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The influence of electronegativity on linear and triangular three-centre bonds

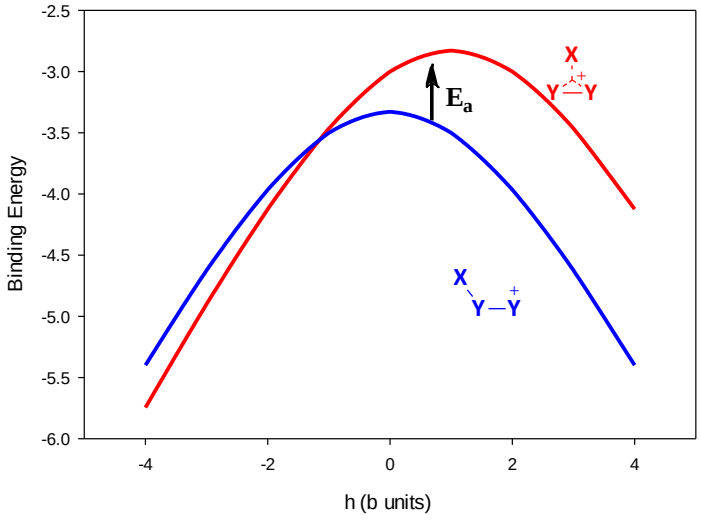
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Abstract

Electronegativity differences between bonding atoms have major effects on the strengths of chemical bonds but they affect two-centre and three-centre bonds in different ways and with different consequences. The effect on two-centre bonds was recognised almost 100 years ago but the influence of electronegativity difference on three-centre bonding has received less attention. Molecular orbital models of three-centre bonding are discussed and their application to the understanding of the properties of three-centre bonded species illustrated.



Keywords: Three-centre bonding, electronegativity, hypervalent, nonclassical carbocations, 2-norbornyl cation, xenon difluoride

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1. Introduction

How does electronegativity influence the stability and reactivity of the hypervalent iodine reagents **1** (X = F, Cl, Br, O_2CR)? Why does argon not readily form stable crystalline colourless difluorides like krypton **2** and xenon **3**? In cationic rearrangements (e.g., **4** → **5**; R = Me or tBu), why is the inherent migratory aptitude of t-butyl greater than that of methyl? How does the nature of the substituents R influence the relative stabilities of the 2-norbornyl cations **7** and the classical cations **6** and **8**? These and many other questions can be rationalised in terms of the influence of electronegativity on the relevant three-centre bonding.

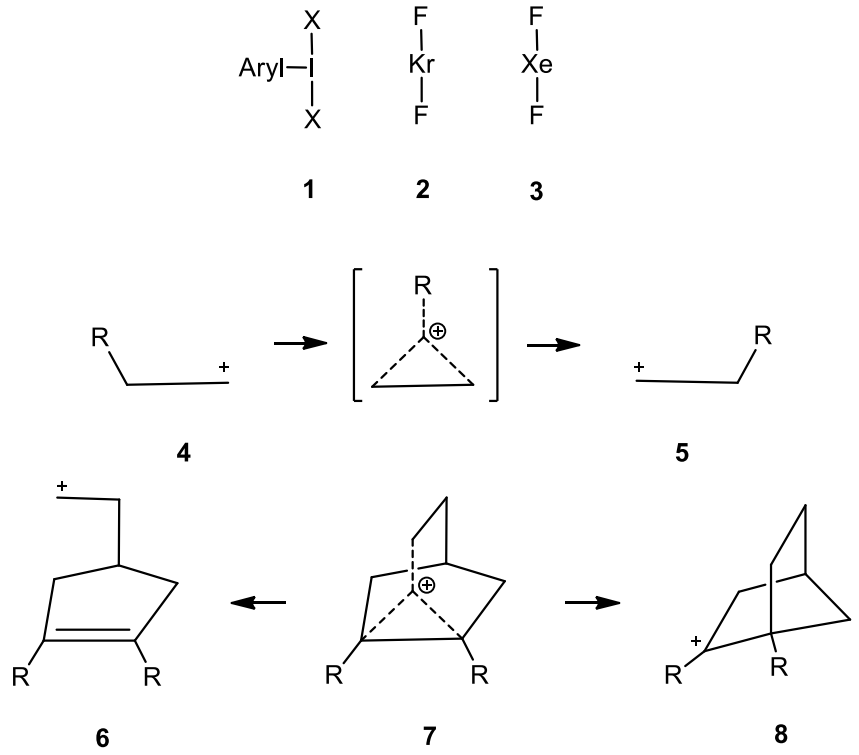


Figure 1. Examples of linear and triangular three-centre bonding.

