



STN[®]: Advanced Structure Searching



Today's presenters are...



Matthew
McBride



Lora
Burgess

Why does structure searching seem so difficult some days?

“Chemistry is all about getting lucky.”

Dr. Robert F. Curl, Jr.

“To think is to practice brain chemistry.”

Deepak Chopra

Structure searching requires a knowledge of chemistry, databases, a little luck, and a good deal of brain chemistry.



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e-Seminar assumptions

For the purposes of today's session, it is assumed you already feel comfortable with:

- Basics of Structure Drawing
- G-groups
- Variable Points of Attachment (VPA)
- Repeating Groups
- Element Counts
- Generic Definitions

Consider reviewing the following STN® Workshops:

- Structure Searching in CAS REGISTRYSM
- Markush Searching in the Patent Literature



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Goals for this e-Seminar

In this e-Seminar, you will learn how to:

- Build successful G-groups, including the use of fragments
- Use Hydrogen and Non-Hydrogen Attachments
- Apply Match Level and Element Counts to MARPAT® queries



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Agenda

- G-groups limits in structure searching
- Connectivity in queries – Hydrogen and Non-Hydrogen Attachments
- Advanced MARPAT search issues
- Review example searches
- Additional resources



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G-groups in structure searching

- Use G-groups to search for structures that have more than one allowable value at a node
- G-groups may include atoms, shortcuts, variables, fragments, and other G-groups
- Use structure fragments to apply generic definitions, element counts, and match level
- Draw the fragment and point of attachment prior to defining the G-group
- Bridging (linking) fragments cannot be embedded in other G-groups

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STN G-group system limits

- Structure drawing has a limit of 200 nodes
- The limit is lower when a query includes attributes, reaction information, or fragments
- G-groups may contain between 2 and 20 items, and you may use up to 20 G-groups
- No more than two points of attachment are permitted on a fragment
- Points of attachment count towards the total G-group item count – bridging fragments count as two items!

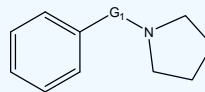
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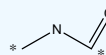
8

Search Question:

Identify substances fitting the following query. G1 is a bridging group, in either orientation.



G1 =



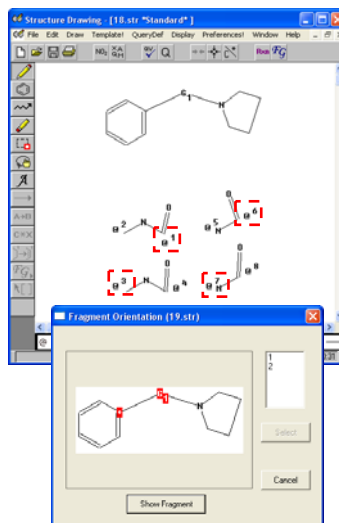
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Bridging G-groups require fragment orientation during SAVE

- Draw fragments twice for alternate bridging options
- When two points of attachment exist in a fragment, the Fragment Orientation dialog box is displayed
- Specify the placement of the fragment relative to the other atoms in the structure query
- Use the Show Fragment/Show Structure button if fragment number's obscured



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Use caution with hydrogens in G-groups

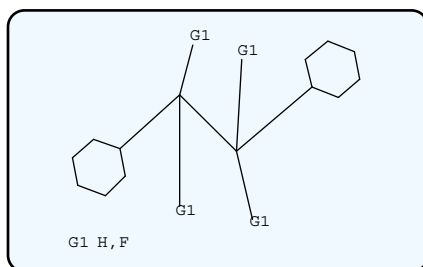
- If the G-group is attached to a node that allows for multiple substituents, false drops can be retrieved – good answers will not be lost
- Once the hydrogen from the G-group definition is satisfied, the system allows for any node or group to fill the open valence state
- Solution is to consider fragments, where appropriate

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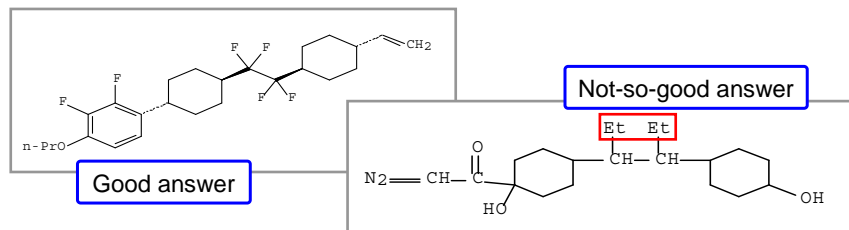
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Incorporating hydrogens in G-groups



Why this happens:

