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Conformations of Six-membered Carbon Rings with Planar Groups

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A systematic account is given of experimental and theoretical data on the steric structures of six-membered rings containing groups with a coplanar disposition of three consecutive bonds within the ring—a fragment with a double bond, a condensed rigid ring, or a bridged bicyclic system. We shall consider rings containing one such fragment, namely cyclohexane, bicyclo-[4.1.0] heptane, and its analogues, as well as rings with two fragments of this kind in the 1,4- or 1,3-positions. Data are presented on the structure of the rings, their inversion, and the orientation of the substituents in various positions. The principal characteristics of the conformational structures of such compounds are described and the possibility of the assumption of the boat form and the relative preferences for the axial and pseudoaxial orientations of the substituents and the condensed planarising fragments are discussed.
The bibliography includes 272 references.

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I. INTRODUCTION

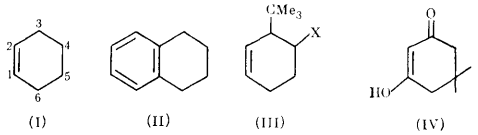
Cyclohexane and its derivatives are classical objects of conformational analysis. Much less attention has been devoted to six-membered carbon rings with planar groups of atoms formed by a double bond or by condensation with a rigid system ensuring an eclipsed conformation of the common bond. The ring may also contain two planar groups in the 1,3- or 1,4-positions. Variation of the nature and positions of such groups and of the configurations of the condensed rings and substituents creates a wide variety of possible types of compounds. Studies on such compounds have been far from uniform; the available reviews concern individual conformational relations for the cyclohexane[1,2] and cyclohexa-1,4-diene[3,4] series.

The stereochemistry of both unsaturated six-membered rings and cyclohexanes or cyclohexenes condensed with three-membered rings or other rigid systems has developed vigorously during the last decade. A theoretical basis for the known facts is being developed and a number of common features have been discovered. This permits a survey and analysis of the results obtained.

II. PRINCIPAL CHARACTERISTICS OF THE CONFORMATIONAL STRUCTURE OF CYCLOHEXENES

1. Ring Conformation

It is known that cyclohexene (I) and its derivatives exist in the half-chair conformation (Fig.1).[5,6] The endocyclic torsional angles ϕ(for the half-chair conformation the angle of twist ψ) serve as a measure of non-planarity. The structure of cyclohexene has been determined by gas electron diffraction[7-11] and microwave spectroscopy[12,13]:



The angles ϕ vary within narrow limits: $\phi(23) = 15.2-15.7°$, $\phi(34) = 44.8-46.0°$, $\phi(45) = 60.2-62.6°$, and $\psi = 25.4°$ (Chiang and Bauer[10]) or 30.1° (Scharpen et al.[13]). The value $\phi(45) = 63°$ was also established by ^{1}H NMR.[14] Theoretical conformational analysis using various computational methods leads to a good agreement with experiment[8,9,15-23]. Ring structure is retained when the substituents are located only at the olefinic atoms in cyclohexene, in tetralin (II), and in its heteroaromatic analogues; a number of data have been published for tetralin derivatives[24,25] and for their solutions[26].

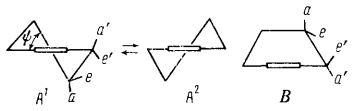


Figure 1. The conformations of cyclohexene and its derivatives; A^1, A^2—half-chair; B—boat.

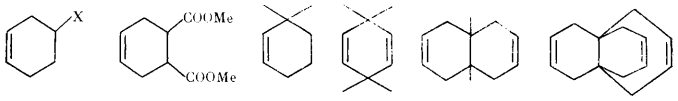
Asymmetric substitution can distort the half-chair, i.e. can lead to different deviations of the C(4), and C(5) atoms from the plane of the double bond, which has been demonstrated by calculation[18,27] and structural studies[24,25]. Marked distortions are observed under the conditions of steric hindrance due to bulky substituents. For example, the angle ϕ(23) in the *trans*-isomers of 4-substituted 3-t-butylcyclohexenes (III) and the angle ϕ(56) in the *cis*-isomers diminish to 7°.[28,29] Further distortion of the half-chair leads to the boat conformation, which has been observed for certain polycyclic compounds[32].

An additional conformational effect, namely conjugation of the C=O bond with the π-electron system, is observed in cyclohexanones and tetralinones. This effect stabilises the 1,2-diplanar form (the envelope conformation); thus the C(5) atom in dimedone (IV) is displaced from the plane of the ring by 0.6 Å.[30,31] The structure of 1-tetralinone is also close to the envelope conformation[32].

2. Ring Inversion

The barrier $\Delta G^{\neq}$ to the transition between two half-chairs A^1 and A^2 in cyclohexene (Fig.1) amounts to 5 kcal mol^{-1} [33] or 7.6 kcal mol^{-1}. [34] The calculated data correspond to the maximum energy of the boat conformation. A point on the sloping section of the energy curve corresponds to the envelope conformation; the energy gain compared with the half-chair conformation is 1.5–2.5 kcal mol^{-1}. [17,22,35,36]

Data concerning the influence of substituents are contradictory. Energy barriers not exceeding 5.1 kcal mol^{-1} have been measured by the ultrasonic method for 4-substituted cyclohexenes (V): [37]



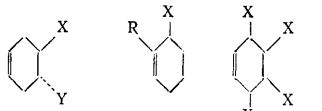
(V) (VI) (VII) (VIII) (IX) (X)

However, ^{1}H NMR studies of compounds (V) and (VI) have shown that the introduction of each substituent increases the barrier by 1 kcal mole^{-1}, which indicates inversions via the boat form[38]. This is confirmed by the increase of $\Delta G^{\neq}$ by 2.2 kcal mol^{-1} on passing from (VII) to (VIII)—the 3,6-flagstaff ("prow") interaction creates a considerable steric hindrance in the intermediate boat form[39]. Finally, the barrier for compound (IX) is approximately twice as high and that for compound (X) three times as high as the usual value, since two or three rings pass simultaneously through the boat form in the inversion process[40].

3. Conformations of the Substituents

The introduction of a double bond into a six-membered ring alters the orientation of the exocyclic bonds, particularly in the allylic positions, where they have a pseudoequatorial (*e'*) or pseudoaxial (*a'*) orientation (Fig.1). The dihedral angles between the planes in which these bonds are located (τ) differ appreciably from the angles in cyclohexane derivatives: $\tau(e'a) = 51°$, $\tau(e'e) = 62°$, $\tau(a'a) = 151°$, $\tau(a'e) = 53°$, $\tau(ea) = 64°$, and $\tau(aa) = 168°$. The bonds between the olefinic atoms form dihedral angles of 46° and 65° with the *e'*- and *a'*-substituents respectively[41]. The introduction of a double bond is responsible for the disappearance of one *syn*-axial interaction and a marked weakening of the second (*aa'*). The conformational energies of 4-substituents are therefore much lower than in the cyclohexane series. For halogen atoms, they are close to zero[38,42–46], and for iodine the *a*-orientation is actually preferred (ΔG = −0.05 kcal mol^{-1}). [38] The same may be noted for the cyano- and nitro-groups[46–48]. The methyl group[49] and the carbonyl functional groups[47,50–52] exhibit a somewhat greater tendency towards an equatorial orientation (but not exceeding 1 kcal mol^{-1}). The stabilisation of the axial position compared with the saturated analogues increases by 0.7 kcal mol^{-1} on passing from atom to atom in the series of halides, in conformity with their polarisabilities[38].

