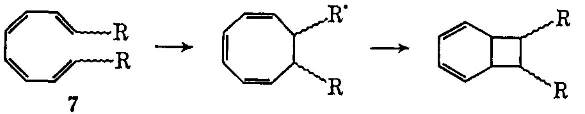
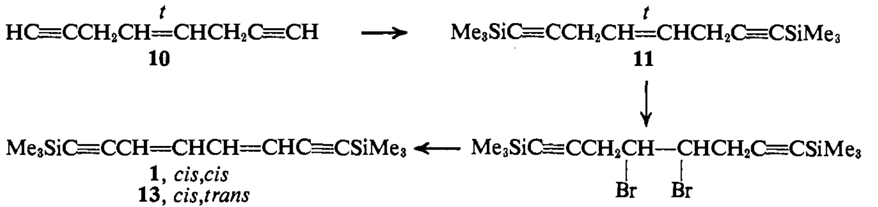
preparative experiment (1 hr), **5** (mp 74–75°)[5] was isolated in 85% yield.

That the conversion of **2** to **5** proceeds by way of benzocyclobutadiene (**4**) was shown by the observation that hydrolysis of **1** in ethanol with aqueous sodium hydroxide in the presence of an excess of cyclopentadiene (40 min, room temperature) gave ~60% of the known adduct **6**[6] (liquid; mass spectrum, molecular ion *m*/*e* 168). This adduct was characterized as the phenyl azide derivative (mp 131–132°; lit.[6] mp 132–133°).

The valence isomerization of **2** to **4** presumably involves cyclization to 1,2,4,5,7-cyclooctapentaene (**3**), followed by a second cyclization to **4** [rather than a direct (2 + 2) addition of the two acetylenes in **2**]. This process is formally related to the isomerization of *cis,cis*-1,3,5,7-octatetraene and its 1,8-disubstituted derivatives (**7**) to 1,3,5-cyclooctatrienes (**8**) and then to bicyclo[4.2.0]octa-2,4-dienes (**9**).[7]



7 **8** **9**



$HC{\equiv}CCH_2CH\overset{t}{=}CHCH_2C{\equiv}CH \longrightarrow Me_3SiC{\equiv}CCH_2CH\overset{t}{=}CHCH_2C{\equiv}CSiMe_3$

10 **11**

$Me_3SiC{\equiv}CCH{=}CHCH{=}CHC{\equiv}CSiMe_3 \longleftarrow Me_3SiC{\equiv}CCH_2\underset{Br}{CH}{-}\underset{Br}{CH}CH_2C{\equiv}CSiMe_3$

1, *cis,cis*
13, *cis,trans*
14, *trans,trans*

12

An indication that the interesting diallenic cyclic hydrocarbon **3** is indeed an intermediate in the transformation of **2** to **4** was obtained from hydrogenation experiments. Platinum oxide in ethanol and aqueous sodium hydroxide was reduced by stirring in hydrogen, a solution of **1** in ethanol was added, and the hydrogenation was continued until uptake ceased. Analysis by glpc showed that one of the components of the resulting complex mixture was cyclooctane (*ca.* 0.5% yield), identified with an authentic sample by the mass spectrum and glpc retention time. The cyclooctane was presumably derived from the intermediate **3**, but attempts to obtain more direct evidence for this substance (*e.g.*, by nmr and infrared spectroscopy) have not yet succeeded.

