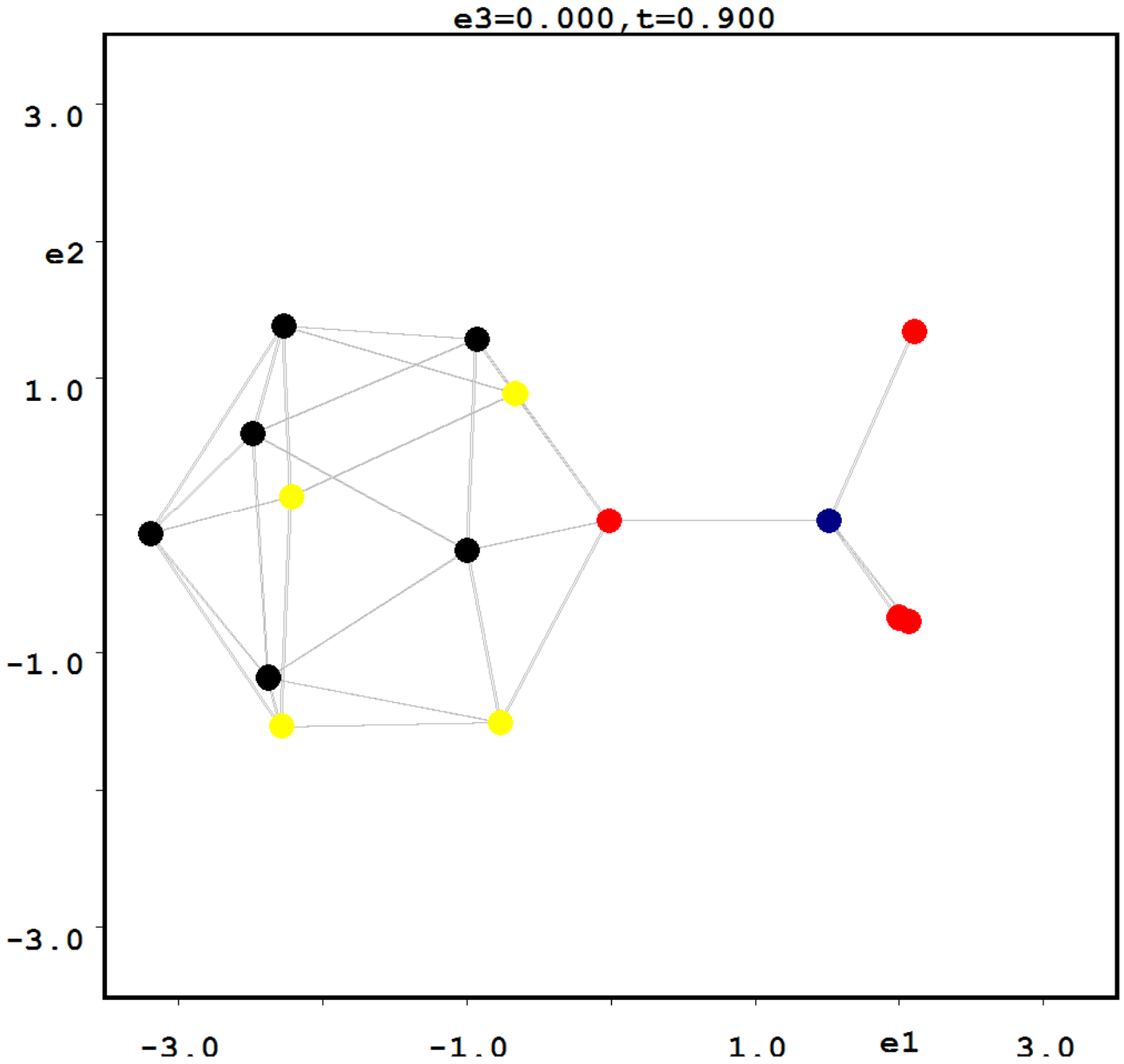
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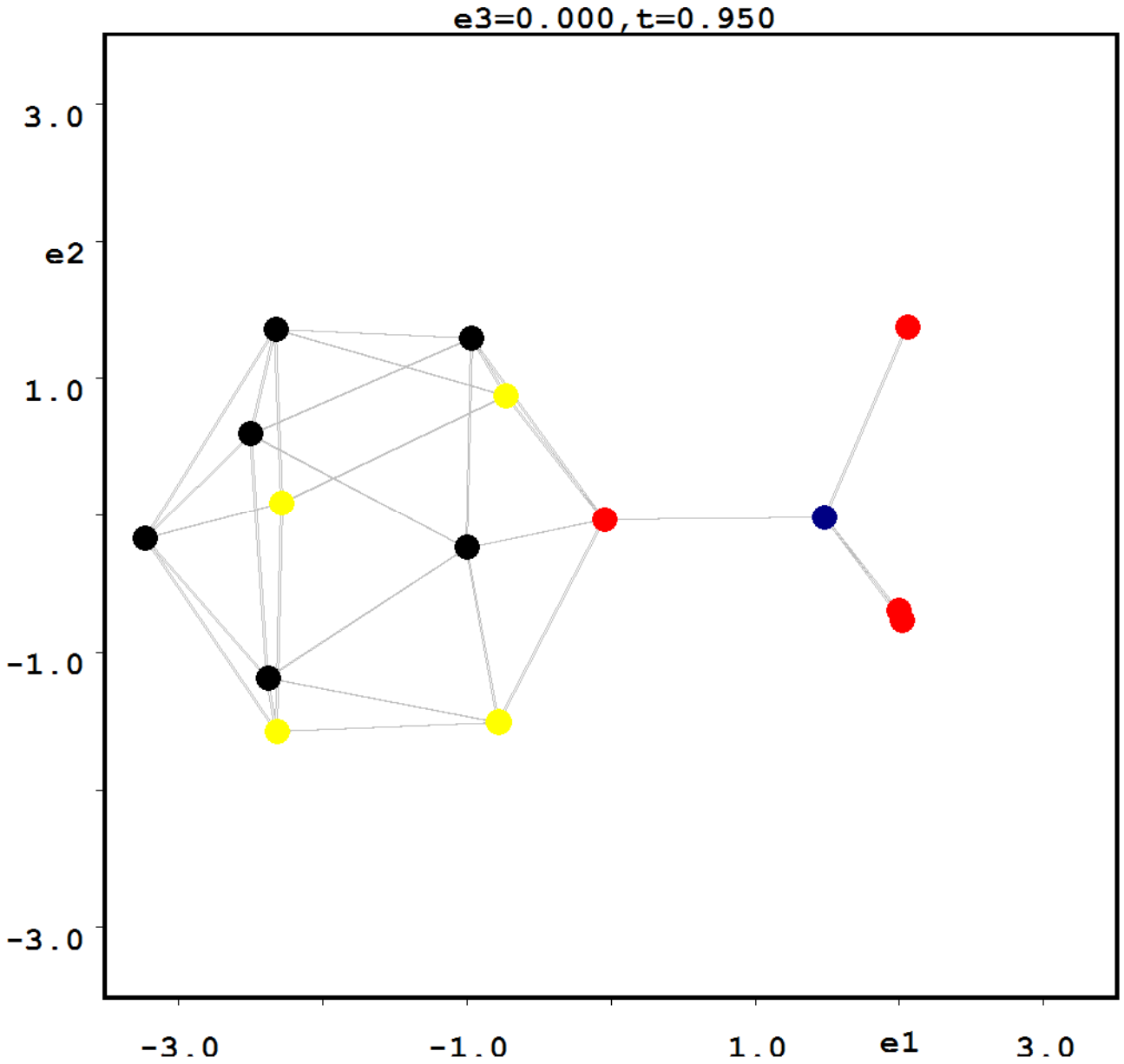
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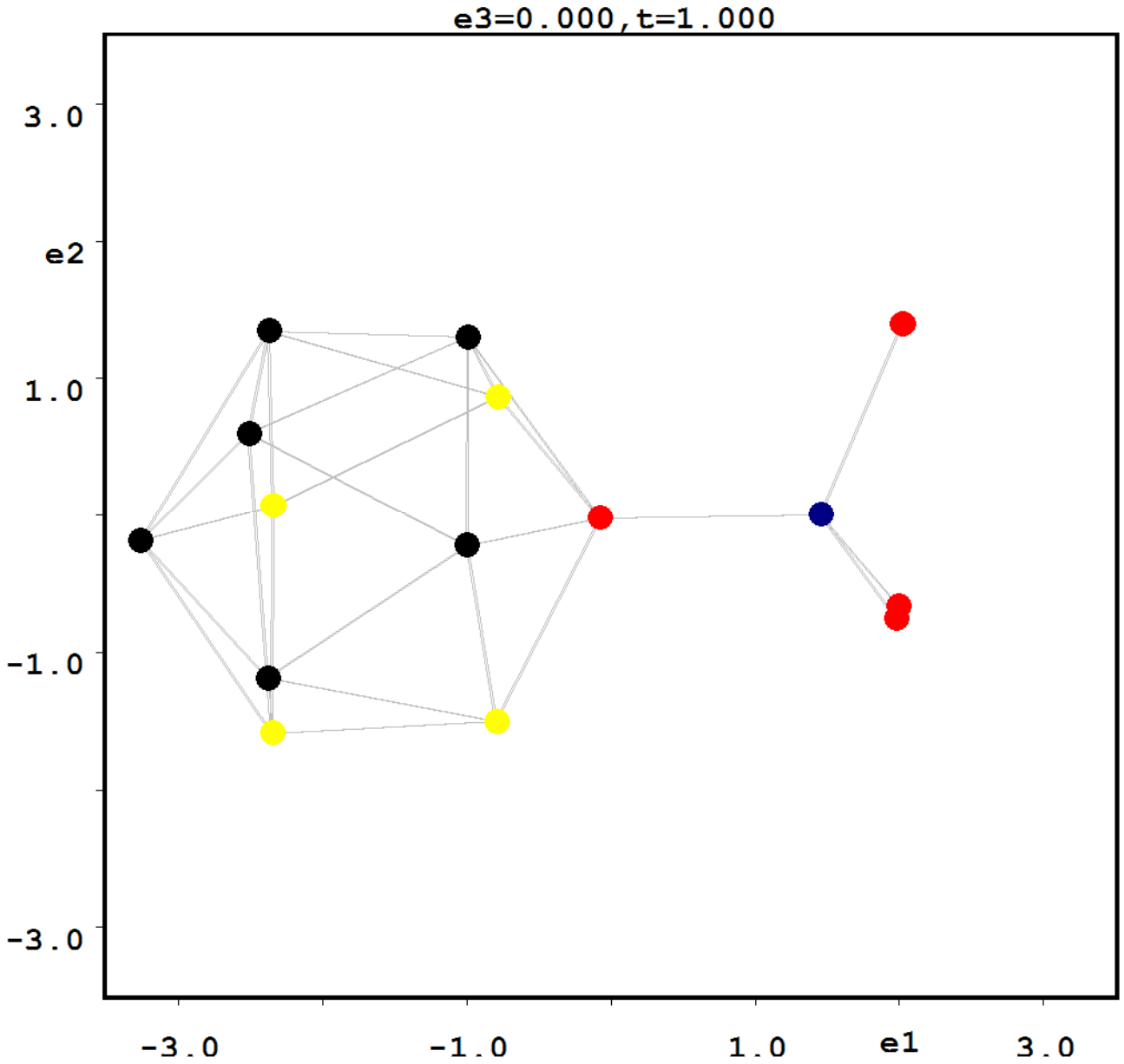
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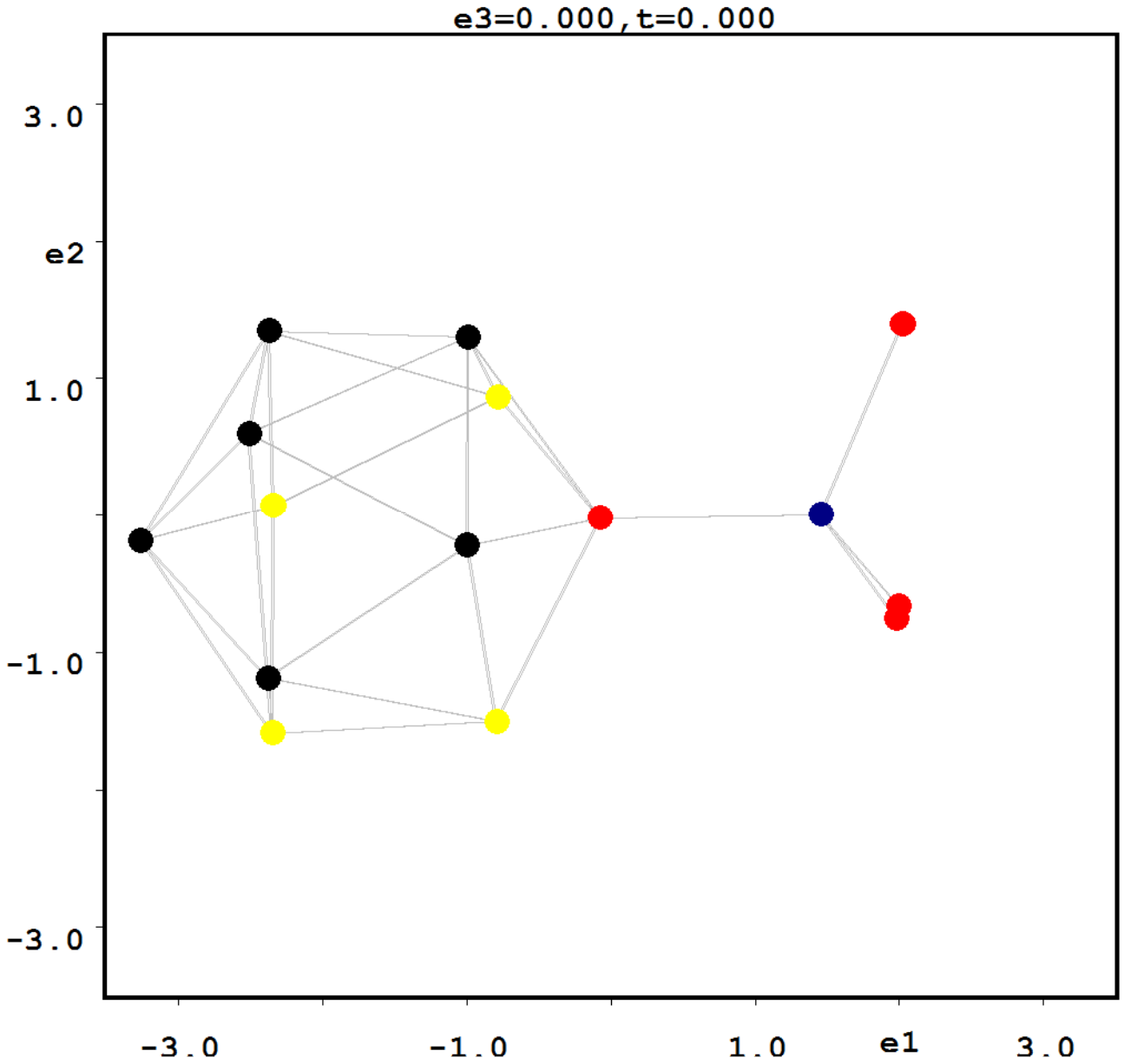
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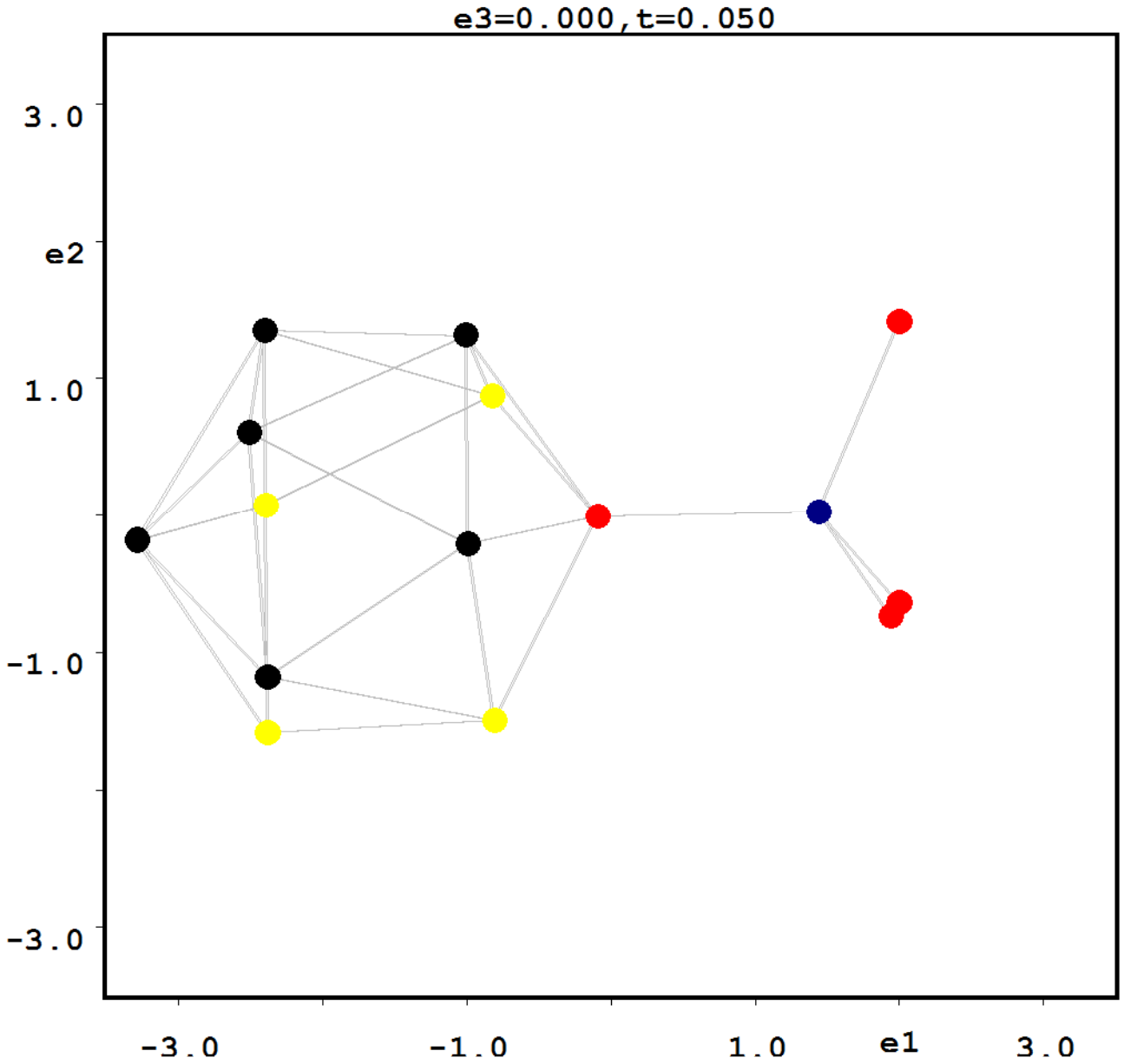
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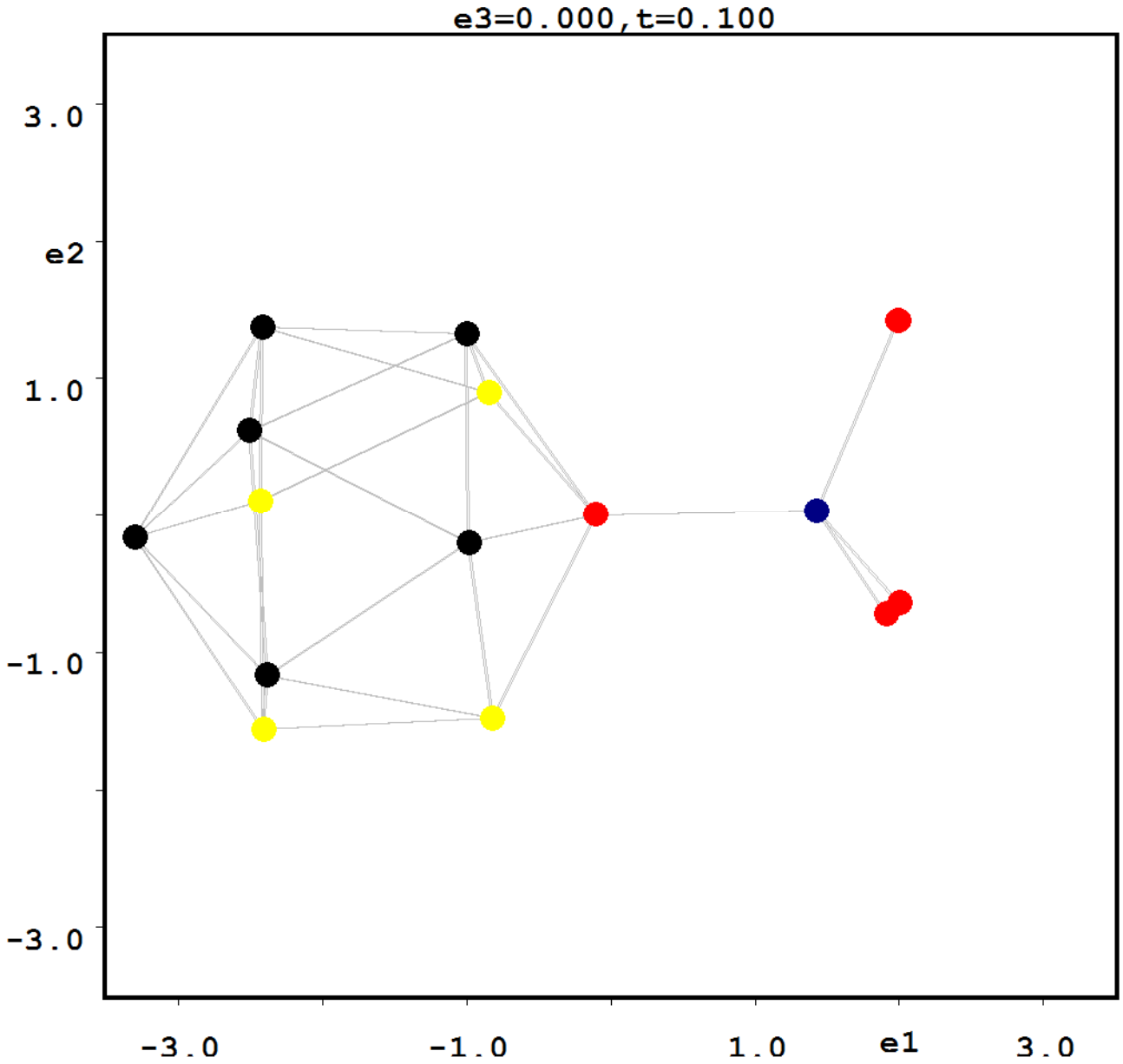
