Available online at www.sciencedirect.com

SCIENCE DIRECT®

Tetrahedron 60 (2004) 3293–3309

Tetrahedron

The influence of electronegativity on triangular three-centre two-electron bonds: the relative stability of carbonium ions, π-complex chemistry and the $-2h\beta$ effect

Christopher A. Ramsden*

Lennard-Jones Laboratories, School of Chemistry and Physics, Keele University, Keele, Staffordshire ST5 5BG, UK

Received 23 October 2003; revised 6 January 2004; accepted 29 January 2004

Abstract—Using the HMO approximation, bond energy equations for triangular three-centre, two-electron [3*c*-2*e*] bonded species AB_2^+ (π-complexes) and the isomeric systems ($AB-B^+$, $BB-A^+$, $BA-B^+$ and $A^++B{=}B$) are described. The electronegativity difference ($\Delta\chi$) between the atoms or groups A and B is assumed to be related to the difference (h) in their Coulomb integrals and the variation of relative energies with electronegativity difference is explored. The bond energy curve for π-complexes is displaced relative to those of the two-centre, two-electron [2*c*-2*e*] bonded species and this displacement accounts for the significant influence of electronegativity difference on reactions proceeding via [3*c*-2*e*] bonded intermediates or transition states. The origin of the displacement of the bond energy versus electronegativity difference curve for the π-complexes is identified as a $-2h\beta_{BB}$ term in the bond energy equation. In contrast to [2*c*-2*e*] bonds, this term makes the influence of electronegativity difference on triangular [3*c*-2*e*] bonds directional, that is, the bond energies of AB_2^+ and BA_2^+ are different in contrast to those of AB and BA. A more electronegative atom A destabilises the [3*c*-2*e*] bond by removing electron density from the bonding interaction BB (β_{BB}) whereas a less electronegative atom A will strengthen the bond by increasing the electron density between the atoms B. Reactions involving [3*c*-2*e*] AB_2^+ bonds are classified as homo- or heteroprocesses and the influence of electronegativity difference on these discrete transformations is discussed in terms of the contribution of h, h^2 and $-2h\beta$ functions to differences in bond energy. The analysis is extended to π-complexes with back-donation and the equivalence of the description of onium ions using either two [2*c*-2*e*] bonds or two [3*c*-2*e*] bonds is demonstrated. Extension of the analysis to 2-norbornyl cations suggests that, due to the shape of the bond energy versus electronegativity difference curve, this cation exists within a window of stability between the alternative isomers. 1,2-Disubstituted norbornyl cations are used as a model of π-complexes and the influence of substituent effects on relative stability is explored using the AM1 method. After allowance for resonance and hyperconjugation effects, the results are found to be consistent with the general conclusions of the simple HMO model.

1. Introduction

Accurate calculations of molecular structure and properties are now readily accessible and can be applied to a wide range of chemical problems.[1] These calculations are structure specific and it is not always easy to make generalisations from the accurate data that they produce. In contrast, simple and approximate semi-quantitative models can produce general analytical expressions for molecular properties but these are lacking in accuracy and reliability. Nevertheless, used with care they can usefully bridge the gap between qualitative theories and specific calculations by (i) providing a semi-quantitative general model of the effects of structure variation on properties and by (ii) directing attention to areas worthy of detailed investigation by accurate structure-specific techniques. Both approaches, particularly when used together, can make a useful contribution to an understanding of structure and reactivity[2] and can focus experimental studies on new areas worthy of investigation.

We have recently described[3] a semi-quantitative model of triangular three-centre, two-electron [3*c*-2*e*] bonds of the type AB_2^+ based on the HMO approximation.[4,5] This model suggests that the bond energies of these [3*c*-2*e*] bonds (AB_2^+ defined relative to $A^{\cdot}+B^{\cdot}+B^+$), like those of two-centre, two-electron [2*c*-2*e*] bonds (AB defined relative to $A^{\cdot}+B^{\cdot}$), are related to the electronegativity difference ($\Delta\chi$) between the atoms or groups A and B. However, for the [3*c*-2*e*] bonds the influence of electronegativity on bond energy is a function of both $(\Delta\chi)^2$ and ($\Delta\chi$) and, in contrast to bonds AB, the influence of $\Delta\chi$ is directional, that is, the bond energies of AB_2^+ and BA_2^+ are different whereas those of AB and BA are the same. This directional relationship may at least in part be responsible for the observation that reactions occurring via triangular three-centre bonds (π-complexes) appear to be significantly affected by electronegativity

---

Keywords: Norbornyl cations; Electronegativity; Three-centre bonds; π-Complex; Carbonium ions; Bond energies.

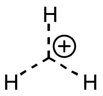
* Tel.: +44-1782-583045; fax: +44-1782-712378;
e-mail address: c.a.ramsden@chem.keele.ac.uk

0040–4020/$ - see front matter © 2004 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2004.01.090

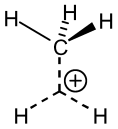
difference. We have described this additional influence of electronegativity difference as the $-2h\beta$ effect because it is this term in the general bond energy equation that gives rise to the directional effect. Details of the derivation of this model have been described elsewhere,[3] where it was discussed primarily using experimental data for reactions involving σ bonds. In this paper we explore the application of this model to three-centre bonds formed from π bonds (π-complexes) and extend the application to include a semi-quantitative model of 'back-donation'. We then explore conclusions and predictions of this model using more accurate structure-specific MO calculations.

2. Background

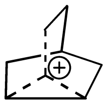
Many organic reactions involving electrophiles proceed via species (intermediates or transition states) that involve triangular [3*c*-2*e*] bonding.[6–10] These species are often, but not always, cations. In the gas phase, cations containing a [3*c*-2*e*] bond are often more stable than isomeric systems in which the electron pair is associated with a [2*c*-2*e*] bond. The simplest examples are the triatomic hydrogen molecular ion H_3^+, which has an equilateral triangle structure **1**,[11,12] and the methonium ion CH_5^+ **2**.[13–16] In solution, solvation usually favours two-centre bonding and only rarely are [3*c*-2*e*] bonded species, such as the 2-norbornyl cation **3**, stable enough to be observed experimentally.[17–19] Nevertheless, their involvement in chemical reactions of both σ and π bonds is now well established.[6]



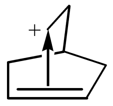
1



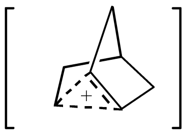
2



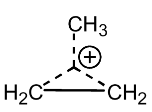
3a



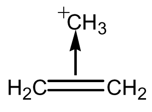
3b



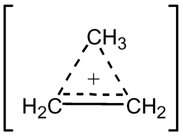
3c



4

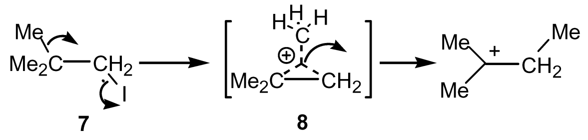


5



6

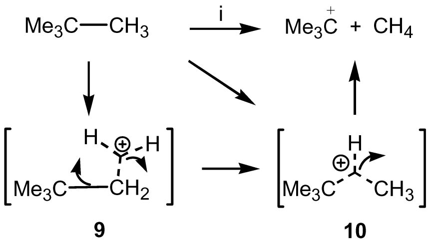
Dewar in 1945, was the first to recognise that alkenes could form dative bonds with electrophiles.[20–23] He described these products as π-complexes, recognised their relationship to aromatic species, and represented them using a dative bond arrow between double bond and electrophile, for example, **5**. Using this representation of [3*c*-2*e*] bonds the 2-norbornyl cation is represented by structure **3b**. Many electrophilic addition reactions of alkenes and 1,2-rearrangements of carbenium ions are interpreted in terms of π-complex formation. A well-known example is the Wagner–Meerwein rearrangement, exemplified by the rearrangement of neopentyl iodide **7** via the π-complex **8**, as shown in Scheme 1.[24,25] Whether the π-complex is an intermediate or transition state in these rearrangements and whether it is preceded by carbenium ion formation (e.g., $Me_3C{-}CH_2^+$) appears to depend on the individual structure and reaction conditions.[26] The π-complex concept was extended by Dewar to incorporate back-donation by an electron pair on the electrophile (a reverse dative bond).[27,28]



Scheme 1.

Based on AIM and ELF studies of the 2-norbornyl cation,[29–31] it has been proposed that the alternative representation of [3*c*-2*e*] bonds by structures of the type **3c** and **6** is misleading and should be avoided. A study of the calculated electron density in the 2-norbornyl cation **3** indicated that there is no 'bond path' connecting the bridging carbon and each of its neighbours. Structures of the type **4** or **5**, implying tetracoordinate carbon, appear to be a more realistic representation of the bonding. Here, and throughout, we represent π-complexes (e.g., **8**) using the branched dashed line convention advocated by Olah[6,32] to represent the three-centre bonding. This provides a consistent representation for both π and σ bonds, facilitates the writing of mechanisms using curly arrows and is consistent with the electron density studies described above.[29–31] Additional reasons for favouring the representation **4** in preference to the dative representation **5**, based on the implications of dative bond arrows, are given in Section 3.1.4.

Sigma bonds are weaker donors than π-bonds and only react with electrophiles under much more severe conditions. It was not until the 1960s that Olah[32–35] and others,[36,37] using superacids and other new methodology, were able to demonstrate the σ-basicity of C–H and C–C single bonds with a range of electrophiles to give products via triangular [3*c*-2*e*] bond formation. Thus, the protolysis of neopentane in HF-SbF$_5$ gives predominantly C–C cleavage with methane formation (Scheme 2).[38] This reaction occurs via the [3*c*-2*e*] bonded cation **10**, which is analogous to a π-complex and could be represented using a dative bond (cf. **4**). Formation of the species **10** may be preceded by C–H bond protonation to give the cation **9** which then undergoes a bond–bond rearrangement (**9**→**10**).[39–41] The universal role of [3*c*-2*e*] bonding in the reactions of σ- and π-bonds (σ and π donors) with electrophiles has been



Scheme 2. Reagents: (i) HF–SbF$_5$.

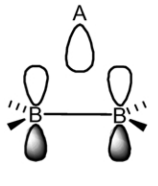
emphasised by Olah.[32] Dewar[22] has emphasised that [3*c*-2*e*] bonded species/π-complexes are associated with strong chemical bonds and are distinct from more weakly bonded van der Waals complexes.

The bonding of π-complexes, carbonium ions and other [3*c*-2*e*] bonded systems has been described by qualitative MO models and by increasingly sophisticated computer-aided MO calculations on specific systems. The HMO model that we have recently described[3] extends the qualitative analysis to a semi-quantitative description of [3*c*-2*e*] bonding in terms of generalised analytical expressions for relative bond energies. This permits some cautious generalisations on the influence of the electronegativity of the participating atoms on the relative strength of three-centre bonds and their ease of reaction. This model, therefore, bridges the gap between qualitative general pictures and sophisticated structure specific calculations and allows some conclusions that are not readily forthcoming from the other approaches, and which may be useful as a general reactivity guide to practicing chemists. We are aware of the limitations of the HMO method[4,5,42] but we emphasise that the objective of this study is to identify general trends and their origins and not to calculate accurate energies. We now explore in more detail the application of this model to structures and reactions involving ‘π-complexes’ and extend the application to include ‘back-donation.’

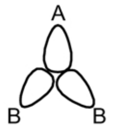
3. Results and discussion

3.1. π-Complex formation: a semi-quantitative model

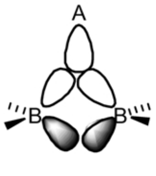
3.1.1. Bond energies. A π-complex can be considered to be formed by overlap of the p_z orbitals of a π bond B=B with a hybrid orbital on atom A (**11**). Here the BB overlap is different to the AB overlap and any interaction with the BB σ bond is neglected. The orbital topology is similar to but different from that envisaged for formation of a three-centre bond by a σ bond (i.e., **12**). A closer relationship between these types of three-centre, two-electron bond is achieved if the double bond forming the π-complex is considered to be formed by overlap of sp hybrid orbitals. The three-centre bond is then formed by overlap with two of these hybrids as shown in structure **13**. This approach has the advantage that participation of the BB σ bond is not neglected.



11

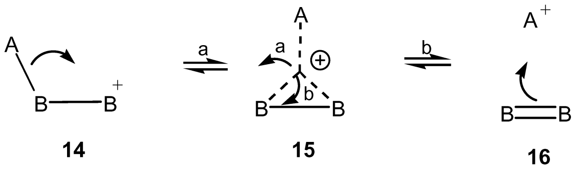


12



13

The purpose of the semi-quantitative model described here is to focus attention on generic features that merit further investigation by accurate structure specific calculations. Considering the approximations used, we do not believe that the extra refinement of the four-electron model **13** is either justified or provides additional insight (see later). Only the two-electron model **11** will be employed in the following discussion.



Scheme 3.