The starting material **1** was obtained as follows. Reaction of *trans*-4-octene-1,7-diyne (**10**)[8] in tetrahydrofuran with ethylmagnesium bromide (3 molar equiv) and then with chlorotrimethylsilane (3 molar equiv) gave the bis(trimethylsilyl) derivative **11** [bp 124–128° (6 mm)][9] in 77% yield. Treatment of **11** with bromine (1.25 molar equiv) in chloroform at 0° led to 63% of the dibromide **12** (mp 137.5–138°),[9] which was dehydrobrominated with 1,5-diazabicyclo[4.3.0]non-5-ene[10] (2.4 molar equiv) in ether at room temperature. Chromatography on silica gel and preparative glpc gave ~35% of the *cis,cis*-dienediyne **1** [mp 35–37°; λ_{max}^{EtOH} 292 nm (ϵ 28,700), 304 (39,500), and 320 (36,900); nmr spectrum ($CDCl_3$), 2 H double doublet (J = 8 and 2 Hz) at τ 3.09, 2 H doublet (J = 8 and 2 Hz) at 4.41, and 18 H singlet at 9.80],[9] ~35% of the *cis,trans* isomer **13** [liquid; λ_{max}^{EtOH} 291 nm (ϵ 32,100), 303 (46,000), and 319 (40,900); nmr spectrum ($CDCl_3$), 4 H complex multiplet at τ 2.72–4.51 and 18 H singlet at 9.80],[9] and ~15% of the *trans,trans* isomer **14** [mp 40–42°; λ_{max}^{EtOH} 290 nm (ϵ 37,300), 302 (58,100) and 318 (62,600); nmr spectrum ($CDCl_3$), 2 H double doublet (J = 12 and 3 Hz) at τ 3.34, 2 H double doublet (J = 12 and 3 Hz) at 4.28, and 18 H singlet at 9.80].[9] Hydrolysis of **13** and **14** in ethanol with aqueous sodium hydroxide led to the corresponding unprotected dienediynes. The last-mentioned substances (together with **5**) could also be obtained directly from **10** by bromination and subsequent dehydrobromination, but the bromination step in this case proceeded in only ~10% yield.

Acknowledgments. We are indebted to the Science Research Council for financial support, as well as to Drs. H. M. R. Hoffmann and P. J. Garratt for valuable discussions.

---

(5) The dimer **5** was identified with an authentic sample (mp 74–75°)[2] by mixture melting point determination and comparison of the infrared, ultraviolet, and mass spectra.

(6) C. D. Nenitzescu, M. Avram, and D. Dinu, *Chem. Ber.*, **90**, 2541 (1957); M. P. Cava and M. J. Mitchell, *J. Am. Chem. Soc.*, **81**, 5409 (1959).

(7) See R. Huisgen, A. Dahmen, and H. Huber, *ibid.*, **89**, 7130 (1967), and references cited there.

(8) Y. Gaoni, C. C. Leznoff, and F. Sondheimer, *ibid.*, **90**, 4940 (1968).

(9) The infrared, nmr, and mass spectra were in accord with the assigned structure.

(10) H. Oediger, H. J. Kabbe, F. Möller, and K. Eiter, *Chem. Ber.*, **99**, 2012 (1966).

(11) Author to whom inquiries should be addressed.

G. H. Mitchell, F. Sondheimer[11]
Chemistry Department, University College
London W.C.1, England

Received October 6, 1969

Cyclooctatetraene and Ions Derived from It[1]

Sir:

In view of the current interest in the [4*n*]annulenes, we wish to report some calculations for cyclooctatetraene (COT) and ions derived from it, using two different semiempirical SCF MO procedures that have been developed here and shown to give satisfactory results for a wide range of hydrocarbons. The first[2] of these is based on the Hückel σ,π approximation, the π electrons being calculated by a variant of the Pople method, while in the second, an improved version (MINDO/2[3a]) of the MINDO[3b] approximation, all the valence electrons are included in the SCF MO calculation. MINDO/2 differs from MINDO/1[3b] in the choice of parameters which allows it to give good estimates of bond lengths as well as heats of formation.

---

(1) This work was supported by the Air Force Office of Scientific Research through Grant No. AF-AFOSR-1050-67.

(2) M. J. S. Dewar and C. de Llano, *J. Am. Chem. Soc.*, **91**, 789 (1969).

(3) (a) M. J. S. Dewar and E. Haselbach, *ibid.*, in press; (b) N. C. Baird and M. J. S. Dewar, *J. Chem. Phys.*, **50**, 1262 (1969).

Table I. Comparison of Calculated and Observed Properties of Cyclooctatetraene

	Bond lengths, A		CCC angle, deg	Heat of formation, kcal/mol	Ionization potential, eV	
	C=C	C—C			Vertical[a]	Adiabatic[b]
Calcd	1.355	1.473	125.3	56.7	8.81	8.17
Obsd	1.340[c]	1.476[c]	126.1 ± 0.5[c]	69.5[d]		8.21[e]

[a] For formation of ion without change of geometry. [b] For formation of ion in its equilibrium state. [c] M. Traetteberg, *Acta Chem. Scand.*, **20,** 1724 (1966). [d] Calculated from the heat of combustion of H. D. Springall, T. R. White, and R. C. Cass, *Trans. Faraday Soc.*, **50,** 815 (1954), and heat of vaporization of D. W. Scott, M. E. Gross, G. D. Oliver, and H. M. Huffmann, *J. Am. Chem. Soc.*, **71,** 1634 (1949). [e] M. J. S. Dewar and S. D. Worley, unpublished results.