The *ee* ⇌ *aa* equilibrium is possible for *trans*-4,5-disubstituted cyclohexenes (XI). In the case of dichlorides and dicyanides the proportions of different forms are virtually the same[53–56], while for X = Y = Br the repulsion of the equatorial substituents leads to a greater stability of the diaxial conformation[57–59]. On the other hand, *trans*-4,5-dimethylcyclohexene has a preferred diequatorial conformation (ΔG = 1.1 kcal mol^{-1}) [60,61] like the analogous acids and esters[62]. In contrast to compound (XI), *trans*-2,3-dihalogenotetralins are characterised by a greater proportion of the *aa*-form (up to 80% for X = Cl and 95% for X = Br. [26,57,63]



(XI) (XII) (XIII)

An extensive investigation of cyclohexane with various *trans*-substitutents in the 4,5-positions has been undertaken [47,50,64–68]. It has been established that compounds with carboxy-groups are fully diequatorial, while others are almost so. An appreciable shift is observed when one of the substituents is CCl_3 (up to 66% of the *aa*-conformer for X = CCl_3 and Y = CH_2OH). [66,67]. This resembles the behaviour of iodocyclohexene. The large bulk of the substituent is not an obstacle to its axial orientation; even the t-butyl group can occupy the *a*-position to a large extent[69].

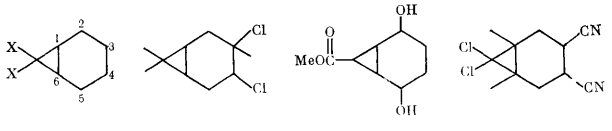
Pseudoequatorial substituents in the 3- and 6-positions are located close to the plane of the double bond, which is sterically unfavourable, particularly in the presence of substituents at the nearest olefinic atom, as in compound (XII). Such interaction is called 1,2-allylic ($A^{1,2}$). [1] The pseudoaxial position is therefore preferred for chlorine and bromine [43,70] and for certain oxygen-containing functional groups[71]. Qualitative analysis of the available data has shown that the proportion of the *e'*-conformer is greater only for 3-methylcyclohexene[72]. The *trans*-3,6-disubstituted derivatives can be fully diaxial[73]. 2,3-Disubstituted cyclohexenes are almost entirely pseudoaxial[74]. There is evidence that such orientation is caused not only by steric factors but also by hyperconjugation[72].

The different conformational conditions for the substituents in the 4(5)- and 3(6)-positions are revealed in the analysis of the structures of molecules of type (XIII), which exist in the form of six-configurational isomers. The *trans*-oriented bonds of the substituents at the atoms in the 4- and 5-positions assume the diequatorial position with the exception of the *a'eea'* ⇌ *e'aae'* equilibrium, but even the latter is 80–90% displaced towards the first form[24,25,41,75–77]. Concordant results have been obtained by calculation for 3,4-dimethylcyclohexene: *ee'* > *ea'* > *ae'* > *aa'*. [21]

III. CONFORMATIONS OF CYCLOHEXANE FRAGMENTS IN BICYLIC SYSTEMS

1. Bycyclo[4.1.0]heptane

The condensation of a six-membered ring with a three-membered ring also gives rise to the coplanarity of four atoms and the loss of a plane of symmetry by the planar group leads to the presence of two different boat conformations (*syn*- and *anti*) and, in the presence of different substituents, also to two half-chair forms (Fig.2). Theoretical calculations predicted the maximum stability of the half-chair conformation of bycyclo[4.1.0]heptane (XIV, X = H), [78,79] but the energy of the boat form is not higher by more than 3.3 kcal mol^{-1}. An electron diffraction study yielded the same results[80] as for the 7,7-dichloro-derivative (XIV, X = Cl) [81,82] and *trans*-3,4-dichorocarane (XV): [83]



(XIV) (XV) (XVI) (XVII)

The half-chair conformation has been found by X-ray diffraction for many compounds, for example, for compound (XVI)[84] and a series of cyclosteroids[24,25]. As a rule, the half-chair is somewhat asymmetric and approaches the envelope form in polysubstituted compounds of type (XVII).[85] This has also been observed after the introduction of an sp^2-atom into the six-membered ring[86].

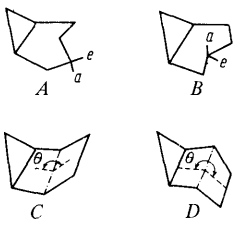


Figure 2. The possible conformations of bicyclo[4.1.0]-heptane; *A*, *B*—half-chair; *C*—*syn*-boat; *D*—*anti*-boat.

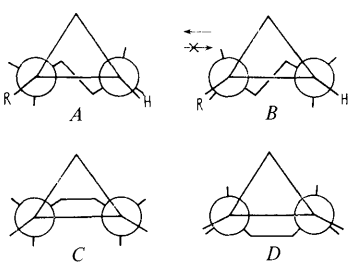
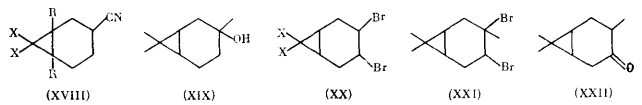


Figure 3. The orientation of the bonds in bicycloheptane systems; for legend, see Fig. 2.

Substituents in the 1-positions stabilise the half-chair form, in which they are less eclipsed (Fig. 3*A*). This has been demonstrated[87] for 1-t-butylbicycloheptane. The equatorial *cis*- and *trans*-substituents in the 3- and 4-positions do not interact with the ring, but the *cis*-axial substituent can be strongly destabilised, particularly for bulky *syn*-7-substituents. In the *trans*-isomers of compound (XVIII, R = H or Me, X = Cl or Br), the cyano-group is therefore 8% axial, while in the *cis*-isomers it occupies only the equatorial position[88,89]; similarly in both caranol (XIX) isomers the *cis*-substituent is equatorial[90,91]. Only the methoxycarbonyl group retains the equatorial position whatever the configuration[92,93].



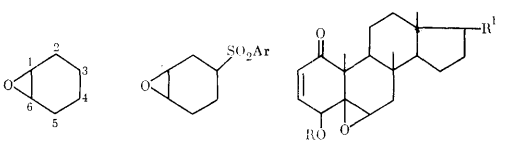
In *trans*-3, 4-disubstituted bicycloheptanes, the unsubstituted three-membered ring does not hinder the diaxial conformation; at any rate, in dibromocycloheptane the latter predominantes significantly[94]. In 1,6-disubstituted derivatives the steric hindrance experienced by the *trans*-axial substituent results in a diequatorial structure of the 3,4-diesters[89,92,95] and the corresponding dinitriles[89].

The introduction of substituents into the *syn*-7-position increases the conformational possibilities. The distortion of the ring in compound (XVII) in the direction of the envelope form in the crystalline phase has been noted. The tetrahalogeno-compounds (XX, X = Cl or Br) exist in solution mainly in the *anti*-boat conformation with the angle $\theta = 200$ to 215 °C.[96] The same form appears in the equilibrium involving dibromocarane (XXI) although the dichloro-derivative consists of a mixture of the *ee*- and *aa*-half-chair conformations: the smaller chlorine atom can be in the *cis*-axial position relative to the *gem*-dimethyl group[97,98]. The *anti*-boat conformation appears also in caranols and caramines with the *cis*-orientation of two substituents in the 3- and 4-positions [99,100]; the conformation of compounds of this type is greatly influenced by the possibility of the formation of hydrogen bonds[101–104].

The half-chair conformation is retained when sp^2-atoms are introduced into the ring[105,106] and in the isomeric caranones (XXII) the carbonyl group approaches the three-membered ring regardless of the orientation of the 3-methyl group[105].

