

### 3 Theoretical Chemistry

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By I. H. WILLIAMS

*School of Chemistry, University of Bristol, Bristol BS8 1TS*

#### 1 Introduction

What has theoretical chemistry had to say to organic chemistry during 1987? If judged by the sheer volume of published literature, the answer is plenty. Increasingly, theoretical methods are being used by organic chemists as tools for the investigation of structure and reactivity; such applications should be guided by awareness of the scope and limitations of the available methods. *Ab initio* calculations for individual molecular species are catalogued annually in a bibliography (the supplement for 1986 contains 1667 references<sup>1</sup>), but a classification of theoretical studies of reactions is lacking. Theoretical organic chemistry is not merely the business of cranking ever-more-accurate numbers from a computer: its primary role is the establishment and refinement of concepts and models for the interpretation and prediction of organic molecular behaviour.

#### 2 Computational Methods

Two volumes (67 and 69) of the series *Advances in Chemical Physics* were devoted to *ab initio* methods in quantum chemistry and contain authoritative reviews of numerous topics, including the use of analytical derivative methods.<sup>2</sup> Handy and co-workers have described the accurate prediction of molecular geometries and spectroscopic constants using SCF and MP2 energy derivatives;<sup>3</sup> the use of large basis sets (triple zeta in the valence region with multiple sets of polarization functions) leads to errors of only  $\pm 0.002$  Å in single bond lengths,  $\pm 0.01$  Å for multiple-bond lengths,  $\pm 0.2^\circ$  for angles, and a mean error of only 1.5% in harmonic vibrational frequencies at the MP2 level.<sup>4</sup> Analytical energy gradients have been implemented at the MP3 and MP4 levels,<sup>5</sup> but the resulting geometries and frequencies do not seem to be better than those at the MP2 level. Schlegel has reviewed methods for optimization of equilibrium geometries and transition structures<sup>6</sup> and Baker has described a numerical version of his efficient saddle-point searching

<sup>1</sup> Quantum chemistry literature database. Supplement 6. Bibliography of *ab initio* calculations for 1986, ed. K. Ohno and K. Morokuma, *THEOCHEM*, 1987, **39**, 1.

<sup>2</sup> P. Pulay, *Adv. Chem. Phys.*, 1987, **69**, 241.

<sup>3</sup> N. C. Handy, J. F. Gaw, and E. D. Simandiras, *J. Chem. Soc., Faraday Trans. 2*, 1987, **83**, 1577.

<sup>4</sup> E. D. Simandiras, N. C. Handy, and R. D. Amos, *Chem. Phys. Lett.*, 1987, **133**, 324.

<sup>5</sup> J. Gauss and D. Cremer, *Chem. Phys. Lett.*, 1987, **138**, 131.

<sup>6</sup> H. B. Schlegel, *Adv. Chem. Phys.*, 1987, **67**, 249.

algorithm which may be used without analytical gradients.<sup>7</sup> Transition-structure computations and their analysis was the subject of a review, by Bernardi and Robb,<sup>8</sup> emphasizing the use of multiconfigurational wavefunctions; the formalism of their diabatic-surface approach to reactivity has been presented in a unified fashion.<sup>9</sup> The CASSCF method has been reviewed,<sup>10</sup> and both gentle<sup>11</sup> and thorough<sup>12</sup> discussions of modern valence bond theory have been given.

Errors in heats of formation calculated with the AM1 semi-empirical method are comparable with those at the 3-21G level of *ab initio* SCF theory but are larger than those calculated at the 6-31G\* level.<sup>13</sup> There is a tendency in this year's literature for the latter basis to be referred to as 6-31G(*d*). The nomenclature for other bases of the same ilk is undergoing similar revision, supposedly to clarify the nature of the polarization functions added to more extended bases [e.g. 6-31G(2*df*, *p*) indicates a basis augmented by two sets of *d* and *f* functions on heavy atoms and a single set of *p* functions on hydrogens], but differing examples of usage betray a lack of consistency. Are the functions in parentheses to be understood as being *in addition* to or *instead* of those implied by the conventional asterisk notation? (*Caveat lector!*) An economical polarized basis set 3-21G(N\*) for nitrogen-containing molecules,<sup>14</sup> and diffuse-function augmented bases for second-row elements (Na to Cl) have been evaluated:<sup>15</sup> the 3-21+G\* basis is recommended particularly for anions containing these atoms. Extended (3-21G-like) bases for first- and second-row transition metals have been reported.<sup>16</sup>

A stochastic method for locating the global minimum on an energy surface, has been reported,<sup>17</sup> and a program, WIZARD, which applies artificial-intelligence methods to conformational analysis has been described.<sup>18</sup> Intrinsic reaction coordinates and dynamic reaction coordinates may be obtained from semi-empirical calculations of molecular trajectories.<sup>19</sup>

The semi-empirical SINDO1 method has been parameterized<sup>20</sup> for second-row atoms (Na to Cl) and may include *d* orbitals (not present in MNDO) which are necessary for the description of hypervalent molecules.<sup>21,22</sup> Jug's SINDO1 differs philosophically from Dewar's MNDO (and AM1) in an important respect. The parameters of Dewar's methods are adjusted directly to experimental heats of formation at room temperature; computation of zero-point and thermal energy corrections to enthalpies of reaction and activation enthalpies, using the calculated vibrational frequencies, in effect includes these quantities twice over. SINDO1 is

<sup>7</sup> J. Baker, *J. Comput. Chem.*, 1987, **8**, 563.

<sup>8</sup> F. Bernardi and M. A. Robb, *Adv. Chem. Phys.*, 1987, **67**, 155.

<sup>9</sup> F. Bernardi, J. J. W. McDouall, and M. A. Robb, *J. Comput. Chem.*, 1987, **8**, 296.

<sup>10</sup> B. O. Roos, *Adv. Chem. Phys.*, 1987, **69**, 399.

<sup>11</sup> J. Gerratt, *Chem. Brit.*, 1987, **23**, 327.

<sup>12</sup> D. L. Cooper, J. Gerratt, and M. Raimondi, *Adv. Chem. Phys.*, 1987, **69**, 319.

<sup>13</sup> M. J. S. Dewar and B. M. O'Connor, *Chem. Phys. Lett.*, 1987, **138**, 141.

<sup>14</sup> N. V. Riggs and L. Radom, *Int. J. Quantum Chem.*, 1987, **31**, 393.

<sup>15</sup> G. W. Spitznagel, T. Clark, P. v. R. Schleyer, and W. J. Hehre, *J. Comput. Chem.*, 1987, **8**, 1109.

<sup>16</sup> K. D. Dobbs and W. J. Hehre, *J. Comput. Chem.*, 1987, **8**, 861, 880.

<sup>17</sup> M. Saunders, *J. Am. Chem. Soc.*, 1987, **109**, 3150.

<sup>18</sup> D. P. Dolata, *J. Computer-Aided Mol. Design*, 1987, **1**, 73.

<sup>19</sup> J. J. P. Stewart, L. P. Davis, and L. W. Burggraf, *J. Comput. Chem.*, 1987, **8**, 1117.

<sup>20</sup> K. Jug, R. Iffert, and J. Schulz, *Int. J. Quantum Chem.*, 1987, **32**, 265.

<sup>21</sup> K. Jug and R. Iffert, *J. Comput. Chem.*, 1987, **8**, 1004; K. Jug and J. Schulz, *ibid.*, p. 1040.

<sup>22</sup> J. T. Sprague, J. C. Tai, Y. Yuh, and N. L. Allinger, *J. Comput. Chem.*, 1987, **8**, 581.

parameterized so as to reproduce experimental heats of formation extrapolated to 0 K and from which the zero-point energy has been subtracted; consequently the consideration of vibrational properties of molecules by this method does not involve any logical inconsistency.