Consider the formation of the π-complex **15** from the classical precursors **14** and **16** (Scheme 3). In the HMO model, details of which we have described elsewhere,[3] the orbital energies (E_{14}, E_{15} and E_{16}) of the localised orbitals accommodating the electron pair involved in the change of bonding are given by Eqs. 1–3.

$$E_{14} = \alpha_B + 1/2h + 1/2[h^2 + 4\beta'^{2}_{AB}]^{1/2} \tag{1}$$

$$E_{15} = \alpha_B + 1/2(h + \beta_{BB}) + 1/2[h^2 - 2h\beta_{BB} + \beta_{BB}{}^2 + 8\beta_{AB}{}^2]^{1/2} \tag{2}$$

$$E_{16} = \alpha_B + \beta_{BB} \tag{3}$$

In Eqs. 1–3, the parameter *h* is the difference between the Coulomb integrals of atoms A and B (i.e., $h = \alpha_A - \alpha_B$) and can be taken as a measure of the electronegativity difference ($\Delta\chi$) between the atoms A and B (i.e., $h \propto \Delta\chi$).[4] The resonance integrals in the π-complex are defined as β_{AB} and β_{BB}, and β'_{AB} is the resonance integral of the σ-bond in the ion **14**. As previously, based on second-moment scaling,[43] we assume that the resonance integral of the σ bond AB (β'_{AB}) is related to the corresponding integral in the π-complex (β_{AB}) by $\beta'_{AB} = \sqrt{2}\beta_{AB}$. Although the choice of $\beta'_{AB} = \sqrt{2}\beta_{AB}$ may appear arbitrary it is not unreasonable (the two-centre bond is shorter) and it is easily shown that the choice does not affect the general conclusions (see later).

The bond energies (BE) of the species **14**, **15** and **16** relative to the energy of the dissociated system $A^{\cdot} + B^{\cdot} + B^{+}$ (i.e., $2\alpha_B + h$) are therefore given by Eqs. 4–6. Note that the choice of the reference point does not matter since we are only interested in the relative energies of the species **14**, **15** and **16** and these are independent of the reference frame chosen. This is illustrated by comparing Figure 1(c) and (d) (see below).

$$BE_{14} = -[h^2 + 8\beta_{AB}{}^2]^{1/2} \tag{4}$$

$$BE_{15} = -\beta_{BB} - [h^2 - 2h\beta_{BB} + \beta_{BB}{}^2 + 8\beta_{AB}{}^2]^{1/2} \tag{5}$$

$$BE_{16} = h - 2\beta_{BB} \tag{6}$$

Eq. 4 is in agreement with Pauling’s empirical relationship for two-centre bond energies:[44–47] bond energy (BE_{14}) is at a minimum when $h = 0$ (i.e., $\Delta\chi = 0$) and increases as electronegativity difference increases. Note that it does not matter if *h* is positive or negative since h^2 is always positive. In the region $h = 0$ the hyperbola (Eq. 4) is relatively flat ($\partial BE_{14}/\partial h = 0$ when $h = 0$). For small values of *h* the variation of bond energy will be small, in agreement with calculated values of intrinsic bond energies.[48,49]

The bond energy equation for the three-centre bond **15**

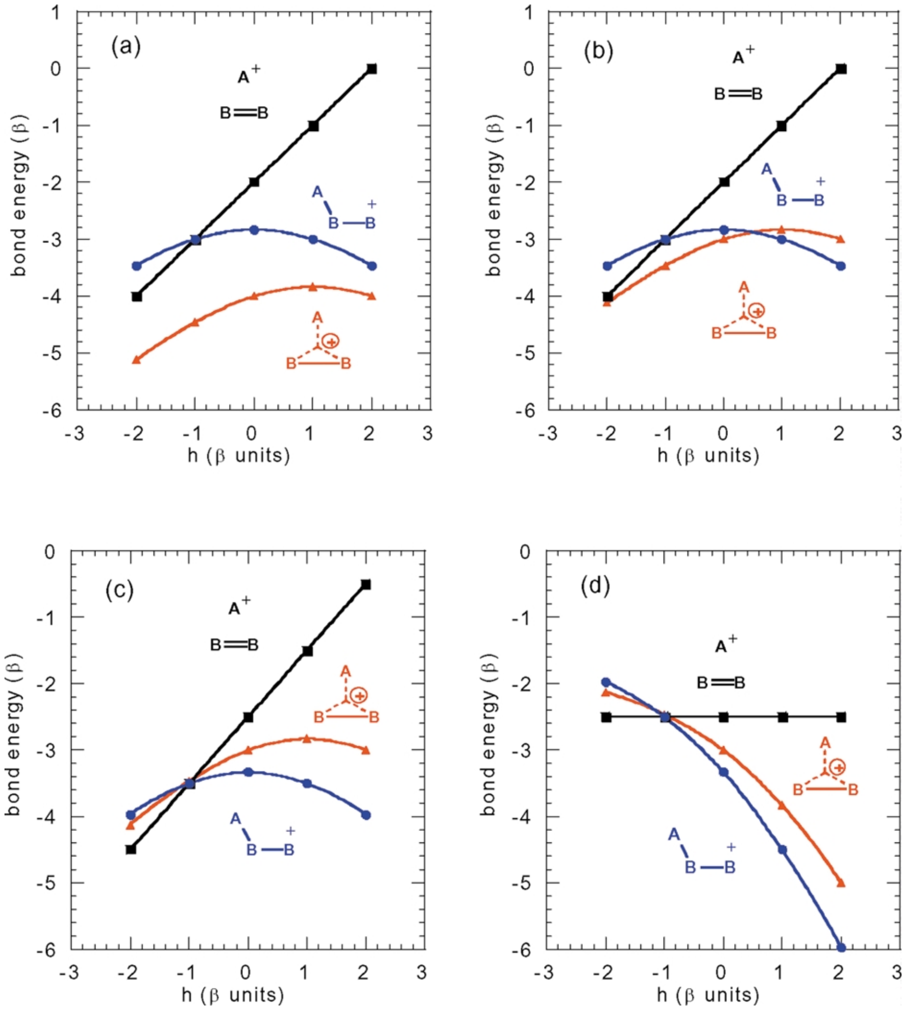


Figure 1. Calculated relative energies of species **14**, **15** and **16** with variation of h: (a) relative bond energies using Eqs. 4–6; (b) relative energies with allowance for nuclear repulsion; (c) relative energies with allowance for nuclear repulsion and solvation; (d) relative energies defined with respect to $A^+ + 2B^{\cdot}$ instead of $A^{\cdot} + B^{\cdot} + B^+$.

(Eq. 5) shows interesting similarities to and differences from the expression for the two-centre bond **14** (Eq. 4). Both curves are hyperbolas but the [3*c*-2*e*] bond curve is displaced along the *h*-axis by β_{BB}. Both bond energy expressions contain h^2 and $8\beta_{AB}^2$ terms, which seems reasonable. Although each A–B bonding interaction in the three-centre bond will be weaker, there are two interactions instead of one, which compensates. For the three-centre bond (Eq. 5) there are three additional terms each involving β_{BB}. The first two terms essentially reflect the new bonding interaction (B–B) that takes place as the bond forms and accounts for the greater stability of the [3*c*-2*e*] bond in the gas phase (Fig. 1(a)). These β_{BB} terms can be considered to describe the favourable cyclic conjugation relative to a linear [3*c*-2*e*] bond (B···A···B).

Figure 1(a) shows a plot of the bond energies given by Eqs. 4–6 against *h*, assuming that $\beta_{AB} = \beta_{BB}$. If the bond energy expression for the π-complex **15** was limited to these two additional terms in β_{BB} then it also would be a symmetrical hyperbola with minimum energy when $h = 0$. If this were the case, then variation of the electronegativity difference between atoms A and B would have little influence on the difference in bond energy between **14** and **15**. However, there is an additional term $(-2h\beta_{BB})$ that considerably modifies the form of the hyperbola. This term in effect displaces the hyperbola along the *h* axis and increases or decreases the bond energy depending upon whether *h* is positive or negative. When *h* is positive there is a negative contribution to BE_{15} and vice versa. The minimum bond energy occurs when $h = \beta_{BB}$ and when $h = 0$ the gradient $(\partial BE_{15}/\partial h)$ is 0.33. The bond energy difference between the isomeric systems **14** and **15** will therefore vary significantly with electronegativity difference (*h*), especially in the region $h = 0$. In other words, in contrast to [2*c*-2*e*] bonds, there is a directional influence of electronegativity difference on the bond energy of [3*c*-2*e*] bonds. We have described this influence of electronegativity difference as the $-2h\beta$ effect because it is this term that accounts for it in the HMO model and this emphasises the contribution of both *h* and β_{BB}. This influence of electronegativity difference (*h*) on the bond energy difference of isomers **14** and **15** is not the result of dative bond formation (e.g., **4**), which would involve a full *h* term in the bond energy difference. The contribution of *h* to dative bonds is discussed in Section 3.1.3.

The bond energy expression for the dissociated system **16** is much simpler and in this model is represented by a linear relationship (Eq. 6) (Fig. 1).

Before allowing for the effects of nuclear repulsion and solvation it is informative to consider the relative values of the energies given by Eqs. 4–6. If we assume that the energies of all the other electrons remain unchanged, Eqs. 4–6 give the relative electronic energies of the isomeric cations **14**-**16**. A plot of Eqs. 4–6 is given in Figure 1(a). This shows that the bond energy for the π-complex is greatest over a wide range of *h* values. However, some allowance for the differences in nuclear repulsion (ΔE_{nuc}) and for solvation (ΔE_{solv}) needs to be made in order to model relative energies. Here it is necessary to take a semi-empirical approach and use values that lead to a model consistent with experimental observations. We have assumed that ΔE_{nuc} and ΔE_{solv} are independent of *h*. The nuclear repulsion energy will be greatest for the cyclic cation **15** and we can allow for this by decreasing the relative bond energy of species **15** by $+\Delta E_{\mathrm{nuc}}$. Using a value of $+\Delta E_{\mathrm{nuc}}=1.0\beta_{\mathrm{AB}}$ gives the gas phase energy profile shown in Figure 1(b). With this allowance for nuclear repulsion the gas phase π-complexes **15** are expected to be more stable than the isomers **14** and **16** over a wide range of *h* values and this is in agreement with experiment and theory. A large part of the extra stability of the gas phase π-complexes **15** relative to the isomers **14** is attributable to the BB interactions in the bond energy expression (Eq. 5).

Most reactions of interest occur in the solution phase, in which the relative stabilities of the classical and non-classical ions are reversed. The [2*c*-2*e*] bonded systems **14** and **16** are more stable and the [3*c*-2*e*] bonded systems **15** correspond to intermediates or transition states. This reversal of stability can be partially attributed to greater solvation of the classical cations **14** and **16** with localised positive charge than that of the non-classical cations **15** with greater delocalisation of charge. This extra solvation of classical ions can be modelled by lowering the bond energies of the cations **14** and **16** by ΔE_{solv}. Again it is necessary to be pragmatic in selecting a value for ΔE_{solv}. It is known that for simple organic reactions (in the region $h=0$) the π-complex is an intermediate/transition state in the degenerate rearrangement of the cations **14** and the activation energy is quite small.[36,50–52] This, therefore, places the hyperbola of the non-classical species **15** only just above the hyperbola of the classical ion **14**. We have therefore used a value of $\Delta E_{\mathrm{solv}}=-0.5\beta_{\mathrm{AB}}$. Using this allowance for nuclear repulsion and solvation, the relative bond energies (RBE) of the species **14**-**16** are modelled by Eqs. 7–9. The resulting plot of relative energies in solution is shown in Figure 1(c) where it is assumed that $\beta_{\mathrm{AB}}=\beta_{\mathrm{BB}}$.

$$\mathrm{RBE}_{14} = -[h^2 + 8\beta_{\mathrm{AB}}{}^2]^{1/2} - 0.5\beta_{\mathrm{AB}}(\Delta E_{\mathrm{solv}}) \qquad (7)$$

$$\mathrm{RBE}_{15} = -\beta_{\mathrm{BB}} - [h^2 - 2h\beta_{\mathrm{BB}} + \beta_{\mathrm{BB}}{}^2 + 8\beta_{\mathrm{AB}}{}^2]^{1/2} + 1.0\beta_{\mathrm{AB}}(\Delta E_{\mathrm{nuc}}) \qquad (8)$$

$$\mathrm{RBE}_{16} = h - 2\beta_{\mathrm{BB}} - 0.5\beta_{\mathrm{AB}}(\Delta E_{\mathrm{solv}}) \qquad (9)$$