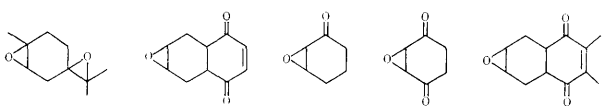
2. 7-Heteroanalogues of Bicycloheptane

Epoxycyclohexane (XXIII) has been investigated by gas electron diffraction[7,107,108] and microwave spectroscopy[109]. The six-membered ring has the half-chair conformation with the endocyclic dihedral angles $\phi(12) = \phi(65) = 16.3°$, $\phi(23) = \phi(54) = 48.8°$, $\phi(34) = 63.9°$,[108] and $\psi = 34.4°$.[109]



The results of calculations by the method of molecular mechanics are consistent with these findings[79]. The half-chair conformation has been established for many epoxycyclohexanes, for example, the isomers of compound (XXIV)[110] and polysubstituted and polycyclic compounds[24,25], including steriods. It is noteworthy, firstly, that the half-chair is usually asymmetric and, secondly, that its form depends to a large extent on the strength of the crystal field. Thus withafevin A (XXV) crystallises in two conformations differing in the direction and degree of bending of the *B* ring[111].

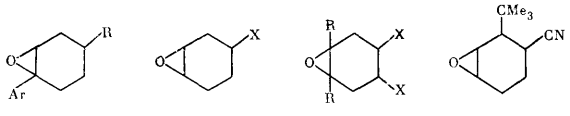
In certain epoxides the cyclohexane ring has the boat conformation. The electrical parameters of the molecule of terpinolene dioxide (XXVI) can be described only in terms of the presence of this form[112]. The boat conformation is to some extent stabilised by the other six-membered ring: for this reason, 10–20% of the *syn*-boat conformation is involved in the equilibrium in the case of compound (XXVII).[113]



The fact that the *syn*-boat form obtains is readily understood from the standpoint of the orientation of the bonds (Fig. 3). According to a calculation[113], the contribution of the torsional interaction energy in the case of the half-chair and the *syn*-boat amounts to ~3 kcal mol^{-1}, while for the anti-boat form it is more than 7 kcal mol^{-1}.

The envelope or highly distorted half-chair conformation is typical for epoxycyclohexanones (XXVIII). If carbonyl groups have been introduced into both α-positions, as in compound (XXIX) then, compared with the chair form, the *syn*-boat form has a more favourable orientation of the dipoles and conditions for the conjugation of the carbonyl groups with the oxiran ring; ultimately, simple calculation predicts the highest stability of compound (XXIX) in the *syn*-boat form. Compound (XXX) has precisely this structure[114]. The substituent in the 1(6)-position is responsible for the "uneclipsed" half-chair conformation being preferred, as in bicycloheptanes (Fig. 3). This has been demonstrated in compound (XXXI) with R = H; however, when R = t-C_4H_9, the ring conformation is determined by the bulky substituent [115].

The orientation of the substituents in the other positions of 7-oxabicycloheptane is determined to a large extent by the direction of their dipoles relative to the epoxy-group. Apart from the general preference for the equatorial orientation, electrostatic repulsion destabilises the *cis*-axial positions of the polar substituents. It has been shown[110] that the *cis*- and *trans*-isomers of compound (XXXII, X = SO_2Ph, NO_2, or CN) exist preferentially in the equatorial form, but the fraction of the axial form of the *cis*-isomers is systematically lower, so that the values of ΔG for these compounds are smaller by 0.7 kcal mol^{-1} than for the *trans*-isomers[110,116];

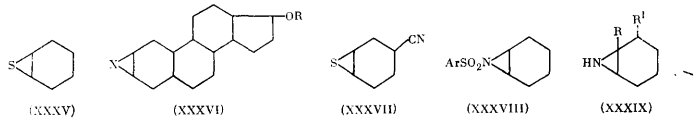


(XXXI) (XXXII) (XXXIII) (XXXIV)

the ratio of the values of ΔG mentioned above holds also for these compounds. Since the *cis*-substituent does not tend to occupy the axial position, the *trans*-3,4-dicyanides and the *trans*-3,4-diesters (XXXIII) exist preferentially in the *ee*-form[116,117].

The substituents in 2- and 5-positions to some extent retain the features of the conformational behaviour of cyclohexanes. This is indicated by the axial orientation of the 3-*cis*-t-butyl group in compound (XXXIV).[116] On the other hand, in general the ring conformation is determined mainly by the substituents in the 3,4- and not 2,5-positions (see, for example, Tadwalkar et al.,[118] Watanabe et al.,[119] and Jackson and Zurqiyah[120]).

The 7-heteroanalogues of bicycloheptane with other heteroatoms have been scarcely investigated. Cyclohexenothiiran (XXXV) has been found to have the half-chair conformation with the angle $\psi = 27.6°$.[121] A similar analogy with the corresponding epoxides has been observed in the structure of epithioandrostanes (XXXIV) with X = S (a) and SO (b).[122,123]



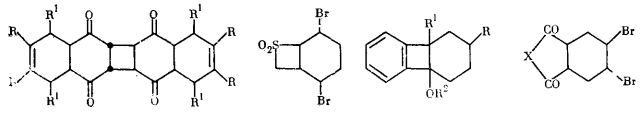
(XXXV) (XXXVI) (XXXVII) (XXXVIII) (XXXIX)

The *A* ring has the distorted half-chair conformation. The similarity of the dipole moment of cyanocyclohexenothiiran (XXXVII) to that of the epoxide has in fact led to the conclusion that the former is involved in an analogous conformational equilibrium with participation of about 40% of the equatorial half-chair conformation[48].

A typical half-chair conformation has been observed in an X-ray diffraction study of 7-(*p*-iodobenzenesulphonyl)-7-azabicyclo[4.1.0]heptane (XXXVIII).[124] Substituted compounds of type (XXXIX) have been investigated by ^{13}C NMR.[125] The substituent R^1 in the *trans*-position relative to the nitrogen atom is pseudoaxial, while that in the *cis*-position is pseudoequatorial, i.e. only one half-chair conformation with an uneclipsed substituent R is realised (Fig. 3).

3. Compounds of the Bicyclo[4.2.0]octane Series

A planar group arises only in the *cis*-condensation of the plane of the four-membered ring with the six-membered ring. Two groups of compounds have been investigated in fair detail. The first comprises the photodimers of hydrogenated naphthoquinones (XL).[126] The central four-membered rings in these compounds are planar and the cyclohexanedione rings have the half-chair conformation distorted to different extents, up to the envelope conformation, depending on the nature of the substituents R and R^1.



(XL) (XLI) (XLII) (XLIII)

The half-chair conformation has also been observed for compound (XLI); the C–Br bonds occupy the pseudoaxial positions, as in cyclohexene[127].

The compounds of the second group contain a six-membered ring condensed with the benzocyclobutene fragment, as in structure (XLII).[128,129] In all the molecules the cyclohexane ring has a fairly symmetrical boat conformation: the atoms in the 2- and 5-positions deviate from C(1)–C(3)–C(4)–C(6) by 0.55 and 0.62 Å respectively[128]. It is of interest that this is the *syn*-boat conformation, i.e. the bonds in the four-membered ring are axial.

4. The Anhydrides and Imides of *Cis*-cyclohexenedicarboxylic Acids

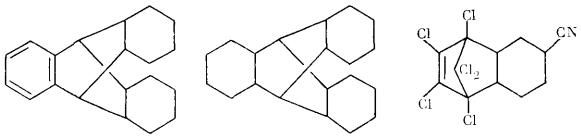
The tendency towards the formation of the boat form is manifested also in those cases where the cyclohexane ring is *cis*-condensed with a planar five-membered ring—anhydride or imide ring, as in compounds (XLIII, X = O or NAr). Compounds of this type have been investigated in solutions by various methods and it has been definitely established that there is an equilibrium between the diaxial half-chair and *syn*-boat conformations in proportions of 4 : 1 for anhydrides and 3 : 2 for *N*-arylimides[130].

