

algorithmic improvements are desirable in these cases and work to devise these improvements is in hand.

We thank Dr Olga Kennard FRS for her interest in this work and Mrs Dee Hughes for preparing Figs. 2(a) and 2(b).

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## Symmetry-Modified Conformational Mapping and Classification of the Medium Rings from Crystallographic Data. III. *endo*-Unsaturated Seven-Membered Rings

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(Received 12 August 1993; accepted 25 January 1994)

#### Abstract

Crystallographic results retrieved from the Cambridge Structural Database (CSD) have been used to

perform systematic conformational analyses for cycloheptene, cyclohepta-1,3-diene, cyclohepta-1,4-diene and cyclohepta-1,3,5-triene. Conformational mappings based on symmetry-adapted deformation coordinates show that, with the exception of cycloheptene (for which a C<sup>4</sup> conformation is dominant),

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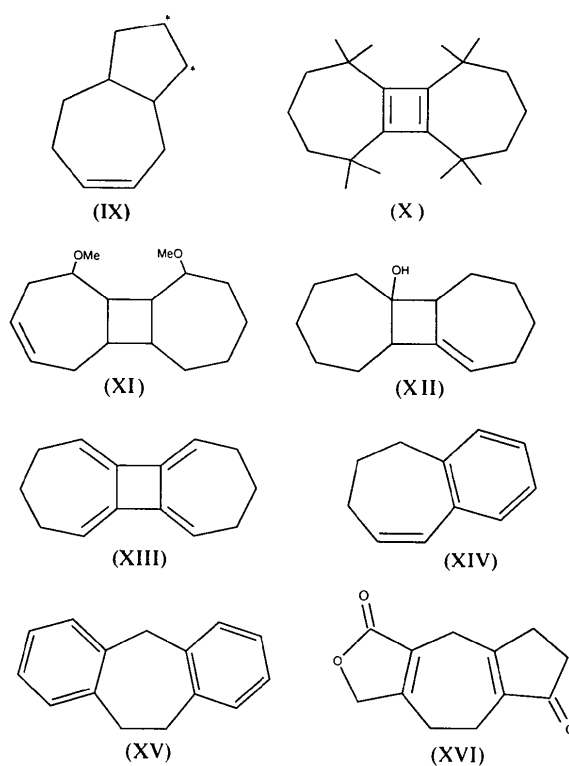
all conformations adopted by these unsaturated systems are intermediate between chair-like and boat-like forms. Conformational classifications, using symmetry-modified Jarvis–Patrick clustering, show a qualitative correlation between class populations and relative energy differences reported in published force-field and *ab initio* studies. Cyclohepta-1,3-diene is an apparent exception: computational methods predict a  $C_s$ -envelope as the most stable form, in agreement with gas-phase structural studies, but the  $C_2$ -twist form, some 8–10 kJ mol<sup>-1</sup> higher in energy, is ubiquitous in the crystallographic literature. However, the majority of crystal structures show that one or both of the double bonds arise from benzo-fusion. Force-field calculations, carried out as part of this study, show that the C conformation of the seven-membered ring is preferred in cases of benzo-fusion to relieve unfavourable H···H interactions.

### Introduction

The aim of this short series of papers is to examine and classify the crystallographically observed conformations of those seven- and eight-membered rings and associated substructures that are well represented in the Cambridge Structural Database (CSD: Allen *et al.*, 1991). Studies of this type are of fundamental chemical interest, since we may reasonably assume that the crystallographic observations will be closely aligned with low-energy features of the relevant conformational hypersurface. In this work we use symmetry-adapted deformation coordinates and symmetry-modified principal component and cluster analyses for conformational mapping and classification (see *e.g.* Allen, Doyle & Auf der Heyde, 1991; Allen, Doyle & Taylor, 1991*a,b*). Wherever possible the results are related to conformational energy differences obtained from the literature, or as calculated by force-field methods as part of each individual study. In part I we applied these methods to parent cycloheptanes [(I) in Fig. 1; Allen, Howard & Pitchford (1993)], whilst part II described conformations of *exo*-unsaturated and heterocyclic seven-membered rings (II)–(IV), *i.e.* common derivatives that contain seven intra-annular single bonds (Allen, Howard, Pitchford & Vinter, 1994). We now conclude our study of seven-membered rings by considering the *endo*-unsaturated systems (Fig. 1) of cycloheptene (V), cyclohepta-1,3-diene (VI), cyclohepta-1,4-diene (VII) and cyclohepta-1,3,5-triene (VIII).

### Conformational space for seven-membered rings

Conformational space for cycloheptane (I), and for related fragments that preserve seven single intra-



annular bonds, is summarized in detail in parts I and II of this series (Allen, Howard & Pitchford, 1993; Allen, Howard, Pitchford & Vinter, 1994, and references therein). The space is four-dimensional and may be described by coordinates  $\theta$ ,  $\rho$ ,  $\varphi_2$ ,  $\varphi_3$  (BPRS coordinates: Bocian, Pickett, Rounds & Strauss, 1975) or by the (equivalent) phase amplitude pairs  $q_2$ ,  $\varphi_2$ ;  $q_3$ ,  $\varphi_3$  (CP coordinates: Cremer & Pople, 1975). For (I) these coordinates describe two pseudorotational subspaces involving interconversion of the 14 equivalent permutation/inversion isomers of the symmetrical chair (C, symmetry  $C_3$ ) and twist-chair (TC, symmetry  $C_2$ ) forms, and of the boat (B, symmetry  $C_s$ ) and the twist-boat (TB, symmetry  $C_2$ ) forms. Pseudorotation is effective due to the small energy barriers between C and TC forms (*ca* 5–6 kJ mol<sup>-1</sup>) and between the B and TB forms (*ca* 1–2 kJ mol<sup>-1</sup>). There exists, however, a higher barrier (> 10 kJ mol<sup>-1</sup>) for interconversions between chair-like and boat-like conformations. The experimental results may be separated into C/TC or B/TB classes by the use of the BPRS  $\theta$  coordinates. Permutational isomers and their enantiomers on the predominant C/TC pathway may be mapped *via* a  $\varphi_2, \varphi_3$ -plot, whilst B/TB variants are mapped by  $\varphi_2$  alone.