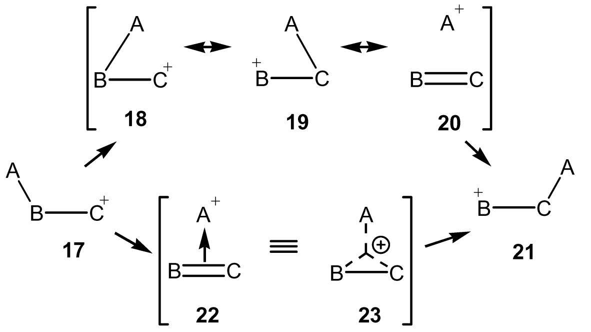
At this stage some comments on the assumptions and estimations used in this model are appropriate. The allowance for nuclear repulsion and solvation is purely empirical and the values are chosen to give a model consistent with the observation that simple π-complexes are not detectable in solution but are accessible during reactions. The separation of the parameters ΔE_{solv} and ΔE_{nuc} is artificial and is done only to acknowledge their contributions. There is some evidence that the difference in solvation energies in aqueous solution is smaller than we have suggested.[53] An alternative approach would be to arbitrarily choose parameters to allow for these and other effects that only move the curves on the *y*-axis and thereby place the bond energy relationships in the same juxtaposition. We also recognise that we have assumed that $\beta_{\mathrm{AB}}=\beta_{\mathrm{BB}}$ without justification and that the relationship $\beta'_{\mathrm{AB}}=\sqrt{2}\beta_{\mathrm{AB}}$ is imprecise. However, variation of the relative β values makes little difference to the general features of Figure 1. For example, different values for β simply move the hyperbola for the classical ion **14** up or down the *y*-axis and the effect is therefore incorporated into the semi-empirical parameters (ΔE_{solv} and ΔE_{nuc}) discussed above. We regard the main value of the model summarised by Figure 1 as providing an approximate evaluation of the relative energies of the species **14**-**16** as electronegativity difference varies. This provides insight into the nature of the bonding that is not forthcoming from either qualitative models or highly accurate calculated properties of a limited number of structures. It is important to reiterate here that the parameters ΔE_{solv} and ΔE_{nuc} and the β values only move the relative positions of the bond energy graphs in Figure 1 up or down the *y*-axis. They do not move the curves along the *x*-axis and this leads to important conclusions. It is relevant to point out here that the use of the four-electron model **13** also only moves the relative positions of the bond energy graphs on the *y*-axis and does not alter the conclusions, which is why we have used the simpler two-electron model **11**.

Figure 1(d) shows the energies of species **14**-**16** calculated relative to $\mathrm{A}^{+}+2\mathrm{B}^{\cdot}$ and demonstrates that their relative energies are independent of the reference frame chosen (cf. Fig. 1(c) and (d)).

3.1.2. π-Complex structure and stability.

Eqs. 7–9 describe a semi-quantitative model for the relative bond energies of the species **14**, **15** and **16** in solution. This model suggests certain features that are worthy of further exploration and which may give further insight into the nature of triangular three-centre bonding. First, because of the $-2h\beta$ effect, there is a crossover of the relative energies of the classical **14** and non-classical ion **15**. However, as the non-classical species (π-complex) becomes more favoured so does the dissociated product **16**. This suggests that simple π-complexes **15** (without back-donation) are never more stable in solution than the isomers **14** and **16**. It is interesting to question how close they come to being the most stable structure in solution or even whether there is always a small window of stability. The special case of the 2-norbornyl cation is discussed in Section 3.3.

A second point that becomes clear from the bond energy expression for π-complexes **15** (Eq. 5) is that the B–B interaction (β_{BB}) makes an important contribution to their stability and that part of this contribution is dependant on electronegativity difference. For molecular rearrangements the contribution of the B–B interaction in terms of qualitative resonance theory was recognised by Wheland.[54] He pointed out that in the general rearrangement **17**→**21** (Scheme 4) the intermediate species is a resonance hybrid of the structures **18**, **19** and **20**. Interestingly, Wheland emphasised the contribution of the structures **18** and **19** but made little comment on structure **20**, other than to say that it may 'also have a significant weight', and its contribution to rearrangement mechanisms was largely ignored in subsequent discussion. Here it is worth noting that the π-complex approach of Dewar (i.e., **22**) clearly emphasises the contribution of hybrid **20** but neither of these qualitative analyses focus attention on the combined influence of $\Delta\chi$ and β (i.e., $-2h\beta$). Later, the relative importance of the resonance hybrids **18**-**20** as electronegativity varies was briefly discussed in qualitative terms by Berson and Suzuki[55] and using qualitative arguments Dewar showed that classical ions, for example, **17**, can be expected to be favoured as the electronegativity of the apical group A increases.[28] Based on the semi-quantitative model described by Eqs. 7–9, the important quantitative contribution of the resonance hybrid **20** in determining relative stability of the intermediate species **23** with respect to the reactant **17** and product **21** can be appreciated. In particular the important β_{BB} terms in Eq. 5 describe the contribution of the hybrid **20**. This contribution is enhanced or reduced depending upon the relative electronegativity of the atoms and the absolute value of the resonance integral (β_{BB} or β_{BC}). This is the $-2h\beta$ effect: rearrangement will be easier when $-h$ and β are maximised. On their own, the hybrids **18** and **19** have little energetic influence relative to the precursor **17** (cf. Eqs. 4 and 5). The HMO model permits the general qualitative analysis of three-centre bonding based upon qualitative resonance[55] and MO[20–22,27,28] theories to be developed into a general semi-quantitative analysis and this is explored further in Section 3.1.3



Scheme 4.

3.1.3. The influence of electronegativity on heterolytic and homolytic cleavage of two-centre bonds (A–B).

To analyse the influence of electronegativity on reactions involving [3*c*-2*e*] bonds, it is useful to recognise a distinction between heterolytic and homolytic transformations. This is also relevant to deciding whether [3*c*-2*e*] bonds are appropriately represented as dative bonds (e.g., **5**) or by alternative representations (e.g., **4**), and this point is discussed further in Section 3.1.4.3. To emphasise similarities to and differences from two-centre bonds, we briefly discuss the influence of electronegativity on two-electron dative bonds ($B^-\rightarrow A^+$) before further discussing three-centre bonds.

All covalent bonds can in principle be regarded as dative bonds: a simple C–C bond can be envisaged as $C^-\rightarrow C^+$. Consider the general case of a dative bond between a Lewis acid A^+ and a Lewis base B^- [$B^-+A^+\rightleftarrows B^-\rightarrow A^+\leftrightarrow B-A$]. The energies of the precursor lone pair and [2*c*-2*e*] bond, relative to $A^{\cdot}+B^{\cdot}$ using the HMO model described above, are h and $-[h^2+4\beta_{AB}{}^2]^{1/2}$, respectively. In other words, the bond energy of the dative bond $B^-\rightarrow A^+$ relative to B^-+A^+ is given by the expression:

$$\{-h-[h^2+4\beta_{AB}{}^2]^{1/2}\}$$

It is made up of two components: these are the energy involved in transferring one electron from donor to acceptor ($-h$) and the bond energy of the covalent bond between $A^{\cdot}$ and $B^{\cdot}$ ($-[h^2+4\beta_{AB}{}^2]^{1/2}$). Depending upon the direction of the reaction, the term $-h$ is characteristic of dative bond formation or heterolytic cleavage and makes an important contribution to the energetics of chemical transformations. After allowing for nuclear repulsion ($+1.0\beta_{AB}$), plots of bond energy versus electronegativity difference (h) for the species B^-+A^+, $B^-\rightarrow A^+\leftrightarrow B-A$ and $B^{\cdot}+A^{\cdot}$ are shown in Figure 2.

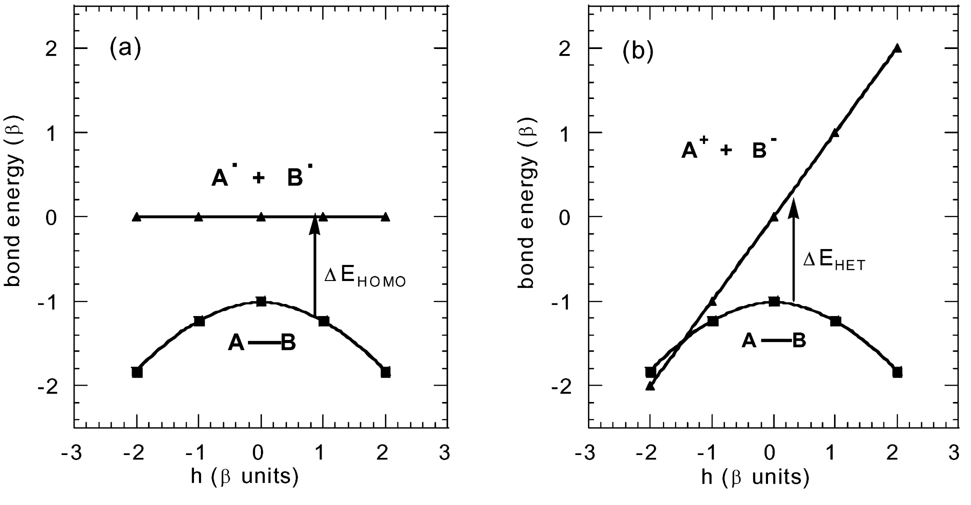


Figure 2. The calculated influence of h on the energy of (a) homolytic and (b) heterolytic cleavage of a two-centre, two-electron bond A–B.

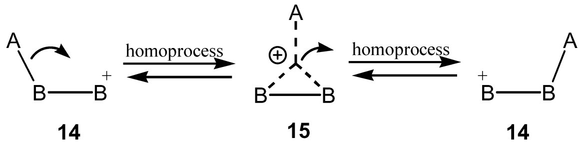
Here, and elsewhere, it is important to recognise the difference between the theoretical bond energy and the experimental bond dissociation energy, which will involve a number of other factors. The HMO model describes important but incomplete contributions to the bond dissociation energy and should only be used to discuss trends rather than actual energies. Within this model, when $h\approx0$ the energy of B^-+A^+ and $B^{\cdot}+A^{\cdot}$ are the same because, among other things, no allowance is made for electron–electron repulsion which is less in the diradical. In reality when $h=0$ the diradical will be more stable than the ion-pair (e.g., $C^{\cdot}+C^{\cdot}$ vs C^++C^-) and homolytic cleavage (ΔE_{HOMO}) of the bond is optimal (Fig. 2(a)). However, when one of the atoms becomes more electronegative ($h<0$) heterolytic cleavage rapidly becomes the energetically favoured mode of reaction (ΔE_{HET}) (Fig. 2(b)). The greater the electronegativity (or more correctly the greater the Coulomb integral) of the donor atom B relative to the acceptor A, the easier heterolytic cleavage (ΔE_{HET}) becomes and this is directly related to the $-h$ term in the bond energy expression. A crossover of the energies occurs when $-h$ reaches a certain value and ionisation predominates. Increasing the electronegativity (Coulomb integral) of an atom facilitates heterolytic cleavage (e.g., $-OH\rightarrow-OH_2^+$ and $-F\rightarrow-FSbF_5$).[56,57]

Although we have described bonds as dative (i.e., $B^-\rightarrow A^+$) in the preceding discussion, the concept of dative bonds is unnecessary, although sometimes convenient, and all dative bonds can be represented as conventional covalent bonds (e.g., $Me_3N^+-{}^-BF_3$ instead of $Me_3N\rightarrow BF_3$).[58] For heterolytic cleavage the bond energy of covalent bonds is related to electronegativity difference (h) by a simple $-h$ term plus an h^2 function and the ease of heterolytic cleavage is highly dependant upon h. As h becomes increasingly more negative the bond rapidly weakens (Fig. 2(b)). For homolytic cleavage there is no $-h$ term in the energy of cleavage (only an h^2 function) and as a result homolytic cleavage is not enhanced as the electronegativity difference (h) increases (Fig. 2(a)). Although not necessarily expressed in terms of a simple HMO model, these features of [2*c*-2*e*] covalent bonds are well known. Figure 2(a) is in good qualitative agreement[23] with Pauling's empirical relationship between [2*c*-2*e*] homolytic bond energies and electronegativity.[44–47] In applying the HMO approximation to [3*c*-2*e*] bonds it is reassuring that a similar application to [2*c*-2*e*] bonds gives a semi-quantitative model that is consistent with general experimental observations.

We have briefly discussed two-centre bonding here so that similarities and differences in three-centre bonding can be emphasised. In three-centre bonding, in addition to energy differences for bond formation and cleavage being related to $-h$ (heterolytic cleavage) and an h^2 function (heterolytic and homolytic cleavage), a dependence on a $-2h\beta$ function, not encountered with [2*c*-2*e*] bonding, influences the energy of some [3*c*-2*e*] bond transformations. Just as for two-centre bonds, it is important to distinguish between the types of transformation involved in the reactions of triangular [3*c*-2*e*] bonded species AB_2.

3.1.4. Homoprocesses and heteroprocesses of [3*c*-2*e*] bonds (AB_2). We refer to the formation and breaking of a [3*c*-2*e*] bond AB_2 as a *heteroprocess* if the pair of electrons moves from an association with only nuclei B to an association with both A and B, or vice versa. We refer to the formation and breaking of a [3*c*-2*e*] bond AB_2 as a *homoprocess* if the pair of electrons retains an association with both nuclei A and B during the transformation. These processes correspond to heterolytic and homolytic mechanisms in two-centre bonds A–B but we use different terms to avoid confusion.

