

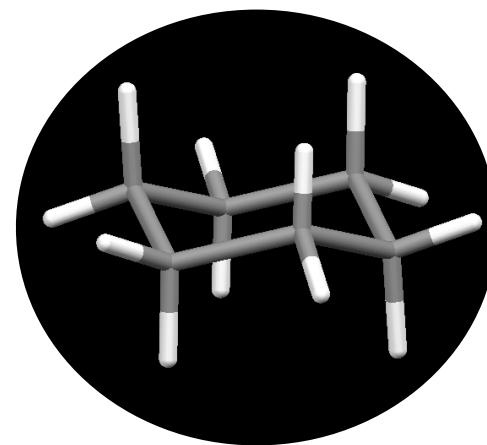
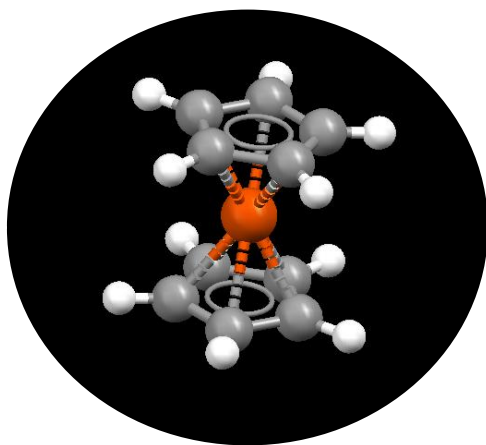


An Interactive Online Teaching Subset of the Cambridge Structural Database

Gary Battle

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battle@ccdc.cam.ac.uk





3D Visualisation

- Chemists need 3D visualisation proficiency
- 3D visualisation shown to enhance students conceptual understanding and spatial abilities

Williamson, V. M. *J. Chem. Educ.*, **2008**, 85, 718-723

Wu, H. K. *Sci. Educ. Res. Pract.*, **2004**, 8, 61-72

Bodner, G. M. *The Chemical Educator*, **1997**, 2

“Because basic 3D spatial relationships in molecules have systematic and profound causal significance, chemistry is an extraordinarily fertile field for visual learning”

2001 NSF Workshop: Molecular Visualisation
in Science Education



Experimentally Measured Data

- Use of experimentally measured data is of great pedagogical value
 - Inherent experimental error and statistical variation provides an opportunity to deal with the uncertainties of chemistry
 - Challenges students to think more critically about bonding and molecular structure
 - Encourages method and limitations of data collection to be considered
- Measured data shown to enhance student learning

DeHaan, R. L. *J. Sci. Educ. Technol.*, **2005**, 14, 253-269

Handelsman, J. *Science* **2004**, 304, 521-522

Prince, M. *J. Eng. Educ.*, **2004**, 89, 1-9



Encouraging the use of Crystal Structure Data in Teaching

- Free on-line interactive teaching subset of the CSD, and associated example teaching units

These educational materials are designed to demonstrate, to the non-specialist, the utility of crystallographic information across the entire chemistry curriculum



Teaching Subset of the CSD

- 500 structures that have important applications in chemistry and chemical education selected from the full CSD of almost half a million crystal structures
- Key molecules typically used in textbooks to exemplify core concepts and principles, e.g.
 - Bonding and structure: benzene (BENZEN02), diborane (GAFLAA), and ferrocene (FEROCE27)
 - Conformational analysis: half-chair and envelope cyclopentane (LISLOO, IHIPOE), cyclohexane (CYCHEX)
 - Stereochemistry: L-(R)- and D-(S)- alanine (LALNIN23, ALUCAL05), tartaric acid (TARTAC, TARTAL04, TARTAM)
 - Reaction mechanisms: bromonium ion (refcode: DAKVUG)