Many simple derivatives of (I), *e.g.* the *exo*-unsaturated rings (II) and the heterocycles (III), have  $C_{2v}$  topological symmetry, a considerable reduction by comparison with the  $D_{7h}$  symmetry exhibited by

Table 1. Theoretical torsion angles ( $\tau_1$ – $\tau_7$ ) ( $^\circ$ ) for low-energy conformers of the parent cycloheptane (I) and for the *endo*-unsaturated systems (V)–(VIII) (Fig. 1).

Conf. is the conformational descriptor used in the text, Sym is the symmetry of each conformer and  $\Delta E$  is the calculated energy difference ( $\text{kJ mol}^{-1}$ ) relative to the minimum energy form in each case.

Conf.	Sym.	$\tau_1$	$\tau_2$	$\tau_3$	$\tau_4$	$\tau_5$	$\tau_6$	$\tau_7$	$\Delta E$	Reference
(I) Cycloheptane										
TC	$C_2$	-39.1	88.1	-72.3	54.3	-72.3	88.1	-39.1	0.0	(a)
C	$C_s$	63.8	-83.5	66.1	0.0	-66.1	83.5	-63.8	5.9	(a)
TB	$C_2$	45.4	-64.4	-17.9	74.6	-17.9	-64.4	45.4	10.0	(a)
B	$C_s$	-57.5	-30.9	69.0	0.0	-69.9	30.9	57.5	11.3	(a)
(V) Cycloheptene										
$C^4$	$C_s$	67.6	-74.9	58.5	0.0	-58.5	74.9	-67.6	0.0	(b)
1-T	$C_2$	-43.1	77.9	-27.9	-7.8	-27.9	77.9	-43.1	1.8	(b)
1-A	1	86.7	-46.6	-10.4	-4.8	63.2	-49.0	-30.0	11.1	(b)
(VI) Cyclohepta-1,3-diene										
1,3-E	$C_s$	70.5	-30.4	1.4	0.0	-1.4	30.4	-70.5	0.0	(c)
1,3-T	$C_2$	40.6	-71.4	3.2	46.4	3.2	-71.4	40.6	10.5	(c)
1,3-T	$C_2$	40.0	-73.8	8.3	38.6	8.3	-73.8	40.0	7.6	(d)
1,3-A	1	-49.9	1.1	2.2	22.7	-1.8	-57.9	85.8	3.4	(d)
(VII) Cyclohepta-1,4-diene										
1,4-A1	1	64.7	-0.4	-69.0	56.1	-4.1	0.5	-49.0	0.0	(d)
1,4-A2	1	0.0	0.0	44.7	-80.0	57.8	1.6	-24.4	3.8	(d)
1,4-T	$C_2$	-10.3	1.7	49.1	-74.9	49.1	1.7	-10.3	4.6	(c)
1,4-C	$C_s$	-70.2	4.2	-46.0	-0.1	46.0	-4.2	70.2	12.6	(d)
1,4-C	$C_s$	-60.1	9.2	-22.1	0.0	22.1	-9.2	60.1	42.8	(c)
(VIII) Cyclohepta-1,3,5-triene										
1,3,5-B	$C_s$	-62.5	-4.9	32.7	0.0	-32.7	4.9	62.5	0.0	(c)

References: (a) Hendrickson (1967); (b) Ermer & Lifson (1973); (c) Saebo & Boggs (1982); (d) Favini, Maggi & Todeschini (1983).

(I). This gives rise to four possible symmetry-independent three-dimensional conformations for each of the canonical subclasses C, TC, B, TB. In part II (Allen, Howard, Pitchford & Vinter, 1994), we identified these different conformations in terms of the ring bond (1 to 4) that is bisected by the  $C_s$ - or  $C_2$ -symmetry element. This bond is the simplest to identify in a fragment-by-fragment torsion-angle listing since, for conformations that are reasonably close to  $C_s$  or  $C_2$  symmetry, it exhibits a clearly unique numerical value. For the  $C_2$ , TC and TB forms, the notations  $TC^1$ – $TC^4$ ,  $TB^1$ – $TB^4$  identify positive values of this unique angle with inverses denoted by  $TC^{\bar{1}}$ – $TC^{\bar{4}}$ ,  $TB^{\bar{1}}$ – $TB^{\bar{4}}$ . The unique angle is zero for the  $C_s$ -symmetric C and B forms and the assignment of positive or negative identifiers is made on the basis of the preceding torsion angle in the list. Because of the symmetry-independence of the various conformers of (II)–(IV) along the C/TC and B/TB pathways, different energy barriers can, and do, exist between them that are sufficiently high to prevent pseudorotation and restrict the observed conformations to narrow ranges of the full pseudorotation itinerary (Allen, Howard, Pitchford & Vinter, 1994).