3.1.4.1. Degenerate rearrangements. Consider the generalised degenerate 1,2-shift occurring via a transition state that is assumed to resemble the [3*c*-2*e*] bonded species **15** as shown in Scheme 5. Both steps in this transformation involve homoprocesses and as a result there is not a large influence of electronegativity difference on the activation energy (i.e., no $-h$ term). However, because of the involvement of the three-centre bonding, there is a contribution of both h^2 and $-2h\beta$ functions to the energy difference. This results in asymmetry of the hyperbolas describing the relative bond energies of reactant and transition state. The relative energies of the species **14** and **15** are given by Eqs. 7 and 8 and a plot of these energies (assuming $\beta_{AB}=\beta_{BB}$) is shown in Figure 3(a). Inspection of Figure 3(a) reveals that the activation energy of the rearrangement can be expected to increase as the electron-withdrawing power (electronegativity) of the migrating group A increases relative to B (i.e., h increasing). Degenerate 1,2-hydride and alkide shifts are usually very fast and a number of factors including steric and conformational effects will also determine the rate of reaction. However, the influence of electronegativity difference summarised in Figure 3(a) is consistent with the general view that the inherent migratory aptitude of groups is H>alkyl and $Me_3C>H_3C$.[59,60]



Scheme 5.

Migratory aptitude of alkyl substituents is often discussed in terms of hyperconjugation and the stabilisation of developing positive charge on atom A. This deserves some comment. In the positively charged [3*c*-2*e*] bonded species **15** the Coulomb integral (electronegativity) of alkyl groups A will vary. Hyperconjugation and the electronegativity/electron-withdrawing power of a charged alkyl group are intimately related. The electronegativity (Coulomb integral) of a methyl cation (Me radical IP 9.8 eV) is greater than that of a *t*-butyl cation (tBu radical IP 7.2 eV) and this can be rationalised in terms of hyperconjugation. The group orbitals of the methyl substituents in the tertiary cation interact with the empty orbital and reduce the Coulomb integral: an electron is held more weakly than by a methyl cation. During the change **14**→**15** the positive charge will increase on atom A and it can be interpreted that more electropositive groups will be better able to stabilise this charge. We suggest that an alternative interpretation of the influence of migrating group A on energy, which is highlighted by the HMO model, is the extent to which an atom or group A draws the pair of electrons away from the

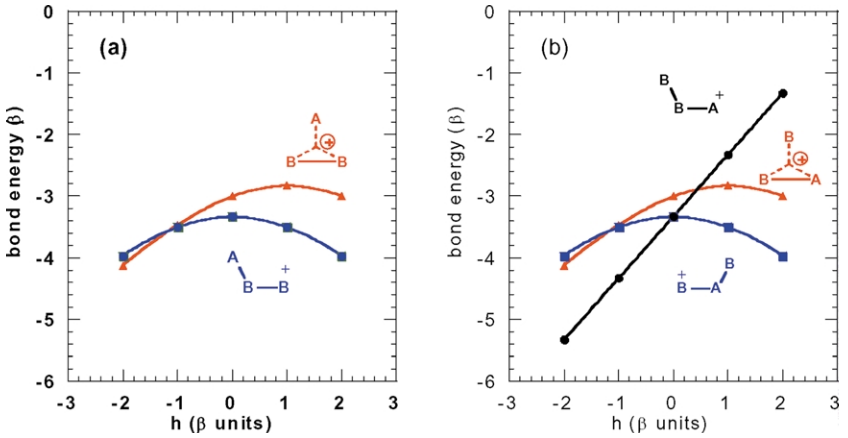


Figure 3. The calculated influence of h on the relative energies of products formed from a three-centre, two-electron bond AB_2^+ by (a) a homoprocess and (b) a heteroprocess.

bonding interaction BB (β_{BB}), or the reverse, and this effect is a function of both h and β_{BB}. This is the interaction that modifies the bond energy (Eq. 5) and this substituent effect on bond energy will also modify the distribution of the electron pair. The influence of $-2h\beta_{BB}$ on energy is therefore reflected in the distribution of positive charge,[61] and also in the bond lengths BB and AB (see Section 3.3.2 and references cited therein). A migrating *t*-Bu group will allow the retention of more bonding between BB in the transition state **15** than the more electronegative Me group and this accounts for a variation in activation energy as h varies (Fig. 3(a)). If this is the case, then it is important not to focus only on substituent effects (e.g., hyperconjugation) on the migrating group A. Substituent effects on the atoms B will also influence the relative energies. The difference in the properties of A and B (e.g., h) should be emphasised rather than effects at a single centre. On the basis of Figure 3(a), 1,2-hydride and 1,2-alkide shifts between secondary carbons can be expected to be faster than those between tertiary carbons.[62]

For a discussion of electronegativity difference of functional groups, group electronegativities are available but these have been derived for application to [2*c*-2*e*] bonds in neutral species.[63,64] In fact the electronegativities of carbon atoms in alkyl groups vary little in these bonds and this is reflected in fairly constant bond energies in CC bonds.[48,49] This is not the case for charged species in which the electron-withdrawing power of alkyl groups will vary much more with structure. Strictly, different values of h should be used for species **14** and **15** but neglect of this does not change the conclusions.

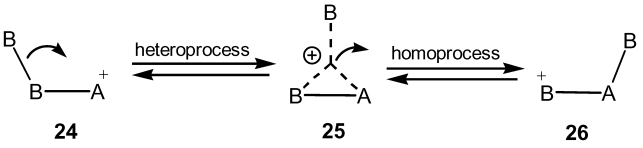
On the basis of the above discussion, more electropositive substituents such as $SiMe_3$ should have a very high migratory aptitude. There is evidence to support this conclusion,[65,66] which is also related to the well known β-effect in silicon-substituted carbocations.[67,68] However, because the electropositive silyl substituent has a weaker hold on the pair of bonding electrons (thereby increasing the bonding interaction BB) elimination is also thermodynamically favoured (i.e., **15**→**16**; A=SiR_3) (Fig. 1(c), h negative) and products related to this alternative mode of cleavage are often formed. In accord with the general features of Figure 1(c), by using the more electronegative $SiCl_3$ substituent both elimination and the β-effect (and presumably the migratory aptitude) are diminished.[69,70] For the same reasons the migratory aptitude of fluoroalkyl substituents (e.g., CF_3) can be expected to be very low.

It is also important to emphasise that the above analysis only concerns the energy of the electron pair involved in the [3*c*-2*e*] bond. Changes in the energies of other electrons may be relevant. For example, the cation B^+ (**14**) may be stabilised by resonance interactions (including hyperconjugation) and similar interactions with empty anti-bonding orbitals may stabilise cation **15**. These are important additional effects and should not be overlooked. They are well understood and are best taken into account on an individual basis (see also Section 3.3.2). Hyperconjugation effects must be separated into those that influence the energy of the bond electron pair and those that influence the energy of other electrons in the molecule (e.g., by stabilising B^+).

3.1.4.2. Non-degenerate rearrangements. Consider the non-degenerate 1,2-shifts shown in Scheme 6. The first step, which is [3*c*-2*e*] bond formation, is now a heteroprocess and, just as for two-centre bonds (Figure 2), the energy difference involves a $-h$ term. Assuming $\beta_{AB}=\beta_{BB}$, within the HMO model the bond energies for the species **25** and **26** are the same as for the isomers **15** and **14** respectively and are given by Eqs. 7 and 8. The relative bond energy for species **24** is given by Eq. 10 (cf. Eq. 9). Figure 3(b) shows a plot of the relative energies.

$$\mathrm{RBE}_{24} = h - 2\sqrt{2}\beta_{BB} - 0.5\beta_{AB}(\Delta E_{solv}) \tag{10}$$

It can be seen from Figure 3(b) that as the atom or group A becomes increasingly more electronegative relative to B the energy difference rapidly increases and there is a strong driving force for rearrangement (**24**→**26**). Even small electronegativity differences will have a big influence on

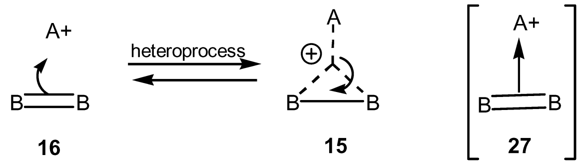


Scheme 6.

relative energies in the region $h \sim 0$. Figure 3(b) suggests that over a narrow range of positive h values the π-complex **25** will be a transition state with the activation energy rapidly decreasing as h increases. Above a certain h value the π-complex is no longer a transition state but simply a point on the energy surface describing the collapse of the cation **24** to the isomer **26**. It is well known that 1,2-shifts rapidly take place towards an electronegative electron-deficient centre such as O or N. The particularly strong driving force and influence of h arises because these rearrangements are heteroprocesses. Resonance stabilisation of the cations by substituents will also contribute to the observed relative stabilities.

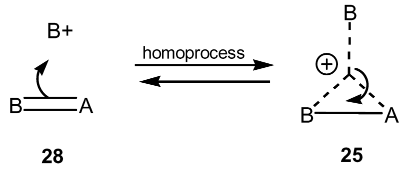
It is worth noting that Figure 3(b) may also provide some insight into concerted reactions such as the Baeyer–Villiger rearrangement[71] in which the transition state is polarised and approximates to three-centre bonding. The relationship is similar to that of cyclopropenone to the cyclopropenyl cation. In the Baeyer–Villiger rearrangement the electronegative CH_3 substituent (B) has a low migratory aptitude and in practice never migrates whereas more electropositive R_3C groups migrate well. It also follows that as A becomes more electronegative, for example if the polarity of the reaction increases, selectivity in the migrating groups can be expected to decrease.

3.1.4.3. Addition–elimination. The addition of electrophiles (e.g., A^+ or B^+) to double bonds to form π-complexes AB_2^+ can also be classified as hetero- or homoprocesses. The relative bond energies for the addition **16→15** are given in Figure 1(c). As A^+ becomes more electronegative the reaction becomes increasingly exothermic due to the direct dependence on electronegativity difference (h) (Scheme 7).



Scheme 7.

For this heteroprocess (**16→15**) the dative π-complex representation **27** is excellent in many ways and is consistent with a $-h$ term in the bond energy difference. However, formation of the same species **15** by the homoprocess **14→15** (Scheme 5) does not involve a $-h$ term and structure **27** is not a meaningful representation of **15** when formed from the precursor **14**. As for two-centre bonds, the dative bond representation (e.g., **27**) is more a characteristic of the mode of formation (a heteroprocess) rather than of the structure. To use structure **27** correctly it is necessary to know the history of the molecule (or its fate).[58]



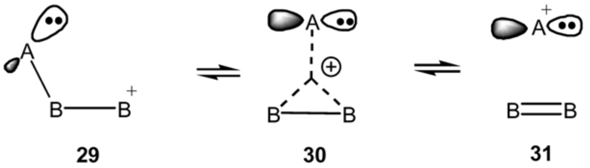
Scheme 8.

It is desirable to have a unique structural representation of [3*c*-2*e*] bonds that has no reaction implications, in the same way that all [2*c*-2*e*] σ bonds can be represented uniquely without the use of the dative notation. For this reason, together with the reasons discussed in Section 2, we prefer the universal use of the dotted line notation **15**.

Addition of an electrophile B^+ to an A═B bond is a homoprocess (**28→25**) (Scheme 8) and the exothermicity of subsequent reactions will be determined by the structure of the alternative products **24** or **26** (Scheme 6). The structure of the thermodynamically more stable product (**24** or **26**) (Fig. 3(b)) is in accord with Markovnikoff's rule.

3.2. π-Complex formation with back-donation

3.2.1. Bond energies and the equivalence of three- and two-centre bonding.



Scheme 9.

