

## CONFORMATIONS OF CYCLOBUTANE

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**Abstract**—The literature concerning the structures of compounds containing saturated, 4-carbon rings is reviewed critically, and the variety of conformations (dihedral angles of  $0^\circ$  to  $30^\circ \pm 6^\circ$ ) of the cyclobutane ring are tabulated and discussed.

## INTRODUCTION

The structures of cyclobutane and substituted cyclobutanes have been extensively investigated using numerous physical methods and theoretical calculations. Cyclobutane itself has been studied from a structural point of view using electron diffraction,<sup>1,2</sup> IR,<sup>3-5</sup> near-IR,<sup>6</sup> Raman,<sup>3,5,7</sup> NMR,<sup>8</sup> CNDO/2 calculations,<sup>9</sup> *ab initio* calculations,<sup>10</sup> and floating spherical Gaussian orbital (FSGO) calculations.<sup>11</sup> As summarized in Table 1, these studies have shown cyclobutane to possess a puckered structure, with a dihedral angle of  $ca\ 30^\circ \pm 6^\circ$  and a barrier to inversion<sup>5</sup> of  $ca\ 1.4$  kcal/mol.

A dichotomy of results has been obtained from

electron diffraction,<sup>12-14</sup> X-ray diffraction,<sup>15-33</sup> microwave spectroscopy,<sup>34,35</sup> and dipole moment studies<sup>36,37</sup> of substituted cyclobutanes (excluding fused rings). Here the cyclobutane rings are either crystallographically required to be planar or are non-planar with a dihedral angle of  $ca\ 26^\circ \pm 3^\circ$  (Table 2). Only molecules that may possess a center of inversion have been found to have planar cyclobutane rings. Interestingly, there is no mid-ground; there have been no structures reported with dihedral angles in the range  $1-18^\circ$ . This contrasts to the variety of dihedral angles observed in fused ring systems including those which do not involve a transition metal (Table 3),<sup>38-51</sup> and those which do (Table 4).<sup>52-61</sup>

The C-C bond lengths have the following mean values:  $1.549\ \text{\AA}$  for the cyclobutane studies listed in Table 1,  $1.544(3)\ \text{\AA}$  for substituted cyclobutanes (Table 2),  $1.551(3)\ \text{\AA}$  for organic fused cyclobutanes (Table 3), and  $1.552(2)\ \text{\AA}$  for organometallic fused cyclobutanes (Table 4). For compounds in Table 3, the C-C bond that is common to two rings is  $ca\ 0.024(4)\ \text{\AA}$  shorter than the C-C bond that is part of only one 4-membered ring; there is no difference in length for compounds in Table 4. The average C-C bond length for the 119 individual determinations by X-ray diffraction methods is  $1.550(2)\ \text{\AA}$ . This

†The weighted mean of  $N$  distances  $d_i$  with ESD  $\sigma_i$  is defined as

$$\frac{\sum_{i=1}^N d_i/\sigma_i^2}{\sum_{i=1}^N 1/\sigma_i^2}$$

and the ESD of the mean  $\bar{d}$  is given by

$$\left[ \frac{\sum_{i=1}^N \frac{(d_i - \bar{d})^2}{\sigma_i^2}}{(N-1) \sum_{i=1}^N \frac{1}{\sigma_i^2}} \right]^{1/2}$$

Table 1. Data on cyclobutane

Technique	C-C, Å	C-H, Å	HCH, deg	Dihedral angle, deg	Methylene rocking angle, deg	Barrier height, kcal/mole	Ref
Electron diffraction	$1.568 \pm 0.020$	$1.098 \pm 0.04$	$114 \pm 8$	$20(+10, -20)$			1
Electron diffraction	$1.548 \pm 0.003$	$1.092 \pm 0.01$	110	35			2
IR, Raman						1.14	3
IR				$37 \pm 6$			4
IR				$35 \pm 5$		1.44	5
near-IR				$34 \pm 0.5$		1.28	6
Raman	$1.558 \pm 0.003$						7
NMR	1.548	1.133	108.1	27	4		8
CNDO/2				20	3	0.31	9
<i>ab initio</i>	1.550	1.092	108.2	15	2.4	0.06	10
FSGO	1.524	1.116	110	32	7	3.5	11

