Effects of Through-Conjugation on the Molecular Structure of *p*-Nitroaniline [1]

Marcello Colapietro, Aldo Domenicano*, Clara Marciante, and Gustavo Portalone

Istituto di Strutturistica Chimica del CNR, I-00016 Monterotondo Stazione; and Dipartimento di Chimica, Università di Roma, I-00185 Roma, Italy

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Through-Conjugation, Benzene Ring Distortions

A new X-ray diffraction study of *p*-nitroaniline shows that through-conjugation has highly significant effects on the geometry of the molecule, as compared to aniline and *p*-nitrobenzoic acid. The effects include a moderate decrease of the internal angles of the ring at substituted carbons, with respect to values derived by superimposing independent angular distortions from each substituent.

Introduction

In view of the fundamental importance of *p*-nitroaniline in the study of through-conjugation (*i.e.*, cooperative interaction between π-donor and π-acceptor substituents) and of our interest in the angular distortions of the benzene ring caused by substitution [2, 3] we have accurately determined the geometry of this molecule by X-ray crystallography.

A paper on the crystal structure of *p*-nitroaniline was published 21 years ago [4]. The study was based on visually estimated photographic data and led to a final R value of 0.095. The accuracy of the molecular parameters was not very high; it appeared that a quinonoid form was contributing to the structure, but, curiously, the amino group was found to interact with the benzene ring to a greater extent than does the nitro group.

Experimental

Crystals grown from ethanol are monoclinic, space group $P2_1/n$, with $a = 12.337(5)$, $b = 6.037(2)$, $c = 8.597(5)$ Å, $\beta = 91.42(7)°$, $V = 640.1(5)$ Å^3, $D_m = 1.430$ g cm^{-3}, $Z = 4$, $D_c = 1.433$ g cm^{-3}. Intensity data were measured in the $\theta/2\theta$ scan mode on a Syntex $P2_1$ diffractometer, using graphite-monochromatized MoKα radiation. Merging of the symmetry-related reflexions led to 1171 independent observations. The final refinement was by full-matrix least-squares techniques, with the heavy atoms treated anisotropically and the hydrogen atoms isotropically, and led to a final R value of 0.044. Lists of atomic parameters and structure factors are available from the authors on request.

* Reprint requests to Dr. A. Domenicano at the Istituto di Chimica Farmaceutica e Tossicologica, Università di Roma, I-00185 Roma, Italy.

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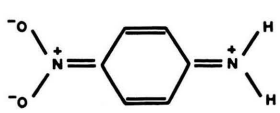
Results and Discussion

When looking at the effect of through-conjugation on the molecular structure of *p*-nitroaniline one should ideally compare this molecule with aniline and nitrobenzene. The molecular structure of aniline is known through an accurate study by microwave spectroscopy [5]; that of nitrobenzene, however, is not yet known with sufficient accuracy (a critical discussion of the present knowledge on the molecular structure of nitrobenzene is given by Di Rienzo, Domenicano and Riva di Sanseverino [6]). Here the comparison will involve *p*-nitrobenzoic acid instead of nitrobenzene.

The choice of *p*-nitrobenzoic acid is dictated by several reasons. Firstly, the –COOH group is known to cause only minor changes in the geometry of the benzene ring [3, 7]. Secondly, cooperative interactions are not expected to occur between –COOH and $-NO_2$, since both groups are π-acceptors. Thirdly, the geometries of both *p*-nitrobenzoic acid [8] and *p*-nitroaniline have been determined in this Laboratory using the same experimental and computational techniques; this makes the comparison especially significant.

The molecular geometry of *p*-nitroaniline is compared in Fig. 1 with those of aniline and *p*-nitrobenzoic acid. The effects of through-conjugation are clearly seen throughout the heavy-atom skeleton of the molecule. The following features are consistent with a substantial contribution of the quinonoid canonical form (I), the two substituents being equally involved in the cooperative interaction:



(I)

(i) The C1–C2 and C1–C6 bonds are 0.009–0.010 Å longer than in aniline (the actual difference may be slightly larger, since aromatic C–C bond distances determined by X-ray crystallography tend to be systematically shorter than those determined by gas-phase techniques).

(ii) The C2–C3 and C5–C6 bonds are shorter than in aniline and *p*-nitrobenzoic acid, by 0.026–0.028 Å and 0.021–0.023 Å, respectively.

(iii) The C3–C4 and C4–C5 bonds are 0.008–0.011 Å longer than in *p*-nitrobenzoic acid.

