CRYSTAL AND MOLECULAR STRUCTURE OF POTASSIUM p-NITROPHENOLATE MONOHYDRATE: SUBSTITUENT EFFECT ON GEOMETRY OF THE RING IN p-SUBSTITUTED NITROBENZENE DERIVATIVES*

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Dedicated to Professor Otto Exner on the occasion of his 65th birthday.

The crystal and molecular structure of potassium p-nitrophenolate monohydrate has been determined by X-ray diffraction methods giving $R = 0.050$. The through resonance effect between $-O^-$ and $-NO_2$ groups resulted in a significant deformation of the ring geometry. Application of the HOSE model yielded in determination of the resonance structure contributions and offered an argument against the classical view of the through resonance effect: percentage contribution of quinoid form with full charge transfer from $-O^-$ to $-NO_2$ was found to be the least significant of all four possible quinoid structures. Contributions of quinoid and benzenoid structures plotted against σ^+ or σ_p constants for 14 p-systems give a reasonable linear dependence. Application of the additive scheme of substituent effect to the same series of compounds proved a strong reasonance effect from electron donating substituents and a much weaker one (and constant in the whole series) from the nitro group.

An anion of potassium p-nitrophenolate monohydrate, hereafter abbreviated as $K^+ p-NPh^-$, is an example of chemical species with a very strong π-electron cooperative effect (through resonance). σ^+ constants for $-O^-$ group is equal to -2.3 $(ref.[1])$ or -4.27 $(ref.[2])$ depending on the method of estimation, but undoubtedly it is one of the strongest electron donating substituents. On the other hand $-NO_2$ group is one of the strongest non-ionic electron accepting substituents with σ^- value equal to 1.23 $(ref.[1])$. Hence for $p-NPh^-$ species one may expect serious distorsion of the ring geometry and large contributions of quinoid structures. This effect should be greater than in p-nitroaniline or N,N-diethyl-p-nitroaniline of which precise geometries are known $(refs[3,4])$, and at the same level as in p-nitrosophenolate of sodium $(ref.[5])$ and magnesium $(ref.[6])$. In order to maintain homogeneity of the sample under study we are going to analyze in this paper, apart from the title compound, also the p-substituted nitrobenzene derivatives. Quantum chemical (VB)

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calculations (ref.[7]) on p-nitroaniline as well as the HOSE-model (ref.[8]) applied to the precise geometry of N,N-diethyl-p-nitroaniline (ref.[4]) revealed that the quinoid structure *VI* has the lowest weight of all the canonical structures considered (Scheme 1), yielding in $0.3 - 1.1\%$ for VB calculations depending on the basis set used (ref.[7]) and 13.1% for the HOSE-model estimation. Both results advocate against the clas-
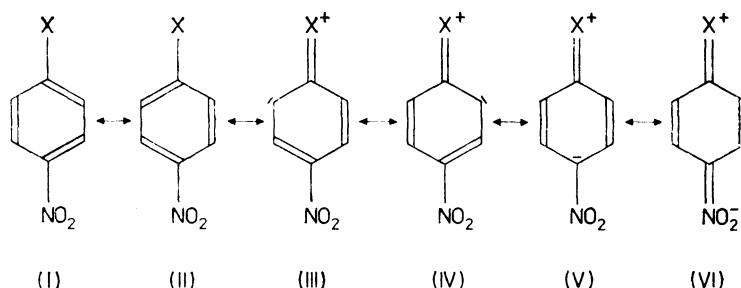
SCHEME 1

sical interpretation of through conjugation which claims that canonical structures *I*, *II* and *VI* dominate over the other ones in description of p-nitroaniline and related systems. Recent structural studies (ref.[3]) as well as structural considerations (ref.[9]) either support the classical view (ref.[3]) or put in doubt the possibilities of getting decisive conclusions from experimental molecular geometry.

The purpose of this paper is to answer the following questions:

1) Does the molecular geometry help in better understanding of the intramolecular interactions?

2) Is the classical view on through conjugation effect supported by molecular geometry of the systems in question?

3) What is the role of the nitro-group in systems with through conjugation?

4) Is it possible to get information about σ- and π-electron contributions to the substituent effect on the geometry of p-substituted nitrobenzenes?

In order to answer these questions a detailed analysis of new structural data of the title compound, together with most precise literature data on p-nitrobenzene derivatives has been carried out.

