

# Non-aromatic endocyclic angle at the ring fusion with the aromatic ring in benzocyclopentene and -hexene, revisited

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X-ray geometries of monocycloalkenobenzenes with a fused-ring size of  $r = 5, 6$  were obtained by the use of the Cambridge Structural Database. In contrast to Allen's study [Acta Cryst. (1981), B37, 900–906], the data were not averaged over exact or imposed  $m_{ad}$  symmetry ( $m_{ad}$  is the mirror plane going through the midpoint of the aromatic ring fusion bond and the aromatic bond parallel to it). The distribution of the non-aromatic endocyclic angle  $\varepsilon$  at the ring fusion clearly shows two and three, respectively, distinct curves for  $r = 5$  and  $r = 6$ . The respective ranges are 104.3–112.6 and 104.4–123.2°. If one of the C atoms directly attached to the aromatic ring is  $sp^2$  hybridized, the bond length  $e$  between the aromatic ring and this atom is shortened by some 0.044 (15) and 0.027 (12) Å for  $r = 5$  and  $r = 6$ , respectively. However, for  $r = 5$ ,  $e$  is only shortened by 0.030 (17) Å when both C atoms directly attached to the aromatic ring are  $sp^2$  hybridized. For  $r = 5$ , the endocyclic angle  $\varepsilon$  is 1.2 (13)° smaller at the side involving the  $sp^2$  hybridized C atom.

## 1. Introduction

In the third paper of a series dealing with the geometry of small rings, Allen (1981) discussed the effect of small-ring fusion on the geometry of benzene. For the X-ray mean geometries of 80 benzocyclopentene (fused-ring size  $r = 5$ ) and 84 benzocyclohexene ( $r = 6$ ) compounds retrieved from the May 1980 release of the Cambridge Structural Database (henceforth CSD), values of 108.5 (4) and 117.2 (9)°, respectively, were found for the endocyclic angle ( $\varepsilon$ ) of the non-aromatic ring at the fusion with the aromatic ring (Fig. 1). It should be noted that atom 9 in the benzocyclopentenes, and atoms 9 and 10 in the benzocyclohexenes can be C, N or O. Consequently, the names benzocyclopentene and benzocyclohexene are not restricted to pure carbon rings, but they also include N or O heterocyclic ring systems.

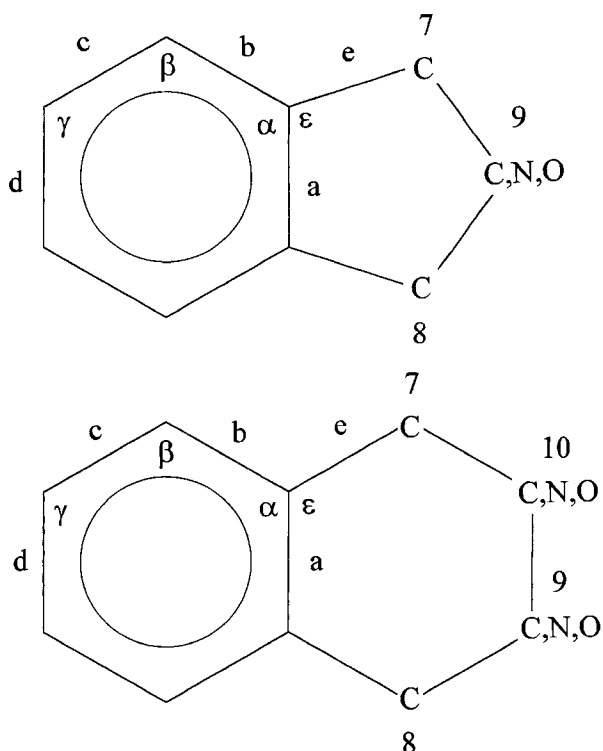
Ianelli and co-workers recalculated a number of Allen's parameters from the 1988 release of the CSD, applying the same criteria. For 127 benzocyclopentene compounds  $\varepsilon = 110.4$  (1)° (Ianelli *et al.*, 1989; Benassi *et al.*, 1991), while for 379 benzocyclohexene compounds  $\varepsilon = 115.9$  (1)° (Ianelli *et al.*, 1990; Benassi *et al.*, 1991). In both cases no value for  $e$  was calculated.