The NMR spectra of the methyl-substituted anhydrides were interpreted as evidence for the twist-boat conformation; the possibility of an equilibrium was not taken into account[131].

5. The Cyclohexane Ring Condensed with a Bridged System

The limiting case in the series of bicyclo[4.*n*.0]alkanes considered consists of a cyclohexane ring *cis*-condensed with a similar ring incorporated in a rigid bicyclic system ensuring the coplanarity of the three consecutively arranged C–C bonds. A series of X-ray diffraction studies have been made of the possible isomers of the hydrogenated triptycenes (XLIV) and (XLV).[132–137]. All the *cis*-condensed rings have the boat conformation owing to the necessity for the optimum blending of the "rigid" and "mobile" halves of the ring.

When the contributions of different energy components are considered it is seen that the *cis,cis,cis*-form (three boats) involves a torsional energy loss of ~10 kcal mol^{-1} relative to the *trans,trans,trans*-form (three chairs), but there is a gain of the same amount of energy due to the Baeyer strain, since the overall destabilisation of the molecule in the "three boat" conformation does not exceed 2.5 kcal mol^{-1}.[136] The boat forms in compound (XLV) are somewhat distorted: the endocyclic dihedral angles formed by the common bond reach 17° for a very small inversion barrier between two directions of twist.



(XLIV) (XLV) (XLVI)

The observation of the stability of the boat conformation of the classical cyclohexane ring is an important achievement in the development of conformational analysis, because it necessitates a review of the structures of many compounds. It is appropriate to mention here that the preference for the boat conformation over the half-chair conformation has been demonstrated by calculations for the inversion of cyclohexane[138].

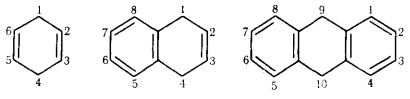
The C-C bonds in the bicyclic systems of compounds (XLIV) and (XLV) occupy an equatorial position in the cyclohexane ring, which is quite understandable from the standpoint of steric factors, although it conflicts with some of the data presented above for the bonds in three-, four-, and five-membered rings.

Substituted derivatives have been hardly investigated. The structure of the isomeric cyano- derivatives (XLVI) with the *cis*- and *trans*-dispositions of the cyano-group and the bicyclic system has been determined by the dipole moment method[139].

IV. 1,4-DIPLANAR SIX-MEMBERED RINGS

1. Aromatic 1,4-Dihydro-compounds

The series considered includes three main types of molecules—cyclohexa-1,4-diene (XLVII), 1,4-dihydronaphthalene (XLVIII), and 9,10-dihydroanthracene (XLIX).



(LXVII) (XLVIII) (XLIX)

The only possibility for a change in conformation involves the bending of the molecule along the C(1)-C(4)-C(9)-C(10) line, so that the ring always assumes the boat conformation specified by the angle θ between the planes of the π-electron systems (Fig.4).

(a) Cyclohexa-1,4-diene and its Derivatives

The planar structure of the molecule of compound (XLVII) is indicated by vibrational spectroscopy[140-143], rotational spectroscopy[144], gas phase electron diffraction[145], and NMR spectroscopy (in a nematic solvent)[146], the potential well being very flat[143], so that the effective angle θ is 167°.[147] This is apparently why it was concluded that the cyclohexa-1,4-diene molecule is non-planar[148]. Theoretical calculations by various methods confirmed the planar structure of compound (XLVII).[23,36,149-154]. Even though calculations indicated an energy barrier at θ = 180°, its height was found to be only ~0.1 kcal mol^{-1}.[155]

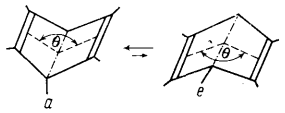
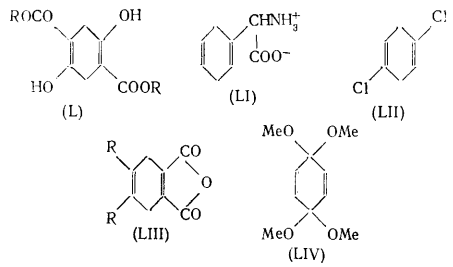


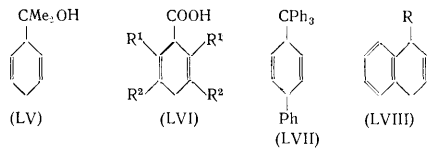
Figure 4. The structure of cyclohexa-1,4-diene and its derivatives.

Substituents at the olefinic atoms do not influence the ring conformation; this was established in an X-ray diffraction study of compounds (L) and (LI),[24,25] although the physical properties of solutions of compounds such as (LII) and (LIII) indicate an appreciable bending of the molecules, which may be effective[156,157]. The 1,1-disubstituted derivatives are also planar, since the bending increases the $A^{1,2}$ strain. An example may be provided by the diketal of the quinone (LIV).[158]



(L) (LI) (LII) (LIII) (LIV)

The conformations of 1-substituted cyclohexadienes are very interesting. When the substituents are not unduly bulky, the NMR spectra indicate the planarity of the ring[159-161]. With increase of the bulk of the substituent, there is an increase of the $A^{1,2}$ strain, so that a pseudoaxial boat conformation was observed for compound (LV).[162] The influence of the substituent on the ring conformation is reflected in the results of the calculation[150]: with increase of the bulk of the 1-substituent, the angle θ changes from 180° to 160° for t-butylcyclohexadiene; there are no energy minima at all corresponding to the pseudoequatorial orientations.



(LV) (LVI) (LVII) (LVIII)

The $A^{1,2}$ strain is equally enhanced after the introduction of substituents at the nearest sp^2-atoms.[163] In particular, in the molecule of compound (LVI), the ring is almost planar for $R^1 = H$ and $R^2 = Me$, but, when $R^1 = Me$ and $R^2 = H$, it is bent at an angle of 8.4°.[164]

1,4-Disubstituted derivatives with the *trans*-configuration have a planar ring (see the data published by Kitaigorodskii et al.[25]) or the more bulky substituent occupies the pseudo-axial position, as in compound (LVII).[165] It is of interest that the *cis*-isomer is diequatorial and not diaxial as might have been expected[166]: the deviation in the opposite direction would not alter appreciably the $A^{1,2}$ strain but would lead to the appearance of the prow-interaction.

(b) 1,4-Dihydronaphthalenes

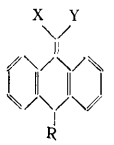
Condensation of cyclohexa-1,4-diene with an aromatic ring increases the $A^{1,2}$ strain and in addition there is a decrease in the torsional barriers in the $C_{sp^2}-C_{sp^3}$ bonds[23]; all this leads to an increase of conformational mobility. Although calculations, predicted a planar structure of compound (LVIII) for R = H,[150,151] experiment indicated a bend, albeit small, in the molecule[167]. Substituents in the 1-position are usually pseudoaxial[161,168–170]. The angle θ depends on the bulk of the substituent[171] and, in the presence of the bulky t-butyl substituent, there is a possibility that the ring form changes completely[172]; however, calculation for all the 1-alkyldihydronaphthalenes indicates the boat conformation with the sole difference that two energy minima correspond to the t-butyl group, with the corresponding angles θ = 132° (*e'*) and 149° (*a'*).[150]

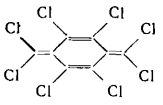
(c) The 9,10-Dihydroanthracene System

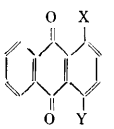
Numerous X-ray diffraction data indicate an appreciable bend in the molecules of 9,10-dihydroanthracene (XLIX) and its derivatives[24,25], which, incidentally, is poorly described by the theory[150,154]. For the two bonds in which the atom in the 9(10)-position is involved, that carrying the larger substituent is predominantly pseudoaxial[161,173] and there is a possibility of equilibrium between two forms[174]. The behaviour of 9-alkyldihydroanthracenes has been satisfactorily accounted for by calculation[150].