- If the G-group contains H, then that requirement is satisfied by the opposing hydrogen, essentially generating a new query

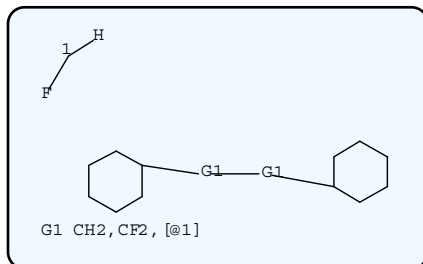


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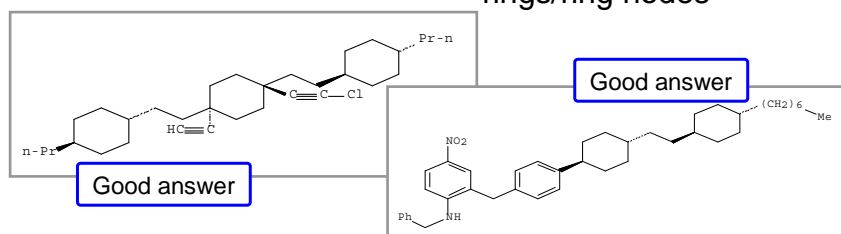
12

The better approach is to build G-groups which “back up” one atom node



Solution:

- Incorporate hydrogens in shortcuts or fragments to obtain precision search
- Same technique applies to G-groups attached to rings/ring nodes



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Connectivity - Hydrogen and Non-Hydrogen Attachments

- Hydrogen and Non-Hydrogen Attachments (Connectivity) allow you to modify the substitution pattern at a specific atom
- In substructure searches, no values are assigned for either option by default
- In closed substructure searches, hydrogen counts are automatically applied to close substitution
- Both options are available via the Query menu or by right-clicking on selected nodes

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Connectivity - Hydrogen Attachments

- Allow you to specify the number of hydrogen connections to a query node
- If no hydrogen counts are specified, any number of hydrogens is retrieved
- Hydrogen counts may be assigned to any node, *except* a G-group, generic, or shortcut symbols
- To apply hydrogen counts to one of the alternatives in a G-group, build that alternative as a fragment

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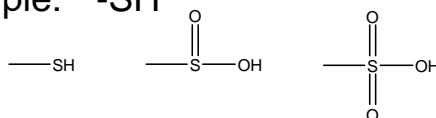
15

STN structure shortcuts have implied hydrogen counts

- All shortcuts contain exact hydrogen counts, except for the point of attachment
- For example: $-\text{CH}_2-\text{CH}_3$ (Et)



- Not all shortcuts behave equally
- For example: $-\text{SH}$



- Hydrogens in tautomer groupings may move to other nodes in the group

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Non-Hydrogen Attachments is also known as Connectivity

- Allow you to specify the number of non-hydrogen connections to a query node and the bond type (ring/chain) of the connections
- When counting the number of connections to a node, include those already drawn in the structure query
- May be assigned to any node in the query except for a G-group node or a shortcut symbol
- Connectivity is the only means of opening a position to substitution if the query is to be used in a Closed Substructure Search (CSS)

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Closed Substructure Searching (CSS) versus Substructure Searching (SSS)

- Substructure Search (SSS) is the broadest type of search
 - Allows for substitution at any open valent positions
- CSS is a special type of SSS
 - Isolates all rings
 - Automatically puts hydrogens at open nodes, UNLESS the position is OPENED for substitution
- Use CSS when:
 - Query has variable nodes such as G-groups or generic variables
 - Only want substitution in a FEW places

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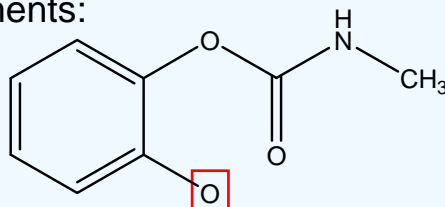
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Using Closed Substructure and Non-Hydrogen Attachments

Search Question:

Locate substances that meet the following requirements:



Substitution is desired only at the terminal oxygen marked with a red box.

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Apply Non-Hydrogen Attachments via right-click or the QueryDef menu

Non Hydrogen Attachments (Connectivity)

Specific Any

Exact Chain

Minimum Ring

Maximum Ring/Chain

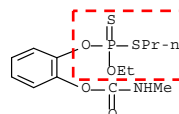
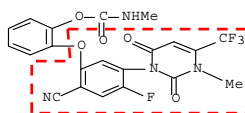
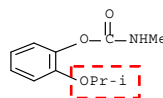
Mixture

Count (0 to 16):

Cancel OK

Connectivity cares about the number of non-hydrogen connections and the bond types – not the connected node characteristics (Ring/Chain).