Within the course of a study of musk compounds (De Ridder, 1992), the X-ray single-crystal structures of a number of indan ( $r = 5$ ; De Ridder & Schenk, 1991, 1992, 1994; De Ridder, Fraanje & Schenk, 1994; De Ridder, Čapková *et al.*, 1994) and tetralin compounds ( $r = 6$ ; De Ridder *et al.*, 1990; De Ridder, Fraanje *et al.*, 1994a,b) were established. In Allen's paper (1981) benzocyclopentene and benzocyclohexene are

used to denote the monocycloalkenobenzenes with  $r = 5$  and  $6$ , respectively, while the terminology indan and tetralin is used for the same of type of compound in De Ridder's (1992) work. For clarity, benzocyclopentene and benzocyclohexene will be used hereafter. The average value of the endocyclic angle  $\epsilon$  for 13 benzocyclopentene compounds was  $111.7(7)^\circ$  (34 observations, range  $109.5$ – $112.8^\circ$ ), while that for seven benzocyclohexene compounds was  $123.0(12)^\circ$  (16 observations, range  $120.5$ – $124.7^\circ$ ). The significantly larger values found in the molecular structures of these compounds compared with the values obtained by Allen (1981) have prompted the present review of X-ray results obtained for monocycloalkenes with fused-ring size of  $r = 5, 6$ .

## 2. Methodology

Crystallographic coordinates for monocycloalkenobenzenes with fused-ring sizes of  $r = 5, 6$  were retrieved from the April 1994 release of the CSD (Version 5.07, 120 481 entries: Allen *et al.*, 1991). In order to enable a comparison with the results from Allen's paper a similar query was defined, which means that the data refer to fragments where the cycloalkene is the sole benzene substituent. With the exception of the bond at the fusion with the aromatic ring, the bonds in the non-aromatic ring were explicitly defined as single bonds. Substitution on the cycloalkene ring was permitted except for additional fused aromatic systems. General search restrictions ensured that only organic compounds were included which did



**Figure 1**  
Definition of the geometrical parameters for benzocyclopentene and benzocyclohexene. The mirror plane  $m_{ad}$  goes through the midpoint of bonds  $a$  and  $d$  (see §3.4.).

not contain heavy atoms, defined as transition elements and the halogens Br and I. It should be noted that an organic compound was retrieved by applying the relevant bit screen which comprises the chemical classes 1–65 and 70, whereas in Allen's paper only the chemical classes 1–60 were taken into consideration. Furthermore, structures were only included in this study if  $R \leq 0.07$ , the mean  $\sigma(C-C) \leq 0.01 \text{ \AA}$  and the coordinate set is error-free. In addition to the restrictions defined by Allen, crystal structures showing disorder were excluded in the calculations performed by *GSTAT* (Allen *et al.*, 1991). Analogous to Allen's study, atom 9 in the five-membered, and atoms 9 and 10 in the six-membered non-aromatic rings were restricted to C, N or O.

There were 317 benzocyclopentene and 254 benzocyclohexene structures retrieved *via QUEST* from the CSD. CSD reference codes for both data sets and full citations have been deposited.<sup>1</sup>

In contrast to Allen's study the data were not averaged over exact or imposed  $m_{ad}$  symmetry when calculations were carried out with *GSTAT*, the reason for which will be explained further on.

Before analysis, the results obtained by *GSTAT* were carefully scrutinized: in those cases in which a CSD reference code had more than one fragment and one of these fragments had an aromatic ring with substituents other than the cycloalkene ring, all fragments were excluded.

In order to avoid confusion with Allen's paper (1981) the same notation and the same atomic numbering was applied (Fig. 1). It should be remarked that this numbering is different from the *IUPAC* numbering system which was also applied in De Ridder's work (1992).

## 3. Results and discussion

The aim of Allen's (1981) work was to study the effect of small-ring fusion on the geometry of benzene. The monocycloalkenobenzenes with fused-ring sizes  $r = 3, 4, 7$  and  $8$ , as well as dicycloalkenobenzenes, are beyond the scope of the present work and therefore only the monocycloalkenobenzenes with fused-ring sizes  $r = 5$  and  $6$  are reported and discussed here. For comparison, all geometrical parameters defined by Allen were calculated. In view of this work, however, only the averaged endocyclic angles of the aromatic ring ( $\alpha$ ,  $\beta$  and  $\gamma$ ), the individual endocyclic angles of the non-aromatic ring at the fusion with the aromatic ring ( $\epsilon$ ), and the bond lengths between the carbon atom of the aromatic ring and the carbon of the non-aromatic ring attached to it ( $e$ ) are compiled in Table 1. All geometrical parameters have been deposited as supplementary material.

### 3.1. Geometry of the aromatic ring

Analogous to the findings of Allen (1981) little variation exists in the aromatic bond lengths: the maximum difference

<sup>1</sup>Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA0141). Services for accessing these data are described at the back of the journal.

**Table 1**Selected geometries with the nomenclature given in Fig. 1 ( $n$  = number of fragments; calculated standard uncertainty in parentheses).

