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THE STRAINED DOUBLE BOND

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CONTENTS

I.	Introduction	88
II.	Types of strain in the double bond	88
	1. Deformation in the plane of the double bond	88
	2. Deformation of the double bond with displacement of the substituents from a single plane	89
III.	Estimate of the strain in the double bond	89
IV.	Physical properties of the strained double bond	91
	1. Nuclear magnetic resonance spectra	91
	2. Infrared spectra	92
	3. Ultraviolet spectra and other properties	93
V.	Chemical properties of strained olefins	94
	1. Addition reactions	94
	2. Complex formation	96
	3. Substitution reactions at the double bond	97

I. INTRODUCTION

The problem of the dependence of the properties of compounds on the deformation of the angle between the bonds is being studied at present very intensively, both theoretically and experimentally; strained compounds such as bicyclobutane[1], diphenyltetrahedrane[2], cubane[3], and others have been synthesised successfully. Compounds with altered valence angles are characterised by an increased content of internal energy, which changes their physical and chemical properties. Thus the far-reaching analogy in the properties of cyclopropane and olefin derivatives is generally known.

The term "strain", introduced by Bayer[4] in 1885, does not explain the significance of the above processes, which are probably of widely different types. Usually it is understood to imply deformation of the valence angles and the associated deformation of the molecules. Since the angles between the orbitals† of the carbon atoms in various hybrid states are different, there is a possibility of representing certain changes in valence angles as a result of rehybridisation. An idea of this kind was applied for the first time in 1949 by Walsh[5] and also by Coulson and Moffitt[6] to account for the structure of cyclopropane. Nowadays this view has been widely adopted.

The strained double bond is of particular interest. All the substituents at a double bond are in the same plane as the olefinic carbon atoms; the normal C=C–X angle is assumed to be 120° (the angle between the orbitals of the sp^2 hybridised carbon atom[7]). Deviation from this geometry requires an expenditure of energy and the internal energy of molecules containing such a fragment is higher. In real compounds the C=C–X angle almost always differs from 120°, if only because of the breakdown of ideality due to different bond lengths[8] (in ethylene 117° 30'), but the deviation of both valence angles at the double bond by 5° causes an energy increase of only 1 kcal mole^{-1}. Since the concept of strain is largely qualitative, we shall regard a double bond as "strained" when the deviation from the "ideal" geometry is so great that it begins to have an effect on the physical and chemical properties of the compounds containing the given fragment.

A considerable number of original studies dealing with the strained double bond have appeared recently in the literature. However, this problem has not been examined as a whole, and the aim of the present review is to fill this gap.

II. TYPES OF STRAIN IN THE DOUBLE BOND

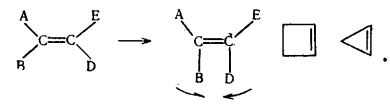
From the formal point of view, the decrease of the valence angle between two bonds of a tetragonal atom can cause the atom to become "olefin-like"; according to Bayer's theory, the double bond may be regarded as a two-membered ring (this description of the double bond is still used, but to a lesser extent than the σ,π-method[8-10]).

In contrast to the tetrahedral atom, strain in the double bond can occur in different ways, which are non-equivalent as regards the induced rehybridisation of the olefinic carbon atom; these will therefore be considered separately.

If the double bond has four substituents A, B, D, and E, then all types of strain in the double bond can be divided into two groups: those occurring in the ABDE plane and those involving the displacement of any one substituent from this plane.

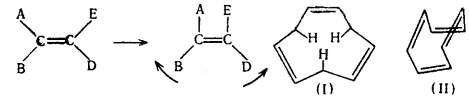
1. Deformation in the Plane of the Double Bond

The deformation of the valence angles in the plane of the double bond (ABDE) can in turn occur in several ways. One of the possibilities is the decrease of the valence angle as a result of the mutual approach of the groups B and D in the *cis*-position ("cisoid compressive strain"):



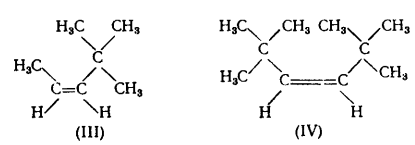
Such strain occurs, for example, in cyclo-olefins with small rings — in cyclobutene or cyclopropene. These examples show that the deformation of the valence angles (considered from a formal standpoint) can become very high. Thus the deviation of the C=C–C valence angle from the normal value in cyclobutene[11] is 26° 06' and in cyclopropene[12] 55° 24'. From the point of view of structural theory, cisoid compressive strain should result in more "acetylenic" character of the double bond; this was apparently foreseen by Bayer[4]. Nowadays it is assumed that such strain should lead to rehybridisation of the olefinic atoms with increase of the *s*-character of the exocyclic bonds (C–H bonds of unsubstituted monocyclic olefins) and the *p*-character of the endocyclic C–C bonds. It is interesting that also from the point of view of Walsh's model of cyclopropene[5] there should be a definite analogy in the properties of acetylene and cyclopropene. Attention will be drawn to this analogy in the properties of strained olefins with cisoid compressive strain and acetylenes in further discussion below.

Another type of strain is the increase in valence angles as a result of the repulsion of the groups B and D in *cis*-position ("cisoid repulsion strain"):



(I) (II)

It would appear that this type of strain should occur in macrocyclic olefins. However, the latter are non-planar and the valence angles are very close to the normal value. Nevertheless in cyclohexene[13,14] the C=C–C angle is already 122°, i.e. slightly higher than the normal value. The increase of the valence angle and hence the strain in the double bond is influenced by the transannular repulsion of hydrogen atoms in cyclic olefins. For example, the C=C–C angle in *cis,cis,cis*-cyclononatriene (I)[15-17] is 124°, due to the repulsion of the mutually non-bonded hydrogen atoms. Cisoid repulsion strain occurs also in cyclo-octatetraene (II), where the C=C–C angle is 126° 46'.[18] The cisoid increase of valence angles can also take place in non-cyclic compounds. An example of this kind is *cis*-t-butylmethylethylene (III)[19] and *cis*-di-t-butylethylene (IV)[19,20]:



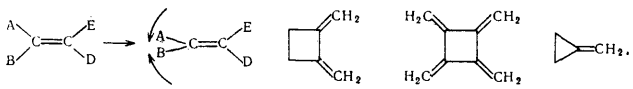
(III) (IV)

† This terminology is used in accordance with the recommendation of the Second Conference on Quantum Chemistry (Vilna, 1962).

Although there are no literature data for the valence angles in compounds (III) and (IV), measurements of the heats of hydrogenation (see below) undoubtedly indicate a considerable strain of the double bond in compound (III) and particularly (IV).

In the case of cisoid repulsion strain rehybridisation with increase of the *s*-character of the endocyclic bonds and the *p*-character of the exocyclic bonds [in compounds (I)–(IV) these are C–H bonds] should also occur and therefore the changes in bond character should be the opposite of those observed for cisoid compressive strain.

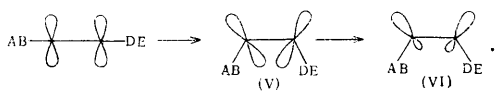
Further, there is a possibility of "unilateral compressive strain" of the double bond in the ABDE plane as a result of the mutual approach of groups A and B:



This type of strain occurs, for example, in dimethylenecyclobutane[21], tetramethylenecyclobutane[22], and methylenecyclopropane[23] molecules. Evidently repulsion strain of this type can also exist in the presence of two bulky groups at one of the carbon atoms of the double bond.

