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Contemporary Ideas About the Conformations of Eight-membered Cyclic Systems with Planar Fragments

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The results of conformational studies on eight-membered cyclic compounds that contain from one to four planar fragments in exo- or endo-cyclic positions of the molecule have been correlated. By analysing the systematic changes in the torsion angles and folding parameters, which were selected as the main quantitative criteria of the conformational state of the class of compounds being examined, it is possible to present a sufficiently complete and consistent picture of their conformational behaviour, which has a diversity that is determined by the relative configuration and nature of both the planar fragments and the heteroatoms contained in the ring. Special consideration has been given to the basis for the NMR spectroscopic criteria used in identification of the respective conformations.
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I. INTRODUCTION

Molecular carbocyclic and heterocyclic systems that are made up of so-called medium rings containing from 7 to 12 atoms in the ring exhibit many specific properties in comparison with well-studied six-membered rings. During the last ten years there has been a substantial increase in the number of published works devoted to eight-membered cyclic systems, among which rings that contain a planar group of atoms with unsaturated bonds (a carbon group, double bond, aromatic ring) constitute a distinctive group of compounds. They can form the basis for the construction of a variety of systems containing from one to four planar fragments in different positions of the eight-membered ring. The design possibilities are increased with the introduction of different heteroatoms into the ring. Inorganic heterocycles made up of a combination of different heteroatoms have been synthesised as well as mixed molecular systems containing heteroatoms and organic aromatic rings (phenyl and naphthyl) as planar fragments.

The extensive synthetic possibilities have also stimulated interest in the stereochemistry of such systems. The development of conformational studies in this field has occurred irregularly. The elaboration of methods of calculation in molecular mechanics made it possible for the basic principles of the conformational analysis of cyclooctenes and cyclooctadienes to be developed as far back as 1968–1973.[1,2] However, the rules developed for carbocyclic systems did not prove to be very suitable for their heterocyclic analogues, since the points on the potential energy surface which are saddle-shaped for the former are often transformed to global minima for the latter. In order to develop the conformational analysis of heterocyclic systems as a whole, the creation of tests and quantitative criteria for the identification of possible conformers was required. Their development was completed in the 1970's mainly on six-membered rings; the progress achieved was reflected in a number of monographs and reviews.[3-7] However, they also proved inadequate for conversion to eight-membered systems because of the greater conformational mobility and flexibility of the latter and also due to the absence of quantitative selection criteria (and in a number of cases even because of the nomenclature system of the respective conformers).

The basic study of Cremer and Pople[8] concerning the quantitative representation of the conformations of cyclic compounds was published in 1975, and in 1981 these concepts were developed for eight-membered rings,[9-11] which stimulated an increase in the number of published works on eight-membered rings. At the present time it has become necessary to interpret the accumulated material on carbocycles and heterocycles within the framework of a single system of nomenclature and a single approach based on the quantitative representation of conformers.

In this review the main focus of attention has been directed to examining the conformational features of eight-membered heterocyclic compounds. We considered it practicable to introduce into the text of the review information on a number of recently synthesised compounds of this type that have not yet been studied in relation to their conformation and were not included in a recent review.[12] The most fundamental and well verified information is reported for carbocycles. The torsion angles about the cyclic bonds and the folding parameters[7,10,15] have been selected as quantitative criteria in discussing the conformational state of the molecules examined. This together with the standardised nomenclature proposed previously for cyclooctane[13,14] and used by us make it possible to build up a unified pattern of conformational behaviour of eight-membered carbocycles and heterocycles which are so diverse in the conformational sense. The basic conformations and their nomenclature for each series of compounds is given in the respective Sections. The effect of the successive introduction of one, two, three, or four planar fragments into a ring is also examined, and for two average cases the effect of the relative configuration of the planar fragments on the conformation of the compounds is also discussed.

II. EIGHT-MEMBERED RINGS WITH A SINGLE PLANAR FRAGMENT

1. General Concepts of the Conformations of Cyclooctane Systems

In examining the conformations of eight-membered rings with planar fragments we have primarily used the nomenclature systems introduced for cyclooctane itself[13,14] as a basis. An eight-membered ring can adopt ten conformations, which constitute four groups (Fig.1): (a) the boat-chair (BC) group which is simply boat-chair (BC) and skewed or twist-boat-chair (TBC); (b) the crown group which is crown, chair-chair (CC), and skewed or twist-chair-chair (TCC); (c) the boat group which is boat-boat (BB), twist-boat (TB), and boat (B); (d) the chair group which is long chair (LC) and twist-chair (TC). For each conformation, Fig.1 indicates the sequence of torsion angles in the ring (namely, the angles between the planes formed by three neighbouring atoms of the ring: angle φ_1 corresponds to the angle along the C(1)–C(2) bond between the planes containing the atoms in positions 8, 1, 2 and 1, 2, 3; angle φ_2 is the angle between the planes containing the atoms in positions 1, 2, 3 and 2, 3, 4; etc.). The line in Fig.1 corresponds to the symmetry element (axis or plane), ± are the signs for the torsion angle values.

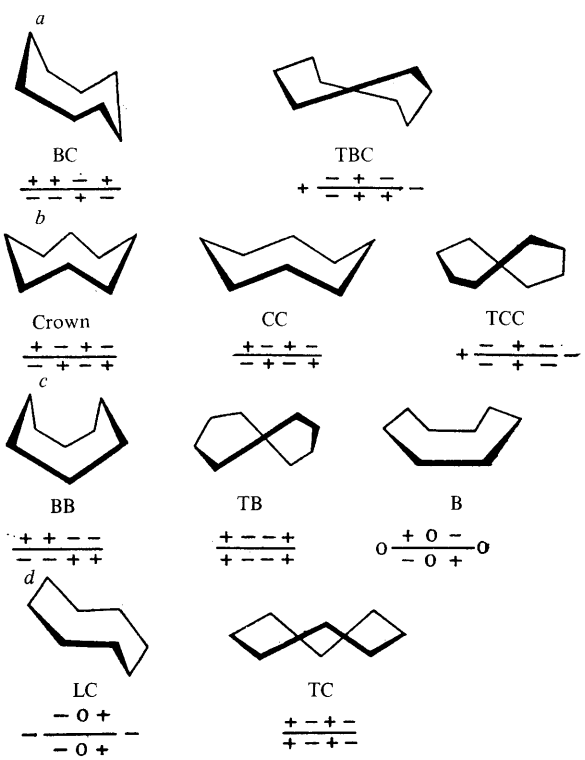


Figure 1. The possible conformations of cyclooctane.[13,14]

In addition to the chemical numbering of the atoms, differentiation of the conformational system has also been proposed for eight-membered rings. This is due to the existence of nonidentical positions in each conformation, which is caused by the unequal distribution of interactions between the chemically nonbonded atoms. For example, when a heteroatom or carbonyl group (which can be labelled X) is introduced, several forms of BC conformation can be distinguished: BC-1, BC-2, ... BC-8. For heterocycles with a single X, conformations BC-2, BC-3, and BC-4 are enantiomeric to conformations BC-8, BC-7, and BC-6 respectively (in the literature isomers with a mirror plane of reflection are indicated by an asterisk—BC and BC*).

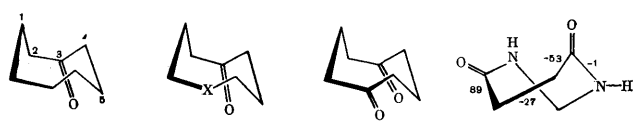


Enantiomeric conformers, like the normal ones, undergo conformational changes as a result of pseudorotation processes (with a partial change in the signs and values of the torsion angles) or inversion (with a partial or complete change in the signs of these angles).[2,14] Sometimes in dynamic NMR spectra it is possible to observe the "freezing-out" of several conformational processes.

The BC form is the preferred conformation of cyclooctane.[2,13,14] Introduction of planar fragments into the *exo* and *endo* positions of the cyclooctane ring affects in different ways the stabilisation of the atoms of the ring in one plane. For *exo* positions (as, for example, in the case of cyclooctanone), as in the saturated rings, three atoms remain in one plane, but in the process the geometrical parameters and torsional configuration about the adjacent bonds change. For *endo* positions, four atoms lie in one plane and one torsion angle is equal to zero. This naturally can assist the stabilisation of conformations with zero torsion angles, as in the B form, especially if two or four planar fragments are introduced into the ring. However, in practice this seemingly indisputable assumption does not always hold. Up to now it remains unclear how the occurrence of planar fragments affects the conformation of eight-membered rings.

2. Mono- and Di-ketones

The simplest example of an eight-membered ring with a single planar fragment is cyclooctanone (I), since the carbonyl group in the molecule can be regarded as a planar fragment that introduces a double bond into the exocyclic position of the molecule. According to the calculations (here and subsequently if a method of calculation is not indicated, conformational energy calculations carried out by means of molecular mechanics are implied) and analysis of the temperature dependences of ^{1}H NMR spectra,[2,16] the most favourable conformation for (I) is BC-3 (or BC-7). The stability of this conformer compared to the other BC forms is due to a reduction in the strong transannular repulsions between the pseudoaxial hydrogen atoms on C(3) and C(7) in the cyclooctane ring. An analogous structure BC-3,7 or BC-7,3 is also established for heterosubstituted analogues with X = 0 (II) and X = S (III).[17,18]

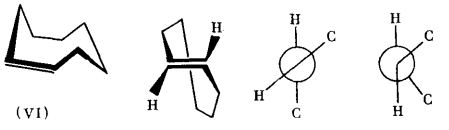


From a study of the temperature dependence of the ^1H and ^{13}C NMR spectra it has been possible to detect in this case two types of conformation process, differing from each by 1.2–1.5 kcal mol^{-1} in energy: a low energy process due to pseudorotation of the form BC-3 $\rightleftharpoons$ BC-7 ($\Delta G^{\neq}$ for (I) is equal to 6.3 kcal mol^{-1}, for (II) it is equal to 6.7 kcal mol^{-1}, and for (III) it is equal to 7.8 kcal mol^{-1}), and the high-energy process for the inversion BC-3 $\rightleftharpoons$ BC-3* via the chair form with $\Delta G^{\neq}$ barriers for (I)–(III) of 7.7, 8.15, and 9.0 kcal mol^{-1} respectively.[18] Both these processes proceed fairly rapidly in the NMR timescale. When substituents are introduced into the ring, the barrier, as a rule, increases. Thus, in 5-t-butyl-substituted cyclooctanone it is 8.0 kcal mol^{-1}.[19] The slight increase in the inversion barriers in (II) is due to a transannular interaction between the oxygen atom and the carbonyl group. Thus, replacement of one methylene group in cyclooctane by a carbonyl group does not produce any substantial changes in the steric structure of the eight-membered ring.

According to IR[20] and NMR spectroscopic data, cyclooctane-1,5-dione has the same structure in the crystalline state as in solution, corresponding to conformation BC-3,7 (IV).[16] Two dynamic processes with $\Delta G^{\neq}$ barriers equal to 6.1 and 7.0 kcal mol^{-1} were found for its deutero-analogue.[16] The two geometrical isomers of 2,4,6,8-tetrabromocyclooctane-1,5-dione also have the BC-3,7 form, and they differ according to the orientation of the C–Br bonds.[21] Ketones in which a heteroatom is situated at the α-position relative to the C=O group should also formally belong to this group of compounds. However, in the case of 2,6-diazocine-1,5-dione (V) it was shown[22] that they comprise systems with an endocyclic planar fragment formed by C=O groups and NH. Thus, compound (V) should be grouped with compounds that contain two endocyclic planar fragments at the 1,5-position relative to each other (see Section V). The torsion angles found for it correspond to those calculated for the TB form of 1,5-cyclooctadiene (LXI).

3. Cyclooctene Derivatives

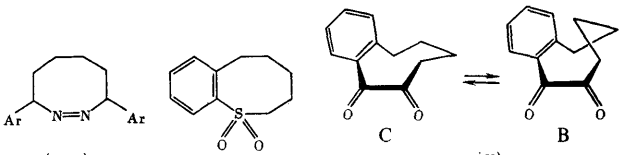
In cyclooctene the ring can be made up in both the *cis*- and *trans*-isomers, and the latter is sufficiently stable to be studied experimentally. It was shown from calculations[23–26] and then also by X-ray diffraction analysis of enantholactam hydrochloride[2] that the most favourable form for the *cis*-isomer is one similar to BC (VI).