Possible answers:



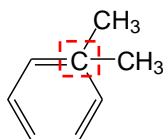
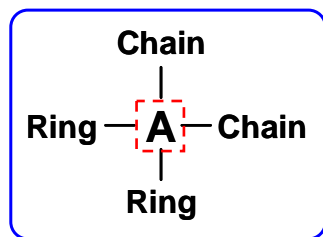
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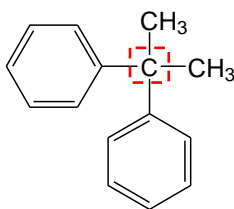
20

Connectivity is just like shaking hands with strangers

- Connectivity counts the number of non-hydrogen connections to a query node and the bond type of the connections (ring/chain) – not the node that it is connected to



4 ring/chain (2 chain / 2 ring) connections



4 chain connections

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Advanced MARPAT search issues

Most MARPAT structure search issues revolve around three areas:

- Applying Generic Definitions and Element Counts
- Applying Match Level
- Element Count (EC) – Limited versus Unlimited

Review the revised MARPAT User Guide or the STN e-Seminar “Revealing the Mysteries of MARPAT” for more details and examples.

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Generic Definitions allow refinement of generic group queries

- Add information about the generic nodes (i.e., Ak, Cb, Cy, Hy) in your queries to increase precision while preserving recall

saturated/unsaturated	monocyclic/polycyclic
branched/linear (Ak)	# of carbon atoms (<7 / >=7)
# of hetero atoms (1 / >1)	

- Same generic definitions that are available in REGISTRY

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Element Counts may be specified for generic groups and implied for real atoms

- By default, no Element Count is specified for a generic group
- Element Count for generic groups is not implied – must be added by searcher
- The number and kind of elements in a generic group may be specified using Element Count
- Real atom rings and chains have implied Element Counts at Match Level CLASS
 - Pyridine at Match Level CLASS retrieves answers with “heterocycle (containing 1 N)” or “heterocycle (containing 0 or more N)”

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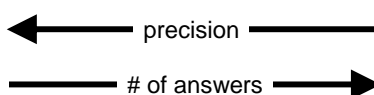
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Match Level determines the degree to which query nodes match with nodes in the candidate answers

- Markush structures include both real atoms and generic nodes – Match Level controls retrieval
- Changing the degree of matching will increase or decrease the number of answers retrieved

There are three Match Levels:

ATOM < CLASS < ANY



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Real atom chain nodes may match at the real atom level or generic class

Query Node	Candidate Node	Match Level	
		ATOM	CLASS
F	F	Yes	Yes
F	Cl	No	No
F	X	No	Yes
X	F or Cl or Br or I or At	Yes	Yes
X	X	No	Yes

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Structure queries automatically include a default Match Level assignment

- This assignment is only taken into account when searching MARPAT
- The default settings for Match Levels are:

Match Level	Assumption
ATOM	<ul style="list-style-type: none">• Ring atoms• Cy, Cb, Hy
CLASS	<ul style="list-style-type: none">• Chain atoms• Ak

Default assumptions attempt to weight precision versus recall.

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What does Match Level ANY mean?

- Match Level ANY is the least restrictive Match Level option
- In addition to specific atoms and generic nodes, candidate answers also include “R-nodes”
- R-nodes are indefinite substituents in the database structure, described with text terms

Indefinite does not mean undefined, just not searchable via a structure search. R-nodes are not text-searchable in MARPAT.

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Why is Match Level ANY important?

Example: Electron withdrawing groups (EWG) often disclosed indefinitely – consider Match Level ANY for halogens, nitriles, carboxylic acids, etc.

R <"leaving group">	R <"ligand">	R <"ligand with metal", (+1 charge)>
R <"bridging group">	(opt. substd.)	R <"wortmannin C20 derivative">
R <"reactive group">	R <"boronate ester">	R <"thermo labile group">
R <"activated moiety">	(SO)	R <"containing zero or more Si, zero or more Ti, zero or more C">
R <"displaceable group">	R	

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Match Level ANY "Rule of Thumb"

Consider applying Match Level ANY to

- Terminal ring substituents – particularly with the 'A' variable node
- Any electron withdrawing group
 - Halogens, nitriles, carboxylic acids
- Protecting groups
- Whenever in doubt – cautiously

If you retrieve too many irrelevant answers, consider a subset structure search with nodes set to Match Level CLASS.

