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Orbital interactions through space and through σ-bonds

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Abstract. The present state of one of the comparatively new theoretical concepts in organic chemistry—the interaction of two heteroatoms having a lone electron pair or of groups incorporating a π-bond through the system of σ-bonds separating them—is considered. Two mechanisms of such interactions are discussed—through space and through the σ-bonds. These interactions are assessed in terms of UV, photoelectron, and electronic transmission spectroscopic and quantum-chemical data. The influence of the above interactions on the reactivity of the molecules is illustrated. The bibliography includes 139 references.

I. Introduction

For a qualitative and quantitative assessment of the mutual influence of substituents in an organic or organoelement molecule, a wide range of various electronic effects are used: the α-effect—interaction of two directly linked heteroatoms having lone electron pairs (LEP);[1,2] geminal interaction (also referred to as the α-effect)—interaction of two substituents separated by one carbon atom or an atom of another element;[3] orbital interaction through space or through σ-bonds—interaction of substituents separated by σ-bonds; the anomeric effect;[4–7] the 'rabbit-ear' or 'hockey sticks' effect;[8,9] vicinal interaction (the β-effect)—interaction of substituents separated by two carbon atoms;[10–12] the alternation effect (the field effect);[13] the inductive effect;[14] hyperconjugation;[15–17] various types of conjugation[18,19] etc.

In 1968–1971, Hoffmann[20,21] examined the interaction between σ-bond-separated heteroatoms having lone pairs or [groups having?] π-electron systems. In relation to biradical systems, he analysed two types of orbital interactions—through space and through σ-bonds. The splitting of the energy levels (ΔE) serves as a measure of the orbital interactions: thus, in the presence of such inte.actions, the energy levels should be [non-?] degenerate, whilst in their absence they should have similar energies. The present state of this problem is considered below. Several reviews on this topic have been published abroad,[17,18,22–28] but these are largely based on the consideration of only individual classes of compounds and differ in the theoretical approach used. Unfortunately, this problem has not been duly considered in Russian literature.

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II. Interactions between equivalent substituents having lone electron pairs or π-electron systems

1. Model ideas

According to perturbation theory, in the interaction of two degenerate electronic levels n_1 and n_2 of a molecule (n_1 and n_2 are the LEP orbitals of identical heteroatoms or the π orbitals of unsaturated groups) through space, two new electronic levels are generated—a low-energy level corresponding to the bonding combination ($n_1 + n_2$) and a high-energy level corresponding to the antibonding combination ($n_1 - n_2$). For a biradical system (for which the initial study was performed) with three separating σ-bonds, the $n_1 + n_2$ combination is symmetrical (S or n^+) while the $n_1 - n_2$ combination is antisymmetrical (A or n^-) relative to the symmetry axis perpendicular to the C(2)–C(3) bond (Fig. 1). The interaction through space reduces the energy of the level S relative to A ($E_S < E_A$). When interactions through σ-bonds are considered, it is assumed that the bonding σ orbital of the C(2)–C(3) bond is symmetrical, while the antibonding σ* orbital is antisymmetrical relative to the symmetry axis. When account is taken of the possibility of

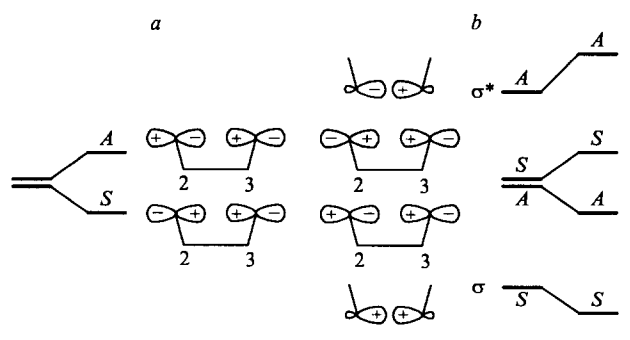


Figure 1. Schematic illustration of the interaction of the orbitals through space (*a*) and through σ-bonds (*b*).[20]

the mixing of only orbitals of similar symmetry, the $n_1 + n_2$ orbital interacts with the σ orbital, while the $n_1 - n_2$ orbital interacts with the σ* orbital. The energy of the level S then increases and that of the level A diminishes. 'Repulsion' of the levels leads to a lower energy of the level A compared with S ($E_S > E_A$). Their splitting ΔE is a function of the overlap of the above orbitals. The influence of the C(1)–C(2), C(3)–C(4), and C–H bonds on the relative positions of E_S and E_A is insignificant.[20,21]

In the general case, the interaction through σ-bonds depends only on the overlap of the LEP of the heteroatoms with the σ and σ* orbitals of the central C(2)–C(3) bond. The degree of overlap is independent of the rotation about this bond but does depend significantly on the rotation about the C–X bonds, since the symmetry is then infringed. On the basis of perturbation theory, displacements of the levels S and A (ΔE_S and ΔE_A) can be calculated by the formula[21]

$$\Delta E_i = \frac{|H_{ij}|^2}{E_i - E_j},$$

where $H_{ij} = \int \psi i_i^* H \psi_j \, d\tau$ is the perturbation matrix element and E_i and E_j are the energies of the interacting levels. Hoffmann did not discuss the influence of the energy difference $E_i - E_j$ on ΔE_S and ΔE_A. One can only note that, if E_j is the energy of an occupied σ orbital, then $|E_i - E_j| \approx 0.3$ eV and, if E_j is the energy of an unoccupied σ orbital, then $|E_i - E_j| \approx 10$ eV.[20] If the terminal substituents in the molecule are close to one another, the interaction through space predominates, but when they are separated by a distance greater than 3 Å the interaction through σ-bonds predominates.

Model calculations carried out by semiempirical methods led to certain important conclusions concerning the orbital interactions through a system of m intervening σ-bonds.[20,21,29–32]

1. The sequence of the energy levels generated on interaction through m intervening σ-bonds depends on their number: $E_S < E_A$ for even values of m and $E_S > E_A$ for odd values of m. It follows from this parity rule that the interactions through space and through m σ-bonds intensify one another in the case of even values of m and weaken one another for odd values of m (when these interactions are opposed).

2. For a given value of m, the orbital interactions through m σ-bonds depend on the geometry of the σ-skeleton and their extent is a maximum for the *trans*-structure of the σ-skeleton. Thus the manifestation of orbital interactions through four σ-bonds weakens in the following sequence of molecular conformations: *trans, trans* > *cis, trans* > *cis,cis*.

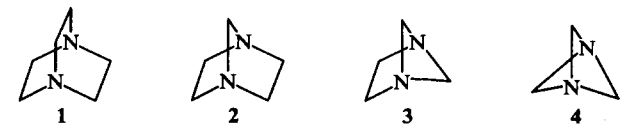
3. The interaction through σ-bonds on the whole stabilises the molecule, but the C–C σ-bond in the X–C–C–X fragment is then weakened.

The principal experimental methods for the investigation of orbital interactions through space or σ-bonds are photoelectron,[33] electronic transmission (electron capture),[34] and UV spectroscopy.

2. Diazabicycloalkanes

The interactions through space and through σ-bonds in diazabicyclic systems have been investigated by photoelectron spectroscopy and quantum chemically.[20,21,35–41] Quantum-chemical calculations by the extended Hückel[20] and MINDO/2 [36] methods for the 1,4-diazabicyclo[2.2.2]octane **1** molecule confirmed that the n^+ level is higher than the n^- level by 1.57 and 1.36 eV respectively. Photoelectron spectroscopy yields 2.13 eV.[35] Analysis of the vibrational structure of the bands in the photoelectron spectrum of compound **1** also confirms that $n^+ > n^-$.[37]

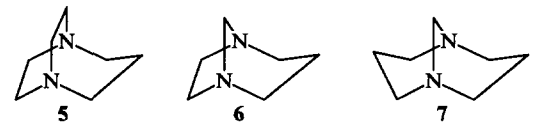
Quantum-chemical calculations for the diazabicycloalkanes **1–4** demonstrated the influence of the intervening σ-bonds on the relative disposition of the levels.[20]



1 **2** **3** **4**

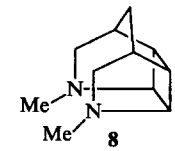
In the series of compounds **1–4**, the number of methylene bridges containing two intervening σ-bonds diminishes, which weakens the interaction through σ-bonds and intensifies those through space as a result of the mutual approach of the nitrogen atoms. The order of the levels S and A is then changed: for compound **1**, the $a_2''(A)$ level lies below $a_1'(S)$ ($\Delta E = 1.573$ eV); for compound **2**, $\Delta E = 0.371$ eV for the levels arranged in the same order; for compound **3**, the opposite order of the levels obtains, i.e. $S < A$ ($\Delta E = -0.605$ eV); for compound **4**, the level S is appreciably below the level A ($\Delta E = -2.878$ eV).

The photoelectron spectra of 1,5-diazabicyclo[3.2.2]nonane **5**, 1,5-diazabicyclo[3.2.1]octane **6**, 1,5-diazabicyclo[3.3.1]-nonane **7**, and various piperazine and hydroxypyrimidine derivatives show that the splitting ΔE for 1,3- and 1,4-diamines depends on the spatial orientation of the LEP of the nitrogen atoms[38] (Fig. 2). The influence of ring strain on the ionisation energies of the bicyclic diamines has been described.[39]



5 **6** **7**

The low ionisation potentials (7.29 and 8.24 eV) of *N,N*-dimethyl-2,7-diazatetracyclo[3.3.3.$0^{4,9}0^{8,11}$]undecane **8** and the appreciable splitting ΔE of the energy levels of the LEP of the nitrogen atoms (0.95 eV) were interpreted in terms of the interaction of the LEP of the nitrogen atoms through space ($n^- > n^+$) (the lone pairs are oriented at an angle of 70° within the undecane skeleton).[41]



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Non-empirical calculations in terms of the STO-3G basis set for 1,4-diazabicyclooctane **1** and two model molecules containing respectively one and two C–C bonds between the two nitrogen atoms indicate that two types of interaction are mainly responsible for the splitting of the two LEP orbitals—the first