Chemical Diversity

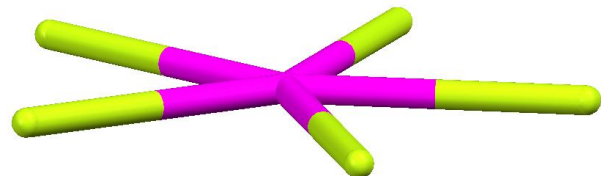
Structure Type	N	%Subset
All structures	500	100.0
Organic	331	66.2
Metal-organic	161	32.2
Organic structures		
Carbohydrates	8	1.6
Nucleosides / nucleotides	6	1.2
Amino-acids and peptides	29	5.8
Porphyrins / corrins	13	2.6
Steroids	12	2.4
Alkaloids	10	2.0
Organic polymers	8	1.6

Metal-organic structures		
Any metal: 3-coordinate	9	1.8
Any metal: 4-coordinate	37	7.4
Any metal: 5-coordinate	21	4.2
Any metal: 6-coordinate	52	10.4
Any metal: 7-coordinate	10	2.0
Any metal: 8-coordinate	10	2.0
Any metal: 9-coordinate	6	1.2
Any metal: 10-coordinate	2	0.4
Any metal: 11-coordinate	2	0.4
Any metal: 12-coordinate	3	0.6
π -complexes	33	6.6
Containing keywords		
'Drug' or 'Activity'	42	8.4
'Polymorph' or 'Form'	80	16.0

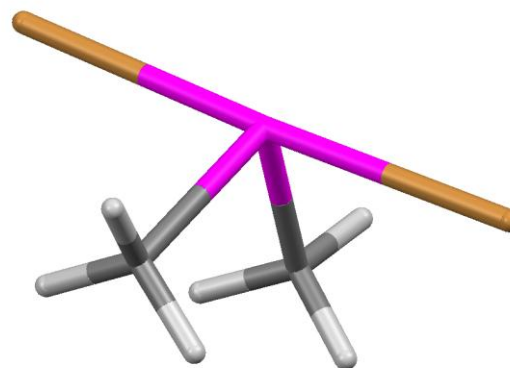


Diverse Molecular Geometries

- Simple examples (composed entirely of main group elements) of all main VSEPR structure types
- Linear, bent, trigonal planar... square antiprismatic



Pentagonal planar
[XeF₅]⁻ anion
(refcode: SOBWAH)

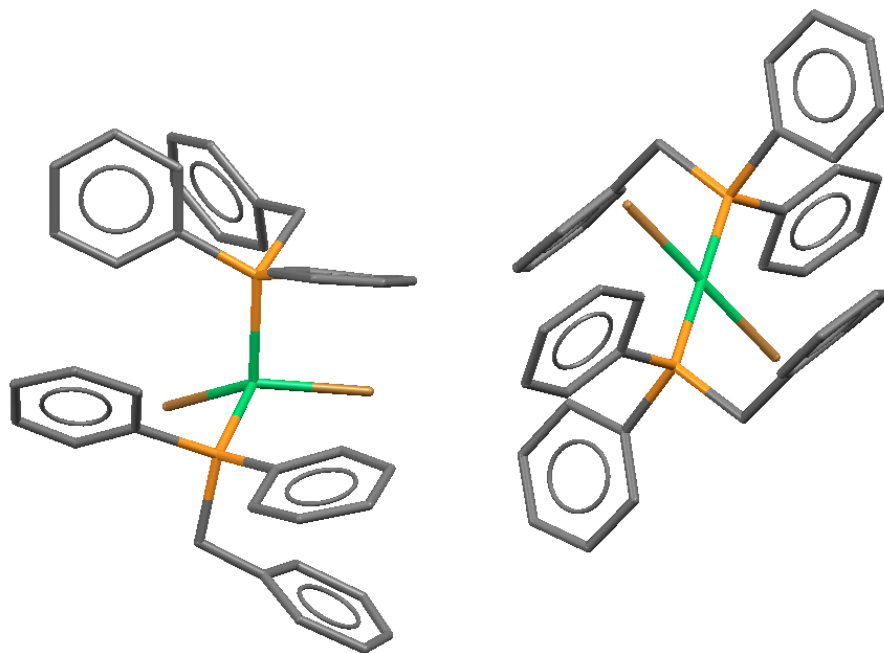


Disphenodial “see-saw”
dibromodimethylselenium
(refcode: RIZMIW)



