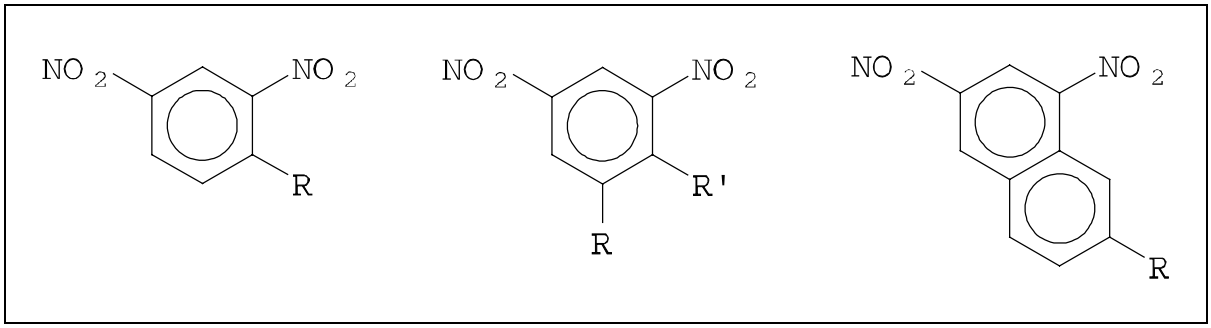
Date: 14 Dec. 1994

DIRDIF.ORBASE GALLERY

A visualization of a database of molecular fragments (file DIRDIF.ORBASE) which can be input to the program ORIENT for the solution of crystal structures using vector search methods.



Why using vector search or molecular replacement for small molecules?

- Because it makes sense to use available chemical information.
- If you have a good fragment, vector search is stronger than direct methods only.
- Because it is fun seeing your fragment growing.
- Because by using vector search you get familiar with it and you can use it when you need it: in some problem cases it is the only way to solve your structure.

And why not?

- It is easier than you might think it is.
- You do not need to be a crystallographer.
- The only thing to do before an automatic structure solution is selecting a proper fragment.

Your interactions with DIRDIF.ORBASE are:

Retrieving ready-to-use fragments: rigid fragments, or fragments with one or more preferred orientations (e.g. nitrobenzene, steroids) are available in this file.

(Let your fingers do the walking!)

Storing your own fragments: when you work on a series of related compounds you can store your coordinates in a file DIRDIF.ORUSER (this is a 'personal' file, analogous to the system-file DIRDIF.ORBASE).

Modifying a fragment to suit your specific needs (e.g. replace C by N, add a methylcarbon, fuse an aromatic ring).

How to use vector search?

When the vector search program ORIENT is called, a molecular fragment is used as input. The program determines its correct orientation, and the DIRDIF system passes automatically control to the program TRACOR to put the fragment on its correct position relative to the symmetry elements. Then control is passed on to the program PHASEX for phase refinement and phase expansion (using direct methods applied to difference structure factors). Finally the program FOUR organizes an automatic recycling procedure for completion of the structure.

Running the program ORIENT: the program reads the parameters of the fragment or model, from a file named ATMOD.

When you want to solve the structure with *ORIENT in the automatic mode* (instruction: DIRDIF CCODE ORIENT), the ATMOD file has to be present in advance.

When you run *ORIENT interactively* (instruction: DIRDIF CCODE) you either select a fragment in advance or during execution of the program. An existing ATMOD file can be modified, or a new ATMOD file can be selected from DIRDIF.ORUSER and/or DIRDIF.ORBASE.

How to use DIRDIF.ORBASE?

Retrieving and modifying fragments: The instruction DIRDIF CCODE ORBASE allows you to retrieve and/or modify a fragment in advance, see page 3 for edit instructions. The resulting fragment is stored in a file ATMOD.

Storing your own fragments: For your own structural research you can build up your own database in a file named DIRDIF.ORUSER which is analogous to the data file DIRDIF.ORBASE. The file DIRDIF.ORUSER is one of the distributed files and its header contains instructions for the addition of your fragments. It contains some examples as well. The atomic parameters of your own fragment may be obtained by previously solved structures, the Cambridge Database, molecular modelling, and so on.