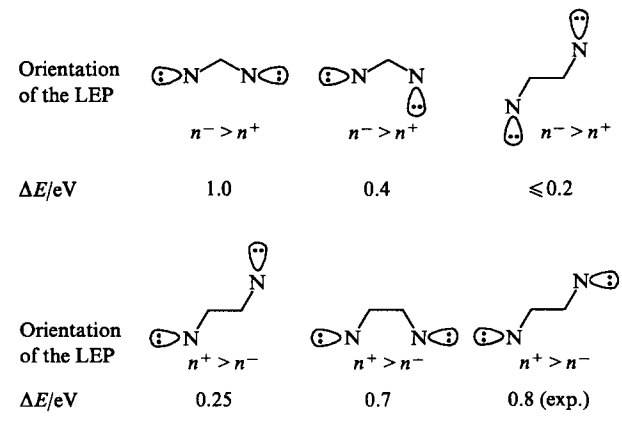


Figure 2. The splittings of the energy levels of the lone pairs in 1,3- and 1,4-diamines.[38]

type involves the interaction between the LEP nitrogen and the central C–C bond in the same N–C–C–N fragment, while the second involves the interaction between the neighbouring N–C bonds in different fragments.[40]

3. Oxygen- and sulfur-containing heterocycles

According to the symmetry of the immediate environment of the oxygen or sulfur atoms in saturated ethers and sulfides, their highest occupied nonbonding MO have a π-type symmetry (p_z-orbitals) (Table 1). A number of studies have been devoted to interaction through space and through σ-bonds in heterocyclic compounds containing at least two oxygen and sulfur atoms.[24,42–47]

Table 1. Vertical ionisation potentials of the LEP of oxygen- and sulfur-containing heterocycles.[42]

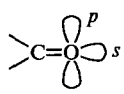
Compound	IP (*n*)/eV		ΔIP(*n*)/eV
1,3-Dioxolan **9**	10.10	10.65	0.55
2,2-Dimethyl-1,3-dioxolan **10**	9.71	10.20	0.49
Tetrahydropyran **11**	9.50		
1,3-Dioxane **12**	10.10	10.35	0.25
1,4-Dioxane **13**	9.43	10.65	1.22
Thiane **14**	8.45		
1,3-Dithiane **15**	8.54	8.95	0.41
1,4-Dithiane **16**	8.58	9.03	0.45
1,4-Thioxane **17**	8.67 (S)	10.0 (O)	

It follows from the analysis of the photoelectron spectra of 1,4-dioxane **13** and 1,4-dithiane **14** that the splitting of the highest occupied levels due to the interaction of the LEP of the oxygen and sulfur atoms is 1.22 and 0.45 eV respectively. The direct overlap of the p_z orbitals of the LEP in these molecules is impossible as they have the chair conformation, so that the interaction through σ-bonds is the main one. The greater splitting for 1,4-dioxane compared with 1,4-dithiane may be a consequence of the better energy correspondence between the LEP orbitals and the σ orbitals of the C–C bonds.

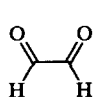
In 1,3-dioxane **12** and 1,3-dithiane **15**, which also have the chair conformation, there is a possibility of the direct overlap of the LEP of the heteroatoms, which is more effective in the case of 1,3-dithiane.[42] Calculations by the MNDO method confirmed that the interaction of the LEP of the sulfur atoms in the 1,3-dithiane is through space, whilst that in 1,4-dithiane is through σ-bonds.[47]

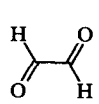
4. Dicarbonyl compounds

In dicarbonyl compounds, there is also a possibility of both types of interactions of the nonbonding *n* orbitals of the oxygen atoms.[17,33,48–60] In the description of the MO of the carbonyl group, taking into account its symmetry, two nonequivalent orbitals of the *p* and *s* types[48] or *p* and *sp* types[19,61] correspond to the LEP of oxygen (the energy of the *p*-type orbital is higher).



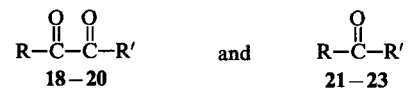
In the molecules containing two carbonyl groups, the interaction of the nonbonding *p*-type orbitals results in the splitting of the energy levels. Their order $n_A < n_S$ follows from quantum-chemical calculations for the *s-cis*- and *s-trans*-conformers of glyoxal on the assumption of ideal geometry.


s-cis


s-trans

The splitting ΔE for *s-cis*-glyoxal is 1.46 eV (EHM) or 2.96 eV (CNDO), whilst for *s-trans*-glyoxal it is 1.46 eV (EHM) or 3.27 eV (CNDO).[48] The experimental splitting ΔE is 1.46 eV.[33] The interaction through space in *s-cis*-glyoxal is insignificant as a consequence of the low value of the overlap integral (0.011) of the two *p*-type orbitals (EHM calculations). However, with decrease in the CCO bond angle, binding through space increases. The energy of the level *A* then increases and that of the level *S* hardly changes.

Similar effects have been discovered[50] in the analysis of the photoelectron spectra of the 1,2-diketones **18–20** and the corresponding ketones **21–23**.


18–20 and **21–23**

18, 21: R = R′ = cyclo-C_3H_5;
19, 22: R = cyclo-C_3H_5, R′ = Me;
20, 23: R = R′ = Me.

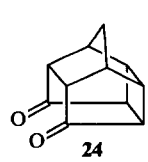
The intense low-energy peaks in the vibrational structure of the spectra of the three monocarbonyl compounds **21–23** are largely determined by the liberation of an electron from the localised *p* orbital of the oxygen LEP. Diffuse bands with higher energies are observed in the spectra of the 1,2-diketones **18–20**. The interaction of the nonbonding *n* orbitals of the oxygen atoms through σ-bonds leads to the splitting of the n_S and n_A levels amounting to ~2 eV (Table 2).

Table 2. Ionisation potentials of carbonyl compounds.[50]

Compound	IP/ eV		Assignment[a]
1,2-Dicyclopropylethane-1,2-dione **18**	9.09		n_S
	10.40	11–12	e_A, e_S and n_A
1-Cyclopropylpropane-1,2-dione **19**	9.33		n_S
	10.78	11.35	e_A, e_S and n_A
Diacetyl **20**	9.57		n_S
	11.41		n_A
Dicyclopropyl ketone **21**	9.28		n_O
	10.43	11.50	e_A, e_S
Cyclopropyl methyl ketone **22**	9.50		n_O
	10.62	11.40	e_A, e_S
Acetone **23**	9.71		n_O

[a] n_O is the nonbonding orbital of the oxygen LEP, e_S and e_A are the symmetrical and antisymmetrical orbitals of cyclopropane, and n_S and n_A are the symmetrical and antisymmetrical combinations of the nonbonding *p* orbitals of the oxygen atoms.

The photoelectron spectrum of pentacyclo-[5.4.0.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$]undecane-8,11-dione **24** indicates an appreciable splitting of the *n* levels of the oxygen LEP (0.55 eV).[60] The contribution to this splitting by the interaction of the two oxygen atoms through space is very low, since they are quite far apart (4.05 Å).[62,63] The interaction of the *n* orbitals of the oxygen LEP with the σ orbitals of the skeleton becomes more intense if the C–C bonds separating the carbonyl groups form part of a strained system (a three- or four-membered ring).[55,57]


24

Analysis of the first two ionisation bands in the photoelectron spectra of cyclohexane-1,4-dione and its derivatives **25**–**32** indicates an increase in the splitting between the n^+ and n^- combinations of the orbitals from 0.2 eV in the spectra of compound **25** to 0.6 eV in those of compounds **29** and **30** and to 0.9 eV in those of compound **26** (Fig. 3). This can be explained by the intensification of the n^-,σ-interaction on passing from compound **25** to compounds **29** and **30** and further to compound **26**, whereas the n^+,σ-interaction in these molecules remains almost constant.[57]

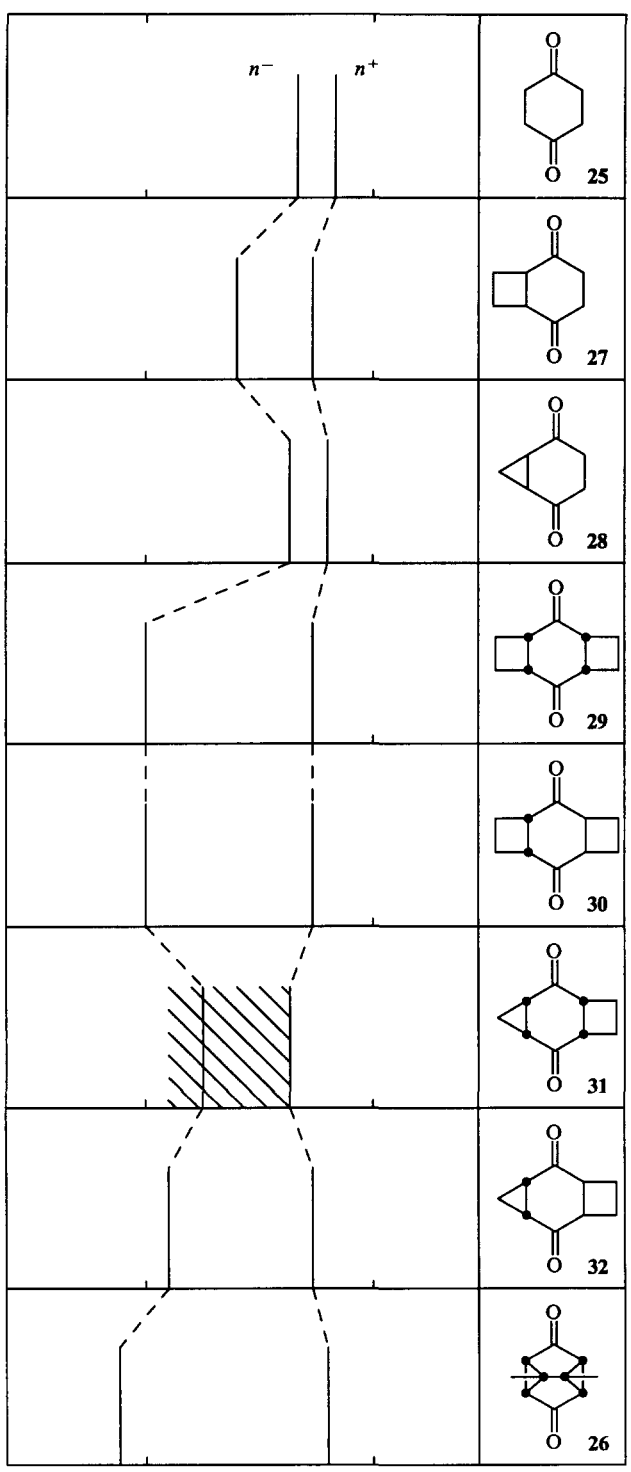


Figure 3. Diagram of the first two bands in the photoelectron spectra of compounds **25**–**32**.[57]

