

A Comparison of the MNDO and AM1 SCF-MO Energy Surfaces For Dipolar Cycloaddition and [3,3] Sigmatropic Reactions

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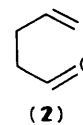
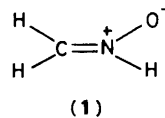
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Difference contour energy maps for several $\pi^4_s + \pi^2_s$ dipolar cycloadditions and for the [3,3] sigmatropic (Claisen) rearrangement of pent-4-enal indicate that the AM1 and MNDO SCF-MO methods differ most significantly at C-C, C-O, and C-N bond distances of approximately 2.3, 2.05, and 2.5 Å, respectively; the AM1 results for bond formation involving nitrogen appear to be incorrect owing to excessive core-core repulsion.

The mechanism of thermally allowed pericyclic reactions such as cycloaddition¹ or the Cope or Claisen rearrangements² continues to attract much theoretical discussion,³ particularly with regard to the structure of the transition states. Theoretical studies at the closed shell (single configuration) SCF level of the Diels-Alder reaction of ethene and butadiene, and of the [3,3] sigmatropic rearrangement of hexa-1,5-diene indicate that the transition states are symmetrical (synchronous) at the *ab initio* level. Recent studies at the correlated multi-configuration (MCSCF) *ab initio* level^{1,2} support the synchronous transition state as the lowest energy pathway for

such reactions. Semi-empirical methods such as MINDO/3 or MNDO, however, tend to favour unsymmetrical transition states both at the closed- and open-shell correlated (CI) levels.³ In contrast, the more recent AM1 semi-empirical



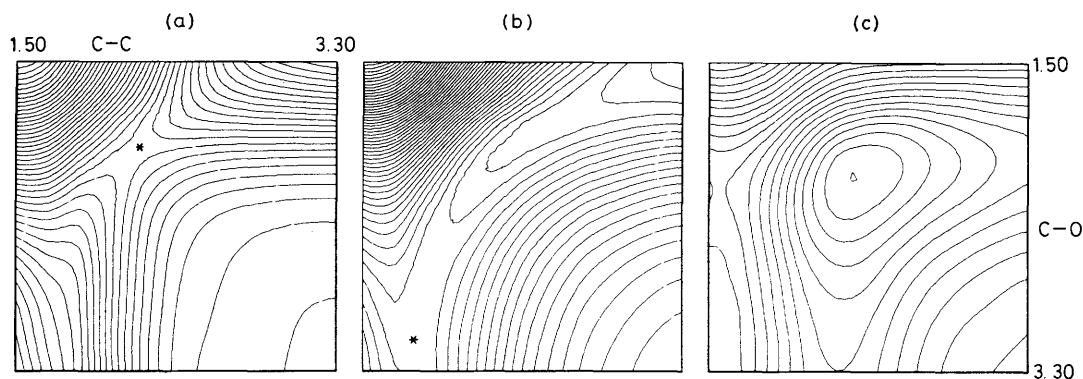


Figure 1. Contour maps for the cycloaddition of (1) and ethene, using the forming C-C and C-O bond lengths as reaction co-ordinates for (a) AM1, (b) MNDO, and (c) the difference map between (a) and (b). All contour levels are separated by 2.0 kcal mol⁻¹ (cal = 4.184 J). Genuine transition states are indicated with an asterisk.