The *trans*-9,10-disubstituted dihydroanthracenes are largely planar, but, in the presence of very bulky substituents, there is a possibility of distortion of the ring[175]; naturally, if the substituents are different, the conformation is determined by the larger substituent. The central ring in symmetrical 9,9,10,10-tetrasubstituted compounds and compounds with condensed benzene rings is also planar[24]. The *cis*-configuration of the 9,10-substituents ensures the possibility of the energetically favourable diaxial conformation. Indeed, it has been observed for a number of dialkyl [25,175] and bis(trimethylsilyl)[176] derivatives. The angle θ is almost constant, varying in the range 150–155.7°. The same conformation is maintained in solutions[177].

The sterically hindered molecules of type (LIX) with an sp^2-atom in the 9-position constitute a special group. An extremely pronounced 1,3-allylic ($A^{1,3}$) strain[1] between the substituents in the methylene group and the nearest hydrogen atoms of the hydroanthracene system is present in these compounds. The molecule therefore assumes that boat conformation, although sterically unhindered compounds of this type are planar[178]. The substituent R in the 10-position assumes the pseudoaxial orientation[179]. The $A^{1,3}$ interaction destabilises the planar structure so much that the height of the inversion barriers exceeds 15 kcal mol^{-1} [178–180] when X,Y ≠ H or for an unsubstituted methylene group and chlorine atoms in the 1- and 8-positions. Even in a quinonoid structure there is a possibility of the breakdown of planarity as a consequence of steric hindrance. Thus compound (LX) has a distinct boat conformation, in which the angle between the directions of the exocyclic double bonds is ~110°.[181]


(LIX)


(LX)

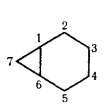

(LXI)

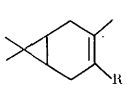
Even the molecules of aromatic compounds, for example, anthraquinones (LXI), can be non-planar as a result of steric hindrance. The bending of the ring requires at least two substituents in the 1,4- or 1,8-positions. For example, the 1,8-dichloroanthraquinone molecule is bent along the C(9)–C(10) line with θ = 168°.[182] The degree of non-coplanarity is still greater if X is a nitrogen atom incorporated in a 1,2-condensed aromatic heterocycle: the atoms in the 9- and 10-positions can be displaced from the plane by 0.2–0.4 Å [183,184].

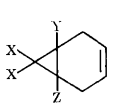
2. Bicyclo[4.1.0]hept-3-ene and Its Analogues

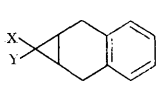
(a) Bicycloheptenes and Epoxycyclohexenes

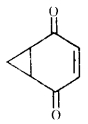
When the cyclohexene ring is condensed with a three-membered ring in the 4,5-positions, there is a possibility of two different boat conformations—*syn* and *anti* (Fig. 5). Bicyclo[4.1.0]hept-3-ene (norcarene) (LXII) and its homologues exist in the *syn*-boat form[185], like 3-carene (LXIII, R = H), whose structure has been determined most reliably by gas-phase electron diffraction[186], NMR spectroscopy[187,188], and the Kerr effect[189]. The angle θ is 165°.[82] The possibility of the involvement of the *anti*-form in the equilibrium in an amount of 5–10% ($\Delta G = 1.48$ kcal mol^{-1}) has been indicated[187]. The structure of 4-methylcarene (LXIII, R = Me) with θ = 172° is even closer to planarity[190]. Steric interactions have been suggested as a factor stabilising the *syn*-form[187], but calculations[189,191] have demonstrated that the torsional term plays the decisive role.


(LXII)


(LXIII)


(LXIV)

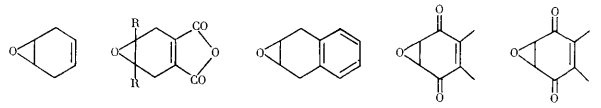

(LXV)


(LXVI)

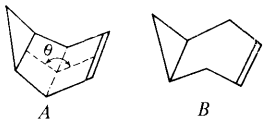
The data for norcarenes with polar substituents in the cyclopropane ring are contradictory. 7,7-Dihalogeno-derivatives exist in the *syn*-boat conformation with θ ≅ 165°.[192] The NMR spectra of the polyhalogeno-compounds (LXIV, X, Y, Z = F, Cl, or Br) indicate the *anti*-structure[193]. Just as contradictory results have been obtained for tetralin derivatives (LXV). If there is no substituent in the *syn*-7-position, the *syn*-boat conformation obtains[191,194]. However, the *anti*-structure with θ = 222° has been established with the aid of various methods for molecules with dichlorocyclopropane and dibromocyclopropane fragments[191,195].

The introduction of carbonyl groups in the 2,5-positions as in compound (LXVI) gives rise to the possibility of conjugation which flattens the ring. On the other hand, the torsional energy minimum retains its position, since the configuration with eclipsed carbonyl groups and C_{ring}–H bonds is favourable. The *syn*-conformations therefore obtain for compounds of type (LXVI) in crystals[24,25] and in solutions[196]. The angle of the bend remains the same as in analogues without carbonyl groups, so that the torsional term is decisive.

The oxygen analogue of norcarene-7-oxabicyclo[4.1.0]-hept-3-ene (LXVII)—has been investigated in fair detail in the gas phase[197,198]. The molecule has the *syn*-boat conformation with the angle $\theta = 160°$.[197] According to Durig et al.[198], the *anti*-boat conformation has an energy greater by 2.33 kcal mol^{-1}, i.e. is hardly involved in the equilibrium; the energy barrier separating the two forms is only 2.81 kcal mol^{-1}. Compound (LXVIII) has a fairly distinct *syn*-boat conformation, but its dipoles are directed to one side[157]. On passing to the tetralin analogue (LXIX), an inversion of conformation takes place, as for compound (LXV) and the *anti*-boat form with the same angle of bend of 219° becomes stable[196].



(LXVII) (LXVIII) (LXIX) (LXX) (LXXI)



A *B*

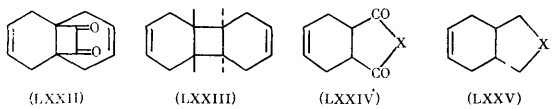
Figure 5. The possible conformation of bycyclo[4.1.0]-hept-3-enes; *A*—*syn*-form; *B*—*anti*-form.

Theoretical calculation[191] predicted the stability of the *anti*-boat form for the 7,7-dihalogeno-derivatives as a consequence of the repulsion of the π-electron systems and electron pairs of the *syn*-halogens. However, at the present time this conformation has been established reliably only for the benzo-derivatives, while the cyclohexene analogues (LXIV, Y = Z = H) and (LXVII) exist in the *syn*-form.