The *endo*-unsaturated substructures (V)–(VIII) represent the imposition of, respectively, 1,2,2 and 3 strong torsional constraints on the cycloheptane conformation. Thus, despite the  $C_2$ , topological symme-

try in each case, the conformational flexibility of these fragments is severely reduced by comparison with their single-bonded analogues. Cycloheptene (V) was originally assumed to exist in the  $C^4$  or  $B^4$  conformations (Pauncz & Ginsburg, 1960; Eliel, Allinger, Morrison & Angyal, 1965) but a variety of spectroscopic data (see Allinger & Sprague, 1972; Ermer & Lifson, 1973, and references reviewed therein) were interpreted in terms of a  $C^4$  chair as the predominant low-energy form. This result was supported by force-field calculations (Allinger & Sprague, 1972; Ermer & Lifson, 1973), but both sets of authors cite a  $C_2$  symmetric twist form (denoted as 1-T in Table 1) at *ca* 2.1  $\text{kJ mol}^{-1}$  higher in energy. Comparison of published torsion angles (Table 1) shows that this  $C_2$  form corresponds to one of the symmetric intermediates involved in a TC–TB interconversion of (I) (Hendrickson, 1967). Ermer & Lifson (1973) cite an asymmetric and heavily distorted boat (1-A in Table 1 at 11.1  $\text{kJ mol}^{-1}$ ) as the next-lowest energy minimum, whilst Allinger & Sprague (1972) cite instead the  $B^4$  boat at 14.2  $\text{kJ mol}^{-1}$ .

The 1,3-diene (VI) has been studied using a variety of experimental and theoretical methods. Electron diffraction (Chiang & Bauer, 1966; Hagen & Traetteberg, 1972) and microwave data (Avirah, Molloy & Cook, 1979) were interpreted unequivocally in terms of a conformation having  $C_s$  symmetry with all atoms except C1 (Fig. 1) coplanar. However, Crews

(1971) proposed a distorted twist conformation of  $C_2$  symmetry on the basis of NMR data. Molecular mechanics calculations (Burkert & Allinger, 1982; Favini, Maggi & Todeschini, 1983) initially indicated that  $C_s$  and  $C_2$  conformers were almost isoenergetic, but that more refined calculations showed a  $\sim 7$ – $8$  kJ mol $^{-1}$  preference for the  $C_s$  form, in agreement with the gas-phase experiments. This result was reproduced by the *ab initio* calculations of Saebo & Boggs (1982). Representative torsional data for the  $C_s$  'envelope' conformation (denoted 1,3-E) and the  $C_2$  twist form (1,3-T) are given in Table 1, together with data for an asymmetric form (1,3-A) identified uniquely by Favini, Maggi & Todeschini (1983). Comparison of the results for the 1,3-E and 1,3-T forms with Hendrickson's (1967) data shows them to correspond, respectively, to the half-boat and twist-chair/twist-boat intermediates of cycloheptane (I).

There appears to be no experimental data available for the 1,4-diene (VII). In this case, a flattened  $C_2$  twist form (1,4-T) is calculated to be energetically preferred over a flattened  $C_s$  chair form (1,4-C), although the energy difference varies considerably from 12.6 (force-field: Favini, Maggi & Todeschini, 1983) to 42.8 kJ mol $^{-1}$  (*ab initio*: Saebo & Boggs, 1982). These symmetric forms were the only ones considered in the *ab initio* study, but the force-field calculations also revealed two diplanar and asymmetric conformers (1,4-A1 and 1,4-A2 in Table 1), which are lower in energy than the preferred symmetric form, 1,4-T.

The 1,3,5-triene (VIII) is shown to occur as a flattened boat by electron diffraction (Traetteberg, 1964), microwave spectroscopy (Butcher, 1965) and by two *ab initio* studies (Saebo & Boggs, 1982; Schulman, Disch & Sabio, 1982). Typical torsion angles for this conformation, denoted 1,3,5-B, are given in Table 1.

The theoretical torsional data of Table 1 represent a useful basis against which to compare the experimental crystallographic results for (V)–(VII). However, it must be remembered that the crystallographic fragments are drawn from a wide variety of chemical environments, and that we have chosen to regard benzo-fusion bonds as 'double bonds' for the purposes of this study. The likely differences in energetic behaviour between the benzo compounds and their ene-counterparts is discussed in some detail by Allinger & Sprague (1972). The effects of benzo-fusion and of more general environment effects will be highlighted in later sections of this paper.

### Methodology

Version 4.5 (January 1992) of the Cambridge Structural Database System was used throughout for sub-structure search, coordinate retrieval and data

analysis, using the programs *QUEST* and *GSTAT* (Allen *et al.*, 1991). Searches were carried out for fragments (V)–(VIII) of Fig. 1, in which the double bonds indicate either formal double or aromatic bonding (bond type = 2 or 5 in the CSD representations). Atoms not involved in multiple bonds were required to be  $sp^3$  hybrids. Searches were further constrained by using the CSD bit-screen mechanism (Cambridge Structural Database, 1992) to locate entries with (a) atomic coordinates available, (b) no residual numerical errors following CSD check procedures, (c) no reported disorder in the crystal structure, (d) a crystallographic  $R \leq 0.12$ , (e) classified as an 'organic' compound according to CSD definitions, and (f) containing no bridged or highly complex ring systems (SCREEN – 620, – 622) as described in part I (Allen, Howard & Pitchford, 1993). Search results are summarized in Table 2 and CSD reftcodes for all hits are in Table 3; full literature citations have been deposited.\*

\* Full literature citations have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71753 (9 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

