

# $\alpha,3$ -Didehydro-5-methyl-6-hydroxytoluene: Matrix Isolation of a Diradical Related to the Neocarzinostatin Chromophore

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**Abstract:** UV photolysis of 2,6-dimethylcyclohexa-2,5-dien-1-on-4-ylidene (**4**), matrix isolated in argon at 10 K, results in the formation of a labile species which is characterized as  $\alpha,3$ -didehydro-5-methyl-6-hydroxybenzene (**5**) by comparison of the experimental IR spectrum with calculations at the ROSS-BLYP/6-31G(d,p) level of theory. This assignment is confirmed by isotopic labeling and by investigating the subsequent photochemistry of **5**, which leads to 3-hydroxy-4-methylhepta-1,2,4-trien-6-yne (**6**). The ring opening of diradical **5** to eneyne–allene **6** corresponds to the reversion of a Myers cyclization.

## Introduction

In 1988 Myers and Proteau<sup>1</sup> presented evidence that the neocarzinostatin chromophore produces a highly reactive diradical upon reaction with methyl thioglycolate even at  $-38$  °C. The formation of diradicals of type  $\alpha,3$ -dehydrotoluene **1** by cyclization of eneyne–allene **2** is believed to be the key step in the in vivo action of neocarzinostatin.<sup>2,3</sup> Despite the current interest in the Myers cycloaromatization reaction to yield derivatives of **1**, no isolation and direct spectroscopic characterization of a derivative of **1** has been reported.



Recently, Squires and co-workers were able to generate **1** in the gas phase and determine the heat of formation using collision-induced dissociation threshold measurements.<sup>4,5</sup> The diradical was found to be a ground-state singlet with the triplet being 3 kcal/mol higher in energy. In another gas-phase study, Chen and co-workers<sup>6</sup> were able to determine the photoelectron spectrum of **1** and to estimate the singlet state to be ca. 5 kcal/mol more stable than the triplet state. Here we report on the matrix isolation, IR spectroscopic characterization, and photochemical ring opening of a derivative of **1** starting from 4-diazo-2,6-dimethyl-cyclohexa-2,5-dienone (**3**) as a precursor.

(1) Myers, A. G.; Proteau, P. J. *J. Am. Chem. Soc.* **1989**, *111*, 1146–1147.

(2) Myers, A. G.; Dragovich, P. S.; Kuo, E. Y. *J. Am. Chem. Soc.* **1992**, *114*, 9369–86.

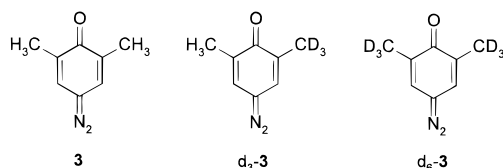
(3) Myers, A. G.; Parrish, C. A. *Bioconjugate Chem.* **1996**, *7*, 322–331.

(4) Wenthold, P. G.; Wierschke, S. G.; Nash, J. J.; Squires, R. R. *J. Am. Chem. Soc.* **1993**, *115*, 12611–12612.

(5) Wenthold, P. G.; Wierschke, S. G.; Nash, J. J.; Squires, R. R. *J. Am. Chem. Soc.* **1994**, *116*, 7378–7392.

(6) Logan, C. F.; Ma, J. C.; Chen, P. *J. Am. Chem. Soc.* **1994**, *116*, 2137–2138.

(7) Ried, W.; Dietrich, R. *Chem. Ber.* **1961**, *94*, 387–391.



## Results and Discussion

Visible light irradiation ( $\lambda > 475$  nm) of quinone diazide **3**,<sup>7</sup> matrix isolated in argon at 10 K, quantitatively produces 2,6-dimethylcyclohexa-2,5-dien-1-on-4-ylidene (**4**) with the carbonyl stretching vibration at  $1518$   $\text{cm}^{-1}$ . The spectroscopic characterization of **3** and **4** as well as the trapping of **4** by molecular oxygen was described earlier.<sup>8,9</sup> In contrast to most other 4-oxocyclohexadienylidenes, which on irradiation with  $\lambda > 470$  nm rearrange to highly strained 1,3-bridged cyclopropenes,<sup>8,10–12</sup> carbene **4** is completely stable toward visible light irradiation. However, several hours of UV irradiation ( $\lambda > 360$  nm, argon 10 K) of **4** results in the formation of at least three products A–C with characteristic IR absorptions.

The highest stationary concentration of the primary product A is obtained after 120 min of irradiation. A very intense IR absorption at  $3635$   $\text{cm}^{-1}$  indicates a phenolic OH stretching vibration (matrix-isolated phenol,  $3634$   $\text{cm}^{-1}$ ; cresol,  $3638$   $\text{cm}^{-1}$ <sup>13</sup>). If **4-d<sub>6</sub>** is irradiated, this vibration is red-shifted to  $2684$   $\text{cm}^{-1}$ , which clearly confirms the assignment of a hydroxyl group and also reveals that it is formed via H-abstraction from one of the *o*-methyl groups. A medium intensity absorption of compound A is found at  $1173$   $\text{cm}^{-1}$ ; the other vibrations of A are of low intensity. The yield of A is much smaller if **4-d<sub>6</sub>** is irradiated, and irradiation of **4-d<sub>3</sub>** preferentially results in the formation of OH and not OD, which indicates a substantial

(8) Bucher, G.; Sander, W. *Chem. Ber.* **1992**, *125*, 1851–9.

