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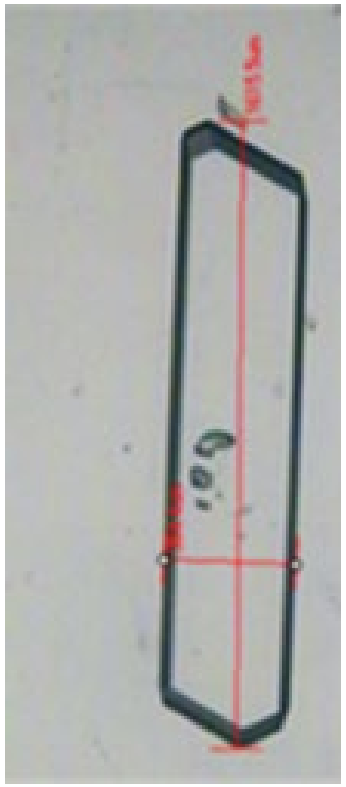
How to curate Morphology Data?

Simon Black
CFC, Cambridge
6th March 2024

What morphology data to curate?

- Needle
- Acicular
- Aspect Ratio ~ 5
- Needle oriented along x axis
- Needle bounded by {011} planes



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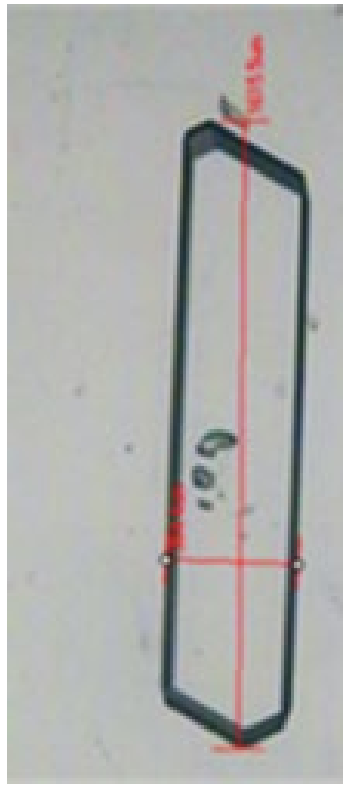
Curate morphology data that are linked to a unit cell

- Needle
- Acicular
- Aspect Ratio ~ 5
- Needle oriented along x axis of BPHEN012
- Needle bounded by {011} planes of BPHENO12



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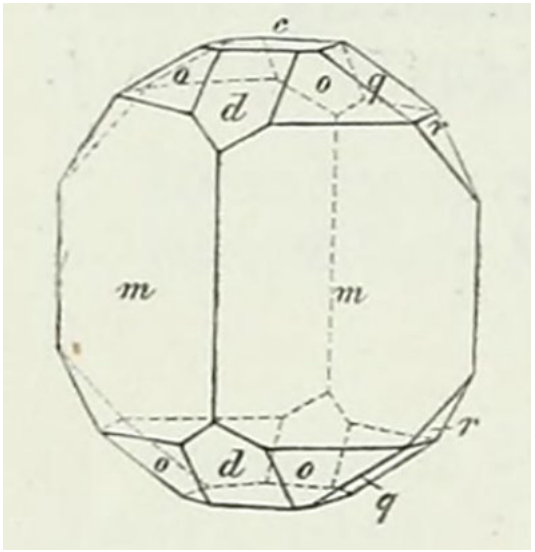
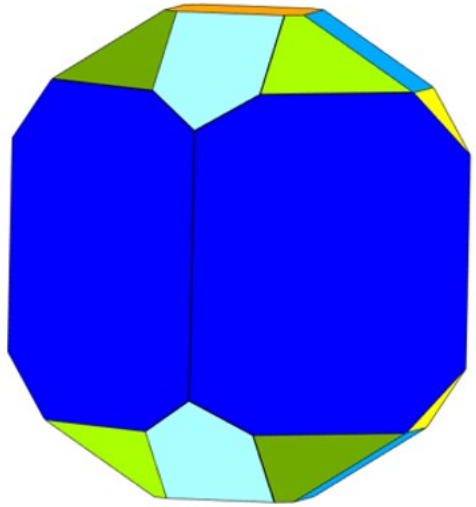
Curating morphology data – benzophenone example





Groth (1919)

Black & Seton (2024)

One of >2000 examples

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“Groth”

Table 1: The five volumes of P. Groth’s “Chemische Kristallographie”

Volume	I	II	III	IV	V
Year of publication	1906	1908	1910	1917	1919
Contents	Inorganics		Organics		
	Elements and simple Compounds	Salts containing oxygen	Aliphatics	one phenyl ring	> 1phenyl ring, heterocycles
Pages	914	930	804	801	1063
Figures	390	522	648	828	955
Figure numbers	1-389	390-911	912 - 1559	1560 - 2387	2388-3342

Morphologies for > 2000 organic compounds

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“Groth” - benzophenone

Summarises
5 references

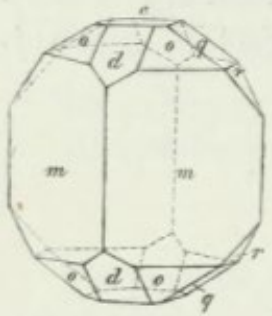
Benzophenon (Diphenylketon) $= (C_6H_5)_2CO$.

Schmelzpunkt 48°,0—48°,5.
Rhombisch bisphenoïdisch.

$a : b : c = 0{,}8511 : 1 : 0{,}6644$ Wickel[25]).

