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The Geometry of Small Rings. VI. Geometry and Bonding in Cyclobutane and Cyclobutene

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Abstract

The molecular geometry, obtained by X-ray methods ($R \leq 0.10$) for 202 derivatives of cyclobutane and 21 derivatives of cyclobutene, has been analysed *via* the Cambridge Structural Database. For cyclobutane a mean ring bond length (d) of 1.554 (1) Å is obtained, but the range (1.521-1.606 Å) is wide; this is attributable to the numbers (n_1, n_2) of exocyclic non-H substituents on a ring bond C(1)-C(2). For n_1 or $n_2 = 0$, $d = 1.547$ (2) Å, but d increases to 1.575 (3) Å for $n_1 = n_2 = 2$. Puckered conformations are preferred in the range $20 < \varphi < 35^\circ$, although a complete range to 67.2° is represented. Whilst d is marginally longer for planar rings at 1.558 (3) Å, a constant d of 1.553 (1) Å is observed as φ increases from 5° and the ring valence angle (θ) decreases from 90° . Thus the transannular C-C distance must decrease and is 2.205 (4) Å at $\varphi = 0^\circ$, $\theta = 90^\circ$, and 2.107 (13) Å at $\varphi = 45^\circ$, $\theta = 85.5^\circ$. Increased transannular non-bonded repulsions are balanced by a decrease in these forces between vicinal 1,2-substituents. The substituent-substituent torsion angle must increase from 0° (eclipsed) as φ increases, and the effect is enhanced by inward rocking of the methylene groups by $\sim 0.12 \varphi$. Each ring C atom uses hybrids of $\sim 27\%$ s character for exocyclic bond formation and of $\sim 23\%$ s character to form the ring σ framework. Ring bonds are bent by *ca* 9° , compared with 22° in cyclopropane. Results for cyclobutene are restricted by the small data set. The C-C bonds, at 1.514 (2) and 1.573 (4) Å, are comparable with gas-phase results, but an unconjugated double bond of 1.323 (4) Å is relatively short.

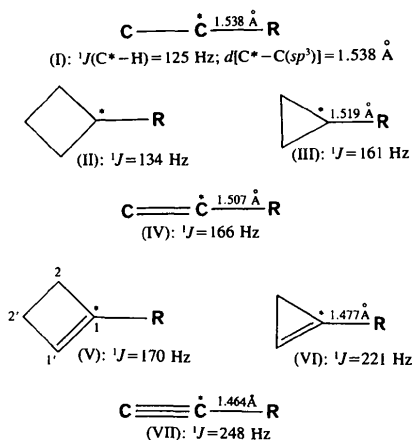
Introduction

The highly strained cyclopropane (III) and cyclopropane (VI) exhibit properties which are atypical of higher cycloalkanes and cycloalkenes. The protons in (III) are markedly vinylic, while 1,2 protons in (VI) are acetylenic, as indicated by the $^1J_{\text{CH}}$ coupling constants. (III) also participates in conformation-dependent conjugative interactions with π -acceptor substituents which are analogous to those for ethylenic links. These anomalies are well explained by a variety of equivalent (Bernett, 1967) bonding models: the bent-bond model (Coulson & Moffitt, 1947, 1949), the trigonally hybridized model (Walsh, 1947, 1949; Sugden, 1947) and the MO approach of Hoffmann (1964). For (III) the models indicate rehybridization at C involving a pair of $\sim sp^2$ hybrids directed towards exocyclic substituents, and a pair of $\sim sp^5$ hybrids contributing to the ring σ framework. For (VI) the exocyclic C(1, 2) hybrids are $\sim sp^1$ while C(3) remains $\sim sp^2/sp^5$ as in (III). Conjugative orbital interactions between (III) and π acceptors were predicted to cause bond-length variations within the ring (Hoffmann, 1964, 1970).

Mean X-ray geometries of fragments containing (III) and (VI) determined by use of the Cambridge Structural Database (Allen *et al.*, 1979) have been examined in some detail in this series. The conjugative ability of (III) has been confirmed and quantified (Allen, 1980) in terms of substituent-induced bond-length asymmetry. It has also been possible to examine C hybridization in (III) (Allen, 1981*a*) and (VI) (Allen, 1982*a*) by a comparison of exocyclic C(ring)-C(sp^3) distances with the C(sp^n)-C(sp^3)

single-bond lengths in (I), (IV), (VII), *i.e.* where $n = 3, 2, 1$ respectively. Non-integral parameters (n) have been approximated for both exocyclic and endocyclic C(ring) hybrids which are consistent with theoretical and NMR estimates. These techniques have also been applied to C atoms in heterocyclic three-membered rings (Allen, 1982*b*). In the present paper the method of mean fragment geometry is applied to a study of cyclobutane (II) and cyclobutene (V), the next higher homologues of (III) and (IV). This paper represents an extension of a previous analysis (Cotton & Frenz, 1974), since a large number of highly accurate studies of (II) are now available.

