# INVESTIGATION OF CRYSTALLINE p-NITROPHENOL AND THE IRRADIATION PRODUCTS OF ITS α-FORM BY MEANS OF THE NUCLEAR MAGNETIC RESONANCE METHOD

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The polymorphous α-form of p-nitrophenol is characterized by the property of becoming durably coloured when irradiated with daylight. NMR-signals have been measured in case of the α- and β-forms of p-nitrophenol as well as in case of samples of the α-form illuminated with daylight. The second moments of the experimental NMR lines are about twice greater than those calculated on the basis of X-ray data. The change in the second moment of the NMR-line which occurs after irradiation of αp-nitrophenol indicates that the photochemical process consists in the jump of the proton from the hydroxyl group to the nitro-group of a neighbour molecule. The molecules formed in this way have quinoidal structure. The concentration of quinoidal molecules in the samples is of the order of several tens of per cent.

## 1. Introduction

Crystalline p-nitrophenol occurs in two phases. The α-form is characterized by the property of being coloured at the surface under the influence of irradiation with daylight. The crystal surface changes its colour from bright yellow to bright red already after a dozen or so minutes of irradiation. After the irradiation for several days it becomes dark red. The β-form is not subject to this effect [1, 2].

Rohleder [1] suggested a hypothesis which explains the difference between the properties of the two forms of p-nitrophenol. According to this hypothesis the colouration of α-p-nitrophenol is caused by the jump of the hydroxyl proton to the nitro group of the neighbouring molecule. The molecules produced in this way have quinoidal structure which fact explains the colouration of the reaction products. In the β form the energy barrier for the jump of the proton is higher since the position of the proton in the crystal is less favourable from the point of view of the process. This is confirmed by crystallographic data. It follows from the detailed X-ray studies of Coppens and Schmidt [2, 3], that in the α-form the proton

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from the OH group is more symmetric with respect to the oxygen atoms of the nitro group of the neighbouring molecule than in the $\beta$-form.

The purpose of the work presented in this paper was the study of this photochemical reaction by means of the nuclear magnetic resonance method. The aim of the NMR measurements of both forms of p-nitrophenol was the verification of the hydrogen atom coordinates given by other authors and also the detection of eventual differences in their structure which may be decisive from the point of view of photochemical properties. The comparison of the second moments of irradiated samples and of the pure $\alpha$-form permits some conclusions about the structure of the photochemical products to be drawn.

## 2. Preparation of samples

Paranitrophenol chemically pure, manufactured by POCh-Gliwice was purified by double recrystallization from its vapour under the pressure of about 30 Tr. Both investigated forms were obtained from solution as well as from vapour (the $\beta$-form crystallizes from vapour under the pressure of several Tr).

The $\alpha$-form was ground to powder and irradiated with white light for more than ten days. In order to obtain a higher yield of the reaction the powder was additionally crushed and mixed. Several samples were irradiated also in nitrogen atmosphere and in vacuum.

## 3. Nuclear magnetic resonance measurements

The measurement have been made with the apparatus for wide lines at the Institute of Nuclear Physics in Cracow. The powdered samples were packed in glass test tubes. The resonance frequency of the spectrometer was 17.455 MHz, the modulation frequency 71 Hz. The measurements were made for two modulation amplitudes: 2.175 Gs and 1.448 Gs. The resonance lines of all samples had a shape shown in Fig. 1 and the width of about 7.5 Gs.

The characteristic parameter used in the interpretation of the results was the second moment of the resonance line. The second moment of a NMR-line $(\Delta H_2^2)$ is the mean square of the local magnetic field strength in the crystal and can be calculated for experimental lines by means of the formula Ref. [4].

$$\Delta H_2^2 = \frac{c^2}{3} \frac{\sum\limits_{-\infty}^{+\infty} n^3 f(n)}{\sum\limits_{-\infty}^{+\infty} n f(n)} \tag{1}$$

where $n$ — is the index corresponding to a consecutive line segment on the ordinate axis (Fig. 1),

$c$ — local internal magnetic strength in Gs which corresponds to the length of the segment into which the ordinate axis was divided,

$f(n)$ — is the value of the first derivative of the resonance line at the point corresponding to the ordinate $n$ (in arbitrary units),