Von Linnemann[26]) aus wässerigem Alkohol erhaltene Krystalle waren nach Handl lange Prismen $m\{110\}$, an den Enden vorherrschend $d\{101\}$ und $q\{011\}$, ferner $r\{021\}$, $c\{001\}$ und $o\{111\}$ in meist unregelmäßiger Entwicklung; außer den Elementen $a : b : c = 0{,}8496 : 1 : 0{,}6535$ wird nur ein gemessener Winkel angegeben: $m : m = (110) : (1\bar{1}0) = 80° 42'$. Arzruni[27]) untersuchte ein Präparat von Merz[28]), aus Ligroïn krystallisiert, wasserhelle Prismen $m\{110\}$, deren Endflächen aus der Combination des Bisphenoïds $o\{111\}$ mit $r\{101\}$ bestanden. Wickel beobachtete an Krystallen, welche Jannasch aus Benzol erhalten hatte, die gleichen Formen, wie Handl, meist ohne $o\{111\}$, welches nur untergeordnet und unregelmäßig auftrat (Wickel übersah offenbar den bisphenoïdischen Charakter der Krystalle, welchen er durch Ätzfiguren leicht hätte feststellen können, und teilte die hier wiedergegebene idealisierte Fig. 2486 mit). Dagegen wurde die bisphenoïdische Symmetrie bestätigt durch Nacken[29]), welcher aus dem Schmelzflusse die Combination $m\{110\}$, $d\{101\}$, $\omega\{1\bar{1}1\}$ erhielt.

Fig. 2486.



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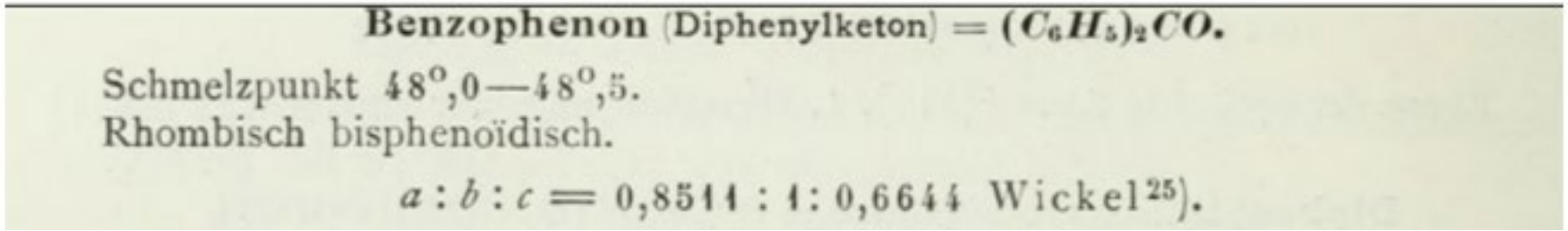
“Groth” – benzophenone symmetry



Benzophenon (Diphenylketon) = $(C_6H_5)_2CO$.

Schmelzpunkt 48°,0—48°,5.

Rhombisch bisphenoïdisch.

$a : b : c = 0{,}8514 : 1 : 0{,}6644$ Wickel[25]).

“rhombisch bisphenoïdisch”

= disphenoidal (International Tables Vol. A, Table 3.1.2.4, p. 728)

= Point Group “222”

“Groth” – benzophenone unit cell

Benzophenon (Diphenylketon) = $(C_6H_5)_2CO$.

Schmelzpunkt 48°,0—48°,5.
Rhombisch bisphenoïdisch.

$a : b : c = 0{,}8514 : 1 : 0{,}6644$ Wickel[25]).