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Limited/Unlimited Element Count option enables better control over answer retrieval

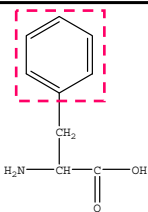
- By default, Element Counts are “Limited”
 - Element Counts in the query must match corresponding Element Counts in an answer
- Element Count “Unlimited” is an alternative
 - Default is overridden and generic groups in an answer that have no Element Counts may also be matched to increase the number of answers retrieved
- Allows balancing recall versus precision in answers with no mention of Element Count

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Element Count ‘Unlimited’ retrieves answers with no mention of EC

QUERY	ANSWER	LIM	UNL
Hy with 2- N	Hy <containing 2-3 N>	Y	Y
	Hy <containing 1 N>	N	N
	Hy	N	Y
	Cb <containing 3-12 C>	Y	Y
	(1-) aryl (opt. substd.)	N	Y
	Cb <containing 5 C>	N	N

NOTE: All rings at Match Level CLASS.

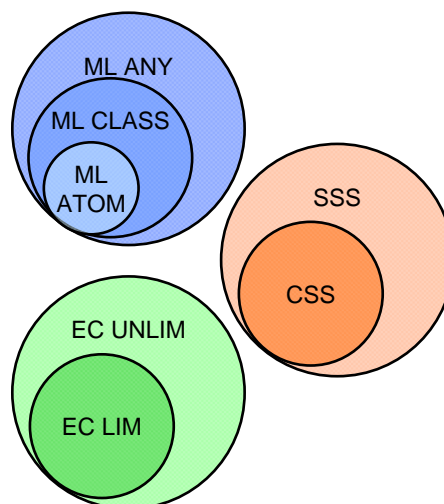
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For Match Level and Element Counts, consider subset searches to control retrieval

- Match Level: All 'ATOM' in 'CLASS'
- Element Count: All 'Limited' in 'Unlimited'
- Subset searches also apply to generic definitions, CSS, SSS, etc.
- Subsets of existing structure searches incur discounts



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Let's look at a few sample queries to reinforce the teaching points

- Allowing/forcing a fused ring
 - Isolated/Embedded versus Specified Fusion
- G-group fragments as a solution to Ring/Chain Bonds limitations in MARPAT
- Complex query based on an actual claim
- Subset searching as a means to an end

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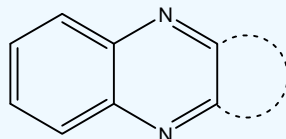
COS
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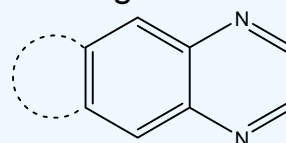
Specifying Ring Fusion Location

Search Question:

Case A – Allow Ring Fusion at dashed site



Case B – Force Ring Fusion at dashed site



Connectivity controls further attachments in substructure searches.

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Connectivity allows Precision Ring Fusion

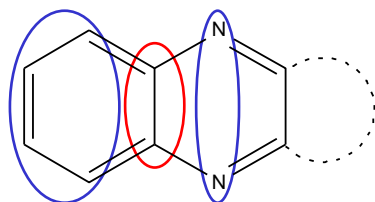
- Ring Isolation (Isolated versus Isolated/Embedded) prevents further ring fusion for entire rings
- Connectivity is used to control the precision of ring fusion in queries
- Either open or lock out positions to further substitution – ring, chain, or ring/chain
- Chain substitutions may occur on nodes with exact ring non-hydrogen attachments

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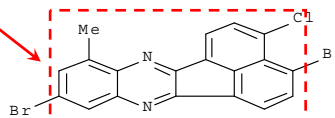
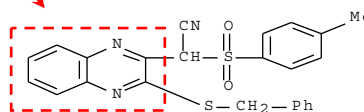
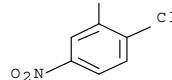
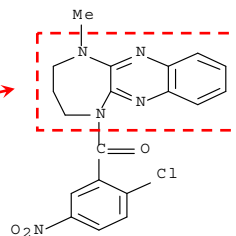
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Allow Ring Fusion at selected sites



- To allow ring fusion, set Non-H Attachments to Exactly 2 (blue) or Exactly 3 (red) Ring
- Additional ring fusion blocked other than open positions

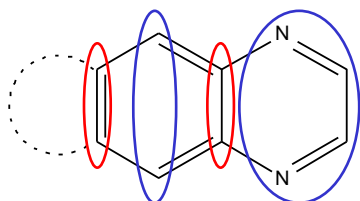


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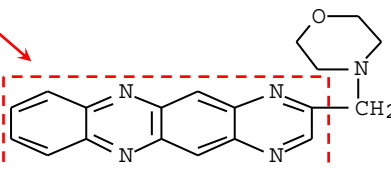
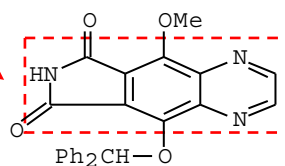
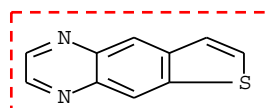
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Force Ring Fusion at selected sites