(VI) (VII) (a) (b)

In the *trans*-isomer the double bond is highly strained. Calculations predict for it form (VII), namely, twist-chair-chair (TCC) and this has subsequently been confirmed by X-ray diffraction[27,29] and electron diffraction.[30] The double bond is distorted, and the torsion angle is considerably less than 180°: 135.4°,[31] 137.7°,[17] 145.3°,[2,23] 138.0°.[24] This is not a simple twisting of the double bond (*a*) (Newman projection along the double bond), but that in which all six atoms adjacent to this bond are tending to align in one plane (*b*); it has been demonstrated by neutron diffraction that the olefinic hydrogen atoms actually protrude from the plane of the double bond.[2] The torsion angles (φ) along the cyclic bonds in (VII) amount to: 135.4°, –86.5°, 50.7°, and 114.4° (here and subsequently the angle formed by the atoms 8,1,2,3 is given first and that formed by 1,2,3,4 is second, and so on in order).[31] In the case of cyclooctene two conformational processes that occur with barriers of 5.8 and 8.2 kcal mol^{-1} have been found by means of dynamic NMR.[19,32] For the 1-fluoro derivative the barrier is higher according to the ^{19}F NMR spectra and it amounts to 6.1 kcal mol^{-1},[33] while in the *cis*-oxide it increases to 8.0 kcal mol^{-1}.[32]

Among heterocyclic analogues of cyclooctene the *cis*- and *trans*-isomers of 3,8-dialkyl-1,2,-diazocines (VIII) have been discussed,[34] but these results based on a possible equilibrium of *cis*- and *trans*-isomers should be re-examined.[3]



(VIII) (IX) C (X) B

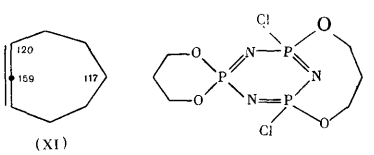
The benzosulphone (IX) has been studied by X-ray diffraction.[35] Introduction of a carbonyl group into the α-position relative to the planar fragment causes them to adopt a coplanar configuration, which has been shown in the case of benzocyclooctene-5,6-dione. In this case five atoms are situated in one plane, and the system becomes analogous to that of cycloocta[d,e]naphthalene (Section III) and its conformational behaviour is such that an equilibrium of C and B forms (X) occurs.

It is evident from the examples given that introduction of a single planar fragment into an eight-membered ring does not lead to substantial changes in its conformational behaviour. For ketones and *cis*-cyclooctenes the most favourable form remains BC as in cyclooctane,[2] and the occurrence of the TCC structure in *trans*-cyclooctene is due solely to steric restrictions that are specific to this case.

III. DERIVATIVES OF 1,2-CYCLOOCTADIENES

1. 1,2-Cyclooctadienes

The calculations made for 1,2-cyclooctadiene (XI)[37] (in the literature there are reports only about attempts to isolate this unstable product in a pure state[38]) revealed two preferred conformers T and TC which have similar energy; their torsion angles and energies are shown in Table 1. The T conformer has a second-order axis of symmetry, and the torsion angles along the cyclic bonds correspond exactly to the T form (see Chapter V). This conformer is defined as TB by the author. The transition barrier between the two forms has been calculated (8.8 kcal mol^{-1}). From the reported values of the bond angles within ring (XI), it is clear that the central allene bond of the molecule is twisted, which produces considerable internal strain in it.



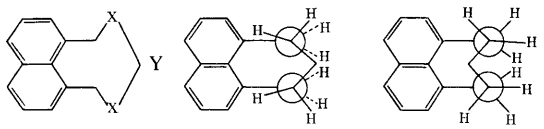
(XI) (XII)

Among heteroanalogues the structure of the inorganic heterocycle (XII) has been studied in the crystalline state.[39] The main structural difference between this molecule and (XI) is determined by the

fact that the central atom in the X–Y–X triad of heteroatoms [see also Chapter VII, compounds (LXXXII) and (LXXXIII)] has a much larger bond angle (about 125°), which is due to the different electronic state of the carbon atom and substituent Y. In the specific case examined, the ring of the *spiro/ansa*-isomer of cyclotriphosphazene (XII) has a BC conformation in which the NP_2O_2 fragment is in the form of a boat.[39] The stability of the BC form is so high that the P(4)N(5)P(6) angle is decreased to 112.7° (this is the smallest of all the values; in a six-membered ring it reaches 124.2°).

2. Derivatives of Cycloocta[d,e]naphthalene

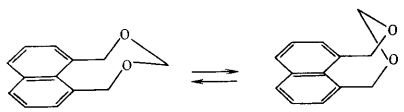
The main feature of compounds of this series [(XIII)–(XVII)] is the occurrence of a *peri* interaction. This dictates the specific type of conformational behaviour that stabilises the B conformation; in it the energy of torsional rotation about the C(1)–C(2) bonds [C(4)–C(5) bonds] is less (skewed conformation) than in the C form.



(XIII)–(XVII) C B

According to the ^1H NMR spectroscopic data, the parent carbon compound (XIII) with X = Y = CH_2 and also its deuterated analogue have the B conformation. By studying the temperature dependence it was possible to determine the energy characteristics of the conformational process B ⇌ B*: $\Delta G^{\neq}$ is equal to 14.5 kcal mol^{-1}, $\Delta H^{\neq}$ to 16.1 kcal mol^{-1}, and $\Delta S^{\neq}$ to 5.4 E.u.[40] Introduction of methyl substituents into the X position (X = CMe_2) assists the relative stabilisation of the B form, so that compounds with Y = CH_2 or C=O, even if they have only one *gem*-dimethyl group at the X position, exist exclusively in this conformation. The inversion barriers of the rings increase by 4.8–5.9 kcal mol^{-1} relative to their nonmethylated analogues.[41]

Among the heterocyclic derivatives of this series 1,3-dioxans (XIV) with X = O and Y = CHR have been studied to the greatest extent. For the simplest acetal (R = H), when the energy is minimised with parametrization,[42] two conformations C and B with ΔH_{C-B} of 1.0 kcal mol^{-1} are predicted;[43] according to the ^1H NMR data for $CHCl_3$ and $C_2Br_2F_4$ (1 : 1) ΔH is equal to 0.7 kcal mol^{-1}.[44] The existence of a conformational equilibrium follows from the IR spectroscopic data, dipole moments, and ^{13}C NMR spectra of different acetals with R = H, Me, iso-Pr, t-Bu, Ph, *p*-ClC_6H_4, and *p*-$O_2NC_6H_4$.[45]



C (XIV) B

In the 3-t-butyl derivative the value of ΔH increases to 1.4 kcal mol^{-1}; and in the crystalline state, according to the X-ray diffraction data, the C form occurs with an equatorial configuration of the t-butyl group.[46] The C conformation is also typical for sulphate (XV) with X = O and Y = S=O, with the S=O bond exclusively occupying the axial position,[43] as in six-membered sulphates.[5] In acetals the C form is destabilised by the *peri* effect; the increase in nonbonded and torsional strains leads to a relative stabilisation of the B conformation.[46,47]

Replacement of the ring oxygen atoms by sulphur [(XVI) with X = S and Y = CHR] makes this form more favourable in thioacetals, and the proportion of C conformer present is reduced to 7%.[48] In contrast to acetals, ketals (XVI) with X = S, $R^1 = R^2$ = Me, $(CH_2)_5$ mainly have the C conformation.[48] The subsequent replacement of Y = CR^1R^2 by a sulphur atom gives trithiocines (XVII) with X = S and Y = S, for which dynamic ^1H NMR spectroscopy was used to detect an equilibrium of two forms in the ratio 10 : 1 (in pyridine-d_5) which participated in two types of conformational process—a relatively rapid process with $\Delta H^{\neq}$ 15 kcal mol^{-1} and $\Delta S^{\neq}$ −1.1 cal mol^{-1} K^{-1} and a slow process with a higher $\Delta G^{\neq}$ barrier equal to 17.9 kcal mol^{-1}.[49] When calculations were applied to interpret the experimental data it was shown that the B form was more stable than the chair form by 0.6 kcal mol^{-1}. The T conformation is obtained on the energy surface by moving out each $C_{sp^3}-C_{sp^2}$ bond 15° from the plane of the naphthalene ring; this leads to a loss of 13.6 kcal mol^{-1}. The conformational processes detected correspond to the exchange B ⇌ B* via the T form and B ⇌ C.[49]

Thus, the steric structure of an eight-membered ring with two planar fragments in the 1,2-position is determined to a considerable degree by the nature of these fragments. In allene systems twisted forms (T, TC) predominate; replacement of sp^2 carbon atoms by heteroatoms decreases the angle in the ring between the double bonds, which helps to remove strain and the system in terms of its parameters approximates to saturated eight-membered rings (XII). In naphthalene derivatives the *peri* effect together with torsional strain and nonbonded interactions controls the stabilisation of the B and C forms. As was shown above in the case of benzosulphone (IX),[35] these principles are applicable to α-keto derivatives of cyclooctenes.

IV. DERIVATIVES OF 1,3-CYCLOOCTADIENES

Initial calculations of the conformational energies of 1,3-cyclooctadiene (XVIII) identified two preferred conformers, approximately equal in energy and defined as TB.[2,50,51] Subsequent calculations led to more accurate notions of the energetics of these basic conformers and provided a basis for developing their nomenclature.[52] The results of the calculations, the energies, nomenclature, and torsion angles are presented in Table 1. It can be seen from this that two conformers stand out in terms of stability—TBC with C_2 symmetry, which is more stable by 0.5 kcal mol^{-1} than the second form (TB) with C_1 symmetry. The remaining forms are less favourable than TB—the boat by 6.3 kcal mol^{-1}, and the half-chair (HC) and twist form by 8.3 kcal mol^{-1}. The decrease in symmetry of the T form of cyclooctadiene derivatives as compared with the TC conformation depicted in Fig.1 and having C_{2h} symmetry is due to the introduction of planar fragments into the ring. As may be seen from the next chapter, when there is a favourable geometric environment its occurrence is possible [compounds (XLII) and (XLIII)].



TBC TB T B HC

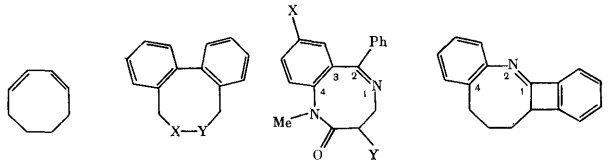
Table 1. The conformations of derivatives of 1,2- and 1,3-cyclooctadienes.

Compound	X	Y	Torsion angles, in deg.*								ΔG^0, kcal mol^{-1}	Notation**	Refs.
			1	2	3	4	5	6	7	8			
(XI)	—	—	—	63	—13	—71	58	—	—	—	14,64	T (TB)	[38]
	—	—	—	68	—75	63	—81	116	—62	—14	14,87	TC	[38]
(XVIII)	—	—	—6	—54	—6	94	—85	59	—85	94	7.12	TBC	[52]
	—	—	—4	—42	—2	92	—52	—59	82	—5	7.66	TB	[52]
	—	—	3	—58	3	28	46	—118	46	28	14.00	B	[52]
	—	—	—	0	—1	65	85	0	—	—	16.30	HC	[52]
	—	—	—	—57	—11	98	—45	—5	—	—	16.25	TBC ⟷ TB	[52]
(XIX)	O	O	3.3	64.9	3.3	—52.1	—31.3	119.5	—31.3	—52.1	—	B	[53, 54]
(XX)	S	S	—	54.32	—	—	—	—	—	—	—	TBC	[55]
(XXI)	O	SO_2	4.3	64.8	—6.7	—90.3	102.6	—64.9	81.3	—92.1	—	TBC (DC)	[54]
(XXII)	S	SO_2	2.1	67.0	2.1	—104.8	86.9	—47.4	86.9	—104.8	—	TBC (DC)	[56]
(XXIII)	Me	Ph	0	—65.9	—12.3	89.2	—31.6	—52.6	7.6	70.2	—	B	[57]
(XXIV)	Br	H	—1.0	—71.6	—3.6	67.3	9.1	—69.3	—12.3	79.4	—	B	[58, 59]
(XXVI)	—	—	—4.2	—56.9	4.9	87.2	—95.7	65.0	—72.2	81.1	—	TBC (C)	[60]

* Torsion angle 1 is formed by atoms 8, 1, 2, 3; angle 2 by atoms 1,2, 3, 4; and so on.

** The labels used by the authors for the conformations are given in brackets; D stands for a deformed conformation, HC is a half-chair, TBC ⟷ TB is a form intermediate between TBC and TB.