Table II. Cyclooctatetraene (COT) and Derived Ions

		MINDO/2				π Approximation			
		Alternating form		Symmetrical form		Alternating form		Symmetrical form	
Species	CCC angle, deg	Bond lengths[a]	ΔH_f[b]	Bond lengths[a]	ΔH_f[b]	Bond lengths[a]	ΔH_f[b]	Bond length[a]	ΔH_f[b]
COT^{2-} (planar)				1.418	128.8			1.422	149.1[d]
COT$^-$ (planar)		1.383; 1.442	44.3	1.413	47.9	1.378; 1.443	39.0[c]	1.412	43.1[d]
(nonplanar)	132.2	1.381; 1.442	47.1	1.413	47.1				
COT (planar)		1.355; 1.475	73.7	1.410	87.6	1.348; 1.477	55.8[c]	1.409	71.2[d]
(nonplanar)	125.3	1.355; 1.473	56.7	1.407	71.3				
COT$^+$ (planar)		1.381; 1.440	248.7	1.410	252.2	1.378; 1.443	236.2[c]	1.412	240.3[d]
(nonplanar)	129.9	1.379; 1.442	245.2	1.409	249.0				
COT^{2+} (planar)				1.414	538.0			1.422	543.4[c]

[a] In ångströms. [b] In kcal/mol at 25°. [c] Equilibrium geometry found by minimizing total energy. [d] Equilibrium geometry found by variable β procedure.[2]

Since the π approximation cannot be used for nonplanar systems, the properties of cyclooctatetraene itself had to be calculated by the MINDO/2 procedure; the results, shown in Table I, are in good agreement with experiment.

Table II shows several sets of calculations for COT and ions derived from it by addition or loss of electrons, for different assumed geometries: (a) planar geometries with alternating bond lengths; (b) planar geometries with equal bond lengths; (c) nonplanar ("tub") geometries with alternating bond lengths; (d) nonplanar geometries with equal bond lengths. In each case the bond lengths were chosen to minimize the energy of the molecule or ion, subject to its conforming to the assumed geometry. In the case of the doubly charged ions, only calculation b is reported since this corresponded to the state of minimum energy. The calculations for planar geometries were carried out by both MINDO/2 and the π approximation; those for nonplanar geometries only by MINDO/2.

Note that the monoions, COT$^+$ and COT$^-$, are predicted to be nonplanar, like COT itself, although the differences in energy from the planar forms are less for the ions and the departure from planarity and the alternation of bond lengths are also less. COT is unusual[4] in that its monoanion tends to disproportionate into (COT + COT^{2-}), a phenomenon which has been attributed to the dianion alone being planar; our calculations are clearly consistent with this. On the other hand we predict the process

$$2\text{COT}^- \longrightarrow \text{COT} + \text{COT}^{2-}$$

to be endothermic by 91.3 kcal/mol; presumably it occurs in solution only because the dianion has a much greater energy of solvation. It is interesting that the corresponding disproportionation of the naphthalene anion, $C_{10}H_{10}^-$, is predicted (by the π MO method[2]) to be much more endothermic (by 121.3 kcal/mol); here the monoanion is stable.

Anet and his collaborators[5] have studied ring inversion in COT, and also a process (bond shift) in which the single and double bonds are interchanged. The latter process was the slower, ring inversion taking place without bond shift; they attributed this to the ring inversion taking place through a planar form of COT in which the original alternation of single and double bonds is retained. The bond shift was attributed to a process involving a similar planar transition state of higher energy, with equal bond lengths.

The calculated difference in energy (17 kcal/mol) between the nonplanar and planar alternating structures for COT is indeed close to the observed free energies of activation (ΔF^*) reported[5,6] for ring inversion (12–15 kcal/mol); however the difference in ΔF^* between ring inversion and bond shift (2.4 kcal/mol) is much less than the calculated difference in energy between the alternating and symmetrical planar forms (MINDO/2, 13.9; π approximation, 15.4 kcal/mol). Since this quantity corresponds in our definition[2] to the (negative) resonance energy of COT, which should be comparable with the (positive) resonance energy of benzene (20.0 kcal/mol[2]), and since the π approximation gives reliable estimates of heats of formation for conjugated hydrocarbons, there seems little doubt that bond shift does not take place, as Anet suggested,[5] *via* the symmetrical planar structure as transition state.