	$n$	$\langle\alpha\rangle$	$\langle\beta\rangle$	$\langle\gamma\rangle$	$\varepsilon_1$	$\varepsilon_2$	$\langle\varepsilon\rangle$	$e_1$	$e_2$	$\langle e\rangle$
Benzocyclopentenes										
5	383	121.0 (6)	117.9 (9)	121.1 (4)	109.3 (17)	109.3 (17)	109.3 (15)	1.495 (22)	1.496 (21)	1.495 (18)
5C	220	120.7 (5)	118.3 (8)	120.9 (4)	109.9 (16)	109.9 (16)	109.9 (13)	1.499 (22)	1.499 (22)	1.499 (18)
5N	115	121.4 (4)	117.3 (7)	121.3 (4)	108.8 (10)	108.8 (10)	108.8 (9)	1.487 (16)	1.486 (15)	1.486 (11)
5O	48	121.3 (4)	117.6 (5)	121.2 (3)	107.7 (19)	107.6 (18)	107.7 (18)	1.492 (25)	1.502 (24)	1.497 (21)
533	158	120.7 (5)	118.4 (8)	120.9 (4)	109.5 (22)	109.4 (22)	109.4 (21)	1.511 (15)	1.511 (14)	1.511 (12)
533C	124	120.6 (5)	118.6 (8)	120.8 (4)	109.9 (18)	109.8 (18)	109.9 (16)	1.511 (15)	1.510 (14)	1.511 (12)
533N	10	120.8 (2)	118.4 (3)	120.8 (2)	110.5 (19)	110.4 (18)	110.5 (18)	1.512 (9)	1.508 (10)	1.510 (8)
533O	24	121.1 (4)	117.8 (6)	121.1 (3)	107.0 (24)	106.5 (19)	106.8 (21)	1.512 (15)	1.513 (15)	1.513 (13)
523	76	121.0 (4)	118.0 (7)	121.0 (3)	109.3 (9)	110.5 (14)	109.9 (10)	1.469 (8)	1.513 (11)	1.491 (7)
523C	37	120.7 (4)	118.4 (6)	120.9 (3)	109.9 (8)	111.8 (7)	110.8 (4)	1.466 (8)	1.515 (11)	1.491 (7)
523N	22	121.2 (3)	117.7 (5)	121.1 (3)	109.0 (6)	109.4 (6)	109.2 (3)	1.474 (7)	1.511 (12)	1.492 (6)
523O	17	121.4 (2)	117.5 (4)	121.2 (2)	108.5 (5)	109.2 (7)	108.8 (3)	1.467 (6)	1.510 (9)	1.489 (6)
522	149	121.3 (5)	117.4 (8)	121.3 (4)	108.9 (9)	108.9 (9)	108.9 (7)	1.481 (13)	1.481 (13)	1.481 (12)
522C	59	120.9 (5)	117.9 (8)	121.1 (4)	109.5 (8)	109.5 (7)	109.5 (6)	1.482 (15)	1.480 (17)	1.481 (15)
522N	83	121.5 (4)	117.0 (6)	121.5 (3)	108.5 (7)	108.5 (6)	108.5 (4)	1.481 (11)	1.483 (9)	1.482 (8)
522O	7	121.5 (3)	117.1 (4)	121.4 (2)	107.9 (6)	107.7 (5)	107.8 (3)	1.464 (6)	1.463 (8)	1.463 (6)
Benzocyclohexenes										
6	357	119.6 (7)	120.1 (12)	120.2 (5)	117.5 (47)	117.5 (48)	117.5 (47)	1.505 (19)	1.510 (15)	1.508 (14)
6C	292	119.7 (8)	120.0 (12)	120.3 (5)	116.9 (49)	117.1 (51)	117.0 (50)	1.506 (19)	1.511 (15)	1.509 (14)
6N	34	119.2 (4)	120.8 (7)	120.0 (4)	121.2 (11)	120.7 (12)	120.9 (6)	1.503 (21)	1.503 (19)	1.503 (18)
6O	31	119.7 (5)	120.1 (8)	120.2 (3)	118.7 (28)	118.9 (23)	118.8 (24)	1.508 (14)	1.504 (15)	1.506 (9)
633	292	119.7 (8)	120.0 (12)	120.2 (5)	116.9 (50)	116.9 (51)	116.9 (50)	1.511 (14)	1.513 (13)	1.512 (10)
633C	243	119.8 (8)	119.9 (13)	120.3 (5)	116.2 (51)	116.3 (53)	116.3 (51)	1.512 (14)	1.514 (13)	1.513 (10)
633N	27	119.0 (3)	121.1 (5)	119.9 (3)	121.3 (12)	120.7 (13)	121.0 (6)	1.512 (10)	1.510 (12)	1.511 (7)
633O	22	119.6 (6)	120.3 (9)	120.1 (3)	119.2 (31)	118.8 (28)	119.0 (30)	1.508 (15)	1.512 (8)	1.510 (7)
623	44	119.3 (6)	120.5 (9)	120.1 (4)	120.2 (11)	120.0 (19)	120.1 (12)	1.477 (15)	1.504 (17)	1.491 (15)
623C	34	119.1 (5)	120.9 (8)	120.0 (4)	120.5 (10)	120.5 (15)	120.5 (9)	1.476 (16)	1.504 (18)	1.490 (15)
623N	1	120.204	119.180	120.612	120.832	120.804	120.818	1.457	1.489	1.473
623O	9	119.96 (15)	119.52 (21)	120.50 (11)	118.9 (4)	117.7 (13)	118.3 (7)	1.483 (9)	1.508 (4)	1.496 (6)
622	21	119.6 (4)	120.0 (6)	120.4 (2)	120.4 (10)	120.6 (7)	120.5 (7)	1.480 (12)	1.482 (11)	1.481 (9)
622C	15	119.5 (4)	120.1 (6)	120.3 (3)	120.3 (12)	120.7 (8)	120.5 (8)	1.485 (10)	1.487 (8)	1.486 (6)
622N	6	119.8 (4)	119.8 (5)	120.4 (1)	120.5 (2)	120.2 (4)	120.4 (3)	1.468 (5)	1.470 (5)	1.469 (4)
622O	0	–	–	–	–	–	–	–	–	–

