

The diatropic σ ring currents of $[\pi 2_s + \pi 2_s + \pi 2_s]$ pericyclic transition states

Remco W. A. Havenith,^{ab} Leonardus W. Jenneskens,^{*b} Patrick W. Fowler^{*a} and Erich Steiner^a

^a School of Chemistry, University of Exeter, Stocker Road, Exeter, UK EX4 4QD.

E-mail: P.W.Fowler@exeter.ac.uk; Fax: +44-1392-263434

^b Debye Institute, Department of Physical Organic Chemistry, Utrecht University, Padualaan 8, 3584 CH Utrecht, The Netherlands. E-mail: jennesk@chem.uu.nl; Fax: +31-30-2534533

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Ab initio current-density maps for the $(4n + 2)$ -electron transition states of two thermally allowed $[\pi 2_s + \pi 2_s + \pi 2_s]$ trimerisations, of ethyne to benzene (**1**), and of ethene to cyclohexane (**2**), show that both support σ diatropic ring currents, dominated by four-electron $\sigma \rightarrow \sigma^*$ virtual excitation of HOMO electrons.

Thermally allowed *pericyclic* reactions are considered to take place *via* a concerted pathway that passes through an energetically favoured ‘aromatic’ transition state involving $(4n + 2)$ delocalised electrons.¹ On the magnetic criterion for aromaticity, the implication is that these transition states should support diatropic ring currents in the presence of an external magnetic field.² Such currents have been inferred in *ab initio* theoretical studies, from various calculated properties [*e.g.* ¹H NMR chemical shifts, exaltation of diamagnetisability ($\Delta\chi$) and nucleus independent chemical shifts³ (NICS)];⁴ in some cases the relative contribution made by σ and π electrons to the induced diatropic current remains a subject of debate.^{4,5}

A direct way to address questions of both the existence and nature of these currents is by visualisation of the induced current density. To this end, we compare here *ab initio* calculated current-density maps for the transition states of the thermally-allowed $[\pi 2_s + \pi 2_s + \pi 2_s]$ trimerisations of ethyne to benzene (**1**, D_{3h}),^{4g} and ethene to cyclohexane (**2**, D_3).^{4k} The maps are computed using the reliable and well-documented⁶ *ipsocentric*⁷ formulation of coupled Hartree–Fock theory for magnetic response. This is the CTOCD-DZ2 (continuous transformation of the origin of current density–diamagnetic zero) method⁸ as implemented in SYSMO.⁹ A particular advantage of this approach from the point of view of interpretation is that it allows partition of the total current density into additive and physically separate orbital contributions.^{7a} As will be seen, the maps for both transition states show a strong diatropic ring current, which arises in both cases from the same translationally allowed nature of the *four-electron* $\sigma \rightarrow \sigma^*$ HOMO–LUMO excitation⁷ and hence points to a general feature of pericyclic reactions.

The transition states **1** and **2** were located at the RHF/6-31G** level of theory using GAMESS-UK¹⁰ and characterised by Hessian calculations (**1**: 1063i cm⁻¹, and **2**: 1221i cm⁻¹) (Fig. 1). The computed CC separations (**1**: 1.217 Å and 2.214 Å, and **2**: 1.381 Å and 2.172 Å) are in reasonable agreement with published results (B3LYP/6-311+G**): **1**: 1.226 Å and 2.295 Å,^{4g} and **2**: 1.388 Å and 2.205 Å.^{4k} The CH bonds are bent back from the carbon frame [RHF/6-31G**]: **1**: $\angle\text{HCC} = 151.5^\circ$ and **2**: $\angle\text{HCC} = 118.4^\circ$ and $\angle\text{HCH} = 115.0^\circ$. In **1** the six carbon atoms are coplanar; in **2** they lie on two triangles, 0.07 Å above and below the median plane. In what follows, the term ‘ σ plane’ will denote the plane of carbon centres in **1** and

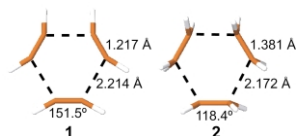


Fig. 1 RHF/6-31G** structures of the transition states **1**, D_{3h} and **2**, D_3 .

the median plane in **2**, and the ‘ π plane’ denotes a plane 1 a_0 above this.

Current densities, calculated with the same 6-31G** basis set as used to determine the geometries, are displayed (Fig. 2) as maps of total current density and of various orbital contributions to it, plotting the current density induced by unit magnetic field acting along the normal to the σ plane, with arrows representing projections of the vector current density in the plotting plane, and contours representing the modulus of the current density. The plotting plane is either the σ plane itself, or the π plane. In the maps, diamagnetic (diatropic) flow is anti-clockwise, paramagnetic (paratropic) flow is clockwise.

The most striking feature of the maps for **1** and **2** is their close similarity, both in overall appearance and in detail. Each transition state exhibits a strong, delocalised circulation in the σ plane, with a consistent diamagnetic sense inside and outside the hexagon of the carbon framework (Figs. 2a and 2d). This