The introduction of carbonyl-containing groups stabilises additionally the *syn*-boat conformation not only as a result of the decrease of the torsional energy but also as a result of the most favourable orientations of the dipoles[199]. It is not surprising that this conformation is characteristic of epoxyquinones (LXX) [196,199] and hydroxyketones (LXXI).[24,200]

(b) Derivatives of Bicyclo[4.2.0]oct-3-ene

The planarity of the four-membered ring condensed with the cyclohexane ring, which is necessary for a fixation of all three bonds of the latter, is by no means always manifested; even the cyclobutene fragment is strongly bent in many instances[24]. The cyclobutane-1,2-dione ring is planar, as a result of which the molecule of compound (LXXII) exists in the crystal with the cyclohexene ring having the *syn*-boat conformation. The four-membered ring then occupies the axial position and the bonds in the second cyclohexene ring are equatorial[201]. Spectroscopic data[202] permit the same conclusion for solutions.



(LXXII) (LXXIII) (LXXIV) (LXXV)

The cyclobutane ring exhibits planarising properties in polycyclic molecules with the skeleton of compound (LXXIII) (but not in all cases)[25]. The degree of bending of the cyclohexene ring can be greater than in the bicycloheptene series—up to $\theta = 142°$.

(c) The Bicyclo[4.3.0]non-3-ene System

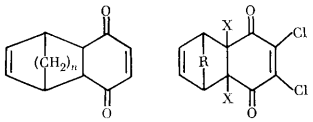
The five-membered anhydride and imide rings are planar in all cases, as a result of which the derivatives (LXXIV) exist in the boat conformation. The view has been frequently expressed that this is the *anti*-boat conformation, but experimental data have shown that the *syn*-form predominates ($n = 90 \pm 10\%$) for anhydrides[203,204], while the imides (LXXIV, X = NAr) exist as a mixture of approximately equal amounts of molecules in the *syn*- and *anti*-boat conformations[192].

Spectroscopic data on the basis of which the equilibrium in solutions might have been inferred unambiguously became available only recently and yielded ambiguous results. According to Larter et al.[205], the anhydride (LXXIV) and its homologues are equilibrium mixtures of the *syn*- and *anti*-forms in proportions of 9:1, in excellent agreement with other data[203]; the degree of bending of the ring was then assumed to be the same as that found in the X-ray diffraction study of cyclohexene *cis*-condensed with a five-membered ring[206]. The study of the temperature variation of the ^1H NMR spectra of compounds (LXXIV)[62] confirmed the *syn*-boat conformation at the usual temperatures, but characteristic signs of equilibrium were observed only on heating above 450 K, which should correspond to an unusually high barrier to inversion.

In the series of bicyclonon-3-enes the *cis*-junction between the cyclohexene ring and the saturated five-membered heterocycle is rigid, as in compound (LXXV). When $X = N^+Me_2$, the degree of bending is very marked: $\theta = 139.7°$.[206] The substance crystallises in the *anti*-boat form, although the *syn*-form is permissible in solution according to NMR data. The equilibrium has been studied in detail for X = O [207] and it has been established that the fraction of molecules in the *anti*-boat conformation is 60–80%.

(d) Adducts of Quinones with Cyclic Dienes

All the compounds investigated in which cyclohexene ring is *cis*-condensed with a bicyclic system can be obtained as adducts in the diene synthesis of *p*-quinones with cyclodienes. The cyclohexenedione ring in compound (LXXVI) with $n = 1, 2$ has the *syn*-boat conformation with an angle of bend close to the canonical value[114,208]: even bulky bicyclic systems can occupy the axial position.



(LXXVI) (LXXVII)

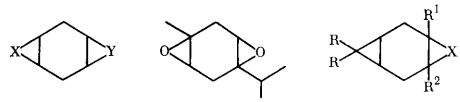
The same conformation has been established for adducts of quinones with hexachlorocyclopentadiene and even with anthracene, although in the latter case the ring is flattened[114,196]. The *syn*-boat conformation has been noted for quinoxalinedione adducts[209].

The adducts of substituted quinones of type (LXXVII) crystallise in the *syn*-boat form[210], but in solution there is a possibility of equilibrium, since in the boat form both the axial and equatorial positions are occupied by the C–C or C–X bonds[114].

3. 1,4-Diplanar Systems Formed by Condensation with Two Rings.

(a) Tricyclo[5.1.$0^{3,5}$]octanes

Mainly compounds (LXXVIII) with a *trans*-junction have been investigated, while only a few data have been obtained for the *cis*-isomers.



(LXXVIII) (LXXIX) (LXXX)

For the symmetrical derivatives (LXXVIII), the main problem was that of the degree of bending of the central ring. It was established ultimately that, for X = Y = CCl_2, CBr_2, or O,[211] and also for the *trans*-dioxide of γ-terpinene (LXXIX)[192], the angle θ between the C(1)–C(2)–C(5)–C(6) and C(2)–C(3)–C(4)–C(5) planes is ~160°. X-Ray diffraction study of compound (LXXX, R = R^1 = Me, R^2 = H, X = CBr_2) showed, however, that the degree of bending varies in the range 0.5–6.1°:[212] similarly, electron diffraction study of the analogous dichloride showed that it is best described by a planar structure[213]. Nevertheless, NMR study of compounds of type (LXXX) demonstrated in all cases the existence of conformational equilibria, which are possible only for a fairly high degree of bending of the molecules[214,215]. The determination of the structure of oxatricyclooctanes methylated to different extents (R = R^2 = H, R^1 = Me; R = H, R^1 = R^2 = Me;[216] R = R^1 = Me, R^2 = H;[217] R = R^1 = R^2 = Me)[187] showed that it depends on the degree of substitution, but the central ring is always significantly non-planar.

In the series of bicyclene oxides, X-ray diffraction data have been obtained for compound (LXXVIII, X = CBr_3, Y = O) and its 1,6-dimethyl derivatives[218]. Extremely small angles of bend of the ring were obtained—7.6° and 6.4° respectively. However, in solutions the polarity and polarisability of the *trans*-oxides of 7,7-dichloro-, and 7,7-dibromonorcarenes cannot be described in terms of a planar conformation; they can be treated only in terms of an equilibrium mixture of two boat forms[208]. The symmetrisation of molecules of this kind in the crystal is encountered fairly frequently.

According to electron diffraction data, the *trans*-oxide of 3-carene (LXXX, R = R^1 = Me, R^2 = H, X = O) has a pseudoaxial cyclopropane fragment and a pseudoequatorial epoxide ring (Fig.6, *syn*-boat)[219] with θ = 160°.[82] Studies in solutions by the NMR[220,222] and Kerr effect[223] methods revealed a conformational equilibrium in which the *syn*-boat form predominates (2:1).[223] The same ratio of conformers obtains for compound (LXXX, R = R^1 = Me, R^2 = COMe, X = O).[224] Equilibria in solutions have been discovered for a number of homologues of 3-carene oxide, the ratio of the conformers depending on the degree of methylation[190,225–227], and for 3-carene *trans*-sulphide (LXXX, R = R^1 = Me, R^2 = H, X = S)[228]. The only exception is a study[218] in which the NMR spectra of the *trans*-oxides of norcarene (LXXVIII, X = CH_2, Y = O) and its 7,7-dimethyl derivative were interpreted as evidence for the planar structure of the central ring.

The *cis*-isomers of compounds (LXXVIII) can exist in the *anti,anti*- or *syn-syn*-conformations (Fig.6), which are significantly different. The *anti,anti*-conformation is doubly destabilised by torsional interactons, while for the *syn,syn*-conformer one may expect stronger interactions between three-membered rings, particularly when these are polar or carry bulky substituents. Studies on the *cis*-oxide of 3-carene (LXXX, R = R^1 = Me, R^2 = H, X = O) by various methods revealed the presence of the *syn,syn*-boat form with θ = 160°,[219,223,229] as for its various homologues[226,227] and 3-carene *cis*-sulphide[228]. The dipole moment of the *cis*-dioxide of γ-terpinene (LXXIX) shows that the oxiran rings have a parallel or nearly parallel orientation, which is possible only for the *syn,syn*-boat conformation[192]. Only certain NMR studies led to the unambiguous conclusion that the *anti,anti*-form is possible or even more stable or that the planar structure obtains[218,221,222,225,228].