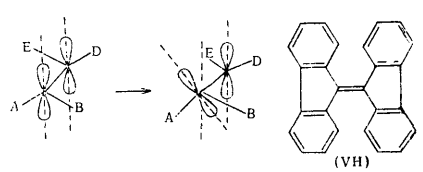
2. Deformation of the Double Bond with Displacement of the Substituents from a Single Plane

The strain of the double bond involving the displacement of the substituents from the ABDE plane can also occur in several ways. Strain in the double bond with displacement of all four substituents below the plane of the double bond ("out-of-plane strain") is possible:



The transition (V) → (VI) should then occur[24]. This is due to the tendency of the olefinic carbon atom to undergo a transition from the sp^2-hybridised state to the sp^3-hybridised state in the presence of such deformation of valence angle. However, examples of compounds of this type are evidently so far unknown. It is also noteworthy that this type of strain in the double bond is to some extent analogous to that in compounds of the type of dehydrobenzene[25].

Another type of strain in the double bond involving the displacement of the substituents from the plane of the double bond is "torsional strain":

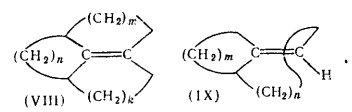


Rotation about the double bond entails a decrease of the degree of overlap of *p*-electrons, which is approximately proportional to the square of the cosine of the angle of rotation[7,26]. Dibiphenylene-ethylene‡ (VII) can serve as an example of a compound with torsional strain; in this case the rotation is due to the repulsion of the mutually non-bonded hydrogen atoms in the *peri*-positions. According to Rummens[27], torsional strain cannot be compensated by rehybridisation.

It is noteworthy that torsional strain causes a much greater increase in the energy of the ground state than in the energy of the excited state. This can be illustrated by the results of the calculation of Coulson and Jacobs[28] which show that the order of the double bond in stilbene in the ground state is 1.820 and in the first excited state only 1.436; therefore the difference between the energies of these states should decrease with increase in torsional strain. For the ground N-state of ethylene, rotation by 90° requires the expenditure of 61 kcal mole^{-1}.[29,30]

Thus strain in the double bond can occur in different ways and sometimes it is difficult to decide to which type of strain a particular case should be assigned. In this respect, *trans*-cyclo-octene is interesting. In early studies it was assumed that the double bond fragment in this compound is planar and that the strain in the molecule is due to the deviation of the valence angles from the normal value[31]. However, in subsequent studies involving the investigation of the dipole moment and the infrared spectrum[24] of *trans*-cyclo-octene and also its separation into optical isomers[32,33] it was assumed that torsional strain occurs in this compound and the angle of rotation was estimated[34] as 17° ± 5°.

In addition, in complex polycyclic systems there is a possibility of cases involving the combination of certain types of strain of the double bond, as, for example, in the hypothetical structures (VIII) and (IX):



III. ESTIMATE OF THE STRAIN IN THE DOUBLE BOND

In many calculations of the conformations of cyclic compounds[35–40] and solvolytic reactivity[39,40] it has been shown that the deformation of the angle between the bonds is not localised but extends to other bonds, so that the energy of the system as a whole is a minimum. Therefore, there is no doubt that the deformation of the angle at the double bond entails a certain deformation of the remaining angles. However, as an approximation the overall strain may be regarded as the sum of the different types of strain [angular strain, bond extension, torsional (Pitzer) strain, interaction between mutually non-bonded atoms[41]] and therefore in favourable cases one may speak of the intrinsic strain of the double bond.

The strain can be estimated experimentally from thermochemical data[42]. Thus comparison of the negative heats of hydrogenation of cyclohexene (27.1 kcal mole^{-1})[43] with those of *cis*- and *trans*-but-2-enes (28.5 and 27.5 kcal × × mole^{-1} respectively)[44] shows that the double bond in cyclohexene is unstrained. The heats of hydrogenation of cyclo-olefins are presented in Table 1. In comparing these data, account must be taken of the fact that they may have been obtained under different conditions; however, the error does not exceed 1 kcal mole^{-1}.[42,45]

The negative heat of hydrogenation of compounds with cisoid compressive strain increases with decrease in ring size and is a maximum in cyclopropene[46] (53.9 kcal mole^{-1}).

‡ Better termed 9,9′-bi(fluorenylidene) (Ed. of Translation)].

TABLE 1. Estimate of the double bond strain in certain cyclo-olefins.

Ring size	Excess strain of cycloalkane (Ref. 57) E_{strain}, kcal mole^{-1}	ΔH_{hydr}, kcal × × mole^{-1}	Excess strain of cycloolefin E_{strain}, kcal mole^{-1}	C=C–C angle in cyclo-olefin	Double bond strain [$(E_{strain}$(double bond)], kcal mole^{-1}	
					calc. from angle by Eqn. (1)	calc. from thermochemical data
C_3	27.6	53.9 [46]	54.3	64°36′ [12]	107.4	45.1
C_4	26.2	—	—	93°54′ [11]	23.8	—
C_5	6.1 *	26.9 [58]	5.9	111°30′ [60]	2.5	2.3
C_6	0	27.1 [13]	0	122°30′ [14]	0.2	0
C_7	6.4	25.9 [48]	5.2	—	—	0.7
C_8 *cis*	9.9	23.0 [59]	5.8	—	—	—
C_8 *trans*		32.2 [59]	15.0	—	—	9.2
C_9 *cis*	12.9	23.6 [59]	9.4	—	—	—
C_9 *trans*		26.5 [59]	12 3	—	—	2.9
C_{10} *cis*	12	20.7 [59]	6.6	—	—	—
C_{10} *trans*		24.0 [59]	8.9	—	—	3.3
Norbornane XIV	13	33.1 [45]	19	109° [55]	4.2	>6

* Calculated from ΔH°_{form},[44] taking E_{C-H} = 98.7 kcal mole^{-1} and E_{C-C} = 82.6 kcal mole^{-1}.[45]

The double bond in bicyclic bridged systems is also strained. Table 1 shows that the negative heat of hydrogenation of norbornene (X) is very considerable. Similarly $-\Delta H_{hydr}$ for bicyclo[2,2,2]octene[43] (XI) is 28.25 kcal mole^{-1}, that for the first double bond in norbornadiene[43] (XII) is 35 kcal mole^{-1} and that for the first double bond of barrelene[47] (XIII) is as much as 37.6 kcal mole^{-1}.



(X) (XI) (XII) (XIII) (XIV)

Compounds with cisoid repulsion strain can also be considerably strained. Thus the negative heat of hydrogenation of *cis*-t-butylmethylethylene (III) is 30.8 kcal mole^{-1} and that of *cis*-di-t-butylethylene[19] (IV) is 36.2 kcal mole^{-1}. The negative heats of hydrogenation of the *trans*-isomers of these olefins are 26.5 and 26.87 kcal mole^{-1} respectively, i.e. close to the value for the unstrained double bond.

However, direct comparison of the heats of hydrogenation cannot always be used to estimate the strain of the double bond. In fact, the heat of hydrogenation characterises the difference between the heat contents of the olefin and the corresponding paraffin, i.e. the difference between their heats of formation. Therefore, the heat of hydrogenation depends not only on the strain of the double bond but also on the strain in the saturated hydrocarbon which obtains on hydrogenation: the greater the strain of the paraffin, the higher is its heat of formation and the lower the negative heat of hydrogenation. This is clearly seen in the heats of hydrogenation of cyclo-octene, cyclononene, and cyclodecene (Table 1). The decrease of the negative heat of hydrogenation is in this case due to the strain in the corresponding cycloparaffins[31]. Similarly the negative heat of hydrogenation of cyclopentene is lower than that of cyclohexene, despite the fact that the deformation of the double bond is higher in cyclopentene; the explanation is that the strain in cyclopentane is higher than in cyclohexane[48]. The excess strains in cycloparaffins relative to the unstrained cyclohexane are also given in Table 1.

Therefore, the strain of the double bond can be estimated directly from the heats of hydrogenation only when the saturated hydrocarbon is unstrained. Thus it follows from the above data that the strain of the double bond in compound (III) is equivalent to 4.3 kcal mole^{-1} and in compound (IV) to 9.9 kcal mole^{-1}. If the strain in the cycloparaffin is neglected, the lower limit to the strain of the double bond can be estimated. Thus the strain of the double bond in norbornene should not be less than 6 kcal mole^{-1} and in *trans*-cyclo-octene it should not be less than 5.1 kcal mole^{-1}.