RESULTS AND DISCUSSION

Crystallographic data are given in Table I. Table II contains fractional coordinates and U_{eq} values whereas Fig. 1 presents numbering of atoms in p-NPh$^-$ together with bond lengths and valence angles. Tables containing U_{ij} and F_o, F_c are available

at the authors on requirement. Table III presents short contacts which are visualized in Fig. 2 presenting projection of the fragment of the crystal lattice along z axis.

TABLE I

Crystallographic data of $K^+[C_6H_4NO_3]^-.H_2O$ at temperature $26.5°C$

$M = 195.22$	$\lambda(MoK_\alpha) = 0.71069$ Å
monoclinic	$\mu(MoK_\alpha) = 5.88\ cm^{-1}$
$a = 10.581(6)$ Å	$F(000) = 396$
$b = 7.366(4)$ Å	$P2_1/n$
$c = 11.317(3)$ Å	$Z = 4$
$\beta = 117.88(5)°$	$D_x = 1.66\ Mg\ m^{-3}$
$V = 779.7(6)$ Å^3	$D_m = 1.66\ Mgm^{-3}$

TABLE II

Final fractional coordinates, equivalent isotropic temperature factors for nonhydrogen atoms and isotropic temperature factors for hydrogen atoms; $U_{eq} = 1/3\sum_i\sum_j U_{ij}a_ia_ja_i^*a_j^*$

Atom	x	y	z	U_{eq}
K	0.84394(3)	−0.01194(4)	0.29448(3)	0.0323(1)
O(1)	0.4436(1)	0.1579(1)	0.8065(1)	0.0314(3)
C(1)	0.5122(1)	0.1542(1)	0.7374(1)	0.0244(3)
C(2)	0.4581(1)	0.2420(2)	0.6110(1)	0.0283(4)
C(3)	0.5313(1)	0.2389(2)	0.5379(1)	0.0280(4)
C(4)	0.6622(1)	0.1474(2)	0.5877(1)	0.0256(4)
C(5)	0.7185(1)	0.0575(2)	0.7109(1)	0.0301(4)
C(6)	0.6458(1)	0.0622(2)	0.7845(1)	0.0303(4)
N(1)	0.7371(1)	0.1395(2)	0.5117(1)	0.0323(4)
O(2)	0.8465(1)	0.0451(2)	0.5508(1)	0.0487(5)
O(3)	0.6891(2)	0.2231(2)	0.4035(1)	0.0506(6)
OW(1)	0.8918(1)	−0.3386(2)	0.4141(1)	0.0404(4)
HC(2)	0.358(2)	0.303(3)	0.572(2)	0.034(5)
HC(3)	0.495(3)	0.300(4)	0.457(3)	0.048(6)
HC(5)	0.803(2)	−0.013(3)	0.738(2)	0.033(5)
HC(6)	0.661(3)	−0.003(3)	0.850(3)	0.036(6)
H(1W1)	0.960(4)	−0.330(5)	0.517(4)	0.108(12)
H(2W1)	0.925(3)	−0.417(4)	0.391(2)	0.044(6)

TABLE III
Short contacts less than sum of respective van der Waals radii taken from ref.[22]

$O1 \cdots OW1^{v}$	2·807(2)	$K^{+} \cdots O1^{ii}$	2·910(1)
$O1 \cdots H1W1^{v}$	1·77(5)	$K^{+} \cdots O1^{xi}$	2·792(1)
$O1 \cdots OW1^{viii}$	2·818(2)	$K^{+} \cdots O2$	2·918(2)
$O1 \cdots H2W1^{viii}$	2·07(3)	$K^{+} \cdots O2^{iii}$	2·914(1)
$C2 \cdots C4^{ii}$	3·497(2)	$K^{+} \cdots O3$	3·015(2)
$C3 \cdots C4^{ii}$	3·405(2)	$K^{+} \cdots O3^{vi}$	2·866(2)
		$K^{+} \cdots OW1$	2·691(1)
		$K^{+} \cdots OW^{iv}$	2·814(1)