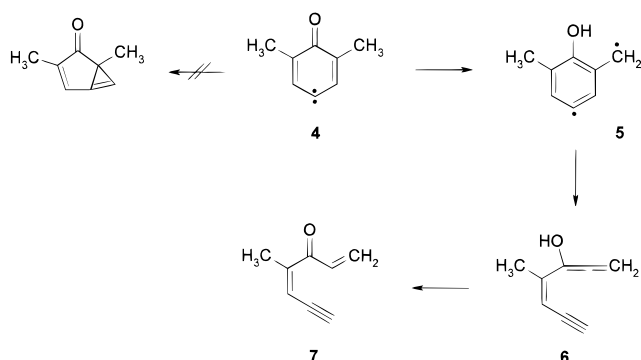
(9) Sander, W.; Bucher, G.; Komnick, P.; Morawietz, J.; Bubenitschek, P.; Jones, P. G.; Chrapkowski, A. *Chem. Ber.* **1993**, *126*, 2101–9.

(10) Sander, W.; Kirschfeld, A., Halton, B., Eds.; JAI Press: London, 1995; Vol. 4, Chapter 2; pp 1–80.

(11) Sander, W.; Bucher, G.; Reichel, F.; Cremer, D. *J. Am. Chem. Soc.* **1991**, *113*, 5311–22.

(12) Bucher, G.; Sander, W. *J. Org. Chem.* **1992**, *57*, 1346–51.

## Scheme 1



kinetic isotope effect. However, the yield of A formed from **4-d<sub>3</sub>** via the deuterium shift is too low to clearly assign IR absorptions other than the OD stretching vibration to this isotopomer, and therefore, the isotope effect could not be quantified. The opening of the benzene ring should result in highly unsaturated molecules with characteristic IR absorptions such as alkene, allene, or alkyne CC stretching vibrations. Since no IR absorptions are observed in the 1700–2000 cm<sup>-1</sup> range, it is reasonable to assume that the benzene ring in A is still intact, and we thus assign A the structure of  $\alpha,3$ -didehydro-5-methyl-6-hydroxybenzene (**5**, Scheme 1).

We carried out density functional theory (DFT) calculations for several C<sub>8</sub>H<sub>8</sub>O isomers to verify the assignment made for compound A. While carbene **4** (triplet state), hydroxyallene **6**, and vinyl ketone **7** are well described with standard DFT using the B3LYP energy functional<sup>14–17</sup> and a 6–31G(d,p) basis,<sup>18</sup> the investigation of diradical **5** cannot be carried out at the single-determinant DFT level. Therefore, **5** has been treated with the recently developed restricted-open-shell singlet DFT (ROSS-DFT) approach, which will be described in more detail in the Experimental Section.

The ROSS-BLYP geometry of **5** (Figure 1a) is similar to the MCSCF3-21G geometry of **1<sup>5</sup>** and suggests that the CC bonds adjacent to the radical centers are slightly shortened, which is in line with the spin polarization pattern shown in Figure 1b. In Table 1, calculated ROSS-BLYP/6-31G(d,p) vibrational frequencies, relative intensities, and calculated isotope shifts are compared with the available experimental data. Each vibrational mode was characterized on the basis of an adiabatic analysis (see Table 1).<sup>22</sup> The adiabatic stretching frequencies are included into Figure 1a and confirm the variation in the CC bond as indicated in Figure 1b.

Comparison of calculated and experimental spectra provides further proof for the existence of **5**. The weak IR bands at 1249

(band 28), 1239 (band 26), 1087 (band 24), 925 (band 20), 809 (band 19), and 744 (band 18) do not appear in the spectrum of the open form **6** (see Table 2) since all of these bands are typical of an intact ring structure with an exocyclic methylene group (CCH<sub>2</sub> stretch, HC<sub>ring</sub> bend, ring stretch, etc., Table 1). In turn, the easily identified asymmetric allene stretching vibration of **6** (1947 cm<sup>-1</sup>, band 36, Table 2) is missing in the spectrum of compound A, thus confirming that A does not possess an acyclic structure with an allene group. On the other hand, those vibrational modes which are normally considered as being typical of phenol derivatives (phenol: OH stretching at 3637 cm<sup>-1</sup>, HOC bending at 1176 cm<sup>-1</sup>, OH torsion at 309 cm<sup>-1</sup>;<sup>23</sup> see also ref 24) appear in the infrared spectrum of both **5** and **6**: OH stretch, 3635/3670 cm<sup>-1</sup> (expt/calcd); HOC bend, 1173/1169 cm<sup>-1</sup>; OH torsion, 318 cm<sup>-1</sup> cal. (**5**, Table 1); OH stretch, 3637/3661 cm<sup>-1</sup>; HOC bend, 1175/1151 cm<sup>-1</sup>; OH torsion, 366 cm<sup>-1</sup> cal. (**6**, Table 2). Other intensive phenol ring vibrations (1412 (band 32), 1546 cm<sup>-1</sup> (band 37), Table 1), which according to ROSS-BLYP results could be used to identify **5**, coincide with bands of **4** and, therefore, cannot be seen in the difference spectrum.

The second photoproduct B builds up on prolonged irradiation (6–12 h) of **5** with  $\lambda > 360$  nm and was identified as 3-hydroxy-4-methylhepta-1,2,4-trien-6-yne (**6**) (Scheme 1). Hydroxyallene **6** exhibits several characteristic IR absorptions: OH stretch, 3638 (band 45); alkyne CH stretch, 3333 (band 44); asymmetric allene stretch, 1947 cm<sup>-1</sup> (band 36, see Table 2). On deuteration (starting from **4-d<sub>6</sub>**) band 44 is not affected, revealing that the alkyne group is not deuterated, while band 36 is red-shifted by 20 cm<sup>-1</sup>. The asymmetrical CCC stretching vibration of allene at 1957 cm<sup>-1</sup> is shifted by 17 cm<sup>-1</sup> in H<sub>2</sub>CCCD<sub>2</sub>,<sup>25</sup> and thus, the observed shift of 20 cm<sup>-1</sup> in B is in accordance with a doubly deuterated terminal allene group. The hydroxyl function is also deuterated and  $\nu_{OD}$  of band 45 shifted to 2685 cm<sup>-1</sup>. The IR spectrum of **6** as well as that of **6-d<sub>6</sub>** is nicely reproduced by B3LYP/6-31G(d,p) calculations (Table 2, Figure 2).