The influence of electronegativity on the bond energies of two-centre bonds (X-Y) is well known and was explored in detail by Pauling in the first half of the 20th century.[1] The relationships between electronegativity and the bond energies of three-centre bonds are less well documented. This short review explores simple molecular orbital (MO) models of the contribution of electronegativity to the bond energies of two- and three-centre bonds and illustrates the conclusions with examples.

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Pauling demonstrated that the bond energy (E_{XY}) of an unsymmetrical single bond X-Y is usually greater than the average of the bond energies of the corresponding symmetrical bonds (E_{XX} and E_{YY}).[1] The additional bond energy of the unsymmetrical bond is attributed to a contribution by the polarised ionic structure X^+Y^- arising from the difference in electronegativity (Δ_{XY}) between atom X and atom Y. The empirical relationship between bond energies and electronegativity difference derived by Pauling is shown in Equation 1.

$$E_{XY} = 0.5[E_{XX} + E_{YY}] + 23\ \Delta_{XY}^2 \qquad (\mathbf{1})$$

Using a simple two-centre MO model of the X-Y bond, formed by overlap of a pair of atomic orbitals on atoms X and Y, the bond energy E_{XY} is given by Equation 2. In this equation, β_{XY} is the resonance integral and α_X and α_Y are the Coulomb integrals of atoms X and Y. The Coulomb integral of an atom is related to its ionisation potential and therefore to its electronegativity. The difference between the Coulomb integrals (α_X - α_Y) is therefore directly proportional to the electronegativity difference (Δ_{XY}) and is conveniently expressed as h, i.e., h = (α_X - α_Y).

$$E_{XY} = -[4\beta_{XY}^2 + (\alpha_X - \alpha_Y)^2]^{½}$$

$$= -[4\beta_{XY}^2 + h^2]^{½} \qquad \text{Equation 2}$$

Dewar has demonstrated that Equation 2 can be transformed into the relationship shown in Equation 3, which is analogous to Equation 1, thus providing a theoretical basis for Pauling's equation.[2]

$$E_{XY} \approx 0.5[E_{XX} + E_{YY}] + h^2/[E_{XX} + E_{YY}] \qquad \text{Equation 3}$$

An important feature of Equations 1 - 3 is that the electronegativity difference (Δ_{XY} or h) always appears as a squared term (Δ_{XY}^2 or h^2) and can never make a negative contribution to the bond energy. Importantly, we will see that this is not the case for three-centre bonds.

2. Linear Three-Centre Bonds (Hypervalent Bonds) (X-Y-X)

Linear three-centre bonds, exemplified by the bonding in iodobenzene difluoride ($PhIF_2$) and xenon difluoride (XeF_2), are three-centre four-electron [3*c*-4*e*] bonds.[3-6] Using a similar model to that described above for two-centre bonds, the binding energy (E_{XYX}) for the bonding in XYX (relative to $2X^{\cdot}$+Y:) is given by Equation 4. The parameter h is again the difference in the Coulomb integrals (α_X - α_Y) of X and Y, which is directly proportional to electronegativity difference (Δ_{XY}), and β_{XY} is the resonance integral between X and Y.

$$E_{XYX} = \mathbf{-h} - [8\beta_{XY}^2 + h^2]^{½} \qquad \text{Equation 4}$$

Equation 4 has a significant difference to the relationship shown in Equation 2. The additional h term in Equation 4 means that there is a directional contribution to the binding energy. If h is positive, i.e., X is more electronegative than Y, the binding energy is enhanced and vice versa.