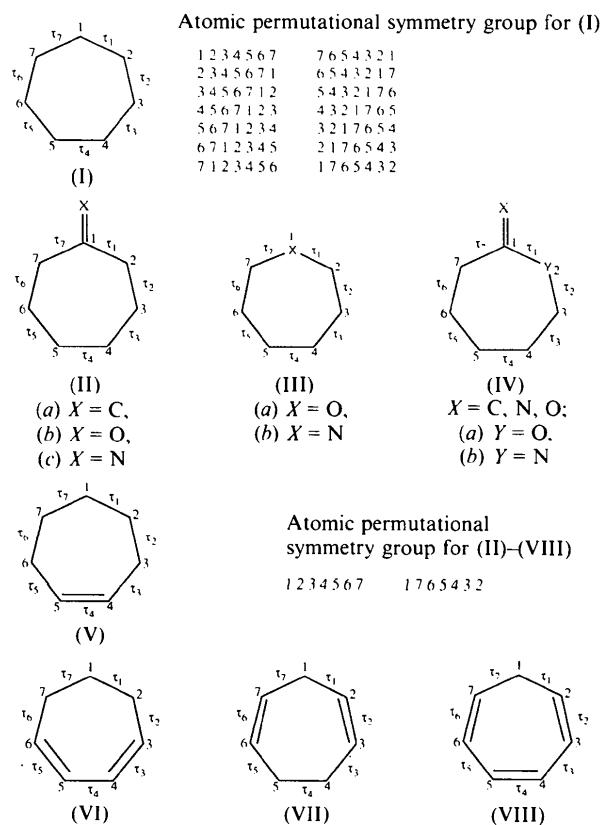


Fig. 1. Chemical substructures (I)–(VIII) and relevant atomic permutational symmetry groups.

Table 2. Search results for substructures (V)–(VIII) of Fig. 1

$N_c$  is the number of CSD entries retrieved,  $N_f$  is the number of chemically independent fragments located in those entries and  $R_{max}$  is the minimum  $R$  factor in each data set. Clustering criteria used in the Jarvis–Patrick analysis are also given.

Substructure	Data set composition			Clustering criteria			
	$N_c$	$N_f$	$R_{max}$	$n$	$K_{NN}$	$K_{JP}$	$D_{max}$
(V)	67	74	0.120	1	12	6	0.08
(VI)	18	20	0.080	2	8	4	0.08
(VII)	11	13	0.094	2	4	2	0.10
(VIII)	29	33	0.088	1	10	5	0.10

Table 3. Refcodes of all entries in each data set

Data set (V) (cycloheptenes)			
AESTME10	CU DTOK	GESJOD	ONYCHL
AHBCPB	CU DTUQ	GESJUJ	PARMOL10
ARTEGA	CU KJIB	GIHCEF	PLENAC
BAHHAT	DAZPID	GIPCAJ	PORTSH10
BEBPED	DEFSEM	INSERR10	PSVALB10
BERLAN	DEFSIQ	IVLBIN	SACSEU
BIHNOV	DIDHIH	JAHHIJ	SEBBUW
BRGAIL10	DOLTAC10	JEXJOL	TAKROM
CAPLAG	DORKIE	KAHDUS	TCTDOL
CAXJUG	DOZMOU	KAMBAB	VEBNUL
CAZXIK	ERGYZN	KEHFIM	VEGTUW
CHEBAR	FICUP	LACTUC10	VEKBUI
CILXAW	FUCVII	MEOCHP	VEZPEV
CILXEA	FUPYAQ	MXSERR10	
CIWCAM10	GASCHA	NPHRBL10	
CIWCEQ10	GAYDUF	OCMETD01	
COVPAE	GAYFAN	OCMETD10	
CUDSUP	GEJYEZ	OHDLST	
Data set (VI) (cyclohepta-1,3-dienes)			
CAJCOF	DUTGAA	KENLUK	SICTED
CEYXAF	EXPOCP	MELOCH	VEFCAK
CHMHAZ	GELWOJ	NACCOL	XMOHAZ
DMITCL10	HCMCHP	PBOPOS	
DOYHUU	ISCHOL	SATGUP	
Data set (VII) (cyclohepta-1,4-dienes)			
BERWOK	CIKVIB	JASGIT	JIDCUU
CHSBHA	DPHTRP	JIDCII	SAHROI
CIKVEX	HBZCHP	JIDCOO	
Data set (VIII) (cyclohepta-1,3,5-trienes)			
BAYRIC	CMCHBZ	DMDPCH	HPHAZO
BAYROI	CPHHTZ	DOZSIU	KEXNIK
BEDWAI	DAJXAN	DUGWOR	MTBCHO
BIDTEN	DALXOD	FAPMOY	TUJBRP10
BSPDOD10	DELCUS	FEKTEU	VAMKAV
BUKTAC	DELDAZ	FUNCOG	
BUZTUL	DIGGEF	GIJXIG	
CIDCEX	DIGGIJ	HPHAZL	

The program *GSTAT* (Murray-Rust & Raftery, 1985a,b; Allen *et al.*, 1991) was used for the calculation and analysis of the following parameters (using the atom and bond enumerations of Fig. 1): the intra-annular torsion angles  $\tau_1$ – $\tau_7$ ; the puckering parameters  $q_2, \varphi_2, q_3, \varphi_3$  (Cremer & Pople, 1975) and their Cartesian equivalents  $CP1 = q_3 \sin \varphi_3$ ,  $CP2 = q_3 \cos \varphi_3$  (mapping C/TC conformers) and  $CP3 = q_2 \sin \varphi_2$ ,  $CP4 = q_2 \cos \varphi_2$  (mapping B/TB conformers); the BPRS coordinates  $\theta, \rho$  (Bocian, Pickett, Rounds & Strauss, 1975) were calculated from  $q_2, q_3$  as described in part II (Allen, Howard, Pitchford &

Vinter, 1994). Fragments (V)–(VIII) have  $C_{2v}$  topological symmetry and raw data sets were symmetry expanded by the use of the atomic permutational symmetry operators of Fig. 1 together with the inversion operator to yield four isomers per fragment. Conformational classifications using the raw torsional descriptors were performed using the symmetry-modified cluster-analysis module of *GSTAT* (Allen, Doyle & Taylor, 1991b).

