A Theoretical Investigation of Some Stereoelectronic Effects

By **Robert J. Elliott** and **W. Graham Richards,*** Physical Chemistry Laboratory, South Parks Road, Oxford OX1 3QZ

MNDO and *ab initio* calculations, in conjunction with the ' sphere-charge ' technique of charge partition, consistently account for stereochemical preferences in the generations and alkylations of allyl and heteroallyl anions. The conventional localised orbital treatments of these phenomena are shown to be inadequate.

THE generation and alkylation of allyl and heteroallyl anions are remarkable in that they are stereospecific and overwhelmingly the preference is for the *syn*-configuration.[1] Isoelectronic neutral systems, such as enols and enol ethers, and carboxylic acids, esters, and imidates, also adopt the *syn*-geometries about the oxygen. Greater thermodynamic stability of the *syn*-anion is generally claimed, although in some cases the possibility of a kinetic preference for formation of the *syn*-anion is recognised. These phenomena have been explained in several different ways; recently it was shown [1] that two explanations, namely homoaromatic stabilisation and metal chelation, were not generally viable, and the possibilities of electrostatic forces and localised orbital interactions remained. Various model calculations indicated that the *syn*-preference arises from the greater electrostatic repulsion between the lone pair and the partial minus charge at C-3 in the *anti*-species and the authors concluded that electrostatics offers the most likely general rationalisation.

However, the remaining possibility of localised orbital interactions [2] continues to receive support.[3] Its basis is represented crudely in Figure 1, the example chosen being that of the *syn*-preference of hydroxyethylene. In each conformation electron delocalisation, and therefore an overall stabilisation of the molecule, can occur as a result of interaction between the *n* orbital on oxygen and σ^* of the antiperiplanar bond. The relative orientation is such that interaction with the synperiplanar σ^* will be much smaller. The hypothesis that σ^*_{CC} is of lower energy than σ^*_{OH} and that therefore the interaction with the former will be greater is then used to conclude that the *cis*-conformer will be favoured over the *trans*.

An attempt to generalise this explanation to all allyl and heteroallyl systems raises a number of problems. First, when both antibonding orbitals are σ^*_{OO}, the assumption presumably has to be made that the energy is lower when the carbons are doubly bonded than when they are singly bonded. This seems rather dubious.

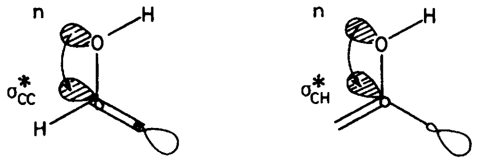


FIGURE 1 Dominant localised orbital interactions in *syn*- and *anti*-hydroxyethylene

Secondly, since an antibonding orbital becomes partially occupied, the implication is that bonds *anti* to lone pairs should be weaker (longer) than the same bonds when in the *syn*-configuration. However, we have performed MNDO geometry optimisations and *ab initio* bond order calculations on a range of molecules which suggest that the reverse is true, by a small but consistent margin. Thirdly, we show that the preference is in general likely to be due to kinetic factors; the preferential formation of the *syn*-species is then inconsistent with delocalisation into σ^* of what is to become the developing double bond.[4]

CALCULATIONS

Wavefunctions and energies were computed at *ab initio* STO-3G level [5] using the GAUSSIAN 76 program [6] on a CDC 7600 computer. Charge distributions were obtained by the method of Dean and Richards,[7] which permits sampling of the charge density in any spherical region in or around the molecule. In this way the method permits far more versatile investigations [8-10] of the chemical properties of molecules than the conventional Mulliken population analysis.[11] The geometries used were the optimal values obtained from the MNDO program.[12a]

This procedure (using geometries obtained from semi-empirical methods for subsequent *ab initio* wavefunction calculations) is reasonably well established, and is followed because of the prohibitive expense of performing routine *ab initio* geometry optimisations on molecules of the size studied. The MNDO method is particularly suitable since it gives highly satisfactory geometries and represents a significant advance on earlier semi-empirical methods due to a superior parametrisation (see the discussion by Dewar [12b]).