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Consider the relationship between the [3*c*-4*e*] bonded species X-Y-X and the product of ligand coupling X-X + Y: (Equation 5). If we assume that $\beta_{XX} = \sqrt{2}\beta_{XY}$,[7] the binding energy of the coupled product X-X is $2\beta_{XX} = 2\sqrt{2}\beta_{XY}$, then the variation of the binding energies of both sides of Equation 5 with h (and thus with electronegativity difference) is shown in Figure 2. The binding energy of the hypervalent species increase with electronegativity difference whereas the energy of the ligand coupling product is constant. There is a crossover point beyond which the hypervalent structure XYX is more stable relative to its components Y: + X-X.

X-Y-X ⇌ X-X + Y: Equation 5

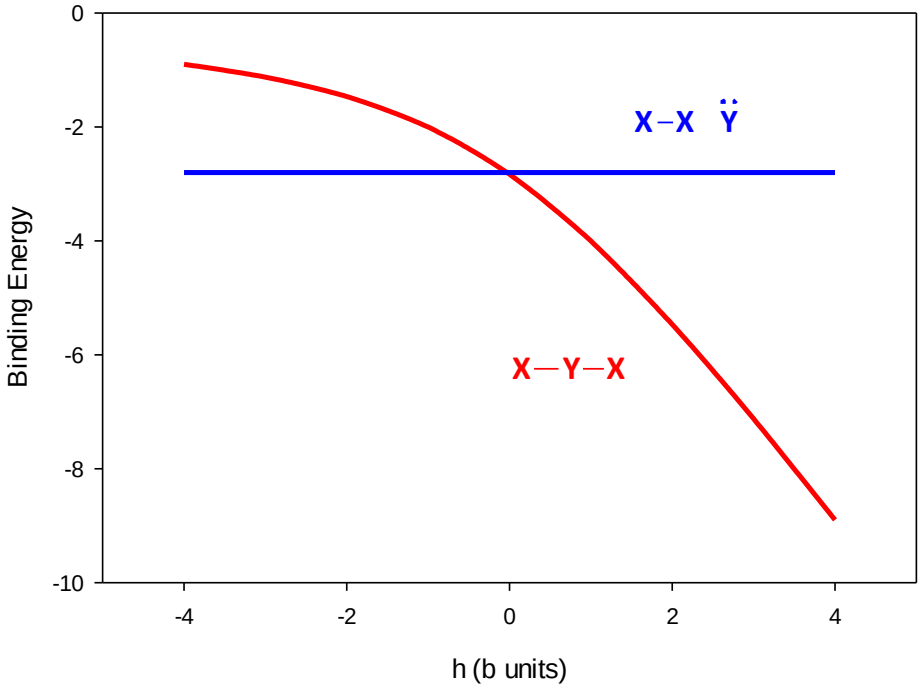


Figure 2. The influence of electronegativity difference measured by h on the binding energies of X-Y-X and X-X + Y: based on Equation 4.

The assumptions made in Figure 2 merit some comment. The approximation that $\beta_{XX} = \sqrt{2}\beta_{XY}$ is made for convenience but it does not change the conclusions. Using a different value based on $\beta_{XX} = a\beta_{XY}$, where a is a constant, would simply change the position of the crossover point and not the main conclusions. Assuming that the binding energy of XX is a constant may seem unreasonable since other factors influence the bond energy. However, for comparison of species with a constant ligand, e.g., difluorides F-X-F (see Table 2) this is a valid assumption. Comparisons between different ligands, where the crossover points may not coincide, needs more caution.