Diverse Molecular Geometries

- Simple examples (composed entirely of main group elements) of all main VSEPR structure types
- Linear, bent, trigonal planar... square antiprismatic
- Unusual and interesting geometries



Interallogon compound

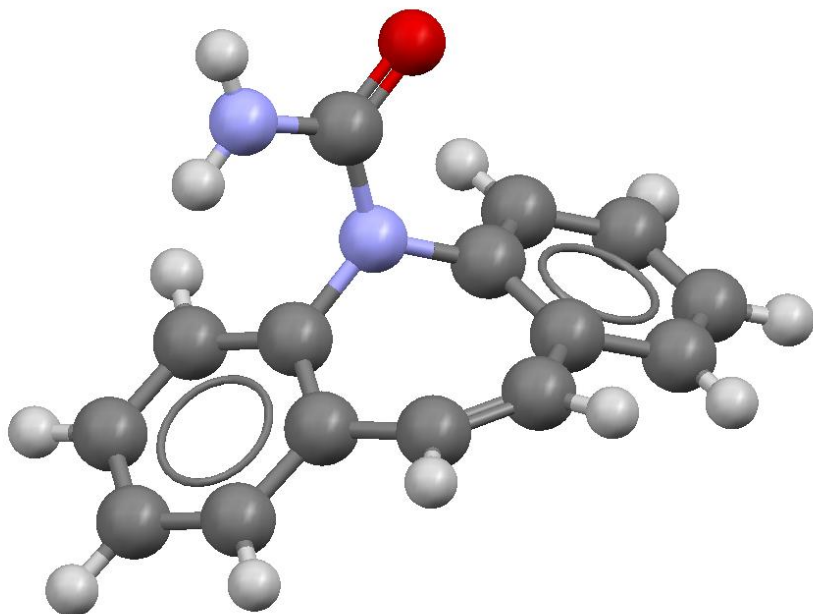
(Greek: allos, other, different;
gonia, angle)

Dibromo-bis(benzylidiphenyl
phosphine) nickel(ii)
(refcode: DBBZPN)



Multiple Determinations

- CSD contains multiple determinations of the same crystal structure, e.g. improved model, temperature study etc.
- Such series can be used to study statistical variation and explore different crystal forms (polymorphism).



Carbamazepine, an analgesic and anticonvulsant drug

6 determinations:

