Analysis of nuclear magnetic resonance spectra of phthalic acid and its diesters

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The n.m.r. spectra of benzene ring protons of phthalic acid, phthalic anhydride, dimethylphthalate, and diethylphthalate were analyzed by means of LAOCN 3 computer programme. The results of analysis were compared with those obtained by direct method. For the given series of compounds it was found that the coupling constants $J_{AA'}$ and $J_{BB'}$ change whereas the constants J_{AB} and $J_{AB'}$ remain practically unchanged.

С применением LAOCN 3 программы были анализированы ЯМР спектры протонов бензольного ядра фталевой кислоты, фталевого ангидрида, диметилфталата и диэтилфталата. Результаты анализа спектров исследуемых веществ были сравнены с результатами полученными прямым методом. Для данной серии веществ определили изменение констант взаимодействия $J_{AA'}$ и $J_{BB'}$ в то время, как константы J_{AB} и $J_{AB'}$ практически не изменяются.

The analysis of n.m.r. spectra for the systems of the type AA'BB' or ABCD consisting of four spins is generally a very difficult problem because of the complicated relationship among the shape of the spectra, chemical shifts, and coupling constants. The given dependence may be described schematically as follows:

$$\nu_0\delta = \nu_A - \nu_B$$
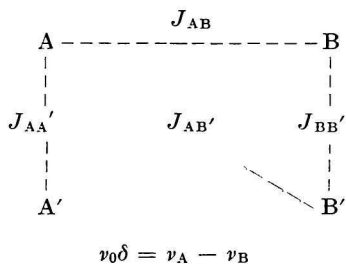
In the present paper, we analyzed the n.m.r. spectra of protons on benzene ring according to the method of *Castellano* and *Bothner-By* [1] using LAOCN 3 prog-

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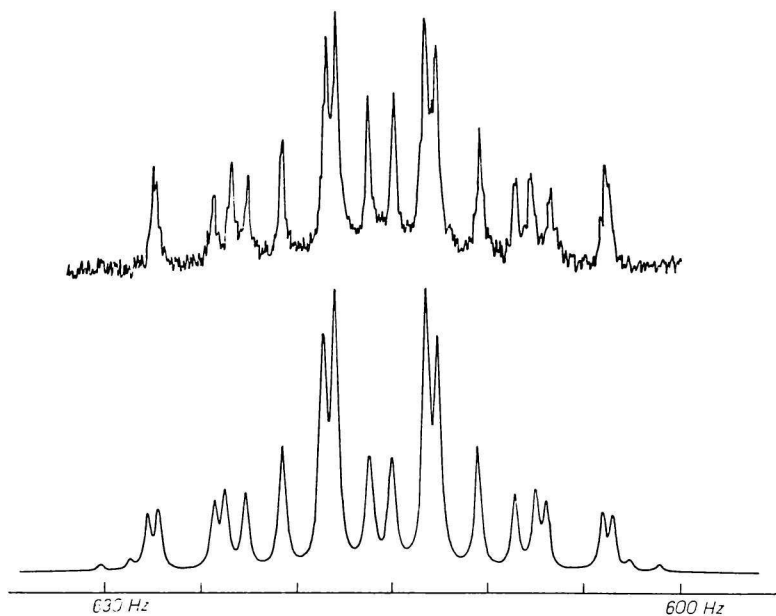
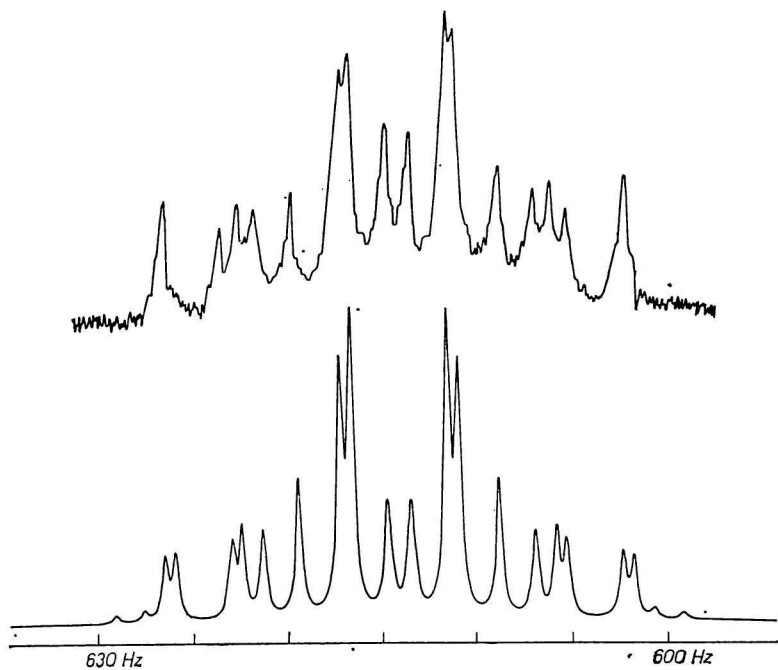*Fig. 1.* Experimental and simulated 80 MHz n.m.r. spectrum of phthalic anhydride.