The total strain energy in (II) at 115 kJ mol⁻¹ is close to the value of 119 kJ mol⁻¹ in (III) (Greenberg & Liebman, 1978, and references therein). However, the strain per CH₂ group in (II) is significantly reduced by comparison with (III) (28.8 *vs* 39.7 kJ mol⁻¹) as might be expected from the expansion of intra-ring angles by some 30°, to within 20° of strainless values. Cycloalkene strain energies are 228 and 143 kJ mol⁻¹ for (VI) and (V) (Greenberg & Liebman, 1978); a simplistic calculation shows that the strain at each unsaturated C(1, 1') is ~42 kJ mol⁻¹ in (V) compared with ~92 kJ mol⁻¹ in (VI). These data, taken together with C-H bond dissociation energies (Greenberg & Liebman, 1978) and the ¹J_{CH} coupling constants (I-VII), indicate that (II) and (V) have properties which are less anomalous than (III) and (VI) and closer to those of relatively strain-free systems, represented here by (I) and (IV). Thus bending of the intra-ring bonds in (II) should be much less than the ~22° predicted (Bernett, 1967) and observed (Fritchie, 1966; Hartman & Hirshfeld, 1966; Allen, 1982*b*) for (III). Similarly C*-C(sp³) distances should lie between 1.519 and 1.538 Å in (II) and between 1.477 and 1.507 Å in (V).



Methodology

The April 1982 release of the Cambridge Structural Database (CSD) has been used for this study. Sub-

Table 1. Statistics for entries containing substructures (II) and (V) retrieved from CSD

	(II)	(V)
Total entries	309	35
Error-free with coordinates (EFC)	240	24
EFC with $R \leq 0.10$	202*	23*
EFC with $R \leq 0.07$	144	14
EFC with $R \leq 0.05$	67	10

* Compound names and literature citations for these entries have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38780 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

structure searches, data retrieval and numeric analyses were performed using computer programs described by Allen *et al.* (1979) and methods developed in earlier parts of this series (Allen, 1980, 1981*a*). Searches for derivatives of (II) and (V) were restricted to those compounds normally regarded as 'organic' (CSD classes 1-61, 63, 64, 70) and some statistics for the derived subset are in Table 1. Geometrical tabulations refer to the designation of atoms and parameters in Fig. 1. Mean values have normally been derived from structures with $R \leq 0.07$ and a mean e.s.d. for C-C bonds (SIG) ≤ 0.01 Å; other values have been used occasionally and R and SIG, representing limiting maxima, are cited in text and tables. In this restrictive situation a recent study (Taylor & Kennard, 1983) suggests that the unweighted mean is a good alternative (*i.e.* has comparable precision) to the weighted mean. The unweighted mean necessitates fewer assumptions (Cochran & Carroll, 1953; Cochran, 1954), and always gives an unbiased estimate of the population mean value. Hence error estimates for mean parameters (\bar{x}) are given by $\sigma(\bar{x}) = [\sum_n (\bar{x} - x_n)^2 / n(n-1)]^{1/2}$ for n independent observations x_i ($i = 1, n$). The relationship $\sigma(\text{sample}) = \sqrt{n} \sigma(\bar{x})$ may be used to estimate the spread within any sample. Values of \bar{x} are quoted as $\bar{x}(\sigma, n)$ throughout. Because of the coincidence of crystallographic and molecular symmetry in some derivatives of (II) and (V) values of n may not be simple multiples of the number of rings cited.

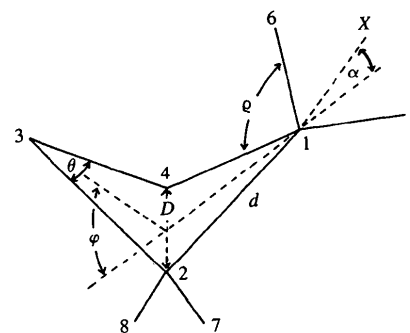


Fig. 1. Geometric parameters for the puckered (D_{2d}) form of cyclobutane. The angle of pucker (φ) is the complement of the dihedral angle between planes 1-2-4 and 3-2-4. The vector 1→X bisects the angle 5-1-6 in the plane of the substituents. The ring torsion angle ω (not shown) is *e.g.* $\omega(4-1-2-3)$.

Cyclobutane

The stereochemistry of (II) has been extensively reviewed by Moriarty (1974). For many years the ring was tacitly assumed to be planar until theoretical work by Bell (1945), reinterpretation of Raman data (Edgell & Weiblen, 1950), and electron diffraction studies (Lemaire & Livingston, 1950; Dunitz & Schomaker, 1952) proved the existence of a puckered ring. Puckering by φ about each diagonal (Fig. 1) gives rise to axial and equatorial substituent directions, and relieves the eclipsed $H \cdots H$ non-bonded interactions which are present in the planar form. Dunitz & Schomaker (1952) obtained $d = 1.568$ (20) Å, $\varphi = 20(+10, -20^\circ)$ for (II), the elongation in d over normal C–C distances being ascribed to transannular (1–3, 2–4) C–C repulsions. More accurate electron diffraction data give $\varphi = 33^\circ$ (Skancke, 1960) and $d = 1.548$ (3) Å (Almenningen, Bastiansen & Skancke, 1961). Finally NMR studies (Meiboom & Snyder, 1970) showed that eclipsing of vicinal H atoms in (II) is further relieved by inward rocking of the methylene groups by $\alpha(\sim 4^\circ)$, Fig. 1) about an axis perpendicular to C(1)–X (X = midpoint of 2–4 diagonal).

Ring geometry in (II) should therefore reflect this delicate balance between ring strain forces and repulsive interactions between vicinal substituents. Ring strain is minimized in the planar form since $\theta = 90^\circ$ and D_{13}, D_{24} are at a maximum, but increases on puckering since $\theta < 90^\circ$ and D_{13}, D_{24} must shorten. Vicinal substituents are maximally eclipsed in the planar form, but repulsion is reduced by ring puckering and methylene rocking. The puckered form is preferred, but only by *ca* 5.9 kJ mol⁻¹ (Stone & Mills, 1970). It is therefore no accident that the only clear characterization of planar (II) occurs in the crystalline state because this energy barrier is of the same order of magnitude as crystal packing forces.