Some idea of the relative stabilities can be gained by inspection of the electronegativity differences in known and unknown compounds. Table 1 shows the electronegativity of non-transition elements on the Allen scale.[8]

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Table 1. Electronegativities of Non-Transition Elements based on the Allen scale[8]

H							**He**
2.30							**4.16**
Li	**Be**	**B**	**C**	**N**	**O**	**F**	**Ne**
0.91	**1.58**	**2.05**	**2.54**	**3.07**	**3.61**	**4.19**	**4.79**
Na	**Mg**	**Al**	**Si**	**P**	**S**	**Cl**	**Ar**
0.87	**1.29**	**1.61**	**1.92**	**2.25**	**2.59**	**2.87**	**3.24**
K	**Ca**	**Ga**	**Ge**	**As**	**Se**	**Br**	**Kr**
0.73	**1.03**	**1.76**	**1.99**	**2.21**	**2.42**	**2.69**	**2.97**
Rb	**Sr**	**In**	**Sn**	**Sb**	**Te**	**I**	**Xe**
0.71	**0.96**	**1.66**	**1.82**	**1.98**	**2.16**	**2.36**	**2.58**
Cs	**Ba**	**Tl**	**Pb**	**Bi**	**Po**	**At**	**Rn**
0.66	**0.88**	**1.79**	**1.85**	**2.01**	**2.19**	**2.39**	**2.60**

Using these values, Table 2 shows the electronegativity differences (Δ_{XY}) for halobenzene and noble gas derivatives of the halogens. Known compounds are shaded blue and unknown derivatives are shaded yellow. For the known compounds the smallest electronegativity difference is for (dichloroiodo)benzene (Δ_{XY} 0.51)(Table 2, Entry 1), prepared in 1885 by Willgerodt.[9,10] (Difluorobromo)arenes (Δ_{XY} 1.50) (Table 2, Entry 2) are known,[11,12] but attempts to prepare a (dichlorobromo)arene (Δ_{XY} 0.18) (Table 2, Entry 2) were unsuccessful,[12] and the corresponding (dibromoiodo)benzenes (Δ_{XY} 0.33) (Table 2, Entry 1) cannot be isolated,[13] We can therefore estimate that compounds with a Δ_{XY} value of 0.4 or less are probably too unstable to be useful as laboratory reagents.

Conversely, compounds with a Δ_{XY} value greater than 0.5 can be expected to be stable. There are two exceptions which are shaded green in Table 2. (Difluorochloro)benzene (Table 2, Entry 3) has a respectable Δ_{XY} value of 1.32, which is greater than that of isolatable krypton difluoride (Entry 5, Δ_{XY} 1.22), but it has not been reported. Nevertheless, chlorine does form [3*c*-4*e*] bonds with fluorine; chlorine trifluoride (ClF_3) is a well-characterised compound,[14] with a linear [3*c*-4*e*] bond consistent with a Δ_{XY} value of 1.32. A clue to the absence of (difluorochloro)benzene derivatives in the literature is the extreme reactivity of ClF_3 as an oxidising agent. It is alleged that in an accidental spill, one ton of ClF_3 burned through 30 cm of concrete and 90 cm of gravel (see Wikipedia). This extreme reactivity probably arises from the mutual bonding of two highly electronegative elements (F and Cl)(see Table 1) resulting in significant lowering of the [3*c*-4*e*] lowest unoccupied molecular orbital (LUMO) and leading to powerful oxidising properties. Under carefully controlled conditions (difluorochloro)benzene might be expected to be stable but very reactive.

Of the known noble gas difluorides, krypton difluoride (KrF_2), which is a volatile, colourless solid, has the lowest electronegativity difference (Δ_{XY} 1.22) (Table 2, Entry 5). The average Kr-F bond energy in KrF_2 is 11 kcal mol^{-1}. Since F_2 has a bond energy of 36 kcal mol^{-1}, KrF_2 presumably lies to the left of the crossover point in Figure 2 and is thermally unstable relative to Kr + F_2. This is consistent with its known decomposition rate of 10% per hour at room temperature.[15,16] XeF_2 is a commercially available colourless solid. It is much more stable than KrF_2 and has a total bond energy of 64 kcal mol^{-1}. It is thermodynamically stable relative to Xe + F_2 and lies on the right hand side of the cross over point in Figure 2.

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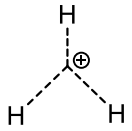
Table 2. Electronegativity differences (Δ_{XY}) between **Y** and **X** in molecules **X-Y-X**.