The MMP2 program and procedures for the treatment of conjugated hydrocarbons have been properly documented,<sup>22</sup> and the deficiencies of this method and MM2 in regard to out-of-plane deformations of aromatic rings have been corrected,<sup>23</sup> the revised MM2(85) program (available from QCPE) contains MMP2. However, partly in response to the further inadequacy of these methods for the description of phenyl-phenyl interactions,<sup>24</sup> Allinger has also announced<sup>25</sup> an entirely new molecular mechanics method, MM3. Not only does this new force field incorporate  $C_{sp^2}-H$  and  $C_{sp^2}-C_{sp^3}$  dipoles for correct descriptions of electrostatic interactions (such as the 'T' structure for benzene dimer), but it also breaks the mould of 'empirical force fields' by virtue of the explicit use of *ab initio* theoretical results, along with experimental data, in the determination of its parameters for non-bonded interactions.

*Ab initio* results have also been used by Houk as a source of MM2 parameters to describe transition structures for intramolecular radical additions<sup>26</sup> and Diels-Alder cycloadditions.<sup>27</sup> MM2 parameters are reported for the anomeric effect in t-butoxy and trimethyl silyloxy derivatives of 1,4-dioxane,<sup>28</sup> for enolate equilibria<sup>29</sup> and boron enolates,<sup>30</sup> for ketones and aldehydes,<sup>31</sup> cyclic ketones,<sup>32</sup> and  $\beta$ -heteroatom-substituted cyclohexanones,<sup>33</sup> and for organophosphines,<sup>34</sup> allenes and non-linear acetylenes.<sup>35</sup>

*Ab initio* theoretical treatments of weakly-bonded systems have been reviewed<sup>36</sup> and the energetics of hydrogen-bonding have been discussed in regard to basis sets,<sup>37</sup> counterpoise procedures,<sup>38</sup> and the effects of correlation.<sup>39</sup> A plethora of modifications to MINDO/3<sup>40</sup> and MNDO<sup>41</sup> semi-empirical procedures for hydrogen bonds have been described. The AM1 method underestimates hydrogen-bond strengths for charged systems and prefers bifurcated geometries for neutral systems.<sup>42</sup>

<sup>23</sup> T. Liljefors, J. C. Tai, S. Li, and N. L. Allinger, *J. Comput. Chem.*, 1987, **8**, 1051.

<sup>24</sup> I. Petterson and T. Liljefors, *J. Comput. Chem.*, 1987, **8**, 1139.

<sup>25</sup> N. L. Allinger and J.-H. Liu, *J. Comput. Chem.*, 1987, **8**, 1146.

<sup>26</sup> D. C. Spellmeyer and K. N. Houk, *J. Org. Chem.*, 1987, **52**, 959.

<sup>27</sup> F. K. Brown, K. N. Houk, D. J. Burnell, and Z. Valenta, *J. Org. Chem.*, 1987, **52**, 3050.

<sup>28</sup> P. Aped, Y. Apeloig, A. Ellencweig, B. Fuchs, I. Goldberg, M. Karai, and E. Tartakovsky, *J. Am. Chem. Soc.*, 1987, **109**, 1486.

<sup>29</sup> G. W. Spears, C. E. Caufield, and W. C. Still, *J. Org. Chem.*, 1987, **52**, 1226.

<sup>30</sup> J. M. Goodman, I. Paterson, and S. D. Kahn, *Tetrahedron Lett.*, 1987, **28**, 5209.

<sup>31</sup> J. P. Bowen, A. Pathiaseril, S. Profeta, and N. L. Allinger, *J. Org. Chem.*, 1987, **52**, 5162.

<sup>32</sup> D. J. Goldsmith, J. P. Bowen, E. Qamhiyeh, and W. C. Still, *J. Org. Chem.*, 1987, **52**, 951.

<sup>33</sup> J. P. Bowen and N. L. Allinger, *J. Org. Chem.*, 1987, **52**, 1830.

<sup>34</sup> J. P. Bowen and N. L. Allinger, *J. Org. Chem.*, 1987, **52**, 2937.

<sup>35</sup> N. L. Allinger and A. Pathiaseril, *J. Comput. Chem.*, 1987, **8**, 1225.

<sup>36</sup> J. H. van Lenthe, J. G. C. M. van Duijneveldt-van de Rijdt, and F. B. van Duijneveldt, *Adv. Chem. Phys.*, 1987, **69**, 521.

<sup>37</sup> Z. Latajka and S. Scheiner, *J. Comput. Chem.*, 1987, **8**, 663, 674.

<sup>38</sup> G. Alagona, C. Ghio, R. Cammi, and J. Tomasi, *Int. J. Quantum Chem.*, 1987, **32**, 207.

<sup>39</sup> J. E. Del Bene, *J. Comput. Chem.*, 1987, **8**, 810; *J. Chem. Phys.*, 1987, **86**, 2110.

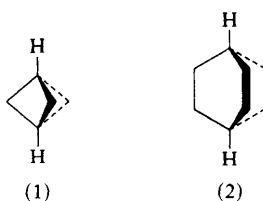
<sup>40</sup> N. U. Zhanpeisov, A. G. Pel'menshchikov, and G. M. Zhidomirov, *Zh. Strukt. Khim.*, 1987, **28**, 3.

<sup>41</sup> A. Goldblum, *J. Comput. Chem.*, 1987, **8**, 835; A. A. Voityuk and A. A. Bliznyuk, *Theor. Chim. Acta*, 1987, **71**, 327; 1987, **72**, 223.

<sup>42</sup> I. H. Williams, *J. Am. Chem. Soc.*, 1987, **109**, 6299.

### 3 Electronic Structure, Bonding, and Properties

**Charge Distributions and Chemical Bonds.**—Molecular structures can be assigned and their relative stabilities and reactivities understood in terms of global and local properties of the electronic charge density, such as bond orders and ellipticities (the tendency for charge density to accumulate in a particular plane) and the Laplacian of the charge distribution (measuring local concentration or depletion of charge).<sup>43</sup> A theory of atoms in molecules yields average atomic electron populations and energies.<sup>44</sup> In unstrained hydrocarbons H is more electronegative than C: thus the order of electron-withdrawing abilities is  $H > CH_3 > CH_2 > CH > C$ . Geometrical strain increases the electronegativity of C, and decreases the atomic energy of C, but increases the energy of H to a greater extent; this provides an explanation for the origin of strain energy. Methyl and methylene groups may often be regarded as transferable units, and group properties are often additive.<sup>44</sup> 'Bonds are a fundamental construct of chemistry', wrote Ritchie and Bachrach,<sup>45</sup> who continued 'nevertheless many chemists are hard pressed to define exactly what a bond is, and, instead, rely upon intuition to identify bonds in unusual structures...'. However, they have claimed (optimistically?) that electron density distribution analysis<sup>46</sup> provides rigorous definitions of bonds, rings, and cages in molecules; an examination of bond paths (paths of maximum electron density joining pairs of bonded nuclei) for some organolithium compounds yielded surprising results.<sup>45</sup> Feller and Davidson<sup>47</sup> described [1,1,1] propellane (1) as just a strained cage, with little intra-bridgehead covalent bonding and commented (pessimistically?) that 'it is not possible to translate the concept of a bond into something which can be universally extracted from theoretical calculations.' Meanwhile Wiberg *et al.*<sup>43</sup> obtained a bond order of 0.73 for this bond, which they described as arising from in-phase overlap of the tails of outwardly directed  $sp^3$  hybrids on the bridgehead carbon atoms. In contrast the bridgehead carbons of [2,2,2] propellane (2) are  $sp^2$ -hybridized and the intra-bridgehead bond, arising from overlap of pure  $p$  orbitals, has a bond order of 1.26.<sup>43</sup>



The fact that standard deformation densities sometimes give rise to (counter-intuitive) charge deficits in regions associated with covalent bonds has been shown to be due to the assumption of spherical atomic charge densities;<sup>48</sup> consideration of bond formation between (non-spherical) valence-state atoms restores the intuitive

<sup>43</sup> K. B. Wiberg, R. F. W. Bader, and C. D. H. Lau, *J. Am. Chem. Soc.*, 1987, **109**, 985.

<sup>44</sup> K. B. Wiberg, R. F. W. Bader, and C. D. H. Lau, *J. Am. Chem. Soc.*, 1987, **109**, 1001.

