

The Geometry of Small Rings.

II.* A Comparative Geometrical Study of Hybridization and Conjugation in Cyclopropane and the Vinyl Group

BY FRANK H. ALLEN

Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, England

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Abstract

The cyclopropane ring (Δ) has many properties which differ from higher cycloalkanes and are more analogous to those of the vinyl group ($C=C$). In particular, the $C(\Delta)$ hybrid orbitals used in substituent-bond formation are closer to sp^2 than sp^3 , while a conformation-dependent conjugative ability is exhibited with π -acceptor substituents. The Cambridge Crystallographic Database (CCD) has been used to obtain the mean X-ray-determined geometries of $\Delta-A$ fragments ($A = C-C, C=C, C=O, C\equiv N$), which are compared with the geometries of analogous fragments where Δ is replaced by $C-C$ and $C=C$. Changes in the $D-A$ bond length ($D = C-C, \Delta, C=C$) have been analysed in terms of hybridization and conjugative effects. The X-ray data indicate that the $C(\Delta)$ hybrid involved in the substituent bond is approximately $sp^{2.2}$, while the relative conjugative ability Δ :vinyl is *ca* 71%. Problems involved in precise retrieval and geometric analysis of high-incidence organic fragments from CCD are discussed in terms of (i) restrictions on substitution and environment, (ii) acceptance criteria for coordinate sets, (iii) geometric screening of derived geometry to obtain unbiased mean values.

Introduction

Part I (Allen, 1980) examined the experimental evidence for bond-length asymmetry in cyclopropane (hereafter Δ) induced by a variety of π -donor and π -acceptor substituents. Molecular geometry from X-ray structural studies, assembled from the Cambridge Crystallographic Database (CCD) (Allen *et al.*, 1979), and augmented by data obtained by other physical techniques, was used to derive quantitative values for the asymmetry parameter δ (Fig. 1a).

Positive δ values are induced by π -donor substituents (F_2, Cl_2 ; see Table 1): the distal (2–3) bond (Fig. 1a) is lengthened, relative to the mean Δ bond length, by $\delta \text{ \AA}$;

* Part I: Allen (1980).

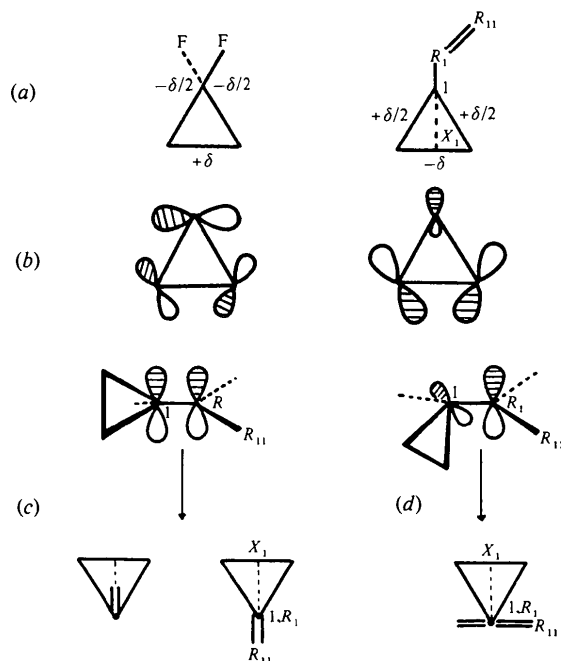


Fig. 1. Some aspects of the geometry of cyclopropane and its derivatives. (a) Bond-length asymmetry due to π -donor and π -acceptor substituents; (b) the $3e'$ orbitals of cyclopropane; (c) the ideal bisected conformations for π -acceptor substituents; $\tau(X_1-C_1-R_1-R_{11}) = 0^\circ$ for *cis*-bisected and 180° for *trans*-bisected; (d) the unfavourable perpendicular ($\pm p$) conformation at $\tau = \pm 90^\circ$.

Table 1. Asymmetry parameters (δ) for various substituted cyclopropane rings

The methods used to obtain δ values are detailed in Allen (1980).

Substituent	δ (Å)	Substituent	δ (Å)
Cl_2	0.025 (7)	$N=C$	-0.018 (-)
F_2	0.060 (-)	Phenyl	-0.018 (2)
$N=N$	-0.014 (-)	$C-C$	-0.022 (4)
$C\equiv N$	-0.017 (2)	$C=C$	-0.026 (5)

the vicinal (1–2, 1–3) bonds are both shortened by $\delta/2$ Å. Such results, first noted in gas-phase studies of cyclopropanone (Pochan, Baldwin & Flygare, 1969), methylenecyclopropane (Laurie & Stigliani, 1970) and 1,1-difluorocyclopropane (Perretta & Laurie, 1975), have been the subject of three recent MO studies (Deakyne, Allen & Laurie 1977; Deakyne, Allen & Craig, 1977; Skancke, Flood & Boggs, 1977).

Results (Allen, 1980) for π -acceptor substituents ($-\text{C}=\text{O}$, $-\text{C}=\text{C}$, $-\text{C}\equiv\text{N}$: Table 1) show a reversal of the π -donor effect: δ is negative, hence the distal bond is shortened and the vicinal bonds are lengthened (Fig. 1a). It was also shown that this effect is dependent on the conformation adopted by the π acceptor (Fig. 1a,c,d): δ values are consistently negative when the torsion angle τ (for $-\text{C}=\text{O}$ and $-\text{C}=\text{C}$) lies within $\pm(20-30)^\circ$ of the bisected conformations (0 or 180° , see below), and the C_1-R_1 bond (Fig. 1a) is systematically shortened. The conjugative ability of Δ is due to transfer of electron density from its $3e'$ orbitals [Fig. 1b: see Jorgensen & Salem (1973) for a complete representation of the MO's for Δ] to low-lying π orbitals of the acceptor (Hoffmann, 1964; Hoffmann & Stohrer, 1971). Maximum orbital overlap occurs (Fig. 1c) when the two orbital systems are parallel (Hoffmann, 1970; Hoffmann & Davidson, 1971) in conformations characterized by τ values (Fig. 1a) of 0° (*cis*-bisected, *cb*) or 180° (*trans*-bisected, *tb*). Minimum orbital overlap occurs at $\tau = \pm 90^\circ$ in the perpendicular (*p*) conformation. All three conformations are depicted in the Newman projections of Fig. 1(d). Orbital mixing in the *cb*, *tb* conformations weakens those Δ bonds for which the $3e'$ orbital has bonding character (the vicinal bonds), but strengthens the distal bond for which the $3e'$ orbital is antibonding (Fig. 1b).

