Table I. Parameters and g Values for the Present and Previous Models[a]

ref	6	5	4	7,1[c]	7,1[d]	8	present work
tetragonal splitting	−945	$D + E =$	−843.8	−2317	+600	−800	$D = -330$
rhombic splitting		+2400	+109.2	−745	−2690	+1600	$E = -2000$
spin–orbit coupling	−1050	+1050	+1000	−1000	−1000	+1000	$\xi = +690$
$\hat{H}_{\mathrm{el}}$[e]			$\epsilon_1 = 0.0$			$\epsilon_1 = 2870$	$\alpha = 10000$
			$\epsilon_2 = 2900$			$\epsilon_2 = 3250$	$J = -6400$
			$\epsilon_3 = 0.0$			$\epsilon_3 = 2120$	
g_x		1.334[b]	f	1.346[b]		1.36	1.36
g_y		2.779[b]		2.799[b]		2.81	2.85
g_z		2.489[b]		2.487[b]		2.50	2.45
coord system	single ion	symmetry-adapted single ion	dimer	symmetry-adapted single ion	dimer[d]	dimer	dimer

[a] All energies in cm^{-1}. [b] Experimental g values. [c] Original numbers used symmetry-adapted single-ion coordinates. [d] Translated into dimer coordinates to facilitate comparison with other treatments. Tetragonal and rhombic splittings muxt be in the same coordinate system for meaningful comparison. [e] ϵ_1, ϵ_2, and ϵ_3 are defined in ref 8 in terms of their symmetries; they are given approximately by $\epsilon_1 \simeq \langle x^2 - y^2{}_{\mathrm{L}}|\hat{H}_{\mathrm{el}}|x^2 - y^2{}_{\mathrm{R}}\rangle$, $\epsilon_2 \simeq \langle xz_{\mathrm{L}}|\hat{H}_{\mathrm{el}}|xz_{\mathrm{R}}\rangle$, and $\epsilon_3 \simeq \langle yz_{\mathrm{L}}|\hat{H}_{\mathrm{el}}|yz_{\mathrm{R}}\rangle$. Note that previous treatments postulate direct coupling between metal d orbitals on the left- and right-hand ions; the bridge is not explicitly included. [f] Fitted g values not reported.

Table II. Optical Absorption (OA) and MCD Transitions[a]

predicted			observed[16,2a,17]		
energy, cm^{-1}	polarization	assignment	energy, cm^{-1}	polarization	assignment
5700	z	bonding → nonbonding or “IT”	6500, m	z	IT, OA
15000	z	nonbonding → antibonding	18200, m		$t_{2g} \rightarrow \pi^*$, OA
16000, w	z	$4d_{x^2-y^2}$ → antibonding, s			
17000, w	z	$4d_{yz}$ → antibonding, s			
16000	x	$4d_{x^2-y^2}$ → antibonding, l	17400		MCD
17000	x	$4d_{yz}$ → antibonding, l	20400		MCD
1500	$x + y$	$4d_{x^2-y^2}$ → nonbonding	~2000, br		MCD
2300	$x + y$	$4d_{yz}$ → nonbonding	~4000, br		MCD
b			12800		MCD, OA, w

[a] w = weak; s = a minor component; l = a major component; m = frequency maximum; br = broad. [b] Not predicted by our model. Might be attributed to doublet → quartet transition.[2a]

effects of delocalization. Delocalization of electron density onto ligands reduces the effective spin–orbit coupling by 20–30% for the 3d subshell.[14]

Of course there are approximations and sources of error in this calculation. Probably the most significant of these are the neglect of spin–spin exchange and the neglect of e$^-$–e$^-$ repulsion. The parameters obtained from the HFS–DVM calculation probably carry at least 10% error and nearly ±100% for the tetragonal splitting.

Even with these approximations, this model makes some very important points. We have shown how to incorporate essential features of the bridging ligand into the g-tensor problem. Although we have only one fit parameter, we have successfully calculated three components of the g tensor.