<sup>45</sup> J. P. Ritchie and S. M. Bachrach, *J. Am. Chem. Soc.*, 1987, **109**, 5909.

<sup>46</sup> J. P. Ritchie and S. M. Bachrach, *J. Comput. Chem.*, 1987, **8**, 499.

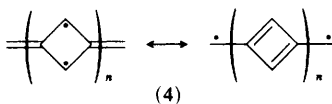
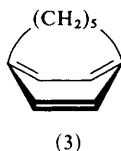
<sup>47</sup> D. Feller and E. R. Davidson, *J. Am. Chem. Soc.*, 1987, **109**, 4133.

<sup>48</sup> K. L. Kunze and M. B. Hall, *J. Am. Chem. Soc.*, 1987, **109**, 7617.

picture. Various alternative definitions of bond orders<sup>49</sup> and atomic charges<sup>50</sup> have been proposed. Molecular electrostatic potentials have been used to investigate the intra-bridgehead bond in bicyclobutane,<sup>51</sup> and the properties of nitroso- and nitroaromatics<sup>52,53</sup> and acetylenes;<sup>54</sup> there is only a minor degree of conjugation between the nitro-group and the phenyl ring in nitrobenzene.<sup>52</sup>

The P—O and P—C bonds of phosphine oxide, hypophosphite and methylene phosphoranes, metaphosphate, and tris(methylene)metaphosphate anions are semi-polar and have little double-bond character.<sup>55</sup> However, phosphorothiolate anions have appreciable P=O double-bond character and a corresponding absence of P=S double-bond character, although these results depend upon the overall charge on the anion.<sup>56</sup>

**Delocalization and Aromaticity.**—The spin-coupled VB description of benzene<sup>11</sup> (involving six equivalent essentially localized spin orbitals) has provoked some interesting exchanges in the pages of *Nature*.<sup>57</sup> Schaefer and co-workers quoted Streitwieser ('There is no operational definition of aromaticity') in their *ab initio* study of [5]paracyclophane<sup>58</sup> (3), some of the properties of which are indicative of aromatic character and others not: bond alternation is modest, but the ring is substantially bent with a consequent loss of thermochemical stability. MNDO calculations on [*n*]metacyclophanes<sup>59</sup> showed that localization of the bonds of the aromatic ring was unfavourable even for highly bent systems. Delocalized structures for [14] and [18] annulene are more stable than localized ones only if interpair electron correlation is included and the Davidson correction added.<sup>60</sup> Correlation is responsible for higher ring currents in charged annulenes than neutral ones;<sup>61</sup> large neutral 4*n*-electron systems become weakly aromatic but charged systems are all anti-aromatic. Aromatic stabilization may be explained in terms of highly corre-



<sup>49</sup> H. O. Villar and M. Dupuis, *Chem. Phys. Lett.*, 1987, **142**, 59.

<sup>50</sup> C. M. Smith and G. G. Hall, *Int. J. Quantum Chem.*, 1987, **31**, 685; L. E. Chirlian and M. M. Francl, *J. Comput. Chem.*, 1987, **8**, 894; K. E. Edgecombe and R. J. Boyd, *J. Chem. Soc., Faraday Trans. 2*, 1987, **83**, 1307.

<sup>51</sup> P. Politzer, G. P. Kirschenheuter, and J. Alster, *J. Am. Chem. Soc.*, 1987, **109**, 1033.

<sup>52</sup> P. Politzer, P. Lane, K. Jayasuriya, and L. N. Domelsmith, *J. Am. Chem. Soc.*, 1987, **109**, 1899.

<sup>53</sup> P. Politzer and R. Bar-Adon, *J. Phys. Chem.*, 1987, **91**, 2069.

<sup>54</sup> P. Politzer and R. Bar-Adon, *J. Am. Chem. Soc.*, 1987, **109**, 3529.

<sup>55</sup> A. Streitwieser, R. S. McDowell, and R. Glaser, *J. Comput. Chem.*, 1987, **8**, 788; A. Streitwieser, A. Rajca, R. S. McDowell, and R. Glaser, *J. Am. Chem. Soc.*, 1987, **109**, 4184; A. Rajca, J. E. Rice, A. Streitwieser, and H. F. Schaefer, *ibid.*, p. 4189.

<sup>56</sup> C. Liang and L. C. Allen, *J. Am. Chem. Soc.*, 1987, **109**, 6449.

<sup>57</sup> L. Pauling, *Nature (London)*, 1987, **325**, 396; J. Maddox, *ibid.*, 1987, **327**, 551; R. D. Harcourt, *ibid.*, 1987, **329**, 491; R. P. Messmer and P. A. Schultz, *ibid.*, 1987, **329**, 492; J. Gerratt, M. Raimondi, and D. L. Cooper, 1987, **329**, 492.

<sup>58</sup> J. E. Rice, T. J. Lee, R. B. Remington, W. D. Allen, D. A. Clabo, and H. F. Schaefer, *J. Am. Chem. Soc.*, 1987, **109**, 2902.

<sup>59</sup> L. W. Jenneskens, F. J. J. de Kanter, W. H. de Wolf, and F. Bickelhaupt, *J. Comput. Chem.*, 1987, **8**, 1154.

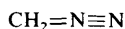
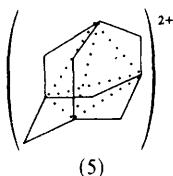
<sup>60</sup> K. Jug and E. Fasold, *J. Am. Chem. Soc.*, 1987, **109**, 2263.

<sup>61</sup> S. Kuwajima and Z. G. Soos, *J. Am. Chem. Soc.*, 1987, **109**, 107.

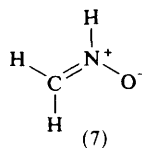
lated Cooper pairs, and a limit of  $n = 6$  or  $7$  for aromaticity in  $4n + 2$  electron systems is predicted.<sup>62</sup> Correlation decreases the amount of bond alternation in linear polyenes.<sup>63</sup>

The electronic properties of a new class of  $(4n + 2)$  alternant hydrocarbons, the dimethylene polycyclobutadienes (4), have been examined by a variety of theoretical methods.<sup>64</sup> Whereas the properties of classical (Kekulé) acenes change progressively with  $n$ , a parity rule is predicted for these non-Kekulé acenes which should have fascinating optical, electronic, and magnetic properties: for even  $n$ , the ground state is a singlet with  $n$  disjoint non-bonding MOs; for odd  $n$ , the ground state is a triplet with  $(n + 1)$  not-fully-disjoint non-bonding MOs. Electronic properties of polycacenes and other hydrocarbon polymers have been studied<sup>65</sup> by a new molecular-orbital based molecular mechanics method.<sup>66</sup>

The topic of  $\pi$ - $\sigma$  interactions has been reviewed,<sup>67</sup> and a  $\pi$ -orbital axis vector/three-dimensional Hückel MO (POAV/3D-HMO) theory, which provides a unified treatment of both planar and non-planar conjugated organic molecules, has been proposed.<sup>68</sup> Deviations of such systems from planarity are aptly described in terms of geometrical pyramidalization.<sup>69</sup> There emerges a natural definition of a homoconjugate bond as one between conjugated atoms whose overlap integral is not dominated by the  $p_\pi$ ,  $p_\pi$  contribution.<sup>68</sup> Four-centre two-electron bonding in a tetrahedral topology has been calculated for the cation (5) – an example of 3D-homoaromaticity.<sup>70</sup>



(6)



Two types of 1,3-dipole may be distinguished at the UHF/6-31G\* level.<sup>71</sup> Molecules such as diazomethane (22 electrons) are hypervalent closed-shell species involving full double and triple bonds to the central nitrogen (6); 24-electron (allyl-type) 1,3-dipoles, such as nitron (7), each have two bonds midway between single and double, and may be described by resonance structures in which the central atom has normal valency.<sup>71</sup> Spin-coupled valence-bond calculations for these molecules are illuminating: the two electrons on the central nitrogen of diazomethane occupy orbitals which overlap very substantially and are coupled, not to each other, but to the terminal atoms respectively, confirming the double bond + triple bond

<sup>62</sup> R. H. Squire, *J. Phys. Chem.*, 1987, **91**, 5149.