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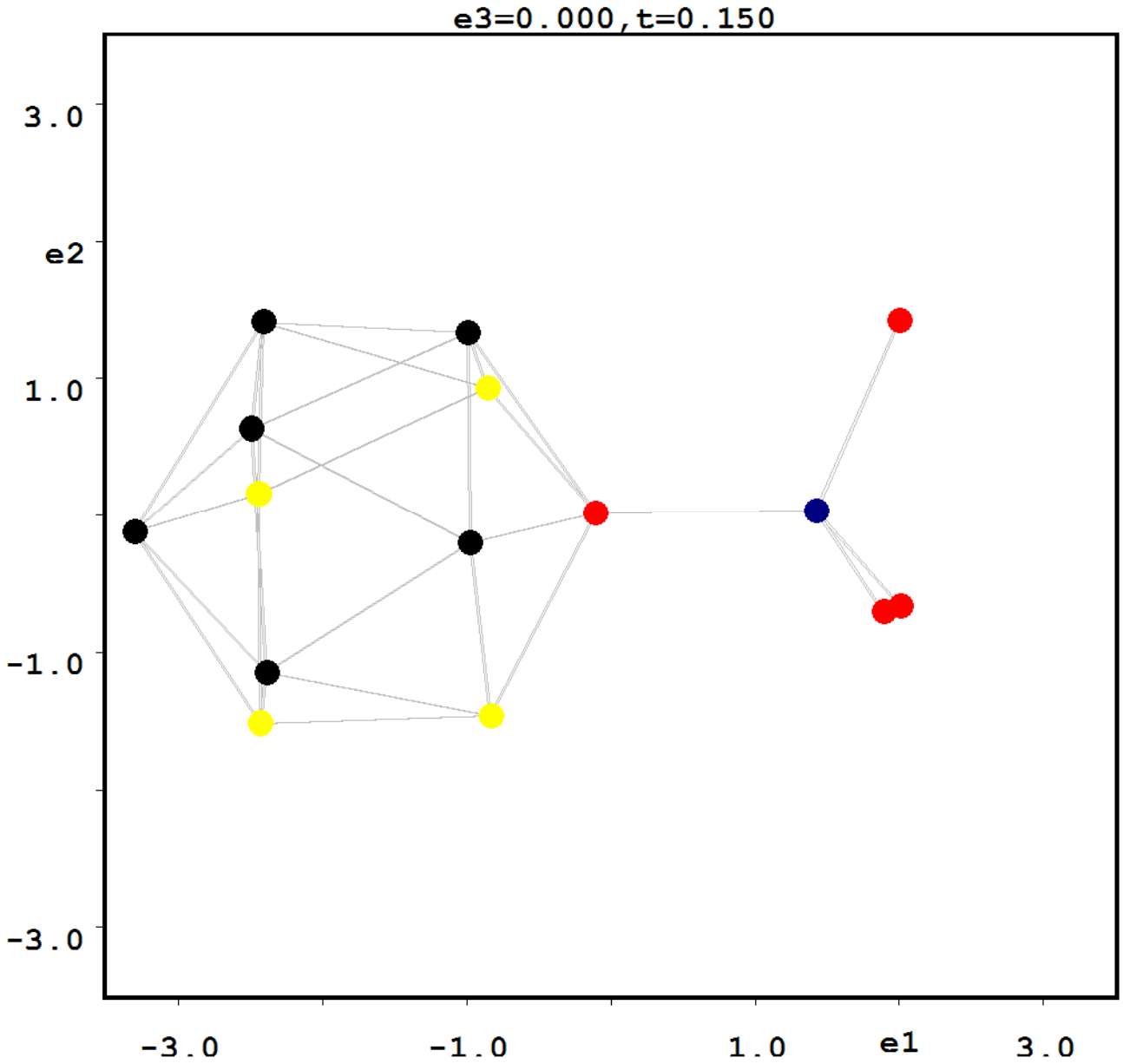
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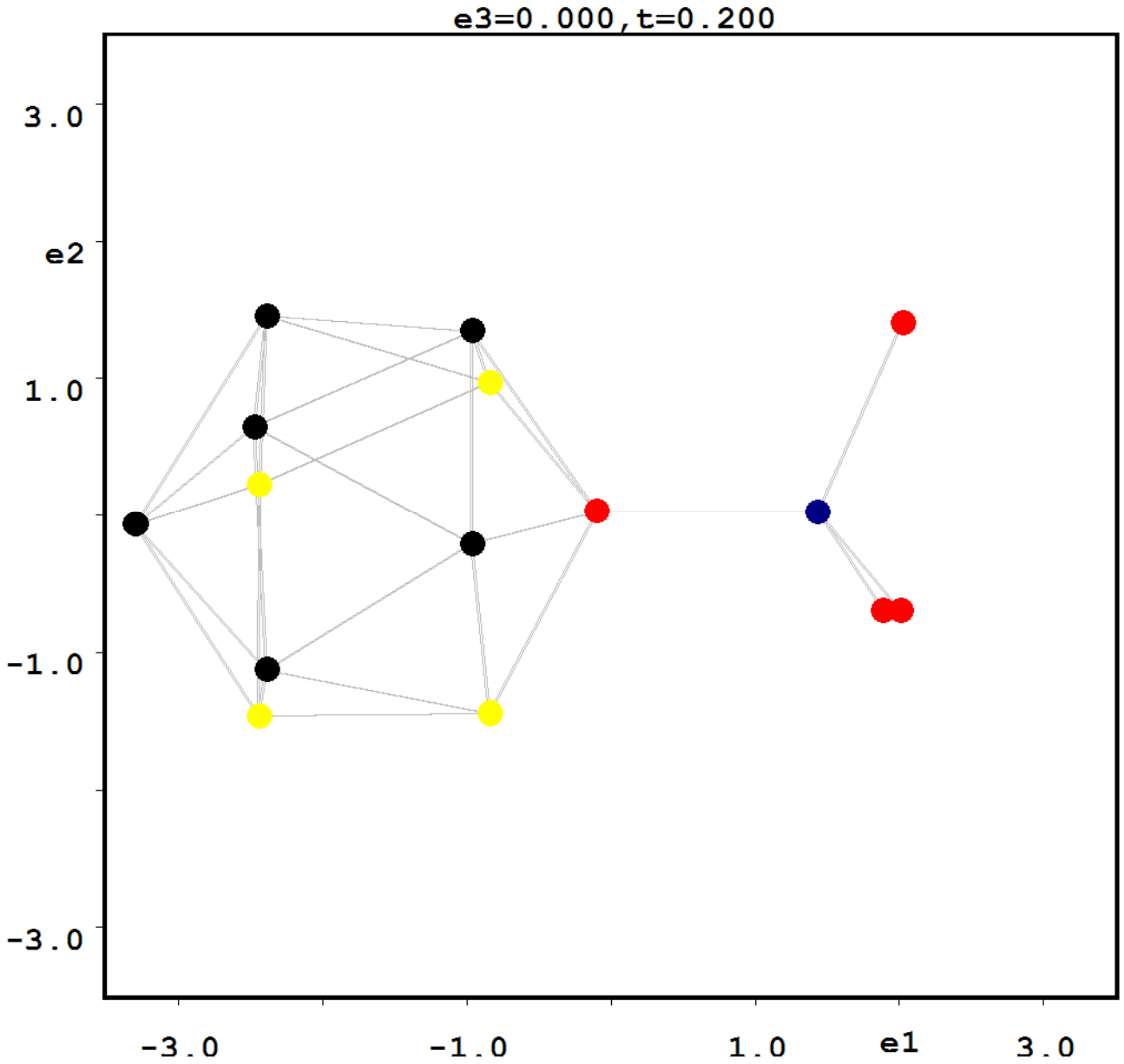
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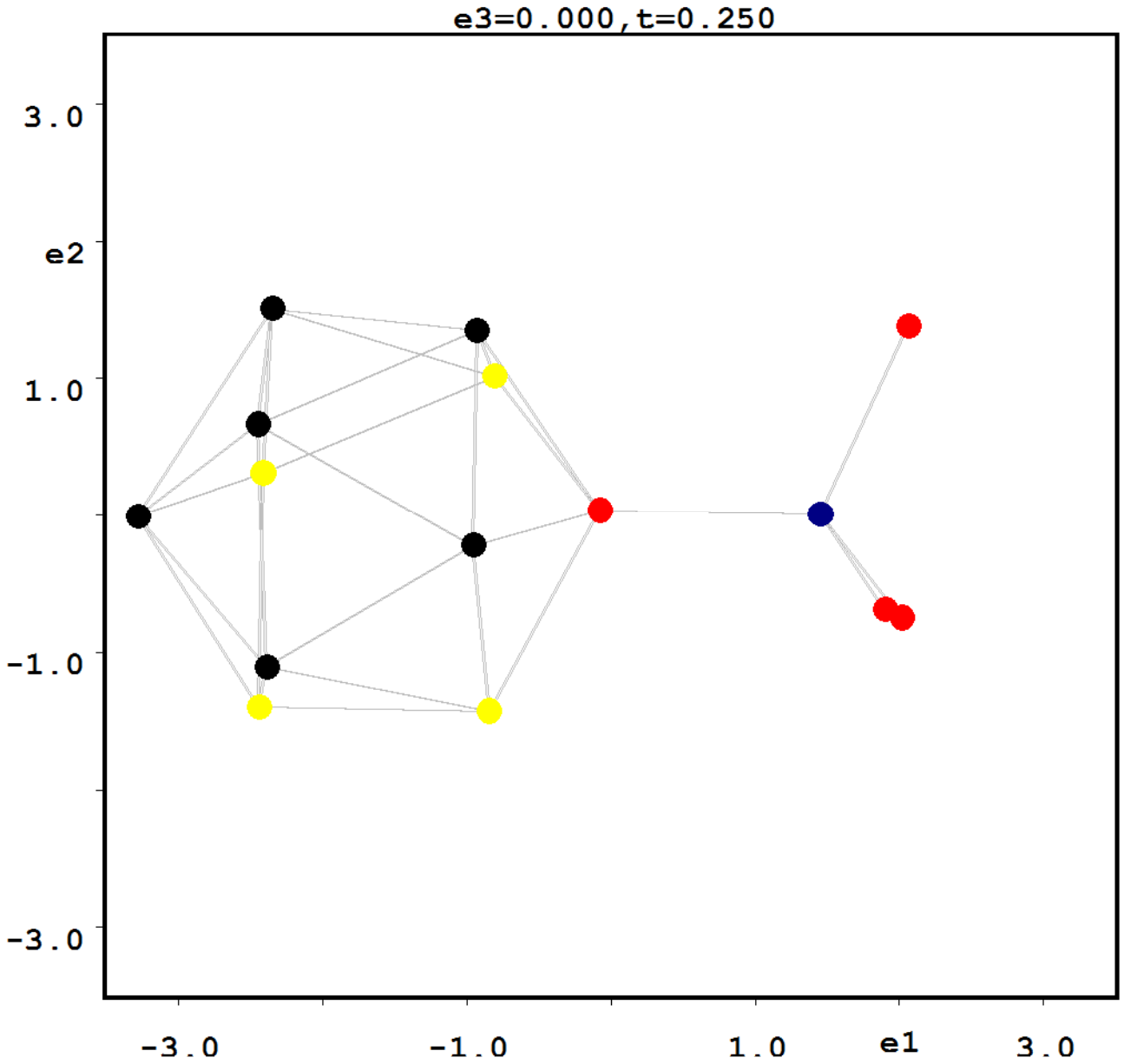
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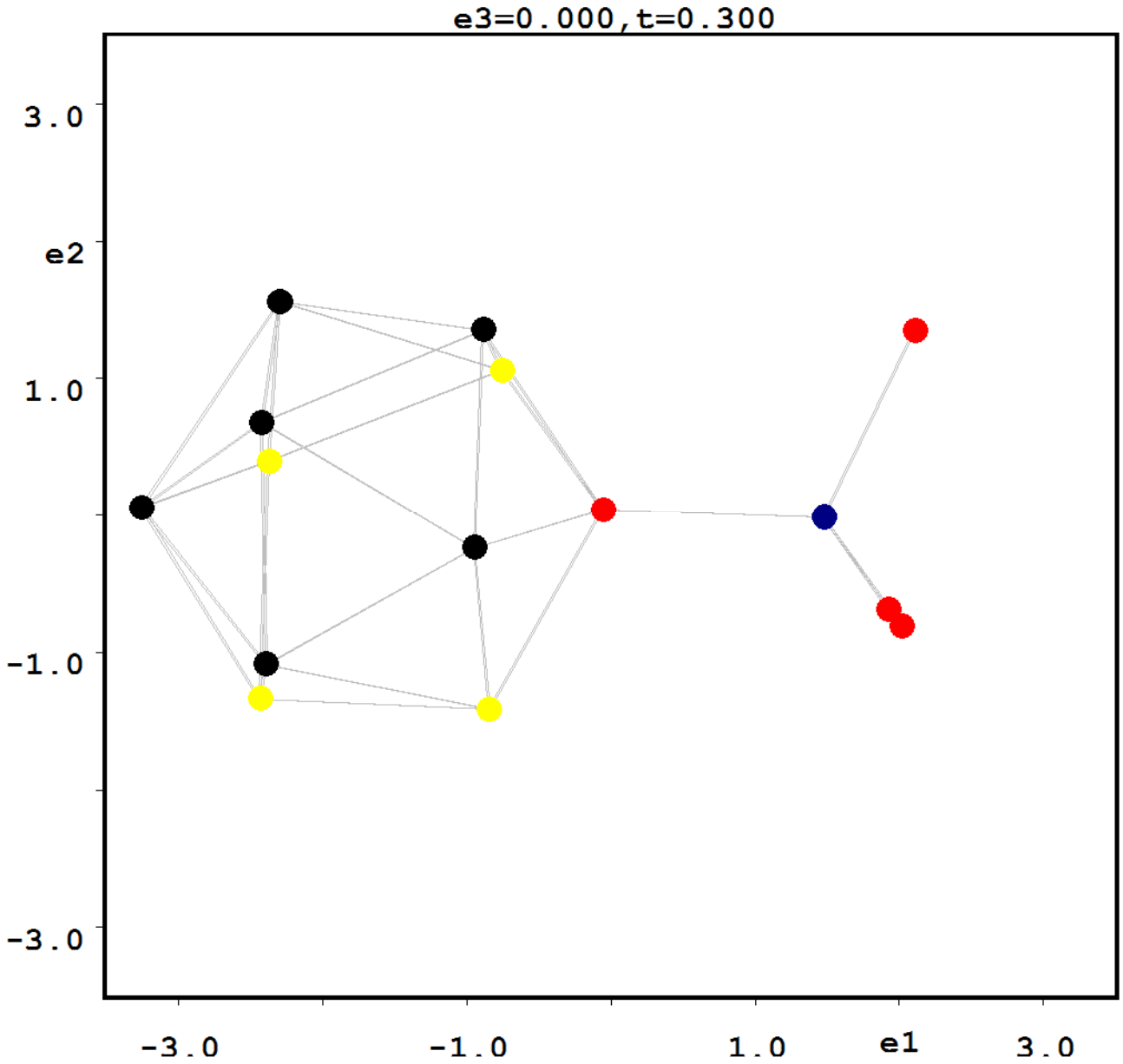
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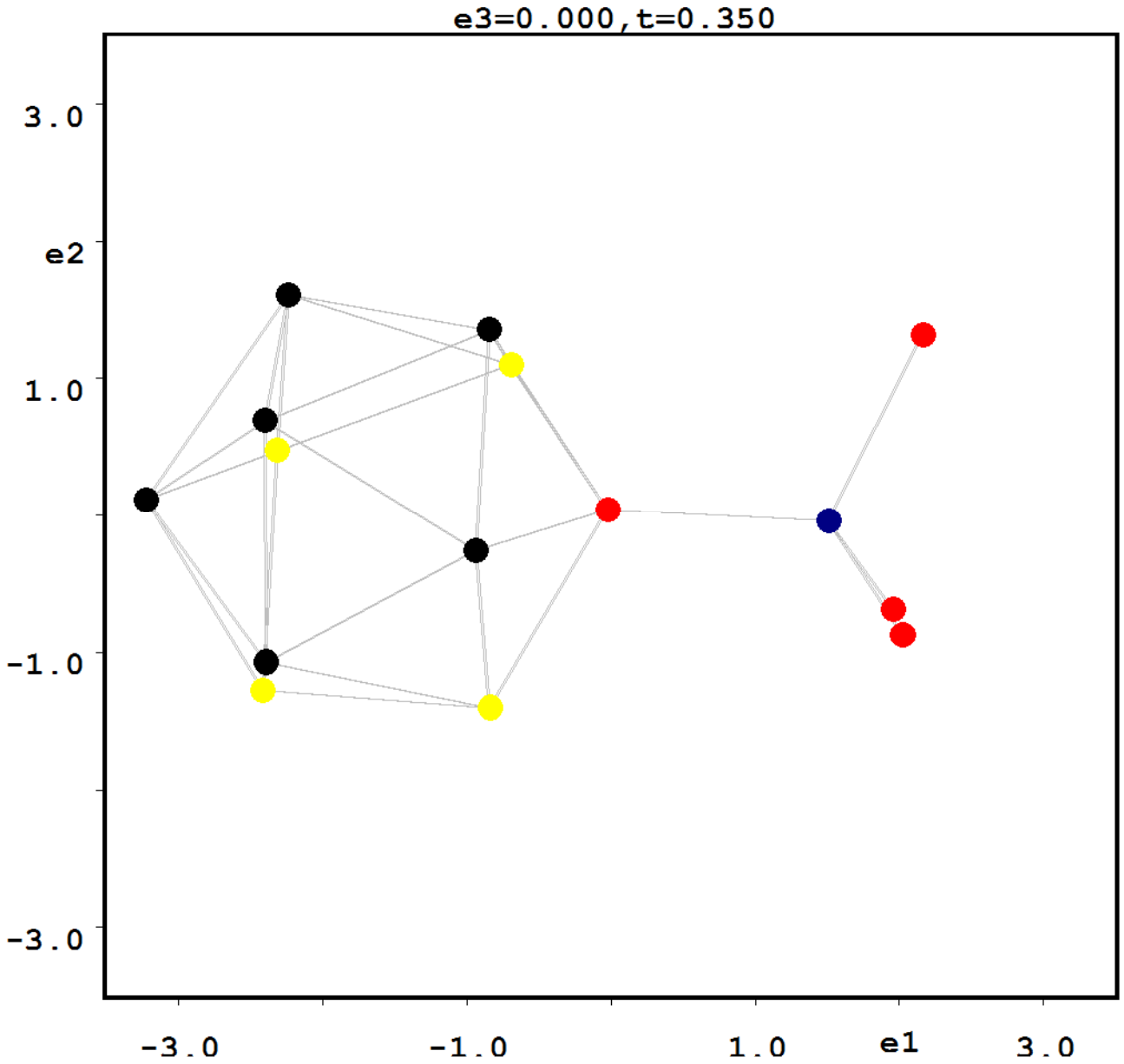