The geometrical survey (Allen, 1980) therefore confirms the conformation-dependent conjugative ability of Δ . It also vindicates the conceptually simple MO explanation of an effect which has long been recognized experimentally (Charton, 1970), particularly in the highly effective stabilization of the cyclopropylcarbiny cation (see, for example, Deno, Richey, Liu, Lincoln & Turner, 1965; Schleyer & Buss, 1969), and by UV spectral shifts (Pete, 1967). Indeed it was UV spectroscopy (Carr & Burt, 1918) which gave the first indication of conjugation involving the Δ ring. Further UV investigations, reviewed by Pete (1967), showed that λ_{max} values for Δ derivatives were approximately midway between those for structural analogues having (i) $\text{C}-\text{C}$ and (ii) $\text{C}=\text{C}$ in place of Δ .

The obvious conformational and geometrical analogies that can be drawn between Δ and vinyl groups have prompted the present work. Here we concentrate not on the geometry of Δ itself, but on the geometry of the substituent grouping $\text{C}_1-R_1-R_{11}$ of Fig. 1. This is compared with the geometry of structural analogues where Δ is replaced by (i) $\text{C}-\text{C}$

and (ii) $\text{C}=\text{C}$, *i.e.* C_1 is affected not only by conjugative effects, which result in a shortening of C_1-R_1 and a lengthening of R_1-R_{11} , but also by changes in hybridization at C_1 . It is well known (Coulson & Goodwin, 1962; Randić & Maksić, 1965; Trinajstić & Randić, 1965; Bennett, 1967; Charton, 1970) that the hybridization of $\text{C}(\Delta)$ in the ring bonds may be approximately represented as sp^5 ; the $\text{C}(\Delta)$ hybrid used to form bonds to substituents is, however, closer to sp^2 than to sp^3 . In the comparative series $\text{C}(sp^3) \rightarrow \text{C}(\Delta) \rightarrow \text{C}(sp^2)$ with a common grouping R_1-R_{11} the C_1-R_1 bond length will always be affected by hybridization changes, even when R_1-R_{11} has no conjugative ability (*e.g.* $\text{C}-\text{C}$). The C_1-R_1 distance will be further foreshortened in $\text{C}=\text{C}$ and Δ substructures where R_1-R_{11} is an acceptor in a suitable conformation for conjugative interactions.

The C_1-R_1 bond length is therefore an ideal probe for examining (i) hybridization changes as C_1 alters from $\text{C}(sp^3)$ through $\text{C}(\Delta)$ to $\text{C}(sp^2)$ and (ii) effects due to delocalization when C_1 is $\text{C}(\Delta)$ or $\text{C}(sp^2)$. In this way an estimate can be made of the $\text{C}(\Delta)$ hybridization in the substituent bond, together with an estimate of the relative conjugative abilities of Δ and $\text{C}=\text{C}$.

Methodology

Scope of the analysis

The analysis is concerned with the geometry of substructural fragments containing pairs of functional groups illustrated in Fig. 2(a). To preserve a loose analogy with the Δ -acceptor interactions summarized earlier, the six independent functional groups are divided into two categories: *donors* (*d*) and *acceptors* (*a*). To complete the geometrical description of hybridization/conjugative effects two groups $\text{C}(sp^3)-\text{C}(sp^3)$ [hereinafter referred to simply as $\text{C}(sp^3)$] and *vi* (vinyl) appear in both categories. With this classification the hybrid orbital at donor C_1 (Fig. 2a) used to form the donor-acceptor bond changes from sp^3 , through some intermediate state for $\text{C}(\Delta)$, to sp^2 for *vi*.

The key geometrical parameter is the acceptor-donor bond length D_{ad} (C_1-R_1 in Fig. 1a; C_1-C_2 in Fig. 2a); its various values are expressed by the acceptor-donor (*ad*) matrix of Fig. 2(b); D_{ad} should decrease in length across row $a = 1$ [$\text{C}(sp^3)$] as a result of the increasing *s* character in the C_1 hybrid orbital used in bond formation by donors $d = 1, 2, 3$. In rows $a = 2, 3, 4$ for donors $d = 2, 3$, D_{ad} is affected both by C_1 hybridization changes (*h*) and by conformation-dependent conjugative effects (*c*). In each of these six fragments conjugative overlap is maximized at $\tau = 0$ or 180° and is a minimum at $\tau = \pm 90^\circ$ (Figs. 1d, 2a). Hence observed values of D_{ad} must be analysed over

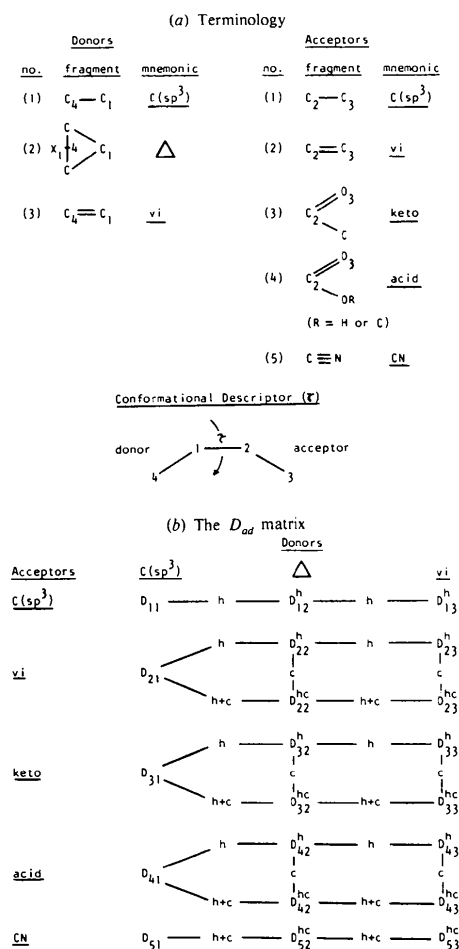


Fig. 2. Summary of the substructural fragments and terminology used in the analysis.

ranges of τ to establish mean values for D_{ad}^{hc} and D_{ad}^h in each case. The differences $D_{ad}^h - D_{ad}^{hc}$ should yield three independent measurements of conjugative ability (for $a = 2, 3, 4$) which may then be compared for the Δ and vi donors ($d = 2, 3$). Results for the cyano acceptor, $a = 5$, are not dependent on conformation and shortening of D_{ad} for $d = 2, 3$ is always a result of hybridization and conjugative effects.

Database search strategies and data retrieval

The analysis was performed with the programs *BIBSER*, *CONNSEER*, *RETRIEVE*, *GEOM78* and *PLUTO78* (Allen *et al.*, 1979) operating on the January 1980 files of the CCD.

A subfile of 330 DATA file entries for compounds containing Δ was constructed as described by Allen (1980). Of the 31 additional structures located since that study (April 1979) only 9 contributed to the effective database for this work (organic structures, error-free coordinate sets, $R \leq 0.10$).

