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22. ^{13}C- and ^{1}H-NMR. Spectra of *ortho*-Benzoquinones 1)
On the Assignment Problem in ^{13}C Spectra

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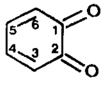
Dedicated to Prof. *Max Viscontini* on the occasion of his 60th birthday

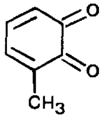
(30. XI. 72)

Summary. ^{13}C- and ^{1}H-NMR. spectra of *ortho*-benzoquinone **1** and its methyl derivatives have been analysed. By means of heteronuclear double resonance experiments it is shown that assignments given in the literature for the olefinic carbon resonances of **1** and of a series of substituted *ortho*-benzoquinones have to be inverted. ^{13}C-carbonyl frequencies of various six-membered cyclic ketones are presented.

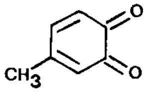
The correct assignment of resonance lines is a major problem in ^{13}C-NMR. spectroscopy. It can often be solved by heteronuclear ^{13}C-[^{1}H] double resonance experiments provided the proton spectrum has been analysed before. In the course of our investigations of the carbon [1] and proton [2] [3] spectra of cyclic unsaturated ketones we have now determined the spectral parameters of the thermally unstable *ortho*-benzoquinone and of its two monomethyl derivatives. The results of a recent analysis [4] of the ^{13}C spectra of *ortho*-benzoquinones agree neither with the sequence of chemical shifts we obtained on the basis of the known assignment of the proton resonances [5] [6] in this class of compounds nor with the sequence of ^{13}C chemical shifts which was found in cyclic unsaturated ketones [1].



1



2



3

The ^{1}H-NMR. data of **1**, **2** and **3** are summarized in table 1. They were extracted from 100 MHz single and double resonance spectra (decoupling of olefinic from methyl

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1) ^{13}C-NMR. Spectroscopy, Part II. Part I see [1].

protons) and were optimized by computational iteration of the four- and six-spin systems respectively.

Table 1. δ_H *[ppm(TMS)] and* J_{HH} *[Hz] of the* ortho-*benzoquinones* **1**, **2** *[0°] and* **3** *[27°] in* $CDCl_3$ *[c* ~ 80 mg/ml]

	1	**2**	**3**
δ H(3)	6.438	–	6.235
δ H(4)	7.110	6.825	–
δ H(5)	7.110	7.021	6.943
δ H(6)	6.438	6.309	6.346
δ (CH_3)	–	2.018	2.195
$J_{3,4}$	10.0	–	–
$J_{4,5}$	6.0	6.2	–
$J_{5,6}$	10.0	10.0	10.0
$J_{3,5}$	1.6	–	2.1
$J_{4,6}$	1.6	1.4	–
$J_{3,6}$	1.0	–	0.9
J_{3,CH_3}	–	–	1.7
J_{4,CH_3}	–	1.7	–
J_{5,CH_3}	–	0.3	0.3
J_{6,CH_3}	–	0.8	0.5

The chemical shift difference between the protons α and β to the carbonyl group in **1** (0.67 ppm in $CDCl_3$) is smaller than in α,β-unsaturated ketones (0.8–1.0 ppm) and compares with the range observed for cross-conjugated ketones, *e.g.* *para*-dienones (0.6–0.8 ppm). The assignment of α-protons at low frequency and β-protons at high frequency, which cannot be obtained from the AA'XX'-spectrum of **1**, is unequivocal in the case of the two methyl derivatives **2** and **3**. For this purpose the coupling constants of the ring protons ($^3J_{HH} > {}^4J_{HH} > {}^5J_{HH}$) and the allylic coupling constants ($^4J_{HH}$) of the methyl and ring protons ($J_{CH_3\overset{|}{C}=CH-} > J_{CH_3\underset{|}{\overset{|}{C}}-CH=}$) can be utilized. Since the effect of the methyl group results in a low frequency shift of all olefinic protons (0.1–0.3 ppm, see also [2]) the assignment obtained for **2** and **3** can also be applied to **1**. Moreover our assignment ($\delta_{H\beta} > \delta_{H\alpha}$) correlates with π-electron density calculations [7] on **1** ($q_{C\beta} < q_{C\alpha}$). The δ_H and J_{HH} data of *ortho*-benzoquinones are very similar to those obtained from *ortho*-cyclohexadienones and 1,3-cyclohexadienes.

The ^{13}C spectra were measured by *Fourier*-transform pulse spectroscopy (25.2 MHz) under simultaneous proton noise-decoupling or coherent off-resonance irradiation. The chemical shifts of **1** and **3** are given in table 2.

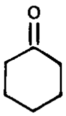
Table 2. δ_C *[ppm(TMS)] of the* ortho-*benzoquinones* **1** *[–20°] and* **3** *[–5°] in* $CDCl_3$ *[c* ~ 50 mg/ml]

	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	CH_3
1	180.4	180.4	130.8	139.7	139.7	130.8	–
3	179.2/180.1		127.7	152.0	143.4	129.5	22.8

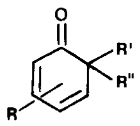
The assignment of the olefinic resonances of **1** follows from the observation of two ^{13}C doublets with different reduced coupling constants ($J_r^{3,6} < J_r^{4,5}$) obtained upon coherent irradiation at 4.7 ppm in the proton spectrum. Hence the sequence of ^{13}C resonances ($\delta_{C\beta} > \delta_{C\alpha}$) corresponds to that of the proton resonances. Analogous double resonance experiments on **3** confirm the position of C(3) and C(6) at low frequencies and of C(5) at higher frequency. C(4) suffers an additional high-frequency shift due to methyl substitution. The olefinic δ_C values for **3** relative to **1** are in very good agreement with shift increments obtained from methylsubstituted *ortho*-dienones [1].

The assignments given by *Berger* & *Rieker* for the olefinic carbon resonances of *ortho*-benzoquinone and of C(4) and C(6) in the six substituted *ortho*-quinones must be inverted. The present example demonstrates that the analysis of the proton spectrum and results of heteronuclear double resonance experiments should be consulted besides other techniques to arrive at an unequivocal assignment of ^{13}C resonance lines.

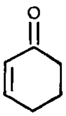
The chemical shifts of the carbonyl group in *ortho*-benzoquinones are the lowest of all six-membered cyclic ketones (δ (ppm), $CDCl_3$):



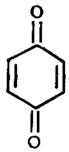
211.6



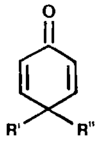
204.5 ± 1.5



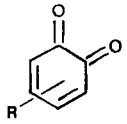
199.2



187.0



185 ± 1



180 ± 1

The wide spread of chemical shifts and high resolution (± 0.1 ppm) obtained in ^{13}C spectroscopy thus allow to distinguish nonequivalent carbonyl groups and to derive considerable structural information in cases where other spectroscopic methods, *e.g.* IR. spectroscopy, fail.

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