Indices denote symmetry codes other than i: ^{i} x, y, z; ^{ii} $1 - x, \bar{y}, 1 - z$; ^{iii} $2 - x, \bar{y}, 1 - z$; ^{iv} $1·5 - x, 0·5 + y, 0·5 - z$; ^{v} $1·5 - x, 0·5 + y, 1·5 - z$; ^{vi} $1·5 - x, -0·5 + y, 0·5 - z$; δ ^{vii} $1·5 - x, -0·5 + y, 1·5 - z$; ^{viii} $-0·5 + x, -0·5 - y, 0·5 + z$; ^{ix} $-0·5 + x, 0·5 - y, 0·5 + z$; ^{x} $0·5 + x, -0·5 - y, -0·5 + z$; ^{xi} $0·5 + x, 0·5 - y, -0·5 + z$.
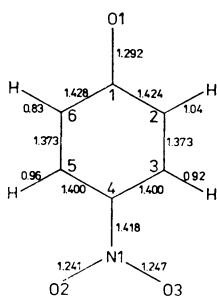

FIG. 1

Bond lengths and valence angles; esd's are all equal to 0·002 Å for all bond lengths except for C1–O1 (0·001 Å), 0·1° for all valence angles formed by nonhydrogen atoms and 0·02—0·03 Å for C–H
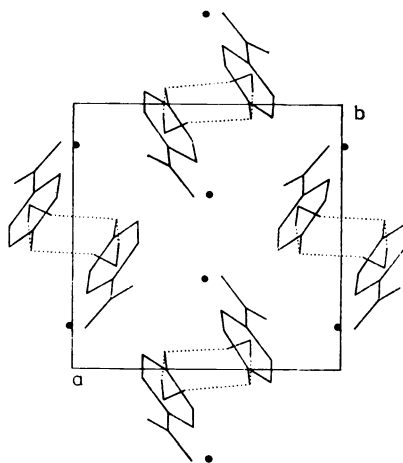
FIG. 2

Projection of the fragment of the crystal lattice along the z axis

Statistical Treatment of the Data

Let us start with the first and the last questions. While looking at the geometry of the p-NPh$^-$ anion it is immediately apparent that the $-NO_2$ and $-O^-$ groups exert different effects on the geometry of the ring. In order to analyze it more quantitatively and statistically correct we construct the null hypothesis, H_0 opposite to this statement and apply simple symmetry properties to test it. If the $-O^-$ and $-NO_2$ groups do not differ in their effect on the geometry of the ring, then the symmetry breaking parameter (SBP) defined as follows

$$SBP = P_i - \hat{S}P_i \tag{1}$$

has to be equal to 0, i.e. H_0: SBP $= 0$. P_i is the structural parameter (bond angle or bond) whereas $\hat{S}$ is the proper for the symmetry problem operator. In our case we take $\hat{S} = \hat{C}_2$ as shown in Fig. 3 whereas application of Eq. (1) to a, b and c bonds and α, β, γ and δ angles gives results gathered in Table IV. In all cases of structural parameters considered for p-NPh$^-$ it can be seen that $|SBP| > 3\sigma$ and rejection of the null hypothesis is statistically correct in 99·73%* of cases. Thus in the case of p-NPh$^-$ we may accept an alternative hypothesis that the effect of substituents $-O^-$ and $-NO_2$ on the geometry of the ring differs significantly. The value of this conclusion depends evidently on the precision of the measurements; for 5 times worse precision (individual $\sigma_i = 0·010$ Å, e.s.d. for the difference equals $(\sigma_a^2 + \sigma_c^2 + \sigma_{a'}^2 + \sigma_{c'}^2)^{1/2} = 0·020$ Å) this conclusion would not be valid any more. Application of this kind of procedure to 14 molecules of p-substituted nitrobenzene derivatives shows that for substituents strongly differing in electron accepting/donating properties and for precise measurements (σ for bond lengths smaller than 0·6 pm) the geo-
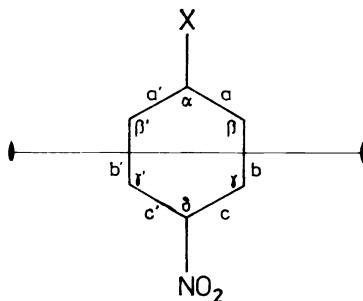

FIG. 3

Action of C_2 symmetry operator in order to test the null hypothesis. See text

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* 3σ rule means that if the difference between two structural parameters normally distributed (it is the usual assumption in this case) is greater than 3σ (σ is the estimated standard deviation) then rejection of the null hypothesis is correct in 99·73% of all cases.

metry changes of the ring are sensitive enough to be significant, provided precise measurements are taken into account. When the SBP's values, estimated for various structural parameters are plotted against the σ^+ (σ_p)-values none of them gives a significant dependence on the nature of X, the best relationship is found, however, for $[|a - c| + |a' - c'|]$. Thus it may be concluded that SBP are good parameters from the point of view of looking for the significance of the substituent effect but they are too sensitive to individual errors, which precludes their use for a deeper analysis of the substituent effect.