Consider the formation of the π-complex **30** (Scheme 9) in which the atom or group A has a lone pair of electrons that can be used for back-donation to the anti-bonding orbital on BB. The bonding MO formed by this interaction is summarised by structure **32** and arises from the interaction of the atomic orbitals shown in structure **33**. Within the HMO approximation, the secular determinant for the system is:

$$\begin{vmatrix} \alpha_B + h - E & \beta''_{AB} & -\beta''_{AB} \\ \beta''_{AB} & \alpha_B - E & \beta_{BB} \\ -\beta''_{AB} & \beta_{BB} & \alpha_B - E \end{vmatrix} = 0$$

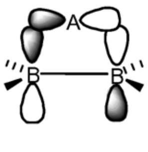
This is the same as the secular determinant for the [3*c*-2*e*] bond interaction **11**, discussed in Section 3.1, except that one of the resonance integrals is negative. Solving this determinant gives the energy of the three-centre MO **32** in the form of Eq. 11.[3]

$$E_{32} = \alpha_B + 1/2(h - \beta_{BB}) + 1/2[h^2 + 2h\beta_{BB} + \beta_{BB}{}^2 + 8\beta''_{AB}{}^2]^{1/2} \quad (11)$$

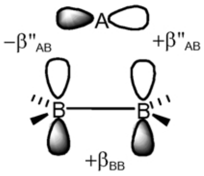
The bond energy (BE_{32}) of the bond **32** relative to an isolated lone pair A: ($2\alpha_B+2h$) is therefore given by Eq. 12.

$$BE_{32} = h + \beta_{BB} - [h^2 + 2h\beta_{BB} + \beta_{BB}{}^2 + 8\beta''_{AB}{}^2]^{1/2} \quad (12)$$

Note particularly that apart from the h term, which is discussed below, this differs from the bond energy



32



33

expression for the simple [3*c*-2*e*] bond **15** (BE$_{\mathbf{15}}$) (Eq. 5) only in that the signs of the β_{BB} and $2h\beta_{BB}$ terms have been reversed. Here we have a $+2h\beta$ effect, which occurs because the interaction is with the anti-bonding orbital of the BB double bond.

Using our common reference points ($A^{\cdot}+A{:}+B^{\cdot}+B^{+}=4\alpha_B+3h$), we are now able to write expressions for the bond energies of all four-electrons in the species **29-31** and these are given by Eqs. 13–15.

$$BE_{29} = -[h^2 + 8\beta_{AB}{}^2]^{1/2} \tag{13}$$

$$BE_{30} = h - [h^2 - 2h\beta_{BB} + \beta_{BB}{}^2 + 8\beta_{AB}{}^2]^{1/2} - [h^2 + 2h\beta_{BB} + \beta_{BB}{}^2 + 8\beta''_{AB}{}^2]^{1/2} \tag{14}$$

$$BE_{31} = h - 2\beta_{BB} \tag{15}$$

Eqs. 14 and 15 both contain an h term. Before discussing the significance of these terms, first consider the bond energy expression for the three-centre bond with back donation **30** (BE$_{30}$). The two square root terms in Eq. 14 only differ in the sign of the $2h\beta_{BB}$ component and the values of the resonance integrals β_{AB} and β''_{AB}. For the purposes of analysis, let us first assume that $\beta_{AB}=\beta''_{AB}$. It can then be shown that because $[h\beta_{BB}]^2 \ll [h^2+\beta_{BB}{}^2+8\beta_{AB}{}^2]^2$ the two $2h\beta$ terms effectively cancel each other out, that is,

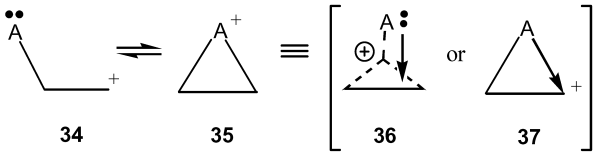
$$\begin{aligned} &-[h^2 - 2h\beta_{BB} + \beta_{BB}{}^2 + 8\beta_{AB}{}^2]^{1/2} - [h^2 + 2h\beta_{BB} + \beta_{BB}{}^2 + 8\beta_{AB}{}^2]^{1/2} \\ &\approx -2[h^2 + \beta_{BB}{}^2 + 8\beta_{AB}{}^2]^{1/2} \\ &= -2[h^2 + \beta_{BB}{}^2 + 4\beta'_{AB}{}^2]^{1/2} \end{aligned} \tag{16}$$

Eq. 16 is effectively the bond energy expression for two σ bonds (cf. Eqs. 4 and 13)—strengthened by some BB interaction (β_{BB}). In other words, with the assumption that $\beta_{AB}=\beta''_{AB}$, the bond energy (BE$_{\mathbf{30}}$) of the [3*c*-2*e*] bond with back donation **30** (i.e., two three-centre bonds) is equivalent to that of two two-centre σ bonds plus an h term, that is,

$$BE_{30} \approx h - 2[h^2 + \beta_{BB}{}^2 + 4\beta'_{AB}{}^2]^{1/2} \tag{17}$$

The h terms in Eqs. 14, 15 and 17 arise because the back-donation of the lone pair A: is a heteroprocess, that is, the lone pair is forming a dative bond with the anti-bonding orbital. This therefore, introduces a strong dependence on electronegativity difference (h) for the transformation **29**→**30**.

The HMO model described by Eqs. 13–17 is therefore, entirely consistent with the representation of bromonium ions and related species (**35**; A=Br, Cl, OH, SR) by two covalent C–A bonds. When formed from the precursors **34** one of these bonds can be regarded as a dative bond (e.g., **37**) and is a heteroprocess. The species **35** can be regarded as being bonded by two three-centre bonds (**36**; Eq. 14) or by a pair of two-centre bonds (**35** or **37**; Eq. 17). The two descriptions are equivalent but the representation **35** is preferred (Scheme 10).



Scheme 10.

In practice the resonance integrals β_{AB} and β''_{AB} in Eq. 14 will not be equal in magnitude. The integral β''_{AB} can be expected to be smaller. Also the Coulomb integral for the lone pair electrons on atom A (α'_A) will be slightly smaller than α_A. If we assume that $\beta''_{AB}=0.5\beta_{AB}$ and $h'=\alpha'_A-\alpha_B$ then the new bond energy expression for the cation **30** (BE$'_{\mathbf{30}}$) is given by Eq. 18.

$$BE'_{\mathbf{30}} = h' - [h^2 - 2h\beta_{BB} + \beta_{BB}{}^2 + 8\beta_{AB}{}^2]^{1/2} - [(h')^2 + 2h'\beta_{BB} + \beta_{BB}{}^2 + 2\beta_{AB}{}^2]^{1/2} \tag{18}$$

If $h-h'$ is small but significant it can be shown that the opposing $-2h\beta_{BB}$ and terms $+2h'\beta_{BB}$ in Eq. 18 still effectively cancel each other out. Eq. 19 is a reasonable approximation and like Eq. 17 describes bonding equivalent to one σ bond and one weaker σ bond.

$$\begin{aligned} BE'_{\mathbf{30}} &\approx h' - [h^2 + \beta_{BB}{}^2 + 8\beta_{AB}{}^2]^{1/2} \\ &\quad - [(h')^2 + \beta_{BB}{}^2 + 2\beta'_{AB}{}^2]^{1/2} \\ &= h' - [h^2 + \beta_{BB}{}^2 + 4\beta'_{AB}{}^2]^{1/2} \\ &\quad - [(h')^2 + \beta_{BB}{}^2 + \beta'_{AB}{}^2]^{1/2} \end{aligned} \tag{19}$$

3.2.2. The influence of electronegativity on onium ion stability.

If we make the same assumptions about internuclear repulsion ($\Delta E_{nuc}=1.0\beta_{AB}$) and solvation ($\Delta E_{solv}=-0.5\beta_{AB}$) as made in Section 3.1 but now include the contribution of back donation to the bond energy of ion **30** in the form of Eq. 18, the relative bond energies of the species **29**–**31** are as shown in Figure 4(a). For the purposes of the plot we have assumed that $h'=h$ and, as previously, $\beta_{AB}=\beta_{BB}$. Note in particular how the stability of the cyclic ion **30** has been increased relative to the acyclic species **29** and **31**. Figure 4(b) compares the bond energies of the onium ion **30** and the π-complex without back-donation **15**. In accord with experimental observation, the π-complex with back-donation is now stable for a wide range of h values and this stability extends to species where A is more electronegative than B ($h>0$) (e.g., A=Br, B=CR$_2$).

Note that as h increases and back donation becomes increasingly difficult, due to the electronegativity of A, the bond energy of the onium ion **35** tends towards that of the simple [3*c*-2*e*] bond **15** (Fig. 4(b)). This can be appreciated from the form of Eq. 18. As h' increases the $2\beta_{AB}{}^2$ term rapidly becomes small compared to $[(h')^2+2h'\beta_{BB}+\beta_{BB}{}^2]$. Eq. 19 then approximates to the form of Eq. 20, which is the bond energy expression for the bond **15** (Eq. 5).

$$\begin{aligned} BE'_{\mathbf{30}} &= h' - [h^2 - 2h\beta_{BB} + \beta_{BB}{}^2 + 8\beta_{AB}{}^2]^{1/2} \\ &\quad - [(h' + \beta_{BB})^2 + 2\beta_{AB}{}^2]^{1/2} \end{aligned}$$

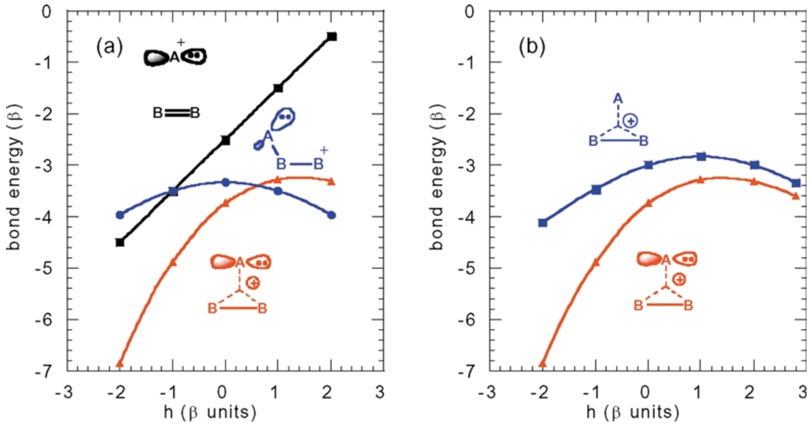


Figure 4. (a) Calculated energies of four-electron species **29**, **30** and **31** with variation of h; (b) comparison of relative energies of three-centre, two-electron bonds AB_2^+ with and without back donation.

If $2\beta_{AB}{}^2 \ll (h'+\beta_{BB})^2$

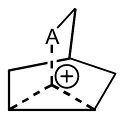
$$BE'_{\mathbf{30}} \approx h' - [h^2 - 2h\beta_{BB} + \beta_{BB}{}^2 + 8\beta_{AB}{}^2]^{1/2} - [(h'+\beta_{BB})^2]^{1/2} \qquad (20)$$

$$\therefore BE'_{\mathbf{30}} \approx -\beta_{BB} - [h^2 - 2h\beta_{BB} + \beta_{BB}{}^2 + 8\beta_{AB}{}^2]^{1/2} = BE_{\mathbf{15}}$$

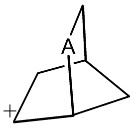
The bond energy expressions discussed above are therefore consistent with the following general conclusions. When formed by rearrangement from an acyclic cation the resulting π-complex can be regarded as being bonded by a σ bond and a weaker σ dative bond as summarised by structure **37**. As the atom or group A becomes more electropositive the dative bond strengthens and as A becomes more electronegative it weakens and tends towards a simple [3*c*-2*e*] bond without back-donation. Eqs. 13–19 therefore, provide a simple quantitative analysis of π-complexes involving back-donation. Back-donation in π-complexes has been discussed extensively by Dewar using both qualitative analysis[7,28] and MNDO calculations[72] and the semi-quantitative model discussed above is consistent with these studies. Detailed MNDO calculations on a number of specific structures were consistent with the earlier postulate that there is a 'continuous transition, with changing electronegativity of the apical group, from species best represented as π-complexes to ones best represented as classical microcycles',[72] (i.e., Fig. 4(b)). The position between the two extremes (**15** and **35**) will be reflected in the molecular geometry and CC stretching frequency of specific species. These aspects have been discussed extensively elsewhere.[72,73] In practice the acyclic ion **34** may well become more stable than the onium ion **35** before it effectively becomes a simple π-complex **15** (Fig. 4(a)).

3.3. 2-Norbornyl cations

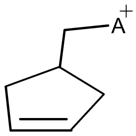
3.3.1. A semi-quantitative model of the influence of electronegativity. There is of course one particularly well-known example of a stable π-complex, namely the 2-norbornyl cation **38a** (R=H). This ion owes its relative stability to the relief of some ring strain in going from the classical structure **39a** to the non-classical structure **38a**.[74] This strain energy can be modelled by increasing the energy of the species **14** relative to **15** and **16**. For the purposes of modelling this effect we have used a value of 0.4β for the extra energy and a plot of the corresponding energies is shown in Figure 5(b). It can be seen that a modest increase in the relative energy of the classical cation results in a window in which the non-classical ion **15** is now more stable than either of the alternatives (**14** and **16**). Presumably the 2-norbornyl cation exists within this window. How large is this window and how much can the 2-norbornyl cation be modified without loss of the non-classical structure? Are there 2-norbornyl cation derivatives or analogues that are relatively more stable than the parent structure? These are interesting questions that are intimately associated with the influence of electronegativity on three-centre, two-electron bonds.



