

Non-Bonding Molecular Orbitals and the Chemistry of Non-Classical Organic Molecules

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1 Introduction

Valence bond structures depicting localized two-centre, two-electron σ and π bonds have proved to be an extremely useful concept for discussing the structures and reactions of molecules. However, there are molecules which cannot be satisfactorily represented by classical uncharged valence bond structures employing atoms in their normal valence states. These 'non-classical' molecules are usually represented either as resonance hybrids of several dipolar canonical forms or as hypervalent structures.¹ Representative examples, (1)–(6), of these molecules are shown in Figure 1.

Ozone is a typical example of a molecule which is represented only by dipolar structures (1a) \leftrightarrow (1b); the alternative hypervalent structure (1c) is not favoured. In contrast, xenon difluoride is 'satisfactorily' represented by the hypervalent structure (2c). The description as a resonance hybrid of two dipolar forms (2a) \leftrightarrow (2b) is seldom used, probably because distinction between these canonical forms and an ionized molecule ($\text{FXe}^+ + \text{F}^-$) is not clear. Examples of non-classical organic molecules include heterocyclic mesomeric betaines such as 1-arylpyridinium-3-olates, (3a) \leftrightarrow (3b), which like ozone participate in 1,3-dipolar cycloaddition reactions, and [hydroxy(tosyloxy)iodo]benzene (4c), a hypervalent iodine derivative which is a useful and versatile reagent.

In spite of the segregation of these non-classical molecules into two camps, the '1,3-dipoles' and the 'hypervalents', all these molecules have fundamental similarities in their bonding and modes of reaction. The purpose of this article is to emphasize the similarities of this large and diverse group of molecules in terms of the three-centre, four-electron bonding model,² which was developed by Pimentel, Hach and Rundle, and Musher,¹⁻³ and to explore applications of this molecular orbital description by reviewing some areas of current interest.

2 Three-centre, Four-electron Bonds

The classical description of molecules in terms of localized two-electron bonds is derived from the interaction of a pair of atomic orbitals on adjacent atoms to form two molecular orbitals of

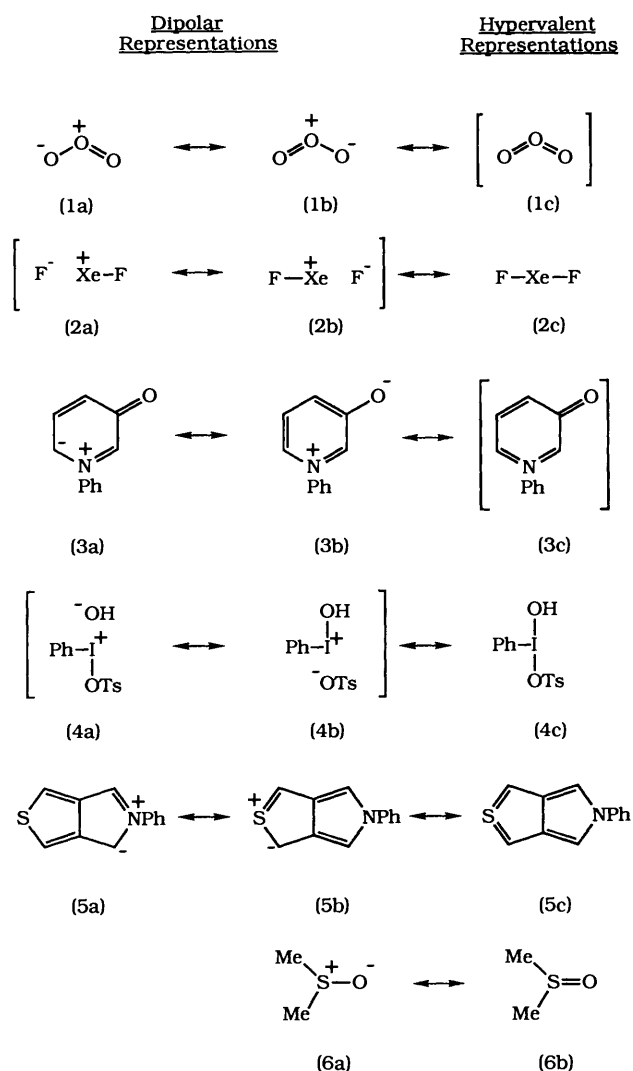


Figure 1 Examples of non-classical molecules represented by dipolar or hypervalent structures.

which one is bonding and the other is antibonding. Two electrons are fed into the bonding orbital leading to a localized bond (σ or π) which can aptly be described as a two-centre, two-electron [2c-2e] bond. This description of the π -bonding in ethylene is summarized in Figure 2a.

The bonding is rather different when three atomic orbitals are placed in linear conjugation – a situation exemplified by the interaction of three carbon $2p_z$ atomic orbitals to give the π -molecular orbitals of the allyl anion. In this case the atomic orbitals combine to form three molecular orbitals of which one is bonding, one is antibonding, but the third is non-bonding (Figure 2b). Two electrons can be placed in the bonding orbital and two in the non-bonding molecular orbital (NBMO) to give an energetically favourable configuration. However, the structure cannot be represented by two-centre bonds. In contrast to ethylene, which can be represented by a single localized bond structure, the structure of the allyl anion can only be represented

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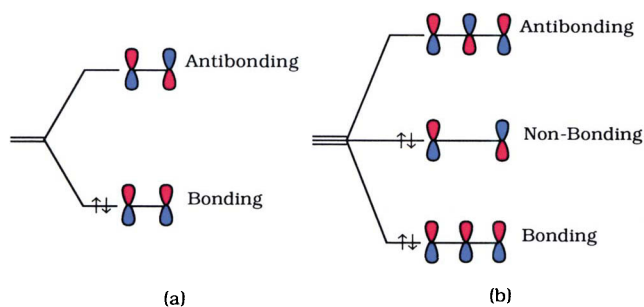


Figure 2 The interaction of (a) two and (b) three $2p_z$ atomic orbitals to form bonding, non-bonding, and anti-bonding molecular orbitals.

as a resonance hybrid of two structures. The bonding is associated with all three atoms, it is fundamentally different from the bonding in ethylene, and can be described as a three-centre, four-electron $[3c-4e]$ bond.² Molecules which are associated with three-centre, four-electron bonds will usually have a high energy occupied molecular orbital which has the topology of a NBMO, and the symmetry and energy of this orbital frequently has a profound influence on the chemistry of these molecules.