The isotopic substitution pattern in **6-d<sub>6</sub>** confirms the mechanism outlined in Scheme 1. The primary step is the transfer of one methyl-hydrogen atom of triplet carbene **4** to the carbonyl oxygen atom to give diradical **5**. Photochemical excitation is required, however, it is not clear if the hydrogen transfer occurs on an excited triplet surface or if this is rather a hot (triplet) ground-state reaction.

Recently we described the photochemistry of *p*-benzoquinone diazide carboxylic acids as a route to 2,4-didehydrophenols.<sup>26</sup> Thus, irradiation of 4-diazocyclohexa-2,5-diene-1-one-2-carboxylic acid with  $\lambda = 435$  nm cleanly yields 2,5-cyclohexadiene-1-one-2-carboxylic acid-4-ylidene (**8**), which on 600–700-nm irradiation eliminates CO<sub>2</sub> and simultaneously transfers the hydrogen atom of the carboxylic acid group to the carbonyl oxygen atom. In contrast, the H-transfer in **4** to give diradical **5** requires UV irradiation. This difference in reactivity results from the short nonbonding O–H distance of only 1.73 Å in **8** (calculated at the B3LYP/6-31G(d) level of theory) compared to 2.79 Å in the lowest energy conformation (C<sub>2v</sub> symmetry) of **4** (Figure 3).

Photochemical ring cleavage of diradical **5** (Myers cycloreversion) results in the formation of **6**. Since the methylene

(13) Gebicki, J.; Krantz, A. *J. Chem. Soc., Perkin Trans. 2* **1984**, 1617–1621.

(14) Becke, A. *J. Chem. Phys.* **1993**, *98*, 5648–5652.

(15) Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J. *J. Phys. Chem.* **1993**, *98*, 11623.

(16) Becke, A. D. *Phys. Rev. A: Gen. Phys.* **1988**, *38*, 3098–3100.

(17) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B: Condens. Matter* **1988**, *37*, 785–789.

(18) Hariharan, P. C.; Pople, J. A. *Chem. Phys. Lett.* **1972**, *66*, 217.

(19) Miehlich, B.; Stoll, H.; Savin, A. *Mol. Phys.* **1997**, *91*, 527–536.

(20) Andrews, J. S.; Murray, C. W.; Handy, N. C. *Chem. Phys. Lett.* **1993**, *201*, 458–464.

(21) Gräfenstein, J.; Kraka, E.; Cremer, D. *Chem. Phys. Lett.*, in press.

(22) (a) Konkoli, Z.; Cremer, D. *Int. J. Quantum Chem.* **1998**, *67*, 1–10.

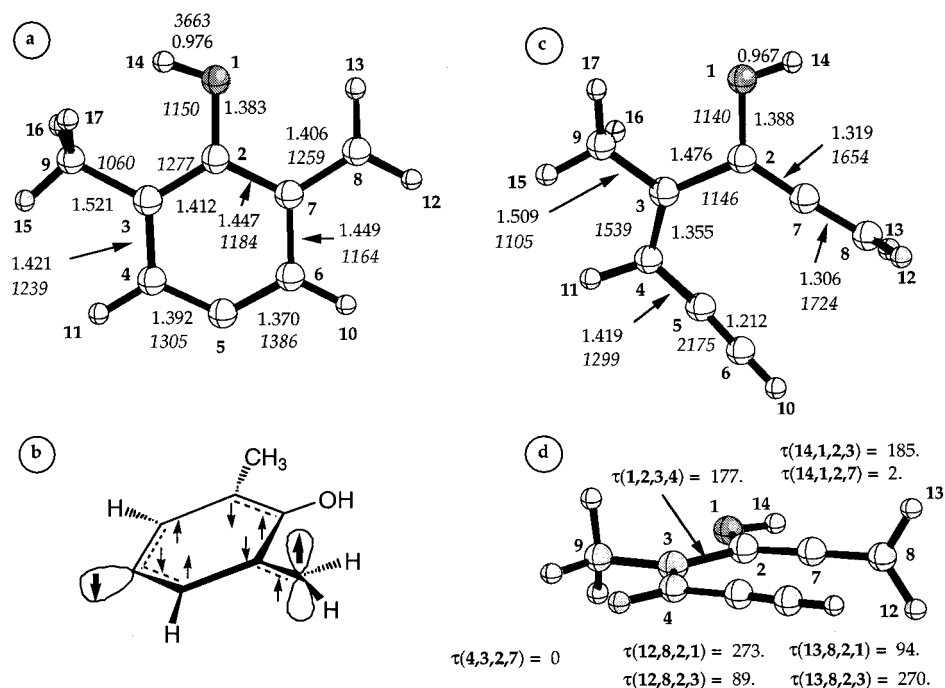
(b) Konkoli, Z.; Larsson, J. A.; Cremer, D. *Int. J. Quantum Chem.* **1998**, *67*, 11–28. (c) Konkoli, Z.; Cremer, D. *Int. J. Quantum Chem.* **1998**, *67*, 29–40. (d) Konkoli, Z.; Larsson, J. A.; Cremer, D. *Int. J. Quantum Chem.* **1998**, *67*, 41–55. (e) Cremer, D.; Larsson, J. A.; Kraka, E. In *Theoretical and Computational Chemistry, Vol. 5, Theoretical Organic Chemistry*; Parkanyi, C., Ed.; Elsevier: Amsterdam, 1998; pp 259–327.

(23) Michalska, D.; Bienko, D. C.; Abkowicz-Bienko, A. J.; Latajka, Z. *J. Phys. Chem.* **1996**, *100*, 17786–17790.