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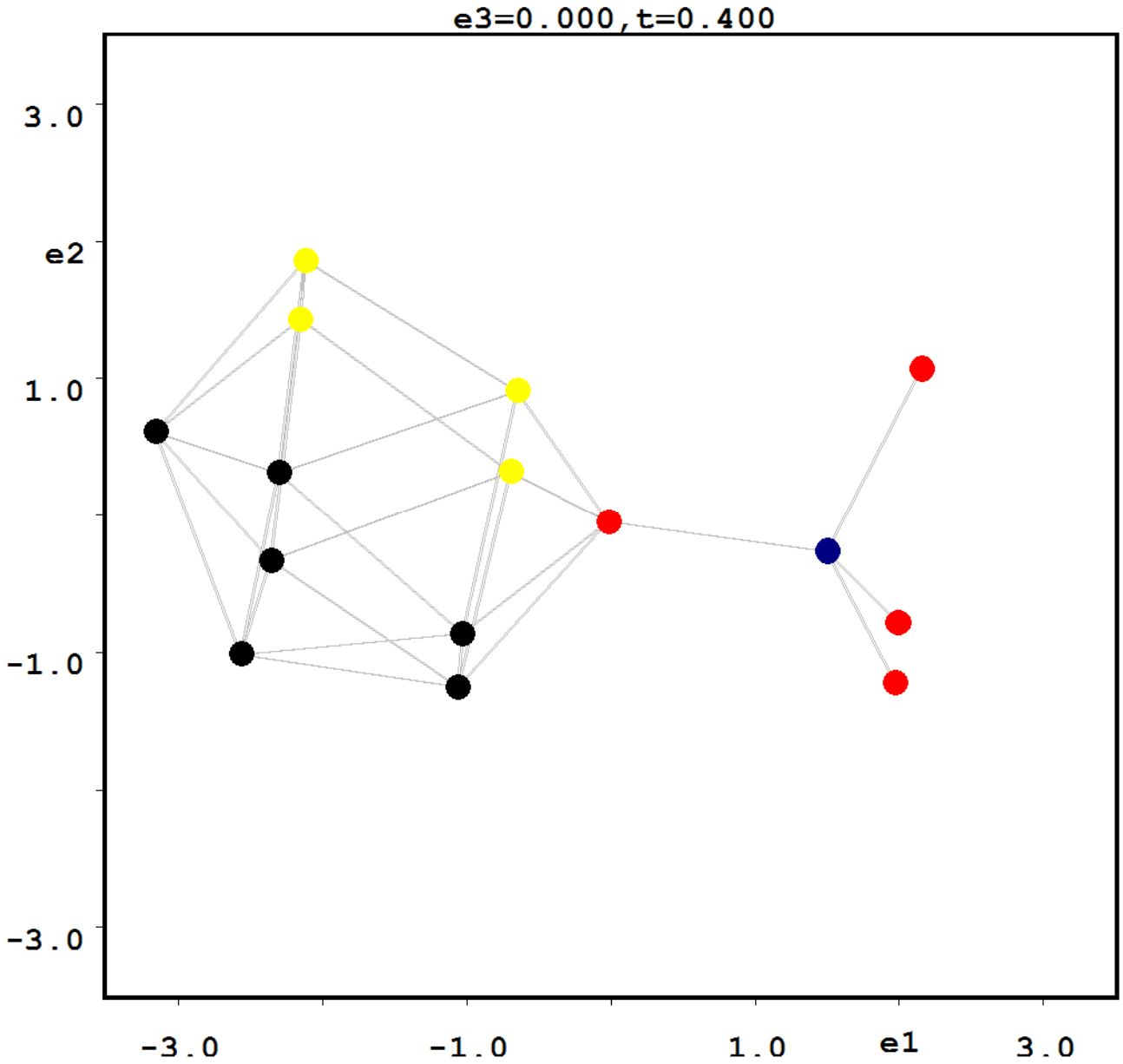
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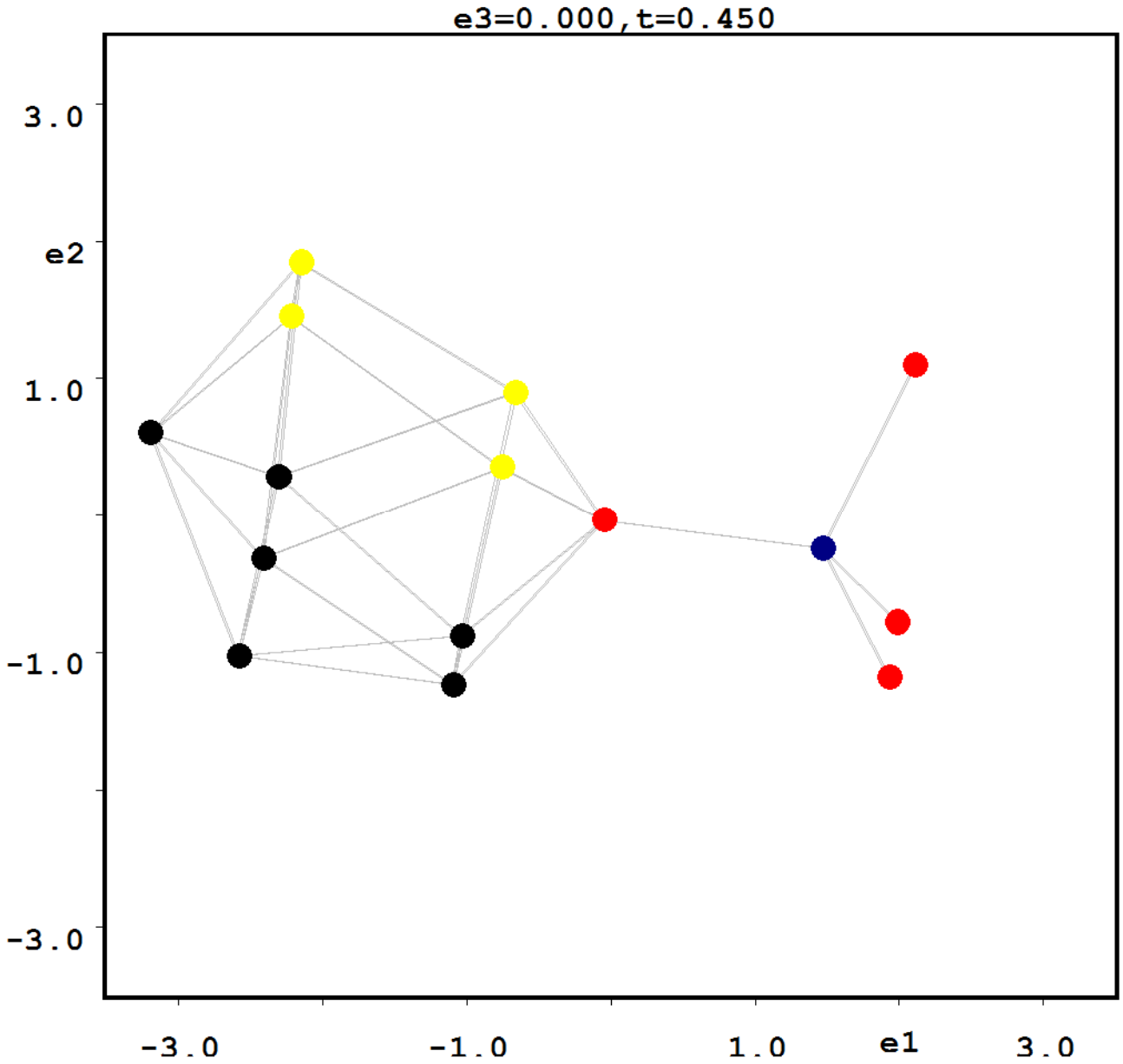
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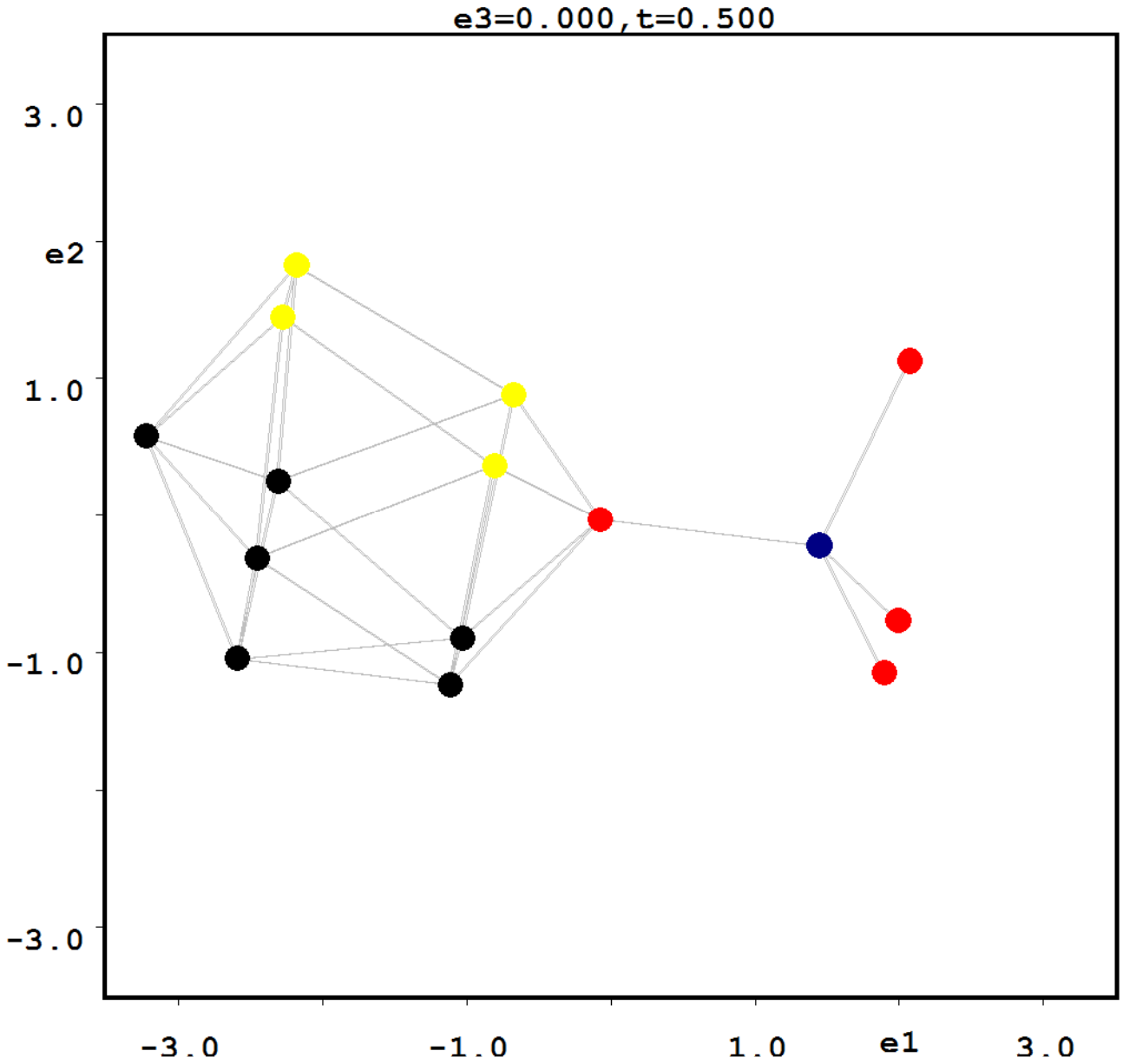
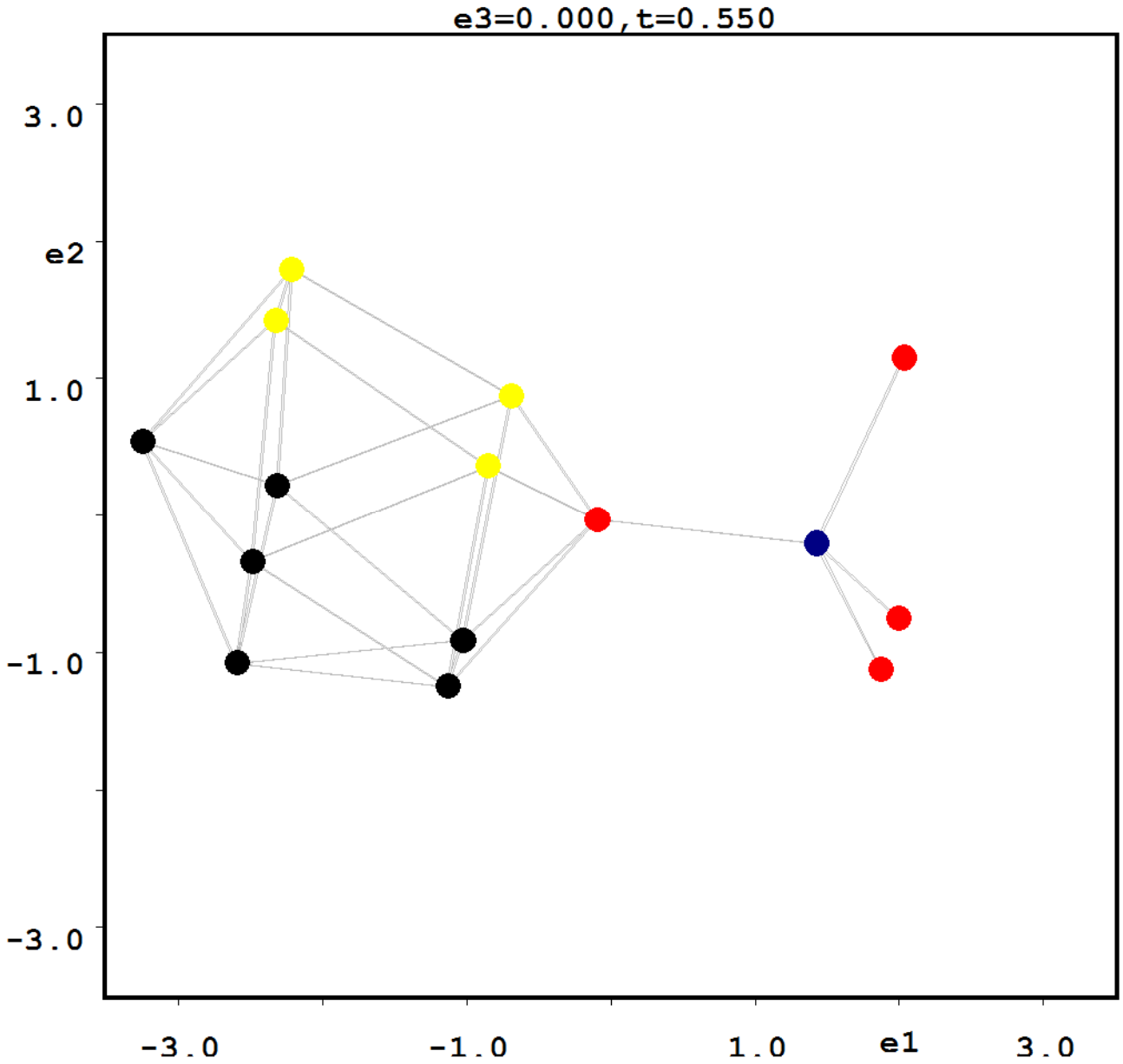


Bruker AXS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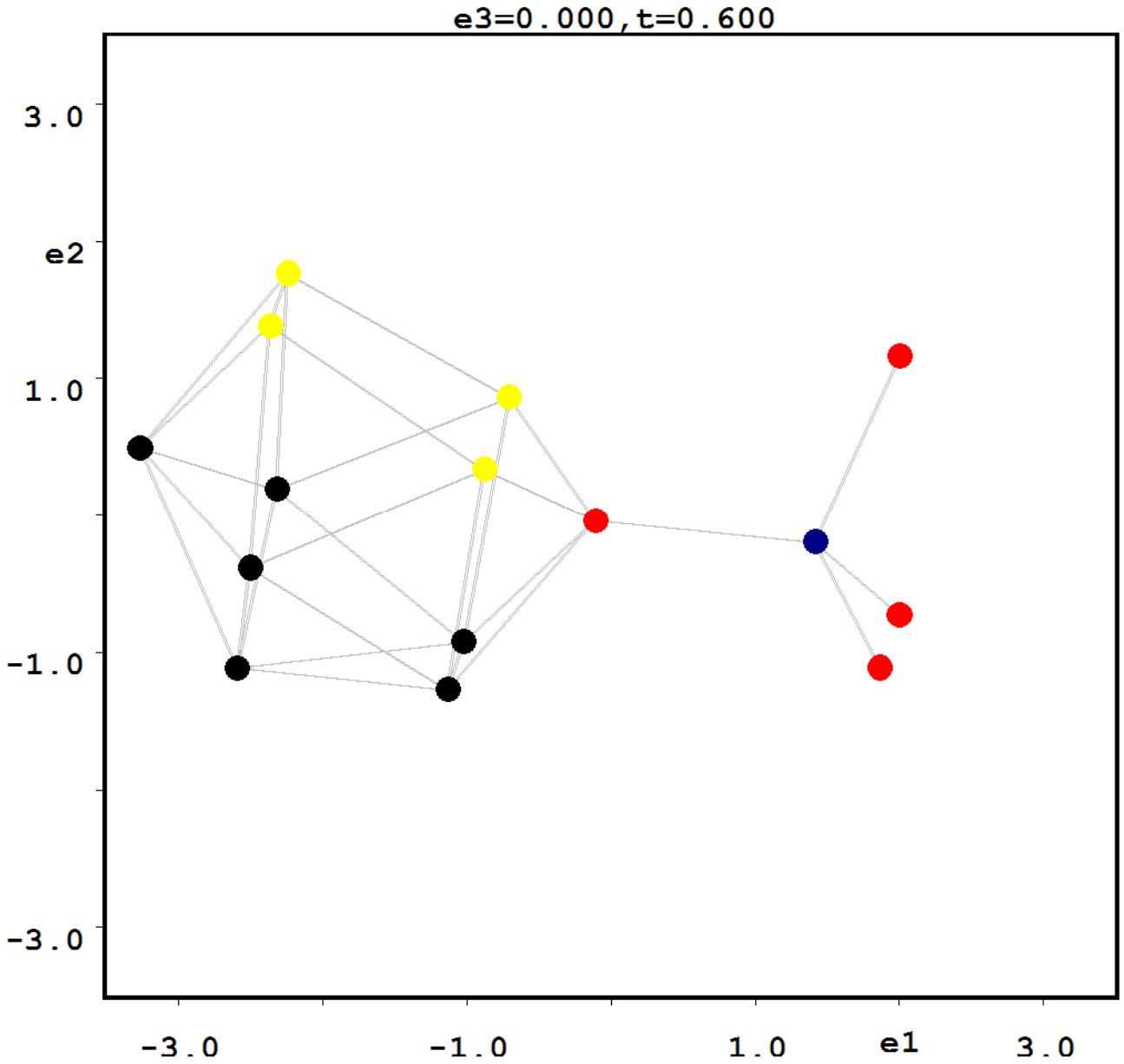
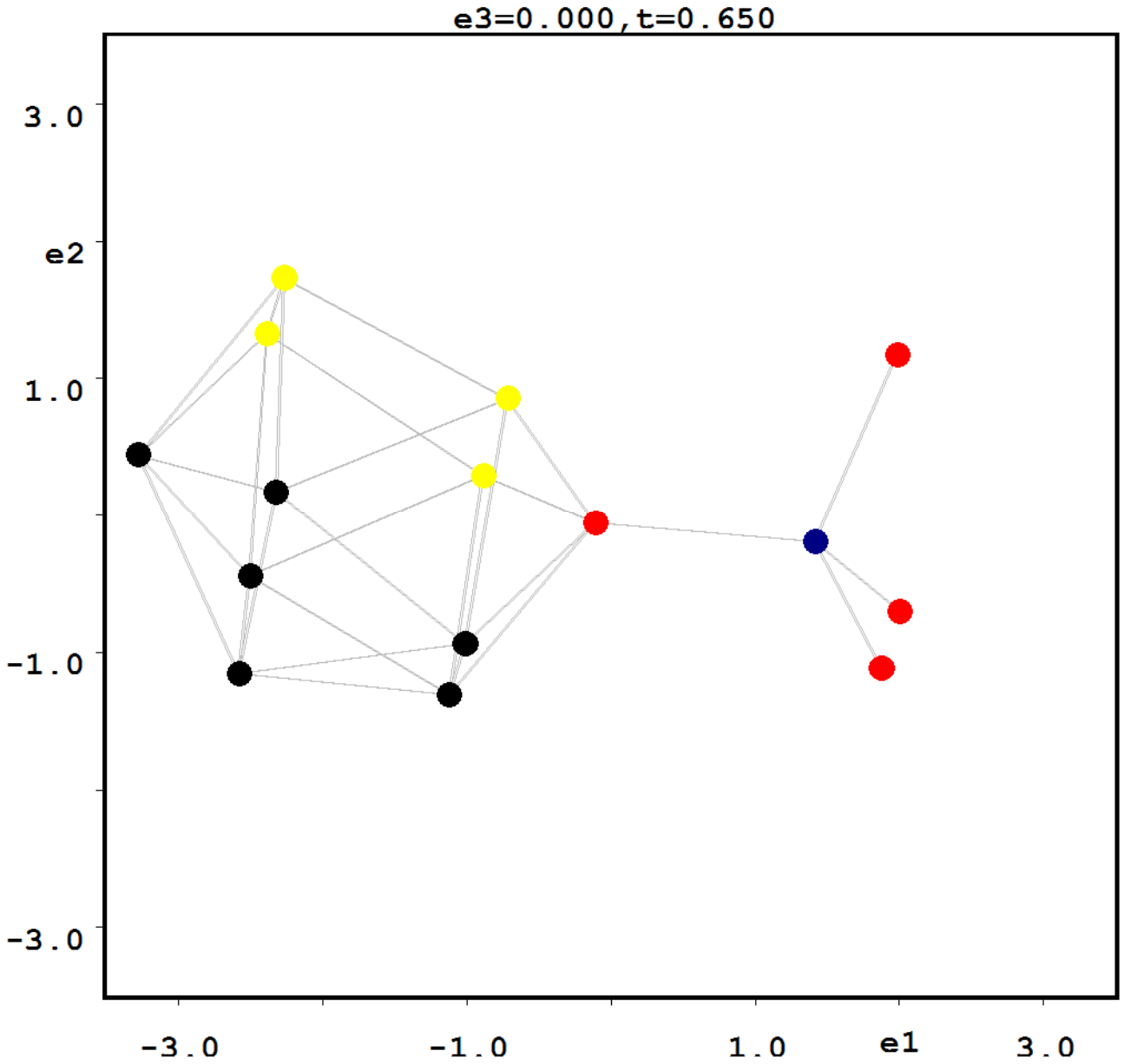


Bruker AXS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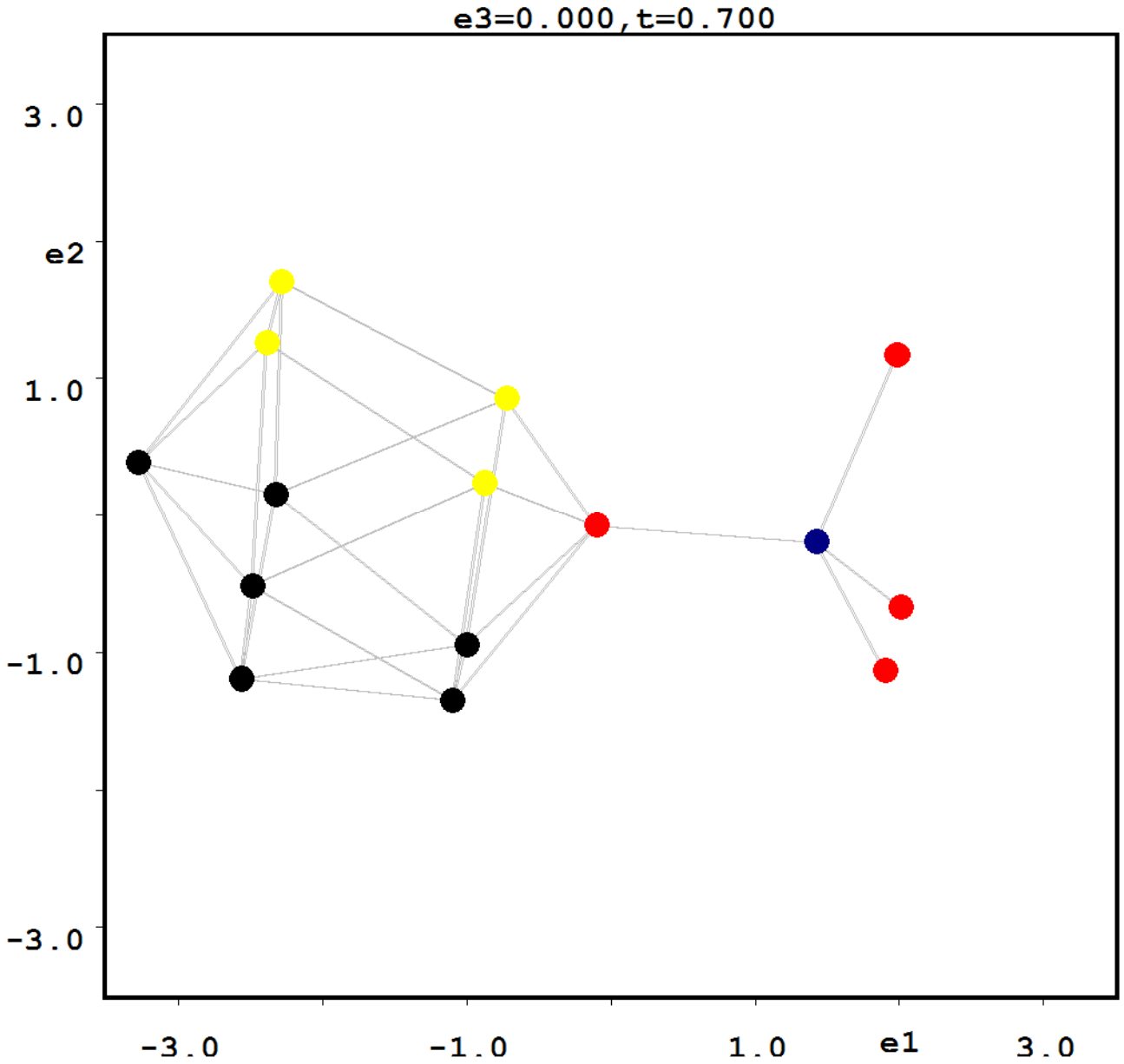