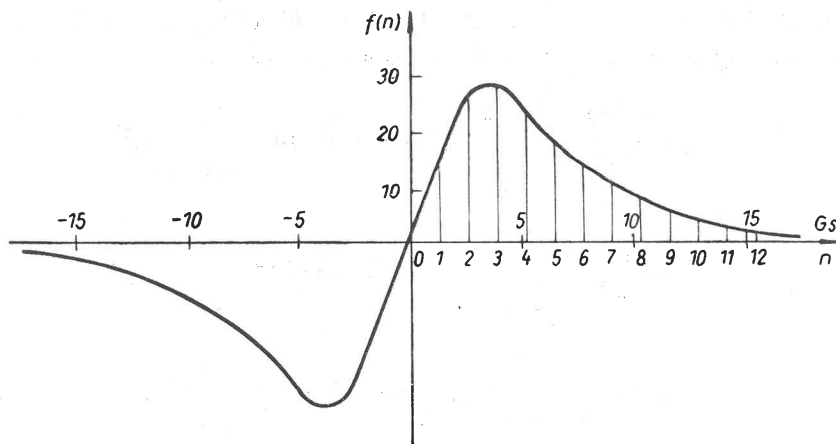$nc$ — is the deviation of the internal field strength from its resonance value.

Fig. 1. Graphical determination of the second moment of the NMR absorption line from the plot of its first derivative

TABLE I

Results of measurements

| Form | $H_2^2(\text{Gs}^2)$ |
|---|---|
| $\alpha$ | $12.01 \pm 0.21$ |
| $\alpha$ irradiated | $10.70 \pm 0.12$ |
| $\beta$ | $12.52 \pm 0.53$ |

It is also necessary to subtract from the calculated value a correction $H_M^2/4$ for the influence of the finite value of the modulation amplitude $H_M$.

The results of measurements are given in Table I.

## 4. Calculation of the second moments on the basis of atomic coordinates determined by means of the X-ray diffraction method

The second moments of the resonance line which resulted from the coordinates of atoms determined by means of the X-ray diffraction method were calculated as follows:

$$\Delta H_2^2 = {}^{ii}\Delta H_2^2 + {}^{N}\Delta H_2^2 + {}^{z}\Delta H_2^2. \tag{2}$$

The first term on the right-hand side of Eq. (2) is the second moment of an isolated molecule (however neglecting the interactions of protons with other nuclei in the molecule), the second term is a correction for interactions of protons with the nitrogen nucleus and the third term takes into account the interactions between protons of different molecules. Thus the second moment of an isolated molecule is equal to ${}^{i}\Delta H_2^2 = {}^{ii}\Delta H_2^2 + {}^{N}\Delta H_2^2$.

The particular terms of the sum on the right-hand side of Eq. (2) have been calculated using the following formulas for polycrystalline samples [4, 5]:

$$^{ii}\Delta H_2^2 = \frac{9\gamma^2\hbar^2}{20\,N} \sum_{j=1}^{N} \sum_{\substack{k=1\\k\neq j}}^{N} r_{jk}^{-6} = 71.616 \cdot 10^{-48} \sum_{j=1}^{5} \sum_{\substack{k=1\\k\neq j}}^{5} r_{jk}^{-6} \tag{3}$$

$$^{z}\Delta H_2^2 = \frac{9\gamma^2\hbar^2}{20\,N} \sum_{j=1}^{N} \sum_{f=1}^{M} r_{jf}^{-6} = 71.616 \cdot 10^{-48} \sum_{j=1}^{5} \sum_{f=1}^{M} r_{jf}^{-6} \tag{4}$$

$$^{N}\Delta H_2^2 = \frac{A}{15\,N} \sum_{j=1}^{N} \mu_N^2 r_j^{-6} = 0.4433 \cdot 10^{-48} \sum_{j=1}^{5} r_j^{-6}. \tag{5}$$

The meaning and the values of the symbols appearing in Eqs (3), (4) and (5) are the following:

$\hbar = 1.05443\cdot10^{-27}$ erg sec — the Planck constant divided by $2\pi$,

$\gamma = 2.67527\cdot10^4$ Gs$^{-1}$ sec$^{-1}$ — gyromagnetic factor of proton,

$\mu^2 = I_N(I_N+1)\,\gamma_N^2\hbar^2$ — square of the magnetic moment of nitrogen nucleus,

$I_N = 1$ — spin of the nitrogen nucleus,

$\gamma_N = 0.19335\cdot10^4$ Gs$^{-1}$sec$^{-1}$,

$N = 5$ — the number of protons in the molecule,

$r_{jk}$ = distance between the $j$-th and the $k$-th proton in a given molecule (cm),

$r_{jf}$ = distance between the $j$-th proton of the given molecule and the $f$-th proton from its neighbourhood,

$r_j$ = distance between the $j$-th proton of a given molecule and the nitrogen atom of this molecule.