## Conformational mapping

### BPRS coordinate plots

Histograms of the BPRS  $\theta$  coordinate (Figs. 2a–2d) provide a rapid visual overview of the conformational complexity of fragments (V)–(VIII). For the cycloheptene (Fig. 2a) the larger peak occurs in the C/TC area ( $\theta > 40^\circ$ ). A smaller grouping is observed at  $\theta = 5$ – $35^\circ$  spanning the area of conformational space between the C/TC forms and the true B/TB conformers at  $\theta = 0^\circ$ . The  $\varphi_2$ – $\varphi_3$  plot for instances of (V) having  $\theta > 40^\circ$  (Fig. 3) shows isolated peaks at  $\varphi_2, \varphi_3 = \pi, 0; 0, \pi; \pi, 2\pi; 2\pi, \pi$ , corresponding to the four permutational isomers and enantiomers of the  $C^4$  conformation. The energy data of Table 1 are in agreement with these observations. For the dienes (VI) and (VII) and the triene (VIII), which have additional conformational constraints, all conformers are intermediate between the chair-like and boat-like conformations with  $\theta$  values in the 5– $35^\circ$  range (Figs. 2b–2d).

### Principal component (PC) and Cremer–Pople (CP) plots

Principal component analysis of symmetry-expanded torsional data sets was an important feature in the conformational mapping of cycloheptanes (Allen, Howard & Pitchford, 1993). Here the PC's occurred in two sets of degenerate pairs, PC1, PC2 mapping the C/TC conformers and PC3, PC4 mapping the B/TB conformers. With decreasing fragment symmetry, the degeneracy disappears and PC coordinates related to directions of maximum variance are less and less easy to interpret in relation to the mutually perpendicular toroidal pseudorotational surfaces of the parent ring (I). This is due to axial rotations within the four-dimensional hyperspace that reflect the reduced symmetry and a greater variability in chair-like/boat-like character than exists for the parent ring (I). For fragments (V)–(VIII) we report that, as expected, four PC's account for >99.9% of total variance in all cases. The PC's occur in pairs as PC1, PC2 and PC3, PC4 where, for each fragment, one member of each pair maps a conformer of  $C_2$  symmetry and the second member maps a conformer of  $C_s$  symmetry.

Plots based upon CP coordinates for (V)–(VIII) are, however, directly comparable to those for the parent cycloheptane (I), since they refer to a consistent axial frame defining the hyperspace. Thus, the CP1,CP2 plot for cycloheptene (V) in Fig. 4(a) shows only two peaks on the C/TC pseudorotation itinerary corresponding to the  $C^4, C^4$  forms. The plot also shows central density due to a number of boat-like conformers and a pair of (symmetry-related) peaks along the CP1 axis representing conformations that are intermediate between the  $TC^4$  and  $TB^4$  forms. By comparison, the CP1,CP2 plot for cyclohepta-1,3-diene (VI) (Fig. 4b) lacks any density on the C/TC circular pathway and shows only the central boat-like region and some  $TC^4/TB^4$  intermediates parallel to the CP1 direction. Plots similar to Fig. 4(b) are obtained for (VII) and (VIII) and are not shown here.

In Table 5 we present orthogonal coordinates, referred to molecular axes, for the most representative fragment (m.r.f.) of each major ( $N_p \geq 4$ ) cluster. The m.r.f. is that fragment whose torsion angles

place it closest to the centroid of a given cluster (Allen, Doyle & Taylor, 1991b) and the coordinates of Table 5 have applications in computational or crystallographic procedures. The conformations represented by these coordinates, and discussed in more detail below, are illustrated graphically in Fig. 5.

### Conformational classification

#### Overview

Results of symmetry-modified Jarvis–Patrick (1973) clustering applied to torsional data sets ( $\tau_1$ – $\tau_7$ ) are collected in Table 4 for fragments (V)–(VIII). Mean torsion angles are given for each discrete cluster having a population  $N_p \geq 3$  fragments and the appropriate conformational descriptor from Table 1 is assigned in each case. The Jarvis–Patrick clustering criteria  $n$ ,  $K_{NN}$ ,  $K_{JP}$  and  $D_{max}$  (Allen, Doyle & Taylor, 1991a,b) that were used to arrive at chemically sensible clustering are reported in Table 2. For the smaller data sets (VI)–(VIII) some experi-

