Evidence for the Möbius Aromatic Character of Eight π Electron Conrotatory Transition Structure. Magnetic Criteria

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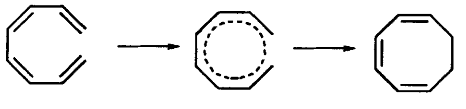
The Möbius aromatic character of the 8π electron transition structure for the conrotatory electrocyclic ring closure of (*Z,Z*)-octa-1,3,5,7-tetraene is demonstrated by downfield and upfield ^{1}H chemical shifts as well as the enhanced magnetic susceptibility computed by the IGLO method. H1,8 (outer) are *deshielded* and H1,8 (inner) are *shielded* in the transition structure.

Heilbronner's original suggestion, that polyene 4*n* π systems would be aromatic if the perimeter were twisted by 180°,[1] has not yet been realized in any stable molecule.[1c] However, such Möbius aromaticity may be manifest in the transition structure of electrocyclic reactions,[1c] *e.g.*, the conversion of (*Z,Z*)-octa-1,3,5,7-tetraene **1** into (*Z,Z,Z*)-cycloocta-1,3,5-triene **2**. The prediction of Woodward and Hoffmann[2] that this eight-electron cyclization would be concerted and conrotatory has been confirmed by experiment (the activation energy is very low, 17 kcal mol^{-1})[3] and by quantum chemical calculations.[4]


1 **3** **2**

As part of an extensive computational investigation of hydrocarbon pericyclic reactions, Houk *et al.*[4] reported the HF/6-31G* geometry for the transition structure (*cf.* **3**) for the **1**→**2** interconversion. At this level, the nearly equal benzene-like C–C bond lengths (av. 1.393, range 1.377–1.411 Å) and the 'coiled arrangement of the eight carbons' point to the potential 'Möbius aromatic' character of **3**.

Our related study of the 1,7-H shift in (*Z,Z*)-hepta-1,3,5-triene[5] showed that the eight-electron Möbius transition structure fulfils the *geometrical, the energetic and, in a new application, the magnetic criteria of aromaticity.*[1c] We now provide a theoretical analysis of the aromaticity of the transition structure **3** for the eight-electron conrotatory electrocyclic process involving only carbon centres.

Computational Method

The geometries of the ground state **1**, the cyclization transition structure **3** and the product **2** were fully optimized at the correlated RMP2(fu)/6-31G* level.[6] The nature of each stationary point was characterized by computing the harmonic vibration frequencies at RHF/6-31G*.[6] Single-point energy calculations were carried out at RMP4sdtq/6-31G* using the correlated geometries. The calculated total energies (in hartree, E_h), the zero-point vibrational energies (E_{zp}, scaled by 0.89),[6] the number of imaginary frequencies (NIMAG), activation enthalpies ($\Delta H^{\ddagger}_{0\,\mathrm{K}}$, **1**→**3**) and reaction enthalpies (ΔH, **1**→**2**, in kcal mol^{-1}) are given in Table 1. The chemical shifts and magnetic susceptibilities were computed using the IGLO[7] (Individual Gauge for Localized Orbitals) method employing the RMP2(fu)/6-31G*, RHF/6-31G* geometries and the DZ basis set as well as BII′ basis set (basis II for carbon and DZ for hydrogen) for the stationary points (**1**–**3**). The natural charges were derived from the natural population analysis (NPA) of Reed and Weinhold *et al.*[8] (Tables 3 and 4).