38



39



40

In structures **38**-**40**: **a**; A = CR_2
b; A = SiR_2
c; A = GeR_2
d; A = SnR_2
e; A = PbR_2

On the basis of the model summarised in Figure 5(b), making the apical atom or group A of a norbornyl system **38** more electropositive can be expected to increase the stability of the non-classical ion **38** relative to the classical ion **39**. The relative ring strain will of course differ depending upon the nature of the atom A. Synthetic studies have demonstrated the stability of the norbornyl cation analogues **38b-e** and NMR studies have fully characterised these species.[75–77] Associated quantum mechanical calculations show that as the electronegativity of the elements Si→Pb decreases, then the intramolecular stabilisation of the norbornyl cations **38** relative to the ring-opened isomeric cations **40** also decreases, in agreement with the general trend summarised in Figure 5(b). This trend arises primarily because the transformation **38**⇄**40** is a heteroprocess (Section 3.1.4) but the relative stability of the norbornyl structure **38** is also favourably influenced by the C1–C2 interaction (β) and the $-2h\beta$ effect. Furthermore, the calculated C1–C2 bond lengths increase along the series **38**

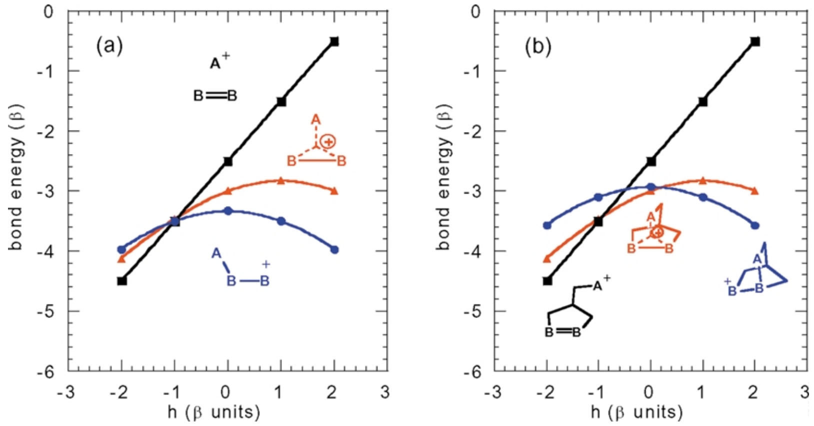
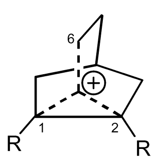


Figure 5. A comparison of (a) the relative energies of species **14**, **15** and **16** and (b) the relative energies of the 2-norbornyl cation and related species with allowance for ring strain in the classical cation.

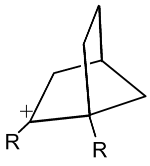
Si→Pb consistent with increasing electron-transfer to the C–C bonding interaction as *h* decreases. These recent preparative and advanced quantum mechanical studies are therefore in satisfactory agreement with the semi-quantitative model summarised in Figure 5(b) but it must be appreciated that in the series **38a-e** other factors neglected in the HMO model will also contribute to the relative stabilities.

The HMO model has been pushed to its limits and further investigations must rely on more accurate MO calculations. In the next Section 3.3.2 we use the 2-norbornyl cation **38a** (R=H) as a model system to probe the influence of 1,2-substituents on π-complex stability.

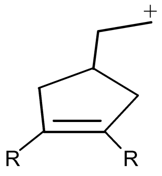
3.3.2. An AM1 study of substituent effects on the 2-norbornyl cation. The 2-norbornyl cation **41** is an excellent model for investigating the influence of substituent effects on the three participating atoms of a [3*c*-2*e*] bond. In this study the variation of electronic effects of substituents is used as a probe of the influence of 'electronegativity' variation. We appreciate that other effects, such as hyperconjugation and resonance interactions, will influence bonding and relative stability and this must be taken into account. We have chosen the AM1 method[78] for this quantitative study of the semi-quantitative model discussed in Section 3.1. For this investigation the AM1 method has advantages and disadvantages. An important advantage is that much less computer time is required than for more sophisticated ab initio calculations thus enabling a large number of substituted cations to be investigated (75 for this study). It does not seem unreasonable to explore the more accessible model first. A disadvantage is that the AM1 method calculates the classical cation **42** (R=H) to be more stable than the non-classical ion **41** (R=H) and therefore does not give an accurate description of the absolute energies. However, we have taken this inherent systematic error into account by correcting the calculated heats of formation of the 2-norbornyl cations **41** (ΔH_f[**41**]) by -22.7 kcal mol^{-1} (ΔH_f^c[**41**]), which gives an energy difference for the unsubstituted non-classical and classical cations **41** and **42** (R=H) of -13.6 kcal mol^{-1} corresponding to accurate ab initio calculations.[79] Since we are specifically interested in the influence of substituents on relative energies rather than absolute energies, we do not regard a systematic error in the calculated absolute energies as a problem.



41



42



43

In the AM1 method, because of the overestimation of the energy of the classical cation, both cations **41** and **42** correspond to energy minima making it straightforward to calculate heats of formation for both species. This is an advantage over ab initio methods in which the classical ion **42** is not necessarily an energy minimum and can be difficult to locate.[79] With these limitations in mind and emphasising that our main interest is the influence of substituents on the relative energies, we have carried out AM1 calculation on 25 symmetrical 1,2-disubstituted-2-norbornyl cations **41** together with the corresponding classical cations **42** and primary cations **43**. These cations correspond to the general species **14**, **15** and **16** (Section 3.1) and the calculated heats of formation are given in Tables 1 and 2.

Table 1 shows the AM1 calculated heats of formation for the cations **41** (ΔH_f[**41**] and ΔH_f^c[**41**]) and **42** (ΔH_f[**42**]) with all geometrical variables minimised. The substituents R were chosen to give a wide range of electronic effects. Table 1 also gives the difference in the calculated heats of formation ($\Delta\Delta H_f^c$[**41-42**]$=\Delta H_f^c$[**41**]$-\Delta H_f$[**42**]). Inspection of Table 1 shows that in general, and as expected based on Figure 5(b), the stability of the non-classical ion **41** increases relative to the classical ion **42** as the electron-withdrawing power of the substituents R increases.

To provide a quantitative basis for evaluating any relationship between relative stability and substituent effect, the correlation of $\Delta\Delta H_f^c$[**41-42**] for the 25 pairs of cations in Table 1 (entries 1–25) with σ_p^+ was investigated by linear regression. The most appropriate electronic parameter for

Table 1. AM1 calculated heats of formation of 2-norbornyl cations **41** and classical isomers **42**

Entry	Substituent	ΔH_f[**41**]	ΔH_f^c[**41**]	ΔH_f[**42**]	$\Delta\Delta H_f{}^c$[**41**-**42**]	σ^+	$\Im$	$\Re^+$
1	H	212.0	189.3	202.9	−13.6	0.0	0.0	0.0
2	$CONH_2$	142.1	119.4	134.9	−15.5	0.36	0.24	0.12
3	CN	292.8	270.1	286.1	−16.0	0.66	0.51	0.15
4	CCl_3	196.9	174.2	190.9	−16.7	0.33	0.31	0.02
5	NO_2	254.5	231.8	253.3	−21.5	0.79	0.67	0.12
6	CF_3	−73.3	−96.0	−74.1	−21.9	0.61	0.38	0.23
7	SOMe	155.6	132.9	157.6	−24.7	0.49	0.52	−0.03
8	SO_2Me	108.0	85.3	112.9	−27.6	0.72	0.54	0.18
9	CH_2CN	268.2	245.5	258.6	−13.1	0.16	0.21	−0.05
10	Cl	202.6	179.9	190.2	−10.3	0.11	0.41	−0.30
11	C≡CH	316.4	293.7	303.3	−9.6	0.18	0.19	−0.01
12	CH_3	191.1	168.4	177.8	−9.4	−0.31	−0.04	−0.27
13	F	128.2	105.5	112.8	−7.3	−0.08	0.43	−0.51
14	SMe	197.5	174.8	171.9	2.9	−0.54	0.20	−0.74
15	OMe	124.4	101.7	98.8	2.9	−0.78	0.26	−1.04
16	NHCOMe	117.2	94.5	85.1	9.4	−0.60	0.28	−0.88
17	CH_2OMe	109.1	86.4	100.1	−13.7	−0.05	0.01	−0.06
18	CO_2Me	58.7	36.0	54.7	−18.7	0.49	0.33	0.16
19	Br	228.0	205.3	219.3	−14.0	0.15	0.44	−0.29
20	Ph	257.4	234.7	233.7	1.0	−0.18	0.08	−0.26
21	Et	177.9	155.2	164.3	−9.1	−0.30	−0.05	−0.25
22	OPh	204.1	181.4	179.3	2.1	−0.50	0.34	−0.84
23	I	252.4	229.7	245.4	−15.7	0.13	0.04	0.09
24	cycloPr	246.1	223.4	231.1	−7.7	−0.41	−0.03	−0.38
25	$PhCH_2$	241.7	219.0	229.3	−10.3	−0.20	−0.08	−0.12

quantifying the electronic effect of each substituent is probably $\sigma_p{}^+$.[80] Although this parameter is derived for p-substituted aromatic systems it should be more relevant to the cations **41** and **42** than the simple Hammett constant σ_p. Values for $\sigma_p{}^+$ are given in Table 1. The relationship shown in Eq. 21 was obtained. Inspection of Eq. 21 reveals that there is a significant correlation and that $\sigma_p{}^+$ accounts for 80% of the variation in energy difference.

Table 2. AM1 calculated heats of formation of 2-norbornyl cations **41** and primary cations **43**

Entry	Substituent	$\Delta H_f{}^c$[**41**]	ΔH_f[**43**]	$\Delta\Delta H_f{}^c$[**41**-**43**]
1	H	189.3	221.3	−32.0
2	$CONH_2$	119.4	146.7	−27.3
3	CN	270.1	294.0	−23.9
4	CCl_3	174.2	197.4	−23.2
5	NO_2	231.8	251.2	−19.4
6	CF_3	−96.0	−75.7	−20.3
7	SOMe	132.9	157.7	−24.8
8	SO_2Me	85.3	110.9	−25.6
9	CH_2CN	245.5	272.6	−27.1
10	Cl	179.9	209.9	−30.0
11	C≡CH	293.7	329.0	−35.3
12	CH_3	168.4	203.9	−35.5
13	F	105.5	136.5	−31.0
14	SMe	174.8	214.6	−39.8
15	OMe	101.7	146.3	−44.6
16	NHCOMe	94.5	131.6	−37.1
17	CH_2OMe	86.4	126.0	−39.6
18	CO_2Me	36.0	63.5	−27.5
19	Br	205.3	232.5	−27.2
20	Ph	234.7	271.5	−36.8
21	Et	155.2	192.2	−37.0
22	OPh	181.4	226.8	−45.4
23	I	229.7	255.4	−25.7
24	cycloPr	223.4	263.0	−39.6
25	$PhCH_2$	219.0	256.4	−37.4

$$\Delta\Delta H_f{}^c[\mathbf{41}-\mathbf{42}] = -10.205 - 18.681\sigma_p{}^+ \qquad (21)$$

$$n = 25,\quad r^2 = 0.802,\quad s = 4.187$$

$$\Delta\Delta H_f{}^c[\mathbf{41}-\mathbf{42}] = -12.572 - 10.704\Im - 21.434\Re^+ \qquad (22)$$

$$n = 25,\quad r^2 = 0.838,\quad s = 3.865$$

The correlation between the calculated energy difference between the isomeric cations **41** and **42** and the parameter $\sigma_p{}^+$ is rather good. Since the energy term is a difference between two calculated values and since $\sigma_p{}^+$ is a general parameter it would be unreasonable to expect to obtain a better correlation using this data. Although values for individual pairs of cations should be treated with caution a general and significant trend is clear. The influence of substituents on the energy difference is entirely in accord with the simple model summarised in Figure 5. In particular the relative stability of the non-classical cation increases as the electron-withdrawing power ($\sigma_p{}^+$) of the substituent increases, that is, as the electronegativity of the carbon atoms increases. Based on Eq. 21, the crossover point of the relative energies of the carbonium ion **41** and the classical carbocation **42** can be expected to occur when $\sigma_p{}^+ \approx -0.5$. From accurate calculations[81,82] and X-ray crystallography,[83,84] we know that the 1,2-dimethyl-2-norbornyl cation (Table 1, entry 12) is more stable than the classical ion **42** (R=Me) ($\sigma_p{}^+ = -0.31$) and the crossover is therefore in the range $0 > \sigma_p{}^+ \leq -0.5$.

However, it is clear that for some substituents, in addition to an electronegativity effect, there is also a resonance/hyperconjugation effect on the relative stability of the cations **41** and **42**. To explore the relative importance of these effects we next investigated the relationship using the Swain and Lupton polar ($\Im$) and resonance ($\Re^+$) constants which separate these discrete effects ($\sigma_p{}^+=\mathfrak{I}+\mathfrak{R}^+$).[80] For the set of substituents used (Table 1) there was no correlation between $\mathfrak{I}$ and $\mathfrak{R}^+$ (r=0.187). Using multiple regression the significant relationship shown in Eq. 22 was obtained.