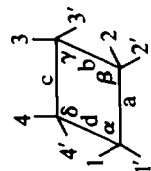
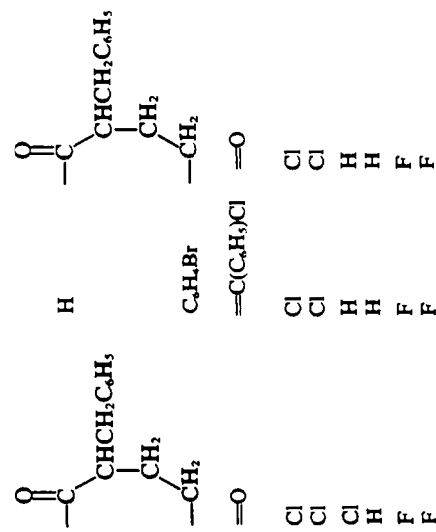



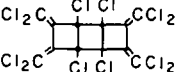
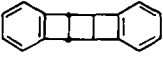
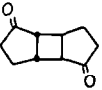



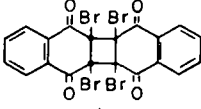
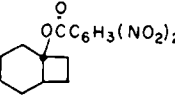
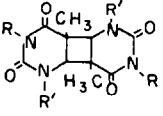
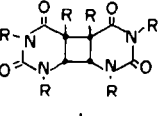
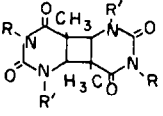
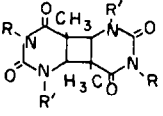
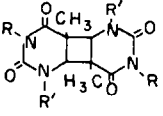
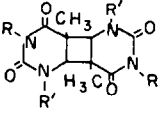
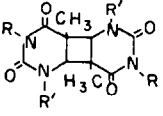
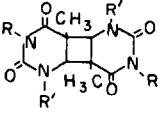
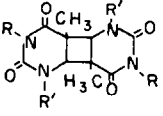
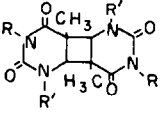
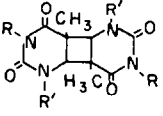
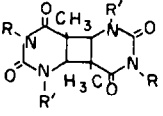
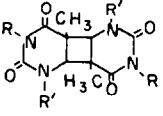
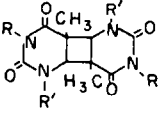
Table 2. Structural data for substituted cyclobutane compounds not involving fused rings

1	1'	2	2'	3	3'	4	4'	a	b	c	d	Dihedral Angle (Deg)	Ref
								$\alpha$	$\beta$	$\gamma$	$\delta$		
COOH		H	H	H	H	H	H	1.567(6)	1.552(6)			0	15
H		H	H	COOH	COOH	H	H	90.5(3)	89.5(3)			0	16
COO <sup>-</sup>		H	H	H	H	H	1.560(9)	1.555(10)				0	
H		H	H	COO <sup>-</sup>	COO <sup>-</sup>	H	H	90.7(5)	89.3(5)			0	17
COOCH <sub>3</sub>		H	H	H	H	COOCH <sub>3</sub>	COOCH <sub>3</sub>	1.541(4)	1.572(5)			0	
H		COOCH <sub>3</sub>	COOCH <sub>3</sub>	COOCH <sub>3</sub>	COOCH <sub>3</sub>	H	H	91.0(3)	89.0(3)			0	18
CN		H	H	H	H	CN	CN	1.547(3)	1.561(3)			0	
H		CN	CN	CN	CN	H	H	90.2(2)	89.8(2)			0	19, 20
C <sub>6</sub> H <sub>5</sub>		H	H	H	H	C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	1.566(15)	1.573(15)			0	
H		C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	H	H	90.6(10)	89.4(10)			0	21
OH		CH <sub>3</sub>	CH <sub>3</sub>	H	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	1.544(5)	1.545(5)			0	
H		CH <sub>3</sub>	CH <sub>3</sub>	OH	OH	CH <sub>3</sub>	CH <sub>3</sub>	91.2	88.8			0	22
OH		OH	OH	OH	OH	OH	OH	1.562(4)	1.564(4)			0	
OH		OH	OH	OH	OH	OH	OH	89.8(2)	90.2(2)			0	23
=O		CH <sub>3</sub>	CH <sub>3</sub>	=O	=O	CH <sub>3</sub>	CH <sub>3</sub>	1.58(2)	1.54(2)			0	
		CH <sub>3</sub>	CH <sub>3</sub>			CH <sub>3</sub>	CH <sub>3</sub>	89.5	90.5			0	24
		H	H			H	H	—	—			0	25
												0	
												19	20, 26
												20 ± 1	34
												20 ± 4	13
												0	25
												19	20, 26
												20 ± 1	34
												20 ± 4	13