Notes

- Do not hesitate to use a model with slightly deviating geometry: vector search methods do not depend critically on precise geometry.
- N-compounds: for many nitrogen compounds the geometry of the corresponding C-compound is sufficiently accurate.
- O-compounds: for many oxygen compounds the geometry of the corresponding C-compound is sufficiently accurate, unless the aromaticity is broken.
- S-compounds: for many sulphur compounds an out-of-ring replacement is sufficiently accurate, but some compounds with S in a ring are listed additionally.
  Warning! Most light-atom structures with S are favourably considered as heavy-atom structures and you had better solve it with PATTY (instruction: DIRDIF CCODE PATTY).
- Building up a large fragment in many steps is likely to introduce too large deviations in the geometry. Try instead to get the fragment from related structures or molecular modelling.

COFRED EDITOR

This editor is a simple COmmon FRagment EDitor, which is called when executing:
DIRDIF CCODE ORBASE, or
DIRDIF CCODE (for an interactive run of ORIENT).

In the editor the following instructions are possible:

H	Help
D C4	Delete atom C4.
R C4 S5	Rename or replace atom C4 by S5; Adjust bond length if end-of-chain.
R C4 N4 1.2	Replace atom C4 by N4 at distance 1.20 from parent atom if end-of-chain.
A C4 C	Add one or more C-atoms to C4. (The number of atoms added and their positions depend on the hybridization of the parent atom C4. The new atoms will be numbered automatically.)
A C4 C -T	Add one or more C-atoms to C4, forcing a specified hybridization. (The number of atoms added and their positions will be determined automatically.) Possible keys are: -T tetrahedral (sp3) -P planar (sp2) -L linear (sp)
A C4 =O	Add =O to atom C4 in planar hybridization.
A C4 -CN	Add -CN to atom C4.
A C4 -NO2	Add $-NO_2$ to atom C4 (Beware of geometry!).
F C2 C3 5	Fuse a 5-membered aromatic ring to bond C2-C3 of an aromatic ring or planar system.
F C2 C3 6	Fuse a 6-membered aromatic ring to bond C2-C3 of an aromatic ring or planar system.
G C4	Supply geometrical information about atom C4.
S	Save (store present atoms in back-up array).
U	Undo (retrieve atoms stored at last save instruction).
X 35	Rotate model around horizontal axis by 35 degrees.
Y 35	Rotate model around vertical axis by 35 degrees.
Z 35	Rotate model in the plane of the screen.
Q	Quit: finish session. Any present H-atom will be removed. (The user will have the opportunity to accept or reject the model obtained sofar.)

After finishing the session the parameters of the fragment are stored in a file ATMOD. When this file is used by the program ORIENT, these parameters are saved in a file called ATOLD.

CLASSIFICATION

The fragments are classified according to chemical classes as given in Molecular Structures and Dimensions Vol.A1, Ed. by Olga Kennard c.s., Crystallographic Data Centre Cambridge (1972). As the 'rigidity' of the fragment is of greater importance than the chemical functionality, we occasionally deviate from these classes.
Note that several classes have no entries, as fragments are not available, or are easily generated.