This type of bonding is not limited to the conjugation of three $2p_z$ orbitals. Any three atomic orbitals in linear conjugation and with positive overlap will be isoconjugate with the allyl anion, and the bonding will be equivalent in terms of molecular orbital (MO) theory. Quantitative differences will arise as a result of variations in the efficiency of overlap and the energies of the orbitals participating, but the molecular orbitals will be topologically equivalent.

Figure 3 shows three arrangements, (8)–(10), of atomic orbitals or their hybrids which are isoconjugate with the π system of the allyl anion (7). In each case interaction of the atomic orbitals leads to molecular orbitals having similar nodal properties: each system has an orbital associated with the characteristics of a NBMO, which vanishes on the central atom. Four electrons can be fed into the two lowest energy orbitals (bonding and non-bonding) to give an energetically favourable configuration.

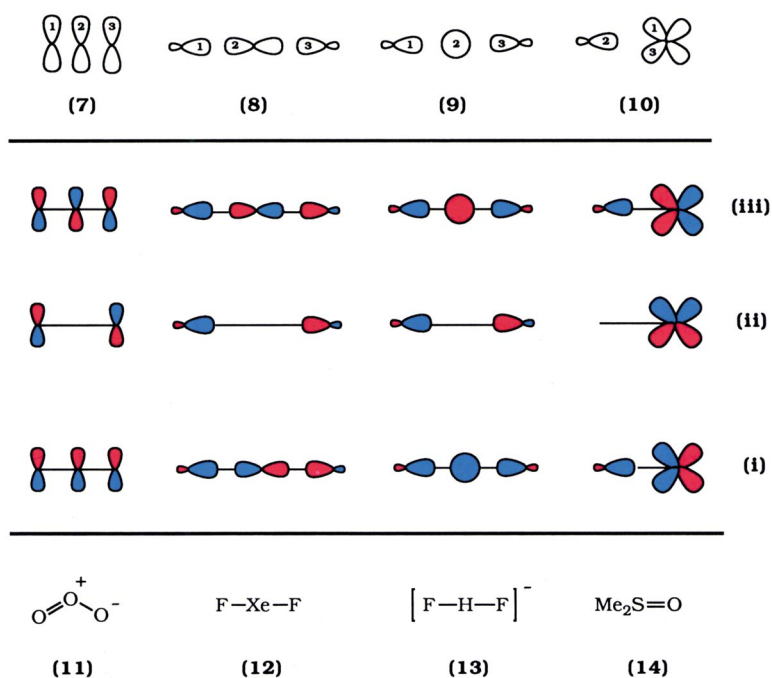
It is instructive to consider molecules and ions which are isoelectronic with these isoconjugate four-electron bonding systems, (7)–(10), and to focus in particular on molecules in which the central atom formally donates two electrons and the

two peripheral atoms each donate one electron to the electron quartet. Examples of such molecules and ions, (11)–(14), are shown at the bottom of Figure 3. The ozone molecule (11) is clearly isoconjugate with the allyl anion and its highest occupied molecular orbital (HOMO) has the symmetry of a NBMO.⁴ For a similar reason, xenon difluoride (12) also has a high energy occupied orbital which is related to a NBMO. The strength of the xenon–fluorine bonds is mainly derived from the bonding MO which has high electron density between the xenon atom and each fluorine atom.^{2,3} In effect electron pairs on the central atoms of ozone and xenon difluoride are participating in bonding interactions with the adjacent atoms while the two electrons originating on each of these peripheral atoms are effectively retained by them because they are located in a NBMO which vanishes on the central atom. Viewed in this way (Figure 3) the similarity between the ‘1,3-dipole’ ozone (1a–c) and the ‘hypervalent’ xenon difluoride (2a–c) is easy to recognize. In molecular orbital terms they are close relatives and the nature of the bonding in the two molecules is essentially the same. Whether we represent them by hypervalent or dipolar structures is purely a matter of convention.

The third example in Figure 3 is the hydrogen difluoride ion (13) and this differs from the previous examples, (11) and (12), in that the central participant is an s -orbital rather than a p -orbital. Nevertheless, the orbital overlap (9) is isoconjugate with the others, (7) and (8), and this bonding scheme accounts for the strong, symmetrical hydrogen bonding in (13) and related species.³

The final example (10) differs from the others in that two of the orbitals are on the same atom.¹ This provides an interesting view of the bonding in, for example, sulfoxides (14) (and ylides) for which both dipolar (6a) and hypervalent (6b) structures are in common usage. In these cases (10) the bonding is correctly described as a two-centre, four-electron $[2c-4e]$ bond, and the NBMO is effectively a lone pair of electrons in a p_z -orbital. In Figure 3 this p_z -orbital is represented as the combination of a pair of degenerate p -orbitals in order to emphasize the relationship with the other NBMOs in the figure (these combinations should not be confused with $3d$ -orbitals). In this article we wish to emphasize similarities between all the types of non-classical

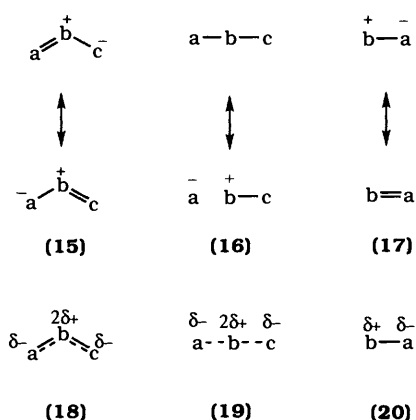
Figure 3 The isoconjugate relationship of sets of three atomic orbitals, (7)–(10), and the resulting bonding (i), non-bonding (ii), and anti-bonding (iii) molecular orbitals together with molecular examples, (11)–(14).



molecule exemplified in Figure 2 and, therefore, we stress here the relationship between the $[2c-4e]$ bonding system (10) and the $[3c-4e]$ bonding systems, (7)—(9), while recognizing that the MOs resulting from overlap (10) can be expressed in other forms