From a detailed study of the contributions of different types of strain to the total energy it is possible, in our opinion, to distinguish the angle strain, namely, the strain occurring as a result of bond angle deformation (ΔE_θ relative to the TBC form is 3.3 kcal mol^{-1} for TB, 4.3 kcal mol^{-1} for B, 7 kcal mol^{-1} for HC, and 5.2 kcal mol^{-1} for T). These observations, in the opinion of the author of this review, indicate that the conformational situation can change when heteroatoms, which have bond angle values that are different from those of the carbon atoms and often undergo angular deformations more easily, are introduced into the ring. That is why Table 1 also contains data on torsion angles and conformations obtained by X-ray diffraction analysis for the heterocyclic analogues of 1,3-cyclooctadiene and includes the dibenzo derivatives (XIX)–(XXVI).[53–60] The author's labels for the conformations in Table 1 are given in brackets. For two compounds [(XXV) and (XXVI)] we have calculated the torsion angles from atomic coordinates reported in two articles.[59,60]



(XVIII) (XIX)–(XXII) (XXIII)–(XXV) (XXVI)

It is evident from the data in Table 1 that TBC is the principal form; compounds (XX)–(XXII)[54–56] and (XXVI)[60] exist in it (see also the results for rhazinilam.[61]). The TB conformer was not detected in a single case, but the B form is fairly representative [(XIX), (XXIII)–(XXV) with X = Me, Br, Cl[53,54,57–59]].

On the whole it should be noted that the TBC form has quite high values for the dihedral angles about the bonds formed by the ring atoms 4–5, 5–6, 7–8, and 8–1 (about 80–100°) and with alternating signs. In the TB form the angle values are lower, one of those adjacent to the double bonds is positioned almost in the same plane with it while the other is very twisted [5° and 92° in (XVIII)]. A B conformation very similar to that predicted by calculation for carbocycle (XVIII) is found in peroxide (XIX). In it the bond opposite the single bond and situated between the two planar fragments is very twisted (about 120°). In the other compounds the single bonds adjacent to the double bond (4–5 and 1–8) are more twisted in comparison with the remaining ones. This helps to flatten out the 4–5–6–7 and 6–7–8–1 fragments so that the B form in compounds (XXIV)[58] and (XXVI)[59] approximates to the classical cyclooctatetraene structure[62] (Section VII).

1,3-Cyclooctadiene (XVIII) has been studied in solution by means of ^{1}H and ^{13}C NMR.[52,53] An interpretation of the results obtained for its mono- and di-epoxides has been carried out from data calculated on the energies of the conformers. They exist in a primary state as a mixture TBC ⇋ TB, and the proportion of TB falls on changing to the diepoxide. Three conformational processes with barriers of 7.2 kcal mol^{-1} (7.4 for the monoepoxide), 9.0 kcal mol^{-1} (9.9), and about 10 kcal mol^{-1} were detected by temperature measurements. The first corresponds to the conversion TB ⇋ TB* via the B form, the second corresponds to TB ⇋ TBC. From among the heterocyclic compounds, nonempirical quantum-chemical calculations[4] were carried out for the disulphide (XX) on the basis of molecular mechanics[65] and also the temperature dependencies of the ^{1}H NMR spectra were studied.[66] The TBC form is recognised as the most favourable since quite a high inversion barrier was found ($\Delta G^{\neq}$ 28.8 kcal mol^{-1}, $\Delta H^{\neq}$ 26.6 kcal mol^{-1}, and $\Delta S^{\neq}$ -6.0 cal mol^{-1} K^{-1}).[66] Such high barriers have also been determined for dibenzo derivatives of 6,7-dicarboxy-1,2,3,4-dibenzocyclooctane.[66] It is apparent that, as in seven-membered heterocycles,[2] replacement of a double bond by a benzo fragment produces an increase in the barriers for conformational conversions.

Table 2. Quantitative characteristics of conformers of 1,4-cyclooctadiene and 1,3,2-dioxaphosphocines.

Compound	Conformation	Torsion angles, deg.*								ΔE, kcal mol^{-1}	Folding parameters				
		1	2	3	4	5	6	7	8		q_2	φ_2	q_3	φ_3	q_4
(XXVII)	BC	87	—87	73	0	—85	85	0	—73	12.20	—	—	—	—	—
	BB	—72	72	4	1	—83	83	1	—4	15.91	—	—	—	—	—
	TB-T	54	54	—89	0	26	26	0	—89	1? 09	—	—	—	—	—
	DTB**	52	55	—88	4	13	38	—3	—90	12.22	—	—	—	—	—
(XXVIII) Y = UEP	BC	95	—95	80	0	—91	91	0	—80	—	0.46	280	0.86	0	0.23
	BB	—93	93	6	0	—89	89	0	—6	—	1.30	180	0.11	180	—0.38
	B	—110	17	51	0	—96	54	0	59	—	1.38	146	—0.18	282	—0.33
	TB	63	54	—111	0	86	39	0	—64	—	1.33	123	0.36	48	—0.13
(XXVIII) Y=O, S	BC	91	—91	80	0	—90	90	0	—80	—	0.51	0	0.80	180	—0.19
	BB	—88	88	5	0	—88	88	0	—4	—	1.27	180	0.06	180	—0.35
	B	—112	14	55	0	—92	51	0	63	—	1.35	—36	0.18	270	0.30
	TB	66	55	—112	0	83	38	0	—67	—	1.30	123	0.36	46	—0.12

* Torsion angle 1 corresponds to the angle formed by atoms 1,8,7,6 (according to the numbering of 1,4-cyclooctadiene); angle 2 corresponds to atoms 8, 7, 6, 5; angle 3 to atoms 7, 6, 5, 4; and so on.
** D stands for a deformed conformation relative to the ideal form.

V. DERIVATIVES OF 1,4-CYCLOOCTADIENES

1. Basic Conformations

Among eight-membered rings with two planar fragments, derivatives of 1,4-cyclooctadiene (XXVII) have been studied in greatest detail. In this chapter we shall examine the possible conformation of this ring on the basis of the X-ray diffraction data and the quantitative properties of the conformers. 1,4-Cyclooctadiene has been the subject of several theoretical studies,[50,67-70] in which three conformations BC, BB, and TB are considered.



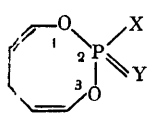
BC BB TB B

Calculations show that BC is the most stable form; its difference in energy from the TB conformation is 0[67] or 1.1 kcal mol^{-1}.[50] The BB form is the transition state in the process TB $\rightleftharpoons$ TB*.[68] Consequently, for (XXVII) the two forms BC and TB are expected to participate. However, as has already been observed above, the situation can alter on changing to heterocyclic analogues.

The basic conformations of compounds of this type have been studied in the case of 1,3,2-dioxaphosphocines with three- and four-coordinated phosphorus[71] (Y is an unshared electron pair (UEP), or an atom of phosphorus or sulphur) using the method of Cremer and Pople[38] developed for eight-membered rings.[9,10]



(XXVII)



(XXVIII)

Calculations have been carried out using X-ray diffraction data for 4,5;7,8-dibenzo-1,3,2-dioxaphosphocines[72,73] [compounds (XXXV) and (XXXIX) in Table 3]. Four basic conformations were obtained—the three proposed for (XXVII) and a distorted B form. Table 2 gives the torsion angles about the cyclic bonds in compounds of three- and four-coordinated phosphorus (XXVIII) and the folding parameters. In this case the torsion angles of the different conformations of (XXVII) and their relative energies[68] are listed.

Before going on to discuss actual conformers, let us consider Table 3, where the X-ray diffraction data that is available at the present time for the heterocyclic derivatives of (XXVII) have been collected. The compounds (XXIX)–(XLIX) are listed according to the increase in the number of heteroatoms in the ring.[72-87] These are mainly dibenzo derivatives and only two examples relate to compounds with dinaphtho residues [(XXXVIII) and (XXXIX)].[73,80] On correlating the calculated and experimental data we observe that when compounds have the same conformations, regardless of the nature of the heteroatoms, the torsion angles vary over quite a narrow range, so that dihedral angles can be used, in our opinion, as a quantitative criterion of the conformers. As in the case of (XVIII), the BC form has high values of the torsion angles about the single bonds with alternating signs. This form is fairly typical in compounds with a methylene bridge—(XXIX),[74] (XXXV)–(XXXVII)[72,78,79]—or a sulphur atom [(XLIV)], as well as in thiazocinium salts (LI), 1,5-dithiocines (XLIX),[97-99] and dibenzosilocine.[100] In the BB conformation the fragments enclosing the single bonds that are adjacent to the planar groups are very flattened out (torsion angles constitute 3–8°). In this form the substituents occurring at the flagpole position approach very close to each other, which contributes to a destabilisation of this conformation. The relatively small difference in energy calculated for the BB form of (XXVII)[68] is due to a substantial flattening out of the fragment made up by the atoms 8,1,2,3,4 in comparison with the related BC form. At the same time it is possible to change from the BB to a distorted B conformer by a small rotation. Proposals about the possible existence of such a conformation in heterocycles were also put forward previously.[88,89] However, their quantitative parameters

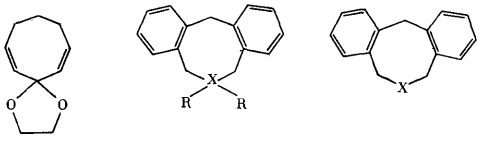
were only obtained recently[71] (Table 2). It was possible to make an unequivocal interpretation of the X-ray diffraction data (Table 3) from a knowledge of the torsion angles. It transpired that this form had been observed by many authors but they had given it arbitrary names. It is typical for azocines (XXX),[75] their sulphur derivatives (XXXI)–(XXXIV),[76,77] 1,3,2-diazaphosphocines (XL),[81–83] and 4,5;7,8-dinaphtho-1,3,2-dioxaphosphocines (XXXVIII) and (XXXIX).[73,80] In some studies this form is also called TB,[76,77] by analogy with a previous study,[88] although it is particularly stressed that this is quite a different conformation from the TB form discussed in the previous studies.[88,89] Thus, only when quantitative criteria were used for the identification of conformers was it possible to avoid ambiguity.

An examination of the T and TB forms deserves particular attention. Even in the basic study of Anet,[68] the dihedral angles for these two forms differed only slightly (Table 2). In the ideal T conformation with the C_2 symmetry, torsion angles 1 and 2 are equal to 60°, and deviations, which are often small (about ±30°) serve to identify the TB form. In the less twisted distorted B conformer these angles have different signs and differ in absolute value by 60–90°. As was predicted in the calculations of Anet[68] and from the folding parameters,[71] this conformation occurs in those cases when the angle at C(6) in the bridge position is readily opened up to 120°. Such a situation must occur in keto derivatives. In fact, the two ketones (XLII) and (XLIII) studied so far[85,86] have a T conformation.

2. Conformational Behaviour in Solution

(a) Derivatives of 1,4-Cyclooctadienes

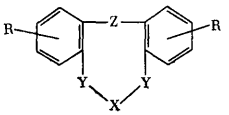
An analysis of the shielding effect from the C(3) atom in the ^{13}C NMR spectra and also the changes in the ^{1}H and ^{13}C NMR spectra on varying the temperature lead to the conclusion[68] that (XXVII) exists as an equilibrium BC ⇋ T (or TB) with an interconversion barrier of 8 kcal mol^{-1}. As a result of the fact that in their studies the authors have not made a distinction between the T and TB forms, the generalised label [TB] is used subsequently in such cases. According to force-field calculations it is proposed that the pseudorotation T ⇋ T* takes place with a very low barrier of 3.8 kcal mol^{-1}.[68]



(XLV) (XLVI) (XLVII)

The ethyleneketal (XLV) is conformationally pure and exists exclusively in the T form, its barrier for pseudorotation is higher than in (XXVII) by 6.0 kcal mol^{-1}.[18] The conformational behaviour of the dibenzo derivative (XLVI) with R = H is considerably different

Table 3. The conformations of dibenzo derivatives of 1,4-cyclooctadienes with the general formula.