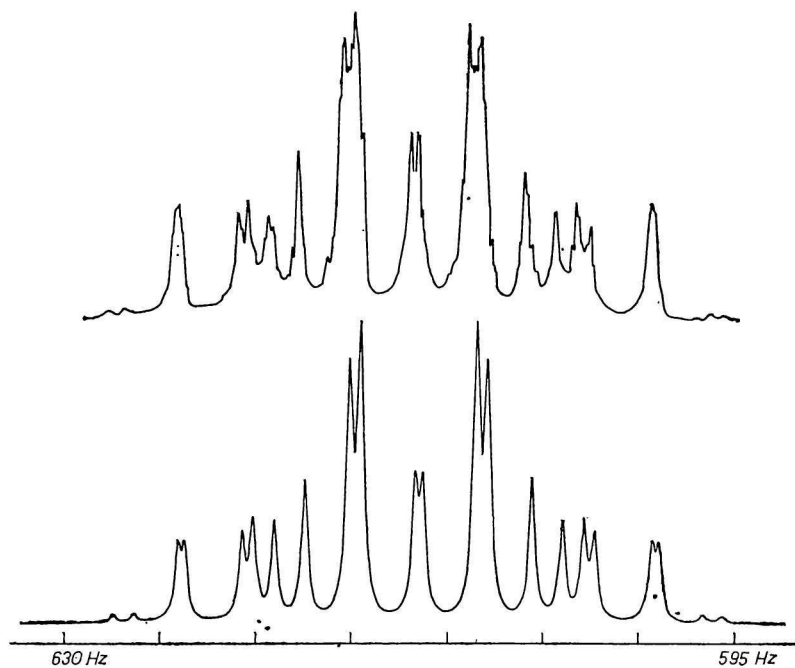*Fig. 2.* Experimental and simulated 80 MHz n.m.r. spectrum of phthalic acid.

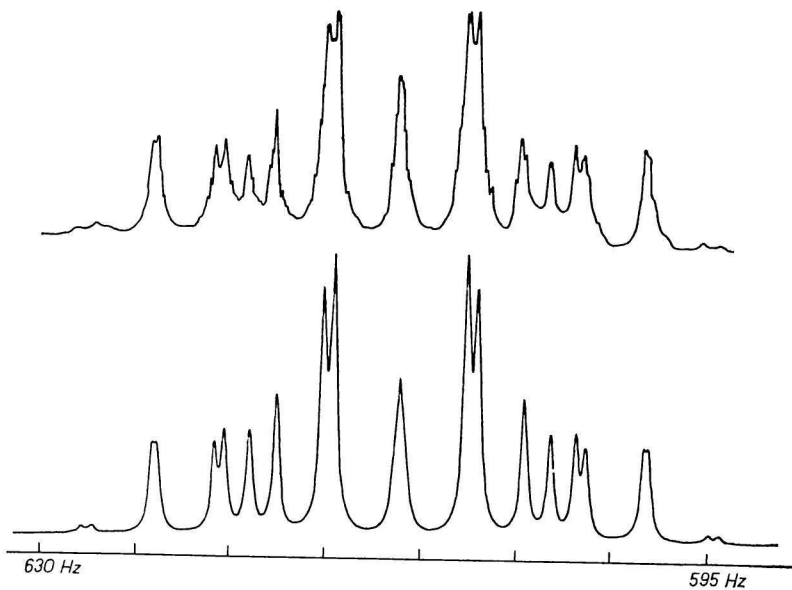*Fig. 3.* Experimental and simulated 80 MHz n.m.r. spectrum of dimethylphthalate.