3 The Stability and Characteristic Reactions of Non-classical Isoconjugates

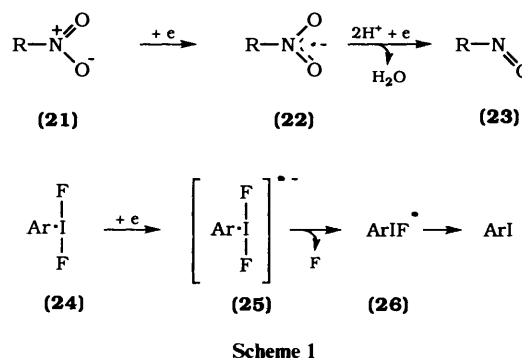
According to the analysis summarized in Figure 3, three large and discrete families of isoconjugate non-classical molecules having the general formulae (15)—(17) can be recognized, and for the purposes of this discussion these can be labelled as *1,3-dipoles* (15), *hypervalents* (16), and *ylides* (17). A simple analysis of the electron distribution in species (15)—(17) based on approximate LCAO coefficients of the molecular orbitals given in Figure 3 shows that the central atoms 'b' (the electron pair donors) are associated with significant positive charge, and the peripheral atoms 'a' and 'c' are associated with corresponding negative charge. The structures (18)—(20) are probably the most realistic general representations of these molecules



Two electrons are accommodated in a high energy NBMO (Figure 3) and the stability of species (15)—(17) increases as the energy of this orbital is lowered. Because the NBMO concentrates the electrons on the terminal atoms (a and c) these molecules are most stable if these atoms have high electronegativity. This is well illustrated by the fact that iodine forms hypervalent iodine(III) compounds with fluorine and chlorine but not with bromine.⁵ Stable oxygen and carbon derivatives can also be obtained when the ligand can stabilize an anion (e.g. MeCO⁻ and NC⁻). For the same reason the 1,3-dipoles (15) and the ylides (17) are most stable when the peripheral atoms are oxygen—the nitro- and sulfoxide functional groups are stable and well characterized whereas the carbon analogues (15) and (17) (a and c = CH₂) are much more elusive.

The factors which result in a lowering of the bonding and non-bonding molecular orbitals in the species (15)—(17) (i.e. the electronegativity of the atoms a-c) will also lower the energy of the empty antibonding orbital. Consequently, those species which are particularly stable are found to function as one-electron oxidizing agents. For example, the nitro-group can be reduced to a radical anion both chemically and electrochemically [Scheme 1, (21) → (22)]. In fact the magnitude of the one-electron reduction potential determines the antibacterial activity of nitroimidazoles, such as metronidazole, which are important anaerobic antibacterial agents.⁶ Introduction of the extra electron into the antibonding orbital (Figure 3) results in weakening of the N—O bonds and further reduction leads to formation of nitroso-derivatives (23) via N—O bond cleavage. Analogous behaviour is seen with many hypervalent species which often function as powerful oxidizing agents. For example, the reaction of iodoarene difluorides (24) with electron-rich dienes can be interpreted in terms of a single electron transfer (SET) to give the radical anion (25) (Scheme 1).⁷ The I—F bonds are now weaker

and the species (25) can collapse to a fluoride ion and the radical (26) which then undergoes further reaction. Some reactions of xenon difluoride (12) can be rationalized in a similar way (XeF₂ → XeF₂^{•-} → XeF[•] + F⁻) (see Section 6)



The isoconjugate bonding in the species (15)—(17) is also reflected in similarities in their chemical reactions. In particular, two general modes of reaction are common to all three species. The first can be termed *ligand coupling* and is generalized in Figure 4a, with representative examples shown in Figure 4b. In the forward reactions the three-centre, four-electron bond is disrupted to give a lone pair on atom b, and the second pair of electrons is used to form a σ bond between atoms a and c (the ligand coupling) or, in the case of the ylides, formation of a nitrene or carbene (which can be regarded as internally coupled ligands). Equation 1 shows an example of the well known ring-opening of aziridines to azomethine ylides.⁸ Similarities with the thermal decomposition of iodobenzene dichloride to chlorine and iodobenzene (equation 2) can be recognized—the reverse process can be achieved by passing chlorine through a chloroform solution of iodobenzene.⁹ The formation of sulfur ylides by addition of carbenes to sulfides (equation 3) is well known and the reverse reaction can be achieved both thermally and photochemically.¹⁰ It must be emphasized that it is the overall reactions which are being compared in Figures 4 and 5—a similarity in the reaction mechanisms is not implied.

The second general mode of reaction can best be described as *syn-addition*. This type of reaction is generalized in Figure 5a with representative examples given in Figure 5b. Again, the driving-force of the forward reaction is isolation of the lone-pair on atom b and at the same time the other pair of electrons of the three-centre, four-electron bond forms σ bonds with the atoms of a π bond. In the case of the 1,3-dipoles (15) this mode of reaction is the well known 1,3-dipolar cycloaddition which is exemplified by the regiospecific addition of the *N*-phenylnitrene shown in equation 4.¹¹ In equation 5 the outcome of treatment of cyclohexene with fluoroxenonium triflate is exclusively the *syn*-2-fluorocyclohexyl triflate.¹² Equation 6 shows a characteristic transformation of sulfimides and sulfur ylides which results in three-membered ring formation in the case of reaction 6 the divalent 'ligand' which can be regarded as undergoing *syn*-addition is HN:¹³

4 Three-centre Bonding and S_N2 Transition States

Three-centre, four-electron bonding is not restricted to neutral molecules. We have already encountered the hydrogen difluoride ion (13). Another anionic system in which this type of bonding makes an important contribution is the transition state of an S_N2 reaction, which is generalized in equation 7, and which has orbital overlap of the type (8) (Figure 3). The distribution of negative charge in these transition states (27) is closely related to the distribution of the NBMO which for simple reactions is localized on the atoms X and Y (equation 7). It is interesting to consider how the nature of these atoms (X and Y) influences the energy of the transition state. This is an exercise which is left to