1	Aliphatic Carboxylic Acid Derivatives
2	Aliphatic Carboxylic Acid Salts
3	Aliphatic Amines
4	Aliphatic N and S Compounds
5	Aliphatic Miscellaneous
6	Enolates (Aliphatic and Aromatic)
7	Nitriles (Al. & Ar.)
8	Urea Compounds (Al. & Ar.)
9	Nitrogen-Nitrogen Comp. (Al. &Ar.)
10	Nitrogen-Oxigen Comp. (Al. & Ar.)
11	Sulphur and Selenium Compounds
12	Carbonium Ions, Carbanions, Radicals
13	Benzoic Acid Derivatives
14	Benzoic Acid Salts
15	Benzene Nitro Compounds
16	Anilines
17	Phenols and Ethers
18	Benzoquinones
19	Benzene Miscellaneous
20	Monocyclic Hydrocarbons (3,4,5-Rings)
21	Monocyclic Hydrocarbons (6-Rings)
22	Monocyclic Hydrocarbons (7, 8-Rings)
23	Monocyclic Hydrocarbons (>8-Rings)
24	Naphtalene Compounds
25	Naphtoquinones
26	Anthracene Compounds
27	Hydrocarbons (2 Fused Rings)
28	Hydrocarbons (3 Fused Rings)
29	Hydrocarbons (4 Fused Rings)
30	Hydrocarbons (>4 Fused Rings)
31	Bridged Ring Hydrocarbons
32	Hetero-Nitrogen (3,4,5-Rings Monocyclic)
33	Hetero-Nitrogen (6-Rings Monocyclic)
34	Hetero-Nitrogen (>6-Rings Monocyclic)
35	Hetero-Nitrogen (2 Fused Rings)
36	Hetero-Nitrogen(>2 Fused Rings)
37	Hetero-Nitrogen (Bridged Ring Systems)
38	Hetero-Oxygen
39	Hetero-Sulphur and Hetero-Selenium
40	Hetero-(Nitrogen and Oxygen)
41	Hetero-(Nitrogen and Sulphur)
42	Hetero-Mixed Miscellaneous
43	Barbiturates
44	Pyrimidines and Purines
45	Carbohydrates
46	Phosphates
47	Nucleosides and Nucleotides
48	Amino-Acids and Peptides
49	Porphyrins and Corrins
50	Antibiotics
51	Steroids
52-57	Terpetines
58	Alkaloids
59	Miscellaneous Natural Products
60	Molecular Complexes
61	Clathrates
62-66	B, Si, P, As, Sb, Bi Compounds
67-68	Group IA, IIA, III Compounds
69-70	Ge, Sn, Pb, Te Compounds
71	Transition-metal compounds
72-75	Metal pi-Complexes
76-86	Metal Complexes
87-99	Miscellaneous

Acknowledgements. Fragments were obtained from published structure determinations, or from a connectivity search in the Cambridge Structural Database. Fragments were also prepared with MODELKS 2.96 (Steliou, Univ. of Montreal, Canada, Jan. 1991) and Chem-X (Chemical Design Ltd., Oxford, UK, July 1991) as made available through the CAOS/CAMM Center, Univ. of Nijmegen.

Revised edition (Apr. 1994): R.M.Beurskens, Univ. of Nijmegen. Update: June 1994.

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DIRDIF.ORBASE GALLERY

'd.a.: 5' denotes a dihedral angle of 5 degrees

0.001 MONOS Test model (7-atom fragment of model 41.41)

1. For anhydrides, see class 38.

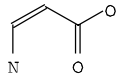
1.11 D-Tartaric acid $COOH(CHOH)_2COOH$

1.12 Ethylacetate $CH_3COOC_2H_5$

1.13 Valeric acid $CH_3(CH_2)_3COOH$

1.14 Valeric acid amide $CH_3(CH_2)_3CONH_2$

1.21 Aminobutenoate



3.11 Butylamine $CH_3(CH_2)_3NH_2$

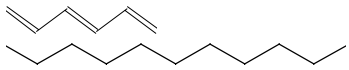
5.11 Butanole $CH_3(CH_2)_3OH$

5.12 Butadiene (trans conformer)

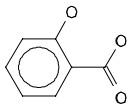
5.13 Butadiene (cis conformer)

5.21 Hexatriene

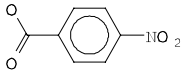
5.31 Undecane



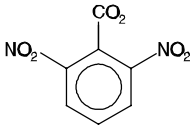
13.11 Hydroxybenzoic acid



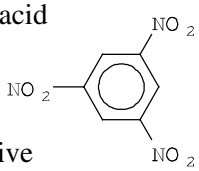
13.12 Nitrobenzoic acid



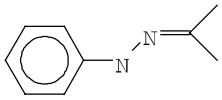
13.21 Dinitrobenzoic acid



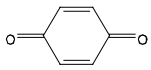
15.11 TNB



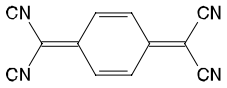
16.21 Azine derivative



18.11 Benzoquinone

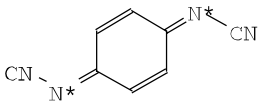


18.21 Tetracyano-p-quinodimethane (TCNQ)

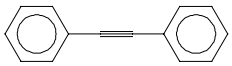


19.11 Benzene

19.21 Dicyanamidebenzene dianion



19.31 Tolane



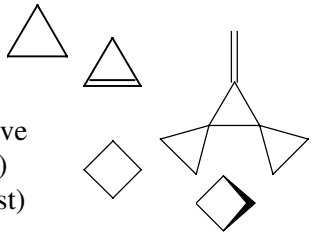
20.11 Cyclopropane

20.12 Cyclopropene

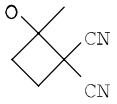
20.13 Cyclopropene-dispiro derivative

20.21 Cyclobutane (flat)

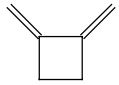
20.22 Cyclobutane (twist)