One unit cell

b always = 1

ratios of unit cell lengths determined from angles between faces

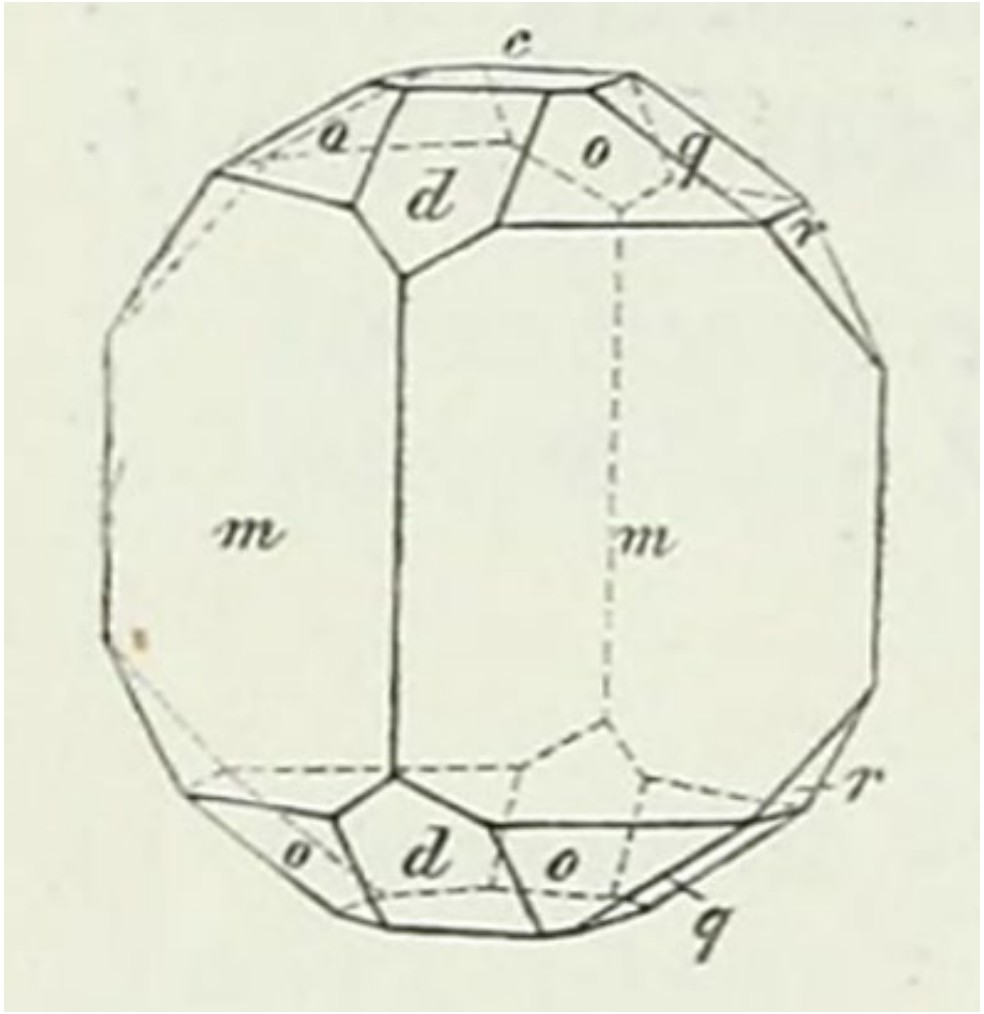
$b > a > c$

“Groth” – benzophenone morphology

- Standard orientation
  just off x -axis

- Faces - {forms} - identified by letters

- For example, *m* is always {110}



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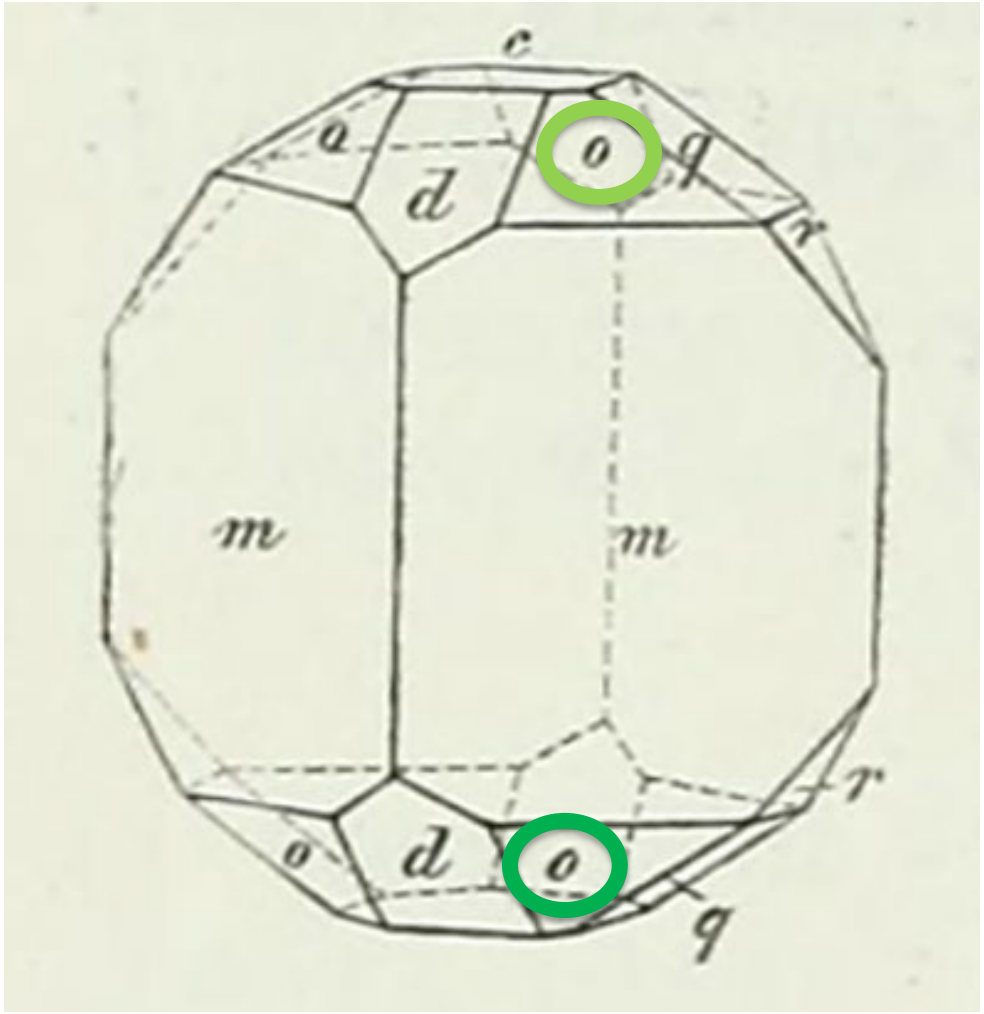
“Groth” – benzophenone morphology

- Notes in the text
- In this case, *o* = {111} is different from *w* = {-111}
- “Verifiable from etch pits”



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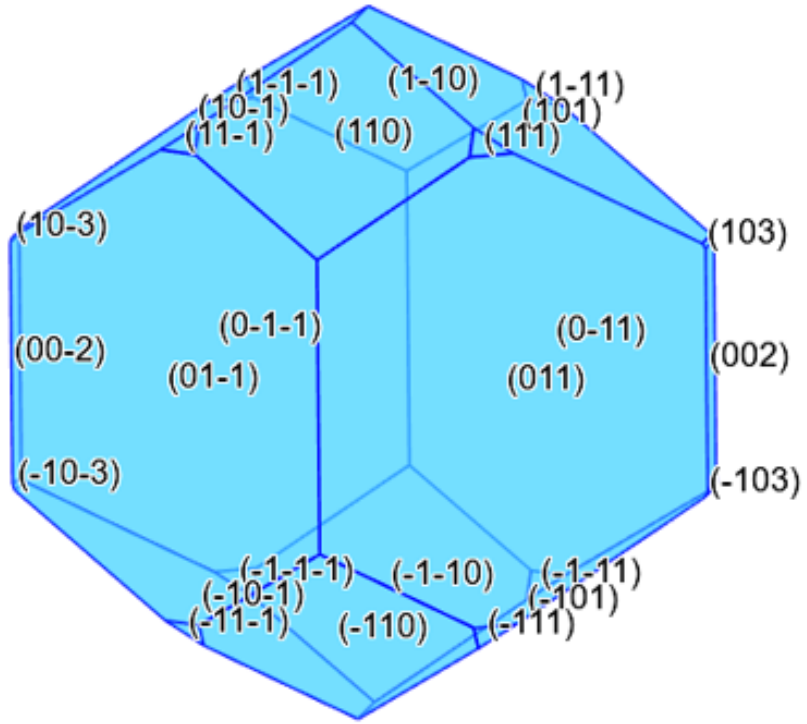
Benzophenone in CSD – 13 options