<sup>63</sup> P. G. Szalay, A. Karpfen, and H. Lischka, *J. Chem. Phys.*, 1987, **87**, 3530.

<sup>64</sup> J. Pranata and D. A. Dougherty, *J. Am. Chem. Soc.*, 1987, **109**, 1621.

<sup>65</sup> J. Kao and A. C. Lilly, *J. Am. Chem. Soc.*, 1987, **109**, 4149.

<sup>66</sup> J. Kao, *J. Am. Chem. Soc.*, 1987, **109**, 3817.

<sup>67</sup> R. Gleiter, *Pure Appl. Chem.*, 1987, **59**, 1585.

<sup>68</sup> R. C. Haddon, *J. Am. Chem. Soc.*, 1987, **109**, 1676.

<sup>69</sup> R. C. Haddon, *J. Phys. Chem.*, 1987, **91**, 3719.

<sup>70</sup> M. Bremer, P. v. R. Schleyer, K. Schötz, M. Kausch, and M. Schindler, *Angew. Chem., Int. Ed. Engl.*, 1987, **26**, 761.

<sup>71</sup> S. D. Kahn, W. J. Hehre, and J. A. Pople, *J. Am. Chem. Soc.*, 1987, **109**, 1871.

structure (6).<sup>72</sup> Nitron (7), with a C=N double bond and a polar N—O bond of order  $\sim 1.5$ , does *not* possess singlet diradical character.<sup>72</sup> A CASSCF wavefunction for nitron may be transformed to a valence-bond space to yield results in agreement with the spin-coupled description.<sup>73</sup> MCSCF calculations on carbonyl ylides have suggested that the allylic resonance is unstable with respect to out-of-plane vibration.<sup>74</sup>

Shaik *et al.*<sup>75</sup> have questioned whether delocalization is a driving force in chemistry, and have argued that the  $\pi$ -electron delocalization of the allyl radical and of benzene is in each case a by-product of the geometric constraint imposed by the  $\sigma$ -bonded framework which prefers a symmetrical structure. Furthermore they have argued that the stabilization conferred by delocalization of a  $\pi$  system *at a given geometry* is not contradictory with the distortive propensity of the  $\pi$ -system towards a lower-symmetry structure.

**Radicals, Carbenes, and Diradicals.**—Accurate calculations (MCSCF/6-31G\* + large CI) on succinimidyl radical have predicted the singlet  $\pi$  state to be 21.5 kJ mol<sup>-1</sup> lower than the singlet  $\sigma_N$  state responsible for most of the known imidyl chemistry; the authors have commented that their calculations 'emphasise the care that is required in applying *ab initio* techniques to many molecular species to produce meaningful results and illustrate the great attention to detail, and awareness of the limitations of the techniques used, which are needed to obtain a minimum qualitative description of a potential-energy surface.'<sup>76</sup>

The spin-coupled orbitals of methylene are highly localized: the singly occupied orbitals of the  $^3B_1$  ground state correspond to the usual  $sp^2(\sigma)$  and  $p_\pi$  description, but those of the  $^1A_1$  excited state are equivalent  $sp^3$  hybrids.<sup>77</sup> The spin-coupled VB method<sup>77</sup> and the simple GVB method<sup>78</sup> both give essentially the same (slightly too high) value for the methylene singlet-triplet separation as does full CI using a DZP basis, but each method is capable of reproducing the experimental value using more extended bases.<sup>77-79</sup> Singlet-triplet separations for substituted carbenes may be reliably estimated by a GVB + CI procedure.<sup>80</sup> It has been argued that the experimental observation of an e.p.r. signal for cycloheptatrienyldiene is not inconsistent with the theoretical prediction of a singlet ground state, since at the optimum triplet geometry the singlet is higher in energy.<sup>81</sup> A singlet ground state has also been predicted<sup>82</sup> for tetramethyleneethane (8), the simplest non-Kekulé hydrocarbon



<sup>72</sup> D. L. Cooper, J. Gerratt, M. Raimondi, and S. C. Wright, *Chem. Phys. Lett.*, 1987, **138**, 296.

<sup>73</sup> J. J. W. McDouall and M. A. Robb, *Chem. Phys. Lett.*, 1987, **142**, 131.

<sup>74</sup> A. Tachibana, M. Koizumi, I. Okazaki, H. Teramae, and T. Yamabe, *Theor. Chim. Acta*, 1987, **71**, 7.

<sup>75</sup> S. S. Shaik, P. C. Hiberty, J.-M. Lefour, and G. Ohanessian, *J. Am. Chem. Soc.*, 1987, **109**, 363.

<sup>76</sup> M. J. Field, I. H. Hillier, and M. F. Guest, *J. Chem. Soc., Perkin Trans. 2*, 1987, 1311.

<sup>77</sup> M. Sironi, M. Raimondi, D. L. Cooper, and J. Gerratt, *J. Chem. Soc., Faraday Trans. 2*, 1987, **83**, 1651.

<sup>78</sup> E. A. Carter and W. A. Goddard, *J. Chem. Phys.*, 1987, **86**, 862.

<sup>79</sup> C. W. Bauschlicher, S. R. Langhoff, and P. R. Taylor, *J. Chem. Phys.*, 1987, **87**, 387.

<sup>80</sup> E. A. Carter and W. A. Goddard, *J. Phys. Chem.*, 1987, **91**, 4651.

<sup>81</sup> C. L. Janssen and H. F. Schaefer, *J. Am. Chem. Soc.*, 1987, **109**, 5030.

<sup>82</sup> P. Du and W. T. Borden, *J. Am. Chem. Soc.*, 1987, **109**, 930.



whose non-bonding MOs are disjoint (i.e. can be localized to different regions of space); this finding contradicts previous theoretical results and also is in apparent conflict with experiment.<sup>83</sup> The problem of spin-orbit coupling and intersystem crossing between singlet and triplet states of diradicals and radical pairs has been addressed by MCSCF calculations for trimethylene and the methyl-methyl pair.<sup>84</sup>

#### 4 Molecular Structure and Energetics

Geometry optimization of individual equilibrium structures at low levels of theoretical sophistication remains a popular pastime, but increasingly there is a trend towards more complete characterization of a potential energy surface corresponding to a particular molecular formula: these studies involve consideration not only of the various energetic minima but also of the saddle points for their interconversion, and hence defy neat categorization into the pigeon-holes of structure and reactivity. Nonetheless conformational and configurational isomerizations may be distinguished.

The structure of fluorine peroxide (FOOF) provides a problem for normally reliable theoretical methods: CI methods including all single and double excitations fail to predict the bond lengths correctly even when high-quality bases are employed.<sup>85</sup> However, the use of externally contracted CI from a large complete-active-space reference does yield reasonable agreement with the experimental geometry.<sup>86</sup>

Epiotis<sup>87</sup> has expounded the thesis that molecular stereoelectronics cannot be understood on the basis of orbital symmetry considerations alone, but requires consideration of what he calls 'colour' - the intrinsic ability of an atom to form bonds by overlap.

A valence-bond approach has been employed to explain the occurrence and extent of non-classical distortion from planarity of double bonds, or from linearity for triple bonds and cumulenes, as related by the singlet-triplet energy separation of the interacting fragments forming the multiple bond.<sup>88</sup>

**Neutral Molecules.**—Bicyclobutene (9) is predicted<sup>89</sup> to have a singlet ground state with a non-planar skeleton and an inversion barrier of  $\sim 50 \text{ kJ mol}^{-1}$ ; the dimethylene-bridged species (10), which has been trapped experimentally, is a minimum on the MP2/6-31G\* surface (but *not* the HF/6-31G\* surface) and is less stable than the as yet unobserved parent (9).<sup>90</sup>



<sup>83</sup> P. Dowd, W. Chong, and Y. Paik, *J. Am. Chem. Soc.*, 1987, **109**, 5284.