It is also possible to estimate the upper limit of the strain of the double bond by a different procedure. The overall strain in the cyclo-olefin relative to cyclohexene is[45]:

$$E_{strain}\,(\text{olefin}) = \Delta H_{hydr}\,(\text{olefin}) - \Delta H_{hydr}\,(\text{cyclohexene}) + E_{strain}\,(\text{paraffin}).$$

The values calculated for these conditions are presented in Table 1. The overall strain in the olefin [E_{strain}(olefin)] relative to cyclohexene includes the excess strain in the double bond and in other groups. The strain of the double bond can be estimated from data on the excess strain in the paraffin per CH_2 group. If it is assumed that this quantity is the same also for the olefin, then the strain of the double bond can be calculated thus:

$$E_{strain}\,(\text{double bond}) = E_{strain}\,(\text{olefin}) - (n-2)E_{CH_2}\,(\text{paraffin}).$$

The data for cyclopropene, cyclopentene, and cycloheptene calculated in this way are also listed in Table 1. Evidently the results represent the upper limit to the strain of the double bond. It is also clear that such calculation for *cis*-cyclo-octene and higher cyclo-olefins gives somewhat indefinite results, since the strain per CH_2 group in the cycloparaffin is significantly higher than in the *cis*-cyclo-olefin due to the transannular repulsion of hydrogen atoms.

Finally the strain of the double bond in *trans*-cyclo-olefins can be roughly estimated from a comparison of the heats of hydrogenation of the *cis*- and *trans*-isomers. For *trans*-cyclo-octene, such comparison yields 9.2 kcal × × mole^{-1}.

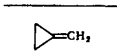
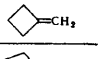
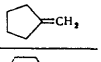
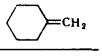
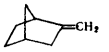
The energy which must be expended to cause the deviation of the valence angle from the normal value may be calculated[8,49] from the equation

$$E = \frac{1}{2}k\alpha^2, \qquad (1)$$

where k is the bending force constant and α the deviation of the angle from the normal value. A large number of semiempirical calculations of the strain energy and of the stable conformations of cycloparaffins have been made[35-38]. Eqn. (1) is also applicable to the calculation of the conformation and strain in cyclo-olefins. It is noteworthy that usually the force constant for the C=C–X angle is higher than that for the C–C–X angle[49,50], which shows that it is more difficult to alter the angle of the sp^2-hybridised atom. The conformation of cyclohexene was in fact calculated in this way[13,14]. The present authors calculated the double bond strain energy for certain cyclo-olefins, the results and the C=C–C angles being listed in Table 1. The bending force constant for the C=C–C angle was taken to be 0.8×10^{-11} erg radian^{-2}, i.e. close to the C–C–C force constant in cyclobutane[51] (for justification of this choice, see Ref. 49).

Critical examination of the limits of applicability of this method among cycloparaffins[49] shows that, whereas for cyclobutane the agreement with experiment is more or less

TABLE 2. Properties of hydrocarbons with unilateral double bond strain.

Substance	$-\Delta H_{hydr}$, kcal mole^{-1} (Ref.61)	Frequencies in the infrared spectra cm^{-1}		K_{eq} for Ag^+ complexes in ethylene glycol at 40° (Ref. 66), litre mole^{-1}
		C=CH$_2$ groups in olefins (Refs. 62 and 63)	C=O groups in corresponding ketones (Ref. 62)	
	—	1730	1815	—
	29.4	1679	1788	5.8
	26.9	1657	1746	4.0
	27.8	1651	1715	6.0
	—	1665 [64]	1751 [65]	4.3

satisfactory, for cyclopropane such calculation yields a strain energy which is much too high and therefore the method can be applied only in the case of small or at any rate moderate deformations of the valence angle. When the deformation of the angle is considerable, involving the formation of "banana" bonds [51-54], the above method of calculation cannot be used. Calculations on the cyclopropene molecule [12] show that, although formally the angle between the bonds in the methylene group of cyclopropene is 50°48', the angle between the orbitals is 105° 35' and therefore "banana" bonds are formed in this case. Table 1 also shows that the calculated value of 109° for the angle in norbornene [55,56] is somewhat too high and therefore the strain of the double bond should be greater. This finding is also confirmed by spectroscopic data (see below).

The application of Eqn. (1) to *cis*-di-t-butylethylene (IV), taking into account the strain of the double bond, permits the calculation of the C=C–C angle in this compound, which is found to be 136°.

Finally, the published data on the heats of hydrogenation of certain compounds with unilateral compressive strain (Table 2) show that the strain of the double bond in methylenecyclobutane is not less than 1.6 kcal mole^{-1}, but it is evident that this value is significantly too low because of the strong repulsion of the mutually non-bonded hydrogen atoms and the methyl group in methylcyclobutane. Nevertheless the strain of this bond is smaller than would be expected from the valence angles in this compound.

IV. PHYSICAL PROPERTIES OF THE STRAINED DOUBLE BOND

From the formal point of view, the decrease of the angle between the bonds of the tetragonal carbon atom results in the atom becoming increasingly more "olefin-like". This was probably suggested by Bayer: it is not fortuitous that he examined the problems of the theory of strain in an article dealing with unsaturated compounds [4]. Formally, it is possible to calculate the "strain" in the formation of the double and triple bond in the same way as for cycloparaffins [4,10].

Similarly cisoid compressive strain should cause the bond to acquire "acetylenic character" and, as already stated above, there should be an analogy between olefins with cisoid compressive strain and acetylenes. Such analogy should undoubtedly be reflected in the physical properties of olefins of this type. However, as mentioned above, different types of strain of the double bond may be non-equivalent from the standpoint of the possibility of the compensation of the strain by rehybridisation and therefore strained olefins can exhibit significantly different relations in their physical properties.

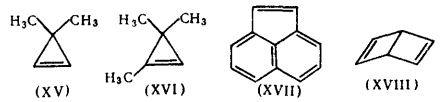
1. Nuclear Magnetic Resonance Spectra

As already stated, compounds with cisoid compressive strain should show an increase of the *s*-character of the exocyclic bond. In recent years estimates of the fractional *s*-character of the C–H bond from the spin–spin interaction constant $J(^{13}C-H)$ have been made extensively. A simple relation was proposed in 1959: [67,68]

$$\% S = \frac{J(^{13}C-H)}{5}. \quad (2)$$

The value of $J(^{13}C-H)$ for the carbon–hydrogen bond of an sp^3-hybridised atom is about 125 c/s (125 c/s for methane [67], 123 c/s for cyclohexane [67]), and for acetylenic compounds it is about 250 c/s (248 c/s for methylacetylene [67], 251 c/s for phenylacetylene [67]). For unstrained olefins, $J(^{13}C-H)$ is in the region of 157 c/s (157 c/s for ethylene [69], 159 c/s for benzene [69], 155 c/s for cyclo-octatetraene [69]).

The values of $J(^{13}C-H)$ for certain cycloalkanes and cycloalkenes are presented in Table 3, which shows that $J(^{13}C-H)$ increases with the cisoid compressive strain. This may be attributed to the increase of the *s*-character of the =C–H bond with increasing strain in the double bond. The value of $J(^{13}C-H)$ for cyclopropene is unknown, but for 3,3-dimethylcyclopropene [70] (XV) and 2,3,3-trimethylcyclopropene [70] (XVI) these constants are 220 and 218 c/s respectively and thus the hybridisation of the carbon atoms at the double bonds in these compounds is significantly different from the hybridisation in ethylene.



(XV) (XVI) (XVII) (XVIII)

TABLE 3. Certain spectroscopic characteristics of cyclo-olefins.