CBMZPN01, CBMZPN02,
CBMZPN03, CBMZPN10,
CBMZPN11, CBMZPN12,



Structure Quality

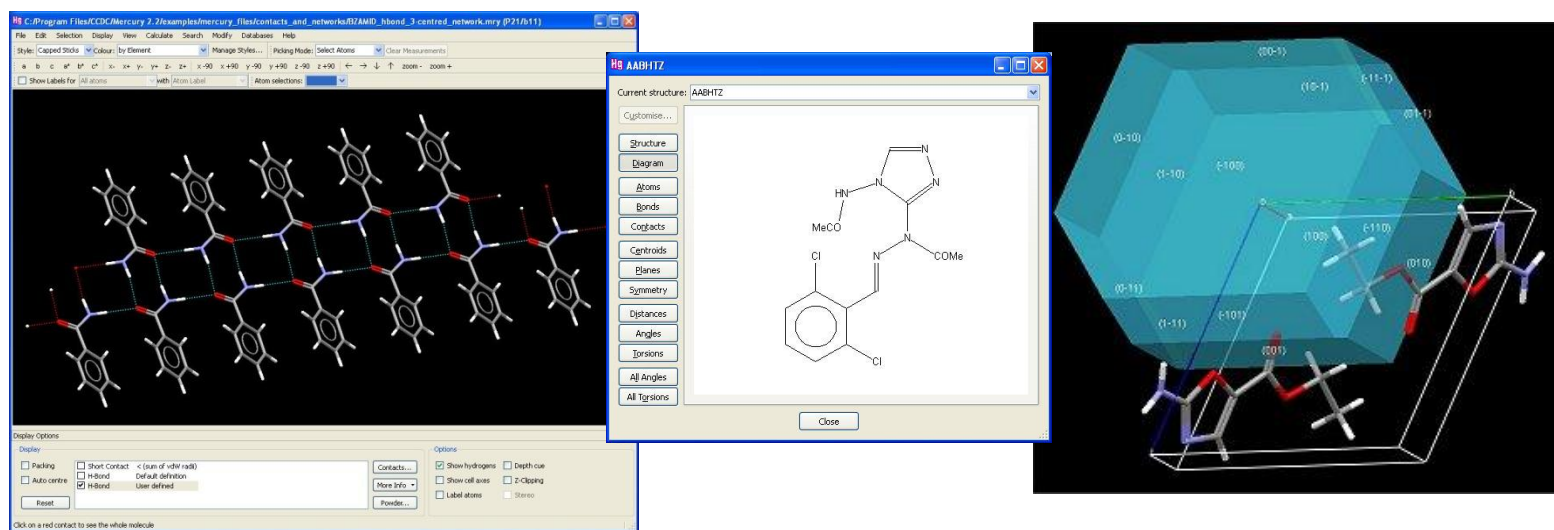
Structure Quality	Teaching Subset		CSD V5.30 +Nov & Feb09 Updates	
	N	%Subset	N	%CSD
All structures	500	100.0	472200	100.0
3D Coordinates determined	500	100.0	433866	91.9
Contain unresolved errors	0	0.0	8345	1.8
Contain disorder	29	5.8	99547	21.1
R factor				
< 0.05	301	60.2	251658	53.3
< 0.075	422	84.4	396521	84.0
< 0.1	461	92.2	438989	93.0



How Can I Access the Subset #1

■ Mercury visualiser

- Advanced crystal structure visualisation program by CCDC
- Freely downloadable desktop application
- Teaching subset embedded and available via Databases menu



http://www.ccdc.cam.ac.uk/free_services/teaching/



How Can I Access the Subset #2

- Interactive web-based interface
 - Uses WebCSD: new on-line search interface to the CSD
 - Not required to download, install or register any software
 - Browse and visualise teaching subset entries using just a standard web-browser

http://www.ccdc.cam.ac.uk/free_services/teaching/



File Filter Help

Find Entry

Entry

- BUFGAE01
- BUVGII
- CAACTY
- CACWOS
- CADVEI
- CAFINE**
- CAFROR
- CAMHFA
- CAMXAP01
- CAQTET
- CARQOB
- CARTEN
- CARTEN02
- CATCOL13
- CBMZPN01
- CBMZPN02
- CBMZPN03
- CBMZPN10
- CBMZPN11
- CBMZPN12
- CCXAPT
- CEBGUL
- CECZEP
- CECZIT
- CEFXOA
- CEHTAK10

< >

500 Hits

100%

Stop Search

Entry loaded

CAFINE : 1,3,7-Trimethyl-purine-2,6-dione monohydrate
D.J.Sutor; *Acta Crystallogr.* (1958), **11**, 453, doi:10.1107/S0365110X58001286