<sup>84</sup> L. Carlucci, C. Doubleday, T. R. Furlani, H. F. King, and J. W. McIver, *J. Am. Chem. Soc.*, 1987, **109**, 5323.

<sup>85</sup> D. A. Clabo and H. F. Schaefer, *Int. J. Quantum Chem.*, 1987, **31**, 429.

<sup>86</sup> C. M. Rohlfing and P. J. Hay, *J. Chem. Phys.*, 1987, **86**, 4518.

<sup>87</sup> N. D. Epiotis, *THEOCHEM.*, 1987, **38**, 1.

<sup>88</sup> G. Trinquier and J.-P. Malrieu, *J. Am. Chem. Soc.*, 1987, **109**, 5303.

<sup>89</sup> B. A. Hess, W. D. Allen, D. Michalska, L. J. Schaad, and H. F. Schaefer, *J. Am. Chem. Soc.*, 1987, **109**, 1615.

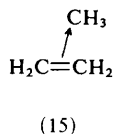
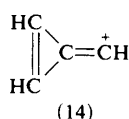
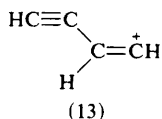
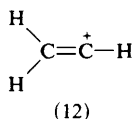
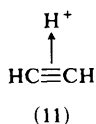
<sup>90</sup> B. A. Hess, D. Michalska, and L. J. Schaad, *J. Am. Chem. Soc.*, 1987, **109**, 7546.



The ring puckering potential of oxetane is primarily due to intramolecular dispersion interactions involving oxygen lone pairs, which are very difficult to calculate accurately.<sup>91</sup> The inversion barrier for azetidine is comparable with that of ammonia and much lower than that of aziridine.<sup>92</sup> Dioxetenes and diazetines tend to be unstable towards ring opening.<sup>93</sup> Dimethyldioxirane<sup>94</sup> is more stable than dioxirane, the peroxide bond of which is strained and weaker than those in hydrogen peroxide and peroxytrifluoroacetic acid.<sup>95</sup>

The concept of strain has been explored by theoretical studies on cyclopoly-silanes:<sup>96</sup> cyclotrisilane is  $\sim 40 \text{ kJ mol}^{-1}$  more strained than cyclopropane, whereas cyclotetrasilane is  $\sim 40 \text{ kJ mol}^{-1}$  less strained than cyclobutane. Silicon analogues of ethene,<sup>97</sup> cyclobutadiene,<sup>98</sup> bicyclobutane,<sup>99</sup> benzene,<sup>100</sup> tetrahedrane, prismane, and cubane<sup>101</sup> have been considered, and theoretical studies of silicon chemistry have been reviewed.<sup>102</sup>

**Cations and Radical Cations.**—The non-classical bridged structure (11) for vinyl cation is more stable than the classical structure (12) by  $21 \text{ kJ mol}^{-1}$  at the MP4SDTQ/6-311G\*\* $(2df)$ //MP2(full)/6-31G\* level,<sup>103</sup> a multi-reference CASSCF-CI study<sup>104</sup> concurs except that (12) is found to be in a shallow minimum rather than at a saddle point. Unsubstituted vinylacetylene (13) is predicted<sup>105</sup> to be less stable than its bridged isomer (14). Corner-protonated cyclopropane prefers an unsymmetrical bridged structure (15) in which the ratio of charges on the basal C atoms is 3:2; the symmetrical structure is at a saddle point.<sup>106</sup> There is no F-bridging in  $\text{CF}_3\text{CH}_2^+$  and its isomers,<sup>107</sup> and the ethyl dication  $\text{CH}_3\text{CH}_2^{2+}$  has an open structure.<sup>108</sup>



<sup>91</sup> H. Sellers, J. Almlöf, S. Saebo, and P. Pulay, *J. Phys. Chem.*, 1987, **91**, 4216.

<sup>92</sup> R. Dutler, A. Rauk, and T. S. Sorensen, *J. Am. Chem. Soc.*, 1987, **109**, 3224.

<sup>93</sup> P. H. M. Budzelaar, D. Cremer, M. Wallasch, E.-U. Würthwein, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, 1987, **109**, 6290.

<sup>94</sup> W. Adam, Y.-Y. Chan, D. Cremer, J. Gauss, D. Scheutzow, and M. Schindler, *J. Org. Chem.*, 1987, **52**, 2800; D. Cremer and M. Schindler, *Chem. Phys. Lett.*, 1987, **133**, 293.

<sup>95</sup> P. Politzer, R. Bar-Adon, and R. S. Miller, *J. Phys. Chem.*, 1987, **91**, 3191.

<sup>96</sup> R. S. Grev and H. F. Schaefer, *J. Am. Chem. Soc.*, 1987, **109**, 6569.

<sup>97</sup> H. Teramae, *J. Am. Chem. Soc.*, 1987, **109**, 4140.

<sup>98</sup> A. F. Sax and J. Kalcher, *J. Chem. Soc., Chem. Commun.*, 1987, 809.

<sup>99</sup> S. Collins, R. Dutler, and A. Rauk, *J. Am. Chem. Soc.*, 1987, **109**, 2564; P. v. R. Schleyer, A. F. Sax, J. Kalcher, and R. Janoschek, *Angew. Chem., Int. Ed. Engl.*, 1987, **26**, 364.

<sup>100</sup> S. Nagase, H. Teramae, and T. Kudo, *J. Chem. Phys.*, 1987, **86**, 4513.

<sup>101</sup> S. Nagase, M. Nakano, and T. Kudo, *J. Chem. Soc., Chem. Commun.*, 1987, 60.

<sup>102</sup> K. K. Baldrige, J. A. Boatz, S. Koseki, and M. S. Gordon, *Ann. Rev. Phys. Chem.*, 1987, **38**, 211.

<sup>103</sup> J. A. Pople, *Chem. Phys. Lett.*, 1987, **137**, 10.

<sup>104</sup> R. Lindh, B. O. Roos, and W. P. Kraemer, *Chem. Phys. Lett.*, 1987, **139**, 407.

<sup>105</sup> K. Hori, T. Yamabe, A. Tachibana, Y. Asai, K. Fukui, S. Kobayashi, and H. Taniguchi, *THEOCHEM*, 1987, **38**, 295.

<sup>106</sup> M. J. S. Dewar, E. F. Healy, and J. M. Ruiz, *J. Chem. Soc., Chem. Commun.*, 1987, 943.

<sup>107</sup> M. Charpentier, J. Fossey, T. T. Tidwell, and S. Wolfe, *Can. J. Chem.*, 1987, **65**, 473.

<sup>108</sup> M. W. Wong, J. Baker, R. H. Nobes, and L. Radom, *J. Am. Chem. Soc.*, 1987, **109**, 2245.

Ylidions are radical cations, with unusual structures, whose neutral (ylide) counterparts are unknown or extremely reactive; theoretical structures and stabilities of ylidions  $\text{CH}_2\text{X}^+\text{H}$  and their corresponding ylides  $\text{CH}_2\text{XH}$  have been surveyed.<sup>109</sup> Structures such as  $(\text{CH}_2\text{CH}_2\text{CO})^{+\bullet}$ ,  $(\text{CH}_2\text{CH}_2 \cdots \text{OC})^{+\bullet}$  and  $(\text{CHCHCHOH})^{+\bullet}$  have remarkable stability on the  $\text{C}_3\text{H}_4\text{O}^{+\bullet}$  surface as compared with ionized methylketene and propenal.<sup>110</sup> An *ab initio* theoretical analysis has provided a coherent description of the gas-phase ion chemistry of metastable ionized methyl acetate.<sup>111</sup> Ionized ethane-1,2-diol undergoes spontaneous intramolecular 1,4-H migration<sup>112</sup> and gives stable hydrogen-bridged radical cation isomers.<sup>113</sup>

**Conformational Isomerism.**—Amide ‘resonance’ involves charge transfer from C to N, *not* from N to O, since in the planar conformation N is more electronegative (has more *s* character) than C.<sup>114</sup> Similarly the *Z* conformers of formic acid, methyl formate, acetic acid, and methyl acetate are stabilized by virtue of the singly-bonded oxygen possessing more *s* character (leading to lower energy) in the *Z* than in the *E* conformers.<sup>114</sup> Comparative studies of the conformational energetics of the monothio<sup>115</sup> and dithio<sup>116</sup> analogues of these species have been performed. The effect of electron correlation on the conformational energy difference in glyoxal is significant;<sup>117</sup> *trans*-dithioglyoxal is more stable than the not-rigidly-planar *cis* conformer, whose energy is close to that of the cyclic structure 1,2-dithiete.<sup>118</sup> The observation of an eclipsed  $\text{C}_{sp^3}\text{—CH}_3$  in the crystal structure of a tricyclic orthoamide, thought to arise from hydrogen bonding to the methyl group by three water molecules, has prompted a theoretical study of  $\text{C—H} \cdots \text{O}$  hydrogen bonding.<sup>119</sup> The interaction between methane and water is worth  $\sim 7.2 \text{ kJ mol}^{-1}$  at the MP4/6-311G(2*d*,*p*) level.