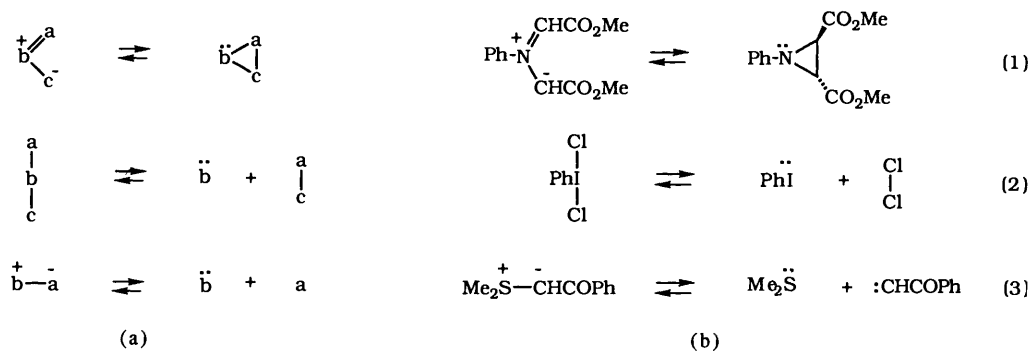


Figure 4 Generalized (a) and exemplified (b) 'ligand coupling' reactions of non-classical molecules

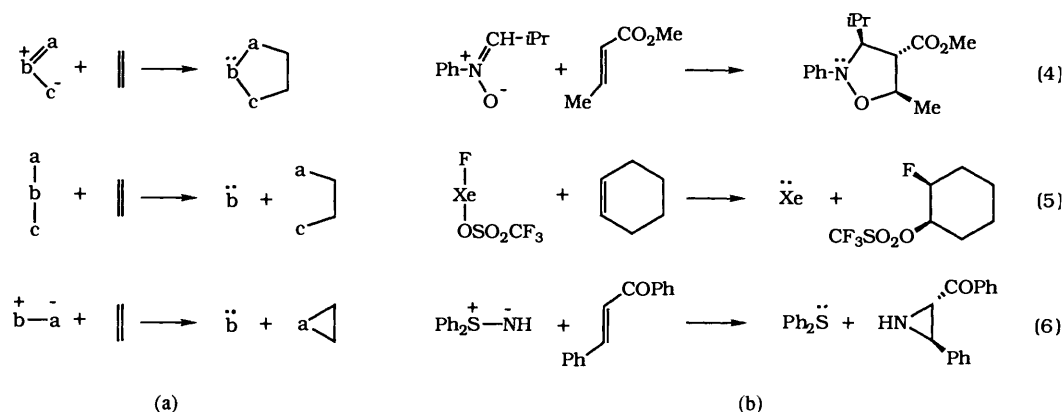
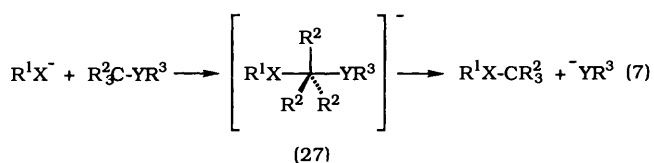


Figure 5 Generalized (a) and exemplified (b) 'syn-addition' reactions of non-classical molecules

the reader who should note that in the gas phase and in aprotic solvents, fluoride ion is the most nucleophilic halide ion ($F^- > Cl^- > Br^- > I^-$), which is the reverse of the generally recognized order based on studies in protic solvents



Recent studies¹⁴ of the gas phase S_N2 reaction shown in Scheme 2 have shown that the transition state (29) is lower in energy than the reactants ($Cl^- + CH_3Br$), clearly demonstrating the positive contribution of three-centre, four-electron bonding in S_N2 transition states. However, the structure (29) is still a transition state and does not lie in an energy minimum since ion-molecule complexes, (28) and (30), held together by ion-dipole forces are more stable. The potential energy surface along the reaction coordinate for this gas-phase reaction (Scheme 2) is shown in Figure 6. Because the negative charge in the transition state (29) is distributed between the entering and leaving groups, the solvation energy of this charge-delocalized species is less than that for the charge-localized reactant and product anions. Hence, in solution the reactants and products have lower energy than the transition state and, in contrast to Figure 6, the reaction profile in solution has the conventional shape. This differential solvation of reactants and transition state is greatest in protic solvents and accounts for the significant rate enhancement of S_N2 reactions in polar aprotic solvents.¹⁵

In contrast to pentavalent derivatives of carbon,¹⁶ pentacoordinated silicon anions are often stable enough to be isolated. X-Ray crystallographic studies have shown a number of anionic fluorosilicates to have a trigonal-bipyramidal geometry, analogous to an S_N2 transition state.^{17,18} Typical examples, which have been characterized as quaternary ammonium salts, are the

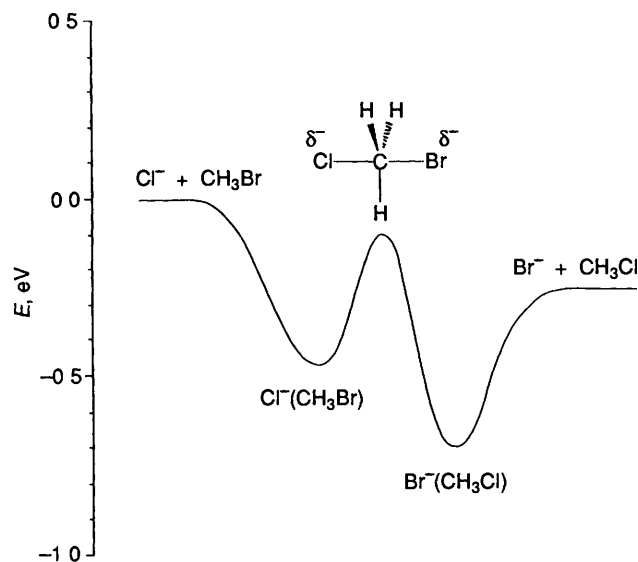
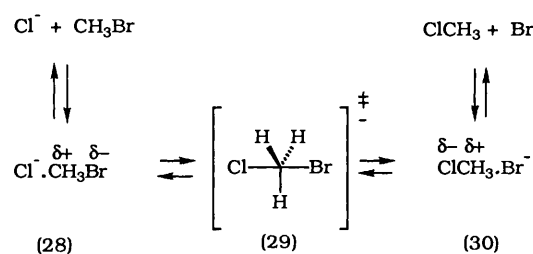
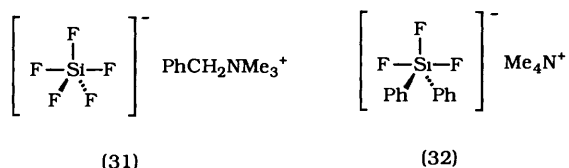