Our model may be used to predict energies of optical transitions, but with the parameters used here these predictions are only approximate. The EPR g tensor is a property of the electronic ground state. Because of electronic relaxation effects, the electronic parameters (α, J, D, and E) for the ground and for each excited state are different. We have used ground-state parameters here and this introduces errors into the transition energies calculated from differences between eigenvalues. These predicted transitions are given in Table II. We can indeed account for the observed optical absorption (OA) and MCD features,[16,2a,17] although our transition energies are too low by 15–20% (and only qualitative at very low energies).[18]

Because the strong through-bridge coupling causes the $|\mathrm{B}\rangle$ state to be shifted far (in energy) from the pure Ru 4d orbitals, the IT transition ($|\mathrm{B}\rangle \rightarrow |\mathrm{N}\rangle$) is not broadened by spin–orbit and low-site-symmetry effects. These effects lead to extra transitions, but not near the IT band.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. We thank the Arthur D. Little Foundation for an Arthur D. Little Fellowship awarded to Jaeju Ko. We are grateful to Professor P. N. Schatz for a copy of ref 8 prior to its publication.

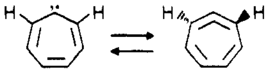
Triplet Ground-State Cycloheptatrienylidene

Robert J. McMahon[†] and Orville L. Chapman*

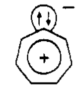
Department of Chemistry and Biochemistry
University of California—Los Angeles
Los Angeles, California 90024

Received June 24, 1985

The role of cycloheptatrienylidene (**1**) in the arylcarbene rearrangements remains unclear.[1] Early trapping studies suggested equilibration of **1** and **2**, although this is now in question.[2]



1 2



1a

1b

---

(14) McGlynn, S. P.; Vanquickenborne, L. G.; Kinoshita, M.; Carroll, D. G. *Introduction to Applied Quantum Chemistry*; Holt, Rinehart and Winston: New York, 1972; p 373.

(15) Ko, J.; Ondrechen, M. J. *Chem. Phys. Lett.* **1984**, *112*, 507–512.

(16) Creutz, C.; Taube, H. *J. Am. Chem. Soc.* **1969**, *91*, 3988–3989.

(17) Krausz, E. *Chem. Phys. Lett.* **1985**, *120*, 113–117.

(18) More accurate transition energies have been obtained from transition operator calculations.[11]

[†] National Science Foundation Graduate Fellow (1980–1983). IBM Corporation Graduate Fellow (1983–1984). UCLA Distinguished Scholar (1984–1985).

(1) (a) Jones, W. M.; Brinker, U. H. In *Pericyclic Reactions*; Marchand, A. P., Lehr, R. E., Eds.; Academic Press: New York, 1977; Vol. 1, Chapter 3. (b) Jones, W. M. In *Rearrangements in Ground and Excited States*; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. 1, Chapter 3. (c) Wentrup, C. In *Reactive Intermediates*; Abramovitch, R. A., Ed.; Plenum Press: New York, 1980; Vol. 1, Chapter 4. (d) Wentrup, C. *Reactive Molecules*; Wiley-Interscience: New York, 1984; Chapter 4.

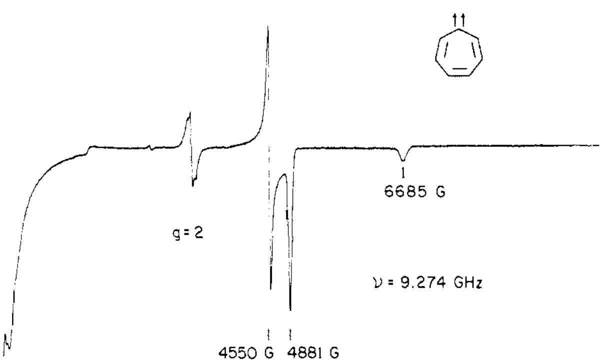
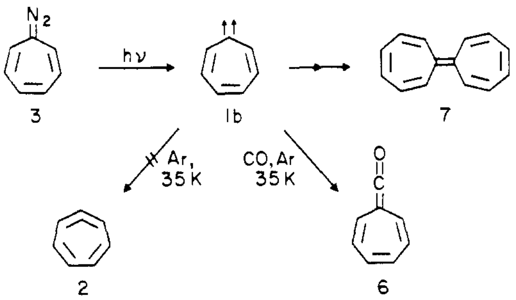


Figure 1. ESR spectrum of triplet cycloheptatrienylidene (**1b**) obtained upon irradiation (>574 nm, 90 min) of diazocycloheptatriene (**3**) matrix isolated in argon at 21 K.

