

## On the $^1\text{H}$ NMR Spectra of Polycyclic Enediones

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**Abstract:** Both isomers of the adduct of 2,5-dibromo-*p*-benzoquinone with cyclohexadiene (*viz.* *endo* and the novel *exo*) were prepared. Their 200 MHz  $^1\text{H}$  NMR spectra were recorded and analyzed with the aid of computational methods for the prediction of chemical shifts (GIAO and CHARGE 7H). The optimized calculated geometries of both, obtained from B3PW91 DFT calculations with 6-31G(d,p) basis sets (Gaussian 98), were used. This allowed the assignment of all proton signals, which we now report.

In the course of our ongoing investigation on the chemistry of polycyclic enediones,<sup>1,2</sup> we have prepared both isomers of the adduct of 2,5-dibromo-*p*-benzoquinone with cyclohexadiene (*endo*-**1** and *exo*-**1**, Figure 1). After obtaining the  $^1\text{H}$  NMR spectra for both isomers of compound **1** (5%  $\text{CDCl}_3$  solutions), which were measured at 4.7 T with a Varian VXR-200 spectrometer, we faced the usual

problem of assigning all the observed signals. For polycyclic enediones, such as these, some signals are unmistakable (*viz.* the signals of H-3 are singlets for both compounds, whereas H-8a is a doublet, with  $J(8,8a) = 1.20$  Hz, for the *endo* isomer but a singlet for the *exo* isomer), assignable by simple inspection. The signals of H-9a, H-9s, H-10a and H-10s give rise to an ABCD system, which can be solved by the method of Reilly and Swalen.<sup>3</sup>



**Figure 1.** The Isomers of Compound **1**

Thus, the signals coupled by  $J_{AB} \approx 10$  Hz should be from the geminal protons in the

$\text{CH}_2$  groups, but it is not possible to discern them, nor to assign individually each proton in

the diastereomeric pairs formed by all the remaining protons. Hence, we employed the most current methods used for the prediction of chemical shifts so as to allow us to make assignments for all the observed signals. We initially calculated the geometries of both adducts using Gaussian 98,<sup>4</sup> after having employed the B3PW91 DFT method with the 6-31G(d,p) basis sets. The chemical-shifts

were computed from the optimized geometries by the GIAO method, also using Gaussian 98 and Abraham's CHARGE 7H program.<sup>5</sup> Our results are presented in Table 1, which shows the correlation coefficients (*r*) and mean standard deviations ( $\sigma$ ) calculated for each set of computed chemical-shifts compared to the experimentally observed data.

**Table 1.** Experimental and Calculated <sup>1</sup>H NMR Chemical Shifts for the *endo* and *exo* Isomers of the Adduct of 2,5-Dibromo-*p*-benzoquinone with Cyclohexadiene

M	Isomer	Proton Number										Statistics		
		Data Type	3	5	6	7	8	8a	9a	10a	9s	10s	r	$\sigma$
endo	Exptl.		7.39	3.48	6.26	6.24	3.44	3.22	2.30	1.94	1.55	1.47		
	Charge		7.38	3.80	6.12	5.97	3.81	3.67	2.75	2.00	1.63	1.52	0.994	0.229
	GIAO		7.25	3.43	6.61	6.54	3.53	3.26	2.42	1.83	1.30	1.32	0.997	0.178
exo	Exptl.		7.25	4.76	6.07	5.70	3.59	3.60	2.02	2.26	1.50	1.83		
	Charge		7.50	3.77	6.29	6.19	3.68	3.51	1.78	2.41	1.61	1.62	0.983	0.421
	GIAO		7.32	3.88	6.88	6.82	3.57	3.24	1.21	1.58	1.07	0.99	0.980	0.542

We consider that these data can provide the basis for assignments in both cases, although such assignments must be regarded as provisional. However, we believe that definitive assignments for these compounds can be obtained only experimentally, by the use of <sup>1</sup>H {<sup>1</sup>H} NOEDIF or related techniques, which is our next step. Our view is that it will be possible to reach unambiguous assignments by computational tools alone in the near future.

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