Figure 6 The schematic reaction coordinate diagram for the S_N2 reaction $Cl^- + CH_3Br \rightarrow Br^- + CH_3Cl$ in the gas phase (Reproduced by permission from *J Am Chem Soc*, 1991, 113, 9696)

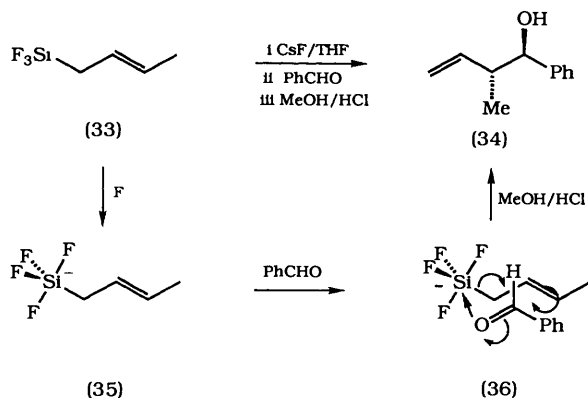


Scheme 2

pentafluorosilicate (31) and the diphenyltrifluorosilicate (32). In these anions two distinct Si—F bond lengths are observed: those associated with the weaker, hypervalent three-centre, four-electron bonds are longer (*ca* 1.65–1.69 Å) than those associated with the stronger, classical two-centre, two-electron bonds (*ca* 1.59–1.65 Å). It is notable that it is electronegative fluorine that forms the most stable pentacoordinate silicon species and that in the organic anion (32) fluorine occupies the hypervalent positions.



In many modern synthetic reactions nucleophilic activation of silicon to form a hypervalent species is a key mechanistic step. The organic chemistry of silicon is extensive and only a single example can be included here. Allylation of benzaldehyde with (*E*)-crotyltrifluorosilane (33) activated by caesium fluoride gives a 92% yield of the alcohol (34) with high diastereoselectivity (Scheme 3).¹⁹ This allylic rearrangement is believed to occur by initial nucleophilic attack by fluoride ion to give the hypervalent anion (35) which then coordinates with the aldehyde to form a hexacoordinate complex (36). Reaction *via* a six-membered transition state in which the phenyl group is equatorial then leads to the observed product (34). Activation of the Si—C bond in the trifluorosilane (33) by nucleophilic attack of the fluoride ion to give the more reactive pentacoordinate species with a hypervalent Si—C bond illustrates an important general principle of modern organosilicon chemistry.



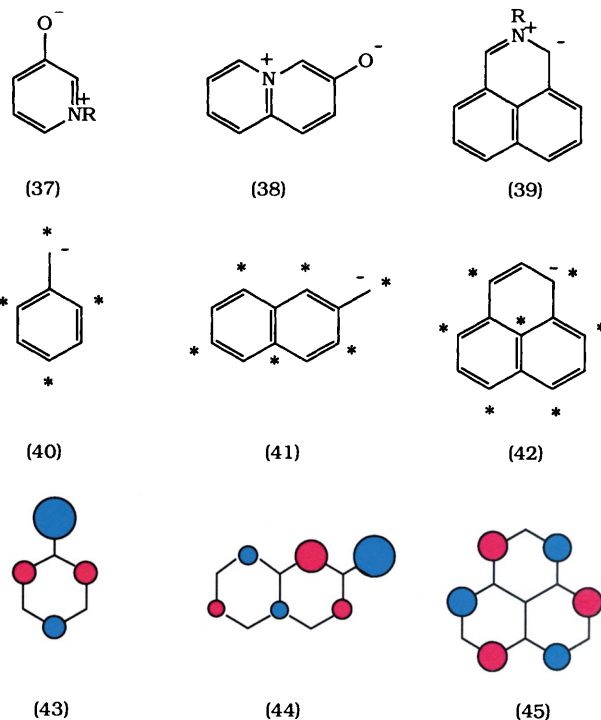
Scheme 3

5 Heterocyclic Mesomeric Betaines and 1,3-Dipolar Cycloadditions

Heterocyclic mesomeric betaines are a large and diverse group of 1,3-dipolar molecules and a number of discrete families of these heterocycles can be recognized. One large family is composed of betaines which are isoconjugate with odd alternant hydrocarbon anions: the essential relationship between betaine and anion can be summarized by the following rule:²⁰

Neutral heterocycles isoconjugate with odd alternant hydrocarbon anions can be represented only by dipolar or hypervalent structures if the heteroatom which donates two π-electrons to the conjugated system is located at an unstarred position.