- To force ring fusion, set Non-H Attachments to Exactly 2 (blue) or Exactly 3 (red) Ring
- Additional ring fusion forced at ring carbons



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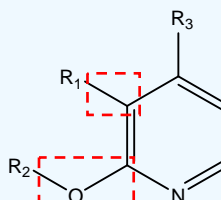
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Structuring queries for MARPAT requires additional considerations

Search Question:

R_1/R_2 = anything
 R_1/R_2 can form a fused ring system
 R_3 = Any ring system
No additional ring fusion



All query building features are allowed in MARPAT *except* the **Ring/Chain** bond characteristics.

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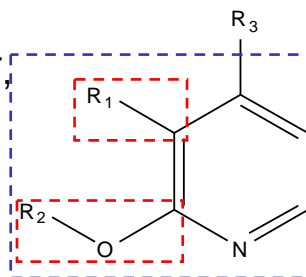
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Solutions to overcoming MARPAT limitations with Ring/Chain bonds

To overcome the limitations with Ring/Chain bonds in MARPAT, we can either:

- Run two structure queries
- Convert existing chains to ring and chain fragments
- Convert majority of query to two fragments



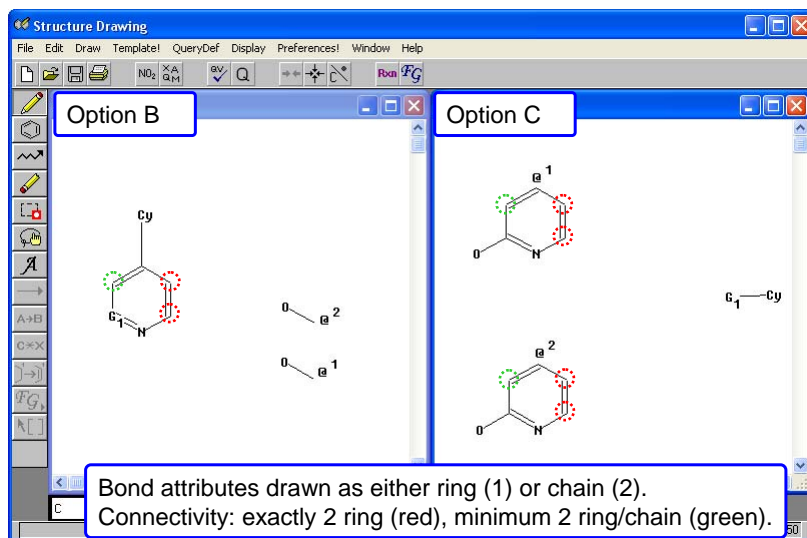
Take care when incorporating a majority of your query as fragments in G-groups to assure proper attachment.

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All options result equal answer sets

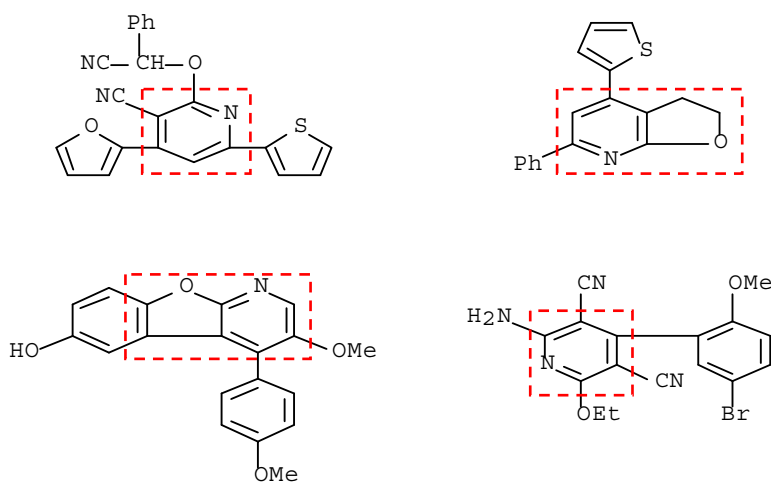


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Sample answers include fused and non-fused ring systems