RESULTS AND DISCUSSION

Complete geometrical optimisations, at the MNDO level, of the species shown in Figure 2 were carried out. Although the differences are small, there is clearly no evidence to suggest that bonds *syn* to lone pairs are stronger (shorter) than those *anti*- and such differences as there are invariably suggest the opposite.

Length is of course only a guide to the strength of a bond; we showed recently [13] how a rigorous bond order could be obtained from an *ab initio* wavefunction using the Dean and Richards technique. A sphere with diameter equal to the bond length is centred halfway along the line joining the two nuclei to obtain the charge density in the internuclear region. For carbon–carbon bonds we parameterised this using ethane, ethylene, and acetylene and showed that the method was of quite general applicability.

Our bond order results for the species in Figure 2 are given in the Table. Again, bonds *anti* to lone pairs are shown to be stronger than those *syn*. This is true of both single and double carbon–carbon bonds. Both *syn*- and *anti*-bonds are strengthened in the protonated species (1), (2), and (5) relative to the corresponding deprotonated forms (3) and (4). Carbon–hydrogen bonds, on the other hand, are weakened on *O*-protonation. Each of the groups of species in Figure 2 will now be discussed in turn.

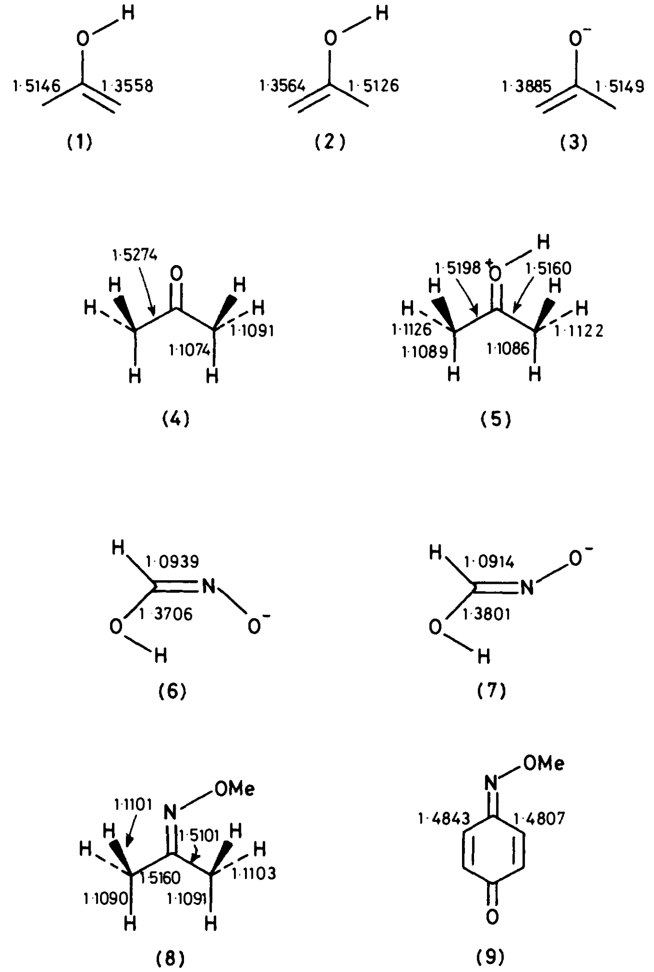


FIGURE 2 Bond lengths (Å) in some species which prefer the *syn*-configuration in solution, and in some reference compounds (MNDO)