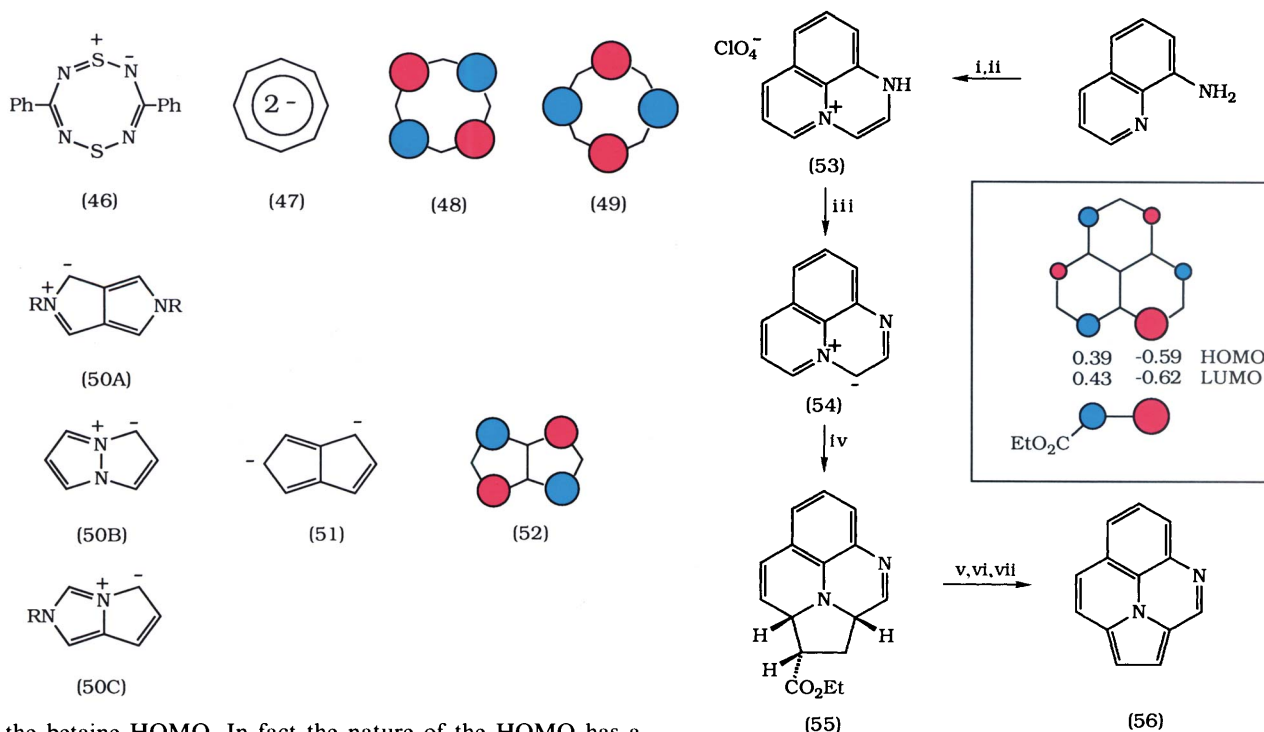
Examples of heterocyclic betaines defined by this rule are the systems (37)–(39) which are isoconjugate with the odd alternant hydrocarbon anions (40)–(42). The number of possible systems is very large.



Because odd alternant hydrocarbon anions are associated with a NBMO [*e.g.* (43)–(45)], which vanishes on the unstarred atoms (the smaller set), then these betaines can also be expected to be associated with a HOMO which has the characteristics of a NBMO, and there is ample theoretical and experimental evidence to support this view.²⁰ We should not be surprised by the association of these betaines with a NBMO. This is characteristic of a system which is associated with three-centre, four-electron bonding and these molecules are indeed systems in which a three-centre, four-electron bond is part of a larger conjugated ring system. This is why they can only be represented by dipolar or hypervalent structures.

Other types of hydrocarbon anion which are associated with NBMOs give rise to different families of neutral heterocyclic betaine when heteroatoms donating a pair of π-electrons are introduced at positions where the NBMO vanishes. Consider, for example, the cyclooctatetraene dianion (47) which is associated with a pair of NBMOs (48) and (49). The heterocyclic betaine (46),²¹ in which the two sulfur atoms are at positions in which one of the NBMOs (48) vanishes, is isoconjugate with the dianion (47). Similarly, the pentalene dianion (51) is associated with a NBMO (52) and the three types of heteropentalene betaine (50A–C) are isoconjugate.²² Again, these ‘non-classical’ heterocycles are examples in which a three-centre, four-electron bond is integrated into a larger π-system.

Using the special properties of odd alternant hydrocarbons, Dewar has developed a perturbation molecular orbital (PMO) theory of organic chemistry which provides deep insight into the structure and reactivity of molecules.²³ The close relationship between the family of betaines exemplified by (37)–(39) and odd alternant hydrocarbon anions encouraged us to employ the PMO approach to develop a model of the structure, bonding, and reactivity of this class of molecule. This model, which is described elsewhere,²⁰ has been successful in generalizing many properties including ionization potentials, absorption spectra, solvatochromism, relative stability, *pK_a* values, and cycloaddition reactions. In considering the betaines [*e.g.* (37)–(39)] as perturbations of the anions [*e.g.* (40)–(42)] the largest perturbation is caused by the heteroatom which donates two π-electrons to the conjugated system (*i.e.* $-\text{RN}^+=, -\text{O}^+=$ or $-\text{S}^+=$). Since this perturbation, by the very nature of the betaines, occurs at a position at which the NBMO vanishes then we might expect the PMO approximation to be particularly good for analysing properties which are closely associated with



Reagents: i, ClCH_2CHO ; ii, HClO_4 ; iii, Et_3N ; iv, $\text{CH}_2=\text{CH}.\text{CO}_2\text{Et}$; v, oxidation; vi, hydrolysis; vii, heat.

Scheme 4

the betaine HOMO. In fact the nature of the HOMO has a profound effect on their properties and this is particularly notable in their cycloaddition reactions and the effect of substituents and aza substitution on these reactions.²⁰

The recognition of the general rule described above provided the opportunity of systematically considering the known and unknown members of the large family of heterocyclic betaines which it defines. Our interest in the relationship between structure and properties and in the use of heterocyclic betaines in synthesis led us to study some simple but novel betaines, including molecules which are isoconjugate with the phenalen-1-ide anion (42). There are two distinct types of unstarred carbon atom in the phenalen-1-ide anion (*cf.* positions 2 and 10). Little was known about isoconjugate betaines in which a nitrogen atom is located at a peripheral bridgehead position and we embarked on a study of the simple tricyclic betaine (54) (Scheme 4).

The species (54) is too reactive to be isolated but it can be trapped *in situ* by treatment of a solution of the salt (53) with base in the presence of a 1,3-dipolarophile.²⁴ In accord with frontier molecular orbital (FMO) theory,²⁵ this betaine with a high energy HOMO (a perturbed NBMO) can be expected to be particularly reactive towards electron-deficient 1,3-dipolarophiles (low energy LUMO) and this proved to be the case. Reaction with ethyl acrylate produced the adduct (55) which after oxidation, hydrolysis, and decarboxylation gave the novel cycloazine (56).²⁴ The regioselectivity of the cycloaddition (54) → (55) is also notable. The asymmetry of the betaine HOMO means that one mode of addition of ethyl acrylate, in which the larger coefficient of the HOMO interacts with the larger coefficient of the LUMO (Scheme 4), is energetically preferred and leads to the formation of a single regioisomer. Both the energy and topology of the betaine HOMO have a decisive influence on the reactivity.