Table III shows the variation in the calculated (MINDO/2) heat of formation of COT with bond angle, from the equilibrium value of 125.3° to that (135°) corresponding to planarity, for the alternating and symmetrical structures. It will be seen that the difference (ΔE) between them is almost independent of bond angle. This seems to suggest rather strongly that bond

---

(4) T. J. Katz, *J. Am. Chem. Soc.*, **82,** 3784, 3785 (1960).

(5) F. A. L. Anet, *ibid.*, **84,** 671 (1962); F. A. L. Anet, A. J. R. Bourn, and Y. S. Lin, *ibid.*, **86,** 3576 (1964).

(6) D. E. Gwynn, G. M. Whitesides, and J. D. Roberts, *ibid.*, **87,** 2862 (1965).

Table III. Energy of COT as a Function of Bond Angle

Bond angle, deg	Unsymmetrical structures Bond lengths, Å	ΔH_f, kcal/mol	Symmetrical structures Bond lengths, Å	ΔH_f, kcal/mol
135.0	1.355; 1.475	73.7	1.410	87.6
132.575	1.353; 1.471	66.1	1.408	79.6
130.15	1.353; 1.471	60.9	1.407	74.2
127.725	1.353; 1.471	57.8	1.407	71.3
125.3	1.355; 1.473	56.7	1.408	70.3

shift in fact takes place *via* a symmetrical nonplanar structure as transition state; the difference in energy between this and COT would then be ΔE, rather than ΔE *plus* the energy required to flatten the COT ring. The nonplanar transition state could indeed correspond to the "crown" structure considered earlier[7] as a possibility for COT itself.

---

(7) E. R. Lippincott, R. C. Lord, and R. S. McDonald, *J. Am. Chem. Soc.*, 73, 3370 (1951).

(8) Robert A. Welch Postdoctoral Fellow.

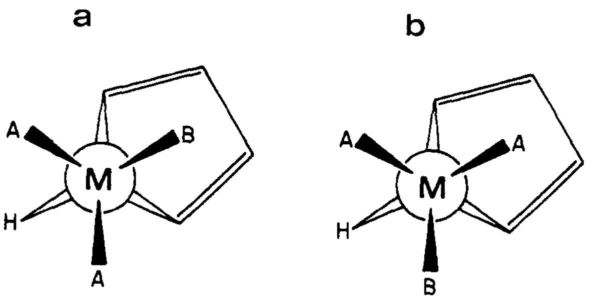
Michael J. S. Dewar, Alan Harget,[8] Edwin Haselbach[8]
Department of Chemistry, The University of Texas
Austin, Texas 78712

Received August 14, 1969

New Evidence for the 1,2-Shift Pathway in Fluxional *Monohapto*cyclopentadienylmetal Compounds[1]

Sir:

A pmr study of $(h^5\text{-}C_5H_5)Fe(CO)_2(h^1\text{-}C_5H_5)^2$ (**1**) showed conclusively that rearrangement of the $(h^1\text{-}(C_5H_5)$ ring occurs predominantly by 1,2 *or* 1,3 shifts as opposed to any process causing random site exchanges. On the available evidence 1,2 shifts were preferred. Further, but indirect, evidence[3] supported 1,2 shifts. Still, this fundamental point merits further attention.



1 M=Fe; A=CO; B=$\underline{h}^5$-C_5H_5
2 M=Ru; A=CO; B=$\underline{h}^5$-C_5H_5
3 M=Mo; A=C_5H_5; B=NO

We therefore report two studies which strengthen the case for 1,2 shifts.[4]