Hide Viewer

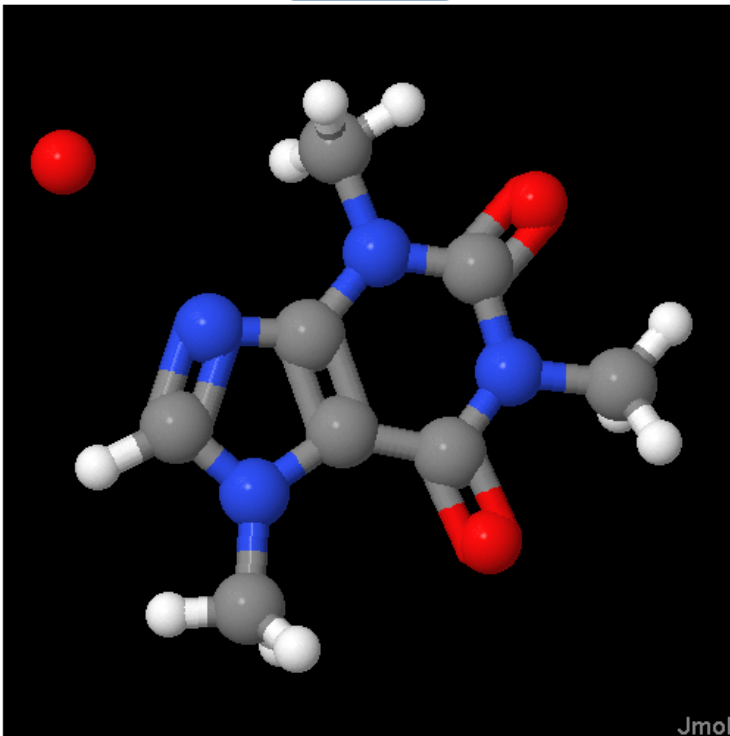
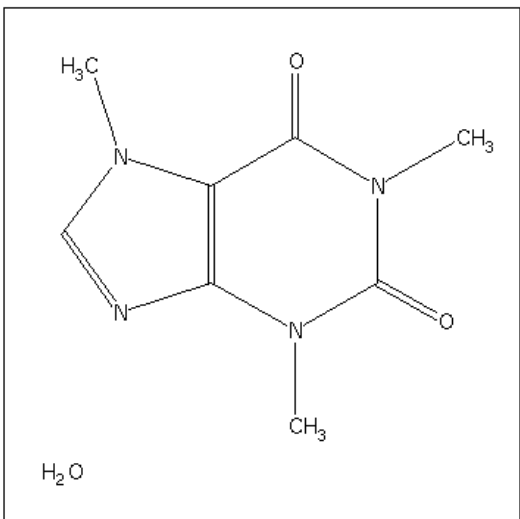


Diagram Details Viewer Export Options Help



$C_8H_{10}N_4O_2 \cdot H_2O$
Space Group: P 2₁/a
a 14.8(1) **b** 16.7(1) **c** 3.97(3)
 α 90 **β** 97.0(5) **γ** 90
R-Factor: 14.6%
Temperature (K): Room Temp. (283-303)

Ball and Stick No Labels

Hydrogens Bond types Disorder

Jmol

http://www.ccdc.cam.ac.uk/free_services/teaching/



File Filter Help

Find Entry

Entry

- BUHQAE01
- BUVGII
- CAACTY
- CACWOS
- CADVEI
- CAFINE**
- CAFROR
- CAMHFA
- CAMXAP01
- CAQTET
- CARQOB
- CARTEN
- CARTEN02
- CATCOL13
- CBMZPN01
- CBMZPN02
- CBMZPN03
- CBMZPN10
- CBMZPN11
- CBMZPN12
- CCXAPT
- CEBGUL
- CECZEP
- CECZIT
- CEFXOA
- CEHTAK10

< >

500 Hits

100%

Stop Search

Entry loaded

CAFINE : 1,3,7-Trimethyl-purine-2,6-dione monohydrate
D.J.Sutor; *Acta Crystallogr.* (1958), **11**, 453, doi:10.1107/S0365110X58001286