It should also be remembered that some exact geometric relationships link various parameters in Fig. 1 (Dunitz, 1979). For an equilateral ring of side d with valence angle θ , torsion angle ω , and pucker φ we have $D_{13} = D_{24} = D$, thus:

$$\sin(\theta/2) = D/2d \quad (1)$$

$$\cos(\omega) = (1 - \cos \theta)/(1 + \cos \theta) \quad (2)$$

$$\cos(\varphi/2) = \tan(\theta/2). \quad (3)$$

Hence a minimal change in θ , *e.g.* from 90 to 88°, corresponds to a significant φ value (30°), which immediately rationalizes the preference for a puckered conformation.

Ring geometry

A variety of mean values for bond length d and diagonal D (Fig. 1), averaged over D_{2d} (puckered)

Table 2. Mean geometries for the cyclobutane ring (distances in Å, angles in deg)

Parameters are defined in Fig. 1.

	n	d	D	θ^*	φ^*
(a) 58 rings with $R \leq 0.05$, SIG ≤ 0.01 Å, any substitution					
Planar	17	1.558 (3, 46)	2.205 (4, 28)	90.08	0.0
Puckered	41	1.553 (1, 150)	2.159 (4, 76)	88.07	29.6†
All rings	58	1.554 (1, 202)	2.170 (4, 101)	—	—
(b) 24 rings with $R \leq 0.10$, SIG ≤ 0.02 Å, acyclic substituents only					
Planar	8	1.559 (3, 16)	2.206 (3, 16)	90.06	0.0
Puckered	16	1.550 (2, 60)	2.167 (4, 32)	88.70	24.3
All rings	24	1.552 (2, 76)	2.180 (4, 48)	—	—

* Calculated from d, D (see text).

† See text for discussion.

or D_{4h} (planar) symmetry, are collected in Table 2. Values of θ, φ are derived from d, D via equations (1), (3). Care has been taken to avoid fragments where additional strain and rehybridization can affect geometry: fusion to three- and four-membered rings, and single-atom bridging as in bicyclo[1.1.1]pentane. A very wide range of d values (1.520–1.606 Å) is represented in Table 2(a), although the majority lie between 1.540–1.575 Å. The overall mean d is 0.006 Å longer than the electron diffraction value for parent (II) (Almenningen, Bastiansen & Skancke, 1961).

In Table 2(a) 17 of the rings have $\varphi \leq 2.5^\circ$ and 12 are strictly planar, since the ring centroid lies at a crystallographic centre of symmetry. Thus five rings in this high-accuracy sample approach planarity which is not dictated by crystal symmetry requirements. The remaining 41 rings of Table 2(a) are puckered with a φ range of 5.2–51.6°. Values of φ above $\sim 40^\circ$ are associated with the geometric constraints of bicyclo[2.1.1]hexane systems {in bicyclo[1.1.1]pentane (Padwa, Shefter & Alexander, 1968) a φ of 67.2° is observed!}. The overall value of 29.6° given for φ in Table 2(a) is probably a distorted value; we note that 27 rings have φ in the narrow range 20–33° and these values average to 27.1 (5)°.

In order to study possible effects of ring fusion the geometry of (II) was examined for compounds which had only acyclic substituent bonds. The R and SIG limits (0.10 and 0.02 Å) were relaxed to obtain the 24-ring sample of Table 2(b). Results are almost identical to those in Table 2(a). All eight planar rings occupy a crystallographic centre of symmetry, while 14 of the 16 puckered rings have φ between 15.8 and 30.3° with a mean of 25.0 (9)°.

In both parts of Table 2 the mean bond length in planar rings is slightly, but not significantly, longer than in the puckered form. This presents the possibility of a variation in d with puckering angle φ , which is examined in Table 3 for the 41 non-planar rings of Table 2(a). In fact Table 3 shows that d remains remarkably constant at all values of φ , even for the

Table 3. Analysis of cyclobutane ring geometry for ranges of puckering angle (φ) (41 rings, $R \leq 0.05$, $SIG \leq 0.01 \text{ \AA}$; n is the number of rings in each range)

φ range ($^\circ$)	n	$\langle \varphi \rangle$ ($^\circ$)	d (\AA)	D (\AA)	θ ($^\circ$)	ω ($^\circ$)*
5–20	7	10.6	1.552 (3, 26)	2.192 (3, 14)	89.7 (2, 26)	8.3
20–26	11	23.8	1.554 (3, 40)	2.178 (5, 22)	88.8 (2, 42)	16.5
26–30	9	27.8	1.552 (3, 36)	2.162 (5, 18)	88.3 (1, 36)	19.5
30–40	8	31.6	1.555 (3, 32)	2.154 (4, 16)	87.7 (2, 32)	22.7
40+	6	44.8	1.553 (3, 24)	2.107 (13, 12)	85.5 (6, 24)	31.3

* Calculated from θ by use of equation (2) (see text).

geometrically constrained group with $\varphi > 40^\circ$. As φ increases from 0° then θ decreases from 90° [equation (3)] and, since d is constant, D must decrease according to equation (1). This increase of intra-ring strain with increasing φ is almost exactly counterbalanced by movement of the vicinal 1,2-substituents out of the eclipsed position. Fig. 2 shows that with static (non-rocking) methylenes the torsion angle (τ) between substituents (5–1–2–7 of Fig. 1) is equal to the intra-ring torsion angle ω . Values of ω , computed from equation (2), are in Table 3. They show that very small reductions in θ (from 90°) produce large changes in ω which effect a dramatic reduction in non-bonded repulsions between vicinal substituents (Dunitz, 1979).