Entry	Y	X			
		F	Cl	Br	I
1	PhI	1.83	0.51	0.33	0.0
2	PhBr	1.50	0.18	0.0	-0.33
3	PhCl	1.32	0.0	-0.18	-0.51
4	Ar	0.95	-0.37	-0.55	-0.88
5	Kr	1.22	-0.10	-0.28	-0.61
6	Xe	1.61	0.29	0.11	-0.22
7	Ra	1.59	0.27	0.09	-0.24

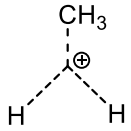
In contrast to Kr,[17] and Xe,[18,19] the difluoride of argon has not been reported. The Δ_{XY} value of 0.95 (Table 2, Entry 4) implies that ArF_2 will be significantly less stable then KrF_2. Also, argon is more electronegative than chlorine (Table 1) and as a result argon difluoride, like (difluorochloro)arenes (Table 2, Entry 3), may also be a very powerful oxidising agent and difficult to isolate and tame in the laboratory. Theoretical studies[20] suggest that high pressure may stabilise ArF_2 (and other noble gas compounds),[21] but handling it may be the problem.

The difluorides of Kr, Xe and Ra have been characterised as solids.[22] High pressure conditions have also been proposed for stabilisation of $XeCl_2$[23] and $XeBr_2$[21] but the low Δ_{XY} values (Table 2, Entry 6) suggest low stability relative to the elements. Xenon dichloride may be accessible/detectable under carefully controlled conditions (gas phase, matrix isolation).[24]

3. Triangular Three-Centre Bonds ($Y^{X}_{\cdots}Y$)



9



10

Triangular three-centre [3*c*-2*e*] bonds are exemplified by the bonding in the trihydrogen cation (H_3^+) **9** and the methanium cation (CH_5^+) **10**.[25] The H_3^+ ion was first detected by J.J. Thomson.[26] It is one of the most abundant ions in the universe and is ubiquitous in interstellar space.[27] CH_5^+ is the simplest of the nonclassical carbocations which are important intermediates in reactions of C-H and C-C bonds in superacids.[28]

Using a similar model to that described above, the binding energy ($E_Y^X{}_Y$) for the bonding (relative to $X^{\cdot}+Y^{\cdot}+Y^+$) is given by Equation 6. The parameter h is again the difference in the Coulomb integrals ($\alpha_X - \alpha_Y$) of X and Y, which is directly proportional to electronegativity difference (Δ_{XY}), and the resonance integrals between X and Y and Y and Y are β_{XY} and β_{YY}. The derivation of Equation 6 has been described elsewhere.[29]

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$$E_Y^X{}_Y = -\beta_{YY} - [\beta_{YY}^2 + 8\beta_{XY}^2 - 2h\beta_{YY} + h^2]^{½}$$ Equation 6

If we assume that $\beta_{XY} = \beta_{XX} = \beta$, then

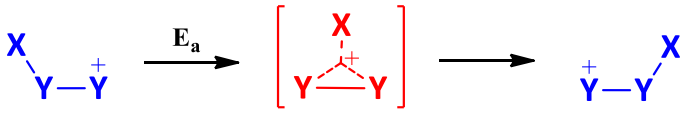
$$E_X^Y{}_X = -\beta - [9\beta^2 - 2h\beta + h^2]^{½}$$ Equation 7

Equation 6 contains a significant new term ($-2h\beta_{YY}$) that is not present in Equations 2 and 4. This $-2h\beta_{YY}$ term also makes a directional contribution to the binding energy which means that, as in Equation 4, the sign of h is significant. The h^2 term has the same significance as in [2*c*-2*e*] and [3*c*-4*e*] bonds. The significance of the additional $-2h\beta_{YY}$ term can be interpreted as follows. If X is more electronegative than Y it pulls electrons away from the bonding interaction Y-Y and makes an adverse contribution to the overall binding energy. Reducing the electronegativity of X reduces this effect. We have referred to this as the -2hβ effect.[29,30] As for two-centre bonds (Equation 2), the relationship between binding energy and h is also a hyperbola but, significantly, the [3*c*-2*e*] curve is displaced along the h axis.