We interpret Eq. 22 to mean that there are two significant electronic effects that determine the relative stability of the 1,2-substituted cations **41** and **42**. A positive inductive effect ($\mathfrak{I}$ positive) increases the relative stability of the non-classical ion **41**. This is entirely consistent with the semi-quantitative model described in Section 3.1 and summarised in Figure 5. These substituents ($\mathfrak{I}$ positive) effectively increase the Coulomb integrals (electronegativity) of the carbon atoms at positions 1 and 2. In addition there is a large resonance effect, which includes hyperconjugation. Substituents with negative resonance effects ($\mathfrak{R}^+$ negative) stabilise the classical ion **42** relative to the non-classical ion **41**. To increase the relative stability of the non-classical 2-norbornyl cation an electron-withdrawing substituent in which both $\mathfrak{I}$ and $\mathfrak{R}^+$ are positive is desirable (e.g., CF_3). Of course, introducing electron-withdrawing groups will also make it increasingly difficult to generate cations (**41** or **42**) and may favour alternative modes of reaction, such as deprotonation to nortricyclane derivatives. These and other limitations need to be considered.

We next investigated the energies of the non-classical cations **41** relative to the primary cations **43**. For the parent carbocations **42** and **43** (R=H) the AM1 calculated energy difference is 18.4 kcal mol^{-1}. This does not seem to be an unreasonable value. We would not expect the energy difference between a primary and secondary carbocation to be less than this. In addition to hyperconjugation, a σ-bond is replaced by a weaker π-bond but there is also significant relief of ring strain. If we accept that the energy difference between cations **42** and **43** (R=H) is at least 18.4 kcal mol^{-1}, then it is appropriate that to compare the energies of the primary cations **43** with the carbonium ions **41** we should use the corrected heats of formation ($\Delta H_f{}^c$[**41**]). The calculated heats of formation $\Delta H_f{}^c$[**41**] and ΔH_f[**43**] and their difference $\Delta\Delta H_f{}^c$[**41-43**] are given in Table 2. For the parent systems **41** and **43** (R=H) (Table 2, entry 1) the energy difference $\Delta\Delta H_f{}^c$[**41-43**] is −32.0 kcal mol^{-1}. This is in good agreement with the results of more accurate calculations which give the energy difference in the range −24 to −32 kcal mol^{-1} depending upon the level of theory.[31]

Again a correlation of the calculated energy difference with $\sigma_p{}^+$ was investigated for all 25 pairs of cations and the relationship shown in Eq. 23 was obtained. This relationship is also significant and suggests a clear trend. As the electron-withdrawing power increases and the carbon atoms become more electronegative the stability of the open chain primary cation increases relative to the non-classical cation. However, the energy difference is so great that it is unlikely that the electron-withdrawing power of substituents would be sufficient to reverse the stabilities of species **41** and **43**. In this sense the simple model represented by Figure 5(b) exaggerates the stability of the primary cation **43** and, on the basis of AM1 calculations, for the 2-norbonyl system the primary cation bond energy is higher. Eq. 23 suggests that the crossover point for the relative energies of the cations **41** and **43** is $\sigma_p{}^+\approx 2$, which is far in excess of any substituent we could realistically encounter.

Using the Swain and Lupton constants the significant relationship shown in Eq. 24 was obtained. Again, there is both a field and resonance effect but note that the signs of the coefficients are opposite to those in Eq. 22 and the contribution of the resonance effect is smaller. We interpret this as a negative resonance effect stabilising the non-classical cation **41** more than the primary cation **43**. In addition a positive field effect increases the bond energy of the carbocation **43** relative to the carbonium ion **41** by increasing the effective electronegativity of the carbon atoms as predicted by the Hückel model (Fig. 5).

$$\Delta\Delta H_f{}^c[\mathbf{41}\text{–}\mathbf{43}] = -32.470 + 15.167\sigma_p{}^+ \qquad n = 25,\ r^2 = 0.822,\ s = 3.176 \tag{23}$$

$$\Delta\Delta H_f{}^c[\mathbf{41}\text{–}\mathbf{43}] = -33.653 + 17.875\mathfrak{I} + 13.883\mathfrak{R}^+ \qquad n = 25,\ r^2 = 0.849,\ s = 2.997 \tag{24}$$

On the basis of these results we conclude that the simple Hückel model described in Section 3.1 combined with resonance/hyperconjugation effects is in good agreement with the AM1 calculated relative stabilities. For the cations **41-43** both the Hückel and AM1 models provide a consistent picture. Electron-donating substituents R ($\sigma_p{}^+<0$, that is, h positive plus hyperconjugation) increasingly favour the classical ion **42** and electron-withdrawing substituents R ($\sigma_p{}^+>0$, that is, h negative) increasingly favour the primary cation **43**. The non-classical ion **41** occupies a position between these two extremes (cf. Fig. 5) but in practise reversing the stability of cations **41** and **43** by substituent effects at positions 1 and 2 is highly unlikely. It should be possible to make relatively more stable 2-norbornyl cations by introducing moderately electron-withdrawing groups at position 1 and 2. Moderately strong and acid stable electron-withdrawing groups such as CF_3 should significantly increase the stability of the carbonium ion **41** relative to the classical structure **42** and more detailed theoretical and experimental investigations of derivatives such as **41** (R=CF_3) may be of some interest.

Clearly, placing electron-withdrawing substituents on a molecule makes it more difficult to generate a cation and, although the relative stability of the cation **41** may increase, the absolute stability and ease of formation will decrease. An alternative strategy for formation of more stable 2-norbornyl cation derivatives is to increase the electronegativity difference (h) by placing electron-donating substituents on the carbon atom at position 6. However, the choice of suitable substituents is not obvious. Several studies of the solvolysis rates of 6,6-dimethyl-2-norbornyl derivatives have been reported but kinetic data is not a reliable guide to the relative thermodynamic stability of products.[85–87]

Table 3 shows the AM1 calculated C–C bond lengths ($r_{1,2}$ and $\check{r}_{1,6}$) that make up the [3c-2e] bond in the norbornyl cations **41**. The absolute values are poor compared to reliably accurate ab initio calculations but the change of bond length with substituent is of some interest here. The

Table 3. AM1 calculated interatomic distances for 2-norbornyl cations **41**

Entry	Substituent	$r_{1,2}$	$\check{r}_{1,6}$
1	H	1.392	2.240
2	$CONH_2$	1.380	2.356
3	CN	1.390	2.354
4	CCl_3	1.388	2.402
5	NO_2	1.372	2.504
6	CF_3	1.367	2.446
7	SOMe	1.383	2.388
8	SO_2Me	1.361	2.613
9	CH_2CN	1.392	2.311
10	Cl	1.400	2.315
11	$C\equiv CH$	1.410	2.269
12	CH_3	1.404	2.244
13	F	1.418	2.288
14	SMe	1.420	2.295
15	OMe	1.425	2.209
16	NHCOMe	1.448	2.235
17	CH_2OMe	1.387	2.309
18	CO_2Me	1.377	2.373
19	Br	1.393	2.354
20	Ph	1.414	2.230
21	Et	1.406	2.239
22	OPh	1.425	2.205
23	I	1.383	2.360
24	cycloPr	1.411	2.233
25	$PhCH_2$	1.402	2.253

bond length $\check{r}_{1,6}$ was taken as the average of $r_{1,6}$ and $r_{2,6}$ where there were small deviations from symmetry. As the electron-withdrawing power of the 1,2-substituents increases the bond length $r_{1,2}$ becomes shorter and the bond lengths $r_{1,6}$ and $r_{2,6}$ increase. The relationship between the bond lengths and electronic parameters are summarised by Eqs. 25–28. Eqs. 26 and 28 suggest that bond length is influenced by both field and resonance effects.

$$r_{1,2} = 1.40 - 0.041\sigma_{\mathrm{p}}{}^{+} \qquad n = 25,\quad r^2 = 0.770,\quad s = 0.010 \tag{25}$$

$$r_{1,2} = 1.394 - 0.021\mathfrak{I} - 0.049\mathfrak{R}^{+} \qquad n = 25,\quad r^2 = 0.835,\quad s = 0.009 \tag{26}$$

$$\check{r}_{1,6} = 2.312 + 0.188\sigma_{p}{}^{+} \qquad n = 25,\quad r^2 = 0.715,\quad s = 0.054 \tag{27}$$

$$\check{r}_{1,6} = 2.279 + 0.273\mathfrak{I} + 0.148\mathfrak{R}^{+} \qquad n = 25,\quad r^2 = 0.755,\quad s = 0.003 \tag{28}$$

Eqs. 25–28 are statistically significant but we do not wish to over-interpret their meaning. Increasing the 'electronegativity' of the carbon atoms at positions 1 and 2 (i.e., positive $\mathfrak{I}$) can be expected to attract the electron pair to these atoms and away from the carbon atom at position 6. This will increase the electron density in the bonding region between C1 and C2 and this is consistent with bond shortening. This interpretation is also consistent with the extra contribution to bond energy that we have referred to as the $-2h\beta$ effect. Both the extra bond energy and the C1–C2 bond length ($r_{1,2}$) are a function of the difference in electronegativity h (related to the $\mathfrak{I}$ parameter) and the C1–C2 resonance integral β. This polarisation inevitably results in lengthening of the C6–C1 and C6–C2 bond lengths ($\check{r}_{1,6}$). The inverse variation of the interatomic distances $r_{1,2}$ and $\check{r}_{1,6}$ with electronegativity difference is also seen in the calculated interatomic distances of protonated alkanes[40,88–91] and related species[92–94] and appears to be a characteristic feature of [3*c*-2*e*] bonds.

Overall, the results of the AM1 calculations on the relative energies and structures of 75 cations are consistent with the semi-quantitative Hückel model described in Section 3.1.

4. Conclusions

We have described an HMO model of [3*c*-2*e*] bonds and their formation and cleavage by homo- and heteroprocesses. This simple model is consistent with general experimental observations and the results of more accurate calculations on specific structures. In particular the model rationalises general trends in the influence of electronegativity difference and substituent effects on reactions occurring via [3*c*-2*e*] bonded intermediates or transition states and provides further insight into the major bonding interactions in these systems.

Important features of this model are the distinct profiles of the bond energy versus electronegativity difference curves (BE vs *h*) of the interconverting isomeric species (**14**-**16**). Key contributions to bond energy difference are a $-h$ term for heteroprocesses and a function of $-2h\beta$ for homoprocess. Although an empirical approach is used to estimate the crossing points of the bond energy curves, the semi-quantitative conclusions concerning energy differences are not dependant upon a precise knowledge of the crossing points. The effect of substituents on transformations involving [3*c*-2*e*] bonds is often interpreted in terms of the ability of an atom and its substituents to stabilise positive charge. The model described here suggests that the relative energies are best understood by an analysis of the influence of electronegativity (electron-withdrawing power) on the bond energies of the isomeric species. Examination of the HMO bond energy equations suggest that significant variation in the relative bond energies is the result of differing dependence on electronegativity difference terms (h, h^2 and $-2h\beta$). It is the contributions of these functions of electronegativity difference that primarily determine the variation in relative energies. In contrast to [2*c*-2*e*] bonded species, the bond energy of a [3*c*-2*e*] bond AB_2 is influenced by a function of $-2h\beta$ that accounts for the extent that the atom A draws electron density away from the bonding interaction BB. In order to focus attention on this term we have described it as the $-2h\beta$ effect. This effect also influences the charge distribution and bond lengths.

In spite of the simplifications inherent in the HMO model, used with caution it continues to give valuable insight into chemical bonding. Although many terms are neglected, those that are retained are major ones that will dominate energy expressions. Many of the most useful theoretical concepts in organic chemistry rely on severe approximations but used within their limitations this does not detract from their usefulness in teaching and practice. We believe that the simple bond energy/electronegativity difference diagrams, exemplified by Figures 1–5, provide a useful basis for understanding substituent effects in structures or reactions in which intermediates or transition states can be approximated to [3*c*-2*e*] bonded species. Ultimately the tests of the usefulness of any model are: (i) does it rationalise existing facts; (ii) does it provide new insights into structure, reactions or properties and (iii) does it direct attention to new areas worthy of further investigation. It is hoped that the simple HMO model described in this paper will fulfil some of these criteria by drawing attention to general trends in the chemistry of triangular three-centre, two-electron bonds and thus contribute to a wider appreciation of the importance of this type of bonding interaction in organic chemistry.