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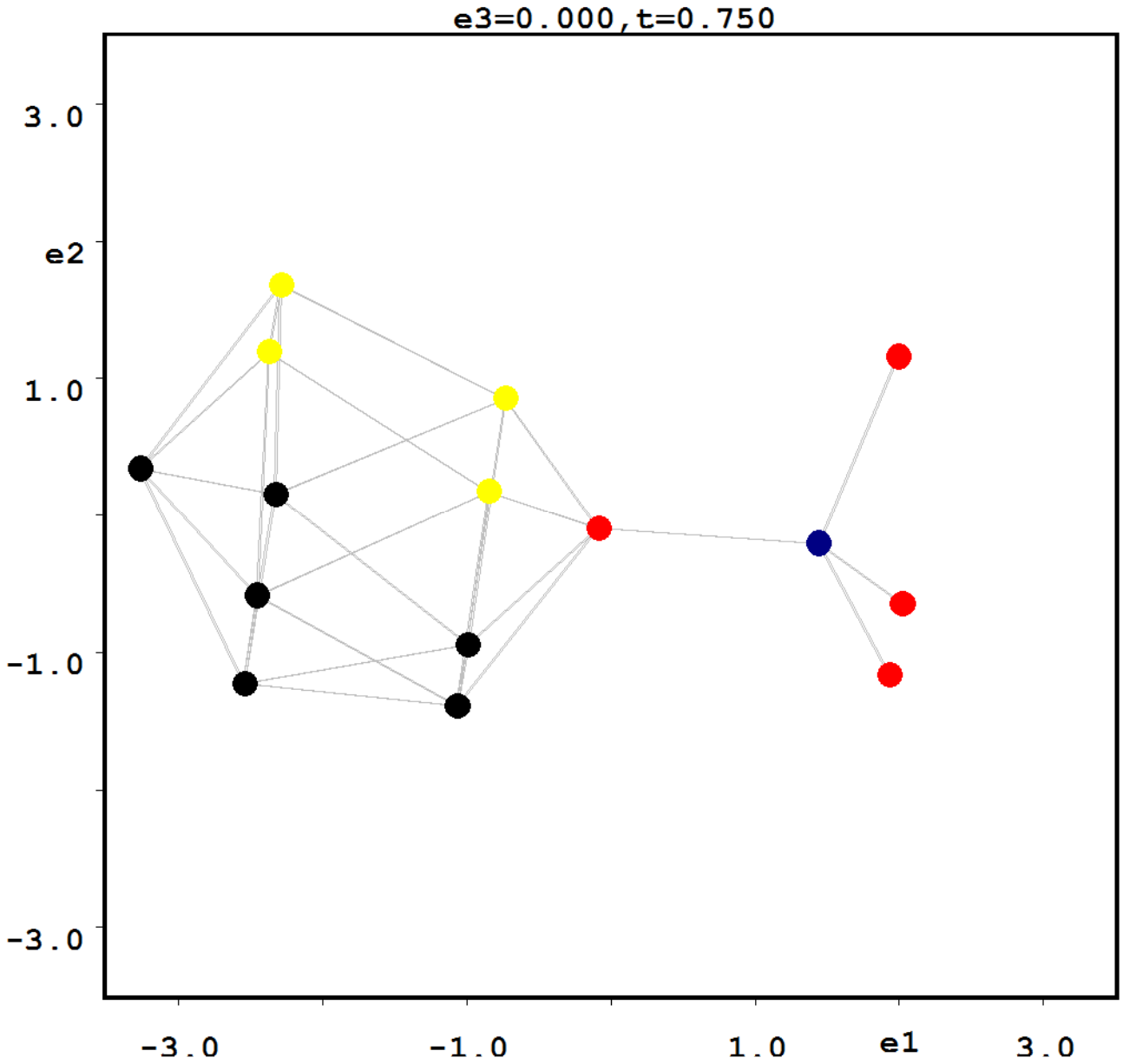
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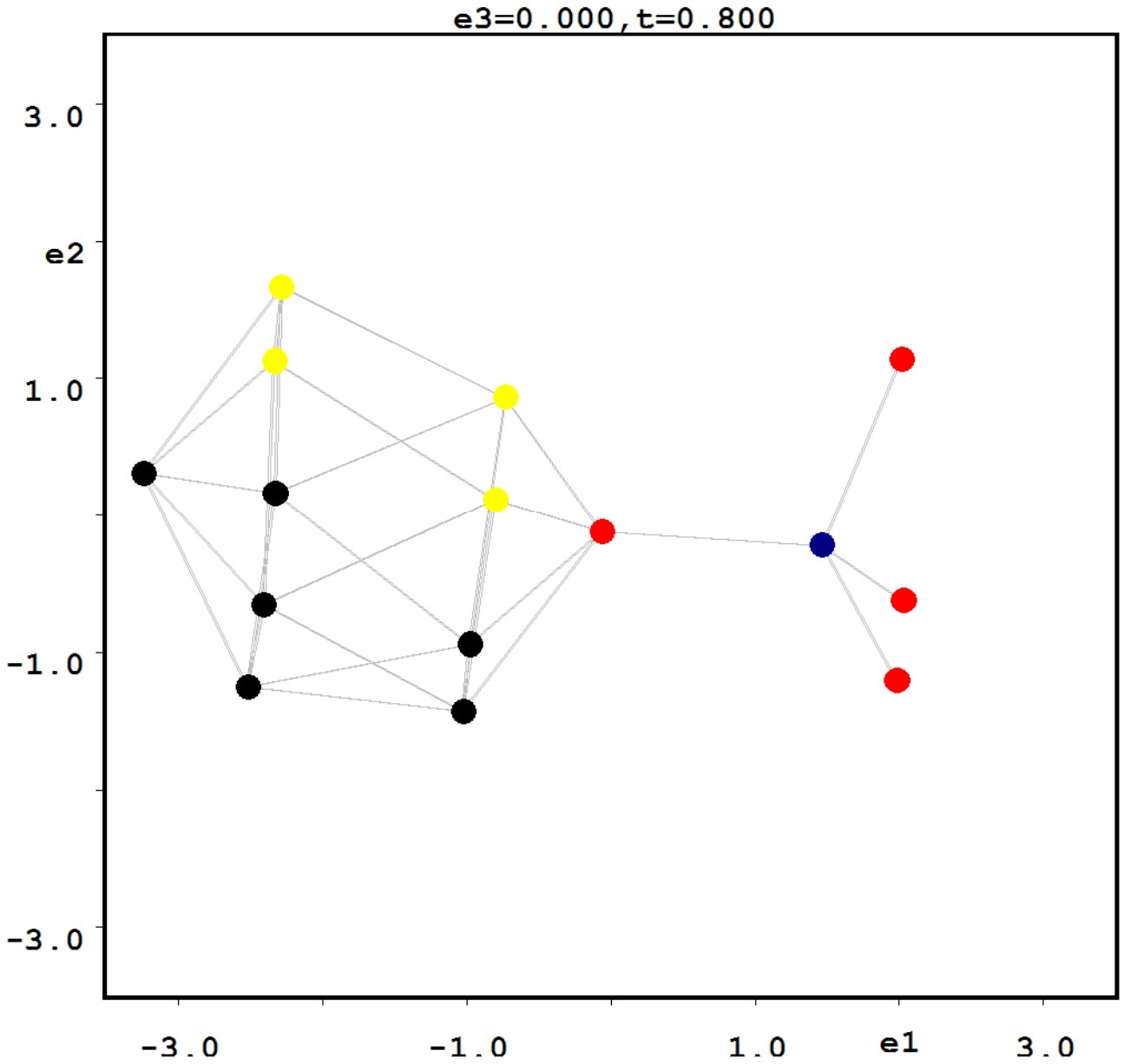
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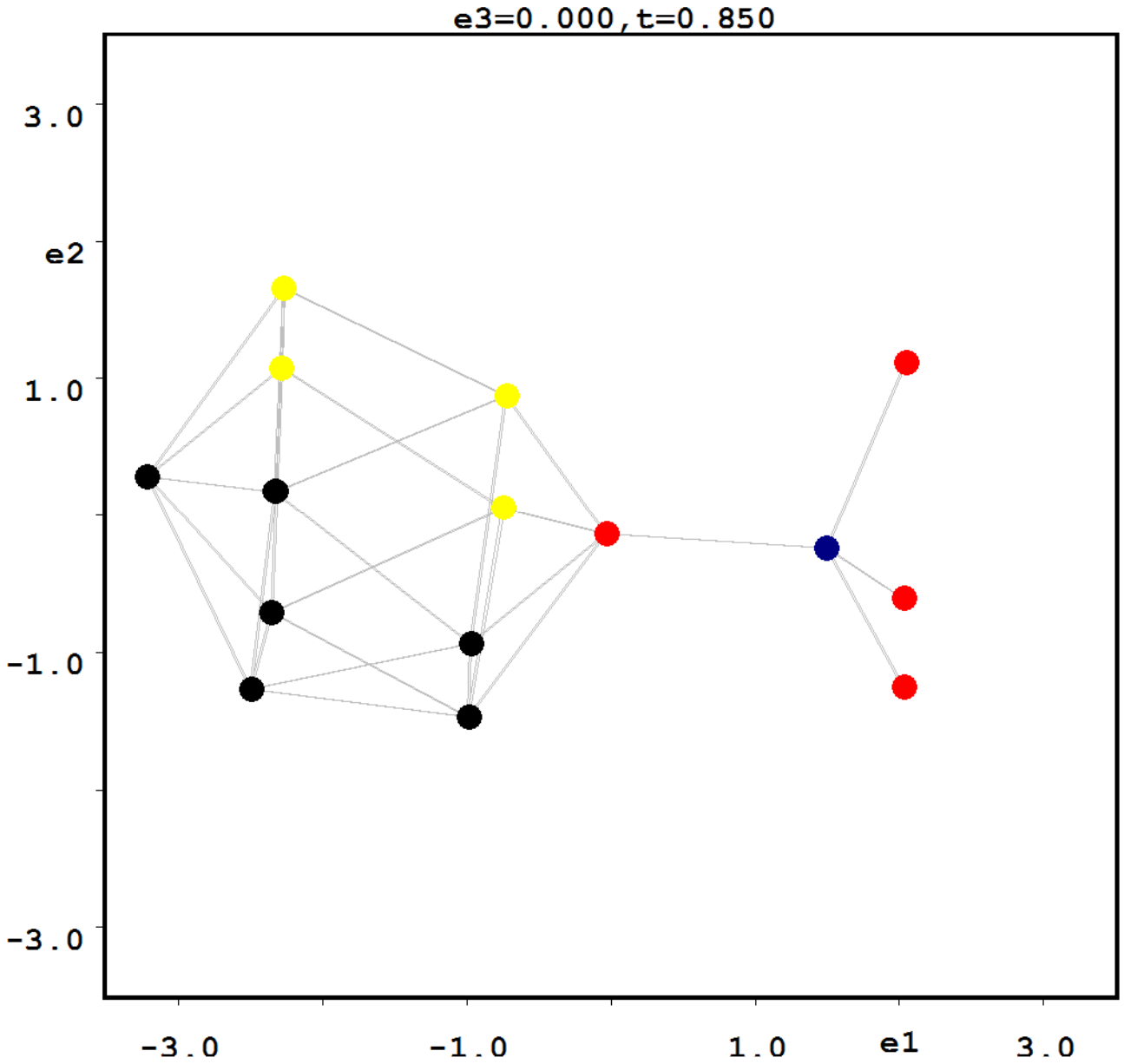
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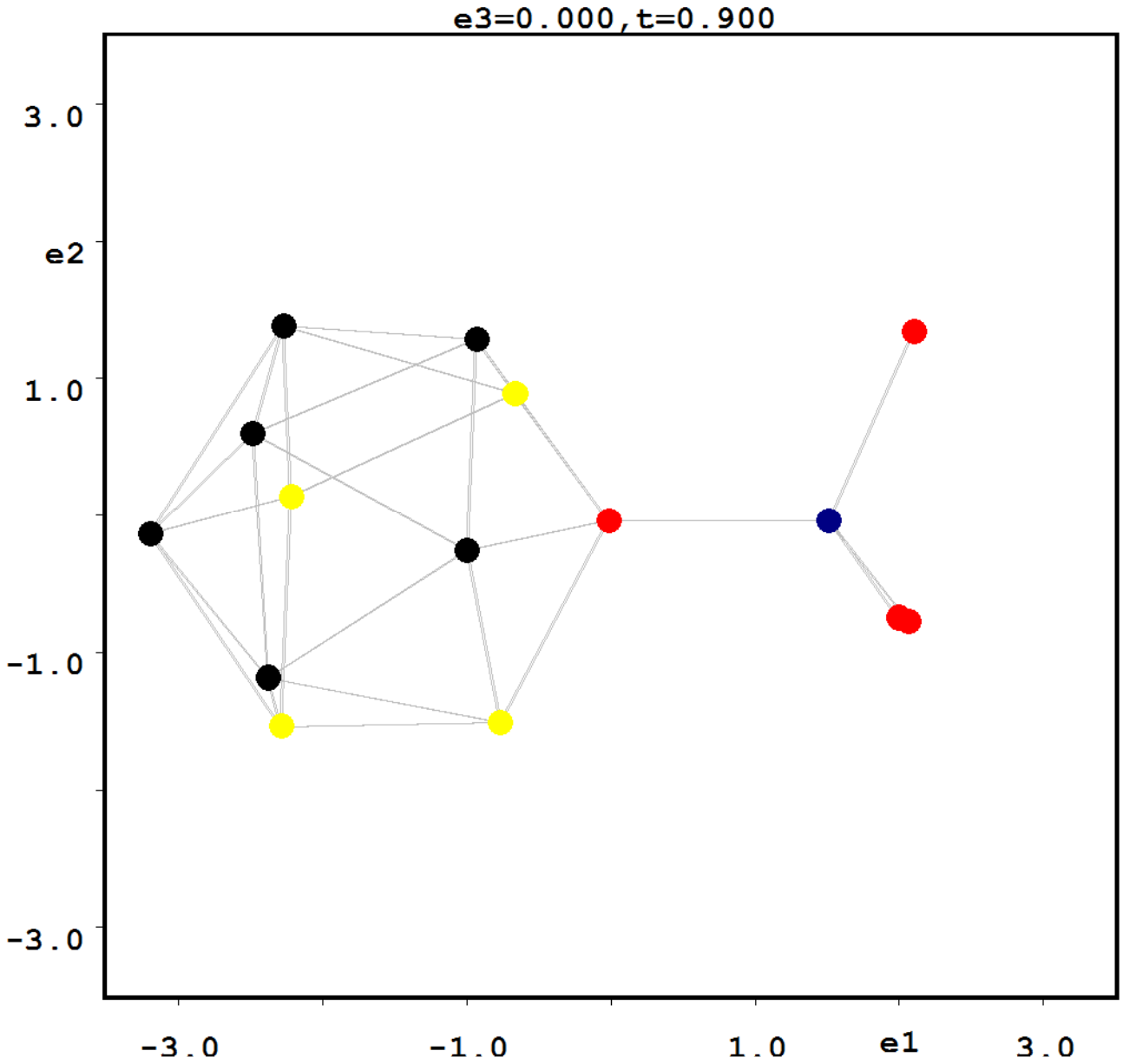
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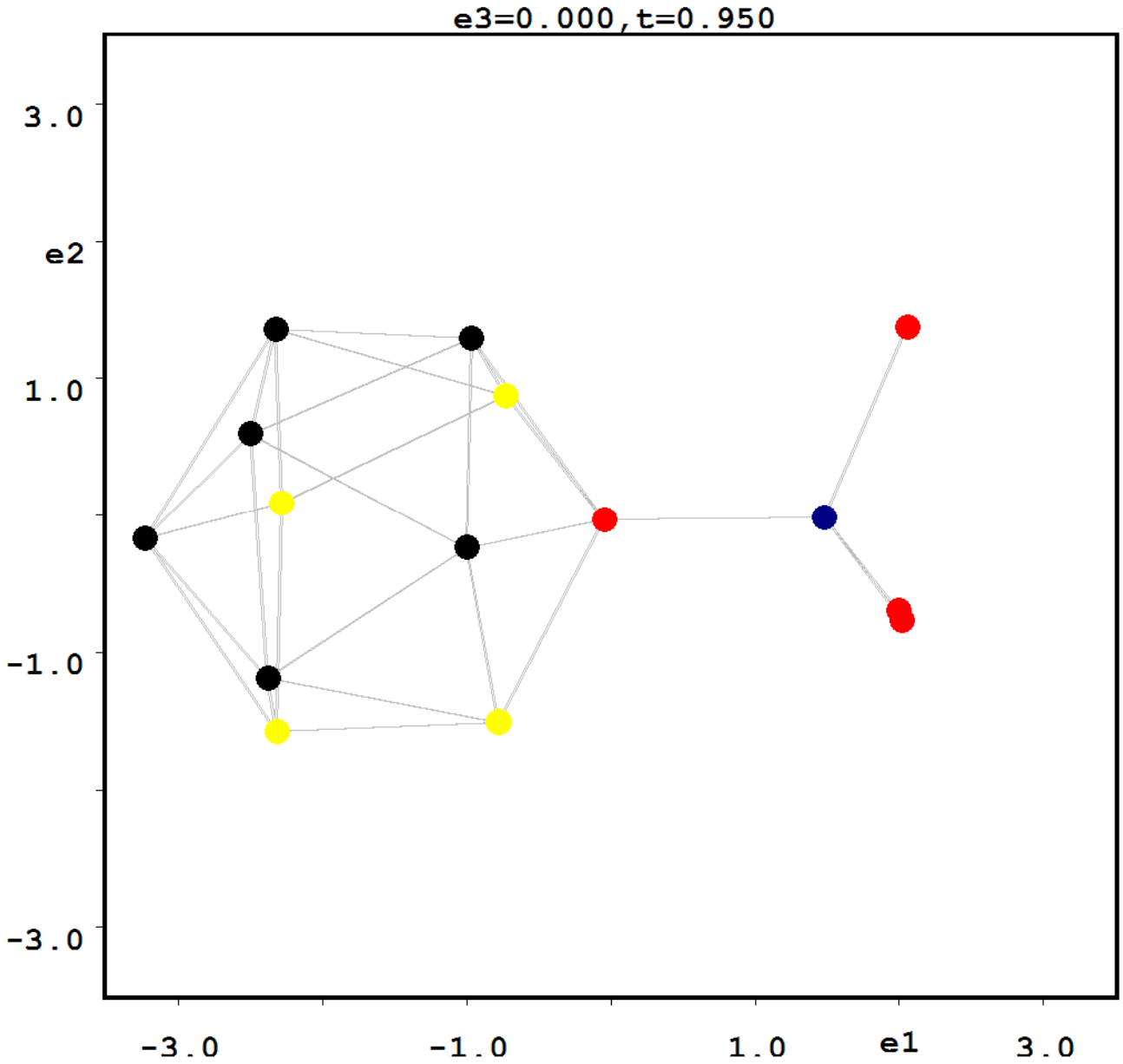