Hide Viewer

Jmol

Ball and Stick No Labels

Hydrogens Bond types Disorder

Packing Options

None Unit Cell 3x3x3

Diagram Details Viewer Export Options Help

Identifier	CAFINE
Author(s)	D.J.Sutor
Reference	<i>Acta Crystallogr.</i> (1958), 11 , 453, doi:10.1107/S0365110X58001286
Formula	C ₈ H ₁₀ N ₄ O ₂ ·H ₂ O
Compound	1,3,7-Trimethyl-purine-2,6-dione monohydrate
SMILES	<chem>CN1C=NC2=C1C(=O)N(C)C(=O)N2C.O</chem>
Synonym	Caffeine monohydrate
Space Group	P 2 ₁ /a
Cell Lengths	a 14.8(1) b 16.7(1) c 3.97(3)
Cell Angles	α 90 β 97.0(5) γ 90
Cell Volume	973.911
Z, Z'	Z : 4 Z' : 1
R-Factor (%)	14.6
Reduced Cell Lengths	a 3.97 b 14.8 c 16.7
Reduced Cell Angles	α 90 β 90 γ 97
Reduced Cell Volume	973.911
Temperature (K)	Room Temp.(283-303)
Density (CCDC)	1.447
Average Sigma (C-C)	0.01 < sigma <= 0.03
Radiation Probe	x-ray
Bioactivity	stimulant agent which increases CNS activity

http://www.ccdc.cam.ac.uk/free_services/teaching/



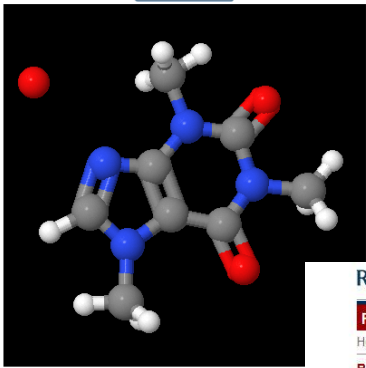
File Filter Help

Find Entry CAFINE

Entry

BUPOAE01
BUV011
BUV012
CAACTY
CACWOS
CADVEI
CAFINE
CAFROD
CAMHFA
CAMKAP01
CAOTET
CAROGB
CARTEN
CARTEN02
CATCOL13
CBMZPN01
CBMZPN02
CBMZPN03
CBMZPN10
CBMZPN11
CBMZPN12
CCXAPT
CEBGUL
CECZEP
CECZIT
CEFXOA
CEHTAK10

Hide Viewer



Ball and Stick No Labels

Hydrogens Bond types Disorder

Packing Options

None Unit Cell 3x3x3

Launch External Viewer

500 Hits

100%

Stop Search

Entry loaded

Diagram Details Viewer Export Options Help

Identifier	CAFINE
Author(s)	D.J. Sutor
Reference	<i>Acta Crystallogr.</i> (1958), 11 , 453, doi:10.1107/S0365110X58001286
Formula	C ₈ H ₁₀ N ₄ O ₂ ·H ₂ O
Compound	1,3,7-Trimethylpurine-2,6-dione monohydrate
SMILES	CN1C=NC2=C1C(=O)N(C)C(=O)N2C.O
Synonym	Caffeine monohydrate
Space Group	P 2 ₁ /a
Cell Lengths	a 14.8(1) b 16.7(1) c 3.97(3)

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Paper

J. Chem. Soc., Perkin Trans. 2, 1997, 1985

Perkin Transactions 2

Perkin Transactions 2 ceased publication in 2002. Chemistry is the RSC's organic chemistry journal for chemistry research.