(24) Kraka, E.; Cremer, D.; Bucher, G.; Wandel, H.; Sander, W. *Chem. Phys. Lett.* **1997**, *268*, 313–320.

(25) Eaton, D. R.; Thompson, H. *Proc. R. Soc. A* **1959**, *250*, 39.

(26) Bucher, G.; Sander, W.; Kraka, E.; Cremer, D. *Angew. Chem.* **1992**, *104*, 1225–1228; *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1230–1233.



**Figure 1.** Calculated geometries and adiabatic frequencies of biradical **5** (a, ROSS-BLYP/6-31G(d,p)) and **6** (c and d, B3LYP/6-31G(d,p)). Bond lengths are in Å, and angles are in deg (all normal print). Adiabatic stretching frequencies are in cm<sup>-1</sup> (italics). Dihedral angles  $\tau$  are given for **6** to show its degree of planarity. The oxygen atom is denoted by a gray ball. (b) Spin polarization pattern of **5**. The spin of the single electrons are indicated by thick arrows. Thin arrows give the spin polarization pattern according to the intraatomic Hund rule (see text).

group of **5** is transformed into the terminal methylene group of the allene moiety in **6**, this group is dideuterated in **6-d<sub>6</sub>**. The DFT calculations confirm that **6** is formed in the *s-Z* conformation (Scheme 1) with a distortion of the butadiene unit from planarity by 34° and with the OH bond being located syn to the allene C=C bond (Figure 1d).

Irradiation of **6** at slightly shorter wavelengths (1 h with  $\lambda > 350$ ) results in the formation of a complex mixture of products. Some of these products might be conformers or stereoisomers of **6**. One of the final photoproducts C exhibits a strong carbonyl absorption at 1724.8 cm<sup>-1</sup>. Other vibrations are found at 1445.6 and 1324.3 cm<sup>-1</sup>. Due to the low intensities of the other IR absorptions, product C was not further characterized. However, it is reasonable to assume that a photochemically induced 1,3-H shift to vinyl ketone **7** takes place, which according to B3LYP/6-31G(d,p) calculations is 24.0 kcal/mol more stable than **6**. A similar rearrangement was described for hydroxyallene, which at -50 °C thermally rearranges to acrolein.<sup>27</sup>

In summary, diradical **5** is the first derivative of a  $\alpha,3$ -dehydrotoluene that has been isolated and characterized by IR spectroscopy. UV irradiation of **5** results in the Myers cycloreversion to give allene **6**. The scope of this reaction is currently being investigated in our laboratory.

## Experimental Section

The NMR spectra were recorded with a Bruker AM-400 spectrometer; chemical shifts are reported in  $\delta$  relative to TMS unless otherwise indicated. Gas chromatography (GC) was performed by the use of a

Siemens Sichromat equipped with glass capillary columns (29.5 m, OVI, 140 °C). Deuterated compounds were obtained from Deutero GmbH (deuterium oxide, isotopic purity 99.9%) and Acros Chimica (methyl iodide 99+ atom % D). 2-Chloro-6-methylphenol was obtained from Aldrich and used without further purification.

**4-Diazo-2,6-dimethyl-1-oxo-2,5-cyclohexadiene (3).** The synthesis of **3** was carried out according to a procedure described by Ried and Dietrich.<sup>7</sup> Purification of the product was accomplished by column chromatography (basic alumina, dichloromethane).

**4-Diazo-2-methyl-6-(trideuteriomethyl)-1-oxo-2,5-cyclohexadiene (3-d<sub>3</sub>).** 2-Chloro-6-methylphenol was methylated with dimethyl sulfate in aqueous sodium hydroxide.<sup>32</sup> The phenyl methyl ether was added to a suspension of lithium in diethyl ether. After heating for 2 h, the solution was cooled; a solution of CD<sub>3</sub>I (Aldrich; 99.5% atom % D) in diethyl ether was added dropwise, and the mixture was heated for 2 h. Water and diluted hydrochloric acid were added, and the reaction mixture was extracted with ether. After drying with MgSO<sub>4</sub>, the solvent was removed and the crude 2-methyl-6-(trideuteriomethyl)-phenyl methyl ether used for the next step without further purification. The phenyl methyl ether was refluxed in 48% HBr/acetic acid until complete ether cleavage (GC analysis). Purification of the product was accomplished by dissolving the phenol in diluted sodium hydroxide solution and extraction of the aqueous phase with ether; acidifying the aqueous phase with diluted hydrochloric acid and extraction with ether yielded the 2,6-dimethylphenol isotopomer in good purity. The phenol was azo-coupled with phenyldiazonium chloride<sup>33</sup> and the azo compound subsequently reduced with sodium dithionite<sup>34</sup> to the corresponding amine.

The amine was dissolved in cold HCl-saturated ethanol and treated with isoamyl nitrite. After stirring for 1 h, the diazonium chloride was quantitatively precipitated by addition of diethyl ether to the reaction mixture. The salt was dissolved in ethanol, cooled, and treated with ammonia-saturated ethanol; the color of the reaction mixture changed rapidly from colorless to orange, and after removal of the solvent, the crude **3-d<sub>3</sub>** was purified by column chromatography (basic alumina,

(27) Hakiki, A.; Ripoll, J. L.; Thuillier, A. *Bull. Soc. Chim. Fr.* **1985**, 911–920.

(28) Mullholland, T. P. C. *J. Chem. Soc.* **1965**, 4939–4953.

(29) Namura, E.; Taniguchi, H.; Otsuji, Y. *Bull. Chem. Soc. Jpn.* **1993**, 66, 3797–3801.

(30) Hakiki, A.; Ripoll, J. L.; Thuillier, A. *Bull. Soc. Chim. Fr.* **1985**, 911–920.

(31) Jackman, L. M.; Petrei, M. M.; Smith, B. D. *J. Am. Chem. Soc.* **1991**, 113, 3451–3458.