Results and Discussion

The computed RMP2(fu)/6-31G* structures for **1**, the (*Z,Z*)-octa-1,3,5,7-tetraene minimum, for cycloocta-1,3,5-triene, **2**, and for the cyclization transition structure **3** are shown in Fig. 1. Houk and co-workers' RHF/6-31G* distances for **3** are given for comparison in parentheses (also for **1** and **2**). Only the *cis,cis* configuration of **1** can lead directly to the transition structure **3**. The computed activation enthalpy [$\Delta H^{\ddagger}_{0\,\mathrm{K}}$ (**1**→**3**)], 15.0 kcal mol^{-1} [RMP4sdtq/6-31G*//RMP2(fu)/6-31G* + E_{zp} (RHF/6-31G*)], is much closer to the measured[3] value of 17.0 kcal mol^{-1} than Houk's 8.4 kcal mol^{-1} result [RMP2(fc)/6-31G*//RHF/6-31G* + E_{zp}]. Our computed reaction enthalpy [ΔH (**1**→**2**)] is −11.2 kcal mol^{-1} (Table 1). Cycloocta-1,3,5-triene geometries were optimized at the RHF/6-31G* level in C_{2v} (planar), C_2 and C_s (boat) as well as in C_1 point groups. The C_1 symmetric **2** is the global cycloocta-1,3,5-triene minimum. Both the C_2 and C_s (boat) are transition structures (NIMAG = 1), while the planar C_{2v} isomer has NIMAG = 2. The RHF/6-31G* relative energies (in kcal mol^{-1}) are C_1 (0.0), C_s (7.1), C_2 (5.5) and C_{2v} (19.0).

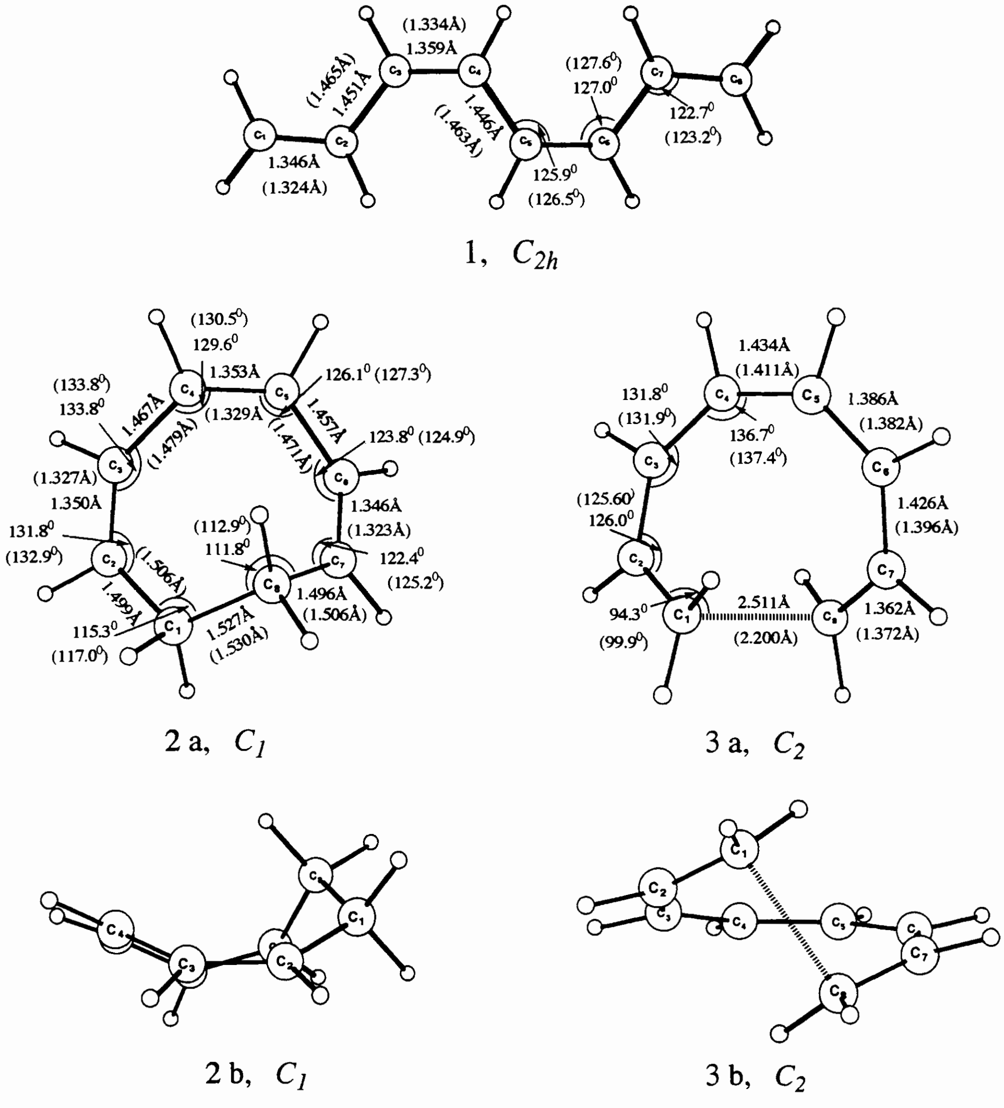
The differences between Houk's RHF/6-31G* (in parentheses) and our RMP2(fu)/6-31G* geometries for **3** are appreciable. The C···C separation involving the C–C bond being formed, 2.55 Å at RMP2(fu)/6-31G*, is 0.35 Å longer than the RHF/6-31G* value, and also than typical C···C separations (*ca.* 2.15 ± 0.15 Å) computed for other pericyclic ring closure processes.[4,5,9] The other C–C bond lengths in **3** differ from the RHF/6-31G* values up to 0.03 Å. The RMP2(fu)/6-31G* lengths in **3** are closer to those in **1** than to the benzene value [1.395 Å, at RMP2(fu)/6-31G*]. In contrast, the C–C lengths are benzene-like in the transition structure for the 1,7-H shift in (*Z,Z*)-hepta-1,3,5-triene (1.395–1.410 Å),[5a] the 1,5-H shifts in penta-1,3-diene (1.396–1.418 Å)[4] and in cyclopentadiene (1.400–1.406 Å).[9] Thus, the *geometrical criterion of aromaticity* is not fulfilled well in **3**. Can this cyclization transition structure still be considered to be 'aromatic'?