The remaining nine unique substructures of Fig. 2(a), *i.e.* those involving $C(sp^3)$ and vi , have a high incidence in the database by comparison with their Δ analogues. Moreover, such common fragments occur in a wide range of structure types with a wide variety of substitution patterns. Since it was desirable that the generation of mean geometry for each fragment should be as automatic as possible, it was decided to use, and if necessary extend, all available features of *BIBSER*, *CONNSEER*, and *GEOM78* to place rigid constraints on (i) the type of compound containing the fragment, (ii) the environment and degree of substitution of the fragment, and (iii) the acceptance criteria for coordinate sets. It was also decided that a full analysis of what might be termed the base fragment in the *ad* matrix (Fig. 2b), the C-C single bond, was not possible. A realistic value for this bond length did, however, emerge during the analysis of other fragments and will be discussed below.

A strategy was developed for using *BIBSER*, *CONNSEER* and *RETRIEVE* to isolate a sample of database entries, constrained by the requirements to criteria (i) and (ii) above, for the remaining eight high-incidence fragments. The scheme is illustrated in Fig. 3 and may be summarized as:

(i) Use of the bibliographic search program *BIBSER* to screen the total database and exclude totally unwanted structures. The query:

Q *CLASS '01-59' AND *YEAR '66-80' NOT
*ELEMENT 'TR' OR 'CL' OR 'BR' OR 'I'

located 8820 references to 7492 distinct organic compounds (CCD chemical classes 1-59), published since 1965. The exclusion of transition elements (TR), Cl, Br and I is an attempt to produce some uniformity in the R -factor- σ (bond-length) relationship for later application of raw-data screening (Murray-Rust & Motherwell, 1978).

(ii) An extended version of *RETRIEVE* was used to create a subfile of chemical connectivity (CONN) entries for the 7492 compounds located above. This subfile, *ca* one third of the total database, was used for all further fragment searching with *CONNSEER*. This pre-screening with *BIBSER* and *RETRIEVE* not only removed unwanted material, but also drastically reduced the c.p.u. time for subsequent connectivity searches.

(iii) The strategy used in defining connectivity search fragments is exemplified in Fig. 4 for (a) the vi - $keto$ substructure (see Fig. 2a for mnemonics) and (b) the vi - $C(sp^3)$ substructure. To avoid perturbation of final mean geometries by the presence of additional conjugation, or electron-donating or -withdrawing substituents, the environment of each search fragment was restricted to $C(sp^3)$ or H substituents only. These are designated C* or H in Fig. 4. In the original *CONNSEER* program (Allen *et al.*, 1979) atomic connectivities within a coded fragment may only be

specified in terms of the two independent variables: *mca*, the minimum number of connected non-H atoms, and *nh*, the number of terminal H atoms. Thus for each substituent C* in Fig. 4 it was necessary to code *individually* the four substitution patterns $-\text{CH}_3$, $-\text{CH}_2-$, $-\text{CH}_2$ and $-\text{C}\equiv$, in order to fix hybridization as sp^3 . This required up to 4^n separate searches for $n\text{C}^*$ atoms in a fragment. For the present study *CONNSEER* was extended so that *mca* and *nh* were linked variables, constrained such that $mca + nh = 4$, for suitably flagged atoms. Fragment location was further constrained in this extended program so that hits were only recorded if substituents on C*, additional to those in the coded substructure, were C or H atoms. No further restrictions were placed on the hybridization states of these secondary C atoms. It should be noted that coding of $\text{C}(sp^3)-vi$ fragments (Fig. 4b) does allow $\text{C}(sp^3) = \text{C}(\text{methyl})$, while the definition of the $\text{C}(sp^3)$ donor (Fig. 2a) requires a $\text{C}(sp^3)-\text{C}(sp^3)$ single bond. The $\text{C}(\text{methyl})$ substructures, discussed in more detail below, were excluded later with fragment geometry routines in *GEOM78*, which give an additional search capability based on crystallographic connectivity and geometric constraints.

(iv) *RETRIEVE* was used in the normal way (Fig. 3) to create *DATA* subfiles corresponding to the

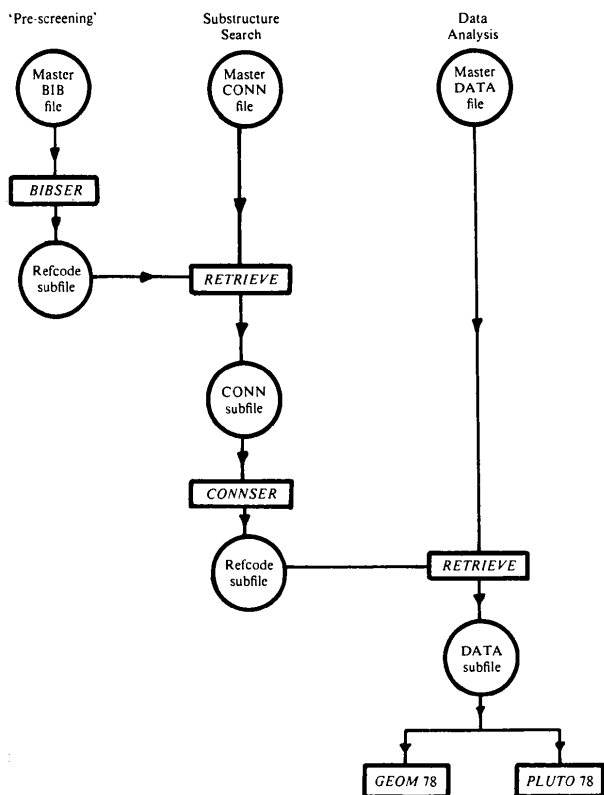


Fig. 3. Strategy for database search and data analysis.

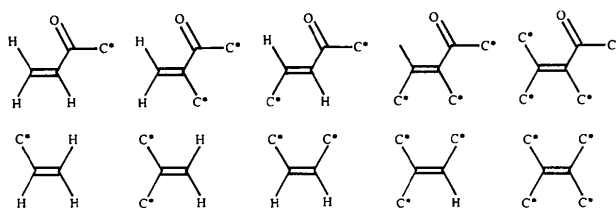


Fig. 4. Substructure search with extended *CONNSEER*. (a) Vinyl-keto fragments and (b) $\text{C}(sp^3)$ -vinyl fragments (ethylene excluded).

CONNSEER results. Each of the eight high-incidence fragments gave rise to more than one subset of *DATA*, due to the restrictions placed on substitution by C* definitions. Thus four subsets are produced for the *vi-keto* fragment (Fig. 4a), and five for $\text{C}(sp^3)-vi$ (Fig. 4b, which excludes the trivial case of ethylene). In some cases the subsets of a complete donor-acceptor substructure were merged prior to geometric analysis, while in others the subsets were analysed separately. The reasons for this decision are discussed below.