20.23 LOXY



20.24 Dimethylene-cyclobutane



20.31 Cyclobutene

20.41 Cyclopentane (twist-envelope)

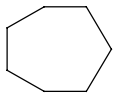
20.51 Cyclopentene

20.61 Cyclopentadiene

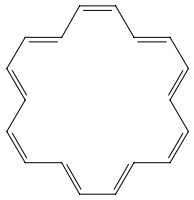
21.11 Cyclohexane (chair)

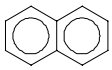
21.12 Cyclohexane (twist-boat)

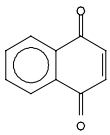
21.21 Cyclohexene

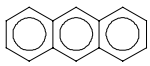
22.111 Cycloheptane, chair
22.112 Same, twist-chair
22.113 Same, bed
22.114 Same, twist-bed 

22.21 Cycloheptatriene
22.22 Same, other conf.

23.11 (18)-Annulene 

24.11 Naphthalene 

25.11 Naphthoquinone 

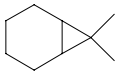
26.11 Anthracene 

27.11 Bicyclo[2.1.0]pentane

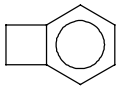
27.21 Bicyclo[2.2.0]hexane

27.22 Bicyclo[3.1.0]hexane

27.31 Bicyclo[3.2.0]heptane

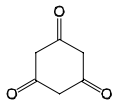
27.32 DiMe Bicyclo[4.1.0]heptane 

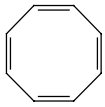
27.41 Bicyclo[3.3.0]octane

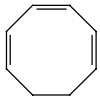
27.45 Benzocyclobutane 

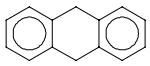
21.31 1,4-Cyclohexadiene (flat)

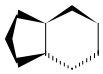
21.32 1,3-Cyclohexadiene

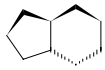
21.41 Phloroglucinol 

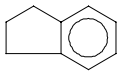
22.31 Cyclooctatetraene 

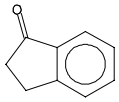
22.32 1,3,5-Cyclooctatriene 
22.33 Same, other conf.

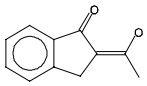
26.211 Dihydroanthracene, d.a.: 4 
26.212 Same, d.a.: 42
26.213 Same, d.a.: 65

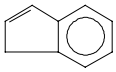
27.51 cis-Hydrindane 

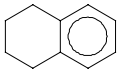
27.52 trans-Hydrindane 

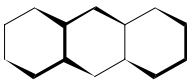
27.53 Indane = Benzocyclopentane 

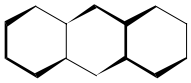
27.55 Indan-1-on 

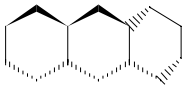
27.56 Acylindanone 

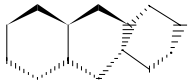
27.57 Indene 

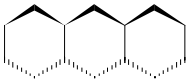
27.61 Tetralin 

28.21 cis-anti-cis-Perhydroanthracene 

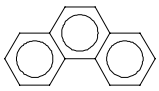
28.22 cis-syn-cis-Perhydroanthracene 

28.23 cis-trans-Perhydroanthracene 

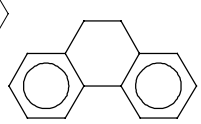
28.24 trans-anti-trans-Perhydroanthracene 