Classical Interpretation of the Substituent Effect

If we follow relatively equal contributions of all canonical structures of Scheme 1, we find that the a-bond is taken five times as a single one, whereas the c-bond only four times, indicating slightly shorter c-bonds than the a-bonds. However, electro-

TABLE IV

SBP-values and their standard deviations. $\sigma = (\sum_{i=1}^{n} \sigma_i^2)^{1/2}$ where σ_i stands for individual estimated standard deviation and summation runs over all individual σ's for parameters involved in SBP. In most cases σ_i stands for individual esd value but in some cases it stands for maximum value of the range given in the paper (refs[3,31-34]).

X		Ref.	SBP^a	σ	SBP^b	σ	SBP^c	σ	SBP^d	σ
O^-		e	0·052	0·004	3·6	0·1	3·6	0·2	7·2	0·2
NEt_2	A	4	0·069	0·010	3·3	0·4	1·7	0·6	5·0	0·7
	B		0·064	0·009	3·0	0·4	1·5	0·6	4·5	0·7
NH_2		3	0·029	0·004	2·5	0·3	2·8	0·4	5·3	0·5
$NHCH_3$		30	0·054	0·008	2·6	0·4	4·0	0·6	6·6	0·7
OCH_3		31	0·045	0·012	2·4	0·7	4·6	1·0	7·0	1·2
OH	α	32	0·011	0·012	1·4	0·6	2·0	0·8	3·4	1·0
	β	33	0·008	0·004	1·6	0·1	2·5	0·2	4·1	0·5
Ph		34	0·036	0·010	3·6	0·4	4·6	0·6	8·2	0·7
COO^-	A	35	0·021	0·006	3·5	0·3	5·3	0·4	8·8	0·5
	B		0·032	0·006	3·7	0·3	4·9	0·4	8·6	0·5
COOH		36	0·026	0·004	2·9	0·1	3·9	0·2	6·8	0·2
NH_3^+		37	0·008	0·011	0·9	0·6	1·3	0·7	2·2	0·9
NO_2		38	0·002	0·004	0·0	0·2	0·4	0·3	0·4	0·4

^{a} SBP $= |a - c| + |a' - c'|$; ^{b} SBP $= |\alpha - \delta|$; ^{c} SBP $= |\beta - \gamma| + |\beta' - \gamma'|$; ^{d} SBP $= |\alpha - \delta| + |\beta - \gamma| + |\beta' - \gamma'|$; ^{e} this paper.

negativities of $-NO_2$ and $-O^-$ differ very strongly, $\chi(NO_2) = 4 \cdot 83$ (ref.[10]) and $\chi(O^-) \ll \chi(OMe) = 2 \cdot 68$ (ref.[11]) and hence a simple application of the Walsh rule (ref.[12]) suggests that the c-bonds should be shorter than the a-bonds, even if the π-electron effects were the same or closely the same for these bonds. Scheme 2 summarizes this reasoning.
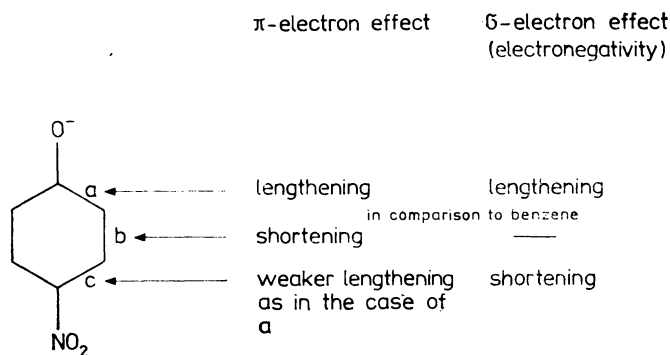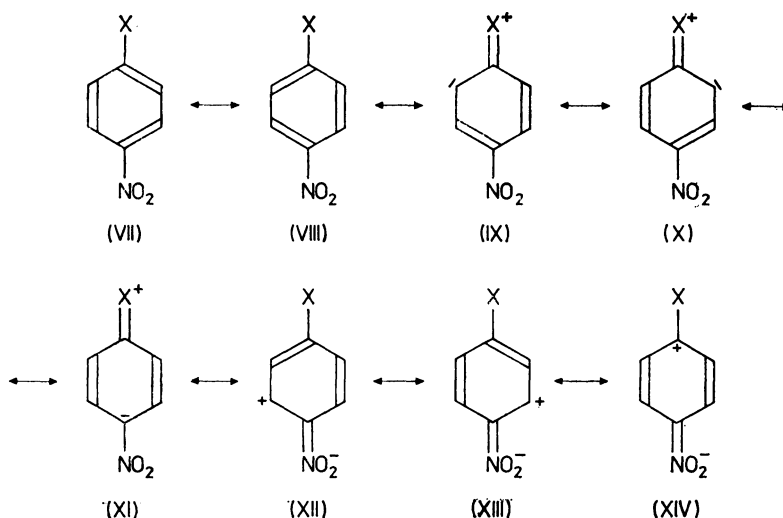