Ring size	NMR spectra			Infrared spectra (cm^{-1})			λ_{max} for phenyl derivatives, nm	
	$J(^{13}C-H)$, c/s			C–H vibrations in cyclo-olefins				
	C–H in cycloalkane	=C–H in cycloalkene	chemical shift τ due to olefinic protons (Ref.62)	ν^{s}_{C-H}	ν^{as}_{C-H}	C=C vibrations	of type (XXV) (Refs. 98, 99)	of type (XXVI) (Ref. 100)
C_3	161 [93]	(220)***	2.99	3076 [62]	—	1641 [62]		308, 317****
C_4	134 [94]	170 [96]	4.03	3060 [83]	(3019)**	1570 [83]		297, 307
C_5	128 [67]	160 [69]	4.40	3060 [85] 3045 [97]	(3039)**	1615 [63]	254	272
C_6	124 [94,95]	157 [69]	4 41	3024 [62]	3067 [62]	1654 [63]	248	253
C_7	123 [94]		4.29	3020 [62]	3059 [62]	1650 [62]	247	254
C_8 *cis*			4.44	3010 [24]		1664 [24]		
C_8 *trans*	122 [94]			3016 [62] 3000 [24]	3053 [62]	1648 [62] 1658 [24]		
Norbornene (XIV)	(135)*	174 [69]	4.06	3070 [97]		1568 [97]	262	

* The value for protons at C_1 and C_4 in norbornadiene (XII). [94]

** Calculated value. [83,85]

*** Value for 3,3-dimethylcyclopropene (XV). [88]

**** Values for 3-hydroxymethyl-1,2-diphenylcyclopropene (XXVII).

The constants for norbornene (X)[69] (174 c/s), norbornadiene (XII)[71] (168 c/s), and acenaphthylene (XVII)[69] (178 c/s) also show that their double bonds are strained. Possibly the high strain of the double bond in acenaphthylene is in fact responsible for the high heat of polymerisation (24.0 kcal mole^{-1}) of this compound[45].

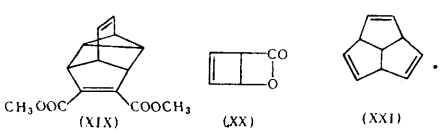
We may note that the above simple equation gives $J(^{13}C-H)$ = 166.5 c/s for the C–H bond of the sp^2-hybridised atom. Nevertheless the fractional s-character of many compounds has been calculated in this way. This procedure has been criticised[72,73]. It has been shown that in some cases (for example, for halogeno-derivatives) other factors exert a dominant effect[74]. Apparently, only when compounds with similar structures are compared is it possible to make fairly reliable conclusions on the basis of the variation of $J(^{13}C-H)$, provided that it is sufficiently pronounced. Here we must point out that so far $J(^{13}C-H)$ has been almost always determined from proton spectra. Burke and Lauterbur[75] compared the values obtained from proton and ^{13}C spectra for a number of cycloalkanes and found certain discrepancies (the greatest discrepancy was found for cyclodecane: 8 c/s). It is very interesting that their calculation confirmed that the observed values of $J(^{13}C-H)$ derived from carbon and proton spectra deviate in different directions from a certain specified value, assumed to be true. It is quite obscure what happens in olefins and therefore care must be exercised in the interpretation of these data, except perhaps for compounds (XV) and (XVI).

Another explanation of the discrepancy in the values of $J(^{13}C-H)$ is possible. It is known from the work of Mislow[8,76] that the s-character of a bond can be expressed in terms of the "hybridisation parameter" of the bond λ_i^2, so that

$$\% S = \frac{100}{1+\lambda_i^2}. \qquad (3)$$

λ_i^2 can be readily calculated if the geometry of the molecule is known. Such calculation for ethylene (adopting the σ,π-model) yields λ^2 = 2.2 for the C–H bond and λ^2 = 1.7 for the C=C σ-bond. Hence on combining Eqns. (2) and (3) we obtain $J(^{13}C-H)$ = 156 c/s, which is almost identical with the experimental value. Thus in simple olefins C–H bonds have a somewhat enhanced p-character (in the case of ethylene we have $sp^{2.2}$) compared with the requirement for an sp^2-hybridised atom.

The increase in the s-character of the =C–H bond should be reflected also in the chemical shift of the olefinic proton. The degree of shielding of the proton then decreases and the signals are displaced in the direction of decreasing field. Data on chemical shifts are presented in Table 3. The shift of the signals due to the olefinic protons with increasing cisoid strain has been observed in a fairly large number of examples. Thus τ for olefinic protons is 3.36 for barrelene (XIII)[77], 3.45 for bicyclo[2,2,0]hexadiene (XVIII)[78], 3.47 for the diester (XIX)[79], and 3.27 for the lactone of 3-hydroxycyclobutene-4-carboxylic acid (XX)[80].



(XIX) (XX) (XXI).

2. Infrared Spectra

In the region of =C–H vibrations unsubstituted cyclo-olefins exhibit two frequencies corresponding to symmetrical and asymmetric vibrations[81] (ν^{s}_{C-H} and ν^{as}_{C-H}), which are given in Table 3. The assignment in some studies[62,82] of the frequency 3126 cm^{-1} in the cyclobutene spectrum to ν^{as}_{C-H} is incorrect; this frequency can be readily interpreted as an overtone of the vibrations of the C=C bond[83]. This is also true of norbornene and some of its derivatives[84]. Calculations on the infrared spectrum of cyclobutene showed that the vibration frequency ν^{as}_{C-H} should be 3019 cm^{-1}, i.e. lower than the vibration frequency ν^{s}_{C-H} (3061 cm^{-1})[83].

The ν^{s}_{C-H} vibration frequency of *cis*-but-2-ene, which is 3023 cm^{-1} according to Wiberg and Nist[62] and 3034 cm^{-1} according to Sverdlov and Krainov[85], may be quoted for comparison. An absorption band near 3300 cm^{-1} is characteristic of the ≡C–H bond[81]. It is evident from the data in Table 3 that the ν^{s}_{C-H} vibration frequency increases systematically with decreasing ring size and hence with increasing double bond strain.

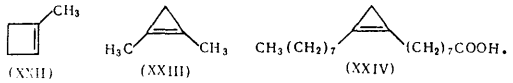
The vibration frequency of the C=C bond in unstrained olefins is near 1650–1660 cm^{-1} (1658 cm^{-1} for *cis*-but-2-ene[62]); data for cyclo-olefins are presented in Table 3, which shows that, as the ring size decreases, this band is initially displaced towards lower frequencies, in cyclopentene and cyclobutene, and then the frequency increases again in the case of cyclopropene. This phenomenon occurs also in the spectra of other compounds. Thus, as already pointed out above, the double bond in cyclononatriene (I) is almost unstrained [according to Eqn. (I), E_{strain} for a single double bond is 0.56 kcal mole^{-1}], which is confirmed by the presence of the frequency 1641 cm^{-1}.[15] However, in triquinacene (XXI)[86], which has a geometry similar to that of compound (I), the strain is higher. This is also shown in the infrared spectrum of compound (XXI), which contains the frequencies 3050 and 1613 cm^{-1}.

Comparison of the C=C stretching vibration frequencies shows that the double bond in norbornene is strained approximately to the same extent as the double bond in cyclobutene. The presence of a frequency in the region 1550–1575 cm^{-1} provides a means of ready identification of the double bond in derivatives of this type[84].

This unexpected decrease of the C=C bond frequency has been explained by a decrease of its force constant[62,82]. However, Sverdlov and Krainov's calculation[83] of the infrared spectrum of cyclobutene showed that the normal value of this force constant can be used. The frequency of the C=C bond depends (for substitution of the same type) on the C=C–C angle. The coefficient of the kinematic interaction of the C=C and C–C bonds is proportional to the cosine of the angle between these bonds. The coefficient is -0.064 for *cis*-but-2-ene, -0.946 for cyclopentene, and -0.009 for cyclobutene; thus the interaction of the coordinates Q(C=C) and Q(C–C) decreases in this series, which results in a decrease of the vibration frequency of the C=C bond. From this point of view, the higher value of this frequency in cyclopropene is reasonable, since the coefficient for the latter compound is 0.054.