28.25 trans-syn-trans-Perhydroanthracene 

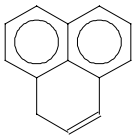
28.31 Phenanthrene



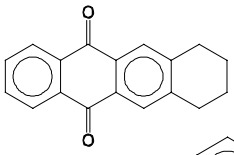
28.32 Dihydrophenanthrene



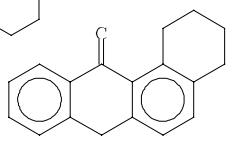
28.41 Phenalene (aromatic)



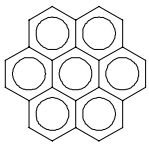
29.31 Tetrahydrobenzo anthrachinone



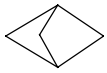
29.41 Tetrahydrobenzo anthrone
(d.a.: 32)



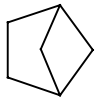
30.31 Coronene



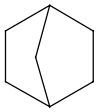
31.01 Bicyclo[1.1.1]pentane



31.11 Bicyclo[2.1.1]hexane

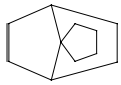


31.21 Bicyclo[2.2.1]heptane = Norbornane

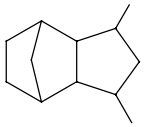


31.22 Norbornene

31.23 Norbornene-spiro derivative

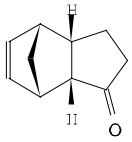


31.251 Fused Norbornane-pentane



31.252 Same
31.253 Same
31.254 Same

31.26 BULAC
31.27 CARBET
31.28 DIENON
31.29 DOLS1



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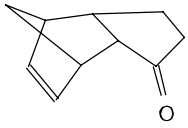
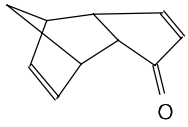
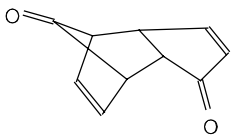
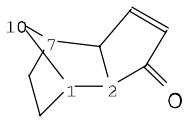
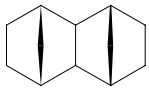




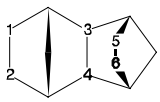




31.31 Fused Norbornanes

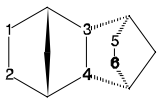


31.32 Fused Norbornanes



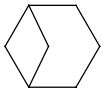
31.331 Same, C5=C6
31.332 Same, C3=C4
31.333 Same, C1=C2, C5=C6

31.341 Fused Norbornanes

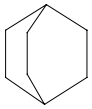


31.342 Same, C3=C4

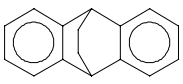
31.41 Bicyclo[3.1.1]heptane



31.51 Bicyclo[2.2.2]octane

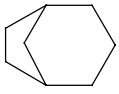


31.521 Dibenzobicyclooctane, bridge: single bond (1.55)

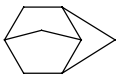


31.522 Same, aromatic bond (1.39)
31.523 Same, double bond (1.30)

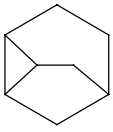
31.55 Bicyclo[3.2.1]octane



31.56 Tricyclooctane

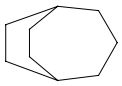
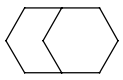


31.57 DELE8

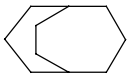
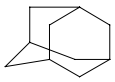
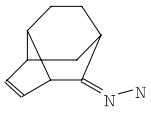
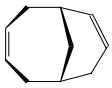


31.58 Cubane

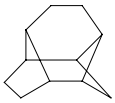
31.61 Bicyclo[3.2.2]nonane
31.64 Bicyclo[3.3.1]nonane

31.71 Bicyclo[3.3.2]decane
31.74 Adamantane
31.75 NN=decane
31.79 Bicyclodecane

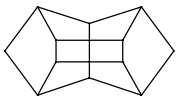
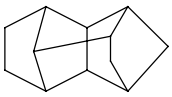
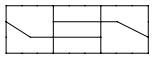





31.81 Tetracycloundecane



31.83 Dodecahedrane (pentagonal dodecahedron)

31.84 Pentacyclododecane
31.86 Hexacyclododecane
31.88 Diamantane C14

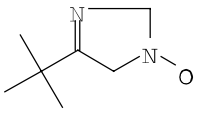
31.91 Buckminster-fullerene (C60 ball)