Owing to the flexibility of the larger carbon skeleton, the transition structure **3** can be reached with less activation and deformation than that in the other electrocyclic processes described above. Indeed, the energy of concert[10] in the **1**→**2** process is large. A non-concerted activation energy of 36–42 kcal mol^{-1} can be estimated roughly by assuming the transition structure to be a diradical. By interpolation from Doering's *et al.*[11] data on a set of rotational barriers for polyenes with an odd number of double bonds, barriers for rotation of **1** of *ca.* 36 kcal mol^{-1} around a central bond or *ca.* 42 kcal mol^{-1} around

Table 1 Calculated total energies (hartree), E_{zp} (zero-point vibrational energies) for octa-1,3,5,7-tetraene (**1**), the cyclization transition structure (**3**) and cycloocta-1,3,5-triene (**2**), activation enthalpies [$\Delta H^{\ddagger}_{0\,K}$ (**1**→**3**)/kcal mol^{-1}] and reaction enthalpies [ΔH (**1**→**2**)/kcal mol^{-1}] as well as number of imaginary frequencies (NIMAG)

	1, C_{2h}	**3**, C_2	**2**, C_1[e]	$\Delta H^{\ddagger}_{0\,K}$ (ΔH)
RHF/6-31G*	−308.690 47	−308.638 29	−308.706 91	33.3 (−7.8)
E_{zp}/(NIMAG)[a]	91.8/(0)	92.4/(1)	94.3/(0)	
RMP2(fc)/6-31G*[b]				8.4[b]
RMP2(fu)/6-31G*	−309.736 08	−309.717 59	−309.761 50	12.2 (−13.5)
MP2(fc)[c]	−309.697 37	−309.678 77	−309.722 47	12.3 (−13.3)
MP3(fc)[c]	−309.752 03	−309.725 03	−309.776 18	17.5 (−12.7)
MP4SDQ	−309.767 03	−309.737 41	−309.789 79	19.2 (−11.8)
MP4SDTQ	−309.812 06	−309.789 09	−309.833 92	15.0 (−11.2)
Expt[d]				17.0

[a] RHF/6-31G* values, scaled by 0.89.[6] [b] Ref. 4 [RMP2(fc)/6-31G*//RHF/6-31G* + E_{zp}]. [c] RMP4sdtq/6-31G* using RMP2(fu)/6-31G* geometries. [d] Ref. 3. [e] The RHF/6-31G* total energies for cycloocta-1,3,5-triene in C_2, C_{2v} and C_s symmetry are −308.698 07, −308.676 63 and −308.695 54, respectively.