## 5 Reactivity and Mechanism

**Theory of Reactivity.**—Diabatic surfaces and the resonance interactions between them have been computed for two-bond cycloaddition reactions.<sup>120</sup> The intersection of the reactant-like and product-like diabatic surfaces determines the topology of the adiabatic surface; these intersections occur at roughly the same energies for different mechanistic possibilities such as concerted synchronous, concerted asynchronous, and stepwise processes. Mechanistic preferences are controlled by the resonance interactions which tend to favour concerted synchronous paths for allowed reactions, in contrast to the dictum that ‘synchronous multibond mechanisms are normally prohibited.’

<sup>109</sup> B. F. Yates, W. J. Bouma, and L. Radom, *J. Am. Chem. Soc.*, 1987, **109**, 2250.

<sup>110</sup> G. Bouchoux, *THEOCHEM*, 1987, **36**, 107.

<sup>111</sup> N. Heinrich, J. Schmidt, H. Schwarz, and Y. Apeloig, *J. Am. Chem. Soc.*, 1987, **109**, 1317.

<sup>112</sup> B. F. Yates, W. J. Bouma, J. K. Macleod, and R. Radom, *J. Chem. Soc., Chem. Commun.*, 1987, 204.

<sup>113</sup> P. C. Burgers, J. L. Holmes, C. E. C. A. Hop, R. Postma, P. J. A. Ruttink, and J. K. Terlouw, *J. Am. Chem. Soc.*, 1987, **109**, 7315.

<sup>114</sup> K. B. Wiberg and K. E. Laidig, *J. Am. Chem. Soc.*, 1987, **109**, 5935.

<sup>115</sup> R. Fausto and J. J. C. Teixeira-Dias, *THEOCHEM*, 1987, **35**, 381; S. P. So, *ibid.*, 1987, **36**, 141; A. Toro-Labbe and C. Cardenas, *Int. J. Quantum Chem.*, 1987, **32**, 685.

<sup>116</sup> R. Fausto, J. J. C. Teixeira-Dias, and P. R. Carey, *THEOCHEM*, 1987, **37**, 119.

<sup>117</sup> S. Saebo, *Chem. Phys.*, 1987, **113**, 383.

<sup>118</sup> J. D. Goddard, *J. Comput. Chem.*, 1987, **8**, 389.

<sup>119</sup> P. Seiler, G. R. Weisman, E. D. Glendening, F. Weinhold, V. B. Johnson, and J. D. Dunitz, *Angew. Chem., Int. Ed. Engl.*, 1987, **26**, 1175.

<sup>120</sup> F. Bernardi, M. Olivucci, J. J. W. McDouall, and M. A. Robb, *J. Am. Chem. Soc.*, 1987, **109**, 544.

A practical formulation of symmetry selection rules for reaction mechanisms has been applied to some electrocyclic processes,<sup>121</sup> and these rules have been re-expressed in terms of permutation-inversion group symmetries.<sup>122</sup> A way of looking at chemical interactions in terms of pairs of interacting localized orbitals has been reviewed<sup>123</sup> and a Riemann geometrical formulation of the principle of least electronic motion has also been applied to electrocyclic reactions.<sup>124</sup> Topological aspects of chemical reactivity have been discussed.<sup>125</sup>

Energy profiles and reaction surfaces have been considered in regard to perpendicular effects on transition states;<sup>126</sup> reaction-surface and curve-crossing approaches lead to similar mathematical descriptions of reactivity. The curve-crossing model has been used to correlate nucleophilicity with vertical ionization potentials in cation-anion recombinations, and to gain insight into the physical significance of the  $N^+$  scale.<sup>127</sup> The roles of transition-state bond order and reaction energy in methyl nucleophilic substitutions<sup>128</sup> and Brønsted relationships in proton-transfer reactions<sup>129</sup> have been studied using an intersecting parabola model. Extremely loose  $S_N2$  transition states give rise to unexpected bond-order relationships in that they are dominated by anti-Hammond effects.<sup>130</sup> A simple modification of the Morse equation yields several relationships among bond lengths, energies, and stretching force constants with interesting consequences.<sup>131</sup>

A general definition of formal steric enthalpies and their differences has been given, which provides the basis for the use of molecular mechanics for calculations of equilibrium and rate constants;<sup>132</sup> the effects of steric hindrance on rates of esterification and acid-catalysed hydrolysis have been studied by molecular mechanics using this formalism.<sup>133</sup> A modified MM2 model for the rates of acid-catalysed lactonizations of hydroxy acids, based upon *ab initio* calculations for  $H_2O + HC(OH)_2^+$ , has reproduced experimental relative activation energies over ten orders of magnitude;<sup>134</sup> no relationship has been found between reactivity and either the angle of nucleophilic attack or the distance between the reacting atoms; hence there is no support for either the concept of 'angularity' (orbital steering) or the 'spatiotemporal hypothesis'.

**Rearrangements.**—The degenerate Cope rearrangement of hexa-1,5-diene is predicted by AM1<sup>135,136</sup> and MP4SDQ/6-31G\*<sup>137</sup> calculations to involve a biradicaloid intermediate with chair geometry; an alternative pathway *via* an aromatic transition

<sup>121</sup> A. Rodger and P. E. Schipper, *J. Phys. Chem.*, 1987, **91**, 189.

<sup>122</sup> A. Metropoulos, *J. Phys. Chem.*, 1987, **91**, 2233.

<sup>123</sup> H. Fujimoto, *Acc. Chem. Res.*, 1987, **20**, 448.

<sup>124</sup> A. Igawa and H. Fukutome, *Chem. Phys. Lett.*, 1987, **133**, 399.

<sup>125</sup> R. Ponec, *Collect. Czech. Chem. Commun.*, 1987, **52**, 555, 1375, 2603.

<sup>126</sup> N. Agmon, *J. Org. Chem.*, 1987, **52**, 2192.

<sup>127</sup> S. S. Shaik, *J. Org. Chem.*, 1987, **52**, 1563.

<sup>128</sup> S. J. Formosinho, *Tetrahedron*, 1987, **43**, 1109.

<sup>129</sup> S. J. Formosinho, *J. Chem. Soc., Perkin Trans. 2*, 1987, 61.

<sup>130</sup> G. P. Ford and C. T. Smith, *J. Chem. Soc., Chem. Commun.*, 1987, 44.

<sup>131</sup> H.-B. Bürgi and J. D. Dunitz, *J. Am. Chem. Soc.*, 1987, **109**, 2924.

<sup>132</sup> D. F. DeTar, *J. Org. Chem.*, 1987, **52**, 1851.

<sup>133</sup> D. F. DeTar, S. Binzet, and P. Darba, *J. Org. Chem.*, 1987, **52**, 2074.

<sup>134</sup> A. D. Dorigo and K. N. Houk, *J. Am. Chem. Soc.*, 1987, **109**, 3698.

<sup>135</sup> M. J. S. Dewar and C. Jie, *J. Am. Chem. Soc.*, 1987, **109**, 5893.