SCHEME 2

Estimation of the Canonical Structure Weights from the Geometry of Chemical Species

The second question may be answered by use of the HOSE-model (ref.[8]) which permits to obtain approximate weights of canonical structures, participating in description of the molecular geometry in question, directly from experimental geometry. The idea of this model is based on the use of deformation energy, E_i, necessary to deform the real molecular geometry to the reference geometry that is expected for particular canonical structures. This energy, E_i, is calculated by use of the simple harmonic oscillator model, whereas the contribution of the i-th canonical structure is assumed to be inversely proportional to E_i, with the normalization condition

$$c_i = (E_i)^{-1}/\sum(E_j)^{-1} .\tag{2}$$

Many applications of the HOSE-model were quite successful in translating the molecular geometry into the language of chemical properties via the analysis of the obtained weights of canonical structures (refs[13-17]).

In HOSE calculations carried out in this paper two schemes of resonance structures are taken into account. First of all, the scheme already presented $1 - VI$ and related to the classical resonance theory, and also the scheme in which resonance effects of substituents D and A (i.e. electron donating and accepting, respectively) are treated solely as additive. These structures are shown in Scheme 3 as $VII - XIV$.

(VII)   (VIII)   (IX)   (X)

(XI)   (XII)   (XIII)   (XIV)

SCHEME 3

Analysis of π-Electron Cooperative Effects Observed in Geometry of p-X-Ph-NO₂ Systems

Table V gives weights of contributions of canonical structures presented in the Scheme 1 calculated using the HOSE-model (ref.[8]) for 14 molecules of *p*-nitro-derivatives of benzene with substituents ranging from strongly electron donating $(-O^-, -NEt_2$, etc.) to electron accepting $(-NO_2, -NH_3^+$, etc.). As it has been shown recently (ref.[18]) the HOSE-model gives these contributions in a relatively good agreement with VB calculations for *p*-nitroaniline (ref.[7]) and hence application of this approach to vast amount of reliable geometries of X–Ph–NO₂ systems may illustrate relationships between structure of these compounds (by means of geometry — bond lengths) and their reactivity parameters i.e. Hammett's constants. Eq. (*3*) shows a dependence of % (*I, II*) (weights of structures *I* and *II* of the Scheme 1) on σ^+ for electron donating X and on σ_p for electron accepting X. The greater is the electron accepting power of X the higher value of % (*I, II*) is observed. The regression line for this plot is

$$\% \,(I, II) = 48.9 \,(1.4) + 10.6 \,(1.2) \, \sigma^+ \tag{3}$$

for $n = 14$ with correlation coefficient $r = 0.929$. In turn when % contribution of structures *III*, *IV*, and *V* is plotted in the same way against σ^+ and σ_p, the equation is as (*4*)

$$\% \,(III - V) = 41.8 \,(1.2) - 8.4 \,(1.0) \, \sigma^+ \tag{4}$$

TABLE V

Weights of contributions of canonical structures $(I - XIV)$ for p-nitroderivatives of benzene