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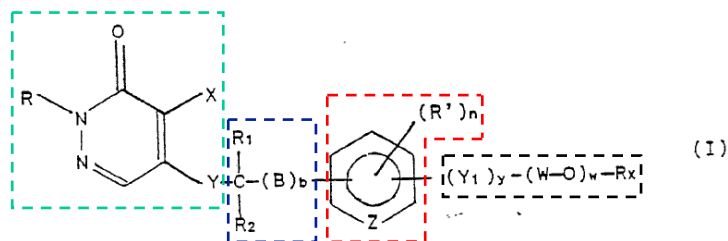
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Over-specifying a query on the first pass can often lead to wasted time

- Use SAMple searches to evaluate your query iteratively as you build it – D SCAN

Claims

1. Pyridazinones of general formula (I) :



wherein:

R represents a linear or branched (C₂-C₆) alkyl group; or a phenyl group, optionally substituted by halogen atoms and/or lower alkyl, haloalkyl, alkoxy and/or haloalkoxy radicals;

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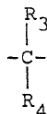
43

Use SAMple searches to evaluate your query as you build complexity

X represents a halogen atom;

Y represents O, S or NH;

B represents:

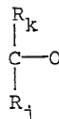


b is O or 1;

R₁, R₂, R₃ and R₄ independently represent H or a linear or branched (C₁-C₄) alkyl or haloalkyl group;

Z represents CH or N;

Y₁ represents O, S, CO or



wherein:

R_k and R_j independently are H or a linear or branched (C₁-C₄) alkyl or haloalkyl group;

W is a linear or branched (C₂-C₆) haloalkylene group;

y and w independently are O or 1;

R_x for w = O, represents a linear or branched (C₂-C₆) haloalkenyl group optionally having a (C₁-C₃) haloalkoxy or phenyl group as substituent, said phenyl group in turn being optionally substituted by one or more halogen atoms, (C₁-C₆) alkyl, haloalkyl, alkoxy and/or haloalkoxy radicals; or represents a (C₃-C₆) halocycloalkyl or (C₄-C₇) halocycloalkyl radical, which radicals may have one or more substituents selected from (C₁-C₄) alkyl or haloalkyl groups; and, for w = 1, represents a linear or branched (C₁-C₆) haloalkyl radical;

R' represents a halogen atom; and

n is O, 1 or 2.

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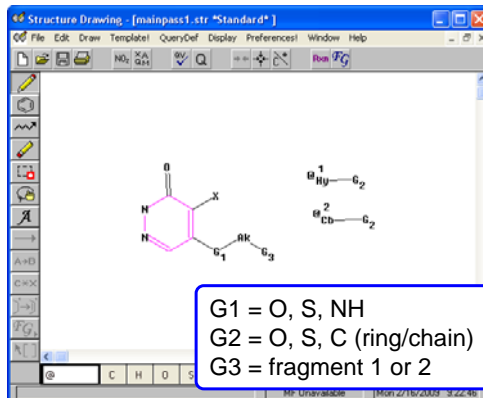
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Prepare a quick query to gather sample answers

First pass to determine correct connectivity and sample answers:

- Replace R with Non-H requirement
- Ring Isolation
- Replaced C-R₁R₂-(B)_b with Ak (1-2 C)
- Element Counts and Generic Definitions for ring system



Verification of smaller queries is often easier – especially with connectivity errors.

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Upload query and run a sample substructure search

```
=> S L1 SSS SAM; D SCAN
```

• • •

```
FULL FILE PROJECTIONS:  ONLINE  **COMPLETE**
                        BATCH   **COMPLETE**
```

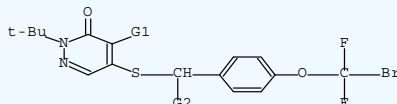
```
PROJECTED ITERATIONS:    5776 TO    7984
```

```
PROJECTED ANSWERS:      4 TO      200
```

```
L2          4 SEA SSS SAM L1
```

```
L2  4 ANSWERS  MARPAT  COPYRIGHT 2009 ACS on STN
```

MSTR 1



G1 = C1

Patent location: claim 1

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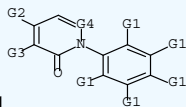
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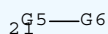
Evaluate answers for appropriateness

L2 4 ANSWERS MARPAT COPYRIGHT 2009 ACS on STN

MSTR 1



G2 = 21

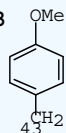


G3 = C1

G4 = N

G5 = NH

G6 = 43



Patent location:

claim 1

STN

CS
Purdue

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Start simple, just like exercising...