<sup>136</sup> M. J. S. Dewar and C. Jie, *J. Chem. Soc., Chem. Commun.*, 1987, 1451.

<sup>137</sup> M. J. S. Dewar and E. F. Healy, *Chem. Phys. Lett.*, 1987, **141**, 521.

structure of boat geometry has a different activation entropy.<sup>136</sup> Rearrangements of 2-phenyl and 2,5-diphenyl hexa-1,5-dienes are also predicted to involve biradicaloid intermediates in very shallow wells, whereas other derivatives rearrange by concerted (but not synchronous) mechanisms.<sup>135</sup> According to Dewar, 'unambiguous [mechanistic] conclusions cannot . . . be drawn from calculations [for a single reaction] by any current procedure because the errors in energies given by even the best of them are too large. A better approach is to calculate a number of examples of the reaction for which activation parameters are available . . . Even if the errors in the calculated activation parameters for the individual reactions are too large for definite conclusions to be drawn from them, the relative values for a number of related reactions are likely to be reproduced, at least qualitatively. Comparison of the predicted pattern of rates with experiment should then provide a more reliable test of the predicted mechanism than any calculation for a single case.'<sup>135</sup>



(16)

A CASSCF and MP4/6-31G\* study<sup>138</sup> of thermal reactions of bicyclopentene (16) has suggested that the degenerate walk rearrangement is probably a stepwise process involving a diradical intermediate, since the activation energy for this symmetry-allowed reaction is  $\sim 40 \text{ kJ mol}^{-1}$  higher than that for the symmetry-forbidden disrotating ring opening to cyclopentadiene. Rearrangement of cyclohexyne,<sup>139</sup> isomerization of allene to propyne,<sup>140</sup> and of acetylene to vinylidene (catalysed by a metal atom),<sup>141</sup> ring opening of cyclopropane (catalysed by palladium),<sup>142</sup> methylenecyclopropane radical cation,<sup>143</sup> three-membered ring carbanions,<sup>144</sup> and ethene episulphoxide anion,<sup>145</sup> have been studied at various theoretical levels. The acyl carbene intermediate involved in the Wolff rearrangement has a singlet ground state which is a pure diradical; the triplet state is important too, and there is almost no barrier to cyclization of either state to oxirene.<sup>146</sup> Rearrangements of  $\text{H}_3\text{PX}$  to  $\text{H}_2\text{PXH}$  have been studied for  $\text{X}=\text{O}$ <sup>147,148</sup> and  $\text{X}=\text{NH}$  and  $\text{CH}_2$ .<sup>147</sup> The importance of using a uniform level of theory to study reaction paths has been illustrated by CASSCF calculations of the ground-state potential energy surface of diazene, its conformational and configurational isomers and the transition structures for their interconversion.<sup>149</sup>

<sup>138</sup> P. N. Skancke, K. Yamashita, and K. Morokuma, *J. Am. Chem. Soc.*, 1987, **109**, 4157.

<sup>139</sup> J. Tseng, M. L. McKee, and P. B. Shevlin, *J. Am. Chem. Soc.*, 1987, **109**, 5474.

<sup>140</sup> T. Kakumoto, T. Ushirogouchi, K. Saito, and A. Imamura, *J. Phys. Chem.*, 1987, **91**, 183.

<sup>141</sup> S. Sakai and K. Morokuma, *J. Phys. Chem.*, 1987, **91**, 3661.

<sup>142</sup> M. R. A. Blomberg, P. E. M. Siegbahn, and J.-E. Bäckvall, *J. Am. Chem. Soc.*, 1987, **109**, 4450.

<sup>143</sup> P. Du and W. T. Borden, *J. Am. Chem. Soc.*, 1987, **109**, 5330.

<sup>144</sup> I. Rajyaguru and H. S. Rzepa, *J. Chem. Soc., Perkin Trans. 2*, 1987, 359.

<sup>145</sup> G. Maccagnani, H. B. Schlegel, and G. Tonachini, *J. Org. Chem.*, 1987, **52**, 4961.

<sup>146</sup> J. J. Novoa, J. J. W. McDouall, and M. A. Robb, *J. Chem. Soc., Faraday Trans. 2*, 1987, **83**, 1629.

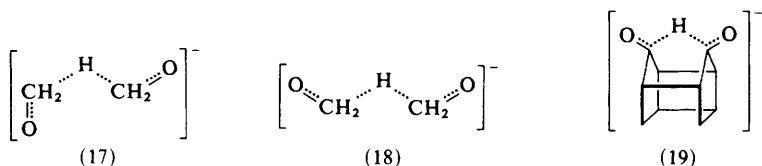
<sup>147</sup> M. T. Nguyen and A. F. Hegarty, *J. Chem. Soc., Perkin Trans. 2*, 1987, 47.

<sup>148</sup> C. J. Cramer, C. E. Dykstra, and S. E. Denmark, *Chem. Phys. Lett.*, 1987, **136**, 17; J. A. Boatz, M. W. Schmidt, and M. S. Gordon, *J. Phys. Chem.*, 1987, **91**, 1743.

<sup>149</sup> H. J. Aa. Jensen, P. Jørgensen, and T. Helgaker, *J. Am. Chem. Soc.*, 1987, **109**, 2895.

**Hydron Transfer.**—The facile suprafacial 1,3-H shift predicted for the radical cation of propene (in contrast to the symmetry-forbidden nature of the process for propene itself) has hinted at the general willingness of radical cations to undergo sigmatropic rearrangements which would be difficult for the neutral parent molecules.<sup>150</sup> Barriers for intermolecular H migrations of ionized amines  $\text{CH}_3(\text{CH}_2)_n\text{NH}_2^{++}$  to  $\dot{\text{C}}\text{H}_2(\text{CH}_2)_n\text{NH}_3^+$  (gas-phase analogues of the Hofmann–Löffler and related rearrangements) decrease with increasing  $n$ , as the angle about the transferring H increases in the respective transition structures.<sup>151</sup> Similarly the activation enthalpy for intramolecular H migration in alkoxy radicals  $\text{CH}_3(\text{CH}_2)_n\text{O}^\bullet$  is lower for  $n = 4$  ( $\varepsilon$ -H abstraction involving a seven-membered cyclic transition structure) than for  $n = 3$ ; the experimental observation of  $\delta$ -H abstraction (*via* a six-membered cyclic transition structure) is due to entropic factors.<sup>152</sup> The suggestion of a planar  $\text{C}_{2v}$  transition structure for the 1,5-H shift of 1,3-pentadiene has been shown to be incorrect owing to the failure to use a uniform level of theory for the alternative pathways; a non-planar  $\text{C}_s$  transition structure is preferred for the suprafacial migration at the MP2 level.<sup>153</sup>

Hydride transfer from methoxide anion to formaldehyde proceeds *via* an unsymmetrical transition structure (17), on a very flat potential energy surface;<sup>154</sup> the 'w'-shaped  $\text{C}_{2v}$  structure (18) has two imaginary frequencies. The primary deuterium kinetic isotope effect calculated for the transition structure (19) is in fair agreement



with experiment.<sup>155</sup> The hydroxide-anion promoted intramolecular hydride transfer of glyoxal is predicted to have a larger primary deuterium kinetic isotope effect than the intermolecular Cannizzaro reaction of formaldehyde;<sup>156</sup> the mechanisms of the benzilic acid and related rearrangements have also been studied.<sup>157</sup> Hydride transfer to methyleniminium cation from methylamine and 1,4-dihydropyridine prefers a *syn* transition structure with a 150–160° angle at the transferring H; the bent *syn* geometry is favoured with respect to the essentially linear *anti* geometry by virtue of stabilizing orbital interactions.<sup>158</sup> The initial step of the ene reaction between the alkoxide anion of propenol and ethene is H-atom transfer, whereas with propenal as the enophile it is hydride transfer.<sup>159</sup>

<sup>150</sup> T. Clark, *J. Am. Chem. Soc.*, 1987, **109**, 6838.

<sup>151</sup> B. F. Yates and L. Radom, *J. Am. Chem. Soc.*, 1987, **109**, 2910.