between the average values of  $a$ ,  $b$ ,  $c$  and  $d$  being  $\leq 0.02 \text{ \AA}$ . The angular distortions in the aromatic ring are a consequence of the strain imposed by the fused ring. For  $r = 5$ ,  $\beta$  is significantly and generally  $< 120^\circ$ , while  $\alpha$  and  $\gamma$  are generally  $> 120^\circ$  and nearly equal to each other, thus imposing almost exact  $mm$  symmetry on the aromatic ring. One mirror plane goes through the midpoints of bonds  $a$  and  $d$  (Fig. 1), while the other perpendicular to it goes through the C atoms *ortho* to the ring fusion. For  $r = 6$ , only small deviations from  $120^\circ$  are observed, indicating an undistorted hexagon. The fusion strain imposed by the cycloalkene ring on the aromatic ring can be expressed by  $\varepsilon$ : Allen (1981) showed that a linear relationship exists between  $\alpha$  and  $\beta$  of the aromatic ring and the cycloalkene angle  $\varepsilon$ . From  $\beta = 96.3 + 0.20 \varepsilon$  (Allen, 1981) and the comparison of the average value of  $109.3 (15)^\circ$  for  $r = 5$  versus  $117.5 (47)^\circ$  for  $r = 6$  it can be seen that the strain is minimal for benzocyclohexene.

### 3.2. Benzocyclopentenes

Phthalocyanine-type compounds were excluded from this study since no distinction could be made in *GSTAT* between its three aromatic rings on one hand and the fourth non-aromatic ring on the other hand.

In the frequency distribution of the averaged endocyclic angle  $\varepsilon$  (Fig. 2) two skewed curves can be distinguished, one

with a maximum around  $106.5\text{--}107^\circ$  and one around  $108.5\text{--}109^\circ$ . A closer inspection of the first curve revealed that this group contains compounds in which C7 and C8 are connected by an ethylene bridge. In the case where there is no supplementary ring fusion and both C7 and C8 are  $sp^3$ -hybridized, C-atom values significantly higher (up to  $113^\circ$ ) than the average value are observed. From Fig. 2 one might ask whether the second curve could be split into two parts: a lower range with a maximum around  $108.5\text{--}109^\circ$  and an upper range with a maximum around  $110.5\text{--}111^\circ$ . Although no general trend was observed, it can be noted that two structure types are frequently found in the upper range, both in which atom 9 is a carbon atom: a first type in which one of the C atoms attached to the aromatic ring forms part of a carbonyl function and a second type in which the cyclopentene ring carries bulky substituents such as *tert*-butyl.

It may be noted that the average value of  $108.5 (4)^\circ$  found by Allen (1981) is in good agreement with the maximum observed in Fig. 2.

### 3.3. Benzocyclohexenes

The compounds in which an additional bond occurs between C7 and C8 or between C7 and C9 (a bond between C8 and C10 is a similar case) have not been included in this study.