Semiempirical[2b,3] and ab initio[4] calculations place singlet **1** (C_{2v}) 16–48 kcal/mol above singlet **2** (C_2). Waali's MNDO calculation predicts a triplet ground state for **1**.[3] The ab initio calculation places triplet **1b** 11 kcal/mol lower than singlet **1a**, but a 25 kcal/mol correction deemed necessary inverted these states.[4] Our work on the arylmethylene rearrangements led to the spectroscopic characterization of cycloheptatraene (**2**) and several of its derivatives but no evidence for **1** or its derivatives.[5,6] We report now the preparation and characterization of diazocycloheptatriene and cycloheptatrienylidene.

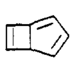
Thermolysis (55–75 °C, 0.1 torr) of the lithium salt of tropone tosylhydrazone (prepared with *n*-BuLi)[7] gives the deep reddish purple diazocycloheptatriene (**3**)[8,10] (IR, Ar, 10 K, 2048 vs, 1565 s, 1408 m, 1311 m, 1191 m, 1120 w, 1108 w, 940 m, 569 m cm^{-1}; UV λ_{max} 520 br, 337, 331, 329, 321, 319, 311, 304 nm) and a clear, colorless liquid when the pyrolysate is trapped in a dry-ice-cooled receiver. The clear liquid consists of isomeric *n*-butylcycloheptatrienes (GC–MS, IR). The *n*-butylcycloheptatrienes and diazocycloheptatriene have similar vapor pressures and thus codeposit in the argon matrix.[12] The *n*-butylcycloheptatrienes do not affect the photochemistry of the matrix-isolated diazocycloheptatriene.[13] Photolysis (550-W Hanovia, Pyrex) of the lithium salt (prepared with *n*-BuLi) in THF at room temperature gave heptafulvalene (**7**) with UV, ^{1}H NMR, and GC retention time identical with those of an authentic sample.[9]

Irradiation (>574 nm, 180 min) of diazocycloheptatriene (**3**) matrix isolated in argon at 21 K produces an intense triplet ESR signal ($|D/hc|$ = 0.317 cm^{-1}, $|E/hc|$ = 0.0087 cm^{-1}) (Figure 1). The Z_1 transition falls at essentially zero field as theory predicts for a triplet with $|D| \sim 0.3$ cm^{-1} at the X-band frequency.[14] This accounts for the drop in the base line at low field. Observation of the ESR signal of cycloheptatrienylidene implies the triplet state is either the ground state or within several calories per mole of the ground state.[15] Shorter wavelength irradiation (>406 nm, 77 min) results in the rapid, irreversible disappearance of the ESR signal, including the low-field Z_1 transition. The small $|D|$ value (0.317 cm^{-1}) accords well with expectation for cycloheptatrienylidene (**1b**) (cf. cyclopentadienylidene 0.409 cm^{-1}).[16]



In separate experiments, irradiation (>574 nm) of **3** matrix isolated in argon led to a decrease in the IR and UV absorptions of **3** and to the appearance of new IR (638 cm^{-1}) and UV (λ_{max} 530, 491, 469, 460, 307, 294, 282, 220 nm) absorptions due to cycloheptatrienylidene (**1b**).[19] Shorter wavelength irradiation (>514 nm) destroys cycloheptatrienylidene and gives rise to new absorptions (IR 1000, 903 cm^{-1}; UV λ_{max} 269, 258, 248, 240 nm) due to an unidentified product.[20] IR spectroscopy excludes cycloheptatetraene (**2**), phenylmethylene, fulvenallene, and the ethynylcyclopentadienes. Structures **4** and **5** are possibilities.


4


5

Irradiation of **3** in an argon matrix doped with carbon monoxide (0.24%) generates cycloheptatrienylidene (638 cm^{-1}) and a trace of a ketene (2103 cm^{-1}), which we presume is **6**. On warming to 35 K for 30 min, the 638-cm^{-1} band of cycloheptatrienylidene disappears with concomitant growth in the ketene absorption at 2013 cm^{-1}.