<sup>152</sup> A. E. Dorigo and K. N. Houk, *J. Am. Chem. Soc.*, 1987, **109**, 2195.

<sup>153</sup> F. Jensen and K. N. Houk, *J. Am. Chem. Soc.*, 1987, **109**, 3139.

<sup>154</sup> Y.-D. Wu and K. N. Houk, *J. Am. Chem. Soc.*, 1987, **109**, 906.

<sup>155</sup> M. J. Field, I. H. Hillier, S. Smith, M. A. Vincent, S. C. Mason, S. N. Whittleton, C. I. F. Watt, and M. F. Guest, *J. Chem. Soc., Chem. Commun.*, 1987, 84.

<sup>156</sup> I. Rajyaguru and H. S. Rzepa, *J. Chem. Soc., Chem. Commun.*, 1987, 998.

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**Additions to Double Bonds.**—The stereochemistry of electrophilic addition to allylic double bonds has been explored by the use of a proton as an electrophilic probe.<sup>160</sup> Electrostatic<sup>161</sup> and steric<sup>162</sup> interactions are important in determining the facial selectivity of Diels–Alder cycloadditions between chiral dienes and/or dienophiles; the frontier molecular orbital (FMO) approach is deficient.<sup>161</sup> While FMO considerations explain the nature of Lewis-acid catalysis on Diels–Alder reactions of propenal, it is secondary orbital interactions which establish their regio- and stereo-selectivities, according to Guner *et al.*,<sup>163</sup> but Fox *et al.*<sup>164</sup> have maintained that steric effects are at least as important, and Sustmann's perturbation MO analyses of cycloadditions have concurred with this.<sup>165</sup> MCSCF calculations for 1,3-dipolar cycloadditions have indicated a preference for concerted mechanisms;<sup>166</sup> pericyclic dihydrogen transfers from HXYH species also prefer concerted pathways,<sup>167</sup> whereas 2+2 cycloadditions of dialkoxyethynes with heterocumulenes may be borderline between non-synchronous concerted and stepwise.<sup>168</sup> The barrier for the concerted ene reaction of propene with formaldehyde is  $\sim 21 \text{ kJ mol}^{-1}$  lower than that with ethene, although the transition structures are remarkably similar.<sup>169</sup> The spin-coupled VB description of carbene addition to ethene has provided a straightforward explanation for the stereospecificity of singlet addition and the lack of it for triplet addition.<sup>77</sup>

Concerted addition of hydrogen halides HX to olefins may be catalysed by a second HX molecule in a cyclic transition structure.<sup>170</sup> Hydrogenation of ethene may be similarly catalysed by HF, but catalysis by  $\text{H}_3\text{O}^+$  involves a cationic intermediate.<sup>171</sup> Barrier heights for addition of OH to ethyne and ethene are overestimated by unrestricted Moller–Plesset perturbation theory calculations, but annihilation of the largest spin component at the PMP4 level provides good agreement with experimental estimates.<sup>172</sup>

The importance of steric effects, and the role of the Felkin torsional model, in determining the facial stereoselectivity of nucleophilic additions to carbonyl compounds has been noted.<sup>173</sup> A concerted mechanism for enamine addition to carbonyl compounds, involving proton transfer in a cyclic transition structure, avoids the unfavourable charge-separation required by the alternative stepwise mechanism *via* a zwitterionic intermediate.<sup>174</sup> Bifunctional catalysis by water of ammonia addition to formaldehyde is effective owing to strong transition-state hydrogen bonding

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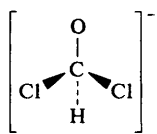
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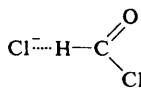
<sup>173</sup> Y.-D. Wu and K. N. Houk, *J. Am. Chem. Soc.*, 1987, **109**, 908; Y.-D. Wu, K. N. Houk, and B. M. Trost, *ibid.*, p. 5560; E. P. Lodge and C. H. Heathcock, *ibid.*, p. 2819.

involving these partial positive and negative charges.<sup>42</sup> Acid hydrolysis of methyl carbamate involves rate determining attack of water upon the *N*-protonated carbamate.<sup>175</sup> Stereoelectronic effects upon nucleophilic addition of phosphite to formaldehyde have been discussed.<sup>176</sup>

A study of the displacement reaction of chloride ion with formyl chloride, at the MP3/6-31 + G\*//3-21 + G level<sup>177</sup> has revealed the tetrahedral  $C_s$  symmetrical species (20) to be a transition structure between the reagent and product ion-dipole complexes (21) on a double-well energy surface; 3-21 + G calculations for the reaction with acetyl chloride have suggested that the transition structure is planar with  $C_{2v}$  symmetry – the ‘tetrahedral intermediate’ is not even a stationary point on the ridge separating reagents and products! Blake and Jorgensen have commented that the central role of tetrahedral intermediates in addition reactions is not as universal as is commonly assumed.<sup>177</sup>



(20)



(21)

A theoretical study of the reactivity of phosphonium and sulphonium methylides with formaldehyde has accounted for the preference of the phosphorus species to undergo the Wittig reaction, yielding ethene, whereas the sulphur compound favours the Corey–Chaykowsky reaction with oxirane as the product.<sup>178</sup>

**Miscellaneous Reactions.**—A study of  $S_N2$  reactions of hydroxide and hydroperoxide anions with methyl chloride has concluded that the  $\alpha$ -effect is due to solvation.<sup>179</sup> Pathways for nucleophilic substitution at silicon<sup>180</sup> and for the Reformatsky reaction<sup>181</sup> have been examined. Unimolecular ring opening of protonated oxirane yields protonated acetaldehyde in a concerted process, but bimolecular attack of water provides a gas-phase counterpart to the classical A2 mechanism for hydrolysis.<sup>182</sup> Methylene insertions into molecular hydrogen,<sup>183</sup> ethane, and cyclopropane<sup>184</sup> have been studied. Calculations relevant to the mechanism of chemical carcinogenesis by *N*-nitrosamines have been performed.<sup>185</sup>

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## 6 Solvation

Jorgensen has exemplified the use of statistical perturbation theory in Monte Carlo simulations of the conformation of butane in water,<sup>186</sup> the  $pK_a$  of ethane in water,<sup>187</sup> and the hydration and energetics of  $t\text{-Bu}^+\text{Cl}^-$  ion pairs in aqueous solution.<sup>188</sup> Free-energy calculations of solvation of organic molecules by computer simulation have been reviewed<sup>189</sup> and a dynamical approach based on a combined quantum and molecular mechanics potential has been applied<sup>190</sup> to the  $S_N2$  reaction  $\text{Cl}^- + \text{CH}_3\text{Cl}$ : the advantages of this method are that it avoids the need for extensive parameterization of the reaction pathway and that it permits the effect of solvation upon the electronic structure of the solute to be ascertained.<sup>190</sup> Tautomeric equilibria of 2-oxopyridine, 2-oxopyrimidine, and cytosine in aqueous solution have been studied by free-energy perturbation methods, giving about  $4 \text{ kJ mol}^{-1}$  uncertainty in the solvation contribution to free-energy differences.<sup>191</sup> The results of an *ab initio* MO study of bifunctional catalysis of 2-oxopyridine tautomerism by one or two specifically solvating water molecules were not greatly affected by the additional treatment of bulk solvation by a reaction field continuum model.<sup>192</sup> Specific solvation effects upon ketonization of vinyl alcohol,<sup>193</sup> 1,3-proton shift of nitrosamine,<sup>194</sup> carbinolamine formation,<sup>42</sup> formic acid dehydration and decarboxylation,<sup>195</sup>  $\text{CO}_2$  hydration,<sup>196</sup> and 1,1-addition to isocyanides<sup>197</sup> have also been studied by *ab initio* methods. Burshtein has described a modified point dipole model to simulate solvent effects<sup>198</sup> and has applied it to studies of carbonyl addition,<sup>198</sup> proton transfer,<sup>199</sup> and  $S_N2$  reactions.<sup>200</sup>

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