Equation 6 also contains an additional $-\beta_{YY}$ term. Within this model, this term describes the extra YY bonding in the three-membered ring compared to the ring-opened or dissociated classical cations (X-Y-Y^+ or X-Y + Y^+). This extra bonding (β_{YY}) accounts for why [3*c*-2*e*] bonded cations are often more stable in the gas phase than classical ions, in spite of greater nuclear-nuclear interactions.

In solution, due to greater solvation, the classical cations are usually more stable. However, at low values of h there may be crossover as shown in Figure 3. The crossover of these hyperbolas is significant and for small changes in electronegativity difference (h) of X and Y the change in energy difference E_a of the two species can be quite large (see Figure 3).

Consider the generalised degenerate Wagner-Meerwein rearrangement shown in Scheme 1. This proceeds through a [3*c*-2*e*] bonded transition state with activation energy E_a. The activation energy will vary significantly with small changes in electronegativity (h), as shown in Figure 3. This is consistent with observed substituent effects. The inherent migratory aptitude of a tertiary butyl substituent (Scheme 1; X = tBu) is greater than that of a methyl substituent (Scheme 1; X = Me).[31] The electronegativity of methyl (Me radical IP 9.8 eV) is greater than that of tertiary butyl (tBu radical IP 7.2 eV) leading to a smaller h value for tBu and a lower activation energy E_a. This also rationalises the migratory aptitude H > alkyl. A more detailed analysis of the -2hβ effect and its relevance to other aspects of carbocation reactions has been published.[29,30]



Scheme 1. A generalised Wagner-Meerwein rearrangement showing migration of a substituent X via a [3*c*-2*e*] bonded transition state.

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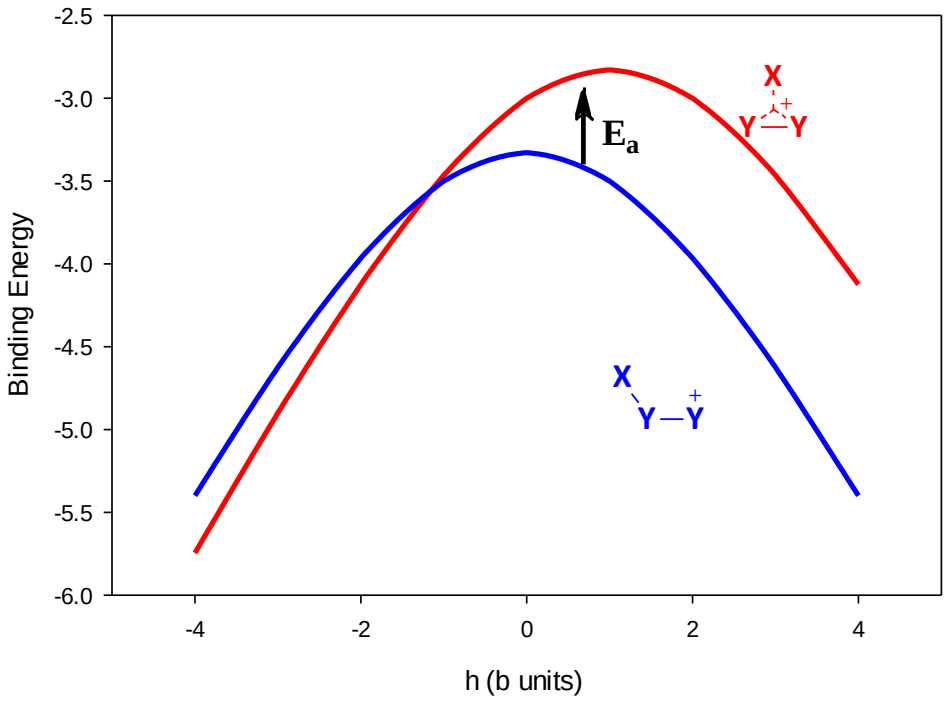
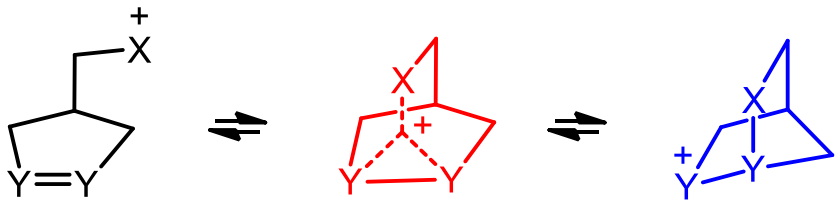


Figure 3. The variation of binding energy of a [3*c*-2*e*] bonded cation (red) and its classical isomer (blue).