X		I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII	XIII	XIV
O⁻		11·9	11·7	18·7	18·7	24·0	15·0	10·5	10·3	16·4	16·4	21·2	7·7	7·8	9·7
NEt₂	A	13·8	12·6	17·1	20·0	23·4	13·1	12·0	11·0	14·9	17·5	20·4	7·3	7·5	9·4
	B	14·2	14·4	18·7	18·2	21·4	13·1	12·2	12·3	16·0	15·6	18·4	7·9	7·9	9·7
NH₂		14·7	14·4	17·5	18·1	22·1	13·2	12·6	12·3	15·0	15·4	19·0	8·0	8·1	9·6
NHCH₃		15·6	15·8	20·0	16·2	19·8	12·6	13·2	13·4	16·9	13·6	16·7	8·0	8·7	9·5
OCH₃		23·2	19·3	13·2	16·2	16·9	11·2	18·3	15·3	10·4	12·8	13·3	9·4	9·3	11·2
OH	α	22·6	22·9	14·8	14·2	15·0	10·5	17·6	17·9	11·6	11·1	11·7	9·8	9·9	10·4
	β	22·0	23·6	14·5	14·2	15·2	10·5	17·3	18·5	11·4	11·1	11·9	9·9	9·5	10·4
Ph		23·0	23·6	15·4	14·2	14·6	9·2	18·7	19·4	12·5	11·5	11·9	8·4	8·5	9·1
COOH		25·2	23·5	14·3	14·7	13·7	8·6	20·5	19·1	11·7	12·0	11·2	8·3	8·6	8·6
COO⁻	A	24·3	24·6	14·3	13·9	13·9	9·0	19·4	19·7	11·5	11·1	11·2	9·0	8·8	9·3
	B	24·7	25·0	14·6	14·0	13·1	8·6	19·9	20·2	11·8	11·3	10·6	8·7	8·7	8·7
NH₃⁺		26·9	27·4	12·5	12·4	12·2	8·6	21·0	21·4	9·8	9·7	9·6	9·5	9·5	9·5
NO₂		27·8	27·8	12·2	12·2	11·7	8·3	21·8	21·8	9·5	9·6	9·1	9·6	9·5	9·1

for $n = 14$ with correlation coefficient $r = -0.919$. In both cases correlation is acceptable and in line with recent views on the through resonance effect, that the main contribution to this effect is described by structures I, II and $III - V$ (refs[7,18]). The less significant role of structure VI is revealed by a much smaller value of regression coefficient for plot % (VI) vs σ^+ (or σ_p) as presented below

$$\% (VI) = 9.2 (0.3) - 2.1 (0.2) \sigma^+ \tag{5}$$

with correlation coefficient $r = -0.934$ for $n = 14$. This means that % (VI) is about four times less sensitive to the changes in electron donating power of substituent X. All these dependences are summarized in Fig. 4.

It may be concluded that classical interpretation of through resonance effect which is represented by a description of p-X–Ph–NO$_2$ derivatives in terms of three main canonical structures I, II and VI should be replaced by a fuller representation of canonical structures $I - VI$ since not only theoretical calculations (refs[7,19]) but also structural evidence presented recently (ref.[18]) and in this paper argue for it.

An interesting conclusion may also be drawn while looking at the correlation between % $(III - V)$ vs % (I, II) and % (VI) vs % (I, II) which yield in the correlation coefficient equal to -0.998 and -0.973, respectively. The negative sign is obvious but a much stronger correlation between % (I, II) and % $(III - V)$ than that of % (VI) might indicate that the contribution of VI is less consistent with the overall picture than that of the other two. This may be due to lower adequacy of this canonical structure in the description of p-X–Ph–NO$_2$ systems.
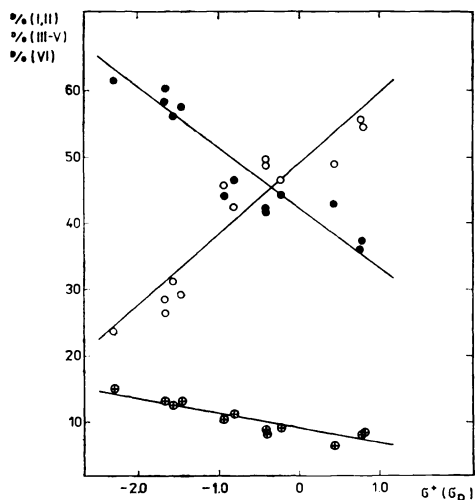

FIG. 4

The dependence of % (I, II) (empty circles) % $(III - V)$ (full circles) and % (VI) (crosses) calculated for the traditional resonance theory scheme of substituent effects on σ^+ for electron donating and σ_p for electron accepting substituents