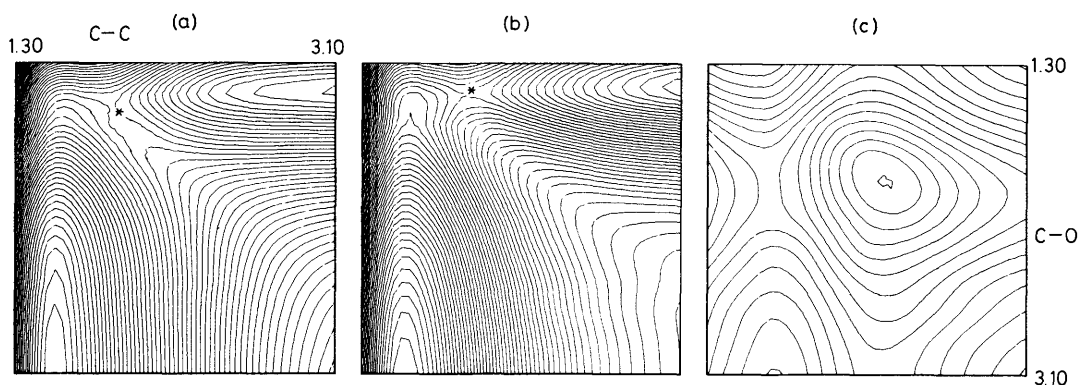


Figure 2. Contour maps for the [3,3] rearrangement of pent-4-enal for (a) AM1, (b) MNDO, and (c) the difference map between (a) and (b). Contour levels are separated by 2.0 kcal mol⁻¹.

method does predict³ *synchronous* transition states for the cycloaddition of butadiene to substituted ethenes, but only at the closed shell level, with *asynchronous* (biradical-like) transition states again favoured at the open shell (CI) level. The closed shell AM1 result was ascribed to the superior treatment of non-bonded interactions compared with MNDO. We report here results at the closed shell level for several pericyclic reactions involving heteroatoms which suggest that the maximum difference between the AM1 and MNDO methods is a function of the two atoms involved in bond cleavage or formation, rather than the type of pericyclic reaction involved.

A contour map of ΔH vs. the C-C and C-O distances of the forming/cleaving bonds in the cycloaddition of nitrene (1) to ethene, obtained with full minimisation of the remaining $3N-8$ degrees of freedom, reveals the AM1 surface (Figure 1a) to correspond to a synchronous reaction, whereas that for MNDO (Figure 1b) is highly asymmetric. The AM1 transition state bond lengths are similar to those recently reported for this reaction at the *ab initio* MCSCF/4-31G level.^{1c} A map of the difference in energies between AM1 and MNDO reveals that the two methods differ most in energy at C-C and C-O bond lengths of 2.3 and 2.1 Å, respectively, approximately coincident with the predicted AM1 transition state. Similar results were obtained for the Claisen type [3,3] sigmatropic reaction of pent-4-enal (2) (Figure 2). In this example, the contour maps reveal quite similar AM1 (Figure 2a) and MNDO (Figure 2b) surfaces, but the region of maximum difference between the two methods is not coincident with

either transition state (Figure 2c). MCSCF calculations² for the Cope reaction of hexa-1,5-diene predict longer transition state C-C bonds (2.063 Å) than predicted by AM1 for the Claisen reaction (Figure 2a).

Surprisingly, the reaction between HN₃ and ethyne is predicted to be highly asynchronous by both AM1 and MNDO, the maximum difference between the two methods occurring at C-N distances of approximately 2.5 Å (Figure 3). The AM1 symmetric stationary point ($r_{\text{HN-C}} 2.051$, $r_{\text{N-C}} 2.051$ Å) had two negative force constants (ν_i 811, 305 i cm⁻¹), the second corresponding to a distortion to a highly unsymmetrical transition state (Figure 3a). The isoelectronic system HCNO + ethyne had only one negative force constant at the AM1 level ($r_{\text{HC-C}} 1.948$, $r_{\text{O-C}} 2.307$ Å, ν_i 683 i cm⁻¹). At the *ab initio* 3-21G level, the HN₃ + ethyne transition state was as expected ($E_{\text{total}} -239.2321$ a.u., $r_{\text{HN-C}} 2.085$, $r_{\text{N-C}} 2.204$, ν_i 655 i cm⁻¹), leading us to believe that the reported AM1 parameters for nitrogen must be incorrect. Indeed, inspection of the gaussian functions used in the core repulsion terms (CRF) in AM1 reveals that whereas carbon and oxygen have repulsive functions centred at 1.85 and 1.44 Å, respectively, the repulsive function for nitrogen is centred at the surprisingly high value of 2.1 Å. If the AM1 calculations are repeated using a value of 1.6 Å for this gaussian function, the symmetrical stationary point for the HN₃ + ethyne reaction now has only one calculated negative force constant ($r_{\text{HN-C}} 2.02$, $r_{\text{N-C}} 2.02$, ν_i 746 i cm⁻¹). This change in the CRF has relatively little impact on ground state energies and geometries (except possibly on hydrogen bonds involving nitrogen,