11 **12** **13**

Under some circumstances even in solution [3*c*-2*e*] bonded carbonium ions are more stable than their isomeric classical carbenium ions. Well-known examples are 2-norbornyl cations **7**. It is now established by X-ray crystallography that the 2-norbornyl cation **7** (R = H) is more stable than the classical cations **6** and **8** (R = H).[32] Allowing for greater ring strain in the generalised cations **13** and greater solvation of the classical cations **11** and **13**,[30] the variation of binding energy with electronegativity (h) for the cations **11** - **13** takes the form shown in Figure 4. Because the hyperbolas are offset, due to the -2hβ term, there is a small window where, for a small range of electronegativity differences, the carbonium ions **12** are more stable than the carbenium cations **11** and **13**.

A theoretical study of the relative energies of seventy five isomeric cations **7** and **8** suggests that substituents R with Hammett σ^+ values in the range $0 > \sigma^+ < -0.5$ will favour the 2-norbornyl structure **7**.[30]

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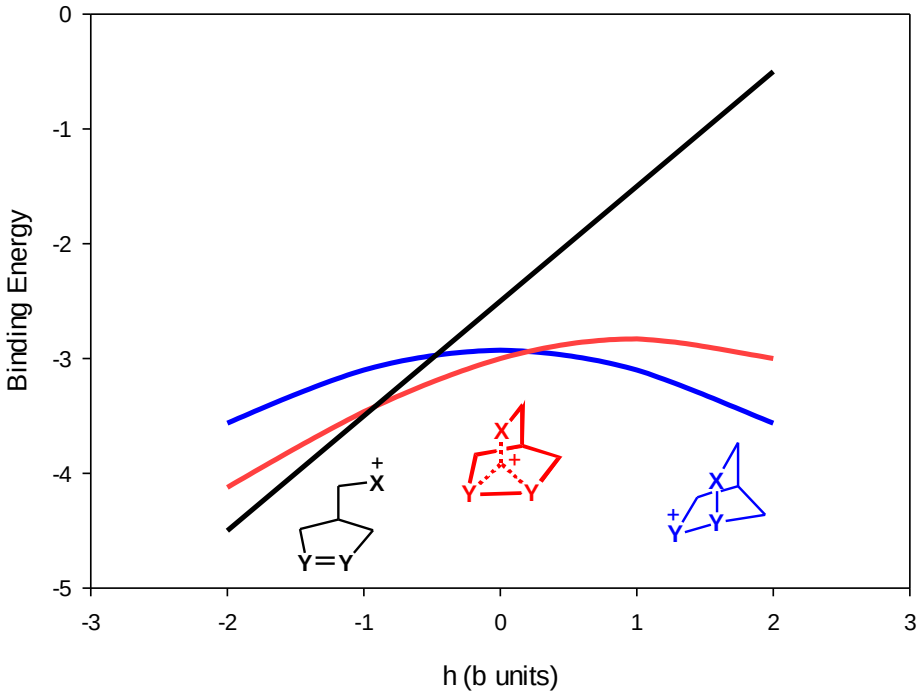


Figure 4. The variation of binding energies with electronegativity difference (h) of 2-norbornyl carbonium ions (red) and isomeric carbenium ions (black and blue).

4. The Localised Bond Model of Two- and Three-Centre Bonds

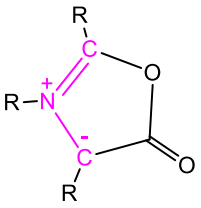
The localised-bond model applied to two-centre bonds has served organic chemists well for many decades. It is an essential part of their toolbox for discussing and predicting molecular structures, reaction mechanisms and substituent effects. It has stood the test of time. Of course, discrete electron pairs are not localised in bonds between atoms. However, provided the model is only used to discuss properties that depend on all the electrons in a molecule (collective properties), it predicts molecular properties corresponding to an energy minimum with an accuracy sufficient to be useful. A theoretical justification for the localised-bond model can be found elsewhere.[33] It is important to emphasise that this type of model should not be used to discuss one-electron properties, such as spectra. For these properties a full knowledge of the distribution of individual electrons in a molecule is necessary.