Geometrical analyses

Mean molecular geometries for each substructure were calculated with the *FRAGMENT-definition* feature of *GEOM78* (Allen *et al.*, 1979). In an analysis involving many high-incidence fragments considerable attention was paid to raw-data screening of retrieved numeric *DATA* entries and to the geometric screening of results (Murray-Rust & Motherwell, 1978) before inclusion in the averaging process.

Raw-data screens were established in terms of: (i) the average e.s.d. of C-C bond lengths (*AS*); (ii) the crystallographic *R* factor (*R*); (iii) the error status (*ERR*) of the coordinate set. These parameters are held in each retrieved *DATA* entry (*Cambridge Crystallographic Data Centre User Manual*, 1978) and the existing version of *GEOM78* was amended to apply the screens. Several trials were made and the screen employed for the vast majority of high-incidence fragments required $R \leq 0.07$, $AS \leq 0.01 \text{ \AA}$ and the exclusion of all error sets ($ERR = 1$). For fragments of lower incidence, notably those involving Δ , *R*, *AS* limits were relaxed to 0.10 and 0.03 \AA respectively, but with close visual scanning of results and reference to the original literature for entries at the higher end of the *R*, *AS* ranges.

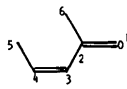
Geometric screening of derived results is of great significance in the study of high-incidence fragments. The extended *CONNSEER* program, described above, made it possible to isolate the required fragments in chemical terms with high precision. They must now be relocated with similar precision with the *FRAG* and *TEST* commands of *GEOM78*.

The *FRAG* command allows the user to code the connectivity of a substructure for which a tabulation of

geometric parameters is required. *GEOM78* then locates the fragment in the DATA entry, transforms the atom labels according to the scheme employed by the user, and outputs geometry tables on this common framework for all entries. Although coding and fragment-search philosophies used in *GEOM78* are analogous to those in *CONNSEER* there is one major difference: the connectivity that is searched is not the complete chemical connectivity (CONN file), but crystallographic connectivity derived from the crystal data and coordinate set by use of a table of covalent radii (Allen, Kennard, Motherwell, Town, Watson, Scott & Larson, 1974). Such crystallographic connectivity is often incomplete by comparison with the corresponding chemical-connection table since H atoms may not have been located by the X-ray study. The most important difference, however, is the lack of explicit bond-type information in the derived crystallographic connectivity.

The problem of bond-type specification is largely obviated by careful use of the TEST command. This permits the user to specify permitted ranges for any distance, angle or torsion angle within the fragment. If any parameter calculates outside its permitted range the fragment-location procedure ceases.

An example of a complete *GEOM78* run, including fragment coding and the resultant geometry table, is





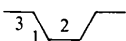
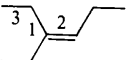
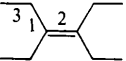
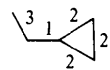

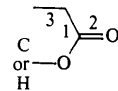
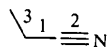
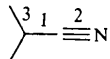
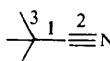
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FRAG VI-KETO
AT1 O 1
AT2 C 3
AT3 C 2
AT4 C 2
AT5 C 1
AT6 C 1
BO 1 2
BO 2 3
BO 2 6
BO 3 4
BO 4 5
TEST DIST 1 2 1.17, 1.26
TEST DIST 3 4 1.28, 1.36
TEST DIST 4 5 1.47, 1.60
TEST DIST 2 6 1.47, 1.60
TEST ANG 1 2 3 114.0, 130.0
TEST ANG 1 2 6 114.0, 130.0
TEST ANG 3 2 6 114.0, 130.0
TEST ANG 2 3 4 114.0, 130.0
TEST ANG 3 4 5 114.0, 130.0
TEST TOR 1 2 3 4 -15.0, 15.0
END
SCREEN RFACT 0.07 ERR 1 AS 2
DEF C = O 1 2
DEF C - C 2 3
DEF C = C 3 4
DEF CO - C 2 6
DEF CC - C 4 5
DEF A1 1 2 3
DEF A2 1 2 6
DEF A3 3 2 6
DEF A4 2 3 4
DEF A5 3 4 5
DEF TAU 1 2 3 4
  
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Fig. 5. Complete coding for extended *GEOM78* for the vinyl-keto substructure.

given in Fig. 5 for the *vi-keto* substructure. In the example a TEST on torsion angle restricts tabulation to *cis* conformations only; a full discussion of torsion-

Table 2. Geometrical analysis (Å) of $C(sp^3)$ -donor substructures

$C(sp^3)$ -vinyl	1	2	3
	1.507 (41, 3)	1.320 (41, 3)	1.539 (64, 3)
	1.510 (46, 3)	1.321 (23, 4)	1.539 (122, 3)
	1.501 (84, 4)	1.318 (42, 3)	1.539 (138, 2)
	1.510 (81, 4)	1.328 (27, 3)	1.539 (128, 3)
	1.510 (32, 4)	1.333 (8, 3)	1.535 (56, 4)
Global mean	1.507 (284, 3)	1.322 (141, 3)	1.539 (508, 4)
Mean of means	-	1.324 (4, 3)	-
$C(sp^3)$ - Δ			
	(a) 1.519 (146, 2)	1.510 (228, 2)	1.534 (214, 2)
	(b) 1.519 (38, 2)	1.508 (81, 3)	-
	(c) 1.515 (35, 3)	-	-
$C(sp^3)$ -keto			
	1.512 (215, 2)	1.213 (139, 2)	1.540 (357, 2)
$C(sp^3)$ -acid			
	1.514 (107, 3)	1.216 (107, 3)	1.535 (211, 4)
$C(sp^3)$ -cyano			
	1.464 (20, 4)	1.134 (20, 3)	-
	1.473 (13, 3)	1.133 (13, 3)	-
	1.478 (15, 3)	1.136 (15, 2)	-
Global means	1.471 (48, 3)	1.134 (48, 3)	-
Mean of means	1.472 (3, 3)	-	-
$C(sp^3)$ - $C(sp^3)$	1.538 (1798, 1)	(see text)	

(a) Means for 76 rings having $R \leq 0.08$.
 (b) Means for 27 structures ($R \leq 0.10$) with $C(sp^3)$ or H as sole substituents: values for $C(sp^3) = C-C$.
 (c) Means derived as for (b) above, but with $C(sp^3) = C(\text{methyl})$.

Table 3. Analysis of the donor-acceptor bond length D_{ad} (Å) for ranges of $\tau(3-2-1-4)$ for vinyl-acid fragments

τ values are normalized to the range 0–90°; i.e. *cis* and *trans* conformations are treated as being geometrically equivalent.