(iv) The C–NH_2 bond is 0.047 Å shorter than in aniline.

(v) The C–NO_2 bond is 0.041 Å shorter than in *p*-nitrobenzoic acid.

(vi) The average length of the two N–O bonds is 0.010 Å greater than in *p*-nitrobenzoic acid (the slight difference in length between N2–O1 and N2–O2 is consistent with their being involved in hydrogen bonds of different strengths).

(vii) The O–N–O angle is 2.7° smaller than in *p*-nitrobenzoic acid.

(viii) The plane of the –NH_2 substituent makes an angle of 7° with the plane of the benzene ring (the corresponding angle in aniline is 37.5°).

(ix) The plane of the –NO_2 substituent makes an angle of 1.9° with the plane of the benzene ring (the corresponding angle in *p*-nitrobenzoic acid is 13.7°).

A more subtle effect occurs at the internal angles of the benzene ring. In a monosubstituted benzene derivative these angles are generally different from 120°, the differences ($\Delta\alpha = \alpha - 120°$; $\Delta\beta = \beta - 120°$; $\Delta\gamma = \gamma - 120°$; $\Delta\delta = \delta - 120°$) being related to the electronic properties of the substituent [2]. Values of the 'angular substituent parameters' Δa, $\Delta\beta$, $\Delta\gamma$ and $\Delta\delta$ have recently been presented by Domenicano and Murray-Rust [3] for 21 functional groups; they have been derived by linear regression from many accurate structural data on monosubstituted and *para*-disubstituted benzene derivatives, assuming additivity of substituent effects. A slightly different set of parameters was presented later by Norrestam and Schepper [9] for 14 functional groups. Angular substituent parameters may be successfully used to predict molecular geometries of other, even highly substituted, benzene derivatives. In the case of *p*-nitroaniline, by superimposing independent angular distortions from the –NH_2 and –NO_2 groups, the internal angles of the ring at atoms C1 and C4 are predicted to be somewhat larger than the present experimental values (Table I). The deviations from the models based on additive angular distortions are relatively

Tab. I. Internal angles of the benzene ring at atoms C1 and C4 in *p*-nitroaniline: predicted *vs* experimental values (°).

Angles	Predicted values			Experimental values
	a	b	c	d
C2–C1–C6	120.1	119.2	119.2	118.4
C3–C4–C5	122.2	121.6	122.0	120.9

[a] From the internal angles of the ring in aniline and *p*-nitrobenzoic acid, as given in Fig. 1.
[b] From the empirical angular parameters of Domenicano and Murray-Rust [3].
[c] From the empirical angular parameters of Norrestam and Schepper [9].
[d] This work. Estimated standard deviations are 0.15°.

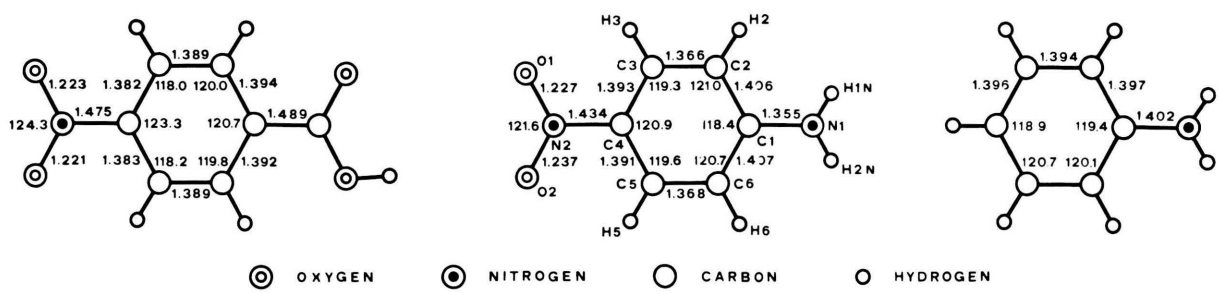


Fig. 1. Molecular geometries of *p*-nitrobenzoic acid (further refinement of the crystal structure, based on the X-ray data of Colapietro and Domenicano [8]), *p*-nitroaniline (this work) and aniline (Lister *et al.* [5]). Bond lengths are given in Å, angles in degrees; estimated standard deviations are 0.002 Å and 0.2° or less.

small (1–2°), but certainly significant. According to the VSEPR model [10], the decrease of the internal angles at atoms C1 and C4 is again consistent with the cooperative interaction between the $-NH_2$ and $-NO_2$ substituents, as depicted by the canonical form (I).

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