It is also interesting to examine the effect of substitution at the double bond on the C=C vibration frequency. In unstrained olefins transition from a *cis*-disubstituted double bond to a trisubstituted double bond causes an increase in frequency from 1650 to 1670–1680 cm^{-1}, i.e. Δ_1 is 20–30 cm^{-1}, and transition to the tetrasubstituted double bond

entails an increase from 1650 to 1680–1690 cm^{-1}, i.e. Δ_2 is 30–40 cm^{-1}. Nevertheless for norbornene derivatives Δ_1 = 60–65 cm^{-1} and Δ_2 = 86–90 cm^{-1},[84] i.e. the frequency increase due to increasing degree of substitution becomes much higher as the strain increases. Similarly, it follows from the infrared spectroscopic data for 1-methylcyclobutene (XXII)[87] that here Δ_1 (relative to cyclobutene) is 70 cm^{-1}.



(XXII) (XXIII) (XXIV).

This relation is shown particularly clearly for cyclopropene derivatives. For 1,3,3-trimethylcyclopropene (XVI)[88] (1768 cm^{-1}), 1,2-dimethylcyclopropene (XXIII)[89] (1898 cm^{-1}), and sterculic acid (XXIV)[90] (1865 cm^{-1}), Δ_1 = 118 cm^{-1} and Δ_2 = 224–257 cm^{-1}.

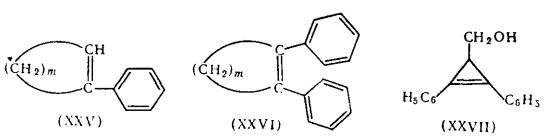
The spectrum of *trans*-cyclo-octene[24] (Table 3) merits special examination. For comparison, the frequencies 3010 and 1650 cm^{-1} in the infrared spectrum of *cis*-oct-4-ene and the frequencies 3027 and 1670 cm^{-1} in the spectrum of *trans*-oct-4-ene may be quoted. Table 3 shows that in the infrared spectrum of *trans*-cyclo-octene the ν^{S}_{C-H} vibration frequency is lower, although this compound is considerably strained. Allinger[24] explained this phenomenon on the grounds of torsional strain in *trans*-cyclo-octene. The presence of a dipole moment (in consequence of torsional strain) explains the appearance of the C=C vibration frequency in the infrared spectrum of *trans*-cyclo-octene, while in the usual symmetrical *trans*-olefins this frequency is forbidden and is observed in Raman spectra.

Thus different relations may obtain in the infrared spectra depending on the different types of strain of the double bond. This can also be illustrated using compounds with unilateral compressive strain of the double bond, the infrared spectroscopic data for which are presented in Table 2. This table also lists the frequencies of the C=O group in the corresponding ketones. It is evident from Table 2 that the frequency of the $C{=}CH_2$ bond increases with decreasing ring size, i.e. in conformity with the mode of rehybridisation. The frequency of the carbonyl group in the corresponding ketones varies similarly. For comparison, we may point out that carbon monoxide[91] has an absorption band at 2143 cm^{-1}, while the absorption band of the carbonyl group in keten[92] in the gas phase is 2151 cm^{-1}.

On the other hand, in olefins with unilateral repulsion strain the C=C frequency decreases from 1661 cm^{-1} in 1-ethyl-1-methylethylene to 1644 cm^{-1} in 1-isopropyl-1-methylethylene and 1638 cm^{-1} in 1-t-butyl-1-methylethylene[27], in agreement with the change in hybridisation.

3. Ultraviolet Spectra and Other Properties

There are a few published data on the ultraviolet spectra of certain simple cycloalkenes[62,101] but it is difficult to arrive at any definite conclusions on their basis.

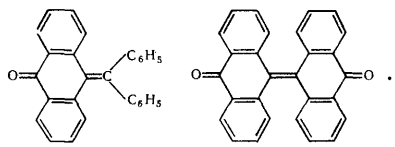


(XXV) (XXVI) (XXVII).

The relations concerning the positions of the absorption bands of derivatives with different functional groups in which the chromophoric group is conjugated with the double bond are also few. Thus Table 3 lists the absorption maxima of the phenyl derivatives of cyclo-olefins of the type of (XXV) and (XXVI). These data show that there is a definite shift of the absorption maximum to the long-wavelength region with increase in the strain of the double bond. There is an indication in the literature of a steady variation in the ultraviolet spectra of unsaturated dicarboxylic acids[102,103], but the available data are incomplete and definite conclusions cannot be arrived at.

Particular interest attaches to an examination of the ultraviolet spectra of olefins with torsional strain of the double bond. As already stated, rotation about the axis passing through the carbon atoms of the double bond causes mutual approach of the energy levels of the ground and excited states. This is evident from Fig. 1, where the potential energy curves for the ground singlet (N) and triplet (T) states and also the excited singlet (V) state for ethylene are plotted schematically; clearly, for those olefins which can give rise to *cis*- and *trans*-isomers, the curves of the type shown in Fig. 1 should be asymmetric.

The ultraviolet absorption band of the usual olefins is due to the $N \rightarrow V$ transition. For an unstrained olefin, this transition is denoted by n_1 in Fig. 1. If the double bond in the ground state is subject to torsional strain and is rotated by an angle φ_1, the ultraviolet absorption maximum in the spectrum of such an olefin is due to the n_2 transition. Hence it is seen that in the presence of torsional strain there should be a bathochromic shift in the ultraviolet spectrum. This has been studied in special detail in the spectrum of dibiphenylene-ethylene (VII)[104]:



(XXVIII) (XXIX).

Eaton and Lin[105] have shown that, on irradiation with ultraviolet light, Δ^2-*cis*-cyclo-octenone isomerises smoothly to Δ^2-*trans*-cyclo-octenone. These workers[106] and also Corey and coworkers[107] obtained in this way the extremely strained *trans*-cycloheptenone, although *trans*-cycloheptene has not so far been isolated[108].

Another very interesting phenomenon, namely thermochromism, is possible for compounds with torsional strain. One of the possible interpretations of this phenomenon was given by Grubb and Kistiakowsky[109], using diphenylmethyleneanthrone (XXVIII), bianthrone (XXIX), and their analogues as examples. A simplified explanation of the phenomenon may be based on Figs. 1 and 2. Torsional strain in

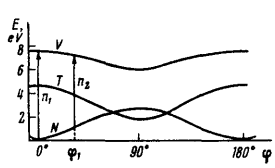


Fig. 1. Potential energy curves as a function of the angle of rotation about the double bond in ethylene; data of Mulliken and Roothaan[29] and Burnell.[30]

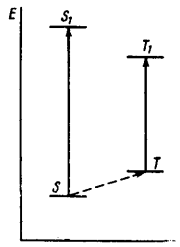


Fig. 2. Schematic representation of the electronic transitions in compounds of the type of (XXVIII), according to the data of Grubb and Kistiakowsky.[109]

systems of the type of (XXVIII) is so much greater than the energy of the ground singlet state that thermal excitation of the molecules to the lower triplet level becomes possible (Figs. 1 and 2). Therefore triplet–triplet transitions can occur in the absorption spectrum of such a compound (Fig. 2). If the excited triplet level is below the excited singlet level, a bathochromic shift occurs. When diphenylmethyleneanthrone (XXVIII) is heated, the colour changes from yellow to red, the colour change being fully reversible as the temperature is varied.

This explanation of thermochromism has been confirmed by quantum-mechanical calculations[110], and also by the study of the temperature variation of paramagnetism. A more rigorous and detailed examination of thermochromism and also other views on this problem have been described by Woodward and Wasserman[111] and Day[112].

Hoijtink[113] showed that the half-wave potential in the polarographic reduction of dibiphenylene-ethylene (VII) is intermediate between the experimental potentials for systems with planar and perpendicular disposition of aromatic rings.