(32) Mullholland, T. P. C. *J. Chem. Soc.* **1965**, 4939–4953.

(33) Namura, E.; Taniguchi, H.; Otsuji, Y. *Bull. Chem. Soc. Jpn.* **1993**, 66, 3797–3801.

(34) Smith, I. *J. Am. Chem. Soc.* **1941**, 63, 1036–1040.

**Table 1.** Measured and Calculated Vibrational Frequencies  $\omega$  and Infrared Intensities  $I$  of  $\alpha,3$ -Didehydro-5-methyl-6-hydroxytoluene (**5**)

band no. <sup>a</sup>	sym	exptl		ROSS-BLYP/6-31G(d,p)				assignment <sup>e</sup>
		$\omega$ (cm <sup>-1</sup> )	$I_{\text{rel}}^b$	$\omega$ (cm <sup>-1</sup> )	$I_{\text{rel}}^b$	$\omega_i/\omega^c$	$\omega_i/\omega^d$	
45	a'	3635	100	3670	36	0.728	0.728	OH stretch
44	a'			3204	4	1.000	0.745	CH <sub>2</sub> stretch
43	a'			3105	7	1.0	0.726	CH <sub>2</sub> stretch
42	a'			3098	7	1.0	1.000	HC <sub>ring</sub> stretch
41	a'			3096	5	1.0	1.000	HC <sub>ring</sub> stretch
40	a'			3051	9	1.0	0.738	CH <sub>3</sub> stretch
39	a''			2976	22	1.0	0.740	CH <sub>3</sub> stretch
38	a'			2934	31	1.0	0.720	CH <sub>3</sub> stretch
37	a'			1546	13	0.996	0.994	CC stretch, ring
36	a'			1493	3	0.997	0.985	CH <sub>3</sub> bend; ring stretch
35	a'			1471	4	0.999	0.958	CH <sub>2</sub> bend; CCH <sub>2</sub> stretch
34	a''			1465	5	0.999	0.720	CH <sub>3</sub> bend
33	a'			1461	6	1.0	0.949	CH <sub>3</sub> bend; ring stretch
32	a'			1412	69	0.999	0.915	ring stretch; CO stretch
31	a'			1402	1	0.998	0.910	ring stretch; HOC bend; HC <sub>ring</sub> bend
30	a'	1375	1	1378	4	0.998	0.887	CH <sub>3</sub> bend
29	a'			1302	7	0.991	0.916	ring stretch; HOC bend
28	a'	1249	5	1259	15	0.998	0.887	CCH <sub>2</sub> stretch
27	a'			1253	14	0.958	0.855	HOC bend; HC <sub>ring</sub> bend; ring stretch
26	a'	1239	6	1224	25	1.0	0.866	HC <sub>ring</sub> bend; CO stretch
25	a'	1173	39	1169	100	0.743	0.731	HOC bend; CO stretch
24	a'	1087	2	1078	11	0.994	0.969	ring stretch; HC <sub>ring</sub> bend
23	a''			1024	1	1.000	0.832	HCC <sub>Me</sub> bend
22	a'	1020	4	1018	13	1.053	0.967	HCC <sub>Me</sub> bend; C <sub>Me</sub> C stretch
21	a'			956	3	1.009	0.885	CH <sub>2</sub> bend; HCC <sub>Me</sub> bend
20	a'	925	8	917	11	1.029	0.824	ring stretch; C <sub>Me</sub> C stretch
19	a''	809	7	821	6	1.000	0.995	HC <sub>ring</sub> oop
18	a'	744	1	784	8	0.988	0.935	ring bend; CO stretch
17	a''	708	2	779	19	1.000	0.984	HC <sub>ring</sub> oop
16	a''			719	6	0.999	0.965	H <sub>2</sub> C oop; ring torsion
15	a''			679	25	1.000	0.836	O oop; ring torsion
14	a'			666	0	0.945	0.944	ring stretch; CO stretch
13	a''			536	1	1.000	0.957	ring torsion; H <sub>2</sub> C oop
12	a'			528	3	0.987	0.958	ring bend; OC <sub>ring</sub> bend
11	a''			522	1	0.998	0.917	ring torsion; C <sub>Me</sub> and CH <sub>2</sub> oop
10	a'			485	0	0.990	0.956	ring bend; OC <sub>ring</sub> bend
9	a''			472	0	1.000	0.760	ring torsion; C <sub>Me</sub> and OC <sub>ring</sub> oop
8	a'			471	2	0.989	0.925	H <sub>2</sub> CC <sub>ring</sub> bend; ring bend
7	a'			330	3	0.976	0.903	H <sub>2</sub> CC <sub>ring</sub> bend; OC <sub>ring</sub> bend; C <sub>Me</sub> C <sub>ring</sub> bend
6	a''			318	77	0.764	0.751	HOC <sub>ring</sub> torsion
5	a''			296	0	1.000	0.844	O oop; C <sub>Me</sub> oop; CH <sub>2</sub> oop
4	a'			287	0	0.996	0.871	C <sub>Me</sub> CC <sub>ring</sub> bend; H <sub>2</sub> CC <sub>ring</sub> bend
3	a''			199	4	0.960	0.914	ring torsion; HOC <sub>ring</sub> torsion
2	a''			138	1	0.993	0.869	ring torsion; C <sub>Me</sub> oop
1	a''			120	0	0.992	0.750	ring torsion

<sup>a</sup> Number of vibration. <sup>b</sup> Relative intensities based on the most intense band (100). <sup>c</sup> Ratio of <sup>2</sup>H/<sup>1</sup>H isotopic frequencies for the *d*<sub>1</sub> isotopomer (OD). <sup>d</sup> Ratio of <sup>2</sup>H/<sup>1</sup>H isotopic frequencies for the *d*<sub>6</sub> isotopomer (CD<sub>2</sub>; CD<sub>3</sub>; OD). <sup>e</sup> Assignments according to adiabatic analysis; diatomic ordering. See ref 22.