- BPHENO02, -03, -11 are the other polymorph
- BPHENO01, -10 have *b* > *a* > *c,* no hydrogens
- BPHENO12, 13-20 have *c* > *b* > *a*
- BPHENO12 as ‘best representative’

BPHENO01	P212121
BPHENO02	C2/c
BPHENO03	C2/c
BPHENO10	P212121
BPHENO11	C2/c
BPHENO12	P212121
BPHENO13	P212121
BPHENO14	P212121
BPHENO15	P212121
BPHENO17	P212121
BPHENO18	P212121
BPHENO19	P212121
BPHENO20	P212121

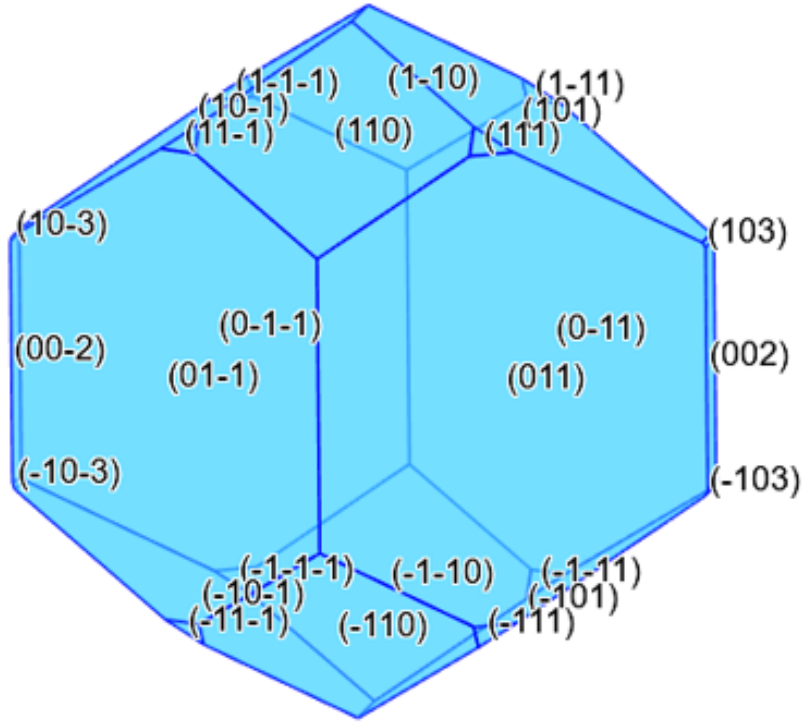
Benzophenone – predicted morphology

- BPHENO12
- “Visual Habit”
- Default view in Mercury



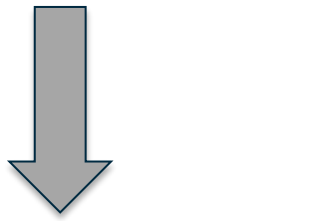
Which pairs of faces are related by symmetry?

1. (011) and (110)
2. (011) and (01-1)
3. (011) and (0-1-1)
4. (111) and (1-1-1)
5. (111) and (-1-1-1)

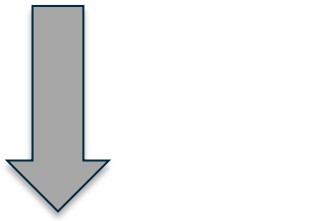


Which pairs of faces are related by symmetry?