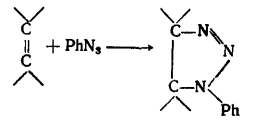
V. CHEMICAL PROPERTIES OF STRAINED OLEFINS

The strain of the double bond is clearly shown not only in physical but also in chemical properties of olefins. These compounds are characterised by high rates of reactions typical of normal olefins. However, reactions characteristic of strained olefins only and also the changes in the stereochemistry of the reactions under the influence of molecular strain are of greatest interest; these will be examined in the present section.

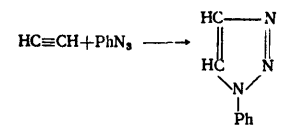
1. Addition Reactions

Addition to the double bond is accompanied by a change in the hybridisation of the carbon atoms — from the sp^2- to the sp^3-hybrid state. The valence angle then decreases from 120° and 109.5°. Therefore, according to the concept of *I*-strain[114], addition should take place readily with compounds having cisoid compressive strain, unilateral compressive strain, and out-of-plane strain. Compounds with torsional strain should also be very reactive, due to the decrease in the degree of overlap of *p*-electrons. The tendency to undergo addition can be inferred from the heat of hydrogenation. Strained olefins react particularly readily by a molecular mechanism involving the formation of cyclic polycentric transition states. 1,3-Dipolar addition and diene synthesis are the most characteristic examples of reactions of this kind.

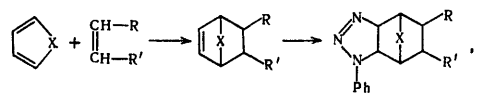
A widely known specific reaction of strained olefins is the reaction with phenyl azide, resulting in the formation of triazolines:



This reaction was investigated in detail by Alder and Stein[115,116] and is widely used nowadays as a kind of "test" for the strained double bond. Unstrained olefins, without electron-acceptor groups, do not undergo this reaction or undergo it with considerable difficulty. According to Dimroth and Fester[117], acetylene reacts with phenyl azide to form phenyltriazole:



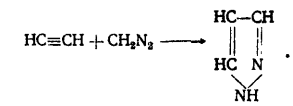
This reaction has been particularly widely used for the identification of diene synthesis adducts of the cyclopentadiene and furan series, since the resulting norbornene and 7-oxabicyclo[2,2,1]heptene contain strained double bonds[118–120]:



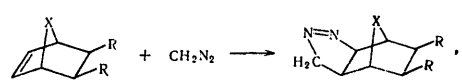
where X = CH_2 and O.

Trans-cyclo-octene reacts extremely vigorously with phenyl azide, while addition to the *cis*-isomer takes place only on standing for several weeks[121]. *Trans*-cyclononene and *trans*-cyclodecene also react with phenyl azide[122–124], while the *cis*-isomers do not react (earlier it was believed erroneously that *trans*-cyclodecene does not give a phenyltriazoline derivative).

Diazomethane does not usually add to the double bond without electron-acceptor substituents[125]. However, Pechmann[126] showed that acetylene readily reacts with diazomethane to form pyrazole:

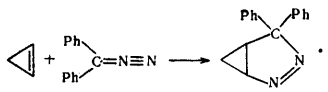


Bearing in mind the analogy between the properties of acetylenes and olefins with cisoid compressive strain, it might have been expected that the latter will also react with diazomethane. Indeed, Zefirov et al. showed that norbornene and also derivatives of 7-oxabicyclo[2,2,1]heptene readily combine with diazomethane to form the corresponding Δ^2-pyrazolines[127,128]:

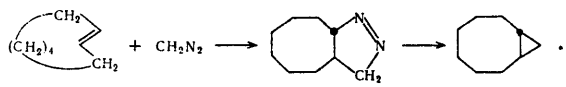


where X = CH_2 and O.

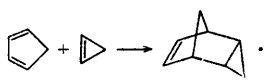
Paul et al.[129] found that cyclobutene also readily combines with diazomethane, but cyclopentene reacts with difficulty, and cyclohexene almost does not react at all (yield 2%). Wiberg and Bartley[130] discovered that cyclopropene readily reacts with diphenyldiazomethane as follows:



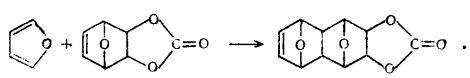
Trans-cyclo-octene also reacts with diazomethane with formation of pyrazoline, which is readily converted into *trans*-bicyclo[6,1,0]nonane under the action of ultraviolet light[131]:



Olefins with cisoid strain of the double bond readily undergo the diene synthesis reaction. For example, cyclopentadiene reacts with cyclopropene at 0°,[130] while the reaction with ethylene requires an elevated temperature and pressure[132]:



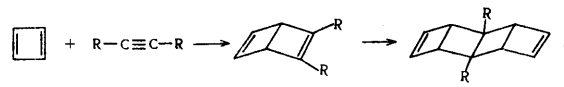
Strained olefins of this type undergo diene synthesis even with relatively unreactive dienes. It has been noted in a number of studies[133,134] that, by virtue of its aromatic nature, furan is an unreactive diene and can react only with very active dienophiles such as maleic anhydride, acetylenedicarboxylic esters, and fumaronitrile. The diene synthesis reaction of furan with dienophiles without electron-acceptor groups takes place under very severe conditions and with a low yield (5% in the case of ethylene[135]) or not at all. However, furan reacts fairly smoothly with bicyclic olefins having a strained double bond[136]:



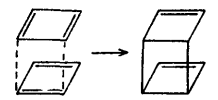
Nowadays diene synthesis with furan is often used for the identification of unstable strained olefins, such as, for example, *trans*-cycloheptene[108], benzocyclobutadiene[137], *trans*-cyclo-octenone[105], and *trans*-cycloheptenone[106]. We may note that compounds of the type of dehydrobenzene are also usually identified by the formation of an adduct with furan[138].

Trans-cyclo-octene also readily undergoes diene synthesis. Ziegler and coworkers[124,139] showed that the reaction of this compound with hexachlorocyclopentadiene takes place easily at 0°, while the *cis*-isomer reacts only on heating to 100°. It is interesting that *cis-trans*-cyclo-octa-1,5-diene readily combines with one mole of hexachlorocyclopentadiene; the second mole adds only on heating.

Strained olefins also readily undergo cyclo-addition reactions. For example, cyclobutadiene reacts with acetylene derivatives to form "Dewar benzene" derivatives[140] and then unusual polycyclobutane derivatives called "pterodactylodienes"[141]:

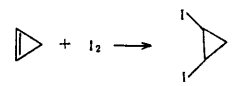


However, in general the reactions of cyclobutadiene can be treated in two ways: as simple cyclo-addition and as a Diels–Alder reaction. The formation of the *syn*-dimer only[140] in the dimerisation of cyclobutadiene is evidence in favour of the second hypothesis (this should be the effect of Alder's rule of "maximum accumulation of double bonds"):

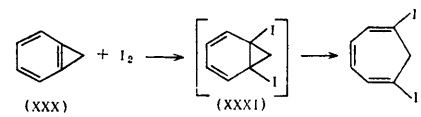


Both possible dimers, *syn*- and *anti*-, were obtained in a pure form by Nenitzescu and coworkers[142,143] by dihalogenation of dichlorocyclobutene.

Iodination of olefins under usual conditions is as a rule reversible; it is well known that the iodide ion is a good 1,2-dehalogenating agent[144]. For this reason, 1,2-di-iodo-derivatives are obtained by photochemical low-temperature iodination of olefins[145]. However, cyclopropene combines with iodine under the usual conditions in carbon tetrachloride solution[130]:



We may note that under these conditions acetylene also combines with one mole of iodine[146]. In 1965 Vogel and coworkers[147] obtained an extremely strained hydrocarbon — benzocyclopropene (XXX) (a substituted system of this type had been obtained earlier[148]), which exhibits reactivity unusual for aromatic compounds. In particular, compound (XXX) combines with iodine in carbon tetrachloride solution, 1,6-di-iodocycloheptatriene being formed together with *o*-iodobenzyl iodide. The authors explain the formation of this compound by the addition of iodine to the "cyclopropene" double bond with formation of the di-iodo-intermediate (XXXI), which then undergoes the Cope rearrangement[149]:



(XXX) (XXXI)

The infrared spectrum of compound (XXX) has an intense band at 1666 cm^{-1}, whose origin is not altogether clear; we may note further that $J(^{13}C-H)$ for the methylene group in compound (XXX) is 178 ± 2 c/s.