In practice the experimental values of τ for 1,2-disubstituted rings are systematically larger than values of ω , especially for highly puckered rings. This can be ascribed (Meiboom & Snyder, 1970) to inward rocking of methylenes by α (Fig. 1). Rocking of 1,2-methylenes, in opposite senses, means that τ will exceed ω by $2\alpha'$ (Fig. 2), where α' is a projection of α onto the plane perpendicular to the 1–2 bond. Table 4 shows an analysis of ω and τ over ranges of φ for 42 rings having *cis*-vicinal C, N, O substituents (*i.e.* $60^\circ \geq \tau > -60^\circ$). Compounds in which the four-membered ring forms part of a complex multi-fused or bridged system are omitted. The mean value of individual α' values, and the mean ring-substituent

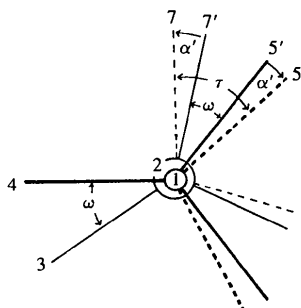


Fig. 2. Newman projection down the 1–2 bond. Before methylene rocking the value of $\tau(5'-1-2-7') = \omega$, the intra-ring torsion angle. After rocking by α° to true positions 5, 7, $\tau(5-1-2-7) = \omega + 2\alpha'$, where α' is the projection of α onto a plane perpendicular to the 1–2 bond.

Table 4. Analysis of methylene rocking angle (α , Fig. 1) determined for 1,2-disubstituted rings, using the parameters in Fig. 2 (42 puckered rings, $R \leq 0.01$, $SIG \leq 0.01 \text{ \AA}$, C, N, O substituents only)

φ range ($^\circ$)	n (rings)	$\langle \varphi \rangle$ ($^\circ$)	$\langle \omega \rangle$ ($^\circ$)	$\langle \tau \rangle$ ($^\circ$)	α' ($^\circ$)	ρ ($^\circ$)	α ($^\circ$)*
Planar	25	0.0	0.0	—	—	113.1 (6, 64)	—
5–20	11	13.4	9.4	12.5	1.5 (4, 33)	113.9 (7, 66)	1.4
20–26	11	23.5	16.5	22.6	2.9 (5, 28)	115.8 (7, 56)	2.5
26–32	10	28.9	20.3	29.4	4.8 (4, 29)	116.7 (6, 58)	4.3
32–50	10	37.2	29.1	39.7	5.1 (6, 27)	112.1 (13, 54)	4.7

* Calculated from ρ , α' via the formula for projected valence angles (Allen & Rogers, 1969).

valence angle (ρ) both increase as φ rises to 32° . For $\varphi > 32^\circ$ the means, especially for ρ , are significantly perturbed by constraints inherent in bicyclo[2.1.1]hexane systems which dominate this φ range. The value of $\alpha = 4.3^\circ$ at $\varphi = 29^\circ$ is in accord with the NMR estimate of 4° (Meiboom & Snyder, 1970), while the φ – α relationship is in close agreement with the calculations of Pasternak & Meyer (1974) and of Bartell & Andersen (1973).

The analyses in Tables 3 and 4 offer no explanation for the wide range of bond lengths (1.520–1.606 \AA) which contribute to the means in Table 2. However an inspection of individual structures shows that d values in octasubstituted rings are consistently high, irrespective of puckering. Thus for two photodimers: $d = 1.578 \text{ \AA}$ at $\varphi = 0^\circ$ (Greenhouse, Borden, Hirotsu & Clardy, 1977), and $d = 1.580 \text{ \AA}$ at $\varphi = 25.1^\circ$ (Courseille, Castellan, Busetta & Hospital, 1975). These values represent a considerable (0.025–0.030 \AA) elongation by comparison with the electron diffraction value of d in free (II) [1.548 (3) \AA (Almendingen, Bastiansen & Skancke, 1961)] or with the X-ray means of Table 2. Thus it appears that d is affected by increased non-bonded interactions due to increased exocyclic non-H substitution at C(1, 2).

The effects of increasing n_1 , n_2 , the number of C, N, O substituents on any ring bond 1–2, are presented in Table 5. In order to differentiate bond-substitution patterns automatically the presence of H atoms was required to complete C(1, 2) connectivities *via* the program GEOM78 (Allen *et al.*, 1979). Thus only those structures having explicit coordinates for the relevant H atoms were included in the analysis. For $n_1, n_2 = 0, 0$ and $2, 0$ the R and SIG criteria were relaxed slightly, while for $n_1, n_2 = 1, 1$ the data set was divided into *cis* and *trans* subsets. Table 5 shows that when only one C atom of a ring bond is substituted (*i.e.* $n_2 = 0$) the mean overall d values are consistently below 1.55 \AA . The mean for $n_2 = 0$, at 1.547 (2, 74) \AA , is now identical to the electron diffraction value of 1.548 (3) \AA for the free ring (Almendingen, Bastiansen & Skancke, 1961). With $n_2 \neq 0$ there are immediate and systematic increases in d , from 1.550 (2) \AA for *trans*-1, 1 substitution to 1.575 (3) \AA for complete non-H substitution at $n_1, n_2 = 2, 2$.