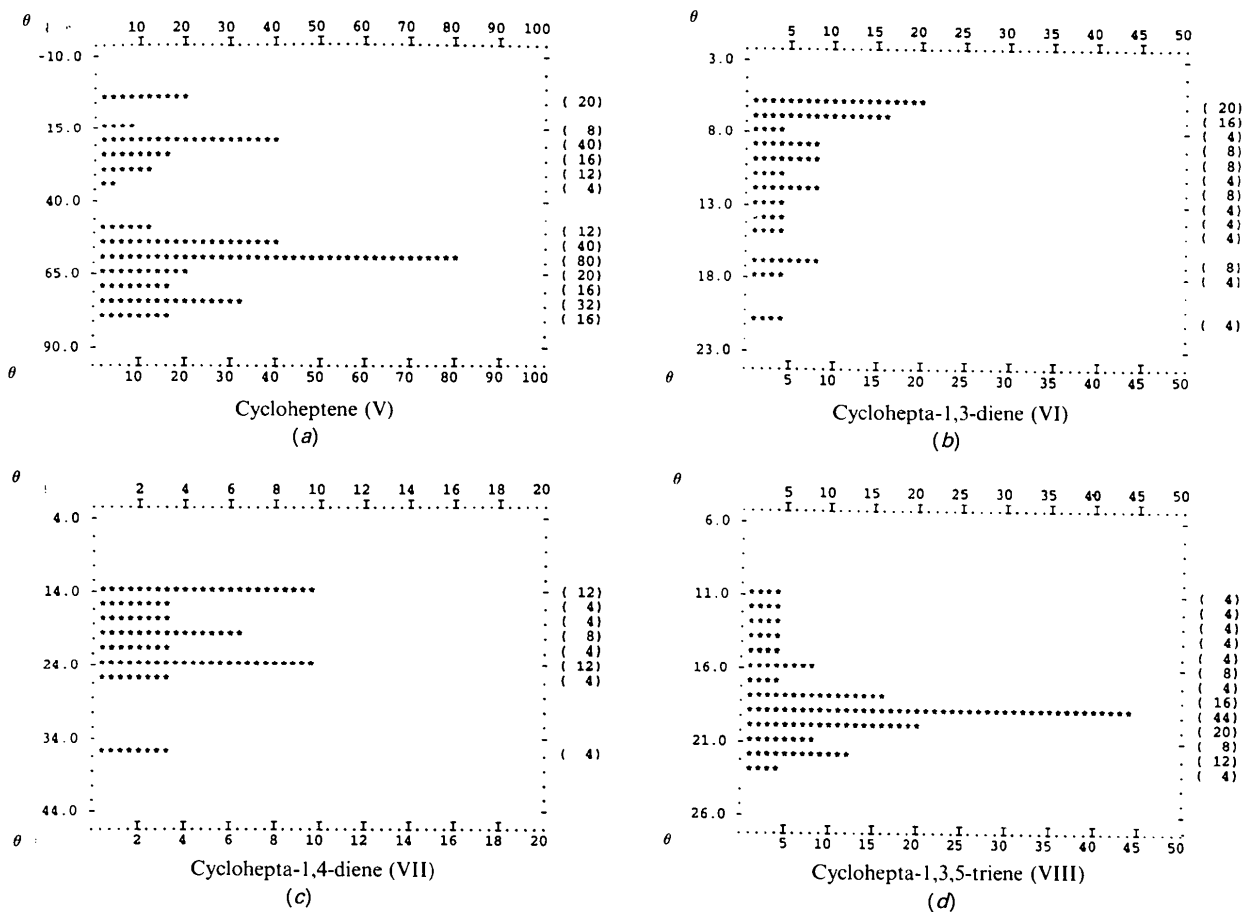


Fig. 2. Histograms of the BPRS  $\theta$  coordinate for the fragments (V)–(VIII).



Table 5. Orthogonal coordinates of the most representative fragments cited in Table 4 and referred to molecular axes

Data set	x	y	z	x	y	z
(V)	OCMETD01 1-T			SACSEU C <sup>4</sup>		
	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
	1.52084	0.00000	0.00000	1.54759	0.00000	0.00000
	2.25363	1.35251	0.00000	2.14699	1.42841	0.00000
	2.05086	1.99874	1.34347	2.02893	2.08859	1.36029
	1.15703	1.82133	2.32094	0.91667	2.30095	2.00808
	-0.18406	1.12689	2.37713	-0.48893	1.95531	1.61368
	-0.70728	0.96814	0.93829	-0.68913	0.46958	1.29907
(VI)	SATGUP 1,3-C <sub>2</sub>					
	0.00000	0.00000	0.00000			
	1.52821	0.00000	0.00000			
	2.12704	1.39586	0.00000			
	2.08799	2.16341	-1.15902			
	1.40616	1.63418	-2.37757			
	0.10876	1.10819	-2.28008			
	-0.57723	1.05769	-0.94417			
(VII)	CIKVEX 1,4-A1					
	0.00000	0.00000	0.00000			
	1.54819	0.00000	0.00000			
	2.35564	1.14628	0.00000			
	1.92899	2.60423	0.02838			
	0.51747	2.98543	-0.35987			
	-0.48175	2.45466	0.64287			
	-0.64526	1.08698	0.86750			
(VIII)	BAYRIC 1,3,5-B			CPHHTZ 1,3,5-B		
	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
	1.51495	0.00000	0.00000	1.49304	0.00000	0.00000
	2.22856	1.13437	0.00000	2.11364	1.20010	0.00000
	1.69860	2.47892	0.15652	1.44514	2.43489	0.31433
	0.61721	2.81712	0.87958	0.38560	2.59681	-1.14237
	-0.24666	1.91095	1.59783	-0.27326	1.54860	-1.86009
	-0.49359	0.64322	1.26432	-0.38672	0.29023	-1.40597
	KEXNIK 1,3,5-B					
	0.00000	0.00000	0.00000			
	1.49886	0.00000	0.00000			
	2.19122	1.21716	0.00000			
	1.46623	2.50230	0.09809			
	0.34427	2.82188	-0.59893			
	-0.34458	1.93904	-1.55800			
	-0.50078	0.56560	-1.30264			

( $P\bar{1}$ , room-temperature data); OCMETD10: Irngar-tinger & Nixdorf, 1988 ( $P\bar{1}$ , data at 100 K)]; (XI) MEOCHP: Jendralla, 1980]. However, (X) is also observed in a flattened C<sup>4</sup> conformation in a mono-clinic ( $P2_1/n$ ) polymorph, while the cycloheptene ring in (XII) (TCTDOL: Courtois, Protas, Fixari & Brunet, 1975) also adopts the lower energy chair form. The chair form of (X) is associated with a planar cyclobutadiene, while the 1-T form is associated with a folded four-membered ring.