The study of the photoelectron spectra of a large series of α-, β-, γ-, and δ-dicarbonyl compounds demonstrated (the n^+ and n^- ionisation energies were calculated by the CNDO/S and CNDO/2 methods) that the most intense interaction through σ-bonds is observed in the α-dicarbonyl compounds ($\Delta IP = 1.5-3.1$ eV).[23] The extent of this interaction is independent of the dihedral angle between the planes of the carbonyl groups,[49] but diminishes rapidly with increase in the number of intervening CH_2 groups between the two carbonyl groups. The sequence of the energies of the nonbonding MO is determined by the assignment of the dicarbonyl compounds to two classes: compounds with coaxial carbonyl groups are assigned to the first class, whilst those with the noncoaxial groups are assigned to the second. Thus the parity rule, which holds for acyclic dicarbonyl compounds with noncoaxial carbonyl groups, breaks down for the cyclic compounds in which the carbonyl groups are coaxial (the C=O bonds are located on a single axis).[23] For example, the order of the levels is $n^+ > n^-$ for 2,2,4,4-tetramethylcyclobutane-1,3-dione **33** in which the LEP of the oxygen atoms interact through the four σ-bonds, whereas for tetramethyl-1,4-benzoquinone **34**, in which the LEP interaction is effected through five σ-bonds, the order of the levels is $n^- > n^+$, although, according to the parity rule, it should have been the opposite for these compounds. The opposite bond order, namely $n^- > n^+$, is also observed for derivatives of cyclohexane-1,4-dione. Since the carbonyl groups in all the symmetrical four- and six-membered cycloalkanediones are located in virtually one plane and are coaxial, their molecules have a centre of symmetry (Fig. 4).[57] In such compounds, the *p* orbital of the oxygen LEP interacts with the group σ orbital incorporating the two C–C bonds formed by the carbon atom of the carbonyl group. In contrast to the model proposed by Hoffmann,[20,21] in which the overlap of mainly the first lobe of the *p* orbital of the LEP of the heteroatom with one σ orbital of the C–C bond was considered, in this case the overlap of two lobes of the *p* orbital with the σ orbitals localised in two C–C bonds is postulated. Here the n^+ combination is antisymmetrical and the n^- combination is symmetrical relative to the centre of symmetry (in contrast to the plane of symmetry). Therefore the parity rule does not hold for compounds with coaxial carbonyl groups.

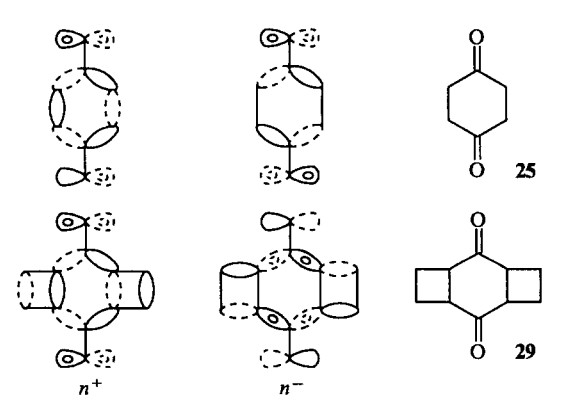


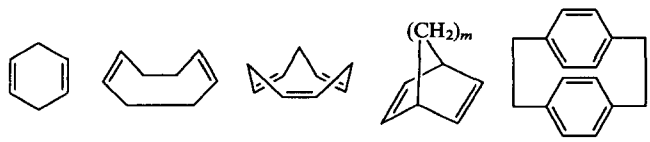
Figure 4. Schematic representation of the highest occupied MO (n^-, n^+) of compounds **25** and **29**. The double contour lines designate a higher electron density.[57]

Four singlet *n*, π* transitions are observed in the polarised UV spectrum of a single crystal of 2,2,4,4-tetramethylcyclobutane-1,3-dione **33** at a low temperature.[51,52] Theoretical analysis (EHM, CNDO/2, CNDO/S) confirmed that the interaction through σ-bonds is in fact the main cause of the greater splitting of the *n* orbitals of the oxygen LEP and of the occurrence of *n*, π* transitions.

5. Nonconjugated π-electron systems

In molecules containing π-electron systems (double or triple bonds, aromatic or heteroaromatic fragments) separated by a system of σ-bonds, both types of interactions considered are also manifested — through space and through σ-bonds.[22,25,27] The interactions through space in compounds of this type are divided into two types — homoconjugation [17,64] and spiroconjugation.[65]

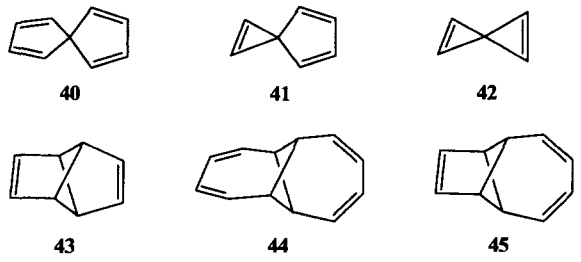
The homoconjugation effect can be demonstrated in relation to cyclohexa-1,4-diene **35**, cycloocta-1,5-diene **36**, cyclonona-1,4,7-triene **37**, [2.2.*m*]bicyclanes **38**, and [2.2]paracyclophane **39**.[22,27,66,67]



35 **36** **37** **38** **39**

The interaction through space predominates in norbornadiene **38** (m = 1).[66] In view of the presence of two symmetry planes (Fig. 5), the energy level corresponding to the symmetrical combination of the occupied π orbitals (*SS*) has a lower energy, while the energy level corresponding to the antisymmetrical combination (*SA*) has a higher energy. Similarly a level with a lower energy corresponds to the symmetrical combination of the unoccupied π* orbitals (*AS*) and one with a higher energy corresponds to the antisymmetrical combination (*AA*).

The spiroconjugation effect is manifested in molecules where the rings linked to one another contain unsaturated fragments located in mutually perpendicular planes (compounds **40–42**).[65,68–70]



40 **41** **42**

43 **44** **45**

Owing to the specific symmetry of these molecules, the interaction of the occupied (π) and unoccupied (π*) orbitals of the unsaturated fragments through space is mainly manifested. The group orbitals constituting a combination of the π(π*) orbitals of two unsaturated fragments have the a_2 and b_1 symmetries.[68] For compounds **40–42** having a spiro-centre, the interaction through σ-bonds is insignificant and the level b_1 lies below the level a_2. For compounds **43–45**, the interaction through the σ-bonds of the intervening four-membered ring is more significant and the opposite order of the energy levels obtains ($b_1 > a_2$).[68,70] These differences determine the characteristic features of the photoelectron and UV spectra of the spiro-compounds.[65,69,70] Thus the splitting of the above levels of the spiro[4.4]nonatetraene **40** is 1.23 eV according to photoelectron and UV spectroscopic data.[65]

In order to estimate the relative contributions of the interactions through space and through σ-bonds, Table 3 presents the experimental π-ionisation energies $IP_{v,1}$ and $IP_{v,2}$ of the bicyclic dienes **38** as a function of the number of methylene groups (m): Dewar benzene (m = 0), norbornadiene (m = 1), bicyclco[2.2.2]octadiene (m = 2), bicyclo[3.2.2]nona-6,8-diene (m = 3), bicyclo[4.2.2]deca-7,9-diene (m = 4), and the hypothetical hydrocarbon with $m = \infty$. The last system is modelled by the planar cyclohexa-1,4-diene **35**. The splitting ΔIP_v should decrease monotonically with increase in the dihedral angle between the planes of the double bonds. However, it passes through a minimum in the case of compound **38** (m = 3) and then again increases to 1.0 eV for the hypothetical hydrocarbon ($m = \infty$). This indicates the mutual cancelling of the interactions through space and through σ-bonds. In compounds with m = 1 and 2, the interaction through space between the π_a and π_b orbitals predominates, whereas in compounds with m = 3, 4, or ∞ the interaction through σ-bonds predominates.

The effective unit connecting the two π-electron systems in a structure of the type $\pi_1-CH_2-\pi_2$ is a single methylene group. For interaction to occur, it is approached by the π-symmetrical combinations of the σ and σ* orbitals (pseudo-π orbitals) localised on the C–H bonds. The interaction diagram[21] illustrates the result of the mixing of the σ and σ* orbitals with the two p orbitals of the trimethylene radical (Fig. 6). The antisymmetrical combination of the p orbitals cannot then become mixed with the pseudo-π orbitals of the CH_2 group for symmetry reasons. In four-membered cyclic systems, the interaction between the endocyclic n_0 or π orbitals also takes place via the pseudo-π orbitals.[26,71,72]

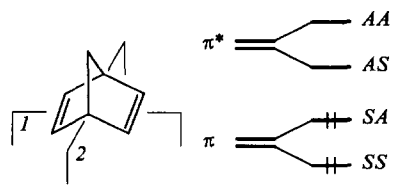


Figure 5. The electronic levels of norbornadiene **38** (m = 1) before and after interaction through space (the designations *S* and *A* refer to the mirror planes *1* and *2* shown on the left).[66]

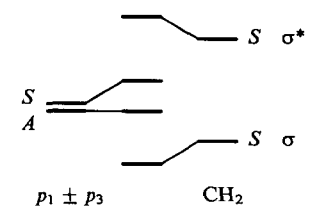


Figure 6. Diagram of the orbital interactions for the trimethylene radical.[21]

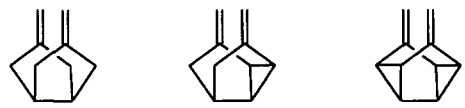
Table 3. Ionisation potentials (eV) of the bicyclic dienes **38** and cyclohexa-1,4-diene **35**.[22]

Ionisation band	Ionisation energy	*m*						**35**
		0	1	2	3	4	∞	
1	$IP_{v,1}$	9.4	8.7	8.8	9.0	8.9	8.6	8.8
2	$IP_{v,2}$	9.7	9.5	9.4	9.2	9.3	9.6	9.8
	ΔIP	0.3	0.8	0.6	0.2	0.3	1.0	1.0

The interaction through σ-bonds is manifested most strikingly in the planar cyclohexa-1,4-diene.[66] In this compound, the π orbitals of the two double bonds overlap with the group σ orbitals (incorporating the two C–H bonds of the methylene groups), which are suitable on symmetry grounds. As a result of the interaction of the π orbitals of the double bonds through the two methylene groups, the opposite order of the splitting of the *SS* and *SA* levels is observed (*SS* > *SA*) compared with that in norbornadiene, where there is interaction through space (*SS* < *SA*, Fig. 5). Quantum-chemical calculations (EHM) for the planar model of cyclohexa-1,4-diene confirmed this order of the levels with a splitting of 0.65 eV (the experimental value is 1.0 eV).[66]

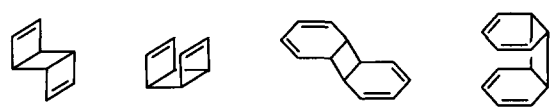
The dependence of the interaction through space and through σ-bonds on distance and the mutual orientation of the basis orbitals has been examined[22] for the model compound **35**. In the boat conformer of cycloocta-1,5-diene **36**, the interaction through space should be considerable. However, the experimental difference between the two π-bonds is only 0.2 eV;[66] on the other hand, the calculated splitting is 1.67 eV with the levels arranged in the order *SS* < *SA*. This is caused by the superposition on the interaction through space in compound **36** of a further interaction of the π orbitals with the *SS* combination of the C(3)–C(4) and C(7)–C(8) σ-bonds which are ideally oriented for the interaction of the two π-electron systems through σ-bonds. This destabilises the π-*SS* combination. When account is taken of this fact, the calculated splitting diminishes to 0.48 eV. In compound **36** in the chair conformation, there is no interaction through space and the interaction through σ-bonds predominates.