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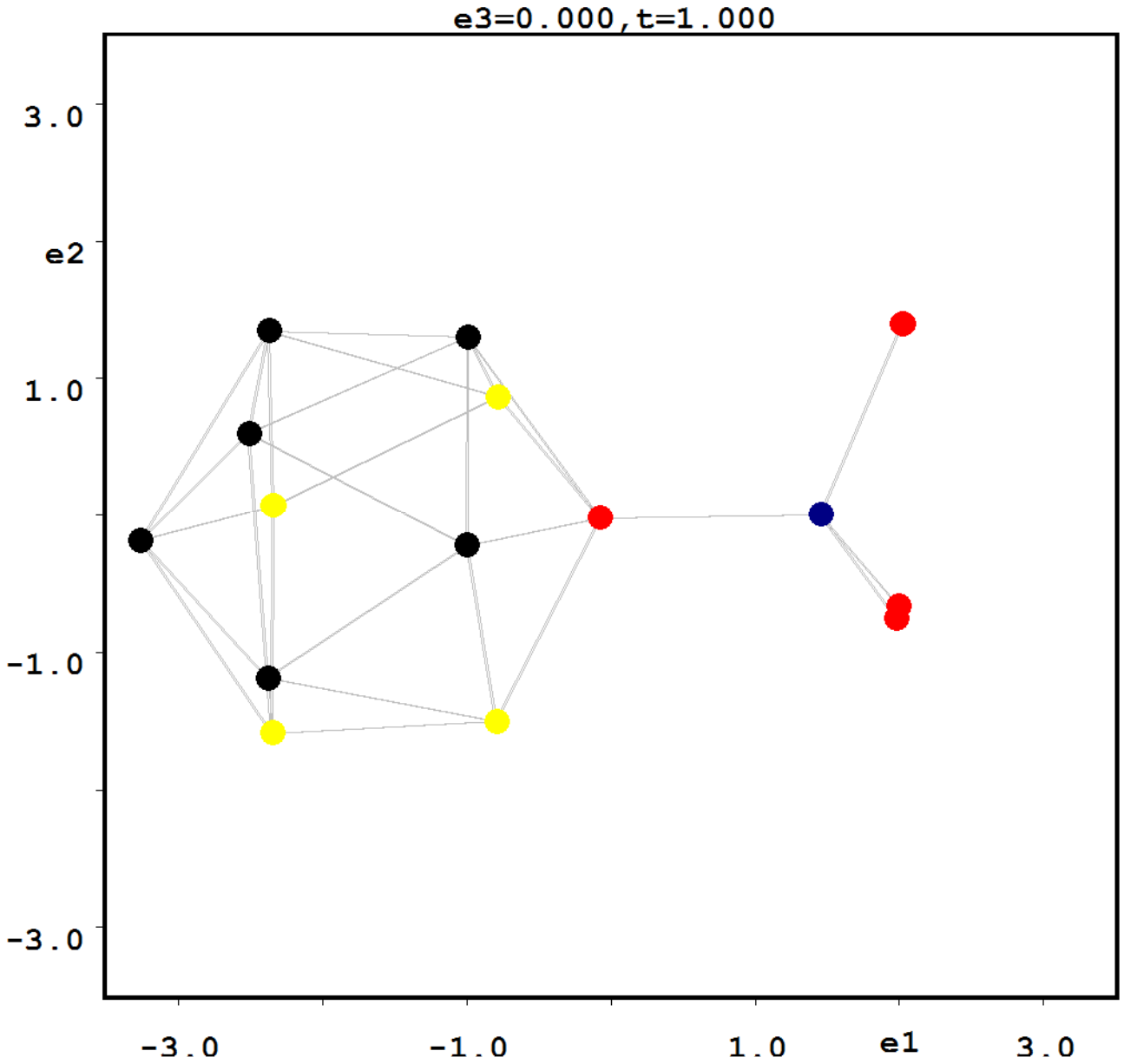
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e2
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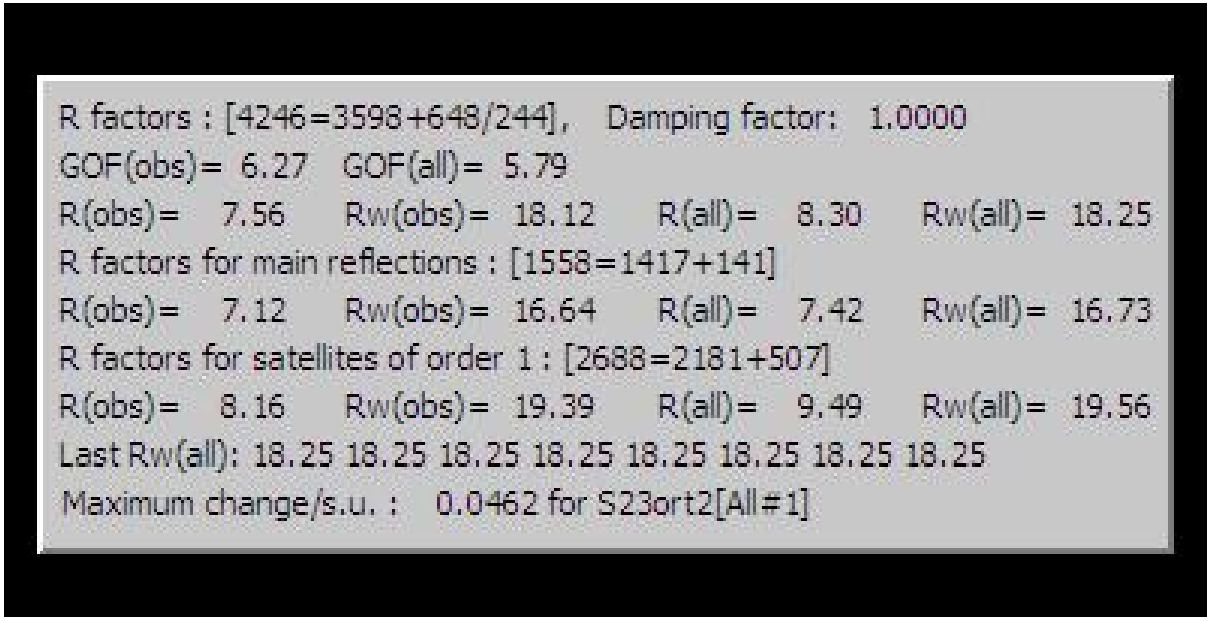
-1.0
1.0
e1
3.0

Example 8 – A Commensurately Modulated Carborane Compound

Modulated structure refinement - JANA2006

Superspace Group – Pnma (00γ) 0s0

Refinement model: whole molecules distributed over two symmetrically related positions