References and notes

1. *Encyclopedia of computational chemistry*; Schleyer, P. v. R., Schaefer, H. F., III, Handy, N. C., Eds.; Wiley: New York, 1998.
2. Munzarová, M. L.; Hoffmann, R. *J. Am. Chem. Soc.* **2002**, *124*, 4787–4795.
3. Ramsden, C. A. *J. Phys. Chem. A* **2002**, *106*, 2777–2780.
4. Coulson, C. A.; O'Leary, B.; Mallion, R. B. Hückel theory for organic chemists; Academic: London, 1978.
5. Heilbronner, E.; Bock, H. *The HMO model and its application*; Verlag Chemie: GmbH, Weinheim, 1976.
6. Olah, G. A.; Prakash, G. K. S.; Williams, R. E.; Field, L. D.; Wade, K. *Hypercarbon chemistry*; Wiley: New York, 1987.
7. DeKock, R. L.; Bosma, W. B. *J. Chem. Ed.* **1988**, *65*, 194–197.
8. McMurry, J. E.; Lectka, T. *Acc. Chem. Res.* **1992**, *25*, 47–53.
9. *Stable carbocation chemistry*; Prakash, G. K. S., Schleyer, P. v. R., Eds.; Wiley: New York, 1997.
10. Mota, C. J. A. *Quim. Nova* **2000**, *23*, 338–345.
11. Gaillard, M. J.; Gemmell, D. S.; Goldring, G.; Levine, I.; Pietsch, W. J.; Poizat, J. C.; Ratkowski, A. J.; Remillieux, J.; Vager, Z.; Zabransky, B. J. *Phys. Rev.* **1978**, *A17*, 1797–1803.
12. Oka, T. *Phys. Rev. Lett.* **1980**, *45*, 531–534.
13. Schleyer, P. v. R.; Carneiro, J. W. de M. *J. Comp. Chem.* **1992**, *13*, 997–1003.
14. Schreiner, P. R.; Kim, S.-J.; Schaefer, H. F.; Schleyer, P. v. R. *J. Chem. Phys.* **1993**, *99*, 3716–3720.
15. Marx, D.; Parrinello, M. *Nature* **1995**, *375*, 216–218.
16. White, E. T.; Tang, J.; Oka, T. *Science* **1999**, *284*, 135–137.
17. Schleyer, P. v. R.; Fort, R. C., Jr.; Watts, W. E.; Comisarow, M. B.; Olah, G. A. *J. Am. Chem. Soc.* **1964**, *86*, 4195–4197.
18. Saunders, M.; Schleyer, P. v. R.; Olah, G. A. *J. Am. Chem. Soc.* **1964**, *86*, 5680–5681.
19. Olah, G. A.; Prakash, G. K. S.; Saunders, M. *Acc. Chem. Res.* **1983**, *16*, 440–448.
20. Dewar, M. J. S. *Nature* **1945**, *156*, 784.
21. Dewar, M. J. S. *The electronic theory of organic chemistry*; Clarendon: Oxford, 1949.
22. Dewar, M. J. S.; Marchand, A. P. *Ann. Rev. Phys. Chem.* **1965**, *16*, 321–346.
23. Dewar, M. J. S. *The molecular orbital theory of organic chemistry*; McGraw-Hill: New York, 1969.
24. Whitmore, F. C.; Wittle, E. L.; Popkin, A. H. *J. Am. Chem. Soc.* **1939**, *61*, 1586–1590.
25. Nordlander, J. E.; Jindal, S. P.; Schleyer, P. v. R.; Fort, R. C., Jr.; Harper, J. J.; Nicholas, R. D. *J. Am. Chem. Soc.* **1966**, *88*, 4475–4484.
26. Ammal, S. C.; Yamataka, H.; Aida, M.; Dupuis, M. *Science* **2003**, *299*, 1555–1557.
27. Dewar, M. J. S. *Bull. Soc. Chim. Fr.* **1951**, C71–C79.
28. Dewar, M. J. S.; Dougherty, R. C. *The PMO theory of organic chemistry*; Plenum: New York, 1975; pp 298–310.
29. Werstiuk, N. H.; Muchall, H. M. *J. Mol. Struct.* **1999**, *463*, 225–229.
30. Werstiuk, N. H.; Muchall, H. M. *J. Phys. Chem. A* **2000**, *104*, 2054–2060.
31. Werstiuk, N. H.; Muchall, H. M.; Noury, S. *J. Phys. Chem. A* **2000**, *104*, 11601–11605.
32. Olah, G. A. *Angew. Chem., Int. Ed.* **1973**, *12*, 173–254.
33. Olah, G. A. *Angew. Chem., Int. Ed.* **1995**, *34*, 1393–1405.
34. Olah, G. A.; Prakash, G. K. S.; Sommer, J. *Superacids*; Wiley: New York, 1985.
35. Olah, G. A. *J. Org. Chem.* **2001**, *66*, 5943–5957.
36. Brouwer, D. M.; Hogeveen, H. *Progress in physical organic chemistry*; Streitwieser, A., Taft, R. W., Eds.; Wiley: New York, 1972; Vol. 9, pp 179–240.
37. Sommer, J.; Bukala, J. *Acc. Chem. Res.* **1993**, *26*, 370–376.
38. Olah, G. A.; Halpern, Y.; Shen, J.; Mo, Y. K. *J. Am. Chem. Soc.* **1971**, *93*, 1251–1256.
39. Olah, G. A. *J. Am. Chem. Soc.* **1972**, *94*, 808–820.
40. Esteves, P. M.; Mota, C. J. A.; Ramírez-Solís, A.; Hernández-Lamoneda, R. *J. Am. Chem. Soc.* **1998**, *120*, 3213–3219.
41. Esteves, P. M.; Ramírez-Solís, A.; Mota, C. J. A. *J. Phys. Chem. B* **2001**, *105*, 4331–4336.
42. Coulson, C. A.; Dewar, M. J. S. *Discuss. Faraday Soc.* **1947**, *2*, 54–62.
43. Lee, S. *Acc. Chem. Res.* **1991**, *24*, 249–254.
44. Pauling, L. *The nature of the chemical bond*, 3rd ed.; Cornell University Press: New York, 1960; pp 91–95.
45. Murphy, L. R.; Meek, T. L.; Allred, A. L.; Allen, L. C. *J. Phys. Chem. A* **2000**, *104*, 5867–5871.
46. Smith, D. W. *J. Phys. Chem. A* **2002**, *106*, 5951–5952.
47. Matsunaga, N.; Rogers, D. W.; Zavitsas, A. A. *J. Org. Chem.* **2003**, *68*, 3158–3172.
48. Exner, K.; Schleyer, P. v. R. *J. Phys. Chem. A* **2001**, *105*, 3407–3416.
49. Grimme, S. *J. Am. Chem. Soc.* **1996**, *118*, 1529–1534.
50. Saunders, M.; Hagen, E. L. *J. Am. Chem. Soc.* **1968**, *90*, 2436–2437.
51. Saunders, M.; Kates, M. R. *J. Am. Chem. Soc.* **1978**, *100*, 7082–7083.
52. Saunders, M. In *Stereodynamics of molecular systems*; Sarma, J., Ed.; Pergamon: Oxford, 1979.
53. Schreiner, P. R.; Severance, D. L.; Jorgensen, W. L.; Schleyer, P. v. R.; Schaefer, H. F. *J. Am. Chem. Soc.* **1995**, *117*, 2663–2664.
54. Wheland, G. W. *Resonance in organic chemistry*; Wiley: New York, 1955; pp 523–524.
55. Berson, J. A.; Suzuki, S. *J. Am. Chem. Soc.* **1959**, *81*, 4088–4094.
56. Olah, G. A.; Tolgyesi, W. S.; Kuhn, S. J.; Moffatt, M. E.; Bastien, I. J.; Baker, E. B. *J. Am. Chem. Soc.* **1963**, *85*, 1328–1334.
57. Olah, G. A.; Baker, E. B.; Evans, J. C.; Tolgyesi, W. S.; McIntyre, J. S.; Bastien, I. J. *J. Am. Chem. Soc.* **1964**, *86*, 1360–1373.
58. Clayden, J.; Greeves, N.; Warren, S.; Wothers, P. *Organic chemistry*; Oxford University Press: Oxford, 2001; p 116.

59. Stiles, M.; Mayer, R. P. *J. Am. Chem. Soc.* **1959**, *81*, 1497–1501.
60. Bethell, D. *Comprehensive organic chemistry*; Stoddart, J. F., Ed.; Pergamon: Oxford, 1979; Vol. 1, p 435, Chapter 2.7.
61. Esteves, P. M.; Alberto, G. G. P.; Ramírez-Solís, A.; Mota, C. J. A. *J. Am. Chem. Soc.* **1999**, *121*, 7345–7348.
62. Olah, G. A.; Olah, J. A. *Carbonium ions*; Olah, G. A., Schleyer, P. v. R., Eds.; Wiley: New York, 1970; Vol. II, p 773.
63. Mullay, J. *J. Am. Chem. Soc.* **1984**, *106*, 5842–5847.
64. Mullay, J. *J. Am. Chem. Soc.* **1985**, *107*, 7271–7275.
65. Cook, M. A.; Eaborn, C.; Walton, D. R. M. *J. Organomet. Chem.* **1970**, *24*, 301–306.
66. Jarvie, A. W. P.; Holt, A.; Thompson, J. *J. Chem. Soc. (B)* **1970**, 746–748.
67. Lambert, J. B. *Tetrahedron* **1990**, *46*, 2677–2689.
68. Siehl, H.-U.; Müller, T. *The chemistry of organic silicon compounds*; Rappoport, Z., Apeloig, Y., Eds.; Wiley: Chichester, UK, 1998; Vol. 2, p 595.
69. Brook, M. A.; Neuy, A. *J. Org. Chem.* **1990**, *55*, 3609–3616.
70. Brook, M. A.; Henry, C.; Jueschke, R.; Modi, P. *Synlett* **1993**, 97–104.
71. Krow, G. R. *Comprehensive organic synthesis*; Ley, S. V., Ed.; Pergamon: Oxford, UK, 1991; Vol. 7, p 671.
72. Dewar, M. J. S.; Ford, G. P. *J. Am. Chem. Soc.* **1979**, *101*, 783–791.
73. Allen, F. H. *Tetrahedron* **1982**, *38*, 2843–2853.
74. Sargent, G. D. *Carbonium ions*; Olah, G. A., Schleyer, P. v. R., Eds.; Wiley: New York, 1972; Vol. III, p 1132.
75. Steinberger, H.-U.; Müller, T.; Auner, N.; Maerker, C.; Schleyer, P. v. R. *Angew. Chem., Int. Ed.* **1997**, *36*, 626–628.
76. Maerker, C.; Schleyer, P. v. R. *The chemistry of organic silicon compounds*; Rappoport, Z., Apeloig, Y., Eds.; Wiley: Chichester, UK, 1998; Vol. 2, p 513.
77. Müller, T.; Bauch, C.; Ostermeier, M.; Bolte, M.; Auner, N. *J. Am. Chem. Soc.* **2003**, *125*, 2158–2168.
78. Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902–3909.
79. Schleyer, P. v. R.; Sieber, S. *Angew. Chem., Int. Ed.* **1993**, *32*, 1606–1608.
80. Hansch, C.; Leo, A. *Substituent constants for correlation analysis in chemistry and biology*; Wiley: New York, 1979.
81. Schleyer, P. v. R.; Maerker, C. *Pure Appl. Chem.* **1995**, *67*, 755–760.
82. Muchall, H. M.; Werstiuk, N. H. *J. Phys. Chem. A* **1999**, *103*, 6599–6602.
83. Laube, T. *Angew. Chem., Int. Ed.* **1987**, *26*, 560–562.
84. Laube, T. *Helv. Chim. Acta* **1994**, *77*, 943–956.
85. Schleyer, P. v. R.; Donaldson, M. M.; Watts, W. E. *J. Am. Chem. Soc.* **1965**, *87*, 375–376.
86. Altmann-Schaffner, E.; Grob, C. A. *Helv. Chim. Acta* **1987**, *70*, 43–48.
87. Kirmse, W.; Mrotzeck, U.; Siegfried, R. *Chem. Ber.* **1991**, *124*, 241–245.
88. Mota, C. J. A.; Esteves, P. M.; Ramírez-Solís, A.; Hernández-Lamoneda, R. *J. Am. Chem. Soc.* **1997**, *119*, 5193–5199.
89. Okulik, N. B.; Sosa, L. G.; Esteves, P. M.; Mota, C. J. A.; Jubert, A. H.; Peruchena, N. M. *J. Phys. Chem. A* **2002**, *106*, 1584–1595.
90. Esteves, P. M.; Alberto, G. G. P.; Ramírez-Solís, A.; Mota, C. J. A. *J. Phys. Chem. A* **2000**, *104*, 6233–6240.
91. Seitz, C.; East, A. L. L. *J. Phys. Chem. A* **2002**, *106*, 11653–11662.
92. Olah, G. A.; Prakash, G. K. S.; Rasul, G. *J. Org. Chem.* **2001**, *66*, 2907–2910.
93. Olah, G. A.; Prakash, G. K. S.; Rasul, G. *J. Org. Chem.* **2002**, *67*, 8547–8551.
94. Sauers, R. R. *Tetrahedron Lett.* **2001**, *42*, 6625–6628.