In the frequency distribution of the averaged endocyclic angle  $\varepsilon$  (Fig. 3) three distinct curves can be detected. The lowest curve with angles in the range 104–107° contains compounds in which C7 and C8 are connected by one C, N or O bridging atom. As expected, the highest frequency in this range is observed in the interval 106.5–107° since this part of the distribution coincides with the lower curve of the benzocyclopentenes in Fig. 2. The medium part of the distribution (110–116°) includes compounds in which C7 and C8 are in general connected by an ethylene bridge, whereas the highest curve (from 116 up to 123.5°) contains compounds in which there is no supplementary ring fusion between C7 and C8.

From Figs. 2 and 3 it can easily be observed that the range of the endocyclic angle  $\varepsilon$  of the benzocyclohexenes is more than twice the range found for the benzocyclopentenes.

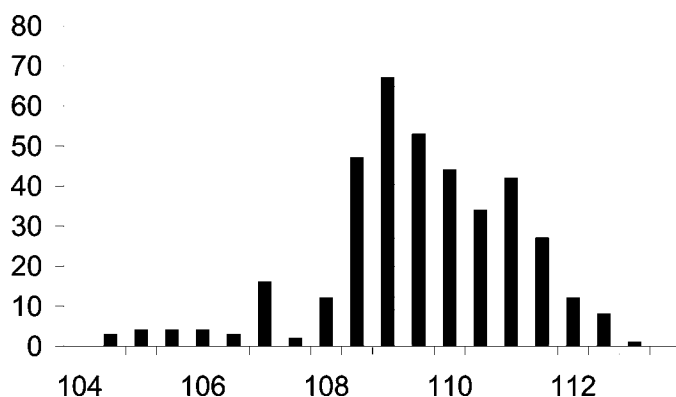
In the case of the benzocyclohexenes the average value of 117.2 (9)° found by Allen (1981) lies in between the middle and the upper curve in Fig. 3. Note, however, that this value is the same as the average value for  $\varepsilon$  given in Table 1.

#### 3.4. Factors influencing the value of $e$ and $\varepsilon$

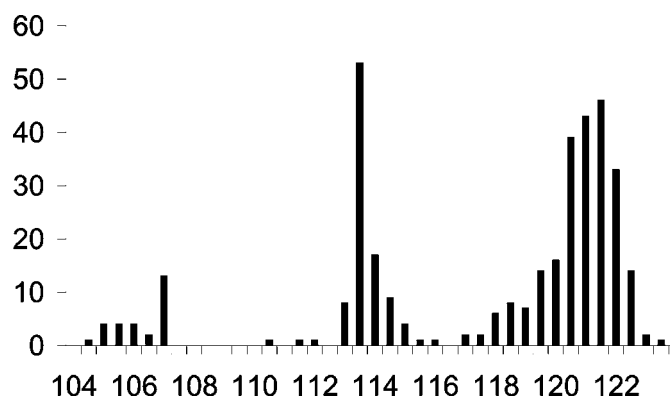
If the substituents on the cyclopentene ring are not taken into account the benzocyclopentene moiety has exact mirror symmetry with the mirror plane  $m_{ad}$  going through the midpoints of the bonds  $a$  and  $d$  and through atom 9 (Fig. 1). In the benzocyclohexene moiety, however, atoms 9 and 10 (Fig. 1) are at opposite sides of the molecular plane going through the aromatic ring and the C atoms directly attached to it. Consequently, if the entire benzocyclohexene moiety is taken into consideration, imposed  $m_{ad}$  symmetry assumes that the moiety is planar and implies that the mirror plane  $m_{ad}$  goes through the midpoints of the bonds  $a$  and  $d$  and through the midpoint of the bond between atoms 9 and 10. Imposed  $m_{ad}$  symmetry also implies that no distinction is made between the types of atoms 9 and 10 which can be C, N or O. In the present work the data were not averaged over exact or imposed  $m_{ad}$  symmetry and for both data sets the geometrical parameters were calculated for three subsets. In the first subset both atoms 7 and 8 are  $sp^3$  hybridized: the subsets are denoted 533 and 633 for the benzocyclopentenes and benzocyclohexenes, respec-