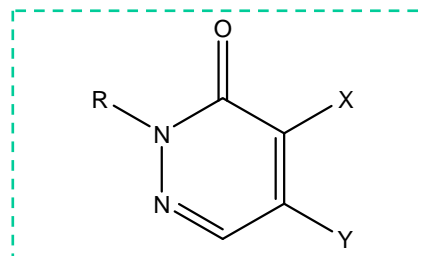
R represents a linear or branched (C₂-C₆) alkyl group; or a phenyl group, optionally substituted by halogen atoms and/or lower alkyl, haloalkyl, alkoxy, and/or haloalkoxy:

X represents a halogen atom

Y represents O, S, NH

Specifications

- R = alkyl (2-6 C), Ph
- X = any halogen
- Y = O, S, NH
- Pyridazinone ring isolated



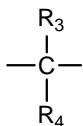
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CS
Purdue

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Watch for G-groups allowing independent hydrogen substitution

B represents:

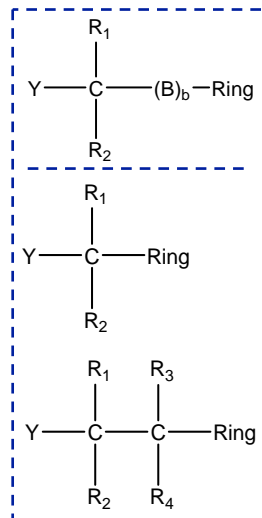


b is 0 or 1

R_1, R_2, R_3, R_4 independently represent H or a linear or branched (C_1 - C_4) alkyl or haloalkyl group

Specifications

- Substitute linear, saturated Ak (1-2 C) for C-(B)_b (covers all H)
- Create fragments for attachment of $R_1, R_2, R_3, R_4 = Ak$ (1-4 C)



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Cannot specify points of attachment for generic ring variables

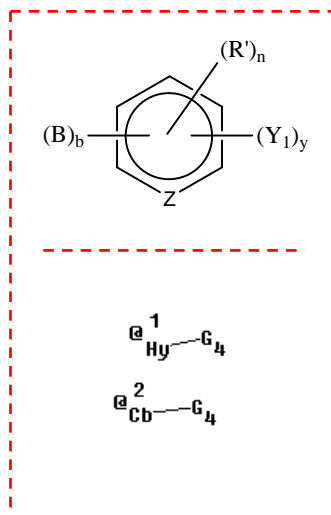
Z represents CH or N

R' represents a halogen atom

n is 0, 1 or 2.

Specifications

- Optionally substituted halogens problematic
- Element Counts for Hy (1 N, 5 C) and Cb (6 C)
- Generic Definitions unsaturated, monocyclic, exactly one heteroatom (Hy)



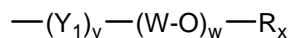
STN

CCS
Purdue

50

And sometimes it's best to know when to re-evaluate sample answers

R_x for $w = 0$, represents a linear or branched (C_2 - C_6) haloalkenyl group optionally having a (C_1 - C_3) haloalkoxy or phenyl group as substituent ...and, for $w = 1$, represents a linear or branched (C_1 - C_6) haloalkyl radical



Specifications

- C (ring/chain), S, O
- Review sample search to determine further

O @ 9
S @ 10
C @ 11

STN

COS
PSEARCH

51

Upload query and run a sample substructure search

```
L3      STRUCTURE UPLOADED

=> S L3 SSS SAM
SAMPLE SEARCH INITIATED 14:00:16
SAMPLE SCREEN SEARCH COMPLETED -      383 TO ITERATE

100.0% PROCESSED      383 ITERATIONS      5 ANSWERS
SEARCH TIME: 00.00.02

FULL FILE PROJECTIONS:  ONLINE  **COMPLETE**
                        BATCH   **COMPLETE**
PROJECTED ITERATIONS:   6496 TO   8824
PROJECTED ANSWERS:     5 TO     234

L4      5 SEA SSS SAM L3

=> D SCAN
```

STN

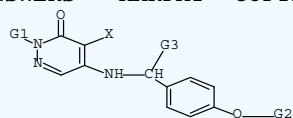
COS
PSEARCH

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Review sample answers for appropriateness

L4 5 ANSWERS MARPAT COPYRIGHT 2009 ACS on STN

MSTR 1

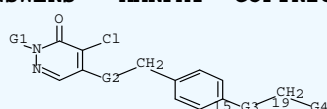


G1 = alkyl <containing 3-5 C>

Patent location: claim 1

L4 5 ANSWERS MARPAT COPYRIGHT 2009 ACS on STN

MSTR 1



G1 = alkyl <containing 1-6 C>

G2 = O

G3 = bond

Patent location: claim 1

STN

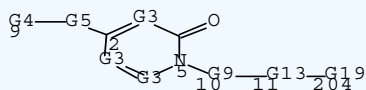
CS
PharmLife

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Review sample answers for appropriateness

L4 5 ANSWERS MARPAT COPYRIGHT 2009 ACS on STN

MSTR 1



G3 = (up to 1) N / CH (opt. substd.)