According to photoelectron and transmission electronic spectroscopic data, which have been confirmed by quantum-chemical calculations, the interaction of two double bonds separated by a σ-skeleton becomes more marked in the series of compounds **46**–**48**.[54,55] The splitting of the energies of the π^+ and π^- orbitals increases on passing from compound **46** to compounds **47** and **48** (0.2 < 0.4 < 1.26 eV respectively). The interaction through σ-bonds, which intensifies with increase in the rigidity of the σ-skeleton, predominates in these compounds[58,59] and leads to the inverted order of the π orbitals ($\pi^- < \pi^+$).



46 **47** **48**

In the series of cyclic hydrocarbons **49**–**52**, the splitting (0.6–1.0 eV) between the π-bonds is greater for the *anti*-isomers of compounds **49** and **51**, which indicates the predominance of the interaction through σ-bonds.[27]

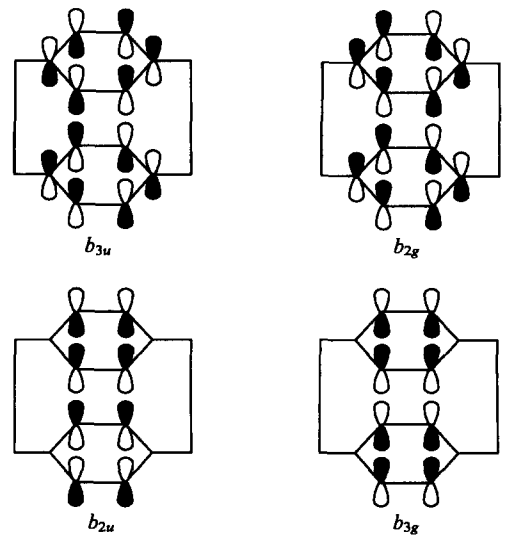


49 **50** **51** **52**

Compound	**49**	**50**	**51**	**52**
ΔIP/eV	1.0	0.3	0.67	0.46

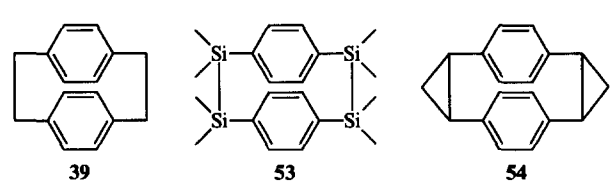
According to electronic, spectroscopic, and Penning ionisation data as well as the results of non-empirical calculations, the differences between the symmetrical and antisymmetrical π orbitals in the molecules of norbornadiene **38** (*m* = 1) and 1,4-diazabicyclo[2.2.2]octane **1** are due to the interaction through space or through σ-bonds.[73] In norbornadiene, where the interaction through space is manifested, the π_S MO is looser than π_A and is characterised by a greater probability of ionisation on electrophilic attack by helium atoms in the metastable excited state. On the other hand, in the case of 1,4-diazabicyclo[2.2.2]octane the n_A MO is looser than n_S owing to the strong interaction through σ-bonds and is distinguished by a greater probability of ionisation.

Orbital interactions have been examined in [2.2]paracyclophane **39** and its analogues, in which two parallel aromatic rings interact through space and through the system of σ-bonds.[67,74] The four $e_{1g}(\pi)$-orbitals of the two benzene rings in compound **39** form the four linear combinations b_{3u}, b_{2g}, b_{2u}, and b_{3g}.



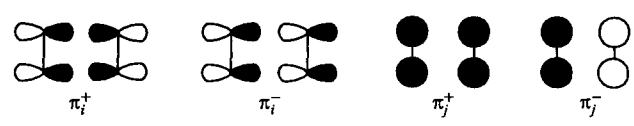
The b_{2g} and b_{3g} combinations, which are antisymmetrical relative to the plane separating the parallel rings, cannot interact with the σ orbitals of the bridging CH_2-CH_2 fragments. The overlap integral between the b_{2u} combinations and the σ orbitals is in fact zero. Their splitting (~1.5 eV) is caused by the interactions through space.[22] Only the linear b_{3u} combination can be effectively mixed with the above σ orbitals (interaction through σ-bonds). Its energy depends significantly on the nature of the bridging fragment.

On passing from the cyclophane **39** to its analogues **53** and **54**, the energy of the σ orbitals of the bridge connecting the benzene rings increases.[73,74] The b_{3u} ionisation energy therefore shifts towards lower values. The opposite shift is observed in *exo*-octafluoro[2.2]paracyclophane as a consequence of the decrease in the energy of the CF_2-CF_2 fragment.[22,27]



39 **53** **54**

As a consequence of the cylindrical symmetry of the π-system of the triple bond, in alka-α,ω-diynes and their analogues, the interaction through space can occur for different orientations of the ethynyl groups.[27] When the two triple bonds are in the same plane, two sets of bonding and antibonding linear combinations of the two in-plane (π_i) and the two out-of-plane (π_j) π orbitals are formed.



For distances between the C≡C bonds ranging from 2.5 to 3.5 Å, small and large splittings may be expected for linear combinations of π_j and π_i respectively. Photoelectron spectroscopic data for the cycloalkanediynes **55–59** indicate a strong dependence of the splitting of the energy levels corresponding to the π_i combinations (Fig. 7) on the distance between the triple bonds.[76]

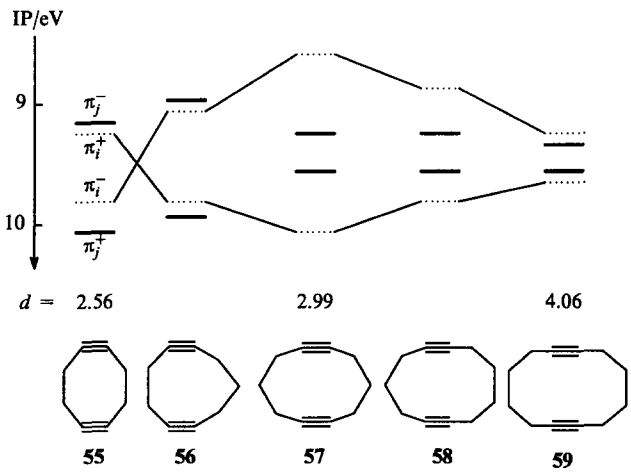


Figure 7. The ionisation potentials in the photoelectron spectra of compounds **55–59** as a function of the average distance (*d*) between the triple bonds. The continuous lines indicate the out-of-plane π_j MO and the dashed lines indicate the in-plane π_i MO.

In the case of the in-plane π MO of the two C≡C groups, separated by several σ-bonds, the interaction through space in compounds **55–59** stabilises the bonding (π_i^+) and destabilises the antibonding (π_i^-) linear combinations which have different symmetries relative to the *xz* planes (Fig. 8*b*). The interaction of

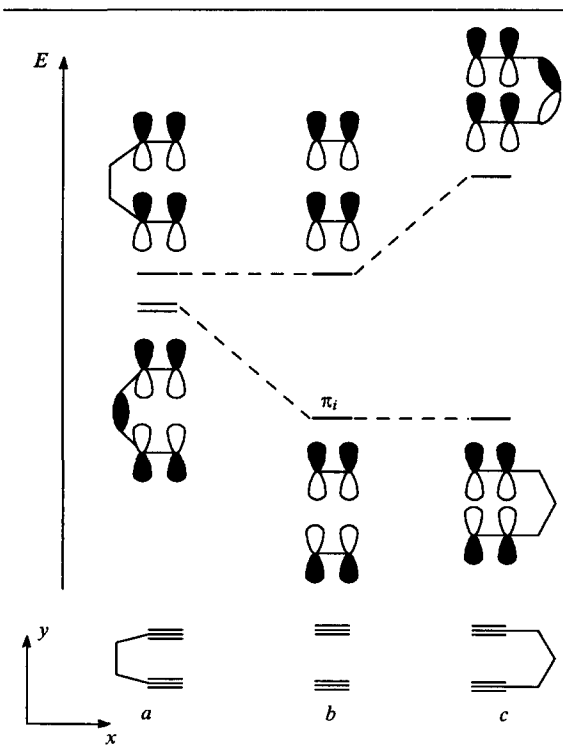
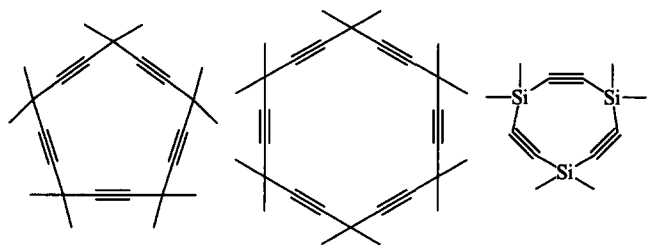


Figure 8. Interaction of the in-plane π MO of the two acetylene fragments in hexa-1,5-diyne **60** (*a*) and hepta-1,6-diyne **61** (*c*) with the σ-skeleton.[27]

the π-system of hexa-1,5-diyne **60** with the σ orbital of the CH_2-CH_2 fragment, symmetrical relative to the *xz* plane, destabilises the π_i^+ energy level but does not alter the energy of the π_i^- orbital (Fig. 8*a*). The splitting of the levels caused by the interaction through space diminishes correspondingly.

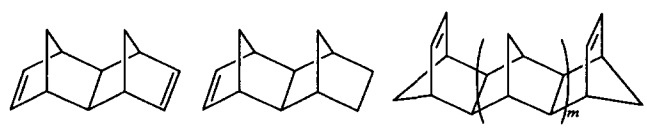
The antisymmetrical σ orbital of the trimethylene chain in hepta-1,6-diyne **61** interacts mainly with the π_i^- orbital, increasing its energy (Fig. 8*c*). In this case, the interactions through space and through σ-bonds increase the splitting of the levels. Thus the interaction of the π_i^+ and π_i^- combinations with the σ-skeleton of the methylene chain depends on the number of CH_2 groups: an even number diminishes the splitting caused by the interaction through space, while an odd number increases it.