Additive Scheme of Substituent Effect on Geometry of the Ring

An alternative interpretation to the typical resonance theory description of p-nitro-aniline like systems expressed by canonical structures $I - VI$ is an additive Scheme 3 presented by canonical structures $VII - XIV$. In this scheme apart from two structures without substituent effect on the geometry of the ring $VII, VIII$ there are three structures in which the donating substituent polarizes the ring, without any co-operative effect from the counter substituent $IX - XI$ and then three other structures in which only the electron accepting substituent polarizes the ring $XII - XIV$. Application of the HOSE-model to this scheme has shown a very interesting feature (Table V). For 14 molecules of p-nitroderivatives of benzene weights for structures $XII - XIV$, i.e. those showing the resonance effect of the $-NO_2$ group are practically constant in the range 24.2% ($-NEt_2$) and 30.1% ($-OH$). In contrast, the weights of structures $IX - XI$ i.e. those taking into account polarization of the ring by the counter substituent vary from 28.2% ($-NO_2$) to 54.0% ($-O^-$). Obviously, the variation of weights for $VII, VIII$ is supplementary to the latter. This finding is in line with the Exner's statement (refs[20,21]) that the nitro-group does not participate in any strong through resonance effect by means of charge transfer from the donating substituent into the $-NO_2$ group but rather inductively interacts with the ring. Almost constancy of $\%(XII - XIV)$ supports this view. Equations (6), (7) and (8) describe the dependences of contributions of particular kinds of canonical structures on σ^+ (or σ_p) whereas Fig. 5 summarizes these considerations: plotting $\%(VII, VIII)$, $\%(IX - XI)$ and $\%(XII - XIV)$ vs σ^+ (or σ_p) of the counter substituent in p-nitro-derivatives of benzene, one can see clearly the difference between the action of the $-NO_2$ group and donating substituents.

$$\%(VII, VIII) = 39.0 \, (1.0) + 7.6 \, (0.8) \, \sigma^+ \tag{6}$$

with correlation coefficient $r = 0.938$ for $n = 14$

$$\%(IX - XI) = 33.5 \, (1.4) - 8.4 \, (1.2) \, \sigma^+ \tag{7}$$

with correlation coefficient $r = -0.896$ for $n = 14$

$$\%(XII - XIV) = 27.5 \, (0.6) + 0.7 \, (0.5) \, \sigma^+ \tag{8}$$

with correlation coefficient $r = 0.36$ for $n = 14$.

Analysis of $\%$ contribution of $IX - XI$ and $XII - XIV$ vs $\%(VII, VIII)$ leads to an interesting finding. There is a relatively high correlation for the first case ($r = -0.983$) but completely weak correlation for the second case ($r = 0.51$). This undoubtedly means that the mechanisms of substituent interaction described by

VII, *VIII* and *IX* − *XI* are mutually consistent whereas that described by *XII* − *XIV* seems to be inadequate (to this scheme). In other words, the resonance effect of the −NO_2 group would seem to be not too realistic description of structural consequences of the substituent effect in *p*-X–Ph–NO_2 systems.

If the additive scheme is enriched by adding the structure *VI* then it represents all main types of interactions: polarization of the ring by electron donating and accepting substituents separately and their joint action which is just the through resonance structure *VI*. Such a scheme gives results which are fully in line with both former schemes and conclusions drawn.

Interactions between p-NPh^- *and Environment in the Crystal Lattice*

Table III gives the closest contacts in which one may differentiate two kinds of data. One type of close contacts which may be a source of deformation due to repulsion are those between neutral C atoms belonging to different species. These contacts are however not too short and do not seem to be of interest. The other type of close contacts are those of attractive nature. These kind of contacts include those between K^+ and oxygen atoms of three types: from water molecules, −NO_2 and −O^- groups. Oxygen atoms of these contacts form antiprisms shown schematically in Fig. 6 which are however deformed significantly from their ideal shape. These deformations
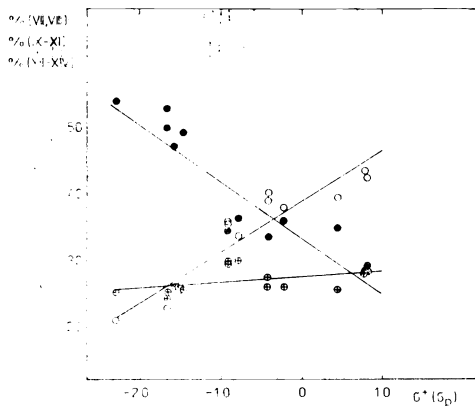