Compounds	X	Y	Z	Torsion angles, deg.*								Conformations***	Refs.
				1	2	3	4	5	6	7	8		
(XXIX)	NMe	CH_2	CH_2	−88.6	88.1	−71.5	1.1	86.9	−88.0	0.3	71.3	*a*-BC	[74]
(XXX)	N-tert-Bu	CH_2	CH_2	−115.4	44.1	41.3	−2.8	−91.0	59.4	−3.1	42.3	*e*-B (TB)	[75]
(XXX)	N-tert-Bu	CH_2	CH_2	−64.5	135.9	−41.3	2.8	−59.4	91.0	3.1	−42.3	*e*-B (TB)	[75]
(XXXI)	NMe	CH_2	SCl	140.7	−72.1	−29.1	−3.9	72.7	−69.3	2.8	−22.8	B (TB)	[76, 77]
(XXXII)	NMe	CH_2	SOMe	−142.5	77.3	−25.3	4.8	70.9	68.0	−6.6	26.9	B (TB)	[76, 77]
(XXXIII)	NMe	CH_2	SMe	132.9	−65.7	−34.0	−1.6	83.2	−66.1	6.4	−29.6	B (TB)	[76, 77]
(XXXIV)	NMe	CH_2	S=O	−129.2	69.1	30.8	4.8	−85.9	66.6	−8.8	27.4	B (TB)	[76, 77]
(XXXV)	POPh	O	CH_2	−94.7	95.3	−80.1	−0.1	90.9	−92.5	1.2	−79.2	*e*-BC	[72]
(XXXVI)	$PNPh_2$	O	CH_2	−95.3	97.7	−77.9	−6.0	95.0	−86.8	−1.9	77.9	*e*-BC	[78]
(XXXVII)	$P(S)NEt_2$	O	CH_2	−94.6	93.2	−74.8	−3.5	90.1	−94.3	6.2	75.9	*e*-BC	[79]
(XXXVIII) **	$PNEt_2$	O	CH_2	−110.8	20.9	48.9	−0.4	−96.2	54.2	−1.5	58.2	*e*-B	[80]
(XXXIX) **	$P(S)NEt_2$	O	CH_2	−101.4	1.5	57.5	9.5	−100.7	50.7	−0.9	61.0	*e*-B	[73]
(XL)	P(O, S)Cl	NMe	CH_2	−96.0	6.0	—	—	—	—	—	—	B (DC)	[81–83]
(XLI)	S=O	O	CH_2	−100.1	98.9	−82.2	3.4	85.8	−91.0	2.1	81.5	*a*-BC	[84]
(XLII)	S=O	O	C=O	71.0	57.0	−92.1	−8.0	39.6	17.9	−1.7	96.7	T (DBB)	[85]
(XLIII)	SO_2	O	C=O	67.7	59.7	−94.2	−6.2	42.4	11.1	1.2	−93.7	T (DB)	[86]
(XLIV)	S=O	O	S	−89.8	90.0	−90.7	0.4	86.4	−79.5	−6.9	92.6	*a*-BC	[87]

* Numbering of the torsion angles corresponds to that in Table 2.

** Dinaphtho derivatives.

*** *a* indicates an axial orientation of the exocyclic bond, *e* indicates an equatorial orientation.

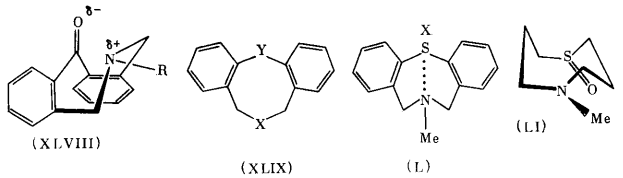
from that of (XXVII);[90,91] the equilibrium BC ⇋ [TB] is displaced 98% towards the first conformer, and the $\Delta G^{\neq}$ inversion barrier between them is much higher (14.9 kcal mol^{-1}), while the barrier for the transition BC ⇋ BC* is even higher (15.3 kcal mol^{-1}).[91] These results are somewhat different from those calculated,[90] according to which the energies of the BC and T forms are equal and the BB form is less favourable than them by 5.3 kcal mol^{-1}. The transition barrier for the process BC → T was also calculated (15.2 kcal mol^{-1}) and its possible pathways indicated.[90]

A change in the nature of the substituents R in (XLVI)—XR_2 = C=O, C=CH_2, CHMe, CHAc, $CMeCH_2OH$, $C(CN)_2$[92]—affects the position of the equilibrium BC ⇋ TB and the inversion barriers to a considerable degree. The population of the TB conformer is essentially small (2–16%). When there is *gem*-substitution it increases to 40–60% [$C(CN)_2$, $CMeCH_2OH$]. As regards the barriers, they increase on changing from a ketone (10.1 kcal mol^{-1}) to a methylene derivative (13–14 kcal mol^{-1}) and then to compounds with XR_2 = CHMe and $C(CN)_2$ (15–16.7 kcal mol^{-1}). The following NMR criteria were proposed for conformational studies on compounds of this class: 1) the flexible T form has a higher entropy than the BC form (ΔS reaches 7 E.u.); 2) the geminal constant ^2J(HH) of the bridge methylene group is determined to a considerable degree by the structure of the ring; for the BC form it is 12–14 Hz, and for the T form it is 19 Hz; 3) in the ^{1}H NMR spectra of the BC form two sets of nonequivalent AB methylene protons occur, and there are two singlets in the exchange T ⇋ T*.[92]

On the whole, it may be stated that replacement of double bonds by aryl residues contributes to an increase in the transition barriers between the BC and T conformers.

(b) 3,4;6,7-Dibenzo-1-azocines and their Heteroanalogues

The first study on dynamic ^{1}H NMR spectra of dibenzoazocines (XLVII) with X = NR_2 and R = H, CN, CH_2Ph appeared back in 1970,[93] but no definite conclusions were then made about the nature of the conformations occurring. This was made possible by a detailed investigation of a series of azocines with R = Me,[94] H, Me, iso-Pr, t-Bu,[95] and CH_2Ph,[88] as well as their carbonyl analogues with a keto group at the bridge position.[96] Dibenzoazocines are conformationally heterogeneous and are characterised by the equilibrium BC ⇋ [TB]. The latter conformation, enclosed in brackets, denotes that its structure has not been established conclusively, and in some studies preference is given to a T conformer with C_2 symmetry[94–96] while in others an asymmetric TB form is preferred. In some cases a BB conformation is considered.[101] The energy factors of the methyl-substituted amine (R = Me) have been obtained (ΔH –3.2 kcal mol^{-1}, ΔS –7 E.u., inversion barrier 15.3 kcal mol^{-1}).[94] The proportion of [TB] conformer increases as the size of the substituent on the N atom increases (in $CDCl_3$—however, the opposite effect was found in CF_3COOH); when R = H the BC conformation occurs with barrier for the transition *e*-BC ⇋ *a*-BC of 16.1 kcal mol^{-1}, when R = t-Bu the barrier is 16.5 kcal mol^{-1},[95] when R = CH_2Ph it is 17.0[88] or 17.4 kcal mol^{-1};[96] on protonation the barriers increase.[95] For aminoketones with R = CH_2Ph and Me, proper consideration was given for the first time in the literature to the distorted B form (XLVIII),[88,96] which is stabilised in these particular examples by a specific transannular interaction between the N atom and the carbonyl group.

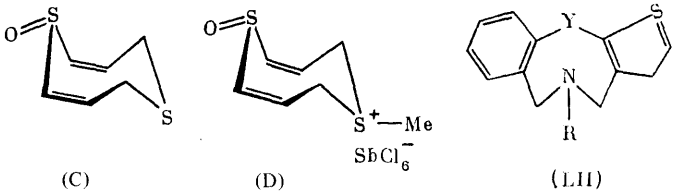


The signals from the two methylene groups in this minor form appear as a singlet at –100 °C, so the authors conclude that the compounds have the B form that occurs during the pseudorotation B ⇋ B* with a barrier of ~8 kcal mol^{-1}. Theoretical calculations carried out for *N*-methylazocine[88,96] show that the BC conformation is actually preferred (ΔE ~4.30 kcal mol^{-1}), and then in increasing energy B (5.54 kcal mol^{-1}), T (5.62 kcal mol^{-1}), and BB (5.94 kcal mol^{-1}). Thus, there is still an open question concerning the steric structure of the minor conformer since the energies of the B and T forms are similar. In our opinion, the use of new, recently obtained spectral criteria of the distorted B form will help to resolve this problem also for azocines (see below).

A fairly extensive group of compounds studied is made up by the heteroanalogues of azocines, in particular thiocines (XLVII) with X = S and SO_2. In the ^{1}H NMR temperature spectra of the sulphone X = SO_2, the protons at C(5) and C(7) appear as an AB system, which is an indication that the BC conformation predominates in the equilibrium BC ⇋ [TB][88] with an inversion barrier of 16.2 kcal mol^{-1} [96] and 15.8 kcal mol^{-1}.[88] According to calculations, the BC form is more favourable in the sulphide than in azocine itself. Introduction of heteroatoms into the bridge position (Y = O, S, SO_2) for those compounds with X = S, SO_2 NCH_2Ph already considered has little effect on the conformational behaviour of (XLIX) compounds, which is manifested in the same dependence on temperature for the NMR spectra.[88] It is therefore concluded that they also exist in the equilibrium BC ⇋ [TB]. The values of the barriers in (XLIX) in relation to the nature of X and Y are given in Fig.2.[88] It can be seen very clearly from it that the energy barriers are determined to a greater extent by the nature of the bridging group Y. The lowest values occur for O-derivatives (10.5–14 kcal mol^{-1}), they are somewhat higher for the CH_2 group (14–16 kcal mol^{-1}), and even higher for the SO_2 group (16–18 kcal mol^{-1}), while for sulphides there is a wide range of barrier values from 12.5 to 16.5 kcal mol^{-1}. As regards the effect of the X group, it is shown less clearly, and it can only be stated that in all of the examples studied the barriers for the sulphones are lower than for the sulphides.

The problem concerning the conformation of the minor component can be resolved in the case of dibenzo-1,5-thiazocines by analysing the current literature; because of the lack of conformity in the terminology this is initially difficult to understand. The authors who hold the opinion that the T form occurs define it as TB;[92,94,95] the same label is given in those cases where a distorted B conformation is being considered.[76,77] Let us consider the data in Table 3 once again. Only for one of the azocines listed there [(XXIX)] is the BC conformation observed in the crystalline state,[74] in all of the remaining cases [(XXXI)–(XXXIV)] the B form occurs,[75–77] while in the thiazocinium salts (XXXI)–(XXXIII) of type (L) this conformation can be recognised as constrained by the transannular $R_3N...SX$ interaction, where sulphur has a trigonal bipyramidal structure. In saturated systems this type of interaction also occurs in the BC form of (LI).[97] However, on going to the dibenzo analogues, such a form where opposing N and S atoms are situated on the base

of the boat cannot occur because of the presence of planar fragments. In the two remaining cases—azocine (XXX) and its sulphoxide (XXXIV)[75-77]—stabilisation of the B form is caused for no other reasons than the inherent properties of this system. In solution (benzene-d_6), according to variable temperature ^{1}H NMR spectra, the sulphoxide retains its structure (the protons of the methylene groups appear as an AB system with ^2J(HH) of 15 Hz at 3.18 and 3.42 ppm).[98] In the thiazocinium salts (L) the S...N attraction is high enough for the B form to be retained even in solution,[77,98,99] and it is predominant although in some cases the presence of the BC conformer is detected (up to 45% depending on the experimental conditions[97]). In the opinion of the authors, when the distorted B form occurs the protons of the methylene group appear as a singlet in the region 3.88–4.25 p.p.m. In 1,5-dithiocines the situation is different; there is an AB system in the spectrum with quite a high $\Delta\delta$ value (0.5–0.8 p.p.m.) and geminal constant of 14–15 Hz, which is associated with the BC conformation of compounds (C) and (D):[99]



(C) (D) (LII)

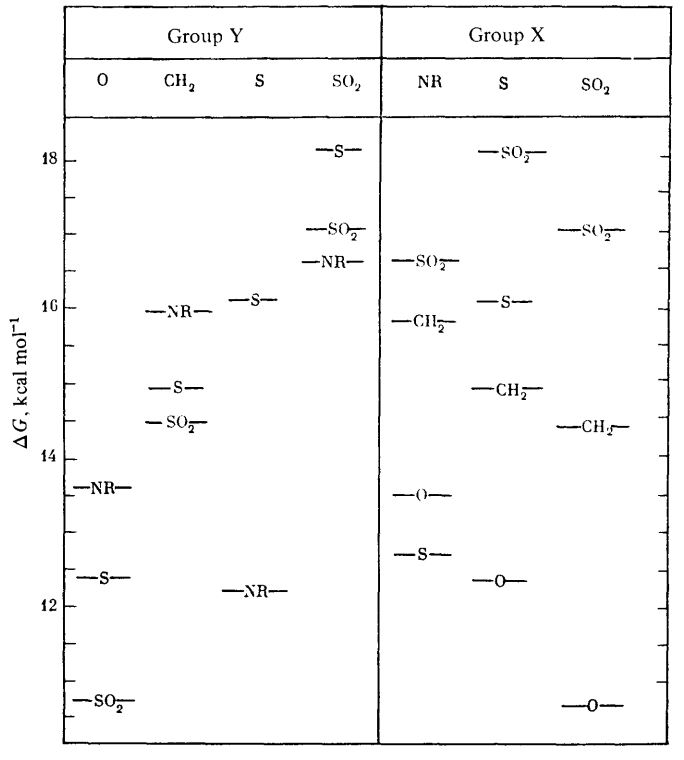


Figure 2. The correlation between the activation barriers $\Delta G^{\neq}$ for the process BC ⇋ B and the nature of groups X and Y;[88] R = CH_2Ph.