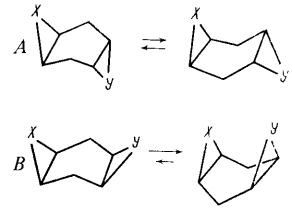
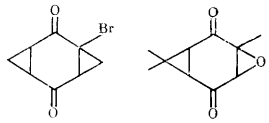


Figure 6. The conformations of 1,4-diplanar tricyclic systems with the *trans*-configuration (*A*) and the *cis*-configuration (*B*).

Ketones of the tricyclopropane series, investigated from the conformational standpoint, have the *trans*-disposition of two three-membered rings. The virtually symmetrical molecule of compound (LXXXI) has an almost planar six-membered ring in the crystal with θ = 175°.[230]



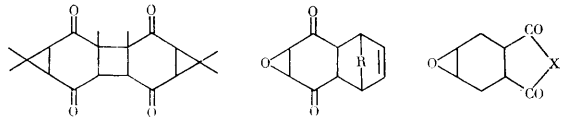
(LXXXI) (LXXXII)

If one of the rings is an epoxide ring, as in compound (LXXXII), it has a pseudoaxial orientation with favourable directions of the dipoles of the carbonyl groups and of the epoxide ring[196].

(b) Conformation of the Cyclohexane Ring in Certain Polycyclic Systems

The number of structures which can be formed on 1,4-condensation of the cyclohexane ring with various rigid fragments is very large; the available data concern only some types of compounds.

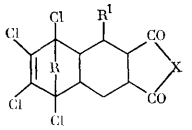
If one of the planarising fragments is a three-membered ring, it occupies the pseudoaxial position, i.e. in relation to this fragment the cyclohexane ring has the *syn*-boat conformation for reasons indicated above. Compound (LXXXIII) in the crystal[25] and the epoxy-derivatives (LXXXIV) in solutions[114,231] have such a structure. This angle of bend of the molecule of compound (LXXXIV) is approximately 150°.



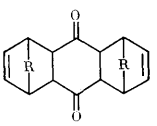
(LXXXIII) (LXXXIV) (LXXXV)

The epoxy-derivatives of the anhydrides and imides of cyclohexenedicarboxylic acids have the *cis*-configuration and exist in the *syn,syn*-boat form[192,203] like the *cis*-tricyclo-octane compounds, although the stabilising role of the torsional interactions is reduced by a factor of two compared with compound (LXXVII), while the electrostatic interactions are clearly unfavourable. These facts have no simple explanation and must be regarded as the manifestation of a specific conformational effect (the Pangolin effect).

In polycyclic anhydrides and imides of the type (LXXXVI, $R = CCl_2$ or CO, X = O or NAr, R^1 = H or Me) the cyclohexane ring has the *syn*-boat conformation in relation to the five-membered ring, so that the more bulky bridge system occupies the equatorial positions[232,233].



(LXXXVI)



(LXXXVII)

The exceptions to this rule are due to the equatorial location of the substituent R^1 *trans*-oriented relative to the five-membered ring.

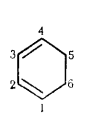
The bisadduct of quinone and cyclopentadiene (LXXXVII, $R = CH_2$)[234] and its tetrahydro-derivatives[235] have been investigated by X-ray diffraction. In the former case the carbonyl carbon atoms are displaced from the plane of the sp^3-atoms of the central ring by 0.37 Å, which corresponds to the classical boat conformation; a planar structure has been obtained by Norment[235]. This shows that small changes in the crystal lattice can give rise to a powerful conformational effect. In solutions the molecules have the boat conformation[208], which undergoes inversion at a high rate[236].

V. 1,3-DIPLANAR SYSTEMS

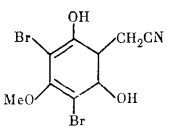
1. Cyclohexa-1,3-diene and Its Analogues

(a) The Ring Conformation

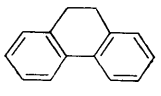
If two planar systems in the ring have a common bond, the only possibility for conformational movements is rotation about this bond [C(2)–C(3) in cyclohexa-1,3-diene (LXXXVIII)] until the distance between the C(5) and C(6) atoms becomes equal to the length of the C–C bond.



(LXXXVIII)



(LXXXIX)



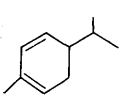
(XC)

In the molecule of compound (LXXXVIII) the angle ω between the planes of the double bonds is 17°,[237] 17.96°,[238] or 18.34°[148] according to electron diffraction data. A microwave study yielded 17.5°.[239] Spectroscopic data confirm the C_2 symmetry[142,240]. Two mirror-isomeric forms are separated by a fairly high inversion barrier, amounting to 3.15 kcal mol^{-1},[142] although a transition can be induced by rotation by only 35°. Theoretical calculations reproduce satisfactorily the height of the barrier and the positions of the potential energy minima (ω = 17–18°);[148,149,155] it is of interest that this angle has been obtained from the analysis of Dreiding models[241]. An X-ray diffraction study of compound (LXXXIX) yielded an angle of 17.3°;[242] in polycyclic systems the angle can diminish to 15° in steroids, 14° in glyotoxin, and 11.8° and 9.1° in laevopimaric acid[24,25].

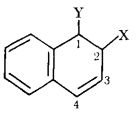
Calculation for the 9,10-dihydrophenanthrene fragment of compound (XC) yielded almost the same value as for cyclohexa-1,3-diene, namely ω = 15.3°.[243] The values of ω found for the crystalline phases of dihydrophenanthrenes[244,245], their benzo-derivatives[25], and their analogues with heteroaromatic rings[246,247] vary in the range 9.3–21°. Thus the cyclohexa-1,3-diene system exhibits a unique conformational constancy associated with the rigidity of its structure.

(b) The Conformation of the Substituents in the 5(6)-Positions

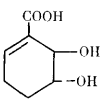
Since both sp^3-atoms are allylic, they are characterised by a pseudoaxial orientation of the substituents. Such orientation of the isopropyl group is in fact preferred for phellandrene (XCI):[248,249] $\Delta G = -0.42$ kcal mol^{-1}.[249]



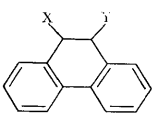
(XCI)



(XCII)



(XCIII)



(XCIV)

A comparison for a series of 5-alkyl derivatives has been carried out by an indirect method based on the ratio of the ring opening products; the pseudoaxial position was found to be energetically more favourable by an amount ranging from 0.24 kcal mol^{-1} for methyl to 2.98 kcal mol^{-1} for t-butyl[250]. The calculation[153] for the 5-methyl derivative predicted a greater stability of the pseudoequatorial form, but only to the extent of 0.025 kcal mol^{-1}. The two possible orientations of substituents such as the fluoro-, cyano-, and nitro-groups were also almost equivalent and the pseudoaxial position is appreciably preferred only for the hydroxyl and amino-groups: $\Delta G \cong -0.6$ kcal mol^{-1}.