The kinetics of reactions involving the addition of diethylaluminium hydride[124] and hexachlorocyclopentadiene[124] to cyclic olefins and also the reduction of the latter by di-isopentylborane[150] and di-imide[151] have now been investigated; these data are presented in Table 4, which shows that, with increasing cisoid strain, the rate of addition increases too. However, an increase of rate has also been observed for cyclo-olefins having rings of moderate

TABLE 4. Relative rates of addition and complex formation reactions for simple cyclo-olefins.

Ring size	Relative rate of addition				Relative complex formation constant	
	of di-imide	of di-iso-pentyl-borane	of hexa-chloro-cyclopenta-diene	of diethyl-aluminium hydride	in water at 25° (Refs. 58 and 153)	in ethylene glycol at 40° (Ref. 66)
C_3					$8.5 \cdot 10^4$ **	
C_4				47		
C_5	15.5	107	22.5	9	6.3	2.0
C_6	1	1	1	1	1	1
C_7	12.1	550 *	30	16	1.2	3.4
C_8 *cis*	17	2046 *	75	21	0.27	4.0
C_8 *trans*						280
C_9	5.7		15	6.5		
C_{10}	0.85		0.9	0.8		
Norbornene	450				14.4	17

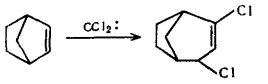
* Data of Garbisch et al.[151]

** Data of Wiberg and Bartley.[130]

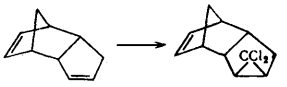
size, with a maximum in the case of cyclo-octene, although these olefins do not have strained double bonds.

Garbisch[152] developed a method of calculation for steric interactions in cyclo-olefins which he applied successfully in an examination of the tautomeric conversions of hydroxymethylene ketones. The application of this type of calculation to reduction with di-imide yielded a satisfactory calculated value of the reaction rate[151]. The success was due to the fact that the polar effects in the reduction with di-imide are very small and the rate of addition is determined by the energy which must be expended in order to change the geometry of the molecule so that a planar transition state arises ("stereotorsional control").

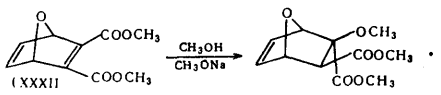
The impression might be created that the increase of molecular strain in all cases results in an acceleration of the rate of addition. However, this is not so. It has been established that norbornene reacts with dichlorocarbene with considerable difficulty[154], a rearrangement product of dichlorocyclopropane being formed:



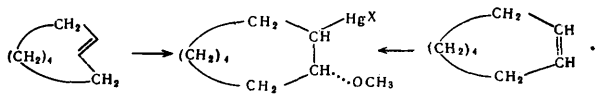
The relative inertness of the norbornene bond is clearly evident in the reaction of dicyclopentadiene from which a monoadduct at the cyclopentene double bond is obtained[155]:



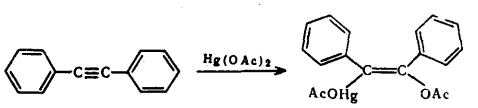
The reason for the retardation of the carbenoid reaction is unknown. We may note, however, that although almost all the "normally" accelerated reactions are of the electrophilic addition type with respect to carbenes, a nucleophilic mechanism cannot be excluded. Nucleophilic addition to a strained double bond has been almost not investigated at all. Thus Zefirov and coworkers[156] showed that nucleophilic addition of methanol to the diester (XXXII) takes place in the normal way without the homoallylic participation of the second double bond:



Finally, the stereochemical aspect of the reactions involving addition to strained olefins must be considered. A number of investigators have shown that the addition of mercury salts to olefins such as norbornene[157-160] or derivatives of 7-oxabicyclo[2,2,1]heptene takes place as *cis*-addition, while hydroxymercuration of unstrained olefins is a *trans*-addition reaction. One of the reasons adduced for the anomalous *cis*-addition is the strain of the double bond in olefins undergoing such addition[160]. Indeed, Sokolov et al.[161] showed that the hydroxymercuration of *trans*-cyclo-octene takes place as *cis*-addition and that of *cis*-cyclo-octene as the normal *trans*-addition:



Burnell[30,162] showed that *trans*-addition reactions at double and triple bonds take place more readily in a twisted conformation. At the same time, such a transition state is difficult to achieve in rigid strained olefins and in the presence of weak electrophilic agents the reaction may take place by a molecular mechanism. In this connection, it is interesting to note that, as shown by Nesmeyanov and coworkers[163,165] and Drefahl[164], the acetoxymercuration of tolane also takes place as *cis*-addition by the mechanism



The reaction with dimethylacetylene does not involve a single pathway[166].

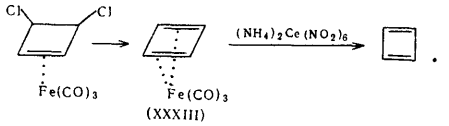
In view of the analogy between the properties of acetylenes and olefins with cisoid compressive strain, in those cases where the stereochemical course of the addition reaction at a double bond is anomalous it would also be useful to investigate the stereochemistry of the addition of the same agent to a triple bond; very little work has been done on this problem.

2. Complex Formation

Lucas and coworkers[167,168] showed that olefins are capable of forming a number of complexes with heavy metal ions and in particular with silver ions. Complexes of this type are formed as a result of the overlapping of the free *s*-orbital of the metal ion and the π-bond of the olefin; the additional stabilisation may be due to the overlapping of the filled *d*-orbitals of the metal and the antibonding π-orbitals of the olefin[6,169,170]. The complexes of silver ions with olefins have been most thoroughly investigated; the instability constants for olefins with unilateral compressive strain are listed in Table 2 and those for olefins with cisoid compressive strain in Table 4. It is evident from Table 4 that in aqueous solutions there is a small but definite increase in the stability of the complexes with increase in the strain of the double bond. Complexes of cyclopropene and also of *trans*-cyclo-olefins are particularly stable. For example, *trans*-cyclo-octene can be extracted from pentane with an aqueous solution of silver nitrate, this being used for its preparative separation from the *cis*-isomer[171]. Data obtained by gas–liquid chromatography on ethylene glycol with added silver nitrate[66] (Table 4) show that the relations which obtain in this case are somewhat different, namely *cis*-cyclo-octene gives a significantly more stable

complex than cyclohexene. The high stability of the complex with norbornene and the extremely high stability of the complex with *trans*-cyclo-octene are striking. There is no correlation between the stability of the complexes of olefins with unilateral compressive strain (Table 2) and the magnitude of the double bond strain itself.

Complex formation is often used for the isolation of unstable olefins. In this connection the history of the attempts made over a period of many years to synthesise cyclobutadiene, which has played an important role in the theory of aromaticity [172], is of interest. Particularly intensive studies have been carried out during the last ten years in the laboratories of Nenitzescu [142,173] and Criegee [174]. The principal idea followed in these studies was stabilisation of cyclobutadiene by formation of a π-complex with a metal. It proved possible to obtain a complex of tetramethylcyclobutadiene with nickel chloride [174]. Only in 1965 was cyclobutadiene synthesised by Pettit's group [140,175], by oxidative decomposition of its iron carbonyl compound (XXXIII), which exhibits the properties of an aromatic system:



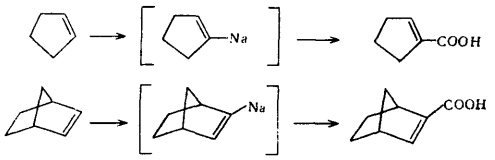
(XXXIII)

According to the calculation performed in 1965 by Dewar and Gleicher [176], cyclobutadiene should have a singlet ground state and its instability should be due to considerable angular strain.