In the calculation of the distance $r$ between the magnetic nuclei the values of Coppens and Schmidt [3] have been adopted for the unit cell. The dimensions of the unit cell of both forms of nitrophenol are the following:

|  | $\alpha$-form | $\beta$-form |
|---|---|---|
| $a$ | 11.66 Å | 15.403 Å |
| $b$ | 8.78 Å | 11.117 Å |
| $c$ | 6.098 Å | 3.785 Å |
| $\beta$ | 107°32′ | 107°04′ |
| space group | $P2_1/n$ | $P2_1/a$. |

Fig. 2 shows the assignments of the atoms in the molecule. The Tables II and III contain the orthogonal coordinates of the magnetic nuclei of one molecule in the $(a, b, c^x)$ system. In the calculation of $^{z}\Delta H_2^2$ all protons from the neighbourhood have been taken into account whose distance from any proton of the molecule is less than 8 Å. A rough estimate of the contribution of farther protons yields less than 2%. In case of the $\alpha$-form the crystallographic data are given at the temperature of 90°K. If it is assumed after Coppens
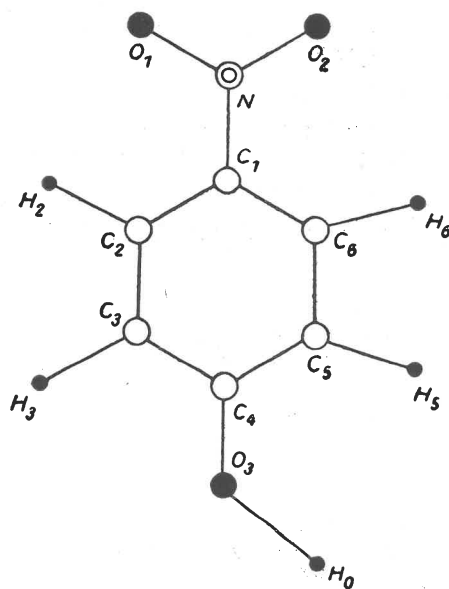
Fig. 2. Denotations of the atoms in the *p*-nitrophenol molecule

TABLE II

Coordinates of the magnetic nuclei of the $\alpha$-form molecule in the orthogonal system ($a$, $b$, $c^x$)

| Atoms | $X$ | Coordinates (Å) $Y$ | $Z$ |
|-------|------|------|------|
| $H_0$ | 3.25 | 4.30 | 2.10 |
| $H_2$ | −0.53 | 4.26 | 5.13 |
| $H_3$ | 1.39 | 5.35 | 4.52 |
| $H_5$ | 1.72 | 2.57 | 1.45 |
| $H_6$ | −0.17 | 1.40 | 2.14 |
| $N$ | −1.738 | 2.115 | 4.210 |

TABLE III

Coordinates of the magnetic nuclei of the $\beta$-form molecule in the orthogonal system ($a$, $b$, $c^x$)

| Atoms | $X$ | Coordinates (Å) $Y$ | $Z$ |
|-------|------|------|------|
| $H_0$ | 5.58 | 4.60 | 0.74 |
| $H_2$ | 0.59 | 5.31 | 1.23 |
| $H_3$ | 2.76 | 6.26 | 1.36 |
| $H_5$ | 4.28 | 2.64 | 0.40 |
| $H_6$ | 2.09 | 1.77 | 0.28 |
| $N$ | −0.133 | 2.900 | 0.748 |

that all distances $r_{if}$ change in the temperature range between 90°K and 293°K on the average by 2% then the value of $^z\Delta H_2^2$ at room temperature can be obtained by multiplying Eq. (4) by the factor $(1+0.02)^{-6} = 1.02^{-6}$.