The calculations reported by Allinger & Sprague (1972) and by Burkert & Allinger (1982) would indicate that the C<sup>4</sup> seven-membered ring conformation in benzocycloheptenes is more energetically favoured (with respect to 1-T) than is the case for the parent (V). Eight of the ten instances of benzo-cycloheptene in our data set are, indeed, highly symmetrical C<sup>4</sup> conformers; the other two instances are distorted by three-ring fusion.

## Cyclohepta-1,3-diene (VI)

This small data set of 20 fragments is dominated by a single cluster comprising 13 instances of the 1,3-T conformation of C<sub>2</sub> symmetry. As with (V), all instances are very close to the ideal symmetry and coalescence of symmetry-related clusters occurs within  $MULT = 1.0$  (Allen & Taylor, 1991). Six of the remaining seven singletons have small-ring fusion (three- and five-membered rings) which generate distorted variants of the 1,3,5-B conformation typical of (VIII) (see Table 1). It is interesting that even a fused and saturated cyclopentane ring consistently has this effect. Only one fragment, from structure (XIII) (VEFCAK: Hashmi, Polborn & Sziemiec, 1989), adopts the C<sub>v</sub> 1,3-E conformation (Fig. 5b) that is observed in gas-phase experiments and which is consistently predicted to be the global minimum for (VI) (see Table 1). Given the fusion of the four-membered ring at the =C—C= single bond, it would be reasonable to regard this 1,3-E conformation as being forced by the local chemical constraints.

At first sight, then, it would appear that the predominance of the C<sub>2</sub> (1,3-T) form of (VI) is at variance not only with the energy calculations, but also with the electron-diffraction (Chiang & Bauer, 1966; Hagen & Traetteberg, 1972) and microwave data (Avirah, Molloy & Cook, 1979). Indeed, the C<sub>2</sub> con-

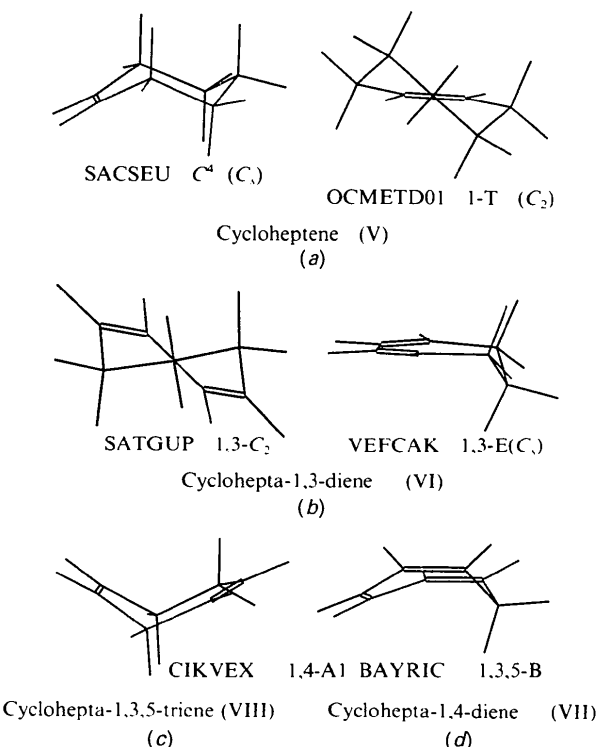


Fig. 5. The most representative fragments for the major conformational subgroups of fragments (V)-(VIII). The 1,3-C<sub>v</sub> form of (VI) is included for comparison purposes (see text).



formation might have been expected by analogy to the structures of 1,3-cyclohexadiene (Traetteberg, 1970) and of 1,3-cyclooctadiene (Oberhammer & Bauer, 1969; Traetteberg, 1968) which show  $C=C-C=C$  torsion angles of 18 and 38°, respectively. However, examination of the chemical environment in the 13 structures that exhibit the 1,3-T ( $C_2$ ) conformation for (VI) show that all of these instances are unrepresentative of the free parent molecule. In 10 of these structures, one (7) or both (3) of the 1,3-double bonds arise from benzo-fusion and in all seven mono-fused rings the ethylenic double bond is further conjugated to  $-C=C$ ,  $-C=O$  or phenyl substituents. In the three remaining cases, one (2) or both (1) of the ethylenic double bonds are conjugated to  $-C=C$  or  $-C=O$  groups.

We have investigated some relevant features of the potential energy hypersurface for the parent (VI) and the mono-benzo fragment (XIV) using three different force-fields in the program systems: (1) the *PCRNGMIN* procedures in *COSMIC90* (Morley *et al.*, 1991; Allen, Howard, Pitchford & Vinter, 1994); (2) the *MM2* force-field within the *CaChe* system (Tektronix Inc., 1990) and (3) the *DISCOVER* module of *INSIGHT* 2.0 (Biosym Technologies, 1992). For the parent (VI), all three systems show the 1,3-E ( $C_s$ ) form as a global minimum with the 1,3-T ( $C_2$ ) form at a consistently higher energy. The  $\Delta E(C_2-C_s)$  values ( $\text{kJ mol}^{-1}$ ) are 6.7 (*COSMIC*), 4.8 (*CaChe*) and 3.4 (*INSIGHT*). The results were obtained using a typical  $C_2$  conformer as the starting point. A similar treatment of a typical example of (XIV) ( $C_2$  starting conformation of the seven-ring) using both *CaChe* and *INSIGHT* retains the  $C_2$  conformation as a global minimum and with torsion angles which differ very little from the X-ray mean values listed in Table 4. Thus, the *ca* 45° twist about the  $C=C-C=C$  single bond minimizes  $H\cdots H$  interactions in the case of benzo-fusion, a point which is discussed at some length by Allinger & Sprague (1972) with respect to conformational differences between cycloheptene (V) and its benzo-derivative.