Table 5. Variation in the 1-2 bond length in cyclobutane with increasing numbers (n_1 , n_2) of exocyclic C, N, O substituents (all distances in Å)

n_1	n_2	R	SIG (Å)	d (total)	d (planar)	d (puckered)	d (sub.)*
0	0	0.10	0.02	1.549 (3, 19)	1.555 (5, 7)	1.545 (4, 12)	—
1	0	0.07	0.01	1.546 (2, 37)	1.553 (3, 6)	1.545 (2, 31)	1.522 (6, 9)
2	0	0.10	0.02	1.547 (3, 18)	1.547 (3, 6)	1.547 (3, 12)	1.523 (4, 17)
1	1	0.07	0.01	1.556 (2, 70)	1.559 (3, 17)	1.555 (3, 53)	—
			<i>trans</i>	1.550 (2, 40)	1.552 (4, 11)	1.549 (3, 29)	—
			<i>all</i>	1.552 (1, 110)	1.556 (2, 28)	1.551 (2, 82)	1.525 (2, 52)
2	1	0.07	0.01	1.561 (2, 57)	1.564 (2, 15)	1.560 (2, 42)	1.528 (2, 73)
2	2	0.07	0.01	1.575 (3, 40)	1.582 (3, 9)	1.573 (3, 31)	1.530 (2, 66)

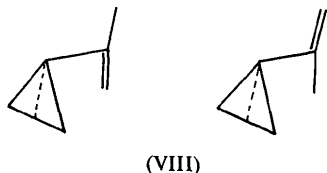
* d (sub.) is the C(1,2)-C(sp^3) substituent bond length.† *cis*-1,2-substituents have $|\tau_{12}|$ between 0 and 40°.

Indeed, if $d = 1.547$ Å is used as a baseline for the free ring, then bond-length increments of ~ 0.01 Å for each *cis*-1,2 interaction and ~ 0.004 Å for each *trans* interaction fit the observations almost exactly. The very slight decrease in d in going from planar to puckered conformations, suggested by Table 2, is consistently shown in Table 5. While statistical significance (3σ) is only attained at $n_1, n_2 = 2, 2$, these small effects are probably a real reflection of eclipsing interactions in the planar form.

The ring-substituent bond length, d (sub.), is included in Table 5 for C(sp^3) substituents. These values agree to within $1.5\sigma_{\max}$ for all substitution patterns and all are within 1σ of the overall mean derived below [1.528 (1) Å, Table 7]. Thus rehybridization is not a factor here, and variations in d with non-H substitution patterns are entirely steric in origin. Hence any mean d value cited for (II) is simply a reflection of the level of substitution of each individual bond. It is no accident that the weighted mean of the 281 ring bonds in Table 5 is 1.556 (2) Å, *i.e.* within 1σ of the 1.554 (1) Å derived in Table 2 for the 58 rings of highest accuracy, since $n_1, n_2 = 1, 1$ is the predominant bond-substitution pattern in each sample.

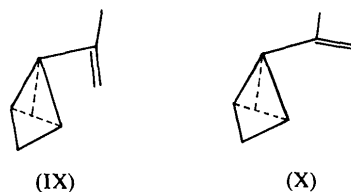
Conjugative ability, or not?

The conjugative ability of cyclopropane (III) with π -acceptor substituents, noted in the *Introduction*, is clearly established. Interactions occur in the bisected conformation (VIII) and, for $-C=O$ substituents, produce a shortening of 0.026 (5) Å in the distal 2-3 bond, with a lengthening of 0.013 (5) Å in the vicinal 1-2, 1-3 bonds (Allen, 1980). The resonance also shortens the C(1)-C(=O) bond from 1.489 (5) Å in unconjugated systems to 1.474 (4) Å in the bisected conformation. These factors are vital to a study of



hybridization in (III) (Allen, 1981a) and before a similar analysis based on exocyclic bond lengths can be performed for cyclobutane, the possible effects of ring-substituent resonance interactions must be examined for (II).

The resonance interactions noted above explain the conformational stability of the cyclopropylcarbinyl cation (Schleyer & Buss, 1969), in which the bisected conformation is preferred by 105 kJ mol $^{-1}$ (CNDO: Wiberg, 1968) or 72.9 kJ mol $^{-1}$ (*ab initio*: Radom, Pople, Buss & Schleyer, 1970). The calculations for cyclobutylcarbinyl indicate considerably lower stability for the comparable bisected form (IX): 31 kJ mol $^{-1}$ (CNDO) and 17 kJ mol $^{-1}$ (*ab initio*). Experimental results do not indicate special conjugative power for (II), but Hoffmann & Davidson (1971) have shown that resonance interactions are possible on the basis of MO calculations. They consider two acceptor conformations: bisected (IX) and perpendicular (X) and predict that the distal diagonal D_{24} should be shorter than the vicinal D_{13} in (IX) and longer in (X).