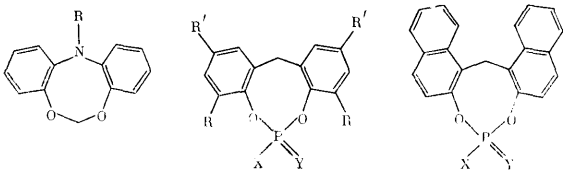
The differences in the conformational behaviour of 1,5-thiazocine and 1,5-dithiocine S-oxides have formed the basis for an explanation of the differences in their reactivity towards electrophiles due to the transannular participation of the amino fragment.[99,102]

There are reports in the literature about the synthesis of benzothienoazocines (LII),[103] 1,5-aza-,[104] and 1,5-oxa(thia)-phosphocines (XLIX) with X = NR, O, S and Y = P(O)R;[105,106] and proposals about their steric structure—whether the BB or TB conformations occur—were deduced by constructing Stewart–Brigleb models. These compounds are very interesting from the point of view of studying the hypervalent bonding of the 1,5-heteroatoms and they will therefore be the subject of future investigations.

On the whole, by examining the conformational behaviour of 3,4;6,7-dibenzoazocines and their 5-heteroanalogues the following conclusion can be made. Despite the discussion which had developed in the literature about the reason for the steric structure of the minor conformer (in certain examples the predominant one), sufficient practical data have so far been accumulated to give preference to a B form that is distorted in one or other direction depending on the geometric parameters of the cyclic fragment. A subsidiary 1,5-transannular interaction helps to stabilise this very conformation. The main competitor to the B form is the BC form, stabilisation of which occurs in compounds that are free of the subsidiary steric interactions.

(c) 4,5;7,8-Dibenzo-1,3,2-dioxaphosphocines and their Heteroanalogues

Compounds of this series have been studied in sufficient detail, which is due to their synthetic asscessibility[101,107] and valuable practical properties.[107-109] Comparatively recently 4,5;7,8-dibenzo-1,3,6-dioxazocines (LIII) were synthesised and their stereochemistry has been studied by means of IR, ^{1}H and ^{13}C NMR, dipole moments, and quantum-chemical calculations using the PPDP/2 method. The latter have also provided the main criterion in selecting the preferred conformer—the BC form. As regards the BB conformation, it has been accepted as not likely to exist[108] because of the strong steric interactions between the methylene and NR groups. It is quite difficult to make definite conformational correlations from the ^{1}H NMR spectra in the compounds examined; a much wider range of possibilities can be admitted in this form of compound with a bridging methylene group, in particular 1,3,2-dioxaphosphocines with different planar fragments (LIV) and (LV).



(LIII) (LIV) (LV)

The spectroscopic characteristics of the CH_2 group [the difference in chemical shift of the protons, geminal ^2J(HH) and long-range ^5J(PH) constants] are closely related to the conformational parameters. Even before the commencement of structural studies, methods had been developed for obtaining compounds of series (LIV) with three-coordinated phosphorus and X = OR,[109] Cl,[110] NR_2[111] and four-coordinated phosphorus with X = H, Y = O,[109,112] X = Cl, Y = S,[113] X = H, Y = S,[114] X = OH, Y = O.[115] The possible steric forms of the cyclic fragment have been examined by means of the folding parameters (Table 2). When these were correlated with the

X-ray diffraction data (Table 3) it was possible to determine the most probable forms—the BC and B conformations. In considering the steric structure of 1,3,2-dioxaphosphocines, one of the main points is also the question concerning the orientation of the exocyclic substituents on the phosphorus atom (we shall take substituent X as a starting point in labelling the conformations). Doubling the number of conformers definitely complicates the solution to the conformational problem, but in many cases, when one form is stable, more reliable conclusions about the steric structure can be made.

Table 4. ^{1}H NMR spectroscopic parameters (δ, p.p.m.; *J*, Hz) of 1,3,2-dioxaphosphocines.[119–121]*

Compound	X	Y	R	$\delta(H^A)$	$\delta(H^B)$	Δδ	^2J(HH)	^5J(PH)
(LIV)	Cl	UEP	tert-Bu	3.68	3.97	0.29	12.6	2.4
	NEt_2	UEP	tert-Bu	3.25	4.31	1.06	12.1	2.3
	NPh_2	UEP	tert-Bu	3.30	4.27	0.97	12.7	5.1
	OEt	UEP	tert-Bu	3.24	4.22	0.98	12.3	3.2
	OPh	UEP	tert-Bu	3.41	4.18	0.77	12.6	2.3
	OC_6H_4-4-tert-Bu	UEP	tert-Bu	3.40	4.28	0.88	12.8	2.3
	O-naphthyl	UEP	tert-Bu	3.51	4.39	0.88	12.8	2.7
	OPh	UEP	$C_6H_4CH_3$	3.38	4.29	0.91	12.8	3.0
	NEt_2	S	tert-Bu	3.31	4.12	0.81	12.6	3.4
	OEt	S	tert-Bu	3.65	4.52	0.87	14.6	—
	H	O	tert-Bu	3.61	4.39	0.78	14.0	—
	H	O	$C_6H_4CH_3$	3.66	4.42	0.76	15.0	—
(LV)	NMe_2	UEP	—	5.12	4.56	0.56	15.9	3.5
	NEt_2	UEP	—	5.06	4.54	0.52	16.3	3.6
	OPh	UEP	—	5.06	4.45	0.61	16.0	—
	NEt_2	O	—	5.28	5.03	0.25	15.6	—
	NEt_2	S	—	5.22	5.12	0.10	16.2	—

*The chemical shift from Me in the benzene ring varies within the limits 2.24–2.30 p.p.m.; that from t-butyl varies within 1.22 to 1.38 p.p.m.

Some ideas about the preferred conformations were provided by nonempirical quantum-chemical calculations of the conformational energies in derivatives of a series of (XXVIII) in which the dibenzo fragments are replaced by double bonds. Calculations were made for 2-chloro-, 2-methoxy-,[116] and 2-hydro-2-oxo-1,3,2-dioxaphosphocines.[117] They showed that the most favourable form is the *e*-BC conformation. The most unstable is the BB form with *e*-X and to an even greater degree with *a*-X because of the close contact between the C(6), *a*-H on C(6), and P(2) atoms. Destabilisation increases if the substituent on P(2) occupies the *a* position. As regards all the other conformations, the differences in energy between them were not large enough for definite conclusions to be made, especially as the calculations were made for model compounds without optimisation of geometry and calculation of the effect of the medium.

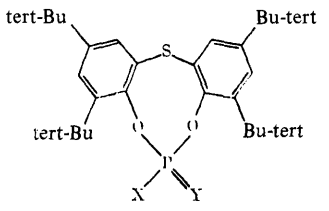
In actual systems studied, the planar fragments are as a rule aryl or naphthyl rings, so it is difficult to expect an absolute convergence of the experimental data and that obtained from calculation.

When we come to consider the spectroscopic characteristics of 1,3,2-dioxaphosphocines, we can turn our attention to the long-range ^5J(PH) constant in azocines. It was originally detected in trivalent phosphorus compounds,[101,118] on the basis of which it was concluded that the BB conformation occurred since the P and H atoms in it are spatially converged. However, as was indicated above,[108,116] the possible occurrence of this structure is very problematic. A single occurrence of this constant cannot yet provide the basis for such a conclusion. Identification of the conformers of 1,3,2-dioxaphosphocines (LIV) and (LV) was made possible from variable temperature ^{1}H NMR spectra.[117,119,122] The spectra of individual conformers were obtained for two of them.[117,122] This assisted the search for spectral criteria of the different conformations. In the ^{1}H NMR spectra the resonance signals from the methylene protons occur in the region 3.24–4.39 p.p.m. for the (LIV) series and at 4.45 to 5.28 p.p.m. for the (LV) series[119–121] (Table 4). They form an AB system, and the low-field doublet in many compounds of the (LIV) series and the high-field doublet in the series of (LV) compounds are split due to long-range interaction with the ^{31}P nucleus. In almost all of the dibenzo derivatives (LIV), with the exception of the phosphorochloridite, a significant (about 1 p.p.m.) nonequivalence (the difference in chemical shifts Δδ) was found in the protons of the methylene group. In addition to the phosphorochloridite, a small Δδ value is also typical for the dinaphtho derivatives (LV). The compounds also differ to a considerable degree with respect to their ^2J(PH) values—12–13 Hz for most of the (LIV) series and 14 to 16 Hz for (LV). Among the P(IV) derivatives of (LIV), ^5J(PH) coupling occurred in one case with X = NEt_2 and Y = S.[122] The spectra of individual conformers were obtained for the phosphorochloridite of (LIV) with R = t-butyl, R′ = Me[117] and the phosphorothioate with X = OEt and Y = S respectively.[122] The energy parameters of the conformational processes of these two compounds were determined: ΔG^0_{195} 0.1 kcal mol^{-1}; $\Delta G^{\neq}_{235}$ 10.85 ± 0.7 kcal mol^{-1} for the first and 0.74 and 12.2 kcal mol^{-1} for the second. In 2-hydro-2-oxo-1,3,2-dioxaphosphocines of (LIV) with R = t-butyl, cyclohexyl, R′ = Me when the temperature was reduced from −40 to −60 °C, there was a sharp increase in Δδ, which corresponds to a slowing down in the intramolecular exchange process with $\Delta G^{\neq}_{220}$ 10.4 ± 0.7 kcal mol^{-1} between the forms,[117] one of which is present in only a small proportion (~10%). In contrast to the dibenzo derivatives, in the (LV) series as the temperature was lowered a regular increase in the difference Δδ was detected, although the spin-spin coupling constant remained virtually constant. This indicates that forms having the same conformation of the cyclic fragment and differing in the orientation of the substituents on the phosphorus atom are taking part in an equilibrium.[120,121] In order to identify the conformers, a quantitative determination of the effect of magnetic anisotropy and electric field of the substituents on the magnitude of Δδ was carried out,[123–125] and also on the contribution from the hyperconjugation effect ΔJ^{π} to the constants ^2J(HH) and ^5J(PH) in the different conformations.[119–121] It was this treatment of the stereospecific nature of the constants in conjunction with dipole moments data that made it possible for the first time to establish spectroscopic criteria for the individual conformers: *e*-BC is characterised by ^2J(HH) of ~12.5 Hz, $^5J(P^{III}H^B)$ and $^5J(P^{IV}H^B)$ are of the order of 3.5–4.0 Hz, Δδ is 1 p.p.m. In the alternative *a*-BC conformation, ^5J(PH) is ~0–2 Hz and the signs for Δδ (H^AH^B) are reversed. Therefore, when there is an equilibrium *e*-BC ⇋ *a*-BC, Δδ is not large (0.2–0.5 p.p.m.), and ^5J(PH) has lower values (1–2 Hz). The *e*-B form has ^2J(HH) of ~14–16 Hz and $^5J(P^{III}H^B)$ of the same order as in the *e*-BC form, but it is less well displayed in P(IV) compounds, Δδ sometimes reaches 1.3 p.p.m.; in the *a*-B conformation ^5J(PH) also cannot be seen. In the equilibrium *e*-B ⇋ *a*-B, as equally in *e*-B ⇋ *e*-BC, Δδ is averaged out and has low values (as a result of the exchange between the *a*, *e*, and *e*′, *a*′ protons). It can be assumed that in the case of compound (LIV) with X = NEt_2, Y = S, R = t-Bu direct evidence has been obtained for the first time for spectroscopic properties of the *e*-BC