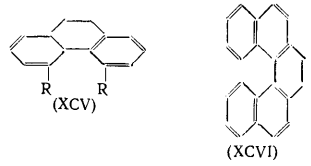
The substituents in the 2-position in the 1,2-dihydronaphthalene system (XCII, X = COR, Y = H) behave in the same manner: $\Delta G = -0.6 \pm 0.1$ kcal mol^{-1} for carbonyl functional groups, while for chlorine the two orientations are energetically equivalent[251]. On the other hand, the substituents in the benzyl 1-position in compound (XCII, X = H, Y = COR) are appreciably more axial[252,253] as a consequence of the $A^{1,3}$ strain. The *trans*-1,2-disubstituted dihydronaphthalenes are also preferentially diaxial and the introduction of a further substituent at the atom in the 8-position renders this form anancomeric [?enantiomeric][253–256]. The *trans*-5,6-derivatives of cyclohexa-1,3-diene have been scarcely investigated. It has only been observed that the conformational composition of dihydroxydihydrobenzoic acid (XCIII) varies sharply as a function of the solvent[257].

The substituents at the C_{sp^3} atoms of 9,10-dihydrophenanthrene (XCIV) are also preferentially pseudoaxial: the methyl, carbonyl, and dimethyl amino-groups are 75–80% pseudoaxial, and bulky substituents such as the t-butyl and trimethylsilyl groups are fully pseudoaxial; the cyano-group is as usual conformationally indifferent[258,259]. The *trans*-9,10-disubstituted derivatives are diaxial[258,260].

(c) Ring Inversion in 9,10-Dihydrophenanthrenes

Unsubstituted compounds with the cyclohexa-1,3-diene fragment have small inversion barriers[253], in agreement with calculation[261]. Their increase to a value measurable by NMR is acheived by the introduction of *cis*-substituents in the 9- and 10-positions in the dihydrophenanthrene

(XCIV) molecule[262], as in the cyclohexene series. The increase of steric hindrance in compounds of types (XCV) and (XCVI) gives rise to the possibility of the separation of the conformers, i.e. the barriers are more than 20 kcal mol^{-1}.



(XCV)

(XCVI)

The racemisation of bridged biphenyls has been the subject of numerous studies[259,263,264].

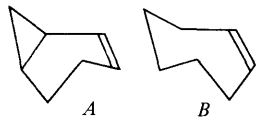


Figure 7. The relative positions of the bonds in the bicyclo[4.1.0]hept-2-ene molecule: *A*) *syn*-form; *B*) *anti*-form.

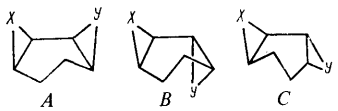
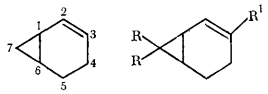


Figure 8. The steric structures of 1,3-diplanar compounds of the tricyclooctane series: *A*) *cis*-form; *B*) *trans,syn,syn*-form; *C*) *trans,anti,anti*-form.

2. The Bicyclo[4.1.0]hept-2-ene Series

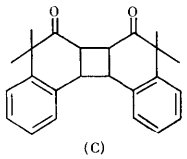
When a three-membered ring is introduced, two directions of the relative movement of the planar groups become non-equivalent. The atom in the 4-position in the (XCVII) system moves towards the three-membered ring (*syn*) or in the opposite direction (*anti*) (Fig.7). The study of compound (XCVII) by gas electron diffraction showed that the dihedral angle of the C(1)–C(2) bond is 15.4°, i.e. it hardly changes compared with cyclohexa-1,3-diene. The ratio of the *syn*- and *anti*-forms is 3:7. The *anti*-form has also been found for 2-carene (XCVIII; R = R^1 = Me) [265] and its 7,7-dihalogeno-derivatives with R = Cl or Br and R^1 = H. [266] The opposite conclusion concerning the stability of the *syn*-boat form has been reached on the basis of the NMR spectrum for R = H and R^1 = Me. [267]



(XCVII)

(XCVIII)

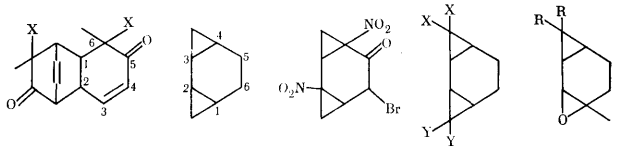

(XCIX)



(C)

The internal rotation potential energy curve has been investigated for the 7-oxa-derivative (XCIX); [198] it has two minima with an energy difference of 1.09 kcal mol^{-1}, also in favour of the *anti*-form. The inversion barrier is the same as in cyclohexadiene (3.82 kcal mol^{-1}). The flattening of the ring has been observed in some derivatives[268].

The tetralin fragment in the molecule of compound (C) has an analogous *anti*-conformation[269]. Among the molecules containing the cyclohexane ring 1,3-condensed with a bicylic system, the keto-derivatives (CI) have been studied.



(CI) (CII) (CIII) (CIV) (CV)

According to the conjugation conditions, they exist in the envelope form with displacement of the C(6) atom from the plane of the ring by 0.70 ± 0.13 Å: [270] the isomer in which the attractive interactions stabilise the *syn*-conformation is an exception[271].

3. Tricyclo[5.1.0.0^{2,4}] Octane and Its Heteroanalogues

As for the 1,4-diplanar analogues, the conformational behaviour of the tricyclic compounds (XCII) depends on their configuration. As a result of the rotation about the C(2)–C(3) bond in the *cis*-isomer, one of the three-membered rings acquires an environment of the *syn*-type while the other acquires one of the *anti*-type (Fig.8). On the other hand, the two conformations of the *trans*-isomer differ. Electron diffraction study of the two isomers of compound (XCII) yielded the angles ω = 17.87–18.20° (*cis*-isomer) and 15.75–16.68° (*trans*-isomer). [272] The *trans*-isomer consists of a mixture of conformers, but, in contrast to compound (XCVII), the *syn,syn*-conformer proved to be more stable (87 ± 5%). Evidently, the direction of the bend in the 1,3-diplanar system depends on very fine structural details. Furthermore, the *syn,syn*-form has been discovered for compound (CIII). [24] The *syn*-orientation is impossible for a three-membered ring with large substituents and for this reason the *anti,anti*-form of all the compounds (CIV, X,Y = Cl, Br, or Me) is stable[266]. The *trans*-oxide of 2-carene (CV, R = Me) exists in the same form[265]. The removal of the *gem*-dimethyl group leads to inversion to the same *syn,syn*-form as for the *trans*-isomer of compound (CII), [226]

The *cis*-isomers have been scarcely investigated. In the *cis*-dioxides of the terpene series the angle ω = 15–16° is retained[25]. If the rings are different, as in the *cis*-oxide of 2-norcarene (CV, R = H), the *syn*-conformation relative to the oxygen atom, which has less stringent steric requirements than the methylene group, is the most stable[226,267].

---oOo---

The data examined show that six-membered carbon rings with planar groups of atoms are characterised by certain common features in their conformational behaviour despite the wide variety of their structures. These include the tendency of the cyclohexane ring to assume the boat conformation on condensation with rigid rings, which may be due to torsional or electrostatic factors, as in the *syn*-boat form of bicyclo[4.1.0]heptane systems, the steric interactions, as

in the *anti*-boat form of polysubstituted bicycloheptanes, and the ring closure conditions, as in perhydrotriptycenes. Next, it is necessary to note the relative stability of the axial and pseudoaxial positions of the substituents, including bonds belonging to planarising cyclic groups. The preferential pseudoaxial orientation of the condensed three-membered rings is responsible for the stability of the *syn*-conformers even in the presence of pronounced steric hindrance.

The extents to which the different types of compounds have been investigated from the conformational standpoint are by no means the same; in a number of instances it is still impossible to speak of rigorous rules. However, the interest aroused by the conformational studies in this field, including the analysis of the stereochemical reactions, gives rise to the hope that considerable advances will be achieved in the immediate future.

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