tively. In this notation the first digit of the subset indicates the ring size of the cycloalkene ring, while the following two digits specify the hybridization of the C atoms directly attached to the aromatic ring. In the second subset atom 7 is  $sp^2$  hybridized and atom 8 is  $sp^3$  hybridized (denoted 523 and 623, respectively), while in the third subset both atoms 7 and 8 are  $sp^2$  hybridized (denoted 522 and 622, respectively). The results of the subsets are also given in Table 1. Both for the benzocyclopentenes and -hexenes the average values of  $e$  and  $\varepsilon$  are equal to within 0.005 Å and 0.1° in the '33' and '22' subsets. For subsets 523 and 623, however, significant differences are observed. The bond length  $e$  involving the  $sp^2$  hybridized C atom is shortened compared with the  $sp^3$  hybridized atom, by 0.044 (15) and 0.027 (12) Å for benzocyclopentene and benzocyclohexene, respectively. In the benzocyclopentenes the endocyclic angles  $\varepsilon$  differ by 1.2 (13)°, the smaller angle observed at the side involving the  $sp^2$  hybridized C atom. In the benzocyclohexenes the difference between the endocyclic angle  $\varepsilon$  is smaller. Fig. 4 shows the distance  $e_1$  versus  $e_2$ , and the angle  $\varepsilon_1$  versus  $\varepsilon_2$  for the benzocyclopentenes and the benzocyclohexenes, respectively; in these figures the sloping line indicates the distances for which  $e_1 = e_2$  and the angles for which  $\varepsilon_1 = \varepsilon_2$ , respectively. In the cases of subsets 533, 522, 633 and 622 the data are more or less equally spread above and below the lines  $e_1 = e_2$  and  $\varepsilon_1 = \varepsilon_2$ , respectively. For both subsets 523 and 623 (Figs. 4a and c) the data are found only above the line  $e_1 = e_2$ , since the bond length of the aromatic ring to the  $sp^2$  C atom is systematically shorter than that to the  $sp^3$  C atom. For the endocyclic angle, the data of subset 523 (Fig. 4b) are mainly observed above the line  $\varepsilon_1 = \varepsilon_2$ , which is in agreement with the fact that the angle at the side involving the  $sp^2$  C atom is smaller by 1.2 (13)° than at the side involving the  $sp^3$  C atom. Inspection of the endocyclic angle for the data of subset 623 (Fig. 4d), however, shows that the difference between the endocyclic angle  $\varepsilon$  is smaller. As expected, three distinct groups of data points can be distinguished in Fig. 4(d), which is in agreement with the three distinct curves in the frequency distribution of the benzocyclohexenes (Fig. 3).

The shortening of the bond is undoubtedly caused by changes in hybridization and probable conjugative interac-



**Figure 2**  
Frequency distribution of the averaged endocyclic angle  $\varepsilon$  for 383 benzocyclopentene compounds. Interval width = 0.5°.