Enols.—Calculations of the total energy of acetone enol as a function of dihedral angle for rotation from the *syn*- to the *anti*-form were carried out at the *ab initio* level. The results, shown in Figure 3, suggest the *syn*-preference to be of kinetic rather than thermodynamic origin. The *syn*-enol is more stable than the *anti*- but only by 2.1 kJ mol^{-1} (*RT ca.* 2.5 kJ mol^{-1} at 298 K). The activation energy, on the other hand, is too great to permit rapid interconversion of the two forms at room temperature. The *syn*-enol must therefore be formed preferentially from the appropriate precursor (in acidic conditions, protonated acetone). This is inconsistent with the explanation of stereoelectronic stabilisation in terms of localised orbital interactions (Figure 1) since such interactions would weaken the *syn*-bond of (5) relative to the *anti* and would therefore favour double bond development on the *anti*-side. The calculated bond strengths, however, correctly predict that deprotonation will occur preferentially on the *syn*-side. The carbon–hydrogen bond lengths are also indicative of this; those C–H bonds on the *syn*-side of (5) are weaker than those on the *anti*-side [similarly for (8)].

Bond strengths in compounds in Figure 2 (MNDO geometries)

Bond	Inter-nuclear sphere-charge (electrons) per unit volume	Bond order
C=C in acetone *syn*-enol (1)	2.7326	1.92
C=C in acetone *anti*-enol (2)	2.7290	1.90
C=C in acetone enolate (3)	2.5938	1.74
C–C in acetone (4)	1.9612	0.99
C–C in acetone *syn*-enol (1)	2.0645	1.11
C–C in acetone *anti*-enol (2)	2.0748	1.12
syn-C–C in protonated acetone (5)	2.0437	1.08
anti-C–C in protonated acetone (5)	2.0286	1.06
syn-C–C in oxime (8)	2.0889	1.14
anti-C–C in oxime (8)	2.0696	1.11
syn-C–CN in oxime (9)	2.1908	1.26
anti-C–CN in oxime (9)	2.1781	1.24
C–OH in (6)	3.1825	
C–OH in (7)	3.1284	

Frontier orbital charges[9] in spheres surrounding the hydrogen atoms in protonated acetone provide further rationalisation (Figure 4); the greater LUMO charges occur on the *syn*-side, although the difference is only *ca.* 2%.

Oximes.—MNDO geometry optimsations and STO-3G calculations were carried out on the anions (10) and (11) (Figure 5). The *syn*-anion is more stable by 0.0145 a.u. (38.07 kJ mol^{-1}). In this case there is therefore a definite thermodynamic preference. Sphere-charge cal-

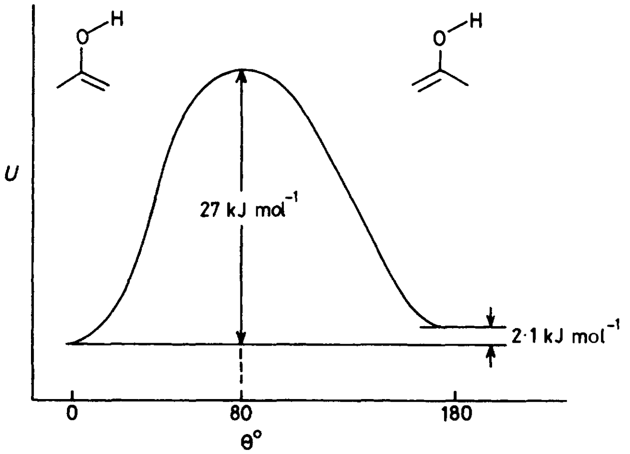


FIGURE 3 Potential energy curve for the rotational interconversion of (1) and (2)

culations still show, however, that under conditions of kinetic control the *syn*-anion will be formed preferentially; the *syn*-bond is stronger, and the hydrogen LUMO sphere-charge is greater on the *syn*-side (Figure 6).