CH<sub>2</sub>Cl<sub>2</sub>). IR (Ar, 10 K): 2101.7 (9), 2067.5 (100), 2052.7 (6), 1648.6 (<1), 1614.7 (20), 1609.4 (19), 1598.7 (4), 1595.3 (1), 1589.6 (3), 1451.4 (<1), 1428.8 (<1), 1380.7 (3), 1366.4 (1), 1262.9 (11), 1258.1 (10), 1218.4 (1), 1150.7 (2), 1078.7 (1), 1036.8 (<1), 1006.5 (2), 953.7 (1), 905.6 (0), 868.6 (2), 521.2 (<1) cm<sup>-1</sup> (relative intensity).

**4-Diazo-2,6-bis(trideuteriomethyl)-1-oxo-2,5-cyclohexadiene (3-d<sub>6</sub>).** Starting material for the synthesis of **3-d<sub>6</sub>** was 2,6-bis(trideuteriomethyl)phenol, which was prepared according to a procedure by Jackman et al.<sup>31</sup> 2,6-Dimethylphenol was refluxed in D<sub>2</sub>O with a nickel on Kieselguhr catalyst. The hydrogen exchange at the methyl positions was nearly quantitative (>99%, determined by NMR). 2,6-Bis-(trideuteriomethyl)phenol was oxidized with Fremy's salt to the corresponding 2,6-bis(trideuteriomethyl)-1,4-benzoquinone. The following steps were carried out analogous to the synthesis of **3**.<sup>7</sup> <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.21 (s, 2H), 2.1 (s, <0.035 H). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  181.9, 134.1, 125.6, 71.7; IR (Ar, 10 K): 2087 (26), 2074.1 (18), 2065.5 (31), 2061.7 (100), 1614.2 (25), 1608 (34), 1605 (47), 1590.5 (6), 1373 (5), 1350.3 (2), 1259.1 (13), 1257.8 (3), 1156.7 (5), 1096.2 (2), 929.8 (8), 907.1 (1), 881.6 (2), 862.7 (4) cm<sup>-1</sup> (relative intensity).

## Computational Methods

The triplet (**4**) and closed-shell singlet (**6** and **7**) systems were treated with standard DFT. For **5**, however, conventional (single-reference) DFT is not appropriate, since here one has to use at least a two-determinant description of the form  $\Psi = \sigma\alpha(1)\pi\beta(2) + \pi\alpha(2)\sigma\beta(1)$  (ignoring paired electrons and normalization) to account for a single electron in a  $\sigma$  orbital and another single electron in a  $\pi$  orbital. This leads to MC DFT, which is at the focus of current research<sup>19</sup> and still bears a number of unsolved problems. We have avoided these problems by retreating to restricted open shell theory for low-spin (ROSS) cases as it was discussed by Andrews, Murray, and Handy<sup>20</sup> for Hartree-Fock and second-order perturbation theory. At the ROSS-DFT level the two-determinant problem is reformulated in a way that one can essentially remain within the realm of single-configuration theory at the cost of building up a more complicated Fock matrix. Also, a new exchange correlation (XC) functional has to be constructed for the ROSS case, which was solved by starting from the one for the corresponding high-spin open shell case and adding an extra term to the exchange energy so that the correlation energy is described properly in the low-spin situation. With this new XC functional, a self-consistent

**Table 2.** Measured and Calculated Vibrational Frequencies  $\omega$  and Infrared Intensities  $I$  of 3-Hydroxy-4-methylhepta-1,2,4-triene-6-yne (6)

no. <sup>a</sup>	argon matrix			B3LYP/ 6-31G(d,p) (scaled by 0.96)			assignment <sup>d,e</sup>
	$\omega$ (cm <sup>-1</sup> )	$I_{rel}^b$	$\omega_i/\omega^c$	$\omega$ (cm <sup>-1</sup> )	$I_{rel}^b$	$\omega_i/\omega^c$	
45	3637.5	31	0.738	3661	30	0.728	OH stretch
44	3333.4	100	1.000	3352	70	1.000	alkyne CH stretch
43				3045	8	0.744	asym allene CH <sub>2</sub> stretch
42				3025	13	1.000	alkene CH stretch
41				3012	14	0.741	asym CH <sub>3</sub> stretch
40				2981	15	0.740	sym allene CH <sub>2</sub> stretch; CH <sub>3</sub> stretch
39	2976.6	15		2980	17	0.735	asym CH <sub>3</sub> stretch; CH <sub>2</sub> stretch
38				2923	23	0.719	sym CH <sub>3</sub> stretch
37				2122	1	1.000	alkyne CC stretch; C4C5 stretch
36	1946.7	15	0.990	1973	22	0.985	asym allene stretch
35				1607	3	0.996	alkene C=C stretch
34	1450.5	11		1451	16	0.944	CH <sub>2</sub> sciss; C7C8 + C2C7 allene stretch; C2C3 stretch
33	1443.9	2		1442	20	0.898	H15C9C3 bend; CH <sub>2</sub> scissor
32				1427	6	0.839	CH <sub>3</sub> deform; H15C9C3C2 torsion
31				1369	2	0.820	C2C3 stretch; H11C4C3 bend; HOC bend
30	1380.2	6	0.996	1368	1	0.758	CH <sub>3</sub> deform
29	1305.3	22	0.994	1291	44	0.799	H11C4C3 bend; HOC bend
28	1222.9	7	0.987	1213	53	0.795	C—O stretch; allene CC stretch
27	1174.7	10	0.762	1151	86	0.735	HOC bend; C3C9 stretch; C2C3 stretch
26	1057.2	99	0.984	1042	82	0.987	C4C5 stretch; CH <sub>3</sub> deform
25	1044.7	56		1027	45	0.981	C3C9 stretch; C4C5 stretch
24	1036.6	11		1021	35	0.863	CH <sub>3</sub> deform
23				988	0	0.846	allene CH <sub>2</sub> wag
22				943	3	0.847	H15C9C3 bend; C4C5 stretch; C3C4C5 bend
21	880.5	35	0.800	875	30	0.802	allene CH <sub>2</sub> oop
20	819.1	10	0.965	824	12	0.958	alkene CH oop
19				705	3	0.940	CO stretch; C2C3 stretch
18				646	6	0.958	O and C2 oop; C2C3C4C5 torsion
17	630.3	93	1.000	609	47	0.998	alkyne CC—H def and torsion
16	597.1	34		596	12	0.921	allene CH <sub>2</sub> wag
15				569	5	0.959	C3C4C5 bend; C3C9 stretch; OC2C3 bend
14	591.4	9	1.008	564	13	0.945	C2C3 stretch; C3C2C7 bend
13	569.6	26	0.973	546	45	0.880	alkyne C—H oop; alkyne C—H def
12				471	0	0.927	C3C4C5C6 torsion
11				436	1	0.923	OC2C3 bend; C9 oop
10				366	100	0.727	OH torsion
9				345	1	0.936	C4C3C9 bend; C4C5C6 bend; C4C13C2 bend
8				317	4	0.942	C9 and O oop; OC2C3 bend
7				277	5	0.913	OCC bend; CCC bends
6				213	6	0.905	C8C7C2 bend; C8C7C2C3 torsion
5				184	2	0.864	C—CH <sub>3</sub> torsion
4				152	0	0.943	C8C7C2C3 torsion; CCC bends
3				143	1	0.792	C—CH <sub>3</sub> torsion; CCCC torsions
2				104	0	0.944	CCC bends
1				40	0	0.930	C7C2C3C4 torsion; CCC bend