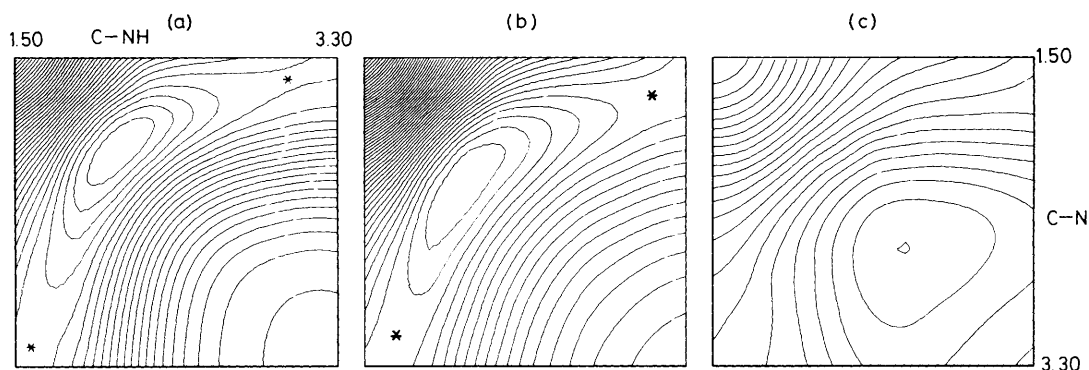


Figure 3. Contour map for the cycloaddition of HN_3 and ethyne for (a) AM1, (b) MNDO, and (c) the difference map between (a) and (b). Contour levels are separated by $2.0 \text{ kcal mol}^{-1}$. Genuine transition states are marked with an asterisk.

where internuclear separations involving nitrogen of 2.6–3.0 Å are important), but it has a *major* effect on transition state geometries, indicating that parametrisation of semi-empirical methods using ground state molecules alone may result in serious deficiencies in calculated potential surfaces.

Difference contour maps thus display the divergence between two different theoretical procedures such as AM1 and MNDO. Similar comparisons between AM1 and *ab initio* closed shell surfaces will allow evaluation of the region of maximum difference between these methods.

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References

- (a) Ethene plus butadiene: F. Bernardi, A. Bottoni, M. A. Robb, M. J. Field, I. H. Hillier, and M. F. Guest, *J. Chem. Soc., Chem. Commun.*, 1985, 1051; (b) F. Bernardi, M. Olivucci, J. J. W. McDouall, and M. A. Robb, *J. Am. Chem. Soc.*, 1987, **109**, 544; (c) Dipolar cycloaddition reactions: J. J. W. McDouall, M. A. Robb, U. Niani, F. Bernardi, and H. B. Schlegel, *ibid.*, 1987, **109**, 4642.
- Cope reaction: D. Feller, E. R. Davidson, and W. T. Borden, *J. Am. Chem. Soc.*, 1984, **106**, 3362; for MNDO calculations on the Claisen rearrangement, see M. J. S. Dewar and E. F. Healy, *ibid.*, 1984, **106**, 7127; for a recent experimental study, see J. J. Gajewski and J. L. Jimenez, *ibid.*, 1986, **108**, 468.
- M. J. S. Dewar, S. Olivella, and J. J. P. Stewart, *J. Am. Chem. Soc.*, 1986, **108**, 5771.