32.21 Pyrrolidine

32.31 Pyrrole

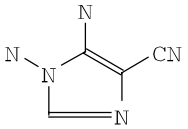
32.41 Imidazolidine

32.43 N-oxyimidazol der.

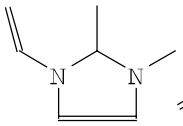


32.51 Imidazole

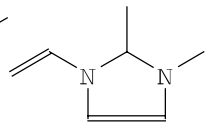
32.52 Imidazolyl derivative



32.53 Imidazolium-ion

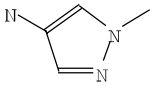


32.54 Same



32.61 Pyrazole

32.62 Pyrazole derivative

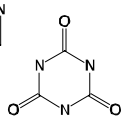


32.81 1,2,4-Triazole

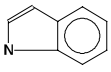
33. For pyridines, see benzene derivatives

33.31 Dihydropyridine

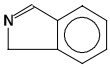
33.51 1,3,5-Triazine (flat)
33.52 Trioxotriazine



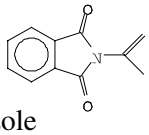
35.11 Indole



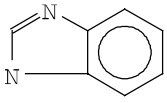
35.21 2H-Isoindole



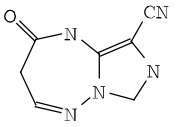
35.22 STRIAN



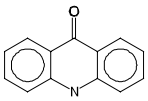
35.31 Benzimidazole



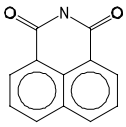
35.51 Imidazotriazepine



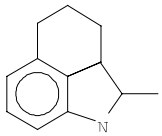
36.21 Oxohydroacridine



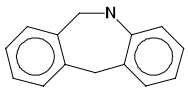
36.31 Naphthalimide



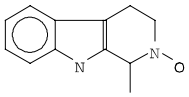
36.32 Ergolin-fragment



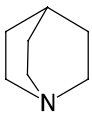
36.411 Dibenzoazacycloheptadiene, fold-line: N-C
36.412 Same, fold-line: C-C



36.51 BEWIJS



37.21 Azabicyclooctane

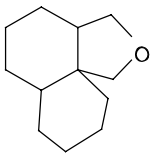


38.11 Oxirane

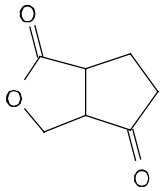
38.21 Oxetane

38.31 Tetrahydrofuran

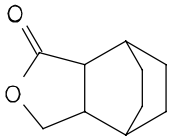
38.32 VADER



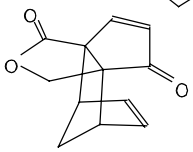
38.33 FENBUT



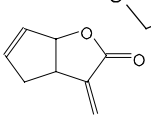
38.34 GAMDEL



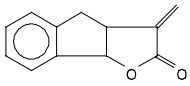
38.35 FENLAK



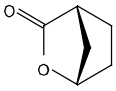
38.36 MANG1



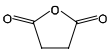
38.37 MANG4



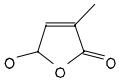
38.38 Camphanic-lacton



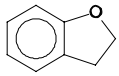
38.41 Succinic anhydride



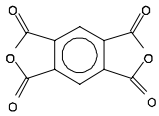
38.42 STRIA



38.43 Dihydrobenzofuran

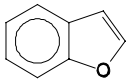


38.44 PMDA

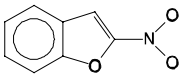


38.51 Furan

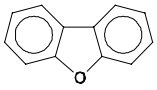
38.52 Benzofuran



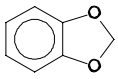
38.53 Nitrobenzofuran



38.54 Dibenzofuran

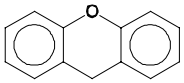


38.61 Benzodioxole

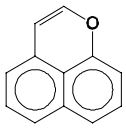


38.62 1,3-Dioxole

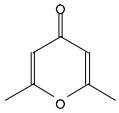
38.72 Xanthene



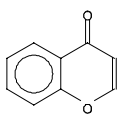
38.73 Oxaphenalene



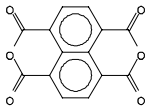
38.74 Dimethylpyrone (flat)



38.75 Benzopyrone

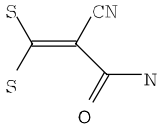


38.76 NTDA



38.81 1,4-Dioxane (chair)