This prediction has been examined using the $-C=O$ group as acceptor. There are only 39 rings with $R \leq 0.10$ which have only one carbonyl substituent and these are grouped as perpendicular, bisected and unconjugated in Table 6. The values for D_{13} - D_{24} appear to follow the prediction, but data are sparse, individual values are inconsistent, and hence the values have little statistical significance. Even if the effect were real the changes in D_{13} , D_{24} would have a minimal effect on intra-ring bond lengths. What is important is that (i) the 'preferred' conformations (IX), (X) are not dominant, as (VIII) tends to be with cyclopropane derivatives, and (ii) there is no significant difference in the C(1)-C(=O) bond length between 'preferred' and unconjugated conformations. Thus we may conclude that resonance

Table 6. Cyclobutane–monocarbonyl interactions (distances in Å)

	$ \tau (^{\circ})$	n	D_{13}	D_{24}	$D_{13}-D_{24}$	C(1)–C(=O)
Bisected	0–2	7	2.191 (10)	2.171 (14)	0.020 (13)	1.507 (8)
	160–180					
Perpendicular	70–110	12	2.164 (8)	2.180 (16)	–0.016 (13)	1.503 (6)
	20–70					
Unconjugated	110–160	20	2.173 (8)	2.173 (8)	0.000 (4)	1.503 (3)

Table 7. Comparison of C*–R bond lengths (Å) in non-conjugated conformations of the substructures (I)–(IV)

Data not generated in this study are taken from Allen (1981a).

	C* in			
	(I) C(sp ³)	(II)† C(□)	(III) C(Δ)	(IV) C(sp ²)
(a) C(sp ³)	1.538 (1, 1798)	1.528 (1, 184)	1.519 (2, 146)	1.510 (2, 820)
(b) C=C	1.507 (3, 284)	1.499 (3, 15)	1.480 (4, 23)	1.472 (5, 5)
(c) C(phenyl)	1.511 (1, 214)	1.504 (2, 25)	1.485 (3, 13)	1.477 (6, 37)
(d) C(keto)	1.512 (2, 215)	1.505 (1, 41)	1.489 (5, 4)	1.482 (5, 10)
(e) C(esters)	1.514 (3, 107)	1.506 (3, 39)	1.504 (6, 9)	1.497 (4, 26)
(f) Mean (b)–(e)	1.510 (2, 820)	1.504 (2, 120)	1.487 (4, 49)	1.484 (5, 78)

† Data for lines (a), (d) have $R \leq 0.07$, $\text{SIG} \leq 0.01$ Å; for lines (b), (c), (e) $R \leq 0.10$, $\text{SIG} \leq 0.02$ Å.

interactions in (II) must be very small by comparison with (III) and have no detectable effect on bond lengths.

Exocyclic bonding

Mean bond lengths for C*–R in substructure (II) have been determined for a variety of substituents R, where C(R) = C(sp³) or C(sp²). These values are compared (Table 7) with analogous values for substructures (I), (III) and (IV) taken from Allen (1981a). Because (III), (IV) enter into conformation-dependent conjugation with R groups on lines (b)–(e) of Table 7, the corresponding C*–R bond lengths cited are for conformations where resonance effects are at a minimum [see Allen (1981a, 1982c) for definition of potential wells]. The lack of data, and high σ values, for (III), (IVb–e) simply reflects the preference of these substructures for resonance-stabilized conformations. Although there is a consistent slight upward trend (b)→(e) in all cases, it is of marginal statistical significance. Hence an overall mean is presented in (f) for R=C(sp²) and lines (a) and (f) form the basis for the ensuing discussion.

The C*–R bond lengths of Table 7(a, f) decrease systematically as C* changes from sp³ in (I) to sp² in (IV). It is possible to derive (Table 8) a covalent radius (r_h) for each different C* (see e.g. Lide, 1962) and values obtained for the R=C(sp³) and R=C(sp²) series are in close agreement. Assuming that r_h differences can be ascribed to electronic effects, then they imply that the s character of the C* exocyclic orbital pair increases from 25% for (II) and (III). An empirical relationship (Allen, 1981a) would predict approximate s characters of 27% for (II) and 32% for (III), which are consistent with NMR and theoretic

Table 8. Covalent radii (r_h , Å) and % s character states for C* in substructures (I)–(IV) established using Table 7(a, f)

Values are compared with NMR and theoretical estimates.

	C* in			
	(I) C(sp ³)	(II) C(□)	(III) C(Δ)	(IV) C(sp ²)
r_h [R=C(sp ³)]	0.769	0.759	0.750	0.741
r_h [R=C(sp ²)]	0.768	0.762	0.746	0.742
r_h (mean)				
% s (X-ray)	25	27†	32	34
¹ J _{CH} (Hz)‡	125	134	161	159
% s (NMR)§	25	27	32	33
% s (theor.)		27¶	29¶	
		24		

† Empirical estimate (Allen, 1981a).

‡ Taken from Breitmaier & Voelter (1978).

§ Calculated using % s = 0.20 ¹J_{CH} (Muller & Pritchard, 1959).

¶ Iterative molecular-orbital overlap (IMOA) method: Kovacevic & Maksic (1974); Eckert-Maksic & Maksic (1982).

|| CNDO: Pasternak & Meyer (1972).

cal estimates, expressed on this common basis in Table 8.