τ (°)	$\langle\tau\rangle$	D_{ad}
0–3	1.5	1.466 (20, 3)
3–15	8.1	1.473 (21, 3)
15–30	23.9	1.493 (13, 4)
30–90	68.3	1.501 (13, 5)

angle ranges for various donor-acceptor pairs is given later. The method used to establish suitable ranges for distances and angles to define bond types was as follows:

(i) Tabulate fragment geometry employing raw-data screens only.

(ii) Examine calculated mean values, and the range of individual values contributing to that mean.

(iii) Establish (empirically) suitable tolerance values t_1 , t_2 about the mean m .

(iv) Set TEST ranges of $m - t_1$, $m + t_2$ and repeat steps (i)–(iii).

In practice initial means were much as expected and tolerances of 0.03–0.04 Å for bond lengths and 4–6° for valence angles were generally satisfactory. Even so it was not possible to relocate all CONNSER fragments uniquely with GEOM78. All tabulations were visually examined for deviant results, the original literature was consulted, and some fragments were omitted from the final averaging.

The geometrical treatment employed here is not designed to locate and study those structures which contain genuinely abnormal features. The procedure outlined has been used to obtain, in a rigorous but relatively automatic manner, the mean geometries of a

Table 4. Geometrical analysis of vinyl-donor substructures

Fragment ^(a)	Conformation ^(b)	1	2	3
	Unconjugated <i>cis/trans</i>	1.472 (5, 5) 1.458 (24, 3)	1.352 (10, 4) 1.340 (48, 2)	– –
	Unconjugated <i>cis/trans</i>	1.482 (10, 5) 1.460 (89, 2)	1.333 (10, 5) 1.340 (89, 2)	1.212 (10, 4) 1.223 (89, 2)
	Unconjugated <i>cis/trans</i>	1.497 (26, 4) 1.470 (41, 3)	1.337 (26, 3) 1.339 (41, 3)	1.202 (26, 3) 1.219 (41, 2)
		1.428 (13, 3)	1.344 (13, 2)	1.141 (13, 3)

(a) Other substituents on the vinyl group restricted to H or C(sp^3).

(b) See text and Table 3 for definition of torsion-angle ranges used to define conformations.

Table 5. Geometrical analysis of Δ -donor substructures

Bond lengths in the ring are omitted here; they are tabulated and discussed in Allen (1980).

Fragment	Conformation ^(a)	1	2
	Unconjugated <i>cb/tb</i>	1.480 (23, 4) 1.470 (11, 6)	1.332 (23, 4) 1.333 (11, 5)
	Unconjugated <i>cb/tb</i>	1.489 (4, 5) 1.474 (12, 4)	1.218 (4, 5) 1.222 (12, 3)
	Unconjugated <i>cb/tb</i>	1.504 (9, 6) 1.484 (21, 4)	1.203 (9, 5) 1.209 (21, 3)
	–	1.441 (14, 4)	1.143 (14, 3)

(a) See text and Fig. 1 for definitions of conformations and torsion-angle ranges used in the analysis.

range of high-incidence fragments as determined in the solid state.

Error estimates and presentation of results

In presenting results for individual donor-acceptor pairs (Tables 2–5) mean bond lengths (\bar{b}) are quoted as $\bar{b}(n, \sigma)$, where n is the number of observations contributing to the mean, and σ is the e.s.d. of the mean expressed in units of the final digit. The e.s.d. of the mean for each set of chemically equivalent bonds has been calculated from: $\sigma(\bar{b}) = [\sum_n (\bar{b} - b_n)^2 / n(n-1)]^{1/2}$, where b_n are the individual contributors to the mean. This is, perhaps, an underestimate due to lack of independence of bonds within a given fragment. Nevertheless, $\sigma(\bar{b})$ is a more accurate reflection of the significance of each mean than $\sigma(\text{sample}) = [\sum_n (\bar{b} - b_n)^2 / n(n-1)]^{1/2}$. The relationship $\sigma(\text{sample}) = \sqrt{n} \cdot \sigma(\bar{b})$ may be used to estimate the spread within any sample.

Results and discussion for individual substructures

The C(sp^3) donor

The term C(sp^3) donor categorizes substructural analogues of Δ -donor fragments having a C(sp^3)–C(sp^3) single bond in place of Δ (Fig. 2a). Geometric analysis of C(sp^3) fragments provides a base line, exemplified by column 1 of Fig. 2(b), for the comparison of hybridization and conjugative effects in the corresponding Δ - and *vi*-donor analogues. The chief parameter of interest within the scope of the present

study is the C_1-C_2 bond length (D_{ad}) of Fig. 2(a). Nevertheless the selection and isolation of suitable fragments *via* CONNSER and GEOM78, and the determination of unbiased mean geometry for such high-incidence fragments, was a non-trivial task:

(i) Although the definition of the $C(sp^3)$ -donor as a C—C single bond is justifiable purely on the grounds of chemical analogy, there is also a crystallographic reason for excluding C_1 (methyl) substructures. In their study of substituent effects on benzene-ring geometry Domenicano, Vaciago & Coulson (1975) note that bond lengths established by the X-ray method are likely to be randomly affected as a result of thermal motion, while the effect on valence angles is not so serious. C_1 (methyl) fragments should, perhaps, be treated with some care, since terminal atoms are more likely to suffer such thermal effects and bias the mean D_{ad} . Some comparative results for one substructure are presented below.

(ii) It is known that the length of any C—C bond (C in any hybridization state) is a function of its degree of substitution (Stoicheff, 1962; Bastiansen & Trætteberg, 1962; Maksić & Randić, 1970; Hencher, 1978, and references therein). Ideally, therefore, mean D_{ad} values cited in this study should be a mean of means (*i.e.* the average of mean values for each substitution level) rather than a global average over all incidences regardless of substitution. This point has been examined here for two $C(sp^3)$ fragments.

(iii) The isolation of a $C(sp^3)$ fragment was a two-stage process. Taking $C(sp^3)$ -*vi* as an example, the CONNSER queries conformed to the fragments illustrated in Fig. 4(a), with $C^* = C(sp^3)$ as described above. This obviously leads to retrieval of entries having $C^* = C(\text{methyl})$; such entries were excluded from the geometric analysis by extending the CONNSER fragments for GEOM78 to demand an extra C' atom bonded to C^* (Fig. 4a), and placing geometric TEST's on the distance $C'-C^*$ and angles at C^* to fix the $C'-C^*$ bond type as unity.