Fig. 4. Experimental and simulated 80 MHz n.m.r. spectrum of diethylphthalate.

ramme [2]. The preliminary analysis was done with the set of parameters obtained
by direct method [3—5]. The calculations according to that method were performed
in [6]. The chemical shifts and coupling constants determined in such a way were
utilized as entrance data in the LAOCN 3 programme. The computed theoretical
lines were ascribed to the experimental ones and all parameters were simultaneously
iterated. From the theoretical lines and corresponding intensities the theoretical
spectra were simulated and compared with those obtained experimentally by means
of NMR PLOT programme. The iteration was performed on 20 experimental lines
for each spectrum.

Results and discussion

Both the experimental and computed n.m.r. spectra of aromatic protons are
shown in Figs. 1—4. From this it follows that the computed spectra are in good
agreement with the theoretical ones and that the differences in frequencies are
within the limits of experimental errors. The computed spectral parameters are
in Table 1. As it follows from the analysis of n.m.r. spectra of aromatic protons
the results obtained by LAOCN 3 programme correspond well to those obtained
by direct method according to [6] and it should be emphasized that in both cases
we have treated the same experimental data. Some slight differences in the obtained
results are caused by different procedures used in calculation of the experimental
error in both cases. Provided that the lines were measured with an infinite accuracy
then according to *Abraham* [7] both methods should give the same results. The differen-
ces in calculated coupling constants between both sets of the results (Table 2) are

Table 1

Computed spectral parameters in Hz*

Compound	$\nu_0\delta$	J_{AB}	J_{AB}'	J_{BB}'	J_{AA}'
Phthalic anhydride	11.99	7.70	1.49	0.75	5.81
Phthalic acid	12.57	7.82	1.48	0.84	6.06
Dimethylphthalate	13.67	7.52	1.36	0.54	7.12
Diethylphthalate	14.51	7.75	1.27	0.30	7.54

* The probable error of parameter sets was less than 0.05 Hz.

Table 2

Difference (in Hz) in calculation of coupling constants by direct method and by LAOCN 3
computer programme

Compound	ΔJ_{AB}	$\Delta J_{AB}'$	$\Delta J_{BB}'$	$\Delta J_{AA}'$	r.m.s. Error
Phthalic anhydride	0.09	0.07	0.00	0.20	0.13
Phthalic acid	0.07	0.04	0.01	0.07	0.10
Dimethylphthalate	0.03	0.02	0.05	0.23	0.04
Diethylphthalate	0.07	0.10	0.10	0.00	0.10

of the same order as r.m.s. error in measurements of line position and are caused only by experimental error and not by different method of analysis. The greater difference obtained in the calculation of the coupling constant J_{AA}' is due to its dependence on correct determination of both side lines in the experimental spectrum which are generally less intense and, therefore, poorly resolved. It brings about the uncertainty in determination of the coupling constant J_{AA}' by direct method.

A set of parameters obtained by computation according to the LAOCN 3 programme should be preferred since this method is more suitable for the treatment of initial data in spectral analysis.

It follows from the comparison of the coupling constants and the inner chemical shift $\nu_0\delta$ in the series phthalic anhydride, phthalic acid, dimethylphthalate, and diethylphthalate, that coupling constants J_{AA}' and J_{BB}' change significantly whereas the constants J_{AB} and J_{AB}' only slightly. The inner chemical shift $\nu_0\delta$ also increases owing to the larger screening of AA' protons and smaller screening of BB' protons.

The analysis has demonstrated that both methods treating the spectra in different way yield the same results which are within the experimental errors. The method by Castellano and Bothner-By seems to be more suitable since it allows to ascribe the experimental lines to the theoretical ones more unambiguously. For the first non-iteration calculation, however, one should choose the appropriate set of parameters; on the other hand the direct method of analysis, in the unambiguous analysis of spectra, requires the record of n.m.r. spectra at two or more intensities of external magnetic fields [8].

Experimental

All proton spectra were measured on an 80 MHz NMR spectrometer Tesla BS 487 with the resolving power 0.4 Hz at 25°C, using tetramethylsilane as an internal standard. The samples were dissolved in deuterated acetone and measured in argon atmosphere. The more detailed description of measurements of spectra is in [6].

The analysis of spectra by using LAOCN 3 programme was carried out on a CDC 3300 computer. The accordance of the observed and simulated spectra was verified by means of NMR PLOT programme with coordinate recorder CALCOMP.

References

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Translated by J. Rychlý