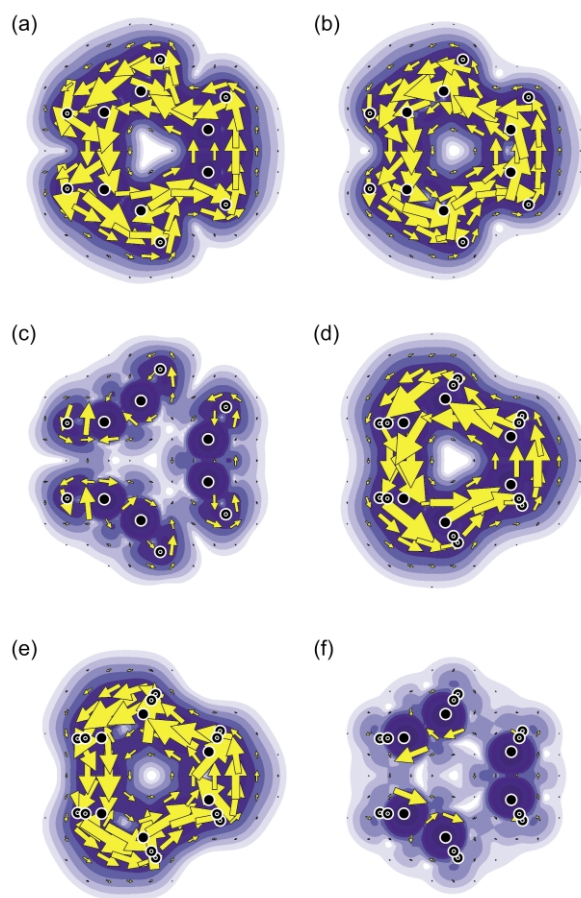


Fig. 2 Maps of current density plotted in the molecular plane for **1**, D_{3h} (a) total, (b) contribution from the $6e'$ HOMO, (c) from all but the HOMO; plotted in the median plane for **2**, D_3 (d) total, (e) contribution from the $8e$ HOMO, (f) from all but the HOMO. (● carbon, ○ hydrogen).

global circulation is in each case dominated by the orbital contribution from the doubly degenerate HOMO of the transition-state structure ($6e'$ for **1**, $8e$ for **2**) (Figs. 2b and 2e). The combined effect of all the remaining orbitals gives hardly any contribution to this ring current (Figs. 2c and 2f), instead bringing in a set of localised circulations within bonds and inner shells (see ref. 6).

The orbital model of current density⁷ that follows from the ipsocentric approach reveals the reason for the similarity of the maps for **1** and **2**. In this approach the current density is built up from contributions from virtual excitations (from occupied to unoccupied orbitals) each weighted by an energy denominator. In a monocyclic system, diamagnetic current arises from those transitions $\Psi_a \rightarrow \Psi_b$ that have translational symmetry, *i.e.* where the product $\Gamma(\Psi_a) \times \Gamma(\Psi_b)$ contains the symmetry of a translation in the plane perpendicular to the magnetic field, and paramagnetic current arises from those transitions that have rotational symmetry, *i.e.* where the product contains the symmetry of the rotation about the direction of the magnetic field.

Now, in both transition states, the sets of σ HOMO orbitals are essentially identical, as are the LUMO set (Fig. 3). The HOMOs consist of a pair of orbitals in which a single nodal plane cuts the carbon framework, and the LUMOs in each case consist of a pair in which two nodal planes cut the framework. They are the exact σ analogues of the π and π^* HOMO and LUMO of benzene, and like them can be classified by their angular momentum about the principal rotational axis, *i.e.* $\Lambda = \pm 1$ for the HOMO and $\Lambda = \pm 2$ for the LUMO. The $\Delta\Lambda = +1$ transitions from HOMO to LUMO are translationally allowed here for the same reason as in benzene itself, and they give rise to the four-electron diatropic current that dominates the magnetic response of these systems; indeed in the simple Hückel treatment of the $4n + 2$ monocycle this is the only contribution to the ring current.^{7b} Thus, the transition states **1** and **2** have a σ ring current for the same reason that benzene has a π ring current.

One possible difference between **1** and **2** remains to be explored. The transition state **2** has no π system, but **1**, the transition state for trimerisation of ethyne to produce benzene, has a π system perpendicular to the plane of the carbon nuclei.

The possibility of a contribution of this π system to the ring current in **1** has been raised.^{4,5} The map of the current density plotted in the $1 a_0$ plane close to a maximum of these π orbitals (Fig. 4) does indeed show a global circulation, but the main orbital contribution to this circulation is still that of the σ HOMO pair and not of the π orbitals themselves. The current density from the π orbitals is weak and localised over the three

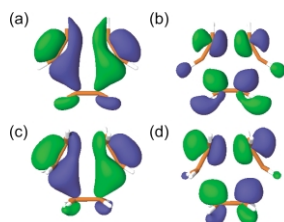


Fig. 3 HOMO and LUMO for **1**, D_{3h} and **2**, D_3 . One member only of each degenerate pair is shown: (a) **1**, $6e'$ HOMO (b) **1**, $7e'$ LUMO, (c) **2**, $8e$ HOMO, (d) **2**, $9e$ LUMO.

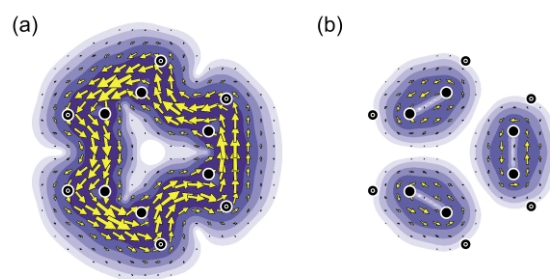


Fig. 4 Maps of current density of $1e'$ HOMO-1 plotted at $1 a_0$ above the molecular plane (in the ' π plane') for **1**, D_{3h} (a) total, (b) π contribution. (● carbon, ○ hydrogen).

CC bonds—it does not constitute a ring current (*cf.* Ref. 5b). In fact, a similar current density is seen in the $1 a_0$ map for **2** (not shown), where there are no formal π orbitals at all. The conclusion from direct mapping is that the ring current in both **1** and **2** is of pure σ type.

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