The relative contributions of the interactions through space and through σ-bonds depend also on the energy of the σ-skeleton. Thus, in the study of the orbital interactions in compounds **62–64**, stronger interactions were observed for hexamethylcyclotrisilethyne **64**, which has higher [energy] σ orbitals than the carbon analogues **62** and **63**. In perfluorocycloalkadiynes with lower energy σ orbitals, the contribution of the π,σ interaction is not high.[27] Thus the homoconjugation of the triple bonds predominates in the pericyclynes **62–64**.[27,77] Photoelectron and transmission electroscopic data indicate a weak homoconjugation in compounds **62** and **63** in the cationic and anionic states. A similar effect has also been observed for compound **64**.[77]



62 **63** **64**

Hoffmann's model, considered above, has been applied mainly to the analysis of the electronic structures of compounds containing three or less intervening σ-bonds.[21,29] Paddon-Row[25,32,78–85] investigated in detail the dependence of the interaction of the π and *n* orbitals through *m* σ-bonds on the value of *m* for compounds with $m \geqslant 3$ and on the mutual orientation of the σ-bonds. In contrast to Hoffmann's model, in his initial approach, Paddon-Row examined the interactions of the π or *n* orbitals only with occupied σ orbitals. Here account was taken of the increase in the energies of both the $\pi^+(n^+)$ and $\pi^-(n^-)$ orbital combinations and the initial $\pi(n)$ orbitals relative to model compounds in interactions with σ orbitals. For an even number *m*, the energy of the $\pi^-(n^-)$ combination increases by a significantly greater amount than for $\pi^+(n^+)$.[25,32] The application of this model to the description of the orbital interactions through four σ-bonds is demonstrated in Fig. 9. An increase in the energy of the basis π orbital in the hex-1-ene molecule by an amount *x* takes place as a result of its mixing with the highest occupied σ MO (here there are no limitations as regards symmetry). Since the highest of the occupied σ orbitals in antisymmetrical, it interacts with the π^- combination, while the symmetrical σ orbital, having a lower energy, interacts with the π^+ combination.



65 **66** **67**

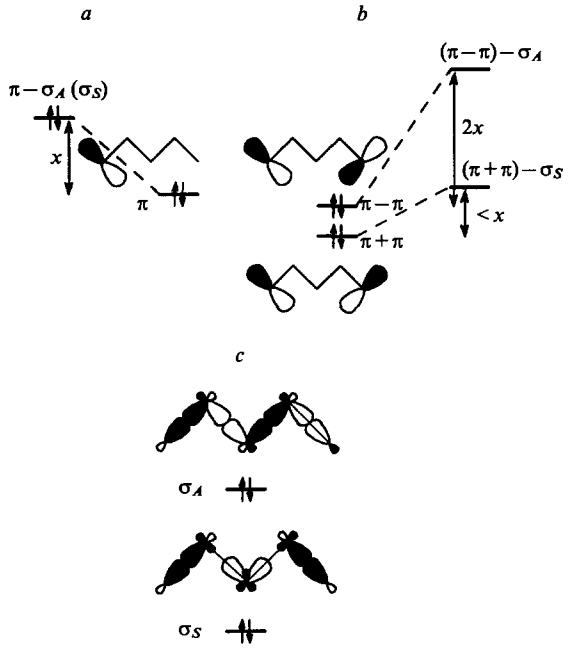


Figure 9. Schematic representation of the σ,π mixing in the molecules of compounds **65** and **66**:[32] (*a*) mixing of the π and highest σ MO: (*b*) mixing of the $\pi^+ - \pi$ combinations with the highest σ MO; (*c*) the π orbital and the two highest σ-type orbitals (*S* and *A*).

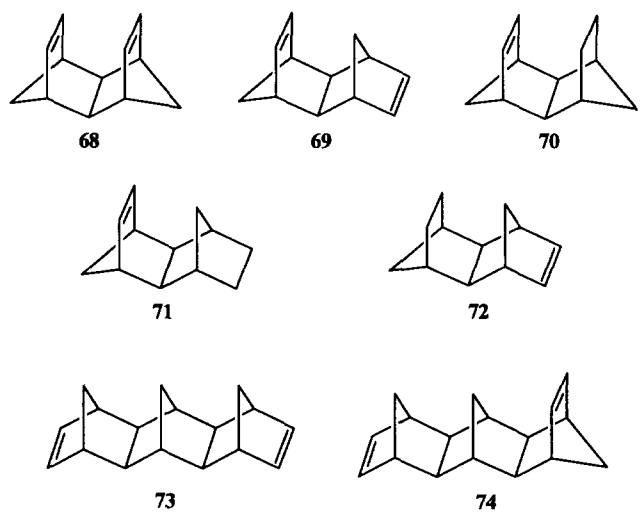
In compounds **67** (m = 1), the energy of the π^- combination increases by an amount $2x$ on mixing with the antisymmetrical highest occupied σ MO. In contrast to this, the energy of the π^+ combination increases only slightly ($\Delta E < x$) on mixing with the symmetrical occupied σ MO having a lower energy. This difference is due to two factors: the energies of the π^- and σ_A orbitals are closer and their overlap is greater than in the interaction of the π^+ and σ_S orbitals.

Analysis of the photoelectron spectrum of the hydrocarbon **67** (m = 1) confirmed the above scheme. The first ionisation π band is wide, which indicates σ,π-mixing. The fairly sharp second band indicates the ionisation of an electron from the more localised π MO.

The orbital interactions through space and through four and more σ-bonds have been examined in relation to the photoelectron spectra of the hydrocarbons **65**, **66**, and **68–72**, the ionisation potentials of which are presented in Table 4. The higher value of ΔIP(π) for compound **65** (0.87 eV) is a consequence of the interactions through four σ-bonds,[32] while the higher values of ΔIP for compound **68** (1.26 eV) is caused by the overall contribution of the interactions through space and through σ-bonds. The value of ΔIP(π) for compound **73** (0.32 eV) demonstrates the appreciable manifestation of the interactions through six σ-bonds.[25]

Table 4. Vertical ionisation potentials (eV) of dimethanonaphthalenes.[25]

Compound	IP(π)	ΔIP	Assignment
65	8.48	0.87	π^-
	9.35		π^+
66	8.85		π
68	8.08	1.26	π^-
	9.34		π^+
69	8.46	0.44	π^-
	8.90		π^+
70	8.60		π
71	8.65		π
72	8.78		π
73	8.58	0.32	π^-
	8.90		π^+



The decrease in the extent of the π-orbital interactions through four bonds in the series **65** (0.87 eV), **69** (0.44 eV) agrees with the rule governing the dependence of the orbital interactions on the geometry of the σ-skeleton: for the same values of m, the interaction in the molecule with a *trans*-orientation of the σ-bonds is a maximum (the *trans*-rule). Indeed the σ-bonds in compound **65** are in the *trans, trans*-positions, whilst in compound **69** they are in the *cis, trans*-positions. However, the *trans*-rule clearly breaks down on passing to compounds where there is interaction through six σ-bonds. ΔIP for compounds **73**, **74**, and **67** (m = 1) increases in the sequence 0.32 < 0.38 < 0.52 eV.[79] This trend has been confirmed by quantum-chemical calculations and indicates the occurrence of an additional orbital interaction, which is manifested to the maximum extent in compound **67**, to a lesser extent in compound **74**, and is virtually absent in compound **73**. In the presence of such additional interaction, called the laticyclic hyperconjugation, the π MO of the two vinyl groups are mixed with the group orbital of the central CH_2 bridge, which embraces the two C–H bonds.[81,83,86,87] In contrast to the pericyclic hyperconjugation of the planar cyclohexa-1,4-diene mentioned earlier, in these compounds the pseudo-π orbital indicated and the orbitals of the double bonds are located virtually in one plane (Fig. 9). (In the planar cyclohexa-1,4-diene, the pseudo-π orbital and the π orbitals of the vinyl groups are located at right angles to the molecular plane.[21]) A direct estimate of the extent of the π-interaction in compound **67** via the intervening CH_2 group has been obtained from the results of non-empirical calculations.[81]

In subsequent studies,[80,82] similar interactions were also examined taking into account the involvement of aromatic rings in them. Laticyclic hyperconjugation—interaction through the so called 'ribbons'—is also observed in the series of polycyclic hydrocarbons with increase in the number of intermediate cyclic units containing CH_2 groups with the orientation indicated (the orbital schemes are illustrated in Fig. 10).[81,86,87] This results in effective delocalisation of the positively charged 'holes' in the radical-cation of the nonconjugated diene containing two double bonds at a distance of 6 Å.[88]

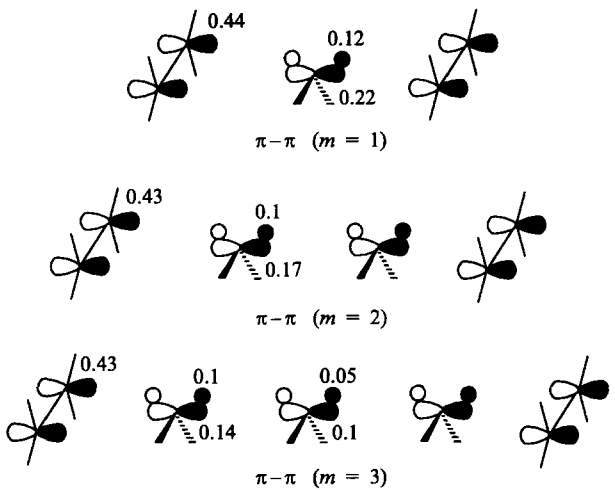
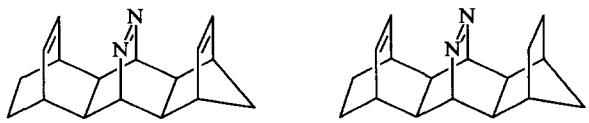


Figure 10. The forms of the orbitals and the coefficients of the π,π interaction calculated by the non-empirical STO-3G method for compound **67** (m = 1–3).[81]

In an experimental study of the electron affinities of compounds **75** and **76**, it was observed that laticyclic conjugation involving the π* orbitals takes place in compound **75**.[78] As the inductive effect and the interaction through σ-bonds in the norbornene fragments of compounds **75** and **76** are identical, the appreciable difference between the ionisation energies (9.02 and 8.40 eV in compounds **76** and **75** respectively) indicates the existence of laticyclic [2 + 2 + 2]-conjugation in compound **75**, which contains three parallel π-bonds.[89,90]



75 **76**

The mechanisms of the interactions under discussion have been analysed[30] on the basis of data derived from semiempirical quantum-chemical calculations in which localised MO were used. With the aid of nonempirical quantum-chemical calculations in terms of different basis sets, a study has been made of the dependence of the splitting of occupied (π^+,π^-) and unoccupied (π^{+*},π^{-*}) orbitals of the vinyl fragments (ΔE) on the number of intervening σ-bonds (m) and their mutual orientation.[91–93] The exponential dependence obtained of $(\Delta E)^2$ on m permits a quantitative prediction of the experimental splittings of the levels and of the rates of electron transfer. The contributions of individual fragments in the transmission of the interaction between π(π*) orbitals have been calculated for similar structures in the analysis of orbitals localised on individual bonds (nature bond orbitals). A more effective transmission of interaction through intervening C–Si bonds has been predicted.