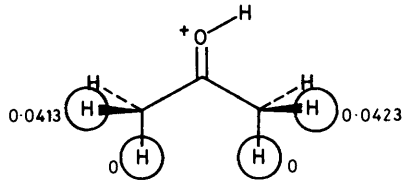


FIGURE 4 LUMO charges in spheres (of radius 0.5 Å) centred on the hydrogen nuclei of protonated acetone

The strength of the *syn*-side carbon–carbon single bond in (9) accounts for the site-selectivity shown in its Diels–Alder reactions;[14] the carbon–carbon double bond on this side is better conjugated with the carbon–nitrogen double bond and its reactivity is thereby increased.

(10) (11)

FIGURE 5 Optimised geometries and total energies (a.u.) for the anions of (8)

Hydroximate Anions.—The reaction of nitrile oxides (12) with nucleophiles has been investigated,[15] experimentally and theoretically, and striking stereospecificity has been observed (Figure 7). The most unequivocal

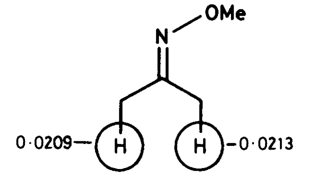
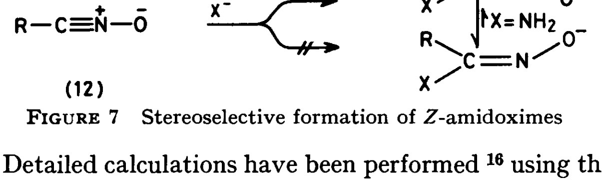


FIGURE 6 LUMO sphere-charges (radius 0.5 Å) for hydrogen atoms in (8)

example is the formation of *Z*-amidoximes on reaction with secondary amines; their formation is undoubtedly kinetically controlled since the *E*-isomer is rapidly formed in a subsequent reaction.



(12)

FIGURE 7 Stereoselective formation of *Z*-amidoximes

Detailed calculations have been performed[16] using the split-valence 4-31G basis set and it has been shown that in the transition state the oxygen on the starting nitrile oxide bends over toward the incoming nucleophile; all other arrangements are of higher energy. Again, the results in Figure 2 and the Table show that the favoured *syn*-arrangement does not result in a weakening of the C–OH bond.

Conclusions.—The stereoelectronic preferences seem to be kinetic rather than thermodynamic, since they can occur regardless of whether the *syn*-configuration is substantially more stable (oxime anions), only slightly more stable (enols), or even less stable (hydroximate anions) than the *anti*-configuration. As we have shown, this is quite inconsistent with the suggestion of more favourable localised orbital interactions in the *syn*-species. Direct evidence that this does not occur may be obtained by

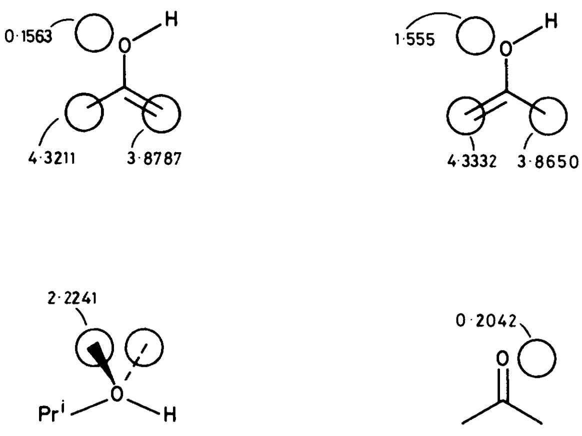


FIGURE 8 Charges in spheres (radius 0.5 Å) centred on the ' lone pair ' regions (1.0 Å from oxygen nucleus) and carbon atomic sphere-charges for (1) and (2)

calculating the charge in ' off-centre ' spheres (Figure 8). There is indeed a considerable delocalisation of charge from the ' lone pair ' region in the enols, as compared with reference compounds such as acetone and propan-2-ol, but this occurs for both forms. In fact this charge is slightly lower for the *anti*-enol.