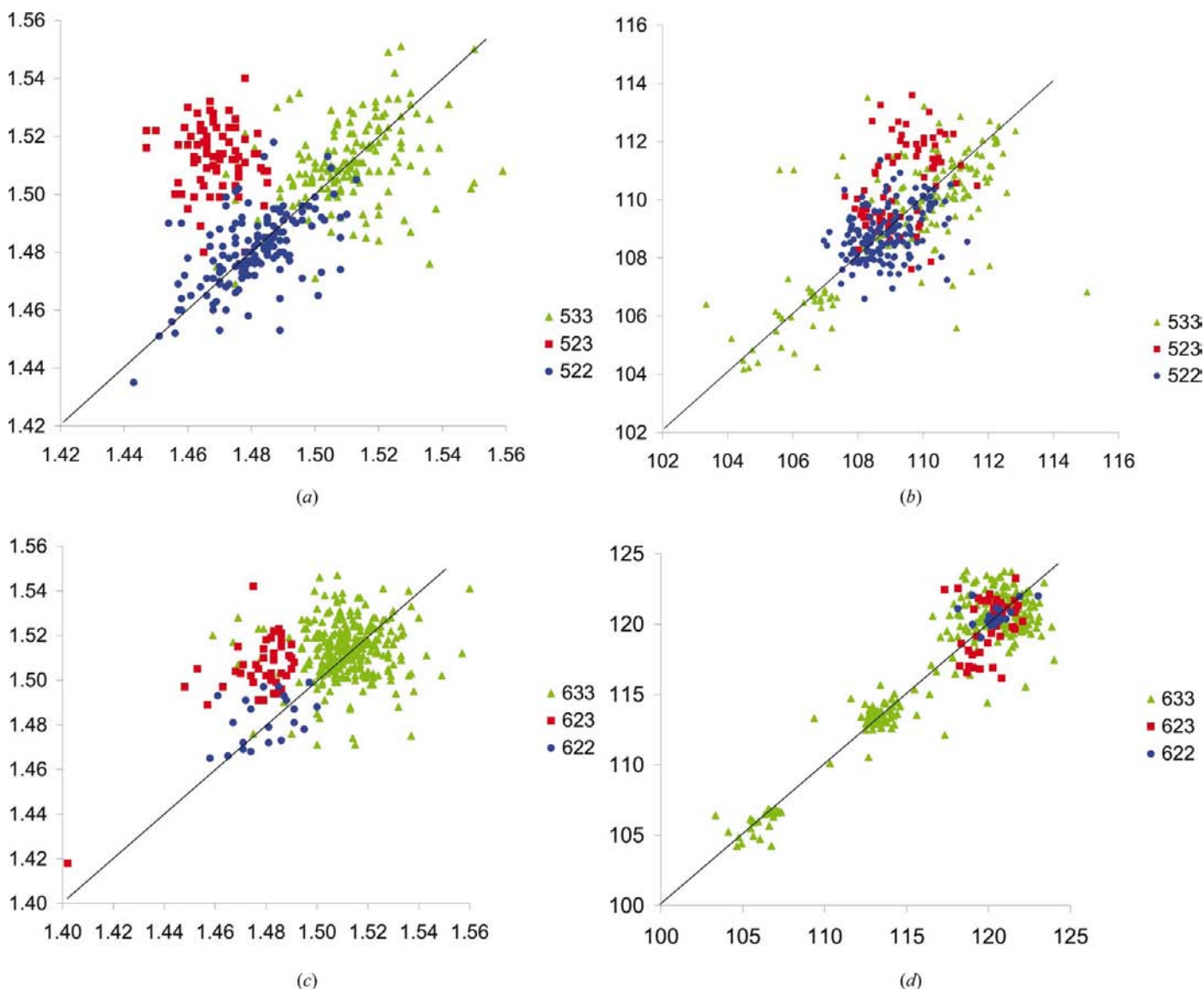


**Figure 3**  
Frequency distribution of the averaged endocyclic angle  $\varepsilon$  for 357 benzocyclohexene compounds. Interval width = 0.5°.

tion(s). However, the degree of shortening depends on the number of atoms which are  $sp^2$  hybridized. Indeed, when both atoms 7 and 8 in the benzocyclopentenes are  $sp^2$  hybridized (subset 522), bond  $e$  is only shortened by some 0.030 (17) Å. In the benzocyclohexenes (subset 622), the shortening can be considered to be the same. As part of an intensive study using the CSD Orpen *et al.* (1994) calculated an average C—C distance of 1.470 (15) and 1.488 (12) Å in  $C_{\text{aromatic}}-C=C$  systems for conjugated and unconjugated systems, respectively. For  $C_{\text{aromatic}}-C(=O)-C^*$  they found an average C—C distance of 1.488 (16) Å. From these values it can be concluded that the conjugative interaction is stronger for the benzocyclopentenes having only one  $sp^2$  hybridized C atom attached to the aromatic ring than for the benzocyclopentenes having two  $sp^2$  hybridized C atoms attached to the aromatic ring or for benzocyclohexenes.

The complete data set and the subsets described above were also split according to the atom type at position 9 in the benzocyclopentenes and at position 9 and/or 10 in the benzocyclohexenes. The results of the subsets are also compiled in Table 1: in this case the atom type is added to the two digits indicating the hybridization of the atoms directly attached to the aromatic ring. For example, subset 533N is the class of benzocyclopentenes with a nitrogen at position 9 and with the C atoms directly attached to the aromatic ring having  $sp^3$  hybridization.

For the whole benzocyclopentene data set as well as for subsets 523 and 522  $\varepsilon$  depends on the atom type at position 9 according to  $C > N > O$ , *i.e.* following the atomic radii. Only for subset 533 is the largest  $\varepsilon$  value found for N such that  $N > C > O$ . It can also be observed that  $\varepsilon$  decreases when the number of  $sp^2$  hybridized C atoms directly attached to the aromatic



**Figure 4**

(a)  $e_2$  versus  $e_1$  for the benzocyclopentene compounds; (b)  $e_2$  versus  $e_1$  for the benzocyclopentene compounds; (c)  $e_2$  versus  $e_1$  for the benzocyclohexene compounds; (d)  $e_2$  versus  $e_1$  for the benzocyclohexene compounds.

**Table 2**

Results of the multivariate analysis of variance on the whole set of bond lengths and endocyclic ring angles (16 variables).

$\nu_1$  and  $\nu_2$  are the degrees of freedom relevant to F,  $p$  is the significance level.