described by the crenel-like modulation; one molecular harmonic used for additional positional and ADP modulations



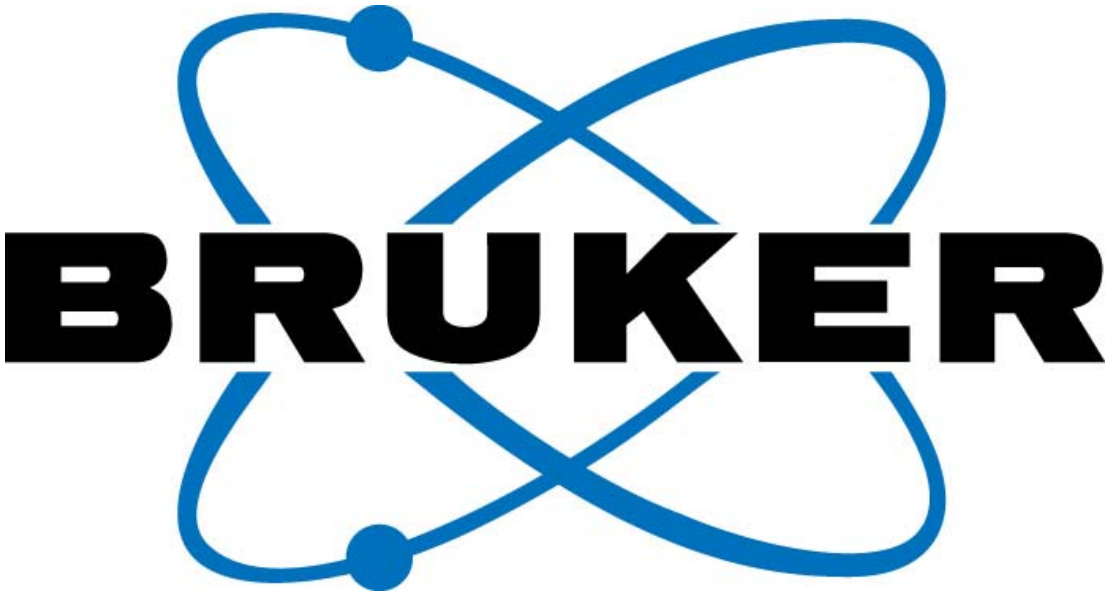
Example 8 – A Commensurately Modulated Carborane Compound

Summary – commensurate structure analysis

- Determine unit cell and q-vector(s)
- Integrate data (including satellite reflections) – write .ram files
- Perform absorption correction and scaling – write .hkl and .hk6 files
- Solve and refine basic structure – SHELXTL