Complete results for $C(sp^3)$ fragments are in Table 2. Degree-of-substitution effects have been studied for the C=C double bond of $C(sp^3)$ -*vi* fragments and for the acceptor-donor bond D_{ad} of $C(sp^3)$ -*cy* (cyano) fragments. No detectable difference in C=C distances was found for mono- and disubstituted bonds [mean = 1.320 (106, 2) Å], but additional $C(sp^3)$ substitution causes an increase in mean C=C to 1.328 (27, 3) Å for $3 \times C(sp^3)$ and 1.333 (8, 3) Å for $4 \times C(sp^3)$. However, the global mean, 1.322 (141, 3) Å, is almost identical to the mean of means, 1.324 (5, 5) Å, even though the longer tetrasubstituted bond has low incidence and makes little contribution to the global value. Similar results are obtained for the D_{ad} value in $C(sp^3)$ -*cy* fragments, although individual means do increase uniformly with increasing substitution. Such results are not exhaustive, but for this study it has been

Table 6. The completed D_{ad} matrix of Fig. 2(b)

All distances are in Å.

	$C(sp^3)$		Δ	<i>vi</i>
$C(sp^3)$	1.538 (1)	<i>h</i>	1.519 (2)	1.507 (3)
<i>vi</i>	1.507	<i>h</i> <i>h + c</i>	1.480 (4) 1.470 (6)	1.472 (5) 1.458 (3)
<i>keto</i>	1.512 (2)	<i>h</i> <i>h + c</i>	1.489 (5) 1.474 (4)	1.482 (5) 1.460 (2)
<i>acid</i>	1.514 (3)	<i>h</i> <i>h + c</i>	1.504 (6) 1.484 (4)	1.497 (4) 1.470 (3)
<i>cy</i>	1.471 (3)	<i>h + c</i>	1.441 (4)	1.428 (3)

assumed that degree-of-substitution variations are not significant and global means are employed throughout.

Comparative geometry for $C(sp^3) = C-C$ and $C(sp^3) = C(\text{methyl})$ is presented in Table 2 for the $C(sp^3)-\Delta$ substructure. The overall mean D_{ad} with $C(\text{methyl})$ excluded is 1.519 (146, 2) Å. The 27 rings having only $C(sp^3)$ or H substituents were analysed further: The value of 1.519 (38, 2) Å was again obtained for $C(sp^3) = C-C$, but a slightly shorter value, 1.515 (35, 3) Å, was given by $C(sp^3) = C(\text{methyl})$. Again, this result is not exhaustive, it simply shows that thermal attenuation of C—C(methyl) distances is not marked for this particular sample.

It was decided at the outset that a full analysis of $C(sp^3)-C(sp^3)$ single bonds was outside the scope of this work; indeed, it would form the basis of a project in its own right. Nevertheless, the mean of the 1798 type 3 distances of Table 2 was calculated to be 1.538 (1798, 1) Å, a value almost identical to the 1.537 (5) Å quoted by Sutton (1965) from a much smaller sample. While it should be noted that no attempt has been made to exclude C—C(methyl) distances from the present mean, the value of 1.538 Å was accepted for use in the final analysis. Other D_{ad} values taken across to the final D_{ad} matrix (Table 6) are shown in bold type in Table 2.

The vinyl donor

The analysis of donor-acceptor interactions for the *vi* donor (Fig. 2) is more complex since D_{ad} is affected not only by the hybridization states at C_1 and C_2 (Fig. 2), but also by conformation-dependent (cyano excepted) conjugative effects. The torsion angle τ (3-2-1-4) (Fig. 2) provides a measure of conjugative overlap for all relevant substructures; τ values close to $\pm 90^\circ$ (*p* conformation) represent minimum overlap with fragment geometry dictated by hybridization effects; τ values close to 0 (*cis*) or 180° (*trans*) provide maximum overlap and additional conjugative distortion of geometry (differences in *cis* and *trans* geometries, caused by differing 1,4 interactions, are ignored).

The two geometries (*p* and *cis/trans*) were separated with the GEOM78 TEST facility. Suitable ranges for τ were established by analysis of the D_{ad} - τ relationship for the 67 *vi-acid* fragments (Fig. 2a). *cis/trans* conformations predominate for most conjugated systems and *vi-acid* was chosen for analysis since it exhibited the widest spread of τ . The results are in Table 3: τ values were normalized to range from 0 to 90° and D_{ad} values were averaged within four ranges of approximately equal population. There is a sharp discontinuity in D_{ad} at $\tau \sim 15^\circ$ and ranges for effective conjugative overlap for *vi* fragments were set at $\tau = 0 \pm 15^\circ$ and $\tau = 180 \pm 15^\circ$.

Complete results for *vi* fragments are in Table 4. The conjugative shortening of D_{ad} (bond 1, Table 4) is 0.014 Å for *vi-vi* interactions, close to the 0.01 Å estimated by Maksić & Rubčić (1977) from orbital-overlap studies. Conjugative shortening for C=O-containing acceptors (Fig. 2a) is somewhat greater at 0.022 for *keto* and 0.027 Å for *acids*. A similar trend is shown by Δ -donor fragments (Table 5 and Allen, 1980). The expected lengthening of conjugated C-C, C=O and C \equiv N bonds is also apparent, in Table 4, in comparison with distances obtained for both unconjugated and C(*sp*³)-donor analogues. All type 1 distances in Table 4 form a row ($d = 3$) in the final D_{ad} matrix in Table 6.

The Δ donor

The work reported in part I (Allen, 1980) was repeated for this study, with a slightly extended sample and with the following modifications (results are collected in Table 5):

(i) The previous analysis distinguished between structures having pure Δ -acceptor interactions, *i.e.* having the π -acceptor [plus C(*sp*³) or H] as sole substituents, and mixed Δ -acceptor interactions, *i.e.* having more than one *different* acceptor substituent. While this distinction was important in establishing Δ -ring asymmetry parameters, it is not relevant here. Table 5 includes results from all interactions; thus for Δ -*vi* fragments results are taken from Tables 4, 6 and 7 of Allen (1980) together with any new material.

(ii) Interactions involving C=O as acceptor have been split into the two subgroups of Fig. 2(a), *viz*: *keto* and *acid*.

(iii) In part I (Allen, 1980) it was noted that the potential well for conjugative overlap in Δ -carbonyl fragments was quite broad. Bond-length asymmetry in Δ was apparent at τ values approaching $\pm 30^\circ$ from the ideal *cb*, *tb* conformations (Fig. 1). For this study τ ranges for effective orbital overlap were set at $\pm 25^\circ$ about the 0 and 180° positions for *keto* and *acid* acceptors, but remained at $\pm 15^\circ$ for Δ -*vi* fragments.

Table 5 shows results which are directly comparable with those for *vi*-donor fragments (Table 4). Conju-

gative shortening of D_{ad} follows the same quantitative trend: *vi* < *keto* \sim *acid*, but at a lower absolute level. By comparison with *vi* fragments the lengthening of the acceptor bond (2 in Table 5) for Δ substructures is not significant.