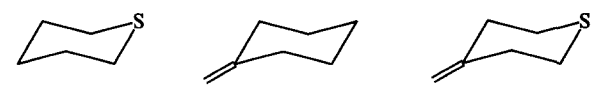
III. Interactions between nonequivalent substituents

Interactions through space and through σ-bonds between nonequivalent substituents are divided into two main types: interaction of occupied π(n) orbitals of two substituents and interaction of occupied n(π) orbitals of a donor (D) with the unoccupied π* or σ* orbitals of the acceptor (A). Interactions of the first type are most strikingly manifested in the analysis of the photoelectron spectra and those of the second type in the analysis of the electronic absorption and emission spectra. In the second case, there is a possibility not only of a change in the energies of the electronic transitions characteristic of the donor and acceptor but also of the manifestation of new transitions accompanied by a significant intramolecular charge transfer (ICT) from the donor to the acceptor.

1. Photoelectron spectra

In the photoelectron spectra of aza-, methyleneaza-, thia-, and methylenethia-cycloalkanones as well as oxygen derivatives, the interaction of the occupied π(n) orbitals of two substituents gives rise to changes in the ionisation potentials referring to the LEP of the heteroatoms (n_S, n_N, n_O) and the π orbitals of the unsaturated fragment. This leads to an increase in the distance between the corresponding energy levels.[94–101]

The increase in the energy splitting of the levels assigned to the n and π orbitals, relative to the difference between their energies in the corresponding monofunctional cyclic compounds (for example, 0.06, 0.29, and 0.35 eV for compounds **14**, **81**, and **82** respectively[96]) is a characteristic feature of the interactions indicated (Fig. 11).



14 **81** **82**

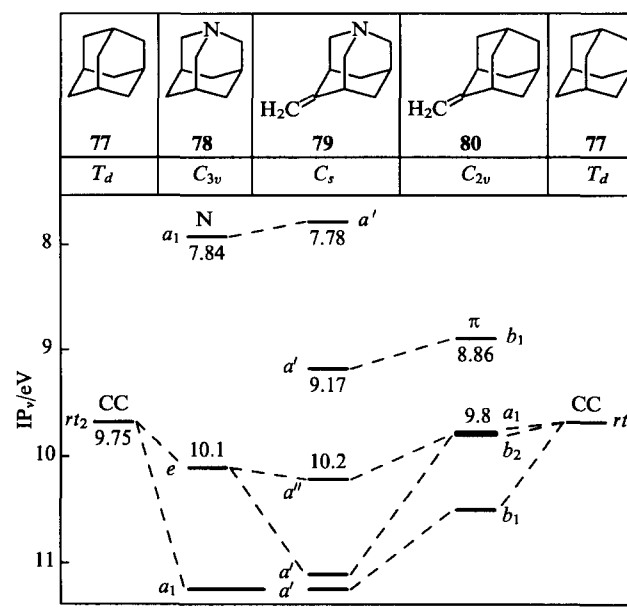
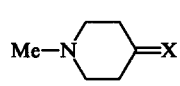


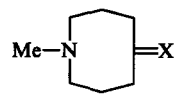
Figure 11. The highest occupied energy levels of compounds **77–80** according to photoelectron spectroscopic data.[95]

The energy splitting of the levels (ΔE = 0.47 eV) in the case of compound **79** is much smaller than in 1,4-diazabicyclooctane (ΔE = 2.1 eV [35]) as a consequence of the greater symmetry of the latter (D_{3h}). For adamantane **79** and thiacyclohexane **81** derivatives, containing an exocyclic double bond or a carbonyl group and having the chair conformation, the interaction through σ-bonds predominates.[94–96] For the analogous derivatives of thiaperhydronaphthalene, a weak interaction through σ-bonds takes place for the *trans,trans*-orientation of the five σ-bonds, such interaction being absent for the *trans,cis*-orientation,[96] which is consistent with Hoffmann's ideas.[20,21]

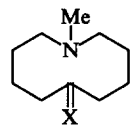
In the azacycloalkanones **83–86** or methyleneazacycloalkanones **87–90**, the increase in the splitting of the levels of the n_N nitrogen orbital and the π orbital of the carbonyl group or the double bond compared with that in the cyclic monofunctional compounds is due to the transannular interaction.[97]



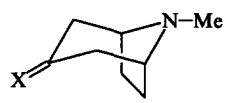
83, 87



84, 88



85, 89

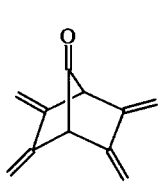


86, 90

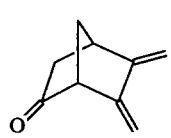
83–86: X = O;
87–90: X = CH_2.

The manifestation of the appreciable n,π interactions in the eight-membered rings of compounds **84** and **88** has been explained by the mutual approach in space of the corresponding structural groups. In 1-azacyclodecan-6-one **85**, n,π interaction also occurs, whereas in 6-methylene-1-azacyclodecane **89** it is not observed, which can be accounted for by the difference between the conformations of these molecules.[97] Furthermore, interactions of the n orbitals of the nitrogen atom and the oxygen atom of the carbonyl group have been observed for compounds **83–86**.[97]

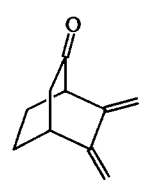
Comparison of the photoelectron spectroscopic data for 2,3,5,6-tetramethylidenebicyclo[2.2.1]heptan-7-one **91**, 5,6-dimethylidenebicyclo[2.2.1]heptan-2-one **92**, 5,6-dimethylidenebicyclo[2.2.2]octan-2-one **93**, and 5,6,7,8-tetramethylidenebicyclo-[2.2.2]octan-2-one **94** with the spectra of other β,γ-unsubstituted ketones and related alkenes as well as the results of nonempirical calculations (STO-3G) for compounds **91–94** confirmed that the appreciable interactions of the n_O orbital of the oxygen LEP and the π orbitals of the double bonds are largely effected through σ-bonds.[98]



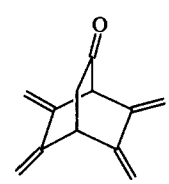
91



92

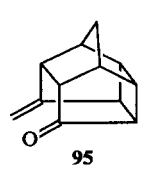


93

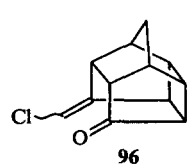


94

In the photoelectron spectra of paracyclophanes containing π-donor and π-acceptor substituents in the aromatic rings, the splitting of the first ionisation bands (~0.3 eV) as a consequence of the interaction of the π orbitals through space is observed.[98] In the study of the photoelectron spectra of 8,11-disubstituted pentacycloundecanes **95** and **96**, the splitting of the peaks (0.4–0.6 eV), caused by the interaction of the two unsaturated fragments through space, has also been observed.[56]



95



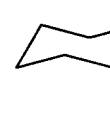
96

In the molecules of ethanolamine and its derivatives containing the O–C–C–N group, there is a possibility of interaction of the LEP of the nitrogen and oxygen atoms with the neighbouring σ-bonds of the skeleton or their interaction through σ-bonds is possible for certain conformations.[100,101] This entails the transfer of electron density from the less electronegative nitrogen atom to the more electronegative oxygen atom. The same effect has been observed in the study of acyclic and cyclic organosilicon compounds containing the Si–O–C–C–N fragment. In these compounds, the basicity of the nitrogen atom is appreciably reduced regardless of the presence or absence of the transannular Si ← N.[102]

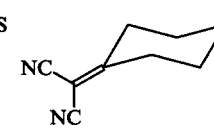
Similar phenomena have been observed also in other X–C–C–Y systems, for example in N–C–C–Cl and S–C–C–Cl, in which the chlorine atom is distinguished by a high mobility (in the O–C–C–Cl system, the chlorine atom is chemically inert), whereas in the X–C–Y systems (for example, in α-chloroethers) electron density is transferred from the more electronegative heteroatom (oxygen) to the less electronegative heteroatom (chlorine).

2. Absorption and emission spectra

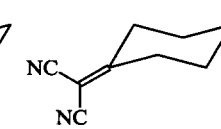
UV spectroscopy has been used widely in the study of interactions through space and through σ-bonds in molecules containing an explicit donor and acceptor separated by σ-bonds.[95,103–108] A new UV band (the ICT band) appears in the absorption spectra of bifunctional compounds with fixed geometries in which the donor and acceptor are separated by three or five σ-bonds. The band is due to charge transfer from an occupied orbital of the donor (nitrogen, sulfur, etc.) to the unoccupied π* orbital of the acceptor [C=C, C=O, $C=C(CN)_2$, $C=CHCO_2R$, $C=C(CN)CO_2R$].[107]



14 (λ = 228 nm)



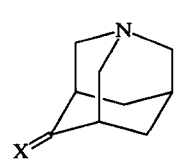
97 (λ = 235 nm)



98 (λ = 230 and 294 nm)

In our view, this transition can take place with a fairly high probability both on partial overlap of the above two orbitals in space and when they are mixed with the occupied (σ) and unoccupied (σ*) orbitals of the intervening system. The charge transfer between the structural groups (D and A) separated in space has been confirmed by the higher dipole moments of these molecules in the excited state (10.5–23.0 D).[104,108]

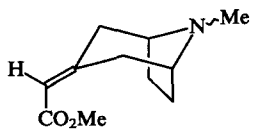
As a consequence of the large distance between the nitrogen atom and the electron-accepting substituent ($C=CH_2$, C=O) and also the unfavourable mutual orientation of the LEP of nitrogen and the π* orbital of the acceptor, in rigid bicyclic systems (derivatives of azaadamantane) direct overlap (through space) is impossible.[94,95,104,106,108] An ICT band has been observed in the UV absorption and emission spectra of compounds **79** and **99** in solutions (at 220 and 241 nm for compounds **79** and **99** respectively); it has a very weak vibrational structure (even in the gas phase).[95,104] It was assigned to the transition from the orbital embracing mainly the nitrogen LEP to the antibonding π* orbital of the $C=CH_2$ or C=O group. Similar ICT bands in the range 280–330 nm (ε ≃ 4500) have been observed for the derivatives of azaadamantane containing the electron-accepting groups $C=CHCO_2R$ (λ = 275 nm), $C=C(CN)CO_2R$ (λ = 316 nm), and $C=C(CN)_2$ (λ = 317 nm). Similar effects have been noted also in the analysis of the UV spectra of nitroazaadamantanes.[109]



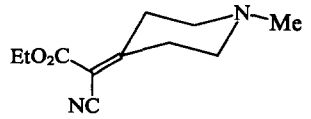
X = CH_2 (**79**), X = O (**99**)

The spectrum of compound **100**, in which the nitrogen atom is separated from the $MeO_2CCH=C$ group by three σ-bonds, also contains an ICT band (at 250 nm).[108] This molecule has a

geometry which is consistent with all the necessary conditions for the mutual orientation of the nitrogen LEP and the σ-bonds suitable for the occurrence of the interactions under consideration.[20,21,30,31] An ICT band is absent from the spectrum of compound **101**, the conformation of which is inconsistent with the above conditions.