38.82 Pyran

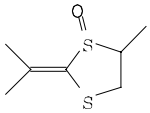
39.01 NOVOA 

39.11 Thiirane

39.21 Thietane

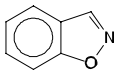
39.31 Thiabicycloheptane

39.32 Thiophen

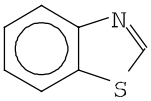
39.34 SULFOX 

39.35 1,3-Dithiole

40.11 Isoxazole

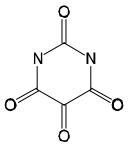
40.22 Benzisoxazole 

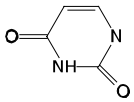
41.11 Thiazole

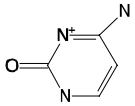
41.12 Benzothiazole 

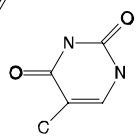
41.22 Thiazocyclohexane
bed, one C-C: aromatic (1.39)

41.23 Same
chair, C-C: single bonds (1.51)

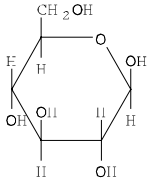
43.21 Alloxan 

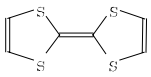
44.11 Uracil 

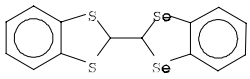
44.12 Cytosine
protonated 

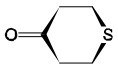
44.13 Thymine 

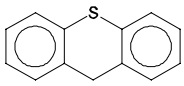
45.11 beta-D-Ribose and 45.111
45.12 alpha-D-Ribose and 45.121
45.21 beta-Fructopyranose

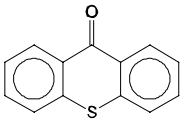
45.51 beta-D-Glucopyranose ---->
45.52 alpha-D-Glucopyranose 

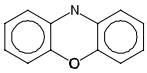
39.36 TTF-Cation 

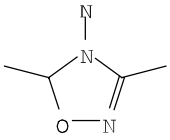
39.37 SSe-fulvalene 

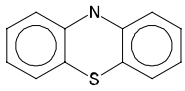
39.41 Thiacyclohexanon, bed
39.42 Same, chair 

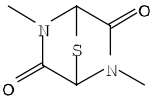
39.511 Thioxanthene, d.a.: 4
39.512 Same, d.a.: 40 

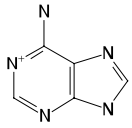
39.52 Thioxanthone 

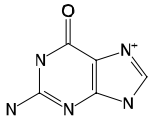
40.311 Phenoxazine, d.a: 5
40.312 Same, d.a.: 33 

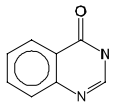
40.41 Oxazo 

41.311 Phenothiazine, d.a.: 5
41.312 Same, d.a.: 29
41.313 Same, d.a.: 42 

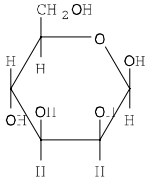
41.41 MONOSX 

44.21 Adenine
protonated 

44.22 Guanine
protonated 

44.31 Benzopyrimidone 

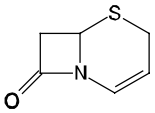
45.61 beta-D-Mannopyranose---->

45.71 beta-D-Arabinopyranose 

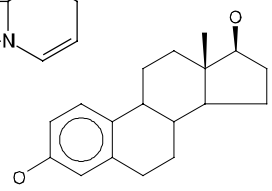
48.11 Glycine (pi = 5.97) NH_2CH_2COOH

48.21 gamma-Aminobutyric acid zwitterion $NH_3^+(CH_2)_3COO^-$

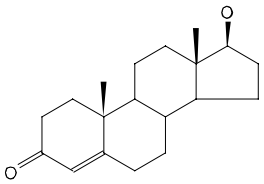
50.11 Cephalosporin-C



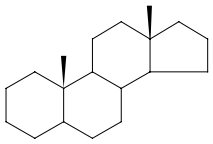
51.11 Estradiol



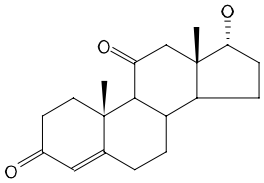
51.12 Testosterone -- -- -- -- -- -- -- -->