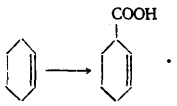
3. Substitution Reactions at the Double Bond

The greater *s*-character of the C–H bond in olefins with cisoid compressive strain results in increased acidity of the hydrogen atoms, similar to that which obtains on going from ethane to ethylene and then to acetylene. The increased acidity of the hydrogen atoms in cyclopropene derivatives has been observed in a number of investigations [88,130]. However, the most convincing data were obtained by Schröder [177] in a study of the base-catalysed deuterium exchange in cyclic olefins. It was found that t-butylacetylene and trimethylcyclopropene readily exchange the hydrogen at the multiple bond even at -20°, the exchange rate constant ratio for these compounds being 1 : 5000. Other cyclo-olefins exchange hydrogen under significantly more severe conditions. Thus bicyclo[3,2,0]heptene slowly exchanges hydrogen even at 110° and rapidly at 139°; cyclopentene exchanges hydrogen at 160°, while *cis*- and *trans*-di-t-butylethylene do not exchange hydrogen at 190°. Norbornene exchanges hydrogen more rapidly than cyclopentene.

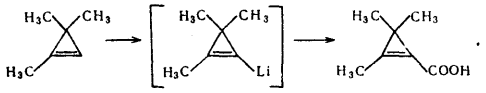
The hydrogen at the double bonds of cyclo-olefins can be substituted by a metal. For example, the action of pentylsodium on norbornene or cyclopentene results in the formation of an organosodium derivative of the cyclo-olefin [178,179], which has been identified by conversion into the corresponding acid:



Cyclohexene yields a $\beta\gamma$-unsaturated acid under these conditions [180]:



Closs and Closs [88] showed similarly that trimethylcyclopropene is readily metallated with butyl-lithium:



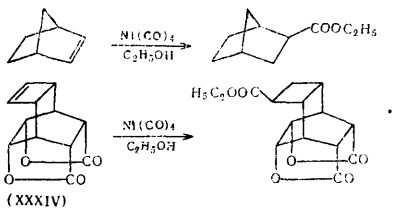
Trimethylcyclopropene reacts with ethylmagnesium bromide similarly as compounds containing a labile hydrogen atom, i.e. with formation of ethane [181]. It is interesting that trimethylcyclopropene forms a fairly stable copper derivative, whose structure, however, has not so far been established [181].

It should be noted that the more pronounced *s*-character of the exocyclic bond in olefins of this type results in a more pronounced electron-acceptor effect in such compounds than in unstrained olefins. Closs and Closs [182] showed that the dissociation constant of trimethylcyclopropenecarboxylic acid is 4.5 times higher than that of *cis*-crotonic acid.

In conclusion we must consider the reaction of unsaturated compounds with nickel carbonyl. Reppe and Kroper [183] showed that this reaction proceeds smoothly with acetylene derivatives having a hydrogen atom at the triple bond, acids being formed:

$$R{-}C{\equiv}CH \xrightarrow{Ni(CO)_4} R{-}CH{=}CH{-}COOH.$$

Ordinary olefins enter into this reaction with difficulty — cyclohexene, for example, yields cyclohexenecarboxylic acid only under very severe conditions. However, Cookson and coworkers [184] showed that norbornene and also the adduct (XXXIV) readily react with nickel carbonyl:



(XXXIV)

The authors explained this course of the reaction by the strain of the double bonds in the reactants.

---oOo---

The above data show that strained olefins exhibit special characteristics both in their physical and chemical properties. Olefins with cisoid compressive strain of the double bond have been most thoroughly investigated. Under favourable conditions it proved possible to calculate the magnitude of the strain in cyclo-olefins and even the rate constants for addition reactions at the double bond. However, many problems have still been little investigated and remain obscure; this applies especially to olefins with other types of strain of the double bond. A detailed quantum-mechanical examination of the problem of strained double

bonds has not been made either. It is still not clear to what extent various types of strained double bonds are chemically equivalent. In this respect olefins with out-of--plane strain are particularly interesting, since, apart from the ease of addition reactions, the rigid structure of certain cyclo-olefins of this type should pre-determine the *cis*-addition of any reagent. There is no doubt that the study of strained cyclo-olefins can lead to the discovery of fundamentally new reactions and also to a deeper understanding of the stereochemical aspects of the known addition reactions.

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EFFECT OF THE SOLVENT ON THE FORMATION AND IONIC DISSOCIATION OF THE ADDUCTS OF ALKALI METALS WITH AROMATIC HYDROCARBONS

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CONTENTS

I. Introduction 100
II. Solvation of cations in adduct formation reactions 101
III. The role of cation solvation in adduct ionic dissociation equilibria 104
IV. The role of the metal and solvent in radical-anio' disproportionation and reduction equilibria 107

I. INTRODUCTION

The chemistry of the organometallic compounds of the alkali metals is developing fairly rapidly. The adducts of alkali metals with aromatic hydrocarbons have attracted much attention because of their unusual structure [1,2] and because they have found wide application in polymer chemistry [3-7] and in synthetic organic chemistry [5,8,9]. The reactions involving the addition of alkali metals to aromatic hydrocarbons were first investigated by Schlenk [10,11], who established, in particular, that in ethyl ether sodium readily adds to anthracene and phenanthrene but not to naphthalene and biphenyl. However, Scott observed [12] that these hydrocarbons react rapidly and quantitatively with sodium when the solvent is 1,2-dimethoxyethane. Subsequently the adducts of benzene and its homologues with alkali metals were obtained in this solvent [13,14].

Scott [12] noted an appreciable electrical conductivity of the solutions of the adducts, indicating their ionic nature. Hückel and Bretschneider [15], who studied the reactions of alkali and alkaline earth metals with aromatic hydrocarbons in liquid ammonia, suggested that the hydrocarbon is converted into an anion by capturing electrons from the metal atom. Weissman and coworkers [16] showed that solutions of aromatic organosodium compounds in tetrahydrofuran exhibit strong paramagnetic absorption and concluded that the aromatic anion is at the same time a paramagnetic species; it has therefore been called a radical-anion ($Ar^{\cdot-}$). The reaction of an aromatic hydrocarbon (Ar) with an alkali metal can be represented by the equation

$$Ar + M \rightleftarrows Ar^{\cdot-}M^{+}. \quad (1)$$

Laitinen and Wawzonek [17] and Hoijtink et al. [18] obtained radical-ions in the electrolytic reduction of hydrocarbons (see also the reviews of de Boer [2] and Hoijtink [19]). The reaction with polycyclic hydrocarbons proceeds further - a second electron adds to the radical-anion and a doubly charged anion (dianion) is formed.

Measurements of the magnetic susceptibility of the solutions of the adducts of anthracene and phenanthrene with sodium [20] showed that, on more prolonged contact between the solution and the metal surface, the paramagnetic compound formed initially ($Ar^{\cdot-}M^{+}$) is converted into a diamagnetic product as a result of the reaction

$$Ar^{\cdot-}M^{+} + M \rightleftarrows Ar^{2-}2M^{+}. \quad (2)$$

Addition of the hydrocarbon to a solution of its dianions results in the appearance of paramagnetism due to the reaction

$$Ar^{2-}2M^{+} + Ar \rightleftarrows 2Ar^{\cdot-}M^{+}. \quad (3)$$

This is an equilibrium reaction and therefore the dianion can be formed not only by the reduction of the radical-anion, but also by the disproportionation of two radical-anions. Recently the possible addition of three electrons to the decacycline molecule has been observed [21].

The properties of radical-anions have been extensively studied by electron spin resonance and electron spectroscopic methods. The ESR spectra were studied by Weissman and coworkers [22-26] and other investigators [27-29]. The