G4 = pyridyl (opt. substd. by 1 or more G18)

G5 = 19-9 20-2 / 21-9 22-2 / 23-9 25-2

$1G6-2G7$ $2G7-2G16$ $2G7-G17-2G7$

G6 = alkylene <containing 1-6 C> (opt. substd.)

G7 = O

G9 = alkylene <containing 1 or more C> (opt. substd.)

G18 = OMe

Patent location: claim 1

Note: or pharmaceutically acceptable salts

STN

CS
PharmLife

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Upload query and run a sample substructure search

```
=> S L3 SSS FULL
```

```
FULL SEARCH INITIATED 14:01:14
```

```
FULL SCREEN SEARCH COMPLETED - 7804 TO ITERATE
```

```
100.0% PROCESSED 7804 ITERATIONS 54 ANSWERS
```

```
SEARCH TIME: 00.00.09
```

```
L5 54 SEA SSS FUL L3
```

```
=> D SCAN
```

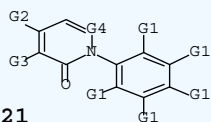
STN

COS
Chemicals

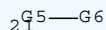
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Take advantage of subset structure searching to refine your searches

MSTR 1



G2 = 21

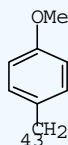


G3 = halo

G4 = N

G5 = NH

G6 = 43



Although our candidate answers look good, we are missing the halogen requirement of R_x.

Patent location:

claim 1

STN

COS
Chemicals

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Be cautious in modifying structure queries when performing subset searches

Uploading Q:\My Documents\...\Queries\AdvSTRSem\14b.str

L6 STRUCTURE UPLOADED

Modified query contains halo substitution requirements.

=> S L6 SSS FUL

100.0% PROCESSED 7801 ITERATIONS 35 ANSWERS
SEARCH TIME: 00.00.06

L7 35 SEA SSS FUL L6

Subset structure searches run at significant cost discount.

=> S L6 SSS SUBSET=L5 FULL

100.0% PROCESSED 54 ITERATIONS 35 ANSWERS
SEARCH TIME: 00.00.01

L8 35 SEA SUB=L5 SSS FUL I

Use SUBSET=L5 to restrict search to answers in L5.

=> D SCAN

STN

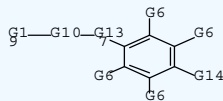
CCS
Chemical Computing Systems

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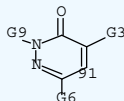
Review candidate answers for appropriateness

L8 35 ANSWERS MARPAT COPYRIGHT 2009 ACS on STN

MSTR 2



G1 = 91



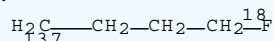
G3 = F

G9 = alkyl <containing 1-6 C> (opt. substd. by G5)

G10 = O

G13 = alkylene <containing 1 or more C>
(opt. substd. by G5)

G14 = 137



Although we've only reduced the search by 19 answers, we've improved our evaluation time using subset.

Patent location:

claim 13

STN

CCS
Chemical Computing Systems

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Summary

- G-groups in structure searching have limits, however they provide flexibility for complex queries
- Hydrogen and Non-Hydrogen Attachments (Connectivity) provide increased accuracy without over-limiting your query
- MARPAT Generic Definitions, Element Counts, and Match Level increase precision versus recall



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Additional STN Training Resources

Recorded CAS e-Seminars:

- Revisiting the Basics of Structure Searching
- Structure Drawing in STN
- Advanced MARPAT Techniques
- Revealing the Mysteries of MARPAT

STN User Documentation:

- Structure Searching in the CAS Registry File on STN
- MARPAT User Guide (revised 11/08)



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Visit www.cas.org for additional STN e-Seminar and training opportunities.

Upcoming 2009 STN e-Seminars

Month	Date	Time	Event Title
March 2009	March 12, 2009	6:00 - 7:00 Pacific DT	STN@: Advanced Techniques for Structure Searching on STN@
	March 24, 2009	10:00 - 11:00 Pacific DT	STN@: Use STN@ to Keep Up-to-Date with Research and Development Trends in Engineering
April 2009	April 9, 2009	6:00 - 7:00 Pacific DT	STN@: Use STN@ to keep up-to-date with research and development trends in Engineering
	April 16, 2009	10:00 - 11:30 Pacific DT	STN@: Go to CAS REGISTRYSM for property data and spectra
	April 28, 2009	10:00 - 11:00 Pacific DT	STN@: Unmasking the World of Antibodies with STN@

<http://casevents.webex.com>

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