#### *Cyclohepta-1,4-diene* (VII)

This very limited data set of 13 fragments proved particularly difficult to analyse using automated clustering methods. The Jarvis-Patrick analysis with  $K_{NN} = 4$  and  $K_{JP} = 2$  yielded a coherent grouping of eight fragments (Table 4) having the asymmetric 1,4-A1 conformation identified by Favini, Maggi & Todeschini (1983) as the minimum-energy form. Two further singleton fragments have significantly flattened versions of this same conformation. All but one of these ten 1,4-A1 conformers are simple derivatives of the 10,11-dihydro-5*H*-dibenzo[*a,d*]cycloheptene substructure (XV). Two further singletons

are effectively 1,3,5-trienes due to cyclopropyl fusion (and have the appropriate 1,3,5-B conformation of Table 1). This leaves a single example of the second asymmetric form (1,4-A2) of Favini, Maggi & Todeschini (1983) in the unique substructure (XVI) (JASGIT: Tochtermann *et al.*, 1989).

#### *Cyclohepta-1,3,5-triene* (VIII)

All 33 examples of the rigid ring (VIII) exhibit the 1,3,5-B ( $C_s$ ) conformation of Table 1. The Jarvis-Patrick analysis, run with a number of  $K_{NN}$  and  $K_{JP}$  variants, consistently dissects the multivariate torsional distribution into three subgroups (Table 4) which are highly coherent within themselves. Both clusters 1 ( $N_p = 25$ ) and 2 ( $N_p = 5$ ) are highly symmetrical and coalesce with their symmetry-related counterparts within  $MULT = 1.0$  (Allen & Taylor, 1991). The mean torsion angles for the largest cluster 1 are very close to the calculated values of Saebø & Boggs (1982). Cluster 2 differs from cluster 1 primarily in the value of  $\tau_3 (= \tau_5)$ . This angle ranges from 20.1 to 35.5° in cluster 1, and from 37.6 to 51.6° in cluster 2. Cluster 3 differs from cluster 1 in having *ca* 11° torsion angles about the 'outer' double bonds. Whilst these dissections of the data are a mathematical nicety, there are no obvious chemical constraints that can be correlated with the individual groupings.

### Discussion

One of the primary aims of this series of papers is to confirm that  $N_p$ -ordered classifications of fragment conformations derived from crystallographic observations are a reliable, albeit *qualitative*, guide to the relative energies of the different conformers. This has been true for the seven-membered ring fragments discussed in parts I and II (Allen, Howard & Pitchford, 1993; Allen, Howard, Pitchford & Vinter, 1994). We remarked there that the fragments studied generally exhibited a wide variety of substitution patterns, *i.e.* they were drawn from reasonably random chemical environments. However, we, and others previously (Bürgi & Dunitz, 1988), have also noted the pitfalls involved in (a) the assumption that chemical environments can be regarded as truly random, followed by (b) the use of conformational population ratios to obtain *quantitative* estimates of relative energies. These pitfalls are starkly illustrated in this paper by the analysis of the crystallographic observations of the cyclohepta-1,3-diene fragment (VI), where any subjective criteria of 'reasonable' randomness are palpably absent. Here, even the qualitative correlation of population ratios with relative energies for parent (VI) are grossly misleading in the absence of a careful study of local chemical environments. Once this is done, the basic thesis of this series of papers remains intact.

We thank Dr Olga Kennard FRS for her interest and encouragement of this work.

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## SHORT COMMUNICATIONS

*Acta Cryst.* (1994). **B50**, 404

### Relationship between the structures of ferroelectric $\text{Pb}_5\text{Cr}_3\text{F}_{19}$ and antiferroelectric $\text{Pb}_5\text{Al}_3\text{F}_{19}$ at 295 K and the phase III–phase IV transition in $\text{Pb}_5\text{Al}_3\text{F}_{19}$ on cooling to about 110 K. Erratum.

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(Received 28 March 1994)

#### Abstract

Six bond-length designations were omitted partially or completely from Table 3 on p. 140 of the paper by Andriamampinanina, Gravereau, Ravez & Abrahams [*Acta Cryst.* (1994), **B50**, 135–141]. The missing bond lengths (Å) are:

Al1—F3 ( $\times 4$ )	1.79(3)	Al2—F4 <sup>21</sup> ( $\times 4$ )	1.77(6)
Al3—F7 ( $\times 2$ )	1.80(3)	Pb1—F4 <sup>3</sup>	2.63(4)
Al3—F6 <sup>17</sup> ( $\times 2$ )	1.81(3)	Pb2—F12	2.61(4)

In addition, on p. 138, column 2, line 2 of the final paragraph should read: 'dipole below  $T_c$  that becomes reversed in sense', and on p. 140, column 1, line 4 of the final paragraph should be corrected to: 'pair of  $6(sp)^2$  electrons with the  $M^3F_6$  octahedra'.

All relevant information is given in the *Abstract*.