COCI H	H H	H H	H H	1.540 ± 0.003	1.540 ± 0.003	21 ± 5	14
COOH H	COOH H	H H	H H	1.546(3) 90.7(2)	1.556(0) 86.3(2)	24	27
COOH H	H H	COOH	H H	1.550(9) 88.2(5)	1.551(10) 88.7(5)	25	16
CH <sub>3</sub> H	H H	H H	H H	1.56 ± 0.03		20 - 30	13
=CCl <sub>2</sub>	=CCl <sub>2</sub>	=CCl <sub>2</sub>	=CCl <sub>2</sub>	1.494(5) 88.8(2)	1.466(7) 88.1(2)	26.5 ± 0.6	28
C <sub>2</sub> H <sub>4</sub> H	H H	F F	H H	1.57(3) 87(1)	1.53(3) 88(1)	27 ± 3	36
COOCH <sub>3</sub> Br	Br COOCH <sub>3</sub>	H H	H H	1.530 - 1.545		27	29
		H	H			28	30
Br H	H H	H H	H H	1.540 ± 0.003 88°41' ± 08'	1.548 ± 0.003 88°06' ± 08'	29°22' ± 08'	35
COOCH <sub>3</sub> Br	COOCH <sub>3</sub> Br	H H	H H	1.58(3) 86(1)	1.55(3) 88(1)	30	29
COOH H	H H	COOH	H H	1.545(12) 88.0(6)	1.563(12) 87.6(6)	1.52(3) 89(1)	
COOH H	H H	H H	H H	1.517(4) 88.8(2)	1.553(4) 88.8(2)	1.547(12) 88.0(6)	32
C <sub>2</sub> H <sub>4</sub> H	H H	H H	H H	1.548 ± 0.004		33.0 ± 2.0	12
COOH COOH	H H	H H	H H			Non-planar	33
NC or CN H	CH <sub>3</sub> CH <sub>3</sub>	NC or CN NC or CN	CH <sub>3</sub> CH <sub>3</sub>			20 - 30	37
NC or CN H	CH <sub>3</sub> CH <sub>3</sub>	NC or CN H	CH <sub>3</sub> CH <sub>3</sub>			20 - 30	37

Table 3. Structural data for cyclobutane fused to other ring systems (not involving transition metals)

Structure	C-C, Å fused	C-C, Å not fused	C-C-C, deg fused	C-C-C, deg not fused	Dihedral angle, deg	Ref
	1.536 ± 0.001	1.528 ± 0.002	90.5	89.5	0	38
	1.60(3)	1.565 ± 0.001	89		0	39
	1.593(7)	1.559(7)	91		0	40
	1.54(2)	1.59(2)	89.5(6)		0	41
	1.59	1.58	90.5(6)		1.0	42
	1.577 ± 0.017	1.557 ± 0.011	90.6		8.1 ± 1.3	43
		1.542 ± 0.020	89.6			
	1.557 ± 0.002				8.0 ± 2.5	44
	1.566 ± 0.003				9.0 ± 2.6	44
	1.55(4)	1.56(4)	88(2)		16	45
	1.53(4)	1.53(4)	89(2)			
	1.532(4)	1.540(4)	86.7(2)	86.8(2)	33	46
		1.556(4)	89.0(2)	87.9(2)		
	1.547(3)	1.587(3)	89.9(2)		0	47
			90.1(2)			
	1.543(4)	1.571(4)	89.6(2)		0	48
			90.4(2)			
	1.529(3)	1.571(3)	86.3(2)		26	49
	1.533(3)	1.577(3)	86.4(3)			
			90.4(3)			
	1.536(3)	1.572(3)	90.7(3)		25	50
	1.543(3)	1.563(3)				
		1.65			>27	51

represents a lengthening of *ca* 0.01 Å over non-cyclic C(sp<sup>3</sup>)-C(sp<sup>3</sup>) bonds.†