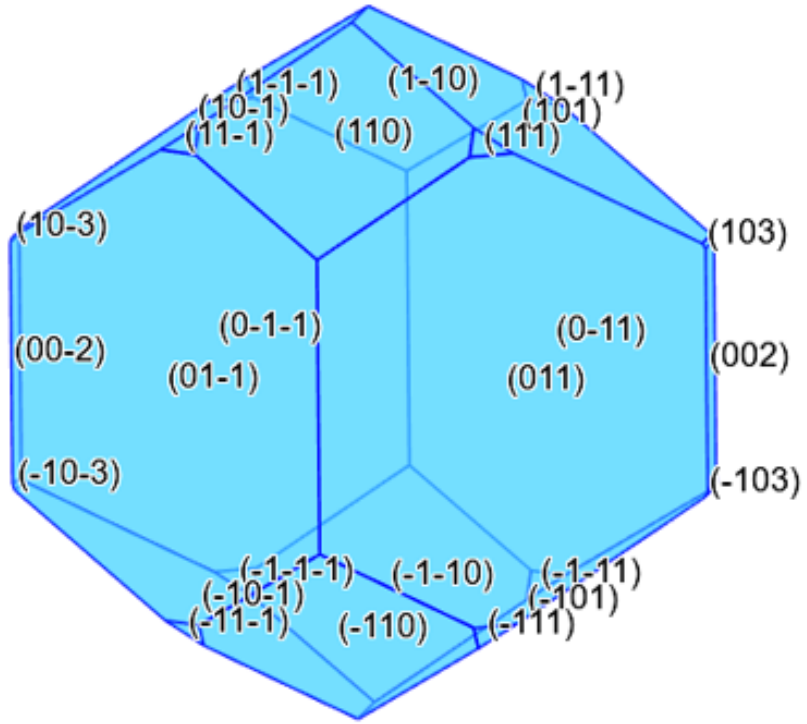
BPHENO12



Space Group $P2_12_12_1$



Point Group 222



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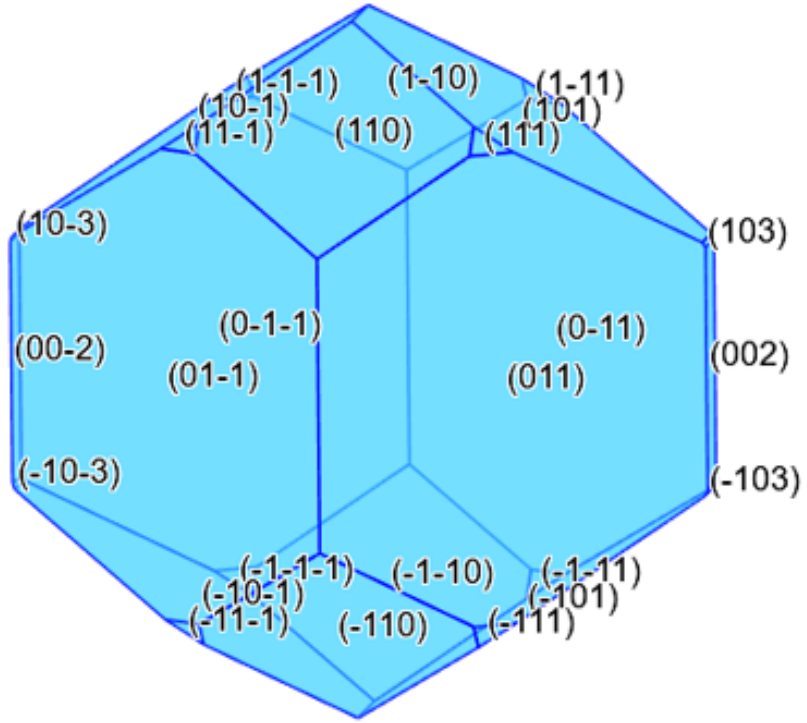
Which pairs of faces are related by symmetry?

1. (011) and (110)
2. (011) and (01-1) {011}
3. (011) and (0-1-1) {011}
4. (111) and (1-1-1) {111}
5. (111) and (-1-1-1)



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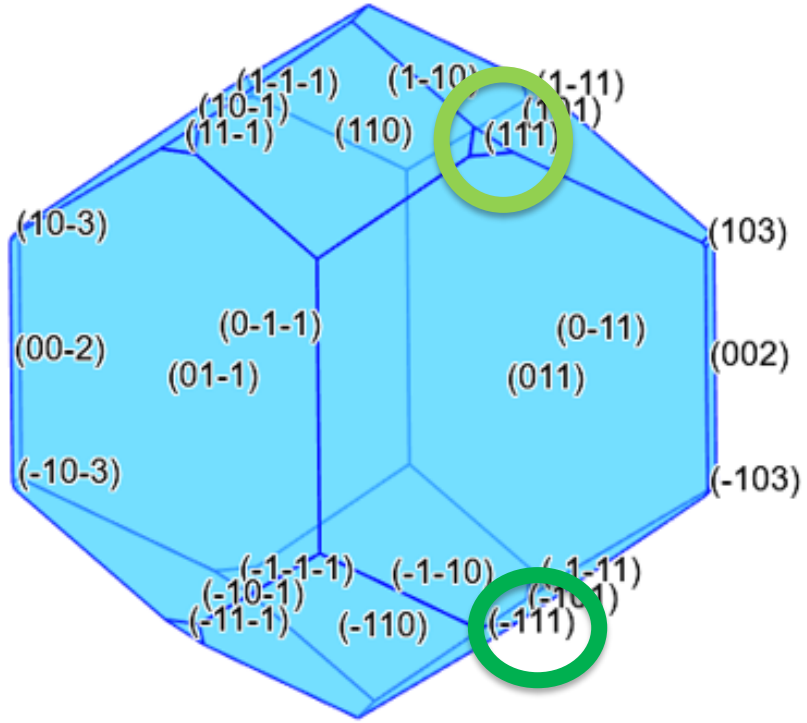
Which pairs of faces are related by symmetry?

1. (011) and (110)
2. (011) and (01-1)
3. (011) and (0-1-1)
4. (111) and (1-1-1)
5. (111) and (-1-1-1)



benzophenone – matching unit cells

Benzophenon (Diphenylketon) = $(C_6H_5)_2CO$.

Schmelzpunkt 48°,0—48°,5.
Rhombisch bisphenoïdisch.

$a : b : c = 0{,}8511 : 1 : 0{,}6644$ Wickel[25]).