J. Chem. Soc., Perkin Trans. 2, 1997, 1985

Metamorphosis of caffeine h

Howell G. M. Edwards, Emma Lawson, Ma

The phase stability, interconversion and (1,3,7-trimethylpurine-2,6-dione) hydrate of the available hydrogen-bonds. A hydrate molecule establishes a weak lattice bond for ambient conditions, transforms to a β -an with an enthalpy of 3.6 kJ mol⁻¹, converts The anhydrous phases are stabilised by

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Metamorphosis of caffeine hydrate and anhydrous caffeine

Howell G. M. Edwards,^a Emma Lawson,^b Marcel de Matas,^a Len Shields^b and Peter York^a

^a Postgraduate studies in Pharmaceutical Technology, School of Pharmacy and ^b Department of Chemistry, University of Bradford, Bradford, UK BD7 1DP

The phase stability, interconversion and physicochemical characterisation of caffeine (1,3,7-trimethylpurine-2,6-dione) hydrate and anhydrous caffeine relate to the strength of the available hydrogen-bonds. A hydrogen-bonded T-branched spine of hydrate molecules establishes a weak lattice bond for the caffeine hydrate which, under ambient conditions, transforms to a β -anhydrous phase which in turn, at 155 °C and with an enthalpy of 3.6 kJ mol⁻¹, converts to a trigonal phase α -anhydrous caffeine. The anhydrous phases are stabilised by weak CH₃ to CO hydrogen bonds.

Introduction

The phase changes associated with caffeine, 1,3,7-trimethylpurine-2,6-dione, are generally related to the state of hydration of the molecule; one disordered and incommensurate hydrate phase will transform in ambient atmospheric conditions to an anhydrous β -phase which converts at high temperature to a second metastable anhydrous α -phase which subsequently sublimates. These phase transformations may be investigated in a number of ways including calorimetry, thermogravimetry, spectrometry and crystalline structure analysis. For example, it is found from the crystal structure that the caffeine molecule possesses a hydrophilic centre at the iminazole nitrogen atom, N9, susceptible to H-bonding and that the hydrate water molecule egresses *via* a molecular escape tunnel through the crystalline structure.

polycrystalline anhydrous β -phase will metamorphose on heating and then by sublimation form crystals of the α -phase, which will revert to the β -phase at room temperature. Consequently, discrimination of the phases is required for a reliable characterisation of the substance and its phase stability.

Experimental

β -Phase material (Lot 79F0469) was obtained from Sigma Chemicals Ltd., Poole, England (purity = 99.6%). Crystals of caffeine hydrate were obtained by slow recrystallisation from water and stored in a sealed vessel at 75% relative humidity in the presence of a NaCl saturated solution at room temp. Microcrystals of the α -phase material were prepared by slow sublimation of the β -phase at 155 °C.



Links to the primary literature



Generating Links to the Teaching Subset

- Easy integration with your own teaching materials, and webpages
- WebCSD interface provides a form that will:
 - Automatically generate a hyperlink that will launch WebCSD and display one or more specified entries
 - `View in WebCSD`



Teaching Units

- Based on structures in the teaching subset
- Provide opportunity to visualise and interact with diverse range of 3D structures
- Illustrate utility of crystal structure data across a broad range of chemical concepts, including:
 - Aromaticity, shapes of molecules (VSEPR)
 - Reaction intermediates, stereochemistry, conformations of rings
 - Metal-carbonyl back-bonding, metal geometry, hapticity
 - Analysing molecular dimensions

http://www.ccdc.cam.ac.uk/free_services/teaching/



WebCSD Teaching Examples



AROMATICITY

AROMATICITY

INTRODUCTION

OBJECTIVES

GETTING STARTED

STEPS REQUIRED

Examine the structure of benzene

Examine the structure of cyclooctatetraene.

Consider what happens when we treat cyclooctatetraene with a powerful reducing agent

Consider what happens if we treat benzene with oxidizing or reducing agents

Do you see a pattern forming?