FIG. 5

The dependence of % (*VII, VIII*) (empty circles), % (*IX–XI*) (full circles) and % (*XII–XIV*) (crosses) calculated for the additive scheme of substituent effects on σ^+ for electron donating and σ_p for electron accepting substituents
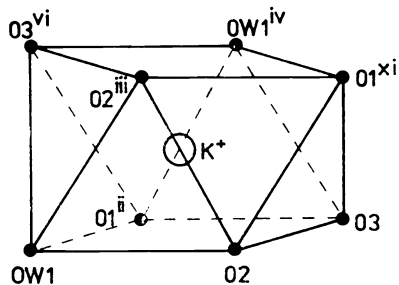

FIG. 6

Eight-coordinated oxygen atoms around potassium cation

from ideal shape are due to a rather low value of binding energy of oxygen atoms and K$^+$ forming an antiprism and on the other hand relatively inflexible position of oxygen atoms since, except of water molecules, all other oxygen atoms are fixed as parts of larger entities. This may result in steric hindrance working against ideal shape of antiprisms.

It should be pointed out that water molecules are also involved in H-bonds with phenolate oxygen. These interactions are shown in Fig. 2 and their geometry is given in Table III. These interactions seem to be relatively strong as may be concluded from values of short contacts.

CONCLUSION

The analysis of structural parameters of the title compound as well as of 13 molecules of other benzene p-nitroderivatives for which the geometry was estimated with high precision permitted to draw the following conclusions.

Molecular geometry estimated with sufficiently high precision is a very valuable source of information and may be decisive in interpretation of intramolecular interactions. The classical interpretation of through resonance in p-nitroaniline like systems with too great weight counted for a structure with a full charge transfer *VI* should be replaced by consideration of all *I − VI* canonical structures, in line with theoretical (VB) calculations (ref.[7]) and other (*ab initio*) data (ref.[19]). The nitro group seems to interact with the ring chiefly via inductive way in line with an interpretation by Exner (refs[20,21]). Precise determination of the molecular geometry of a system like p-NPh$^-$ as well as p-nitroaniline like systems permits to distinguish between the σ^- (electronegativity) electron effect and the π-electron effect of substituents on the geometry of the ring.

EXPERIMENTAL

Yellow crystals suitable for X-ray analysis were obtained by slow evaporation from methanol. Accurate values of unit-cell parameters were determined by least-squares treatment of setting angles of 25 reflections measured on a Enraf–Nonius CAD4 four-circle diffractometer using MoK$_\alpha$ radiation with a graphite monochromator. Profiles of 4 538 reflections with $2\theta \leq 78°$ were measured using $\omega − 2\theta$ scan technique*. Monitored intensities of three standard reflections ($\bar{2}20$, $\bar{3}11$ and $\bar{1}2\bar{4}$) showed no significant variation during data collection. 3 652 reflections were considered as observed on the ground of the $|F_0| \geq 3 \cdot 5\sigma(F_0)$ criterion. The structure was solved with direct methods using MULTAN 80 (ref.[23]) (positions of all non-hydrogen atoms were revealed), and refined with SHELX 76 (ref.[24]). The anisotropic refinement of non-hydrogen atoms followed by the difference syntheses led to the location of all hydrogen atoms. Positional parameters and isotropic temperature factors of all hydrogen atoms were included in the refinement.

The process of refining was stopped when shifts in all parameters became less than $0\cdot1$ esd. The maximum electron density on final difference Fourier map was $0\cdot56$ eÅ^{-3} (in a distance $0\cdot80$ Å from C2) and the largest hole was $-0\cdot44$ eÅ^{-3}. The final refinement converged to a conventional $R = 0\cdot050$, $wR = 0\cdot059$ and $s = 1\cdot85$ for 3 630 observed reflections. The weights were $w = k/[\sigma^2(F_o) + gF_0^2]$, where $k = 0\cdot5019$ and $g = 0\cdot0005$. The empirical isotropic extinction parameter x was used to correct F_c according to $F_c' = F_c(1 - xF_c^2/\sin\theta)$, x converged at $1\cdot9(3) \cdot 10^{-6}$. Scattering factors for neutral atoms were taken from International Tables for X-ray Crystallography (ref.[25]) and for K^+ from refs[26,27]. Additional calculations were performed with programs GEOME (ref.[28]) and PLANE (ref.[29]).

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