Identifier	BPHENO12
Literature Reference	J.Moncol, P.Coppens, *CSD Communication* (2004)
Formula	C_{13} H_{10} O
Compound Name	Benzophenone
Space Group	P 2_1 2_1 2_1 (19)
Cell Lengths	**a** 7.7378(2) **b** 10.2421(3) **c** 12.0395(3)
Cell Angles	**α** 90 **β** 90 **γ** 90

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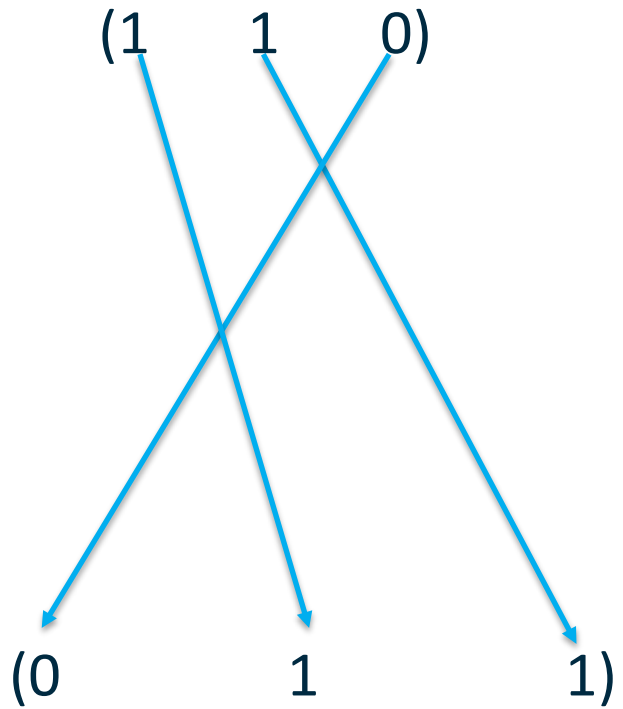
benzophenone – matching unit cells

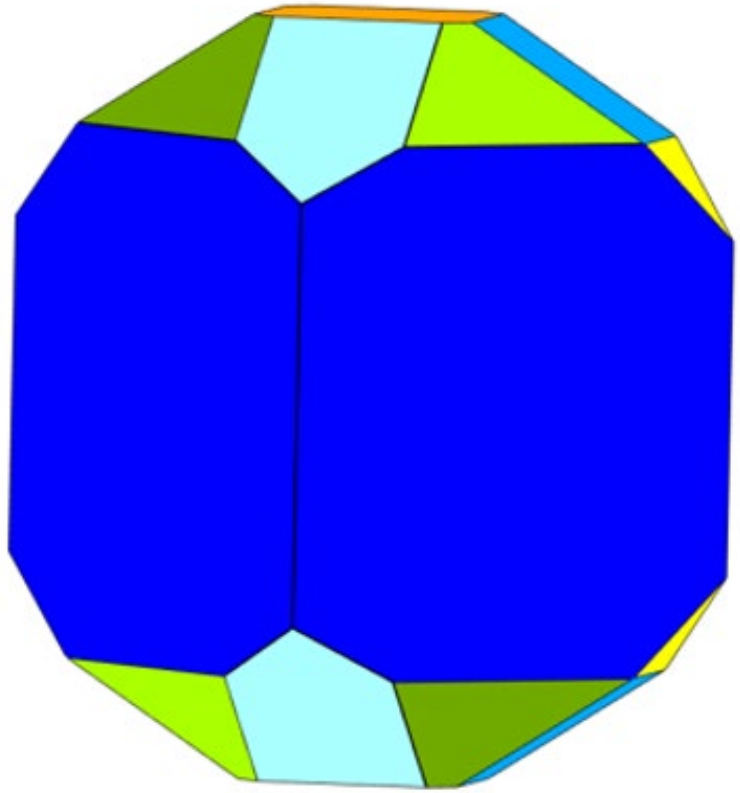
Groth Fig. 2486



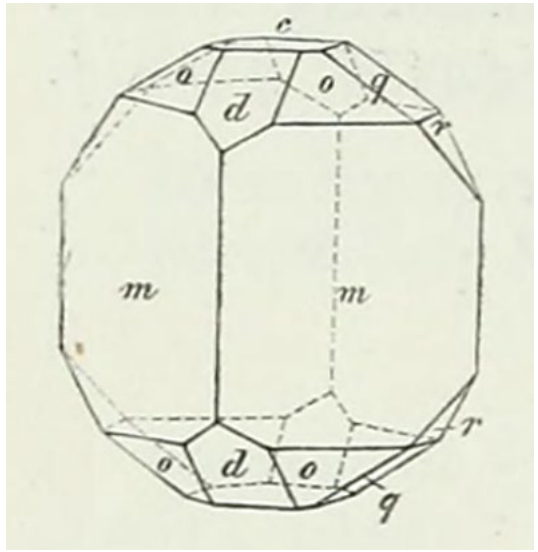
BPHENO12

benzophenone – Groth morphology in Mercury

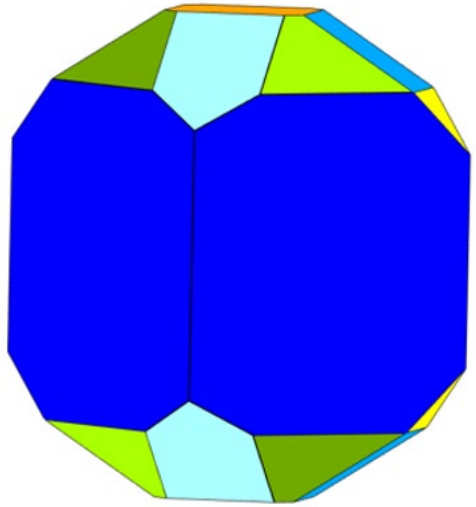
- Approximation to standard orientation
- Forms identified by colours
- Easy to recognise which faces are symmetry related
- {111} different from {-111}