Results of the analysis

The D_{ad} values reported in Tables 2, 4 and 5 are collected in Table 6 to form the final matrix of Fig. 2(b) expressed in numeric terms. Table 7 reports the shortening (d), relative to C(*sp*³), of D_{ad} for Δ and *vi* donor fragments. This is calculated for both hybridization effects (h) and for hybridization plus conjugative effects ($h + c$). The net conjugative effect is derived when applicable. Thus we have:

$$d(\Delta, vi)_{h, h+c} = D_{ad}(\Delta, vi)_{h, h+c} - D[C(sp^3)]_h$$

$$c(\Delta, vi) = d(\Delta, vi)_{h+c} - d(\Delta, vi)_h$$

Finally, Table 7 reports the relative shortening due to h , $h + c$ and c effects for Δ and *vi* fragments expressed as a percentage: $d(\Delta)/d(vi) \times 100$. Compounding of errors in taking differences and ratios would indicate e.s.d.'s for d values of 0.003–0.004 Å and for d ratios of 5–7%. Comparison of Δ and *vi* geometries might more properly be expressed in terms of bond orders, or by the bond-number (n) relationship: $d = -0.71 \log n$ (Pauling, 1947). The small size of the d values in Table 7 covers a narrow range and may be treated linearly. Thus the percentage (61%) in the first line of Table 7 changes only to 60% in terms of $n(\Delta)/n(vi) \times 100$.

Discussion

Hybridization in the Δ -substituent bond

There are three fundamental models for bonding in Δ : the trigonally hybridized model of Walsh (1947a,

Table 7. The net shortening (d) in D_{ad} (Å) for Δ and *vi* donors with respect to values for the C(*sp*³) donor due to hybridization effects (h) and hybridization plus conjugative effects ($h + c$)

The net conjugative shortening is also given where applicable.

		$d(\Delta)$	$d(vi)$	$d(\Delta)/d(vi)$ (%)
C(<i>sp</i> ³)	h	-0.019	-0.031	61
	$h + c$	-0.027	-0.035	77
	c	-0.037	-0.049	76
<i>vi</i>	h	-0.010	-0.014	71
	$h + c$	-0.023	-0.030	77
	c	-0.038	-0.052	73
<i>keto</i>	h	-0.015	-0.022	68
	$h + c$	-0.023	-0.030	77
	c	-0.038	-0.052	73
<i>acid</i>	h	-0.010	-0.017	59
	$h + c$	-0.030	-0.044	68
	c	-0.020	-0.027	74
<i>cy</i>	$h + c$	-0.031	-0.044	71

1949) and Sugden (1947), the bent-bond model of Coulson & Moffitt (1947, 1949), and the MO approach initiated by Hoffmann (1964). Extensions and modifications of these models have been variously used to explain the observed properties of Δ and its derivatives, and Burnett (1967) has shown the essential equivalence of the three descriptions. Theoretical work to define the hybrid orbitals used by Δ C atoms to form (i) bonds within the ring and (ii) bonds to substituents arose from the bent-bond model of Coulson & Moffitt (1947, 1949) which initially indicated hybridization as (i) $sp^{4.12}$ and (ii) $sp^{2.28}$. Extension of this work with the method of maximum overlap has given other estimates in the ranges: (i) $sp^{3.69} - sp^5$ and (ii) $sp^2 - sp^{2.49}$ (Coulson & Goodwin, 1962; Randić & Maksić, 1965; Trinajstić & Randić, 1965; Kovacević & Maksić, 1974).

In the present study individual values of $d(\Delta)/d(vi)_h$ range from 59–77% (Table 7), with a mean of 69%. This agrees well with the theoretical predictions and confirms the results of an earlier study (Charton, 1970) based on Δ -substituent bond lengths. Charton (1970) used the limited data available at that time from X-ray, electron diffraction, microwave spectroscopy *etc.*, and was able to conclude that the $C(\Delta)$ orbital involved in substituent bond formation had a hybridization state between sp^3 and sp^2 , and was probably closer to sp^2 .

To obtain an empirical estimate of the $C(\Delta)$ hybridization state in the substituent bond from the present work the results for the $C(sp^3)$ acceptor (lines 1 of Tables 6 and 7) have been analysed further in Table 8. In the acceptor–donor link bond (C_2-C_1 in Fig. 2a) for $C(sp^3)$ -acceptor fragments the hybridization state of C_2 remains constant (at, or close to, sp^3) while the p character of the C_1 hybrid decreases as the donor changes from $C(sp^3)$ through $C(\Delta)$ to $C(sp^2)$ for vi ; D_{ad} therefore shortens from 1.538 through 1.519 to 1.507 Å. We may therefore assign a covalent radius $r(h)$ which differs for the various hybridization states. If we now add to this analysis the acetylenic linkage as an additional donor we can obtain $r(h)$ for the $C(sp^1)$ hybrid to give an additional fixed hybridization point. A tabulation of $C(sp^3)$ – $C\equiv C$ distances, performed in the manner described earlier, gave a mean D_{ad} of 1.464 (33, 2) and a mean $C\equiv C$ distance of 1.185 (33, 2) Å, values in good agreement with data collected by Hencher (1978). The $r(h)$ values were found to fit the empirical relationship $r(h) = a \log p$ where p is the % p character of the C orbital used to form the bond. The

resultant a values are given in Table 8 and average to 0.408. If the equation is now applied to $C(\Delta)$ for which $r(h)$ is 0.75 we obtain $p = 68.9\%$ or $C(\Delta) = C(sp^{2.22})$.

Charton (1970) has collected extensive tables of experimental data from other physical methods. For example, the IR spectra of Δ and Δ derivatives yield a C–H stretching-force constant of 0.5 N mm⁻¹ (Linnett, 1947). This may be compared with 0.479 for methane and 0.51 N mm⁻¹ for ethylene (Walsh, 1947b) giving a K_{C-H} ratio of 68%. Muller & Pritchard (1959) have used the ¹³C–¹H NMR coupling constant to estimate that the $C(\Delta)$ –H orbital is less than, but very close to, 33% s character. These, and other results cited by Charton (1970) indicate that the present, relatively automatic, analysis of the X-ray data has produced a quantitatively acceptable result, and lends some credence to the empirical estimate of the $C(\Delta)$ –substituent hybridization state.

Conjugative ability of Δ

In his review, Charton (1970) presents results which clearly indicate the conjugative ability of Δ and were obtained by a variety of methods, *e.g.* IR, UV, NMR, NQR, EPR and Raman spectroscopy, molar refractivity determinations and dipole-moment measurements. The earliest indications of conjugation by Δ came from UV studies by Carr & Burt (1918) on benzoyl, and anisoylcyclopropanes, whose spectra closely resembled those of vinyl analogues. It is UV spectroscopy which provides the most coherent body of spectral information with which to assess the relative conjugative abilities of Δ and vi .