Effect of	Data set	No. of cases	No. of groups	Wilks' $\Lambda^*$	F value	$\nu_1$	$\nu_2$	$p$
Ring size	5 + 6	740	2	0.3205	95.7	16	723	< 0.1%
Hybridization	5	383	3	0.2479	69.6	32	730	< 0.1%
	6	357	3	0.6371	12.1	32	678	< 0.1%
Nature of atom	533	158	3	0.4698	4.19	32	280	< 0.1%
	523	76	3	0.0433	13.8	32	116	< 0.1%
	522	149	3	0.1190	15.5	32	262	< 0.1%
	633	292	3	0.7017	3.31	32	548	< 0.1%
	623	44	3	0.0398	6.52	32	52	< 0.1%
	622	21	2	0.0172	10.72	16	4	$\approx 2.5\%$

ring increases in the case of N. Presumably, the different behaviour of N at position 9 is because of the possible intra-annular conjugation with the free N electron pair.

A different order is found for the benzocyclohexenes: for the complete data set and for the subsets 633 and 622  $\epsilon$  follows the order  $N > O > C$  (note that no data are available for subset 622O), while for subset 623 the order  $N > C > O$  is observed. In both cases, however, no sufficient explanation for this behaviour can be given.

### 3.5. Multivariate analysis of variance

The original geometrical variables (eight bond lengths and eight endocyclic ring angles, *cf.* Fig. 1) of the benzocyclopentene and the benzocyclohexene compounds were submitted to a multivariate analysis of variance procedure (Johnson & Wichern, 1992). This procedure allowed the detection of the significant effects of the parameters that affect the geometrical variables. Three classification factors were taken into consideration:

- (i) the ring size of the cycloalkene ring;
- (ii) the hybridization type of the C atoms directly attached to the aromatic ring;
- (iii) the type of atom which is not bonded to the aromatic ring (*i.e.* atom 9 for the cyclopentenes, and atoms 9 and 10 for the cyclohexenes).

The calculations were performed with the *MATLAB* (The MathWorks, Inc., 3 Apple Hill Drive, Natick, MA 01760-2098, USA) package and the results are compiled in Table 2.

The results indicate that the ring size of the non-aromatic ring, the type of hybridization of atoms 7 and 8 and also the nature of atom 9 in the benzocyclopentenes, and atoms 9 and 10 in the benzocyclohexenes, respectively, have a highly significant effect ( $p < 0.1\%$ ) on the whole set of geometrical variables taken into consideration. The nature of atoms 9 and 10 in subset 622 seems to be less significant ( $p \approx 2.5\%$ ), presumably because of the lower number of cases available (also note that only two groups are considered as no data are available for subset 622O).

### 4. Concluding remarks

Originally an attempt was made to retrieve the data sets obtained by Allen based on the May 1980 release of the CSD. Although no restriction was put on the bond type of the bonds of the fused ring (except for the aromatic ring fusion bond), no positive results were obtained. Therefore, all bonds in the cycloalkene ring were defined as single bonds in the present study. Consequently, conjugation between the aromatic ring with the fused system is only possible with extra-annular bonds. This is in contrast with Allen's work (1981) which also allowed for the possibility of intra-annular bonds, *i.e.* by introducing one or two double bonds in the fused ring. Allen defined a subset for the benzocyclopentenes with a carbonyl group at positions 7 and 8, and an O atom at position 9, corresponding to phthalic anhydride rings. Several queries were tried but none of these resulted in an acceptable number of retrieved compounds. From the number of compounds retrieved in this study, on one hand, and by the fact that the geometrical results of the present subset 522N corroborate very well with those obtained by Allen's subset (1981), on the other hand, it can be assumed that both data sets refer to phthalic imide rather than phthalic anhydride compounds. If it is finally taken into account that Allen excluded benzoquinones in the case of the benzocyclohexenes, it can safely be assumed that the same type of compounds were retrieved in both studies. Consequently, the additional requirement to have only single bonds in the non-aromatic ring will have only a small, if any, influence for the comparison of the results of both studies.

In contrast to Allen (1981) the geometries were not averaged over exact or imposed  $m_{ad}$  symmetry. The present results obviously show that such averaging cannot be allowed in the case of the '23' subsets. First,  $\epsilon$  is systematically smaller at the side of the  $sp^2$  hybridized C atom. Secondly, a shortening of bond  $e$  by 0.044 (15) Å is observed, a value which is significantly larger than the 0.025 Å given by Allen (1981). Undoubtedly, the symmetry-averaging has resulted in a underestimation of this shortening.

For the benzocyclopentenes it has been shown that  $e$  and  $\epsilon$  not only depend on the ring size, but also on the number of  $sp^2$  hybridized C atoms directly attached to the aromatic ring and on the atom type at position 9. In the case of the benzocyclohexenes these influencing parameters seem to have less effect, which can undoubtedly be attributed to the fact the fusion strain will be smaller the larger the cycloalkene ring.

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