Groth's experimental morphology displayed in Mercury

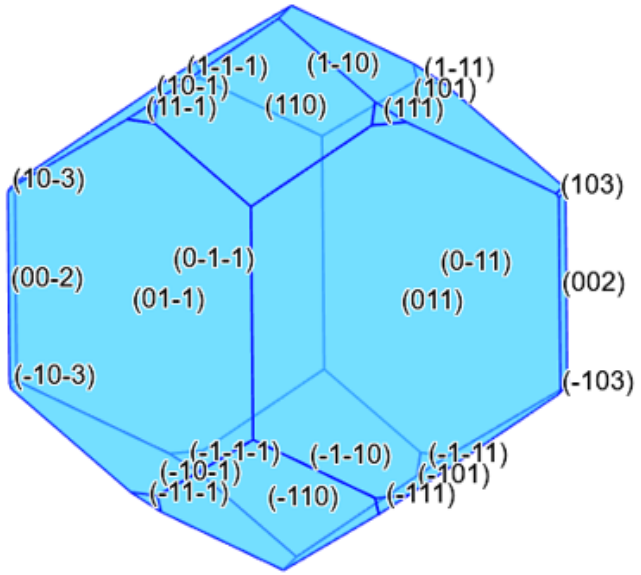


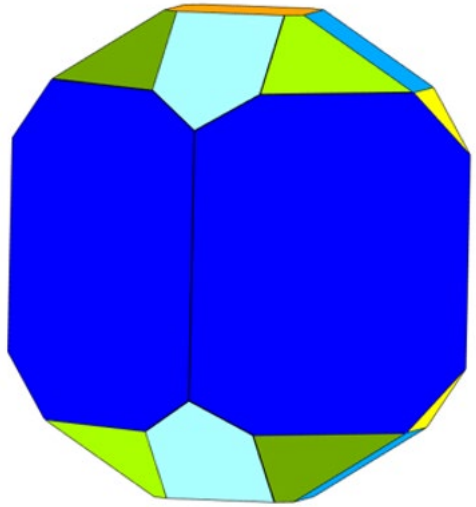
Groth (1919)



Black & Seton (2024)

Groth's experimental morphology compared with prediction





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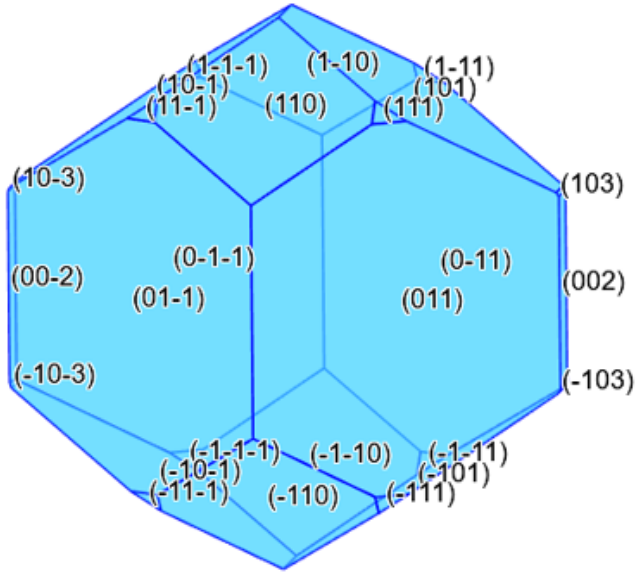
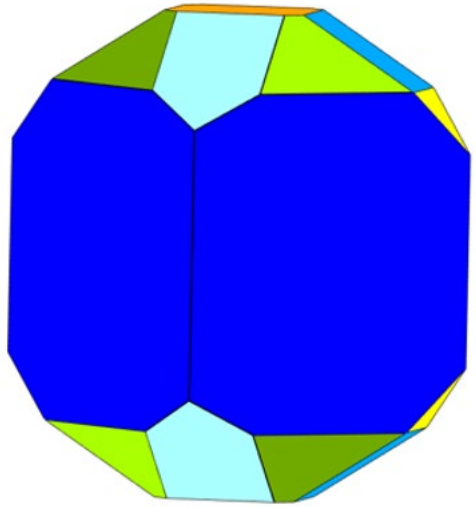
How to store these morphologies?





The “morphology .cif“

- CSD Reference
- Space Group
- Unit Cell
- Centre…face distances

```
data_BPHENO12
_symmetry_cell_setting              orthorhombic
_symmetry_space_group_name_H-M      'P 21 21 21'
_symmetry_Int_Tables_number         19
_space_group_name_Hall              'P 2ac 2ab'
loop_
_symmetry_equiv_pos_site_id
_symmetry_equiv_pos_as_xyz
1  x,y,z
2  1/2-x,-y,1/2+z
3  -x,1/2+y,1/2-z
4  1/2+x,1/2-y,-z
_cell_length_a                      7.7378(2)
_cell_length_b                      10.2421(3)
_cell_length_c                      12.0395(3)
_cell_angle_alpha                   90
_cell_angle_beta                    90
_cell_angle_gamma                   90
_cell_volume                        954.146
loop_
_exptl_crystal_face_index_h
_exptl_crystal_face_index_k
_exptl_crystal_face_index_l
_exptl_crystal_face_perp_dist
0 1 1 10
1 1 1 15
1 1 0 15
1 1 -1 15
2 0 0 16
1 0 1 16
1 0 2 16.5
```

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The “morphology .cif“ - what’s not there

Point group
- deduce from Space Group

Multiplicity of each form
- Deduce from point group

Display Changes
- Orientation
- Changes to face labels
- Changes to face colours

```
data_BPHENO12
_symmetry_cell_setting              orthorhombic
_symmetry_space_group_name_H-M      'P 21 21 21'
_symmetry_Int_Tables_number         19
_space_group_name_Hall              'P 2ac 2ab'
loop_
_symmetry_equiv_pos_site_id
_symmetry_equiv_pos_as_xyz
1 x,y,z
2 1/2-x,-y,1/2+z
3 -x,1/2+y,1/2-z
4 1/2+x,1/2-y,-z
_cell_length_a                      7.7378(2)
_cell_length_b                      10.2421(3)
_cell_length_c                      12.0395(3)
_cell_angle_alpha                   90
_cell_angle_beta                    90
_cell_angle_gamma                   90
_cell_volume                        954.146
loop_
_exptl_crystal_face_index_h
_exptl_crystal_face_index_k
_exptl_crystal_face_index_l
_exptl_crystal_face_perp_dist
0 1 1 10
1 1 1 15
1 1 0 15
1 1 -1 15
2 0 0 16
1 0 1 16
1 0 2 16.5
```

The “morphology .cif“

A standardised way of recording morphology data

The standardised way of recording morphology data?