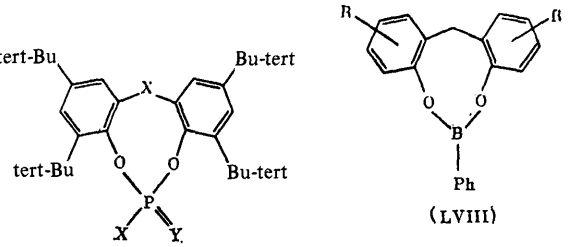
conformer. The compound is conformationally pure in solution, and according to the Raman spectra its steric structure is retained when going from the crystalline form into solution,[126] and its structure in the crystalline state (*e*-BC conformation) has been demonstrated by X-ray diffraction analysis.[79] Similar results have also been obtained for the phenyl phosphite of (LIV) with X = OPh, R = t-Bu, the main conformation of which in solution[119] corresponds to that found in the crystalline state (*e*-BC).[72] An equilibrium of the type *e*-BC ⇋ *a*-BC with a small content of *a*-conformer is also typical for the other dibenzo derivative phosphites with X = NPh_2, NEt_2, OEt, and O-naphthyl. In the phosphorochloridite the population of the second form reaches approximately an equal level (56:44%). In the dinaphtho derivatives of (LV) the BC and BB forms are unlikely to occur because of strong steric repulsions of the α-hydrogen atoms of the neighbouring naphthyl fragments. In the crystalline phase the 2-diethylaminophosphite (XXXVIII) and the diethylaminophosphorothioate (XXXIX) have the *e*-B form.[73,80] The small value of Δδ, ^2J(HH) of ~15.5 Hz, and ^5J(PH) of ~0 Hz must correspond to an equilibrium of the type *e*-B ⇋ *a*-B in the case of P(V) compounds, and similar results have been obtained experimentally. In P(III) compounds the population of the *e*-B conformer is greater with X = NR_2 and less with X = OPh than the *a*-B form.[120,121] If the results obtained for compounds (LIV) with X = H, Y = O[117] are considered in these terms as well as taking into account dipole moment data, a three component equilibrium *e*-B ⇋ *e*-BC ⇋ *a*-BC with population ratio 47:43:10 is acceptable. If the B form is consistent with a geminal constant of 15.6 Hz and the BC form with 12.5 Hz, with the population level of conformers occurring the constant must appear as 14 Hz in the spectra, which is in accord with experiment. The sudden changes in Δδ observed in the variable temperature spectra are due to freezing out of the *a*-BC conformer, which has a Δδ value that is opposite in sign relative to the *e*-B and *e*-BC conformers. The phosphorothioate of (LIV) with X = OEt, Y = S, R = t-butyl exists as an equilibrium mixture of two conformers with population ratio 86:14. In this case the spectral parameters of the minor conformer is consistent with the *a*-BC form (as in the conformationally pure diethylaminophosphorothioate): ^2J(HH) 12.2 Hz, ^5J(PH) 3.5 Hz, Δδ 0.78 p.p.m.; and the predominant conformer is the *a*-B form; 15.5 Hz, 0 Hz, and 1.33 p.p.m. respectively.[122]

An examination of the spin-spin coupling constants ^nJ(PC) was carried out for the 1,3,2-dioxaphosphocines (LIV) and (LV) considered here in order to establish ^{13}C NMR spectroscopic criteria of use in conformational studies.[121,127] The application of observations reported in the literature concerning the stereospecific nature of the $^2J(P^{III}OC_{sp^2})$ constant[128-130] to the four cyclic conformations led to the conclusion that in the BC form the constant (6.6−6.8 Hz) is greater than in the B conformation (1.5−2.2 Hz).[121,127] The vicinal constants $^3J(POC_{sp^2}C_{sp^2})$ are not large; zero values for (LV) and 2.9−4.4 Hz for (LIV) were obtained with P(III) and somewhat higher values with P(IV). They were correlated with the stereospecific dependences of the $^3J(POCC_{sp^3})$ constants.[131-133] In 1,3,2-dioxaphosphocines the dihedral angle in the POCC fragment is close to 0° in the BB conformation (6°). It is for this type of *cis* orientation that the maximum values for the constant can be expected (of the order of 10−15 Hz). In the *a*-BC conformation a constant close to zero should occur since the dihedral angle has a value of about 90° (80°). In the remaining conformations the order of magnitude of the spin-spin coupling constants is: ^3J(B) > ^3J(TB) > ^3J(*e*-BC). Since from a comparison of the correlations made with the experimentally found values the BB form can be excluded from consideration, it may be assumed that for the first time direct experimental evidence for the absence of the BB conformation has been obtained using ^{13}C NMR spectroscopy.[127] The dihedral angles in the $POCC_{(4)}$ and $POCC_{(2)}$ fragments are related by the equation $\theta(PC_{(4)}) = 180° - \theta(PC_{(2)})$; both angles θ are equal (~90°) in the case of the BC conformation, so the equal value of the two vicinal constants (3.7−4.4 Hz) can serve as a spectroscopic criterion for the BC form. The equality was also found experimentally in dibenzo-1,3,2-dioxaphosphocines (LIV) with P(III).[121,127] As regards the long-range spin-spin coupling constants ^4J(PC) and ^5J(PC), it is difficult at present to make definitive conclusions since the stereochemical relationships have not yet been determined for these constants. In the systems investigated the constant $^4J(PC_{(1)})$ is observed in those cases where ^5J(PH) also has a zero value. However, the reverse does not always occur; the $^5J(PC_{(6)})$ spin-spin coupling constant is as high as 1.5−2.2 Hz in compounds that have a BC conformation.

^{1}H and ^{13}C NMR spectroscopy have been extensively used to study the conformational behaviour of 1,3,2-dioxaphosphocines of the (LIV) series, containing benzene rings into which two t-butyl groups, R = R′ = t-Bu, have been introduced (into the *meta* position relative to the bridging group), and the bridge is an alkylmethylene group CHR (X = OR,[101,134,135] Cl,[119,136] Ph.[136] Bicyclic systems with a POXOP bridge have been reported,[101] and also the corresponding pentaoxyphosphoranes,[134,137] sulphides (LVI) [137-139] with P(III) and X = Cl, Ph, OMe,[139] with P(IV),[139] and with P(V).[137]



(LVI)

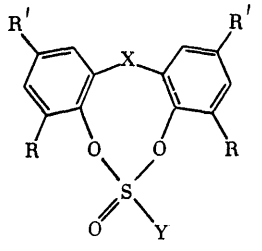


(LVIII)

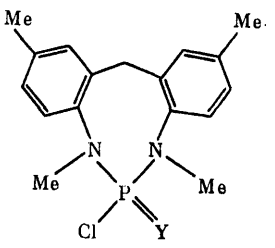
The ^{1}H NMR spectra of the P(III) phosphorus compounds are similar to those reported above for the (LIV) series, and from the existence of a long-range ^5J(PH) constant, the possible occurrence of the BB conformation was proposed.[101,136] In pentaoxyphosphoranes pseudorotation was detected with $\Delta G^{\neq}$ equal to 15.4−15.7 kcal mol^{-1} depending on the nature of the alkoxyl groups at P(V).[135-137] The eight membered ring occupies a diequatorial position in the trigonal bipyramid of the P(V) atom, and pentaoxyphosphoranes with a sulphide bridge have a BC structure.[137] When the temperature is lowered, the doublet of the methylene group (with chemical shift 3.75 p.p.m. and a ^5J(PH) coupling constant equal to 2.7 Hz) from one of the phosphoranes with X = CH_2CF_3 splits into two doublets with chemical shifts 3.52 and 4.11 p.p.m. and ^5J(PH) 1.9 and 2.8 Hz,[135] indicating the presence of a conformational equilibrium.

Recently studies on dibenzo-1,3,2-dioxasilocines (LVII)[139-141] and dibenzo-1,3,2-dioxaborocines[119] were begun. In the methyl derivative of (LVII) with an $SiMe_2$ fragment, the methyl groups are equivalent at room temperature but below 6 °C they become nonequivalent; $\Delta G^{\neq}$ for the process is 13.9 kcal mol^{-1}. The ^{13}C NMR spectra of this compound also change with temperature, and as regards the protons of the methylene group, above T_{coal} they appear as a singlet with δ = 4.12 p.p.m. while below it they appear as a doublet with δ = 3.61 and 4.50 p.p.m., $\Delta\delta$ = 0.89 p.p.m., ^2J(HH) = 14 Hz.[139] The authors came to no definite conclusions about the conformational behaviour (in their opinion there could be BC or BB forms having a plane of symmetry or an equilibrium between identical asymmetric conformations). The inversion barrier in 1,3,2-dioxaborocine (LVIII) is of the same order of magnitude (14.4 kcal mol^{-1}). Since the methylene group in this compound at room temperature appears as a doublet at 3.81 and 4.27 p.p.m. with a geminal constant of 13 Hz, it is suggested that the conformations of (LVII) and (LVIII) are similar.[118] It will be possible to reach definite conclusions about the steric structure of the compounds when detailed variable temperature measurements are carried out, taking into account the spectroscopic criteria (indicating the definite presence of the BC conformer) found in the case of 1,3,2-dioxaphosphocines.

There are also similar spectroscopic parameters for sulphites (LIX) with X = CH_2 and Y = UEP (δ 3.52 and 4.27 p.p.m., ^2J(HH) 12.6 Hz for one of them) existing as equilibrium mixtures given by *a*-BC ⇋ *e*-BC, and the *e*-BC form predominates when R = Cl, R′ = H and R = t-Bu, R′ = Me, the *a*-BC form predominates when R = R′ = H.[142] In accordance with the spectroscopic criteria found,[120] the dinaphthosulphite with δ 4.64 and 4.84 p.p.m. and ^2J(HH) 16 Hz was assigned the *e*-B form.[142] When the methylene group is replaced by a carbonyl (X = C=O) an equilibrium between the *a*-BC and [TB] forms occurs,[143] whereas the corresponding sulphate with Y = O is conformationally pure and has the BC conformation.[143] These conclusions were based on the IR and ^{13}C NMR spectra. The authors claim that the presence of seven lines in the latter is an indication that the molecule has a plane of symmetry.



(LIX)



(LX)

However, since, as was indicated above, such a situation is also possible with a rapid pseudorotation of the type T ⇋ T* or B ⇌ B*, it should once again be considered whether the same conformation that was found for the molecule of this sulphate in the crystalline state is retained in solution.[86]

As in the case of 1,3-dioxaphosphocines a reasonable amount of attention has also been given in the literature to diazaphosphocines (LX).[81,144] The phosphorochloridate with Y = O is conformationally heterogeneous; in the ^1H NMR spectra at low temperatures its methyl groups on the two N atoms are nonequivalent. This may be because the compound either retains the distorted boat conformation found in the crystalline state[71,81-83] or in solution a simultaneous inversion of the two nonplanar nitrogen atoms is occurring in it.

In concluding this Section it may be observed that the results obtained made it possible to establish clearly the effect, caused by the nature of the planar fragments, of exocyclic substituents and the electron configuration of three heteroatoms on the conformational behaviour of derivatives of 1,4-cyclooctadienes. The criteria developed in this case can be used to undertake the conformational analysis of other systems of a similar type. In dibenzo derivatives the most favourable conformation in the majority of cases in the BC form, although in some situations a distorted B form also occurs. Less varied in the conformational sense are dinaphtho derivatives; introduction of two bulky planar groups into them destabilises the BC conformation and the distorted B form becomes more typical. Therefore dinaphtho derivatives can be used as specific models for investigation of B conformers of this type.

VI. DERIVATIVES OF 1,5-CYCLOOCTADIENES

The stereochemistry of 1,5-cyclooctadiene (LXI) has been examined repeatedly in calculations with several force-fields.[67,70,145-148] The energy minimum here corresponds to the TB conformer with C_2 symmetry. The C conformation with C_{2h} symmetry is less favourable than it by 4.09 kcal mol^{-1} [148] or 1.45 kcal mol^{-1}.[145] The differences in ΔE are due in this case to the different values of the dihedral angle ω_3 (Table 5) obtained by calculations with different force fields and energy minimisation procedures. It is claimed that in such cases the Newton–Raphson method is more accurate in determining the minimum.[2,148] The angle ω_3 calculated for the TB form is 52.5°[148] or 37.9°,[145] and the first value is close to that found by electron diffraction for (LXI) with R = R′ = H[149] and by X-ray diffraction for its *syn*-3,7-dibromo derivative with R = H, R′ = Br (LXI)[157] and 4,8-dimethyl-3,7-dicarboxamide derivative with R = Me, R′ = $OCNH_2$ (LXI).[158]

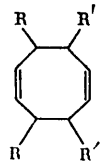


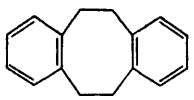
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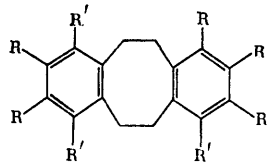
A similar structure was also determined for several organometallic complexes of (LXI),[152,153] dibenzodiazocines,[154-156] and dibenzosilocine.[157] In this conformation there is quite a substantial interaction between the chemically nonbonded H atoms on C(3) and C(7) (distance H...H is 1.992 Å). The energy of the C form is higher because of unfavourable torsional strain along the two types of single C–C bond in comparison with the TB conformer.