In planar cyclobutane compounds the average C-C-C angle is necessarily 90°. Puckering the ring decreases the average C-C-C angle by *ca* 1.6° for compounds in Tables 2 and 3. For the organometallic fused cyclobutane structures given in Table 4 the average angle deviates from perpendicular by only 1.3 times its ESD, reflecting the near planarity of most of the four-membered rings.

Dihedral angles in organometallic fused cyclobutane structures range from 0.2(3)° to 16.4(12)° (Table 4). Before discussing why these angles differ, it is important to consider whether the differences are real, i.e., whether the measurements are of sufficient accuracy to make deviations of this sort meaningful. First, how reproducible are our results? The structure of **5** was determined twice using different crystals, different diffractometers, different temperatures at data collection, and different computer programs.<sup>55</sup> The dihedral angle in the 4-membered ring was determined to be 1.4(4)° and 1.3(3)° for the two studies. Since all of the compounds that we have investigated (1-7) were

†"Tables of Interatomic Distances and Configuration in Molecules and Ions, Supplement," L. E. Sutton, ed., Chem. Soc. Special Publication No. 18 (1965).

Table 4. Structural data for organometallic compounds involving cyclobutane fused to other ring systems

Compound	C-C, Å fused	C-C, Å not fused	C-C-C, deg fused	C-C-C, deg not fused	Dihedral angle, deg	Distance (Å) of fourth atom from plane of 3	Ref
6	1.536(4) 1.565(4)	1.554(4) 1.564(4)	90.9(2), 90.2(2) 89.5(2), 89.4(2)		0.2(3)	0.004(5)	52
3	1.541(8)	1.553(8) 1.559(8) 1.572(7)	89.5(4) 91.0(4)	90.0(4) 89.5(4)	0.6(6)	0.01(1)	53
4 <sup>a</sup>	1.547(9) 1.532(7)	1.552(8) 1.557(8)	90.4(4), 90.1(4) 89.7(4), 89.7(5)		1.1(7)	0.02(1)	54
5	1.545(3) 1.562(3)	1.563(3) 1.564(3)	89.7(2), 90.3(2) 90.3(2), 89.6(2)		1.3(3)	0.25(5)	55
9	—	—	—		1.9	—	56
6	1.533(4) 1.550(4)	1.552(4) 1.565(4)	90.4(2), 90.2(2) 90.0(2), 89.4(2)		2.1(3)	0.040(5)	52
4 <sup>b</sup>	1.547(9)	1.547(9) 1.521(10) 1.511(11)	89.6(5)	89.0(6)	2.7(9)	0.05(2)	54
8 <sup>c</sup>	1.59(2) 1.60(2)	1.56(2) 1.51(2)	89(1), 91(1) 91(1), 89(1)		5.6	0.11	57
10	1.55(3) 1.51(3)	1.53(2) 1.53(2)	91(1), 89(1) 89(1), 91(1)		6.5(26)	0.12(5)	58
8 <sup>c</sup>	1.58(2) 1.60(2)	1.56(2) 1.61(2)	91(1), 89(1) 89(1), 91(1)		7.4	0.14	57
1	1.531(6)	1.541(6) 1.534(6) 1.525(7)	89.5(3) 89.8(3)	90.2(3) 89.5(3)	10.5(5)	0.20(1)	59
7	1.534(10) 1.531(15)	1.568(10) 1.563(12)	89.3(6), 89.5(6) 89.6(6), 89.6(6)		15.0	0.28	60
2	1.56(1)	1.53(2) 1.49(2) 1.54(2)	87.6(8) 88.9(9)	89.5(10) 91.7(9)	16.4(12)	0.31(2)	61

<sup>a</sup>Cyclobutane fused to 6-membered ring.<sup>b</sup>Terminal cyclobutane.<sup>c</sup>Cyclobutane fused to 8-membered ring.

studied using one or the other of the procedures used to study 5, we can state with some confidence that the reported values are reproducible within their ESD's.