<sup>a</sup> Number of vibrations. <sup>b</sup> Relative intensities based on the most intense band (100). <sup>c</sup> Ratio of <sup>2</sup>H/<sup>1</sup>H isotopic frequencies for the *d*<sub>6</sub> isotopomer (CD<sub>2</sub>; CD<sub>3</sub>; OD). <sup>d</sup> Assignments according to adiabatic analysis; diabatic ordering. See ref 22. <sup>e</sup> For numbering of atoms see Figure 1.

procedure was derived to determine the Kohn–Sham orbitals for ROSS-DFT.<sup>21</sup> The ROSS-DFT XC functional was tested in connection with standard DFT procedures, and ROSS-BLYP results turned out to be the best for small test systems (for more details, see ref 21).

**Matrix Isolation.** Standard techniques with an APD CSW-202 Displex closed-cycle helium cryostat were used. Matrices were produced by deposition of argon (Linde, 99.9999%) on top of CsI (IR) or sapphire (UV–vis) window with a rate of approximately 0.15 mmol/min. Infrared spectra were recorded by using a Bruker IFS66 FTIR spectrometer with a standard resolution of 1 cm<sup>-1</sup> in the range 400–4000 cm<sup>-1</sup>. Irradiations were carried out with use of Ushio HBO 500-W mercury high-pressure arc lamps in Oriel housings equipped with quartz optics. IR irradiation from the lamps was absorbed by a 10-cm path of water. For broad-band irradiation, Schott cutoff filters were used (50% transmission at the wavelength specified), and for narrow-band irradiation, interference filters in combination with dichroic mirrors (“cold mirrors”) and cutoff filters were used.

**4-Diazo-2,6-dimethyl-1-oxo-2,5-cyclohexadiene (3).** IR (Ar, 10 K): 2068.7 (94), 2062.1 (100), 2053.4 (3), 2010.6 (1), 1671.8 (1), 1617.8 (93), 1608.8 (49), 1456 (1), 1428.6 (2), 1382.6 (4), 1379.1 (1),

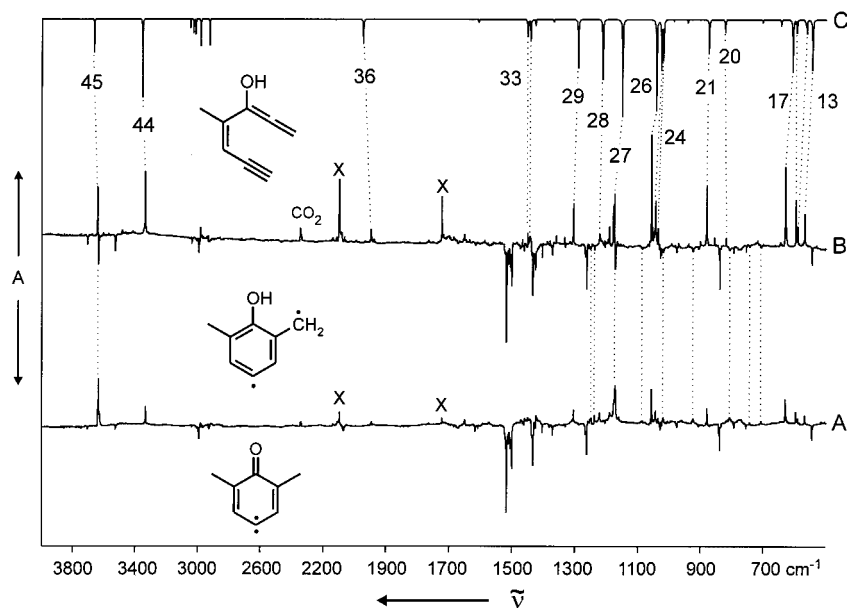
1366.4 (3), 1269.3 (2), 1254.9 (55), 1135.4 (4), 1037.3 (1), 1010.7 (7), 942.8 (2), 932.6 (2), 872.4 (6), 767.2 (<1), 531.2 (4) cm<sup>-1</sup> (relative intensity).