Cycloheptatrienylidene must be planar or nearly so. A tub-shaped conformation or any conformation that significantly reduces π-orbital overlap is inconsistent with the small $|D|$ value (0.317 cm^{-1}) and with the very long wavelength visible absorption (λ_{max} 530 nm). The triplet ground state of cycloheptatrienylidene necessitates a reevaluation of both qualitative arguments, which favored the aromatic, singlet carbene **1a**, and the calculations. Chemically, the most interesting observation is that triplet cycloheptatrienylidene (**1b**) does not convert to cycloheptatetraene (**2**) photochemically or thermally at temperatures up to 35 K.

Acknowledgment. The National Science Foundation provided financial support for this research (Grant CHE 8404949).

Supplementary Material Available: Experimental details of diazocycloheptatriene (**3**) preparation and visible spectra of diazocycloheptatriene (**3**) and cycloheptatrienylidene (**1b**) (3 pages). Ordering information is given on any current masthead page.

---

(2) For a critical discussion of this point, see: (a) Harris, J. W.; Jones, W. M. *J. Am. Chem. Soc.* **1982**, *104*, 7329–7330. (b) Balci, M.; Winchester, W. R.; Jones, W. M. *J. Org. Chem.* **1982**, *47*, 5180–5186.

(3) Kassaee, M. Z.; Nimlos, M. R.; Downie, K. E.; Waali, E. E. *Tetrahedron* **1985**, *41*, 1579–1586. Waali, E. E. *J. Am. Chem. Soc.* **1981**, *103*, 3604–3606. Dewar, M. J. S.; Landman, D. *J. Am. Chem. Soc.* **1977**, *99*, 6179–6182.

(4) Radom, L.; Schaefer, H. F.; Vincent, M. A. *Nouv. J. Chim.* **1980**, *4*, 411–415.

(5) West, P. R.; Chapman, O. L.; LeRoux, J.-P. *J. Am. Chem. Soc.* **1982**, *104*, 1779–1782.

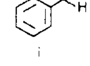
(6) Chapman, O. L.; McMahon, R. J.; West, P. R. *J. Am. Chem. Soc.* **1984**, *106*, 7973–79747.

(7) Experimental details of diazocycloheptatriene preparation are available as supplementary material.

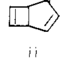
(8) Jones observed a trace of diazocompound upon thermolysis of tropone tosylhydrazone sodium salt (ref 9, footnotes 29 and 29a).

(9) Jones, W. M.; Ennis, C. L. *J. Am. Chem. Soc.* **1969**, *91*, 6391–6397.

(10) We specifically rule out the isomeric diazocompounds i and ii, based on comparison with the IR and UV spectra of the authentic materials and based on the subsequent photochemistry.[5,11]



i



ii

(11) Chapman, O. L.; Abelt, C. J. *J. Org. Chem.*, in press.

(12) Small amounts (ca. 2 mg) of pure **3** can be obtained by pumping away the slightly more volatile impurity at –29 °C. This material was used for the UV studies.

(13) IR spectroscopy shows the impurity to be photostable under the irradiation conditions used in the experiments (>416 nm).

(14) Wassermann, E.; Snyder, L. C.; Yager, W. A. *J. Chem. Phys.* **1964**, *41*, 1763–1772.

(15) Platz, M. S. In *Diradicals*; Borden, W. T., Ed.; Wiley: New York, 1982; p 208.

(16) In general, vinylmethylenes (including cyclopentadienylidene and cycloheptatrienylidene) are triplets.[17] The large bond angle in **1b** favors the triplet over the singlet.[18]

(17) Trozzolo, A. M.; Wasserman, E. In *Carbenes*; Moss, R. A., Jones, M., Eds.; R. E. Kreiger: Malabar, FL, 1983; Vol. 2, Chapter 5.

(18) Lapin, S. C.; Brauer, B. E.; Schuster, G. B. *J. Am. Chem. Soc.* **1984**, *106*, 2092–2100.

(19) The best model for the UV/visible spectrum of **1b** is cycloheptatrienyl. Unfortunately, its spectrum is not known.

(20) Short-wavelength irradiation (>200 nm) of the unidentified product does not generate a detectable concentration of phenylmethylene (ESR).