Second, is the conformation of the fused ring system independent of its crystal packing environment? A survey of intermolecular contacts would

suggest that crystal packing effects are minimal, if present at all. Stronger evidence is available from a comparison of structures 5 and 6 where the same organic moiety appears in three (the two C<sub>11</sub>H<sub>14</sub> units are crystallographically independent in 6) different packing environments.<sup>52,55</sup> The dihedral angle in 5 is 1.3(3)<sup>o</sup> and does not differ significantly

from the dihedral angles of  $0.2(3)^\circ$  and  $2.1(3)^\circ$  in **6**. However, the difference of  $1.9(4)^\circ$ , between the dihedral angles in **6** is either significant or the ESD's have been underestimated. In either case this difference is small compared to those between **5** and **7** or **4** and **7**, as discussed below. Thus it is reasonable to assume that the differences in the 4-membered rings listed in the Table are the result of the differing ring systems fused to the cyclobutane and are relatively independent of how the molecule packs in the crystal.

This statement contrasts with evidence apparent from an examination of the compounds listed in Tables 2 and 3. The fact that the only planar cyclobutane structures known have a crystallographic center of symmetry imposed on them suggests that this conformation is not the preferred one and that it is only present because of crystal packing forces. This is dramatically pointed out by the studies<sup>15,16</sup> of Margulis and coworkers on *trans*-1,3-cyclobutane dicarboxylic acid where the ring is crystallographically required to be planar in the crystal of the compound itself, but has a dihedral angle of  $25^\circ$  in the crystal that also contains the sodium salt of the acid. Thus the evidence presented in Table 2 suggests that for simple substituted cyclobutanes the preferred dihedral angle is  $ca\ 26 \pm 3^\circ$ , unless packing forces require the ring to be planar. The steric and electronic nature of the substituents has only limited effect on the puckering of the cyclobutane ring. Hence no structures have been reported with intermediate degrees of puckering, *i.e.*, in the range  $1-18^\circ$ .

Fusing other rings to the cyclobutane has a more dramatic effect than varying substituents in simple cyclobutanes. For many of the fused structures given in Table 3, the complex electronic and steric nature of the moieties fused to the cyclobutane ring make it difficult to analyze the structural results, much less predict these features in advance of structural work. However, several observations can be made. Again, those compounds that chemically can exhibit a center of inversion, usually are required to have a crystallographic center in the crystal. (An exception is compound **h** which shows a dihedral angle of  $16^\circ$ ,<sup>45</sup> intermediate between the two extremes of  $0^\circ$  and  $ca\ 26^\circ$ .) Packing forces obviously do not apply to the gaseous electron diffraction studies<sup>43,44</sup> of compound **f** and the *syn* and *anti* forms of compound **g**. Thus it is not surprising that the dihedral angles of  $ca\ 10^\circ$  differ significantly from  $0^\circ$ . However the fact that these angles are considerably less than the "normal" cyclobutane dihedral angle of  $ca\ 26^\circ$  must be the result of a compromise between a tendency to pucker and the constraint imposed by the *cis* fusion of the rings.

An especially intriguing structure is that of com-

pound **i**, where cyclobutane is *trans* fused to cyclohexane.<sup>46</sup> The *trans*-fusion allows the cyclohexane ring to achieve a highly desirable chair conformation and at the same time allow the cyclobutane ring to be puckered with a somewhat larger-than-normal dihedral angle of  $33^\circ$ .