However, the mean bond lengths of Table 7 are obtained by averaging over all degrees of substitution of that bond. Thus R=C(sp³) includes substituents which may be formalized as R = Me, Et, *i*-Pr, *t*-Bu, and adopting a variety of conformations. Each mean therefore covers a range of non-bonded repulsive interactions across the bond, and Bartell (1978, and references therein) has pointed out that such interactions are a contributory factor to bond-length variations. The results of Table 5 are evidence of this for a relatively constrained system. A similar analysis of the means in Table 7(a) shows some correlation with

Table 9. Ring geometry in cyclobutene in the nomenclature of (V) (distances in Å, angles in deg)

Compound	1-1'	1-2	2-2'	1'-1-2	1-2-2'
X-ray mean	1.336 (4, 23)	1.514 (2, 44)	1.573 (4, 23)	94.4 (2, 44)	85.5 (2, 44)
X-ray conjugated	1.349 (5, 11)	1.514 (3, 22)	1.568 (3, 11)	94.1 (3, 22)	85.7 (4, 22)
X-ray unconjugated	1.323 (4, 12)	1.514 (4, 22)	1.578 (5, 12)	94.7 (3, 22)	85.3 (3, 22)
(V)*	1.342 (4)	1.517 (3)	1.566 (3)	94.2	85.8
cis-2,2'-Dichloro-(V)†	1.349 (6)	1.505 (4)	1.583 (13)	94.4	85.6
Perfluoro-(V)‡	1.342 (6)	1.508 (3)	1.595	94.8	85.2

* Microwave: Bak, Led, Nygaard, Rastrup-Andersen & Sorensen (1969).

† Electron diffraction: Bastiansen & Derissen (1966).

‡ Electron diffraction: Chang, Porter & Bauer (1971).

bond substitution, but conformational variety prevents an adequate systematization. In fact the means of Table 7(a) are dominated in each case by the formal substituent types $R = \text{Me, Et}$ (68–73%); contributions from $R = t\text{-Bu}$, which give rise to severe interactions, are < 7% in each case.

Of greater importance here is the extent to which the consistent differences between the means for (I)–(IV) (Tables 7 and 8) are determined by electronic rather than steric factors. The experimental data cannot, of themselves, provide a clear distinction, but there are cogent arguments which suggest that interpretation of these differences in electronic terms has some validity:

(i) There is a clear consistency between the trend in mean C^*-R bond lengths and changes in $^1J_{\text{CH}}$ NMR coupling constants in the parent hydrocarbons. Both are translated (Table 8) to empirical % s values for comparison. The $^1J_{\text{CH}}$:% s proportionality was first proposed by Muller & Pritchard (1959), but there is now a body of evidence to show that this empirical observation has a good theoretical basis for simple hydrocarbons (Newton, Schulman & McManus, 1974; Ellis & Ditchfield, 1976) and for a range of small-ring compounds (Ellis & Maciel, 1970).

(ii) The bicyclopopyl substructure is adequately represented in the X-ray literature and a mean value for the (III)–(III) link bond is 1.492 (3, 11) Å for structures with $R \leq 0.070$. Eight of these values lie in a narrow range, 1.483–1.499 Å, and exhibit a variety of relative ring conformations. The r_h value is 0.746 Å, almost identical to the 0.748 Å obtained in Table 8. There is a lack of data for the substructures bicyclobutyl (II–II) and cyclopropyl–cyclobutyl (III–II), where the system is not part of a complex highly strained molecule.

For cyclobutane the 27% exocyclic s character ($sp^{2.7}$) yields an inter-orbital angle of 111.3° ; the mean valence angle for *gem*-di- $C(sp^3)$ derivatives of (II) determined here is 111.5 (5, 31) $^\circ$. The exocyclic bonding implies that endocyclic hybrids are 23% s ($sp^{3.3}$), have an inter-orbital angle of 107° and $r_h = 0.769$ Å. Thus the interatomic C–C vectors deviate from the orbital directions by 8.5° in planar (II), and by 9.3° in a puckered ring with $\varphi \sim 28^\circ$. Harel & Hirshfeld (1975) have shown experimentally that the centroid of C–C bonding electron density in (II) lies ~ 0.08 Å

outside the C–C vector in a planar ring where $d = 1.573$ (3) Å. This yields a bending angle of $\sim 6^\circ$. As expected the bond bending in (II) is considerably less than the 22° found for (III) (Fritchie, 1966; Hartman & Hirshfeld, 1966; Allen, 1982*b*). Assuming that the 'bent' C–C bond has a length $2r_h = 1.538$ Å, then the C–C internuclear vector may be calculated as a chord of this arc (Allen, 1982*a*) and is 1.531 Å. If the value of 1.547 Å, derived above from Table 5, is taken for C–C in the free ring, then elongation due to transannular and 1,2-H,H non-bonded repulsions together is 0.016 Å.

Cyclobutene

We consider here those rings which contain a localized endocyclic double bond as the only point of unsaturation (V). Cyclobuten-3-ones and -3,4-diones are excluded, as are benzocyclobutenes which have previously been discussed (Allen, 1981*b*).

Ring geometry

There are 23 examples of (V) in 21 structures with $R \leq 0.10$ and $\text{SIG} \leq 0.02$ Å. Mean ring geometry, averaged over C_2 symmetry, is compared with relevant gas-phase results in Table 9. The gas-phase work assumes planarity, and 20 of the X-ray studies have a mean dihedral fold (φ) of 1.0 (3, 20) $^\circ$. Three rings, all having bulky vicinal substituents (Hanson, 1981; Lerbscher & Trotter, 1971; Muir & Sim, 1968), have φ between 5 and 12° .