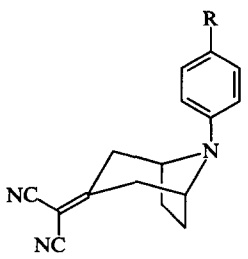


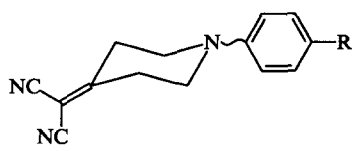
100



101

The influence of the conformation on the extent of the interaction through σ-bonds has been studied in relation to compounds **102**–**105** containing donor and acceptor centres.[110]





102 (R = H), **103** (R = OMe) **104** (R = H), **105** (R = OMe)

In compound **102**, the phenyl group occupies an axial position relative to the piperidine rings, which leads to an antiparallel orientation of the nitrogen LEP and of the central C–C bond. This conformation is retained also in solution in the solid phase (according to X-ray diffraction data). The spectrum of compound **102** contains an ICT band, the intensity of which hardly changes with decrease in temperature (Table 5).

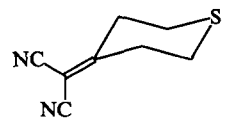
Table 5. The ICT bands in the spectra of compounds **102**–**105** (293 K, solvent — CH_2Cl_2).[110]

Compound	λ_{CT}/ nm	ε/litre mol^{-1} cm^{-1}
102	360	6100
103	378	5100
104	352	3065
105	368	2130

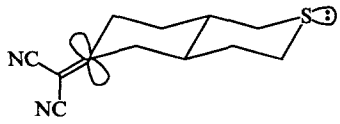
Similar results were also obtained in the study of the structural and spectroscopic characteristics of compound **103**. The spectrum of compound **104** likewise contains an ICT band, but its intensity is appreciably lower, increasing significantly with decrease in temperature. This feature of the compound can be explained by the existence in solution of an equilibrium between conformers with axial and equatorial disposition of the phenyl group, although in the solid phase compound **104** has only one (axial) conformation.[110] In the spectrum of compound **105**, the intensity of the ICT band is lowest and equilibrium between the conformers is observed, but the relative content of the axial conformer is low (in the crystalline state, this compound exists in the equatorial conformation). According to X-ray diffraction data, the length of the central C–C bond in compound **102** is much greater (1.559 Å) than in compound **105** (1.526–1.529 Å).

In compound **98**, having the chair conformation, the mutual orientation of the LEP of the sulfur atom and the C–C π-bonds is favourable for their interaction. An ICT band is observed in the spectrum of compound **98** at 294 nm (ε = 2860).[107]

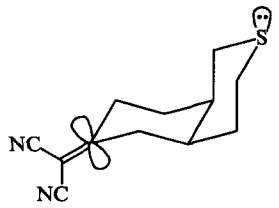
For the fixed *trans*-orientation of the bicyclic compound **106a**, an ICT band is also observed in the spectrum of the latter (at 270 nm), indicating the interaction of the sulfur LEP with the π-acceptor through five σ-bonds. For the *cis*-orientation in compound **106b**,[107,108] there is no such interaction, in conformity with Hoffmann's requirement that the σ-bonds must have the *trans,trans*-orientation.



98

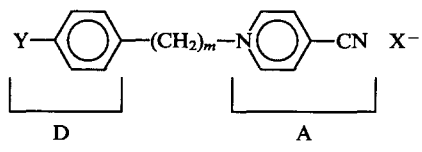


106a



106b

The band due to the intramolecular charge transfer between the aromatic fragment (the donor D) and the pyridinium cation (the acceptor A) is observed in the electronic spectra of compounds **107** having the general formula.[111–113]



107

m = 1–4, Y — electron-donor substituents.

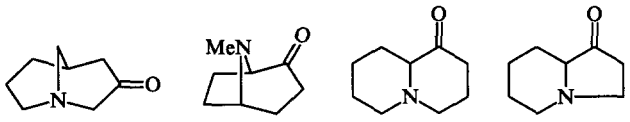
The transition energy is determined by the difference between the π and π* energy levels of the donor and acceptor. Accordingly the length of the methylene chain has little influence on the position of the band but does have a significant effect on its intensity.[111] For certain conformations of compound **107** (m = 1), there is a possibility of a direct overlap of the π orbitals of the donor and the acceptor.

The *trans*- and *gauche*-conformations are believed to be the main ones in compound **107** (m = 2). They are described by the angle φ (rotation about the central C–C bond). For $\varphi > 60°$, only the interaction through σ-bonds takes place, whilst for $\varphi < 60°$ there is in addition also direct π,π overlap due to the interaction through space. The interaction through σ-bonds depends on the overlap of the π orbitals of the donor and the π* orbitals of the acceptor with the σ and σ* orbitals of the intervening C–C bond. The intensity of the ICT band is then determined by their mutual orientation and varies from 225 litre mol^{-1} cm^{-1} ($\varphi \sim 60°$) to 1715 litre mol^{-1} cm^{-1} ($\varphi \sim 144°$).

Quantum-chemical calculations have made it possible to estimate the extent of the interaction of the LEP of the nitrogen atom and the carbonyl oxygen atom with the occupied and unoccupied σ and σ* orbitals of the intervening C–C bond and also with the π orbitals of the carbonyl group in α-aminoketones containing the N–CH_2–C=O group.[105,114,115] It was established at the same time that the interactions under consideration depend on the mutual orientation of the functional groups. The conformations of the molecules of these compounds are specified by the angles φ and θ ($\varphi = 0$, if the C–N bond eclipses C=O and $\theta = 0$ if the nitrogen LEP eclipses the C–C bond).[105]



The interaction through σ-bonds is a maximum in the (φ, 0) and (φ, 180) conformations, whereupon there is maximum overlap between the orbitals of the nitrogen and oxygen LEP and of the adjoining σ-bond. As a consequence of the manifestation of the above interactions, the band due to the $n \rightarrow \pi^*$ transition at 290 nm in the UV absorption spectra of unsaturated cyclic ketones shifts to the region 300–335 nm in the spectra of the cyclic α-aminocarbonyl compounds **108–111** (Table 6).[105]



108 **109** **110** **111**

Table 6. Spectroscopic parameters for certain α-aminoketones with a fixed conformation.[105]

Compound[a]	φ/deg	θ/deg	Solvent	λ/nm (ε)
108	160	165	Hexane	330 (55)
109	180	330	Ethanol	314 (68)
110	150	300	Isooctane	314 (48)
111	170	270	Isooctane	293 (29)

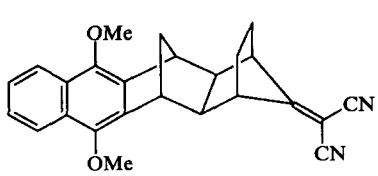
[a] The compounds are quoted in order of increasing deviation of n_O and n_N from coplanarity.

The angle φ for these compounds is close to 180° and the interaction through space is hardly manifested. The energy of the $n \rightarrow \pi^*$ transition depends mainly on the angle θ. When the orbital of the nitrogen LEP is oriented at right angles to the N–C–C=O plane (θ = 90°), the interaction through σ-bonds is ruled out and the energy of the $n \rightarrow \pi^*$ transition is the same as in saturated ketones.

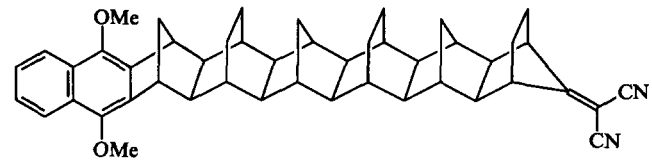
Appreciable changes are observed in the circular dichroism spectra of azacyclohexanones containing the $N-CH_2-C=O$ group when the nitrogen LEP is antiperiplanar relative to the $C_\alpha-C(O)$ bond. Such effects are absent when the nitrogen LEP is in the *gauche*-conformation relative to this bond.[114,115] This demonstrates the influence of the conformations on the interaction through σ-bonds and shows how the interaction with charge transfer differs in stereoisomers containing donor and acceptor fragments with different orientations.

The characteristics of the ICT bands are more sensitive to the interaction through the σ-bonds of nonequivalent groups than photoelectron spectroscopic data.[96]

Studies by pulse radiolysis and photoinduced electron transfer methods of the interactions between the donor and acceptor separated by saturated σ-bridges in rigidly fixed systems containing between 4 and 13 intervening σ-bonds (for example, in compounds **112** and **113**) confirmed the theoretical ideas concerning the mechanism of the interaction through σ-bonds.[28,116] The very rapid intramolecular electron transfer between the donor and the acceptor separated by distances ranging from 7 to 14.9 Å is due to the interaction of their π and π* orbitals with the σ and σ* orbitals of the hydrocarbon bridge.