6 Do NBMOs Control the Reactions of Hypervalent Molecules?

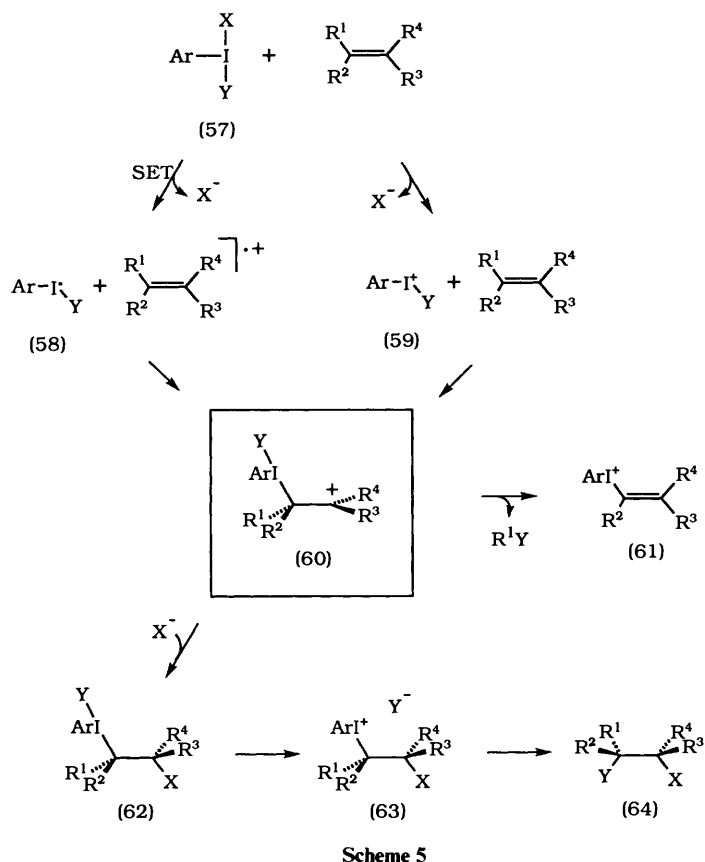
In the preceding discussion we have emphasized the view that the NBMO-like molecular orbitals of '1,3-dipoles,' including heterocyclic mesomeric betaines, have an important influence on their reactivity. This observation has prompted us to wonder if the NBMO-like orbital of 'hypervalent' species (Figure 3) might similarly influence their rate and mode of reaction. The chemistry of hypervalent iodine compounds is an area of

considerable current research interest,^{26,27} and the reactions of hypervalent xenon compounds are also attracting increasing attention. The mechanisms by which these reagents react is not clear. Plausible proposals involving carbocation intermediates have been described^{12,26} but as far as we are aware the possibility that the NBMO of a hypervalent three-centre, four-electron bond might play an essential role in stabilizing cationic intermediates has not been discussed. We conclude this review by considering this interesting possibility.

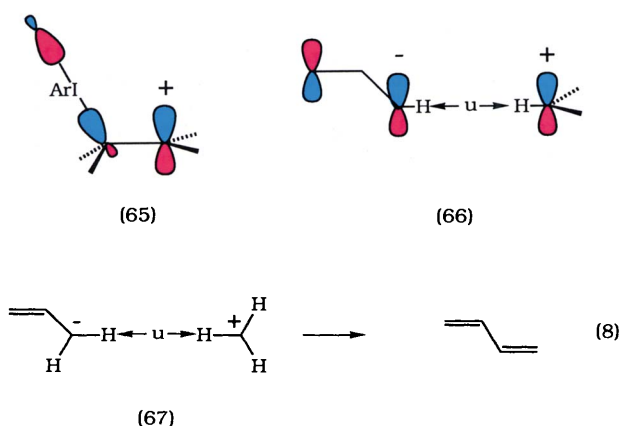
For the purposes of discussion we consider a mechanism (Scheme 5) for the *syn*-addition (Figure 5) of a generalized hypervalent iodine reagent (57) to a simple double bond. The same mechanistic principles can be applied to the rationalization of reactions of hypervalent reagents with a wide variety of substrates.

There are two possibilities for the initial step (Scheme 5). The hypervalent reagent (57) may oxidize the π -system by single electron transfer (SET) to form a radical cation and a radical [*e.g.* (58)] which then combine to give a cationic intermediate (60). Alternatively, the iodine reagent may dissociate to an iodonium ion (59) which then undergoes electrophilic addition to the olefin yielding the same intermediate (60). The cation (60), which contains a hypervalent I–C bond, may then react with the counter ion (X^-) to give molecule (62). Subsequent dissociation to the iodonium salt (63) followed by $\text{S}_{\text{N}}2$ displacement of aryl iodide gives the *syn*-adduct (64). When the substituent R^1 is H or SiMe_3 an alternative reaction of the cation (60) may lead to the vinyl iodonium salt (61). This sequence of events (Scheme 5) provides an interesting example of umpolung in which the iodine species function first as an electrophile and then as a leaving group.

A crucial intermediate in this mechanistic interpretation (Scheme 5) is the hypervalent cation (60) which may well be stabilized by an energetically and topologically favourable interaction between the hypervalent NBMO and the empty p -orbital of the cationic centre (65). This orbital interaction is isoconjugate with the interaction between an allyl anion and a methyl cation (66) when they are combined by intellectual 'union' ($\leftarrow \mathbf{u} \rightarrow$) to form butadiene (equation 8).²³ Since the total π -electron energy of butadiene is demonstrably lower than that

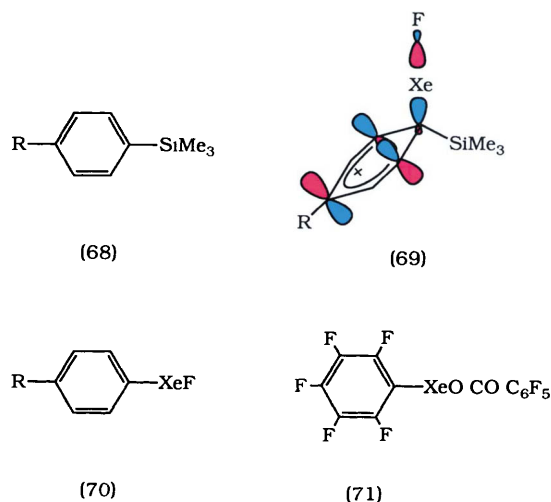


of the separate ions, we might expect the hypervalent cation (65) to be similarly stabilized. Note that during the union (67), one of the allyl π -bonds becomes stronger (*i.e.* becomes the 1,2-bond in butadiene) whereas the other is weakened (*i.e.* becomes the 2,3-bond). The same effect might also be expected in the hypervalent cation (60) with the I–Y bond strengthened but the I–C bond weakened. When the cation (60) reacts with an anion (60) \rightarrow (62) (Scheme 5) this stabilization of the hypervalent system is lost. Simultaneously, the C–I bond should strengthen but the I–Y bond weakens making it easier to dissociate to the salt (63), thus transforming the iodine function into a good leaving group and achieving the umpolung.