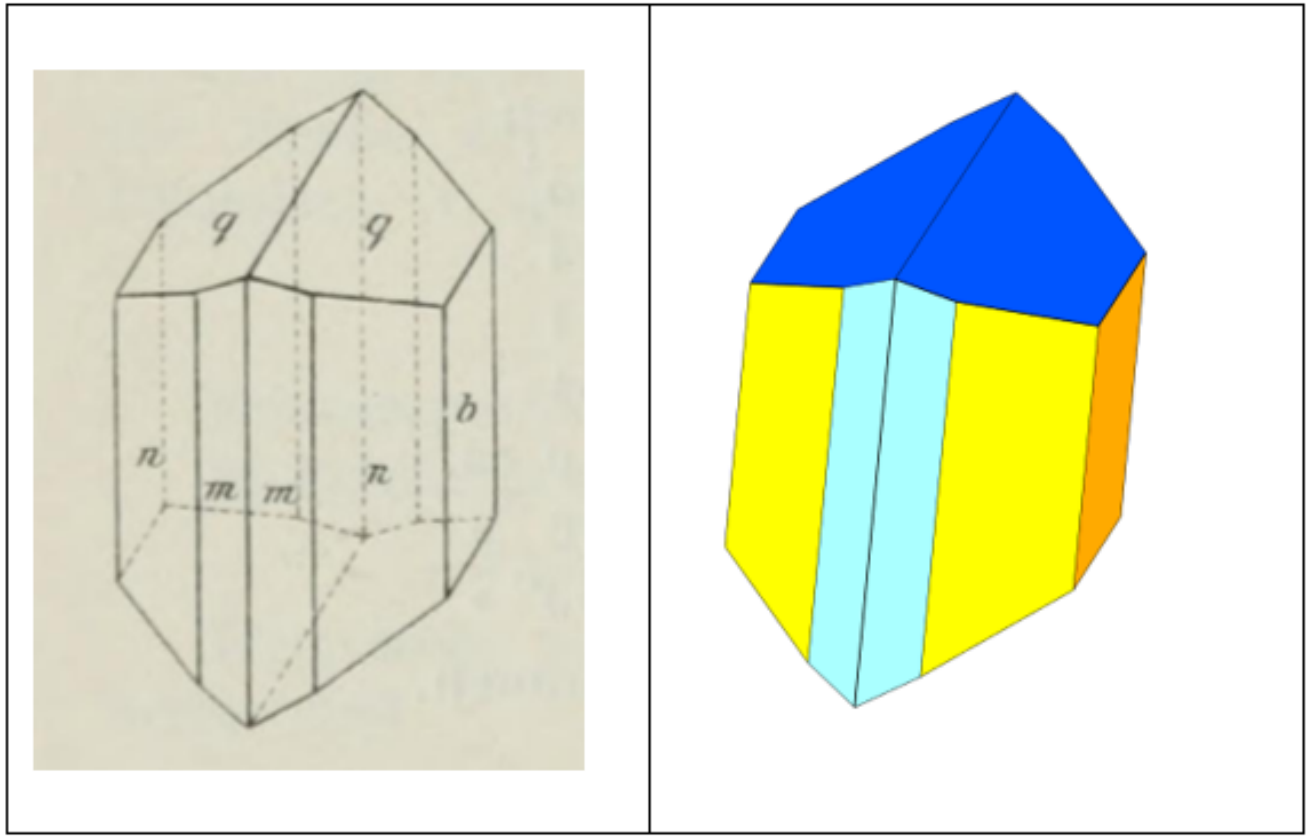
```
data_BPHENO12
_symmetry_cell_setting              orthorhombic
_symmetry_space_group_name_H-M      'P 21 21 21'
_symmetry_Int_Tables_number         19
_space_group_name_Hall              'P 2ac 2ab'
loop_
_symmetry_equiv_pos_site_id
_symmetry_equiv_pos_as_xyz
1 x,y,z
2 1/2-x,-y,1/2+z
3 -x,1/2+y,1/2-z
4 1/2+x,1/2-y,-z
_cell_length_a                      7.7378(2)
_cell_length_b                      10.2421(3)
_cell_length_c                      12.0395(3)
_cell_angle_alpha                   90
_cell_angle_beta                    90
_cell_angle_gamma                   90
_cell_volume                        954.146
loop_
_exptl_crystal_face_index_h
_exptl_crystal_face_index_k
_exptl_crystal_face_index_l
_exptl_crystal_face_perp_dist
0 1 1 10
1 1 1 15
1 1 0 15
1 1 -1 15
2 0 0 16
1 0 1 16
1 0 2 16.5
```

Another example - glycine

Only 143 CSD entries for glycine

GLYCIN02 matched the unit cell in Groth

>2000 other examples of organic crystal morphologies in Groth



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Roger Davey
Sally Price
Brian McMahon
Andy Maloney
Ghazala Sadiq
Paul Black

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Link the other ~2000 morphologies in “Groth” to the CSD?

A standardised way of recording Morphology Data?

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Thank you

Comments?

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