The overall X-ray means of Table 9 appear to be consistent with gas-phase data. However, a wide variety of substituents are represented, especially conjugative $-C=C$, $-C=O$ and phenyl groups at 1, 1' in (V). The major geometrical difference between conjugated and unconjugated rings is the length of 1–1'; the double bond apparently elongates by ~ 0.025 Å on conjugation. This is reminiscent of the resonance stabilization of cyclopropene and cyclopropenylidenes where a similar lengthening of the double bond is noted (Allen, 1982*a*). A very short inter-ring sp^2-sp^2 single bond of 1.439 (4) Å in a 1,1-bicyclobutene (Rettig & Trotter, 1977) perhaps reflects this resonance, although σ effects (discussed below) undoubtedly play a part. There remains a discrepancy

Table 10. % *s* Character for C*C*–C(*sp*³) bond lengths (Å), covalent radii (*r*_h, Å) and % *s* character for C* in substructures (IV)–(VII).

	(IV)	(V)	(VI)	(VII)
C*–C(<i>sp</i> ³)†	1.510 (2, 820)	1.498 (6, 9)	1.477 (6, 7)	1.464 (2, 33)
<i>r</i> _h (C*)	0.742	0.729	0.708	0.695
% <i>s</i> (X-ray)‡	34	39	46	50
¹ J _{C-H} §	159	170	221	248
% <i>s</i> (NMR)¶	32	34	44	50
IMOA (theor.)	—	35	38 #	—

† Data not generated in this study are taken from Allen (1981*a*, 1982*a*).‡ Empirical estimate (Allen, 1981*a*).

§ Taken from Breitmaier & Voelter (1978).

¶ See footnote § of Table 8.

|| Kovacevic & Maksic (1974).

Eckert-Maksic & Maksic (1982).

between the unconjugated 1–1' length and the gas-phase results, but both are considerably more 'ethylenic' than the 1.2959 (4) Å obtained for (VI) (Stigliani, Laurie & Li, 1975).

The 1–2 and 2–2' distances are, as expected, longer than their acyclic counterparts. The overall 1–2 distance of 1.514 (2) Å is 0.007 Å longer than the –C=C–C(*sp*³) value of 1.507 (3) Å from Table 7(*b*). For cyclobutane a suitable comparator would be the overall mean of 1.553 (1) Å (Table 2) which is 0.015 Å longer than a normal *sp*³–*sp*³ bond. Thus the elongation in (V), although marginally significant at ~2.5σ, is sensible since 1,2 substituents are now far from the eclipsed position. The 0.007 Å lengthening thus reflects primarily the 1',2-transannular non-bonded repulsions which contribute about one-half of the total strain energy in (II) (Greenberg & Liebman, 1978). The 2–2' bond is cyclobutane-like and is long at 1.573 (4) Å. However, 15 of the 23 bonds of Table 9 carry three or four substituents, whose interactions in (V) are not relieved by ring puckering. The figures for *n*₁, *n*₂ = 2, 1 and 2, 2 for planar (II) in Table 5 show that the 2–2' bond of Table 9 is quite normal.

Exocyclic bonding

There are only nine bonds of the type C(1, 1')–C(*sp*³) in the sample. The mean value (Table 10) of 1.498 (6, 9) Å lies between the corresponding C*–C(*sp*³) means for (IV) and (VI) as expected. However, Table 10 does show that the sparse data set for (V) gives a rather poor comparison with NMR data. A similar treatment of exocyclic bonds at saturated C(2, 2') gives 1.534 (3, 27) Å for C(*sp*³) substituents and 1.499 (5, 12) Å for C(*sp*²). The resultant *r*_h for C(2, 2') exocyclic bonds are 0.765 and 0.757 Å respectively, which average to 0.761 Å as in Table 8. Thus C(2, 2') are closely comparable to cyclobutane C atoms, but the situation at C(1, 1') is less clear. The presently available X-ray data for both exocyclic and endocyclic bonding at these atoms are not as consistent with other experimental results as might be

expected, even allowing for inherent differences between the techniques involved.

Conclusion

For cyclobutane (II) the following geometric factors have been established additional to those imposed by the constraints inherent in the framework [Dunitz (1979); equations (1)–(3) above]:

(1) The ring bond length (*d*) is marginally longer in the planar form, but remains constant for puckering angles $\varphi \geq 5^\circ$. The transannular C–C distance *D* therefore decreases systematically with increasing φ and decreasing intra-annular angle θ . By combining (1) and (3) we obtain $D = 2d \cos(\varphi/2) \cos(\theta/2)$, where $d = 1.553$ Å (Table 3).

(2) The strain due to increased transannular non-bonded repulsion as φ increases is balanced by a reduction in non-bonded repulsion between vicinal 1,2-substituents. This reduction is enhanced by inward rocking of the methylene groups by α° , where $\alpha \sim 0.12\varphi$.

(3) The wide range of bond lengths encountered in (II) is a function of the number of exocyclic non-H substituents, *n*₁, *n*₂, on a ring bond C(1)–C(2). For *n*₁ or *n*₂ = 0, $d = 1.547$ (2) Å, but for *n*₁ and *n*₂ ≠ 0, *d* increases by ~0.01 Å for each *cis*-1, 2 interaction, and by ~0.004 Å for each *trans*-1, 2 interaction.

(4) Possible conjugative interactions with π-acceptor substituents cannot be quantified; they must be small or non-existent in comparison with (III).

(5) Each ring C atom uses hybrids of ~27% *s* character for exocyclic bond formation and of ~23% *s* character to form the endocyclic framework. Ring bonds are bent by ~9° compared with 22° in (III).

(6) Results for cyclobutene (V) are qualitatively correct but lack of data prevents quantification at the level achieved for (II).

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