1, C_{2h}

2a, C_1

3a, C_2

2b, C_1

3b, C_2

Fig. 1 The RMP2(fc)/6-31G* geometries for octa-1,3,5,7-tetraene, **1**, the cyclization transition structure **3** and cycloocta-1,3,5-triene, **2** (RHF/6-31G* values in parentheses)

a terminal bond can be estimated. As the measured activation energy for **1**→**2** is only 17 kcal mol^{-1},[3] the energy of concert is about 20 kcal mol^{-1}. This is much larger than the energy of concert for many other electrocyclic processes, *e.g.*, Diels–Alder reactions.[10]

We have found that the transition structure for the concerted 1,7-H shift[5a] as well as for Diels–Alder reactions[5b] to be aromatic based on *geometric, energetic and magnetic* criteria. The magnetic susceptibility exaltation ($\Delta\chi_{tot}$), activation energies E_{calc} (E_{exp}) as well as the energy of concert (E_{con}) compared with the 1,7-H shift and Diels–Alder reactions are given in Table 2. Aromaticity was indicated by the computed (IGLO)[7] δ_H values (shielded and deshielded due to ring current effects) and by the magnetic susceptibility exaltation ($\Delta\chi_{tot}$).[5,12] The computed δ_H values for the 1,7-shift transition structure are very close to the benzene value for the equatorial hydrogens, and δ_H for the migrating H as well as for the axial terminal hydrogens are shifted upfield due to strong ring current effects.[5a] The behaviour of transition structure **3** is similar to those in the Diels–Alder reactions.[5b] As in the cycloaddition of ethylene to butadiene, we have explored the variation of the magnetic susceptibility (χ) along the **1**→**3**→**2** reaction coordinate (the C1–C8 distance). The geometries of discrete points along this reaction coordinate were optimized at the RMP2/6-31G* level, and for IGLO calculations were carried out using the standard DZ basis set (Fig. 2).

As shown in Fig. 2, the calculated magnetic susceptibility, as well as the energy profile, is a function of the reaction coordinate. The position of the maxima for the relative electronic energy (E_{rel}, $r = 2.55$ Å) and the magnetic susceptibility (χ, $r = 2.22$ Å) correspond roughly, although they do not coincide exactly. Both educt and product have similar χ values, much less than that found at the maximum.

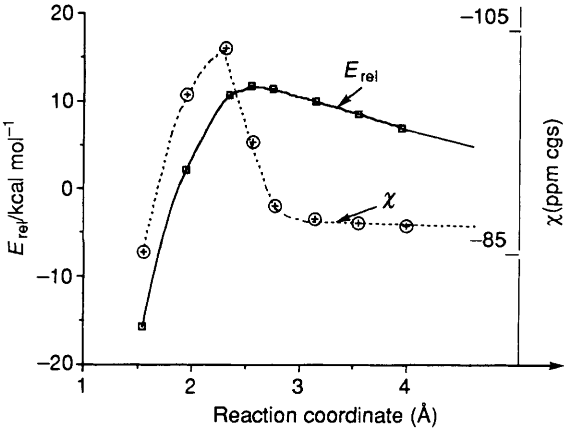


Fig. 2 Calculated relative electronic energies, E_{rel} (RMP2/6-31G*) and magnetic susceptibilities, χ (IGLO/DZ//RMP2/6-31G*) as a function of the reaction coordinate (the C1–C8 distance)