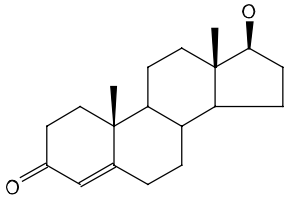
51.13 5a-Steroid



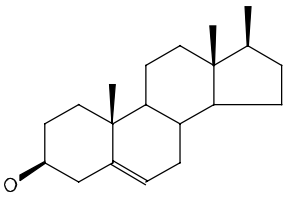
51.14 Cortisone -- -- -- -- -- -- -- -->



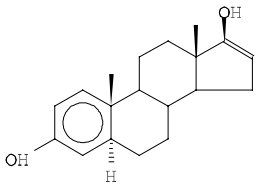
51.15 Progesterone skeleton



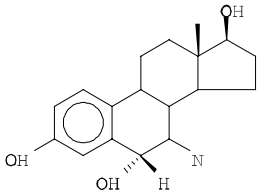
51.16 Cholesterol skeleton -- -- -- -- -- -- -- -->



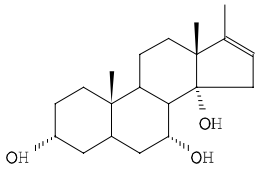
51.17 Ster1



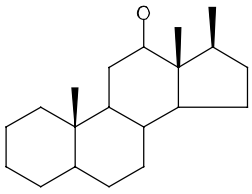
51.18 Ster2 -- -- -- -- -- -- -- -- -- -- -->



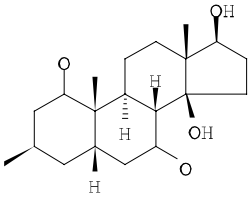
51.19 Ster3



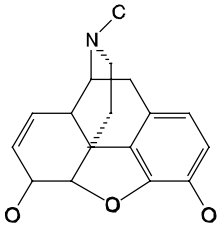
51.20 Ster4 -- -- -- -- -- -- -- -- -- -- -->



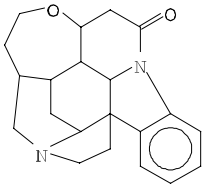
51.21 Ster5



58.11 Morphine skeleton -- -- -- -- -- -- -- -- -- -- -- -- -->

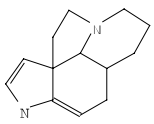


58.21 Strychnine -- -- -- -- -- -- -- -- -->

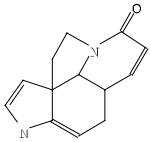


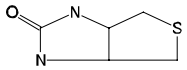
58.22 Same: cation

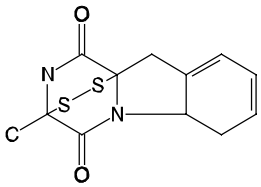
58.51 Vincadifform.

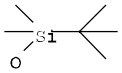


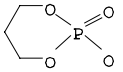
58.52 Oxotabersonine

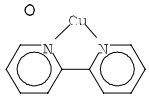


59.11 (+)Biotin skeleton 

59.21 Gliotoxin skeleton 

63.11 Silano derivative (staggered) 

64.31 CLAM2 

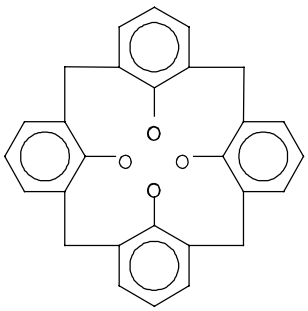
67.51 Cu-bipyridine 

90. Calixarenes

90.01 HUMMEL

six more different geometries:

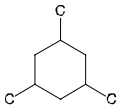
90.02, 90.03, 90.04, 90.05, 90.06, 90.07



DIRDIF.ORUSER GALLERY

Molecular fragments in DIRDIF.ORUSER analogous to those in DIRDIF.ORBASE (see header lines of the file DIRDIF.ORUSER for instructions and suggestions for use). The distributed file may contain additional fragments.

0.1 IODINE I_2

0.2 PHENA 

0.3 PO4 PO_4

0.4 GOLD $AuPC_3$

0.5 PF6 PF_6

8 BASKET A basket-shaped fragment used in supramolecular chemistry.