Table IV gives the calculated values of second moments of both forms of p-nitrophenol and for two structure models of the products of photochemical reaction assumed in accordance with the hypothesis of Rohleder [1]. These models are illustrated schematically in Fig. 3. In the case of the model $a$) it was assumed that in the molecules of the irradiation products
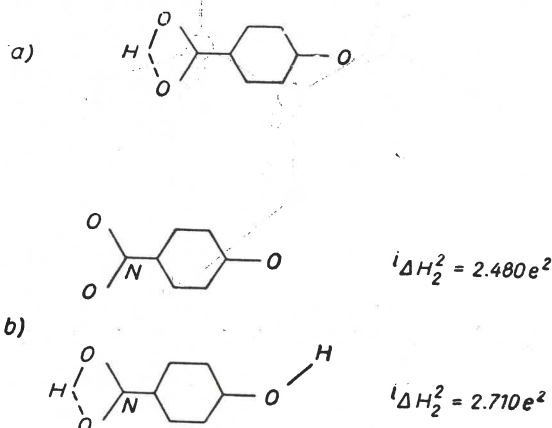


Fig. 3. Models of molecules of the photochemical reaction products

TABLE IV

Second moments resulting from the magnetic nuclei coordinates (Gs²)

|  | Form $\alpha$ | Form $\beta$ | Photochemical reaction products | |
|---|---|---|---|---|
|  |  |  | Model $a$) | Model $b$) |
| 1 | 2 | 3 | 4 | 5 |
| $^{ii}\Delta H_2^2$ | 2.90 | 2.65 | 2.33 | 2.59 |
| $^N\Delta H_2^2$ | 0.01 | 0.01 |  |  |
| $^z\Delta H_2^2$ | 2.38 | 2.18 |  |  |
| $\Delta H_2^2$ | 5.29 | 4.84 | 4.72 | 4.97 |

one hydroxyl proton is bound with the nitro group, whereas in the model $b$) one half of the molecules has two hydroxyl protons per molecule while the other half has no hydroxyl protons at all. The second moments of these molecules are shown in the figure. The second moments of the molecules in which the proton is bound with the nitro group have been calculated under the assumption that this proton is located at the centre of the segments connecting the two oxygen atoms of this group. In both cases the value assumed for $^z\Delta H_2^2$ was that calculated for the $\alpha$-form.

## 5. Discussion of the results

The experimental values of the second moments are more than twice as great as those calculated from the structural data. These discrepancies cannot be explained in terms of the experimental error since the results obtained in several series of measurements were similar. The possibility of systematic errors in the calculation of the second moments from the crystal structure has also been ruled out.

The large experimental values of the second moments obtained by means of the NMR method cannot be explained by the presence of paramagnetic impurities. The measurements of electron paramagnetic resonance [6] have shown that the concentration of free electron spins in the investigated samples is negligible. This concentration amounted to about $6 \cdot 10^{16}$ per gram for the coloured sample and at least half order of magnitude less in non-irradiated samples.

The experimental material available does not enable us to find the reasons for such big discrepancies. It is possible that they are the consequence of lack of accuracy in the assumed distribution of protons in the molecule (in particular the benzene protons). Such explanation is favoured by the similar value of the discrepancies in both forms. On the basis of this fact one can make an approximate assumption that in case of the $\alpha$-form and of the photochemical reaction products the experimental values of the second moments are proportional to the values calculated theoretically. Such an assumption permits the interpretation of the changes in the second moment of the $\alpha$-form caused by its irradiation.

## 6. Conclusions

The experimental values of the second moment of the irradiated substance is about 10.9% less than the corresponding values obtained in case of pure $\alpha$-form. The theoretical values of the second moments given in Table IV which have been calculated for the models a) and b) of the photochemical reaction products are smaller than the theoretical value of the non-irradiated $\alpha$-form by 12% and 6.0%, respectively. It should be pointed out that the values of these changes have been obtained by assuming that the hydroxyl proton bound with the nitro group is as close to the nitrogen atom as possible. This proton lies, however, much farther from the nitrogen atom and thus also from the other protons of the molecule. Thus the second moments of molecules which have one proton bound to the nitro group may be considerably smaller, which in turn means that in case of both models (particularly in case of the model a) these differences of the second moments will be greater than those obtained in the present paper. Thus, 12% and 6% are the lower limits of the changes in the second moment of the $\alpha$-form resulting from the models a) and b), respectively.

The studies on the magnetic susceptibility of irradiated samples have shown that more than 40% of the molecules have quinoidal structure [6]. Thus one can conclude that the model which is in better agreement with experiment is the model a) of the structure of the irradiated substance or perhaps a mixture of both models, however, with the predominance of the first one.

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