Table 2 Calculated magnetic susceptibility exaltation ($\Delta\chi_{tot}$, ppm cgs), activation energies E_{calc} (E_{exp}) and energy of concert (E_{con}/kcal mol^{-1}) for this cyclization reaction compared with the 1,7-H shift and Diels–Alder reactions

Reactions	$\Delta\chi_{tot}$	E_{calc} (E_{exp})	E_{con}
1,7-H shift[a]	−23.1	19.7 (20.8 ± 0.7)	*ca.* 60
Buta-1,3-diene + C_2H_4[b]	−19.3	22.4 (23.6)	5.7[c]
Cyclopentadiene + C_2H_4[b]	−17.7	17.5 (17.5)	13.7[c]
1→**3**[d]	−12.6	15.0 (17.0)	*ca.* 20

[a] Ref. 5(*a*) and references cited therein. [b] Ref. 5(*b*). [c] Ref. 10. [d] This work.

To refine these results, we reexamined the magnetic properties of the stationary points, *e.g.*, octa-1,3,5,7-tetraene, **1**, the cyclization transition structure **3** and cycloocta-1,3,5-triene, **2**, at a higher theoretical level (IGLO/BII′//RMP2/6-31G*). For **1**, the δ_{IGLO} computed for all Hs using the RMP2(fu)/6-31G* geometry are in the range 5.4–6.6. In the product **2**, the ^{1}H chemical shifts are quite normal (Table 3). In contrast, in the transition structure **3**, a dramatic change, indicating strong shielding ring current effects, is the shift to $\delta = -0.2$ of the two inner terminal hydrogens. These point toward the centre of the carbon spiral. The chemical shift difference of the terminal hydrogens at C1,8, H(inner) and H(outer), is 6.4 ppm. In the 1,7-H shift transition structure (using the correlated geometry), the upfield shifts are even larger and the corresponding δ_H(inner)–δ_H(outer) difference is 12 ppm.[5a] δ_H computed in **3** for H3,6, H4,5 and for the two terminal hydrogens (outer) at C1,8 (which point away from the centre of the eight-carbon skeleton), are shifted downfield towards the value calculated for benzene (7.2 ppm).

These chemical shift differences are not related to the hydrogen or carbon charges. All hydrogens in the transition structure (**3**) have nearly the same NPA charge (0.22–0.24), and differ only 0.01–0.02 from **1**. The C2–7 charges are 0.01–0.05 more negative in **3** than in **1**, whereas C1,8 are 0.04 more positive in the **3** than in **1**. These negligible charge differences contrast with the remarkable changes in the chemical shifts, **1**→**3**, especially for H1,8(inner) (Table 3).

The exaltation of magnetic susceptibility, attributed to the presence of a diamagnetic ring current,[5,12] applies well to transition structure **3** as a criterion of aromaticity. The calculated total magnetic susceptibility (including diamagnetic, paramagnetic and non-local contributions, ppm cgs) is −80.1 for **1** and −77.0 for **2**, but quite different, −92.7, for **3** [IGLO/BII′//RMP2(fu)/6-31G*]. The magnetic susceptibility exaltation ($\Delta\chi_{tot}$) of −12.6 for **3** may be compared with −23.1 for the 1,7-H shift transition structure,[5a] −19.3 and −17.7 for the Diels–Alder transition structures of ethylene with buta-1,3-diene and with cyclopentadiene[5b] as well as the value computed

Table 3 Calculated NPA (natural population analysis) charges [RHF/6-31G*//RMP2(fu)/6-31G*] and the ^{1}H chemical shifts at IGLO/BII′//RMP2(fu)/6-31G* (IGLO)/BII′//RHF/6-31G* values are given in parentheses) for (*Z*,*Z*)-octa-1,3,5,7-tetraene (**1**, C_{2h}), the cyclization transition structure (**3**, C_2) and cycloocta-1,3,5-triene (**2**, C_1)