Molecular orbital description

Requirements for aromaticity

Use Huckels rule to predict aromaticity

SUMMARY OF KEY CONCEPTS

Online Resources

[More Teaching Resources](#)

[Learn more about the full version of WebCSD](#)

Contact us

[For a full CSD evaluation](#)

[To share your CSD teaching materials](#)

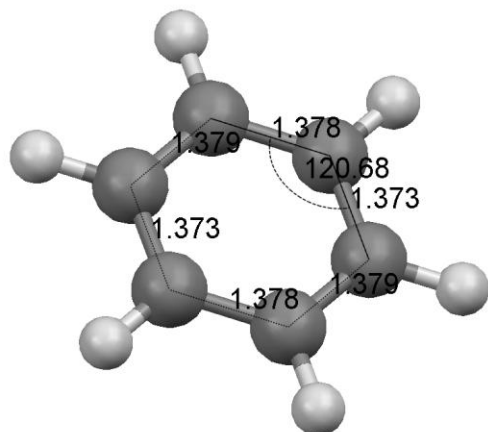
CCDC

[News Events](#)

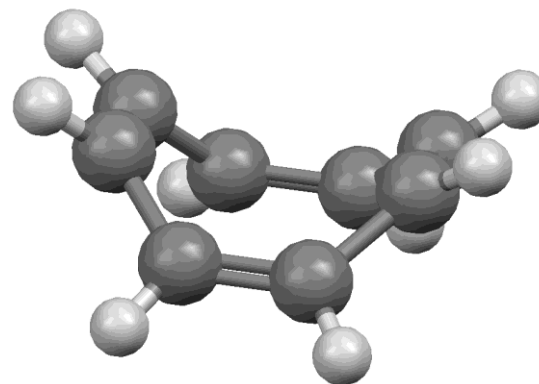


Teaching Unit: Aromaticity

- Note difference in reactivity of benzene compared to cyclooctatetraene, e.g. addition of Br
- Measure and compare the carbon-carbon bond lengths and planarity of the structures



benzene (BENZEN02)

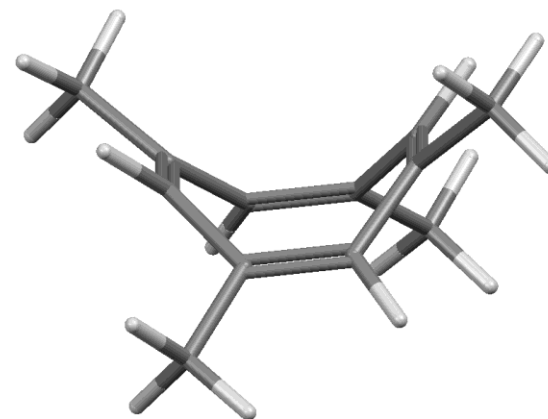


cyclooctatetraene (ZZZSAE01)

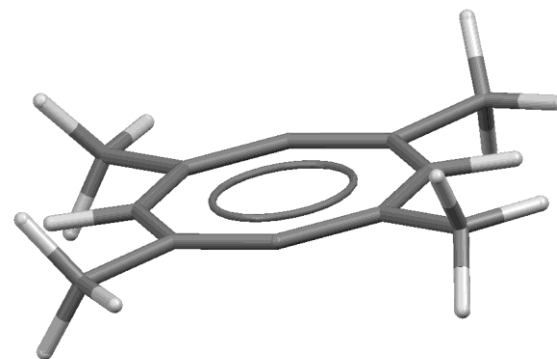


Teaching Unit: Aromaticity

- Inspect a number of oxidised and reduced benzene and cyclooctatetraene derivatives
- Relate structural characteristics to number of π -electrons
- Arrive at Huckel's rule
- Use findings to predict whether or not certain compounds are aromatic



puckerd (*TMCOTT*)



planar dianion (*TMOCKE*)



Further Information

- Battle, G. M.; Allen, F. H.; Ferrence, G. M.
An interactive web-accessible teaching subset of the
Cambridge Structural Database
J. Chem. Educ., **2009**, submitted
- Battle, G. M.; Allen, F. H.; Ferrence, G. M.
Example teaching units that utilise an interactive web-
accessible subset of the Cambridge Structural Database
J. Chem. Educ., **2009**, submitted

http://www.ccdc.cam.ac.uk/free_services/teaching/