**2,6-Dimethyl-1-oxo-2,5-cyclohexadien-4-ylidene (4).** IR (Ar, 10 K): 1518.3 (100), 1501.3 (28), 1438.6 (9), 1434.5 (37), 1426.9 (13), 1404.5 (7), 1371.9 (8), 1330.4 (2), 1263.4 (28), 1204.8 (2), 1028.8 (4), 1026.5 (5), 977.4 (8), 907.9 (1), 840.3 (33), 795 (3), 755.5 (5), 544.9 (15) cm<sup>-1</sup> (relative intensity).

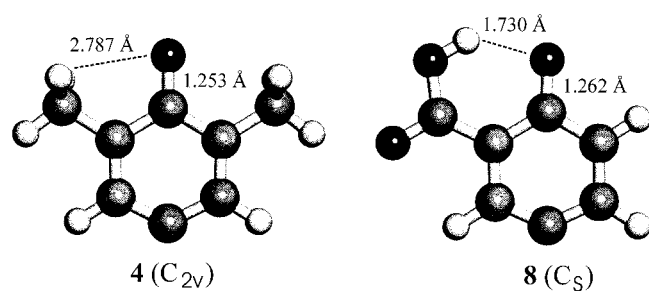
**6-Methyl- $\alpha$ ,4-didehydrocresol (5).** IR (Ar, 10 K): 3634.9 (100), 1374.9 (1), 1253.4 (<1), 1249.7 (5), 1238.8 (6), 1172.6 (39), 1087.3 (2), 1020.5 (4), 925.1 (8), 809.5 (7), 744.1 (1), 708.3 (2) cm<sup>-1</sup> (relative intensity).

**3-Hydroxy-4-methylhepta-1,2,4-trien-6-yne (6).** IR (Ar, 10 K): 3637.5 (31), 3333.4 (100), 2976.6 (15), 1946.7 (15), 1450.5 (11), 1443.9 (2), 1380.2 (6), 1305.3 (22), 1222.9 (7), 1174.7 (10), 1057.2 (99), 1044.7 (56), 880.5 (35), 819.1 (10), 630.3 (93), 597.1 (34), 591.4 (9), 569.6 (26) cm<sup>-1</sup> (relative intensity).

**2-Methyl-6-(trideuteriomethyl)-1-oxo-2,5-cyclohexadien-4-ylidene (4-d<sub>3</sub>).** IR (Ar, 10 K): 1515.4 (34), 1510.8 (100), 1459.4 (6), 1438.4 (10), 1435.3 (9), 1408.1 (17), 1371.4 (2), 1325.1 (2), 1261.5 (30), 1220.6 (1), 1197.7 (2), 1074.9 (2), 1039.6 (7), 1024



**Figure 2.** Difference matrix IR spectra in absorbance showing the photochemistry of carbene **4**. (a) Bands of carbene **4** disappearing and bands of diradical **5** and allene **6** appearing after 120 min of 360-nm irradiation. (b) Bands of **5** and remaining **4** disappearing and more allene **6** as well as other photoproducts (**X**) appearing after 12 h of 360-nm irradiation. (c) IR spectrum of **6** calculated at the B3LYP/6-31G(d,p) level of theory.



**Figure 3.** Structures of carbenes **4** and **8** (B3LYP/6-31G(d)) showing the distance of the carbonyl oxygen atom toward the closest hydrogen atom and the C=O bonding distance.

(3), 1021.5 (2), 996.1 (2), 902.9 (4), 894.4 (4), 838.7 (45), 836.7 (—), 811 (1), 808.7 (2), 757.4 (1), 718.3 (1), 534.4 (12), 472.0 (1)  $\text{cm}^{-1}$  (relative intensity).

**4-Diazo-2,6-bis(trideuteriomethyl)-1-oxo-2,5-cyclohexadiene (3- $d_6$ ).** IR (Ar, 10 K): 2087 (26), 2074.1 (18), 2065.5 (31), 2061.7 (100), 1614.2 (25), 1608 (34), 1605 (47), 1590.5 (6), 1373 (5), 1350.3 (2), 1259.1 (13), 1257.8 (3), 1156.7 (5), 1096.2 (2), 929.8 (8), 907.1 (1), 881.6 (2), 862.7 (4)  $\text{cm}^{-1}$  (relative intensity).

**2,6-Bis(trideuteriomethyl)-1-oxo-2,5-cyclohexadien-4-ylidene (4- $d_6$ ).** IR (Ar, 10 K): 1510.5 (100), 1493.7 (3), 1442.7 (1), 1414.3 (22), 1324.4 (14), 1268 (17), 1221 (5), 1089.1 (7), 1044.3 (13), 1037.3 (29), 895.7 (8), 857 (5), 829.5 (46), 797.1 (1), 524.1 (9)  $\text{cm}^{-1}$  (relative intensity).

**6-(Trideuteriomethyl)- $\alpha,\alpha,O$ -trideutero- $\alpha,4$ -didehydrocresol (5- $d_6$ ).** IR (Ar, 10 K): 2683.6 (100)  $\text{cm}^{-1}$  (relative intensity).

**3-Hydroxy-1,1, $O$ -trideutero-4-(trideuteriomethyl)hepta-1,2,4-trien-6-yne (6- $d_6$ ).** IR (Ar, 10 K): 3334.3 (100), 2684.7 (35), 1926.6 (20), 1374.7 (15), 1297.6 (45), 1207.3 (50), 1190.6 (50), 1141.3 (20), 1052.9 (5), 1040.8 (—), 983.6 (15), 895.6 (40), 790.8 (4), 704.8 (10), 630.1 (75), 596.4 (39), 554.0 (14)  $\text{cm}^{-1}$  (relative intensity).

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