	1, C_{2h}		**3**, C_2		**2**, C_1	
	NPA	δ_H	NPA	δ_H	NPA	δ_H
C1,8/H1,8	−0.39/0.21	5.6 (5.2)	−0.35/0.22	−0.2 (−5.8)	−0.45/0.23	1.4–2.1 (1.1–1.6)
	/0.22	5.4 (5.0)	/0.23	6.2 (6.8)	−0.46/0.23	
C2,7/H2,7	−0.24/0.22	6.6 (6.1)	−0.29/0.24	6.4 (6.7)	−0.18/0.22	5.9–6.3 (5.3–5.8)
C3,6/H3,6	−0.22/0.22	6.0 (5.5)	−0.23/0.23	6.5 (6.9)	−0.27, −0.25/0.22	5.3–5.9 (5.0–5.5)
C4,5/H4,5	−0.23/0.22	6.2 (5.7)	−0.25/0.23	6.6 (7.0)	−0.23/0.22	5.8–5.9 (5.4)

Table 4 Calculated magnetic susceptibility χ (diamagnetic, paramagnetic and non-local contributions), anisotropy σ_{anis} and the enhancement $\Delta\chi = \chi(\mathbf{3}) - \chi(\mathbf{1})$ (ppm, cgs)[a,b] for octa-1,3,5,7-tetraene (**1**), the cyclization transition structure (**3**) and cycloocta-1,3,5-triene (**2**)

	1, C_{2h}	**3**, C_2	**2**, C_1	$\Delta\chi = \chi(3) - \chi(1)$
χ_{anis}	−35.2 (−44.3)	−72.4 (−106.8)	−2.1 (−2.9)	−37.2 (−62.5)
χ_{dia}	−96.3 (−94.2)	−101.0 (−110.5)	−91.9 (−90.7)	−4.7 (−16.3)
χ_{para}	13.4 (+12.4)	+8.4 (+6.4)	+9.5 (+8.7)	−5.0 (−6.0)
χ_{nl}	2.8 (+2.8)	−0.1 (−3.3)	+5.4 (+5.0)	−2.9 (−6.1)
χ_{tot}	−80.1 (−79.0)	−92.7 (−107.4)	−77.0 (−76.8)	−12.6 (−28.4)

[a] IGLO/BII′//RMP2(fu)/6-31G*. [b] IGLO/BII′//RHF/6-31G*, *i.e.*, at Houk's *et al.* geometry for **3**,[4] given in parentheses.

for benzene (−13.4) (Table 2). The large magnetic anisotropy for **3** (much larger than for **1** and **2**) also indicates the aromaticity of **3**. (The magnetic susceptibilities, calculated at IGLO/BII′ using RHF/6-31G* geometry of Houk *et al.* for the transition structure are given in parentheses) (Table 4).

The eight-electron electrocyclic transition structure **3** fulfils the geometrical, energetic and magnetic criteria of aromaticity [albeit to a lesser extent than the 1,7-H shift transition structure in (*Z*,*Z*)-hepta-1,3,5-triene].[5a] On going from **1**→**3**, the double bonds lengthen and the single bonds shorten by *ca.* 0.02 Å. The changes are about three times larger in the 1,7-H shift transition structure, as is the energy of concert (*ca.* 60 kcal mol^{-1} for the latter, *vs. ca.* 20 kcal mol^{-1} for **3**). The 'ring current' downfield and especially the upfield δ_H shifts, although quite marked in **3**, are even larger in the 1,7-H shift transition structure, where the greater degree of twisting results in inner central location of the terminal hydrogens. Möbius aromaticity,[1] in Heilbronner's original sense,[1a] does exist, at least in transition structures.

Acknowledgements

This work was supported by the *Fonds der Deutschen Industrie*, by the *Deutsche Forschungsgemeinschaft* (DFG) and by the Convex Computer Corporation. We also thank Prof. Dr. W. Kutzelnigg and Dr. U. Fleischer (Bochum) for comments and helpful suggestions, and the Shanxi Normal University (China) for a scholarship (to H. J.).

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Paper 3/06293G
Received 21*st October* 1993
Accepted 10*th December* 1993