Other dihedral angles of  $ca\ 26^\circ$  are shown for compounds **j** (*cis-syn*) and **k** ( $R=H$  or  $CH_3$ ).<sup>49-51</sup> In each of these the conformation of the fused rings is *syn* and the cyclobutane ring is puckered to reduce non-bonded repulsions between the rings fused to one side of the cyclobutane ring and between the methyl and hydrogen atoms on the opposite side of the ring. On the basis of these structures one would also expect compound **e** to exhibit a puckered cyclobutane ring. However, the dihedral angle calculated from the reported<sup>42</sup> positional parameters is only  $ca\ 1^\circ$ . In the crystal structure the molecules are required to have  $C_2$  symmetry; thus the CN groups are disordered and it is quite likely that the ring pucker is also disordered. In this case one would expect the disorder to show up in the refinement in the form of large thermal vibrations perpendicular to the cyclobutane ring. Since the thermal parameters were not reported one cannot rule out the possibility that this structure also exhibits a puckered cyclobutane ring.\*

Except for this dubious structure and for the structures crystallographically required to be planar, the only example of a compound in Tables 2 or 3 for which the cyclobutane ring is near planarity is compound **a**.<sup>38</sup> Here the fused cyclopropane ring undoubtedly forces the cyclobutane ring to be planar, and in this respect, the structure is analogous to many of the structures of organometallic fused ring compounds listed in Table 4. In these compounds the conformation of the cyclobutane ring is a function of the distortions imposed on it by the rings to which it is fused. Except for compounds **1** and **2**, the cyclobutane ring is fused to a cyclohexadiene ring in a rigid boat conformation. This would force planarity on the 4-membered ring and, in the absence of significant distorting influences of the second fused ring, we would expect the cyclobutane rings to have dihedral angles not significantly different from  $0^\circ$ . This is indeed the case for compounds **3-6** and **8-10**. In **4** the fact that neither 4-membered ring deviates significantly from planarity must mean that the energy gained by puckering ( $ca\ 1.4\ kcal\ mole^{-1}$  for cyclobutane itself) is less than the energy lost in distorting the cyclohexadiene ring from its rigid boat conformation. In **5** and **6** the small expenditure of energy in forcing the 4-membered ring to be planar permits both the preferred boat conformation for the 6-membered ring and the preferred envelope conformation for the 5-membered ring.<sup>32,55</sup> In **8** the tub conformation of the 8-membered ring is most compatible with a planar 4-membered ring.<sup>57</sup> Although the dihedral angles of  $5.6$  and  $7.4^\circ$  are larger than for the previous struc-

\*Discussions, with Mr. A. J. White, relative to this structure are gratefully acknowledged.

tures, the corresponding ESD'S suggest that these are just barely significantly different from 0°.

In contrast to these structures, compound 7 exhibits a dihedral angle of 15·0° for its cyclobutane ring.<sup>60</sup> Here a planar 4-membered ring would promote either a boat conformation or a half-chair conformation for the cyclohexane ring. However, the cyclohexane ring prefers a chair conformation, which would force the cyclobutane ring into a puckered conformation similar to that observed<sup>46</sup> in the *trans*-fused structure (compound i in Table 3). In this *cis*-fused structure 7 we see a compromise whereby the cyclohexane ring assumes a conformation midway between chair and half-chair and the cyclobutane ring exhibits a geometry midway between planar and the puckered conformation of cyclobutane itself. The non-planarity of the 4-membered ring, in turn, perturbs the cyclohexadiene boat conformation and the dihedral angle of this ring is smaller than all of the others.<sup>53</sup>

Compounds 1 and 2 also have puckered cyclobutane rings.<sup>59,61</sup> In neither of these is the geometry of the 4-membered ring restricted by a planar section of a ring fused to it, as is the case in all of the other structures in Table 4. In 2 one might have expected, *a priori*, that the planar cyclopentadienyl ring would force an envelope conformation on the 5-membered ring, which, in turn, would favor a puckered 4-membered ring. Actually the central 5-membered ring has a conformation intermediate between envelope and half-chair and the 4-membered ring has a dihedral angle intermediate between planar and that observed in the puckered structures of simple cyclobutanes.

Although it is possible to interpret many of the conformations observed from these crystal structure investigations, it is clear that it would have been difficult to predict accurately the conformations without the aid of the diffraction studies. It would be interesting to see whether with the aid of recent methods of calculating conformational energies one could predict the geometries of these more complex fused ring systems in organometallic compounds.

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