For the reasons discussed in the preceding paragraph, provided the same limitations are accepted, there is no reason why the localised-bond models of three-centre bonds described in Sections 2 and 3 should not also be useful tools for organic chemists. For the discussion of collective properties the three-centre bond can be conveniently regarded as localised, as for two-centre bonds, and the effects of electronegativity difference similarly considered.

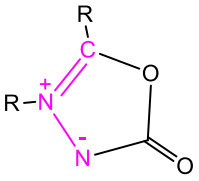
Three-centre bonds are not restricted to σ bonding and examples of three-centre π bonding are 1,3-dipoles, exemplified by the type A mesoionic rings **14**-**16**,[34-36] the sulfur heterocycles **17** and **18**, and nitro substituents (-NO_2). In fact sulfur 1,3-dipoles are sometimes depicted by hypervalent structures; for example, structures **19**, **20**,[37] and sulfur dioxide (O=S=O). The effect of electronegativity difference on these species is analogous to that on hypervalent iodine derivatives and the noble gas halides. This is illustrated by the mesoionic heterocycles **14** – **16**. The munchnones **14** are very reactive azomethine ylides which undergo 1,3-

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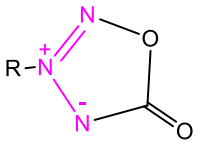
dipolar cycloaddition with a wide variety of dipolarophiles.[38] The sydnones **15**,[39] associated with a azomethine imine, also undergo 1,3-dipolar cycloadditions but the more electronegative ring nitrogen makes them less reactive. This is attributable to the –h term in Equation 4. In the case of the 1,2,3,4-oxatriazol-5-ones (azasydnones) **16**, in which two nitrogen atoms stabilise the three-centre bonding, 1,3-dipolar cycloaddition reactions are surprisingly absent from their chemistry.[40-43] Similar electronegativity effects contribute to the stability of the nitro group ($-NO_2$) and the instability of its thio analogue ($-NS_2$), which is unknown.



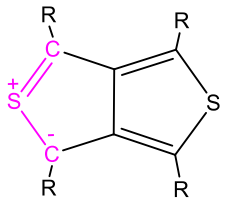
14 münchnones



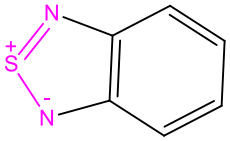
15 sydnones



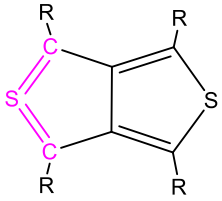
16 azasydnones



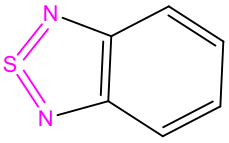
17



18



19



20

5. Conclusions

Electronegativity and particularly electronegativity difference has a major effect on the strengths of chemical bonds. Furthermore, electronegativity difference between bonding atoms affects [2*c*-2*e*], [3*c*-4*e*] and [3*c*-2*e*] bonds in different ways with different consequences. Although the influence of electronegativity difference on two-centre bonds was recognised almost 100 years ago, there has subsequently been little interest in the influence of electronegativity difference on three-centre bonding.

Here we should introduce some final words of caution. Although Equations 2, 4 and 6 model major contributions to bonding, other factors will contribute to bond strength. These include, for example, lone pair-lone pair repulsion, bonding pair-bonding pair repulsion, nuclear-nuclear repulsion and, when comparing systems, solvent effects. This account is intended to highlight the significant contribution of electronegativity difference to bonding and is not a comprehensive study of bond energies. Nevertheless, the simple molecular orbital models described here give some insight into the properties and relative stabilities of three-centre bonded species.

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Author's Biography

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