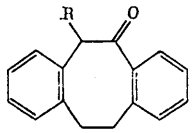
When the double bonds are replaced by benzene residues to give (LXII) (so-called 6,8,6-systems), according to the calculations the difference in energy between the TB and C forms decreases to 1.30 kcal mol^{-1} [145] and the boat form is less favourable by only 0.59 kcal mol^{-1}. This difference in conformational behaviour between compounds with double bonds and those with aromatic fragments is due to the difference in torsional interactions along the $C_{sp^2}-C_{sp^3}$ bonds. In diene systems H/H shielding occurs, with an energy estimated at 1.98 kcal mol^{-1}. Since in the dibenzo derivatives the H/C_{sp^2} shielding is less than 0.5 kcal mol^{-1} in energy,[145] in the latter a pseudorotation process readily occurs while in the

dienes inversion occurs. Introduction of methyl groups into the *o*-position of the benzene rings considerably destabilises the TB form, making the C and B conformers more favourable, and moreover, the transition barriers increase substantially.[154]


(LXI)


(LXII)


(LXIII)


(LXIV)

On turning to an examination of the conformational behaviour of these types of compounds in solution, we should note that when variable temperature ^1H and ^{13}C NMR spectra of (LXI) were recorded two processes with low barriers of 4.4 and 4.9 kcal mol^{-1} were detected.[146] On the basis of calculations of potential energy profiles Ermer asserts that the low-energy barrier corresponds here to the exchange TB ⇋ T ⇋ TB (calculated as 4.15 kcal mol^{-1} at 100 K), while two other processes occur, according to the calculations, via an intermediate boat or chair state with similar barriers of 5.73 and 5.91 kcal mol^{-1}. The experimentally determined barrier of 4.9 kcal mol^{-1} [146,148] apparently corresponds to a combination of these processes. *syn*-3,7-Dibromo-1,5-cyclooctadiene (LXI) with R = H, R′ = Br retains the TB form both in solution and the crystalline state.[150]

The first studies of dynamic ^1H NMR spectra of dibenzo derivatives showed that compound (LXII) was conformationally heterogeneous[159] and two processes for it were found with energies of 7.5 and 10.2 kcal mol^{-1}. At a normal temperature a mixture of TB and C conformations is observed in this case with a predominance of the former.[159] The effect of *o*- and *m*-methyl groups[158,160,161] and of tetra- and hexa-methyl substitution[159] on these processes was also studied. For all of them the equilibrium TB ⇋ C was characteristic, and in the *o,o,o′,o′*-tetramethyl derivative (LXIII) with R = H, R′ = Me the population ratio was 88 : 12 and the interconversion barrier proved to be higher (12.1 kcal mol^{-1}) than in the unsubstituted compound. Thus, the presence of *o*-substituents in this case leads to an increase in energy of the transition state. If four methyl groups are introduced into the *m*-position [(LXIII) with R = Me, R′ = H, the inversion barrier is virtually unchanged (10.5 kcal mol^{-1}), while in the conformational equilibrium of the two forms the chair type predominates (40 : 60).[162] Different dibenzo-3-octanols with methyl groups in the 4-, 7-, and 8-positions also, according to the ^1H NMR spectroscopy data, prefer the TB conformation with an *a*-orientation of the hydroxyl group. Compounds that contain one methyl group each at C(4) or C(8) are conformationally heterogeneous and exist as the equilibrium mixture *a*-TB ⇋ *e*-TB (the difference in energy between these conformers is not large—0.33 and 0.44 kcal mol^{-1}.[163]). Similar behaviour is shown by dibenzocyclooctenes containing fragments such as Br and AcO.[163,164] As was indicated above, introduction of a carbonyl group into an eight-membered ring has little effect on its conformational behaviour, which is also confirmed in the case of ketone (LXIV); when R = H the equilibrium TB ⇋ C, which is usual for dibenzo derivatives, occurs, whereas when H is replaced by Me the equilibrium is displaced towards mirror-image TB conformers.[164]

Dynamic spectroscopy has been widely used to study heterocyclic analogues of the type (LXV)–(LXVII), for which the experimental results on inversion barriers have been correlated with those calculations on the transition state energies. Azocines (LXV) with X =

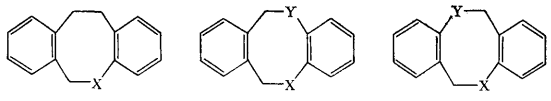
Table 5. The conformations of derivatives of 1,5-cyclooctadienes, cycloocta-trienes and -tetraenes.

Compounds	R	R	Torsion angles, deg.*								ΔE, kcal mol^{-1}	Notation**	Refs.
			1	2	3	4	5	6	7	8			
(LXI)	H	H	—	−89.8	52.5	21.8	5.3	—	—	—	—	T (C_2)	[148]
			0	6.7	−62.6	89.0	0	—	—	—	—	C (C_{2h})	[148]
			0	72.2	−100.0	72.6	0	—	—	—	—	B (C_{2v})	[148]
(LXI)	Br	H	—	−82	65	11	−1	—	—	—	—	TB (C_2)	[150]
(LX)	$OCNH_2$	Me	—	−74.9	76.0	−1.9	−3.4	—	—	—	—	TB	[151]
(LXI)	H	H	—	−86.5	63.3	8.1	6.2	—	—	—	—	TB	[149]
(LXXI)	—	—	−4	−54	−4	51	1	−12	−63	97	0	TB (C_1)	[31]
	—	—	0	64	7	−68	0	68	7	−64	4.8	B (C_s)	[31]
	—	—	−2	−12	−1	66	−114	—	—	—	6.6	HC (C_2)	[31]
(LXXV)	—	—	0	−44	87	−8	−58	—	—	—	0	TBC (C_2)	[31]
	—	—	0	84	−57	0	0	—	—	—	1.8	HC	[31]
	—	—	7	22	16	−7	−36	−4	89	−88	4.1	TS	[31]
(LXXVI)	—	—	−3.1	−63.0	−1.8	69.2	—	—	—	71.3	—	B	[174]
(LXXVI) — octamethyl	—	—	4.2	−66.3	−5.4	−61.8	5.4	—	—	78.8	—	B	[62]

* Numbering of the angles corresponds to that given in Table 1.

** TS is transition state; symmetry of the conformers is given in brackets.

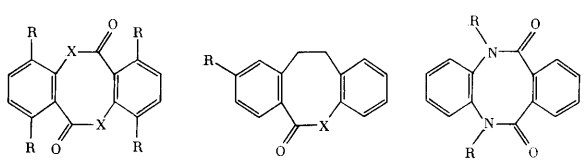
NAc, NBz, NSO_2, Ar, NCH_2Ph, and NH are characterised by an equilibrium of the C and B forms with transition barrier between them of 10.6–11.1 kcal mol^{-1} (calculated 13.2 kcal mol^{-1}); the barriers for the transitions B ⇋ B* or B ⇋ TB are much higher (14.3–20.1 kcal mol^{-1}).[160]



(LXV) (LXVI) (LXVII)

Diazocines (LXVI) and (LXVII) are also conformationally heterogeneous, but the difference in energy between the alternative C and B forms is low—less than 0.28 kcal mol^{-1} with the exception of diazocine (LXVI) for which the inversion barriers are 12.9 to 14.1 kcal mol^{-1}.[160,165] 3,8-Thiazocine (LXVI) with X = S and Y = NAc also exhibits a temperature dependence in its ^1H NMR spectra, which is due to its conformational heterogeneity. The transition barrier between its forms is substantially higher than in diazocines and amounts to 18.6 kcal mol^{-1}.[165] In contrast to diazocines, in dithiocines (LXVI) and (LXVII) with X = Y = S the conformational equilibrium C ⇋ B is displaced up to 80% towards the B conformer. In the corresponding disulphones (X = Y = SO_2) only one conformer is detected at low temperatures. The barriers for the inversion B → C in compounds (LXVI) (9.0 and 11.9 kcal mol^{-1}) for the sulphide and sulphone are substantially lower than in the corresponding (LXVII) compounds (12.4 and 18.6 kcal mol^{-1}).

When coming to consider the conformations of keto derivatives (LXVIII)–(LXX), we should remember that since the carbonyl group situated in the vicinity of the heteroatom forms a planar fragment, diketone (V) in a conformational sense behaves in a similar manner to 1,5-cyclooctadienes. In this respect diketones (LXVIII) and (LXX) can also be regarded as derivatives of cyclooctatetraene (see next Section). In fact, the conformational properties of diketones (LXVIII) with X = NH, NCH_2Ph,[166] O,[167] S[168] are controlled by a reversible equilibrium inversion of the ring between the B ⇋ B forms. The activation energy of these conformational transitions is high—in diazocines it is 27 kcal mol^{-1},[166] while in dioxocines and dithiocines it is reduced to 17.7–18.4 kcal mol^{-1} [167] and amounts to 24.6 kcal mol^{-1} when R = Me.[168] It has been confirmed by X-ray diffraction analysis of dithiosalicide (LXVIII) with R = H, X = S that the preferred conformation in this case is the boat form with a pseudoplane of symmetry passing through the centre of the S–C(O) bonds.[169]



(LXVIII) (LXIX) (LXX)

The barrier in the lactam (LXIX) with R = H, X = NCH_2Ph is also lower (21.4 kcal mol^{-1} [170] (the symmetrically substituted dilactam (LXX) is conformationally pure.[166]) There are indications that the dipole moment of lactone (LXIX) with R = Br (4.09 D) is consistent with the B conformation.

Thus, it may be seen that the conformational behaviour of derivatives of 1,5-cyclooctadienes has as yet been studied insufficiently and to a considerably lesser degree than for 1,4-cyclooctadienes.

Nevertheless, the results obtained indicate that the remote relative configuration of the two planar fragments helps to stabilise flexible (TB or B) rather than chair-like forms. Introduction of heteroatoms or keto groups into the ring produces an increase in the degree of preference for the B conformer relative to TB, which is due to their occurring in a state analogous to cyclooctatetraene systems.

VII. DERIVATIVES OF CYCLOOCTA-TRIENES AND -TETRAENES

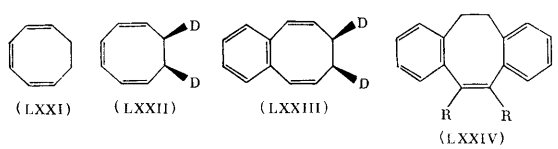
1. 1,3,5- and 1,3,6-Cyclooctatrienes

Since in 1,3,5-cyclooctatriene (LXXI) the alternation of double bonds and single bonds is conducive to conjugation, the theoretical examination of compounds of this type is based on a model of conjugated bonds, assuming a small rotation about the single C_{sp^2}–C_{sp^2} bonds.[31,171,172] It was shown that the most stable form is TB conformer in which the dihedral angle along the CH_2–CH_2 bond is equal to 63°, in contrast to the B form where it has a value of zero. The torsion angles of the three conformers, including the half-chair (HC), are listed in Table 5. The difference in energy between the TB and B forms is due to conjugation effects and torsional interactions. The results of calculations are consistent with dynamic ^1H and ^{13}C NMR spectroscopy data for (LXXI); it was found that the difference in energy between the TB conformer and the B and HC forms is 4.3 and 6.2–6.7 kcal mol^{-1}, and ring inversion occurs with a barrier of 6.6 kcal mol^{-1}.[171]



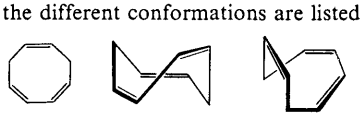
TB B HC

The introduction of benzene rings in place of double bonds increases the barriers. Thus, on going from (LXXII) to (LXXIII) it increases from 6.7 to 9.2 kcal mol^{-1},[173] and the presence of a second benzene ring contributes to a twofold increase to 18.7 kcal mol^{-1} in the dibenzo derivative, this trend being maintained in the tribenzo analogues.[173] The effect of alkyl substituents on the multiple bond in dibenzo derivatives (LXXIV) on the magnitude of the barrier was studied; in the monomethyl derivative it is higher than in the unsubstituted compound with R = R′ = H and lower than in the disubstituted compound with R = R′ = Me.[158]



(LXXI) (LXXII) (LXXIII) (LXXIV)

For 1,3,6-cyclooctatriene (LXXV) calculations have identified two energy minima, which correspond to the TBC and HC conformers with C_2 and C_s symmetry. The energy difference between them is 1.8 kcal mol^{-1} and the transition barrier 4.10 kcal mol^{-1}.[31,171] The torsion angles in the different conformations are listed in Table 5.