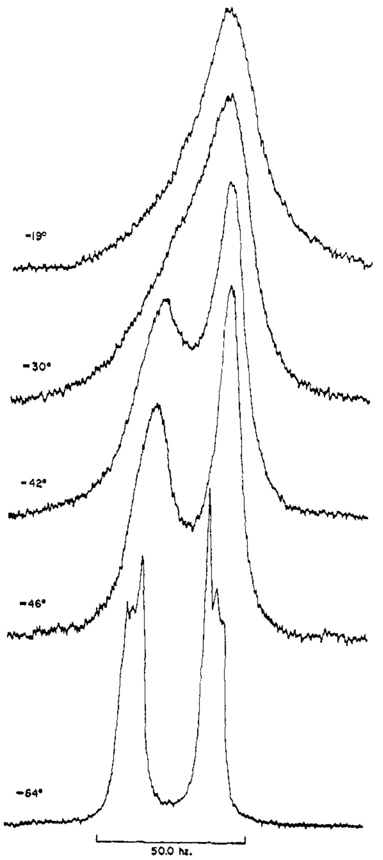


Figure 1. Spectra of the olefinic multiplet of $(h^5\text{-}C_5H_5)\text{-}Ru(CO)_2\text{-}(h^1\text{-}C_5H_5)$ recorded at several temperatures in 3:1 (v/v) CS_2–$C_6D_5CD_3$ at 100 MHz.

(1) $(h^5\text{-}C_5H_5)Ru(CO)_2(h^1\text{-}C_5H_5)$ (**2**) has been prepared.[5a] Pmr spectra of both **1** and **2** have been studied at low temperatures. Both show unsymmetrical collapse of the olefinic multiplet (Figure 1), with the low-field side collapsing more rapidly.[5b] As explained before, assignment of this part of the multiplet to H(2), H(2′) proves 1,2 shifts, while assigning it to H(3), H(3′) proves 1,3 shifts. Strong evidence for its assignment to H(2), H(2′) comes from the limiting low-temperature spectra, as shown in Figure 2 for **2**. The very similar limiting spectra of **1** and **2** are well reproduced by computer-simulated spectra, obtained after iterative refinement of coupling constants[6] to the values of Table I. These sets of J values, which the comparisons in Table I show to be very plausible, assume that the low-field part of each multiplet is due predominantly to H(2), H(2′). Because the H(1) resonance (a broadened triplet, well reproduced in the simulated spectra) is ~250 Hz upfield, the profile of the olefinic multiplet is negligibly altered by reversing the assignment and simultaneously the values of J_{12} and J_{13}. However, the values $|J_{12}| \approx 0$ and $|J_{13}| \approx 1.2$ are not acceptable.[7] Thus only the assignment leading to 1,2 shifts is acceptable.

---

(1) Stereochemically Nonrigid Organometallic Molecules. XXVI. Previous paper in this series: F. A. Cotton and T. J. Marks, *J. Organometal. Chem.*, **19**, 237 (1969). The present study was supported in part by the Petroleum Research Fund administered by the American Chemical Society, and the National Science Foundation under Grant No. 7034X.

(2) M. J. Bennett, F. A. Cotton, A. Davison, J. W. Faller, S. J. Lippard, and S. M. Morehouse, *J. Amer. Chem. Soc.*, **88**, 4371 (1966).

(3) F. A. Cotton, A. Musco, and G. Yagupsky, *ibid.*, **89**, 6136 (1967).

(4) 1,2 shifts may not predominate in *all* such molecules, as for example those with nontransitional or borderline metals.

(5) (a) Made in yields of 1–5% by treating $Ru(CO)_2Cl_2$ or $Ru(CO)_2I_2$ with NaC_5H_5 in 1,2-dimethoxyethane. *Anal.* Calcd for $C_{12}H_{10}O_2Ru$: C, 50.17; H, 3.52. Found: C, 50.2; H, 3.55. (b) For **1**, $E_a = 9.8 \pm 0.1$ kcal mol^{-1} and $\log A = 11.7 \pm 0.1$; for **2**, $E_a = 10.3 \pm 0.3$ kcal mol^{-1} and $\log A = 11.2 \pm 0.2$.

(6) NMRPLOT, a modified version of the computer program LAOCN3 by A. A. Bothner-By and S. M. Castellano, was kindly supplied by Professor G. M. Whitesides of this department.

(7) (a) H. Günther, *Z. Naturforsch*, **24b**, 680 (1969), shows that J_{13} varies from +1 to −1.8 Hz with dihedral angle, γ, being 0 for $\gamma \approx 60°$. (b) M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959); *J. Amer. Chem. Soc.*, **85**,