Rogers (1947) compared the UV spectra of ethylbenzene, phenylcyclopropane and styrene and found that the bathochromic shift due to Δ was about 40% of the shift due to vi . Robertson, Music & Matsen (1950) derived spectroscopic bond orders from UV data on a similar series of compounds and a relative bond-order ratio ($\Delta:vi$) of *ca* 60% was obtained. Pete (1967) reviewed the UV results on Δ derivatives and noted a definite relationship between the spectra of vinylcyclopropanes and the dihedral angle between the vinyl and Δ moieties. He found that conjugation was apparent (but reduced) for angles $\pm 25^\circ$ from the ideal bisected conformation for both vinyl and keto derivatives, a value almost identical to that deduced here and in Allen (1980) from the X-ray data. Pete (1967) collated the results of many UV studies and gives the bathochromic effect of Δ on vinyl and keto groups in the bisected conformation as 16 and 20 nm respectively. The corresponding shift due to an additional conjugated vinyl group is 30 nm (Woodward, 1942; Fieser & Fieser, 1959). These results indicate a $\Delta:vi$ conjugative ratio of *ca* 60%.

The net conjugative shortening (c) of D_{ad} determined from the X-ray data for Δ and vi analogues is in

Table 8. Analysis of hybridization in $C(sp^3)$ -acceptor fragments

Donor	D_{ad}	$r(h) = D_{ad} -$		p (%)	a
		$r(sp^3)$	Hybrid		
$C(sp^3)$	1.538	0.769	sp^3	75.0	0.410
vi	1.507	0.738	sp^2	66.7	0.405
$C\equiv C$	1.464	0.695	sp^1	50.0	0.409

Table 7. D_{ad} shows the largest, and hence the most measurable, change of all the bonds involved in the delocalized system. The $c(vi)$ values are, as expected, greater than the corresponding $c(\Delta)$ values, in agreement with the experimental results cited by Charton (1970). The c value for the $vi-vi$ fragment (-0.014 \AA) may be compared with a value of $ca -0.01 \text{ \AA}$ derived by Maksić & Rubčić (1977) from maximum-orbital-overlap methods. The ratios $c(\Delta)/c(vi)$ (Table 7) vary from 68–74% with a mean of 71% over vi , *keto* and *acid* acceptors. Although the method of estimating c values is, perhaps, simplistic (since it ignores other electronic effects) the X-ray results are in broad quantitative agreement with the UV data, and fit well into the general pattern of comparative data for Δ and vinyl analogues.

Table 7 also permits a comparison of the conjugative ability of vinyl and carbonyl groups. The c values for C=O-containing acceptors are greater than $c(vi)$ for both the Δ and vi donors. The ratio $c(vi):c(C=O)$ is 0.57 in both cases. A similar trend is also exhibited by the asymmetry parameters (Table 1 and Allen, 1980), which are $-0.022 (4) \text{ \AA}$ for vi and $-0.026 (5) \text{ \AA}$ for C=O, a ratio of 0.84. The UV results of Pete (1967) also indicate stronger conjugation in $\Delta-C=O$; the bathochromic-shift ratio is 0.80.

Conclusions

The analyses presented here and in part I (Allen, 1980) show that the mean geometry of substructural fragments, as obtained by X-ray methods, does provide a probe of fine details of molecular structure. A particular effect is not very likely to be revealed by an individual X-ray study; it is only when the results of many studies are analysed in some systematic manner that effects or trends become apparent. In many cases the geometrical changes are small, often at or below the significance limits of individual X-ray studies. Nevertheless, when all pertinent X-ray data are used, an encouraging general level of agreement is obtained with theoretical models and with other experimental findings.

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The Geometry of Small Rings.

III.* The Effect of Small-Ring Fusion on the Geometry of Benzene

BY FRANK H. ALLEN

Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, England

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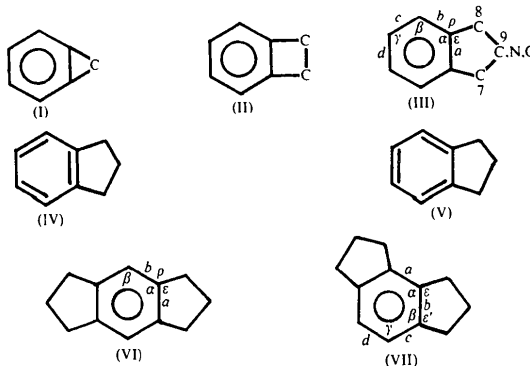
Abstract

X-ray mean geometries of mono- and dicycloalkenobenzenes with fused-ring sizes $r = 3, 4, 5$ have been obtained by use of the Cambridge Crystallographic Database. The tabulations show no significant variations in aromatic bond lengths. A high proportion of the strain induced in the benzene ring by fusion to small-ring cycloalkenes is reflected in systematic angular deformations. The intra-annular aromatic angle (β) *ortho* to a single fused ring is contracted by 2.2 (2), 4.9 (3) and 10.8 (5)° for $r = 5, 4, 3$; the *ipso* angles (α) expand by *ca* one-half those values. A linear relationship exists between α and β and the cycloalkene angle (ϵ) at the point of fusion. For monocycloalkenobenzenes with $r = 3-8$ the relationship is $\beta = 96.3 + 0.20\epsilon$. Limited data for *p*- and *m*-dicycloalkenobenzenes indicate that angular deformations are approximately additive. Experimental results are compared with simple force-field calculations of angle-bending strain.

Introduction

The idea that small-ring fusion to benzene might cause partial double-bond fixation in the aromatic ring was proposed by Mills & Nixon (1930) to explain anomalous electrophilic substitution results for benzo-

cyclopentene (indan, III). A theoretical study of indan (Longuet-Higgins & Coulson, 1946) favoured fixation in Kekulé structure (IV) by indicating shortening of bond a , lengthening of d and contraction of angle β . Since that time the two highly strained lower homologues in the series have been isolated: benzocyclobutene (II) (Cava & Napier, 1956) and benzocyclopropene (I) (Anet & Anet, 1964). The series up to benzocyclohexene has been studied by the CNDO/2 method (Cheung, Cooper & Manatt, 1971). Their geometrical results, summarized in Table 1, favour Kekulé structure (V): lengthening of a and c , shortening of b , contraction of β .



Early X-ray results on derivatives of (I) (Carstensen-Oeser, Muller & Durr, 1972; Billups *et al.*, 1973) and (II) (Hardgrove, Templeton & Templeton, 1968; Lawrence & MacDonald, 1969; Allen & Trotter, 1970a,b) indicated severe angular strain in the benzene

* Part II: Allen (1981).