- Determine superspace group; refine modulated structure – JANA2006
- Analysis and presentation of results

Application of Advanced Tools to Problem Structures

- **Non-Merohedral Twins**
  - Diagnosis – CELL_NOW, RLATT, ROTAX
  - Processing – SAINT (w/ multiple OM), TWINABS
  - Solution – XM or XS (HKLF 4 data)
  - Refinement – XL (BASF + HKLF 5)
- **Pseudo-Merohedral Twins**
  - Diagnosis – XPREP, ROTAX
  - Processing – SAINT, SADABS
  - Solution – XM or XS
  - Refinement – XL (BASF + TWIN)
- **Merohedral Twins**
  - Diagnosis – XPREP, ROTAX
  - Processing – SAINT, SADABS
  - Solution – XM or XS
  - Refinement – XL (BASF + TWIN)
- **Inversion (Racemic) Twins**
  - Diagnosis – XPREP, ROTAX
  - Processing – SAINT, SADABS
  - Solution – XM or XS
  - Refinement – XL (BASF + TWIN)
- **Modulated Structures**
  - Diagnosis – SMART, APEX2, RLATT
  - Processing – SAINT (w/ QVEC inst.), SADABS
  - Solution – XM or XS
  - Refinement – JANA 2000(Petricek & Dusek)



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