112



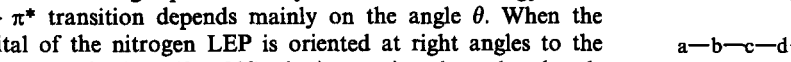
113

The experimental rate constant for the intramolecular electron transfer depends on the number of intervening σ-bonds (m). A similar dependence has been obtained with the aid of nonempirical calculations in the analysis of the interaction through σ-bonds in model compounds.[28] The intramolecular electron transfer rate constant is also determined by the geometry of the intervening bridge. It decreases by a factor of approximately five on passing from the *trans,trans*- to the *trans,cis*-conformation (m = 8) and diminishes from 10^{11} s^{-1} to 4×10^8 s^{-1} on passing from compound **112** to **113**. The high electron transfer rate constants have been explained by the interaction through σ-bonds, including the σ,π interaction.[28,116] Electron transfer processes between equivalent and nonequivalent groups joined by different hydrocarbon bridges have been investigated by the luminescence and EPR methods and by electronic spectroscopy.[117–121]

IV. The influence of the interaction through σ-bonds on the reactivity of organic compounds

Electronic interactions cannot fail to influence the reactivity of organic compounds. We shall consider this influence in relation to several examples.

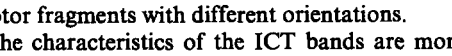
The heterolytic fragmentation



is a very common reaction in organic chemistry and has been studied in detail by Grob.[103,122] The fragmentation of 1-amino-3-halopropanes to ethylene and the corresponding iminium salt can also serve as an example.



Reaction may occur either via a concerted mechanism or as a two-stage process. In the former case, the C^1-C^2 and C^3-X bonds are ruptured simultaneously, while in the latter the cation

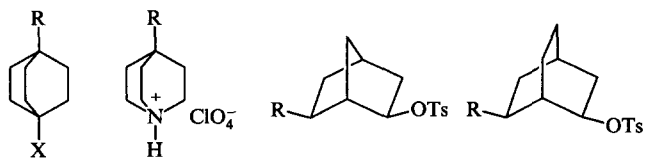


is formed initially. Analysis of the experimental and theoretical results led Grob to the conclusion that the concerted fragmentation occurs if the nitrogen LEP and the C^1-C^2 and C^3-X σ-bonds lie in the same plane and are oriented approximately parallel to one another. Such orientation of the fragments presupposes their interaction through σ-bonds. As a result, the C^1-C^2 bond is weakened, which leads to fragmentation.

For the antiperiplanar orientation of the nitrogen LEP, the C^1-C^2 σ-bond, and the free p orbital of the C^3 atom, the interaction in the cation through σ-bonds likewise induces a weakening of the C^1-C^2 bond; the following order in the arrangement of the levels has been established: A(HOMO) < S(LUMO). Thus both mechanisms presuppose a definite role of the interaction through σ-bonds in the fragmentation reaction.

It has been established that, in the solvolysis of 4-substituted bicyclo[2.2.2]oct-1-yl *p*-nitrobenzenesulfonates **114**, 4-substituted quinuclidinium perchlorates **115**, and the 2-substituted norbornyl tosylate **116** and bicyclo[2.2.2]octyl tosylate **117**, the

influence of the substituents R on the reaction centre X is largely determined by their inductive effect.[123-125] However, for R = $HOCH_2$, CH_3OCH_2, H_2NCH_2, $AcOCH_2$, $ClCH_2$, $TsOCH_2$, and H_2NCO, the rate of reaction increases by a factor of 2–8 compared with the rate calculated from the inductive constant of the substituent R. The increase in the rate of reaction has been explained by the interaction through σ-bonds. For the same reason, the solvolysis of compound **114** with R = $Sn(CH_3)_3$ is 3000 times faster than for R = Alk.[126]



114 **115** **116** **117**

X = p-$NO_2C_6H_4SO_3$

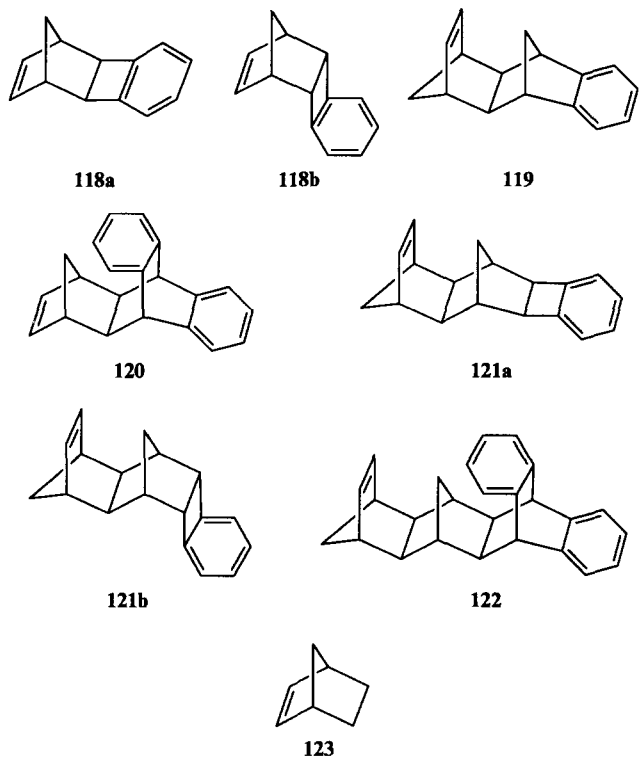
According to quantum-chemical calculations (EHM), the interaction through σ-bonds between the lowest unoccupied MO of aryl cations, localised on a positively charged centre, and the occupied $n(\pi)$ orbitals of the substituents leads to their stabilisation compared with the unsubstituted phenyl cation.[29,127] Similarly, electron-accepting substituents stabilise the aromatic carbanion $XC_6H_4^-$.[29] The photolysis of cyclobutanones entails ring expansion with formation of the corresponding tetrahydrofurans. This has been explained by the interaction through σ-bonds in the intermediate radical.[128]

The high stereospecificity of the cycloaddition of tetracyanoethylene to alkyl propenyl ethers with the intermediate formation of the 1,4-dipoles has also been explained by the predominance in the latter of the interaction through σ-bonds.[29,129]

A striking example of the influence of the interaction through σ-bonds on the reactivity of unsaturated organic compounds is provided by their Birch reduction with a solution of an alkali metal in liquid ammonia.[25,130,131] Isolated double bonds are usually not reduced by this method. However, when they approach one another or an aromatic ring, the rate of hydrogenation increases sharply, which is largely due to the interaction through space. Thus norbornadiene **38** (m = 1) and the related compounds **118–122** are reduced 10^5 times faster than norbornene **123** (Table 7).

Table 7. The coefficients (k_D^E) of the increase in the rate of the Birch reduction of double bonds[25] (*tert*-butyl alcohol served as the proton donor).

Substrate	Standard	Metal	k_D^E
38 (m = 1)	**123**	Li	10^5
118a	**123**	Li	140
	123	Na	169
	123	Na/cryptand[2.2.2]	206
118b	**123**	Li	78
69	**71**	Li	26
65	**66**	Li	18
119	**71**	Li	96
120	**66**	Li	2900
121a	**71**	Li	3
121b	**71**	Li	3.5
122	**71**	Li	5
71	**123**	Li	5.8
66	**123**	Li	0.6



118a **118b** **119**

120 **121a**

121b **122**

123

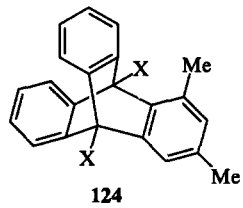
In the Birch reduction of the polycyclic unsaturated hydrocarbons **65**, **69**, and **118–122**, in which the unsaturated fragments are separated by three (compounds **118a, b**), four (compounds **65**, **69**, **119**, and **120**), five (**121a, b**), or six (compound **122**) σ-bonds, the rates of reduction of the double bonds (k_D^E) reflect the interaction of these fragments through σ-bonds (Table. 7).[25] Thus the double bond in the *exo*-compound **118a** is reduced 140 times faster than in norbornene **123**. The lower value of k_D^E for the *endo*-compound **118b** compared with the *exo*-compound **118a** can be explained very successfully by the competition in this system of the interaction of the π orbitals through space and through σ-bonds.[131] An example of the chemical manifestation of the interactions through four σ-bonds is provided by the Birch reduction of the hydrocarbons **119** and **120**, in which the rate constants k_D^E are 96 and 2900 respectively.[132] In terms of the mechanism adopted for this reaction, the interaction between the π* levels of the double bonds and the aromatic ring diminishes the energy of the lowest unoccupied MO and increases the probability of the formation of a radical-anion.[25,131] This has been confirmed by quantum-chemical calculations (EHM, INDO) for compound **118a**, indicating an appreciable mixing of the π* MO of the double bond and the aromatic ring.

The interaction through space and through σ-bonds of the vinyl groups in hexa-1,5-diene and hepta-1,6-diene determines their capacity for photochemical [2 + 2]-cyclisation.[133,134]

The change in reactivity in many intramolecular reactions proceeding with formation of intermediate radicals or biradicals can be explained by the effects of the interaction through space or through σ-bonds of two p orbitals with unpaired electrons (a biradical) or of p orbitals with an unpaired electron and an occupied π orbital (a radical).[135] The stability of the cyclic transition state depends on the number of intervening σ-bonds, the state incorporating ($4m$ + 2) σ-electrons being energetically more favourable. This concept of the 'σ-cooperation' indicates the preferential formation in the transition state of odd-membered rings on biradical cyclisation and of even-membered rings on intramolecular hydrogen or hydride migration.[136]

Analysis of the unoccupied π* orbitals and reactivities of triptycene derivatives **124** showed that the deprotonation of compound **124a** (X = H) takes place preferentially with

participation of the methyl group in the 1(C_α)-position, whereas the corresponding reaction of compound **124b** (X = Cl) takes place with participation of the methyl group in the 3(C_β)-position.[137]



124

X = H (**124a**), Cl (**124b**)

By virtue of the interaction of the π* orbitals of the benzene rings of triptycene through σ-bonds, the relative energies of the degenerate unoccupied levels are $e' < e''$. In interaction through space, this relation is reversed. On passing from X = H ($e' < e''$) to an electronegative substituent (X = Cl), the interaction through σ-bonds is weakened and the order in the arrangement of the levels changes ($e' > e''$). The reactivity agrees with the nature of the lowest unoccupied orbitals e' and e''.

Yet another example of the chemical effect of orbital reactions through σ-bonds and through space on the reactivity of molecules may be provided by the reactions of unsaturated cyclic sulfones with ethyl azidoformate and peracids, which is accompanied by the formation of the corresponding aziridine and oxiran derivatives.[138] There is a correlation between the reactivity of the double bond and its π-ionisation potential, which is higher in the compounds investigated compared with olefins. This increase is caused by the orbital interaction through σ-bonds and/or through space between the sulfone group and the double bond.[138] Similar effects have been noted in the interaction of a series of bicyclic olefins with nitrenes.[139]

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