An electrostatic explanation of the thermodynamic stability of *syn*-forms of anionic species is obviously appealing, but at first sight it is not applicable to neutral systems (see carbon sphere-charges in Figure 8). However, this is simply a limitation of being confined to atomic regions of charge; Figure 9 shows charges in

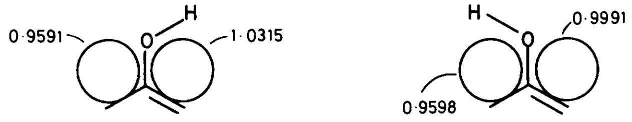


FIGURE 9 Sphere-charges measuring the electrostatic repulsion experienced by the lone pairs in (1) and (2)

spheres which are tangential to the C–C bonds at their mid-points (again, the diameter is equal to half the internuclear distance). Here we can see that the lone pair will experience a greater electrostatic repulsion in the *anti*-species, by a small amount. The *syn*-species is therefore correctly predicted to be slightly more stable.

In conclusion, *ab initio* molecular charge distributions can readily account for kinetic *syn*-preferences in allyl and heteroallyl anion-type systems. Thermodynamic preferences can be explained on the basis of electrostatic interactions. Generalised explanations in terms of localised orbitals are not possible.

[1/1916 *Received*, 11*th December*, 1981]

REFERENCES

[1] K. N. Houk, R. W. Strozier, N. G. Rondan, R. R. Fraser, and N. Chaquia-Offermans, *J. Am. Chem. Soc.*, 1980, **102**, 1426.

[2] R. Hoffmann, *Acc. Chem. Res.*, 1971, **4**, 1.

[3] J. R. Larson, N. D. Epiotis, and F. Bernardi, *J. Am. Chem. Soc.*, 1978, **100**, 5713, and references therein.

[4] The idea of $n \rightarrow \sigma^*$ donation is well supported, by i.r. stretching frequencies, in the case of sp^3 hybridised C–H bonds, however. See D. C. McKean and I. A. Ellis, *J. Mol. Struct.*, 1975, **29**, 81; D. C. McKean, *Chem. Commun.*, 1971, 1373. For a comparison with calculations see V. Bachler and G. Olbrich, *Theor. Chim. Acta*, 1980, **57**, 329.

[5] W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, 1969, **51**, 2657.

[6] J. S. Binkley, R. A. Whiteside, P. C. Hariharan, R. Seeger, J. A. Pople, W. J. Hehre, and M. D. Newton, QCPE, 1978, **11**, 368.

[7] S. M. Dean and W. G. Richards, *Nature* (*London*), 1975, **258**, 133; W. G. Richards and J. Wallis, *Proc. R. Soc. London, Sect. B*, 1977, **199**, 291; J. Wallis, QCPE, 1981, **13**, 411.

[8] A. F. Marchington, S. C. R. Moore, and W. G. Richards, *J. Am. Chem. Soc.*, 1979, **101**, 5529.

[9] R. J. Elliott, V. Sackwild, and W. G. Richards, *J. Mol. Struct.*, (*Theochem*), 1982, **86**, 301.

[10] R. J. Elliott and W. G. Richards, *J. Mol. Struct.* (*Theochem*), 1982, **87**, 247.

[11] R. S. Mulliken, *J. Chem. Phys.*, 1955, **23**, 1833.

[12] (*a*) W. Thiel, QCPE, 1978, **11**, 353; (*b*) M. J. S. Dewar and W. Thiel, *J. Am. Chem. Soc.*, 1977, **99**, 4899, 4907.

[13] R. J. Elliott and W. G. Richards, *J. Mol. Struct.* (*Theochem*), 1982, **87**, 211.

[14] J. E. Baldwin and R. K. Norris, to be published.

[15] K. J. Dignam, A. F. Hegerty, and P. L. Quain, *J. Org. Chem.*, 1978, **43**, 388.

[16] G. Leroy, M. T. Nguyen, M. Sana, K. J. Dignam, and A. F. Hegerty, *J. Am. Chem. Soc.*, 1979, **101**, 1988.