This possibility that the NBMO of hypervalent bonds may stabilize strategic cationic intermediates encouraged us to investigate a potential new method for introducing fluoro-substituents onto aromatic rings using xenon difluoride. In particular, we considered that xenon difluoride might react with aryltrimethylsilanes (68) to form an intermediate of the type (69) in which the cation is stabilized not only by the β -effect of the trimethylsilyl substituent but also by the hypervalent xenon

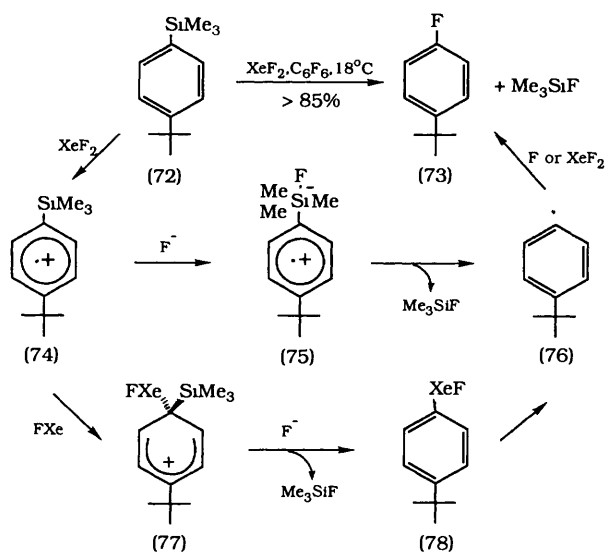
bonds. Subsequent fluorodesilylation by F^- could then give the arylxenon intermediate (70) [*cf.* Scheme 5 (60) \rightarrow (61)] which could be expected to undergo rapid ligand coupling (*cf.* Figure 4) to form an arylfluoride. When we embarked on this study the idea of generating an arylxenon intermediate [*e.g.* (70)] of even transient stability was considered rather 'speculative'. However, within a few months a paper appeared describing the preparation, isolation (80% yield), and X-ray structure determination of the stable xenon derivative (71).²⁸ Furthermore, in accord with the general properties summarized in Figure 4 this compound (71) was shown to undergo thermal ligand coupling to form the ester $C_6F_5O CO C_6F_5$.



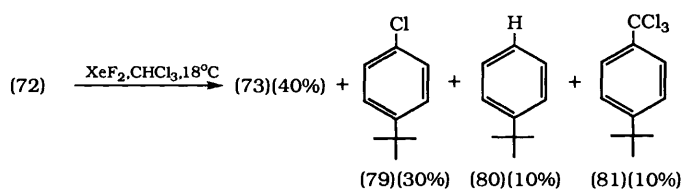
When 4-*t*-butylphenyltrimethylsilane (72) was reacted with xenon difluoride in hexafluorobenzene solution at room temperature a clean reaction took place giving 1-*t*-butyl-4-fluorobenzene (73) in high yield, together with trimethylsilyl fluoride (Scheme 6).²⁹ The actual mechanism of this transformation (72) \rightarrow (73) has not yet been elucidated, but at present we consider that it may proceed *via* either the hypervalent xenon intermediates (77) and (78) or the hypervalent silicon intermediate (75). Since xenon difluoride is a powerful oxidizing agent, the first stage is probably a SET to form the radical cation (74). This species may then react to give the cationic intermediate [(77), *cf.* (69)] or alternatively may undergo immediate fluorodesilylation *via* the pentavalent silicon radical (75) (*cf.* Section 4). Both pathways lead to the aryl radical (76) which may then react with F^- or XeF_2 to form the observed product (73). Although we cannot discriminate between these two pathways (Scheme 6) at present, results using $CHCl_3$ or $CFCl_3$ as solvent do suggest that the reaction proceeds *via* an aryl radical. For example, when the reaction of compound (72) with xenon difluoride was repeated using chloroform as solvent the yield of the fluoroderivative (73) was much lower (40%) and it was accompanied by the chloro (79)(30%), proto(80)(10%), and trichloromethyl (81)(10%) derivatives (Scheme 7), suggesting that an intermediate radical (76) had reacted with the solvent.²⁹

7 Concluding Remarks

The electrons in two-centre σ and π bonds are not localized between pairs of atoms; they occupy molecular orbitals which are delocalized throughout the molecule. Nevertheless, for the rationalization of many properties, particularly those which depend on the total number of electrons in a molecule (collective properties), the localized σ and π bond model is very successful. Similarly, three-centre, four-electron bonds are not localized but, provided the same limitations which apply to two-centre bonds are recognized, the concept can successfully rationalize many properties of the large and diverse group of molecules which are described as dipolar or hypervalent. In some molecules *d*-orbitals have the correct symmetry to mix with the



Scheme 6



Scheme 7

NBMO to form a weakly bonding MO. Present evidence suggests that this contribution of d -orbitals is small and does not appear to affect the qualitative conclusions of the [3c-4e] bonding model significantly. A critical quantitative analysis of the role of d -orbitals in hypervalent molecules has recently been published.³⁰

We are interested in using the ideas reviewed in this article as an aid to the discovery of reactions which may be of general value in synthetic organic chemistry: new reactions of hypervalent derivatives of tellurium, iodine, and xenon are of particular interest. The chemistry of hypervalent compounds is deservedly attracting increasing attention from synthetic organic chemists³¹ but the mechanisms of many of their transformations remain uncertain. We hope that a combination of theoretical and experimental studies will lead to both a better understanding and useful applications of this interesting class of molecule.

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