(LXXV) TBC HC

2. Cyclooctatetraenes

Although in 1,3,5,7-cyclooctatetraenes (LXXVI) the alternation of double and single bonds is conducive to conjugation, in a planar system strong angular and torsional interactions occur—and for that reason the B form occurs in this case as a compromise. This has been demonstrated by electron-diffraction data[174] and the results of calculations[1] for (LXXVI) and by X-ray diffraction analysis for its octamethyl derivative.[62] The torsion angles about the cyclic bonds of the B form are given in Table 5. According to the X-ray diffraction studies, introduction of substituents into the ring changes the degree of flattening in the B conformation. It is determined by the magnitude of the so-called external dihedral angles (α). Carboxy-substituted cyclooctatetraene,[175] the 1,4-dinitro derivative,[176] and the 1,3,5,7-tetramethyl derivative[177] have dihedral angles in the range 39–45°.



The proximity of the two pairs of substituents at the 1,4,5,8-positions of the ring (R = $CH_2OC_6H_4Me$-*p*) [178] causes the angle to increase to 48°. The degree of flattening of the octasubstituted compounds is determined by the steric requirements of the substituents. For fluorine atoms which are small in volume the angles are not large (α is 41.0° and 41.7°),[179] on substitution with methyl groups it increases by 8.7–11.0°,[62] and a further increase in substituent volume (phenyl groups) causes the angles to increase to 58.0° and 53.3°.[180,181] In paracyclophane systems no distinctive changes have been found,[182,184] and the conformational state of tetra-annulated systems is determined by the nature of the annulated ring. The tetracyclopentane derivative has the B form (α is 41.4° and 42.3°)[184] and the tetracyclobutane derivative has a planar structure (0.5° and 2.1°).[185]

As regards dynamics, according to the NMR spectroscopic data cyclooctatetraene and its derivatives are characterised by two processes—ring inversion and bond displacement.[186–188] The first of these processes occurs via a planar transition state of D_{4h} symmetry with localised double bonds, and the inversion barrier amounts to about 10 kcal mol^{-1},[189] while for the second process it is higher by 4 kcal mol^{-1}. It is open to question whether a planar structure of D_{8h} symmetry with equivalent C–C bonds[190,191] should also be considered, and in this connection a detailed examination of factors such as resonance destabilisation (antiaromaticity),[192] angle strain, van der Waals repulsion,[193] and related interactions[190] is required. The introduction of alkyl or aryl groups adds a chirality element, with the result that the possibility arises for isolating optically active isomers.[194–198] From the difference between the ^1H NMR spectra of the isomers it is possible to determine the degree of flattening in the ring. Thus, for derivatives with a 1,2-annulated four-six membered ring system it was shown that flattening of the cyclooctatetraene ring increases as the size of the annulated ring decreases.[199]

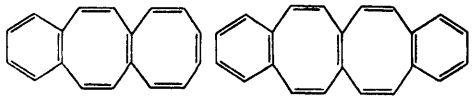
The boat conformation is preserved in mono- and di-benzooctalenes (LXXVII) and (LXXVIII).[200,201] Such systems are of interest for studying the inversion barriers between the B and B* conformers using dynamic NMR spectroscopy. In dibenzooctalenes it is quite high (12.3 kcal mol^{-1} for (LXXVIII) with R = CH_2F [202]) and shows little dependence on the nature of R, while in dioctalenes the barrier is even higher (15.3 kcal mol^{-1} [201]). The conformational behaviour of di-, tri- and tetra-benzooctalenes is similar to that of the biphenyl derivative.[199]

The conformational situation can change, as indicated above, when heteroatoms are introduced. In fact, dibenzodiazocine (LXXX) has a distorted B form, the torsion angles of which are also listed in Table 5.

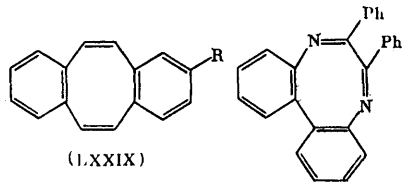
Table 6. The conformations of cyclotetraphosphazenes.

Compounds	Torsion angles, deg.								Conformations	Refs.
	1	2	3	4	5	6	7	8		
$N_4P_4Cl_4(NMe_2)_4$	38.4	49 8	29.3	67 3	31 6	25.8	67.2	46.8	BB	[207]
$N_4P_4(OMe)_8$	34	45	42	55	30	43	40	52	BB	[208]
cis-$N_4P_4F_4(NMe_2)_4$	33.5	43.8	34 7	48.7	31.6	53.3	18.8	36 6	B	[210]
$N_4P_4Ph_4(NMe_2)_4$	95	—53	—21	73	—95	53	21	—73	CC	[211]
trans-$N_4P_4Ph_4Cl_4$	75	—41	—24	62	—75	41	24	—62	CC	[212]
$N_4P_4Cl_2(NMe_2)_6$	76	—44	—19	61	—76	44	19	—61	CC	[213]
$N_4P_4Cl_6(NMe_2)_2$	77	—41	—26	65	—77	41	26	—65	CC	[214]
$N_4P_4Cl_8$	76	—45	—20	59	—76	45	20	—59	CC	[215]
trans-$N_4P_4F_4(NMe_2)_4$	66	—50	—5	40	—66	50	5	—40	CC	[216]
cis-$N_4P_4Cl_4Ph_4$	69	—43	38	—56	53	—34	40	67	CC	[217]
$N_4P_4F_7(C_5NH_6)$	14.4	—13.0	—6	5,7	3.3	4 3	—21.7	12.4	*	[218]

* Structure is almost planar.



(LXXVII) (LXXVIII)

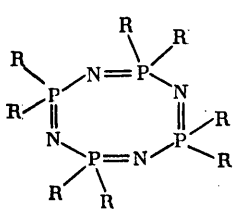


(LXXIX) (LXXX)

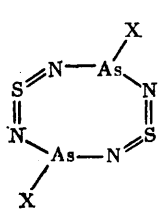
3. Inorganic 8-Membered Heterocycles with Planar Fragments

Extensive opportunities for studying the effect of geometric parameters and intramolecular electronic interactions on conformations are provided by the data on cyclotetraphosphazenes (LXXXI), where by varying the substituents on the phosphorus atom it is possible to obtain a wide variety of compounds, including geometric isomers. X-Ray diffraction studies indicate that the endocyclic PNP and NPN angles are determined to a considerable degree by the nature of the exocyclic substituents on phosphorus and can vary over a very wide range. For F-substituted compounds an almost planar structure of the P_4N_4 ring is characteristic.[204] Some of the compounds studied have a distorted saddle-shaped conformation (BB according to the terminology used in this review); these are $N_4P_4Cl_4Ph_4$,[205] $N_4P_4Cl_2(NMe_2)_6$,[206] $N_4P_4Cl_4(NMe_2)_4$,[207] $N_4P_4.(OMe)_8$.[208,209] A structure similar to the B form was found in $N_4P_4F_4(NMe_2)_4$.[210] A large proportion of the cyclotetraphosphazenes have a CC conformation in which four P atoms are situated in one plane.[211-217] In one case the CC form is stabilised with four coplanar N atoms—this is in the *cis*-isomer of $N_4P_4Cl_4Ph_4$.[217] An increase in the number of F atoms to seven helps to flatten out the ring. In the last of the examples on cyclotetraphosphazene given in Table 6 a nearly planar conformation is present, which is seen very clearly from the values of the dihedral angles.[218]

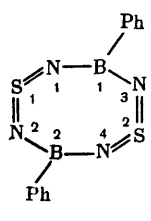
X-Ray diffraction data have been obtained for compounds that contain two adjacent diplanar fragments. The first of them (LXXXII), as for cyclotetraphosphazene, has a BB conformation in which the As atoms occupy the flagpole position and the t-butyl groups are in equatorial positions.[219] In diborocine (LXXXIII)[220] the boron atom is tending to retain a coplanar configuration for three bonds, so the conformation of the compound changes, being characterised by a bend along the line $N_1...S_2$ and by the presence of two planar groups $N_1B_1N_3S_2$ and $S_2N_4B_2N_2S_1N_1$ (the angle between these two planes is 126°).



(LXXXI)

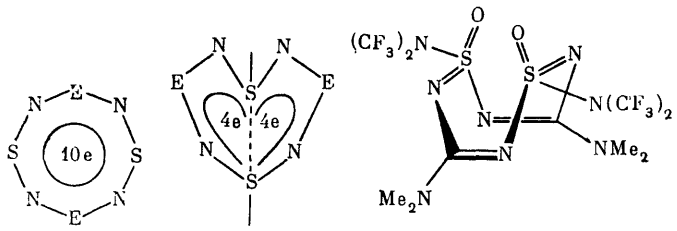


(LXXXII)



(LXXXIII)

Compounds of the type E(NSN)E with 10 π-electrons (obeying the $4n + 2$ aromaticity rule) can exist, depending on the nature of E, either in a planar form (LXXIV) with E = CPh,[221] S as in $S_4N_4^{2+}$,[222-224] $S_4N_4Cl_2$,[225] $[S_4N_4Cl]^+.X^-$ [X = $FeCl_4$,[226] $ZrCl_{10}$[227]] or in a butterfly conformation (LXXXV) with E = PMe_2,[228] $CNMe_2$ [221] and with a transannular interaction between the two sulphur atoms. At the same time in adducts of type $S_4N_4.AsF_5$ a BB (saddle) form occurs with the four sulphur atoms in one plane.[229] A deformation of the BB form to the B conformation is also possible, as is shown in the case of the dioxide (LXXXVI).[230]



(LXXXIV) (LXXXV) (LXXXVI)

- - - o 0 o - - -

It is possible to draw the following conclusions from what has been stated above. Eight-membered rings with planar fragments are conformationally mobile systems whose behaviour is closely related to the nature of the heteroatoms and the planar fragments and their relative configuration. The main and most clearly expressed trend is the tendency to adopt a chair-type conformation that corresponds the closest possible to the most stable BC form of cyclooctane. This is opposed by purely geometric limitations—the preservation of a planar configuration of the cyclic atoms that form a planar fragment and the two atoms adjacent to them. As a result, the TBC or C form occurs instead of the BC form. However, the introduction into the ring of heteroatoms capable of producing large angular deformations can contribute to inclusion in the ring also occurring in the BC form. An indication of this is the case of 1,2-cyclooctadiene and 1,5,2,4,3-dioxadiphosphazocine corresponding to it—they exist in the TC and BC forms respectively. Since the occurrence of the BC form is extremely difficult in compounds with four planar fragments, the majority of cyclotetraphosphazenes have a CC structure. 1,3-Cyclooctadienes and cyclooctatetraenes have a TBC conformation while 1,5-cyclooctadienes have the C form. The introduction of heteroatoms into the ring can lead to a greater stabilisation of the B conformer relative to the TB form. In all of the examples with diplanar fragments examined it is the B conformation that occurs in a particular proportion. In addition to heteroatoms, the nature and relative configuration of planar fragments also have a substantial effect on conformational behaviour. Changes can be seen clearly on going from rings with double bonds to benzo and naphtho derivatives; the main consequence of this transition is related to the increase in inversion barrier. It will therefore be of particular interest in the future to study heterocycles containing multiple bonds.

It can be seen from the material presented that not all types of compounds have been studied sufficiently. This must mainly concern the initial stage of the studies, when it is still premature to make far-reaching general conclusions. The most complete and interesting results have been obtained for dibenzo and dinaphtho derivatives of 1,4-cyclooctadienes, but many of them still require further tests and checks. It is still necessary to apply much effort in

order to determine all the electronic factors that govern the preference for one or other structures. Matters are much more complex than they appeared to be previously concerning compounds that contain four planar fragments and whose heterocyclic representatives all the time reveal new cases of conformational diversity. While for cyclooctatetraene it would be possible to talk about a single preferred form, namely, the boat form, in heterocyclic derivatives other structures are found that are typical, it would appear, only for saturated systems—structures such as the CC and BB forms. As can be seen, eight-membered rings with planar fragments are promising models for the development of conformational analysis as a whole. The correct analysis of compounds that are so complex in terms of conformation is possible on the basis of quantitative criteria for representing the conformations. The development of principles of conformational analysis for the class of compounds considered here will be a stage in proceeding towards saturated eight-membered rings and large-sized rings that are more complex in terms of conformation.

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