Crystallographic Studies of Intra- and Inter-molecular Interactions. Crystal and Molecular Structure of *N,N*-Dimethyl-4-nitro-3,5-xylidine. Structural Evidence against the Classical Through-resonance Concept in *p*-Nitroaniline and Derivatives

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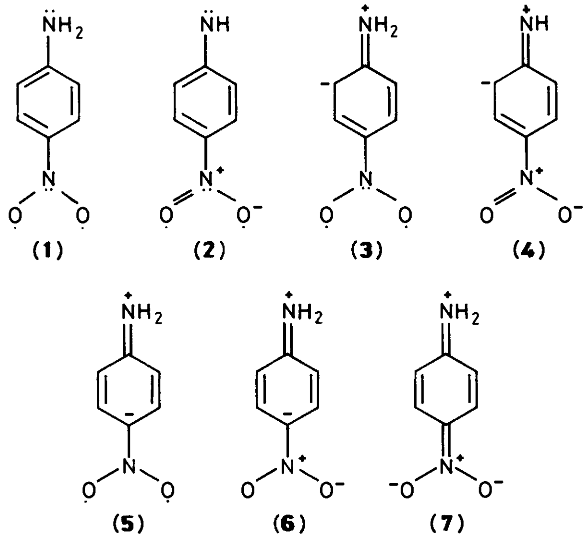
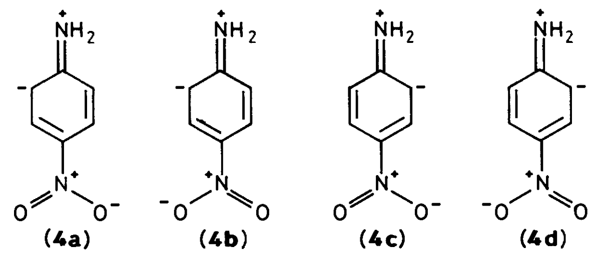
An analysis of the geometry of *N,N*-dimethyl-4-nitroaniline and its 3,5- and 2,6-dimethyl derivatives presents structural evidence against the classical concept of *through-resonance* (through-conjugation), according to which the most important contribution is the quinoid structure with full charge transfer from the amine to the nitro group. Application of the HOSE model gives results which are in line with calculations performed by Hiberty and Ohanessian on *p*-nitroaniline.

For a long time the interactions between the substituents in *p*-nitroaniline, and related π-electron systems, have been described in terms of intramolecular charge transfer from electron-donating substituents to the electron-accepting substituents[1,2] *i.e.* the dominant contribution of structure (**7**) (Scheme 1) has been postulated. This kind of interaction is often named as the through-conjugation[3] or through-resonance[4] effect and sometimes as a π-electron co-operative effect.[3] The theory above appeared many years ago in order to describe the unusual reactivity (and several other physicochemical properties) of this kind of system, requiring the introduction of additional scales of substituent constant (σ^-,σ^+).[5] Early[6] as well as recent[3] structural studies on *p*-nitroaniline have reached similar conclusions. This classical interpretation has been criticized in the last decade on the basis of quantum chemical calculations[4,7,8] as well as gas phase measurements on the acid–base equilibria of the related systems.[7] Moreover, an analysis of the energy of the isodesmic reaction,[9] or the macroincremenation reaction in the case of calorimetric data[10] seems also to weaken the old interpretation. From a structural point of view, the paper on the VB description of *p*-nitroaniline[4] is of great interest. Out of seven main resonance structures (Scheme 1) contributing to the description of *p*-nitroaniline, structure (**7**) is the least important. All these structures should be understood as 'symmetrized',[4] so structure (**1**), for example, includes all possible neutral arrangements of the ring, *i.e.* two Kékulé and three Dewar structures whereas structure (**4**) combines the four structures (**4a**–**d**) (Scheme 2). The calculated weightings of resonance structures (**1**)–(**7**) depend on the level of calculations, but the ratio between weightings [(**7**):(**6**) + (**5**)] is always *ca.* 1:10, or even less. This means that the partial through-resonance effect (**5**) + (**6**) is ten or more times stronger than the full through-resonance effect (**7**). This result is in line with relatively low values of net π-electron population (based on Mulliken analysis):[11] the charge transfer from the NH_2 to NO_2 group equals[4] only 0.037e, which is in agreement with earlier calculations of this type.[12,13] This is of great importance for an interpretation of the relatively large dipole moment of *p*-nitroaniline. Namely, it means that it is not necessary to invoke the high weighting of structure (**7**) to explain this phenomenon, since the partial charge transfer from NH_2 to the ring is manifested in a very strong alternation in net π-electron charge at the ring carbon atoms:[4] 1.155 e at the *para*-position, 0.935 e at the *meta*, 1.104 e at the *ortho*, and 0.896 e at the position *ipso* to the amine group. These results evidently cast doubts on the classical interpretation of through-resonance in *p*-nitroaniline in which a great weight of structure (**7**) is required.



Scheme 1.



Scheme 2.

The aim of this paper is to provide structural support for rationalization against the classical view of the through-resonance effect. An analysis of carefully determined geometries of *N,N*-diethyl-*p*-nitroaniline[14] (hereafter abbreviated DPNA), *N,N*-dimethyl-4-nitro-2,6-xylidine[15] (2,6-DNXy), and *N,N*-dimethyl-4-nitro-3,5-xylidine (this work; 3,5-DNXy) will serve for this purpose. *N,N*-Dialkyl derivatives have been chosen

Table 1. Positional parameters and their estimated standard deviations.

Atom	x	y	z
C(1)	0.117 1(2)	0.421 2(2)	0.635 5(2)
C(2)	0.247 3(2)	0.414 3(2)	0.571 0(2)
C(3)	0.252 1(2)	0.336 8(2)	0.474 9(2)
C(4)	0.124 3(2)	0.261 0(2)	0.445 5(2)
C(5)	−0.004 6(2)	0.260 5(2)	0.510 6(2)
C(6)	−0.007 8(2)	0.341 5(2)	0.603 4(2)
N(1)	0.110 6(2)	0.501 8(1)	0.725 2(2)
C(7)	0.241 1(3)	0.582 6(2)	0.759 5(2)
C(8)	−0.013 2(3)	0.503 0(2)	0.802 1(2)
C(9)	−0.144 7(2)	0.179 0(2)	0.479 8(2)
C(10)	0.398 6(3)	0.334 7(2)	0.411 8(2)
N(2)	0.126 2(2)	0.179 4(1)	0.343 3(2)
O(1)	0.108 6(2)	0.083 7(1)	0.369 5(2)
O(2)	0.145 8(2)	0.201 1(1)	0.233 5(1)

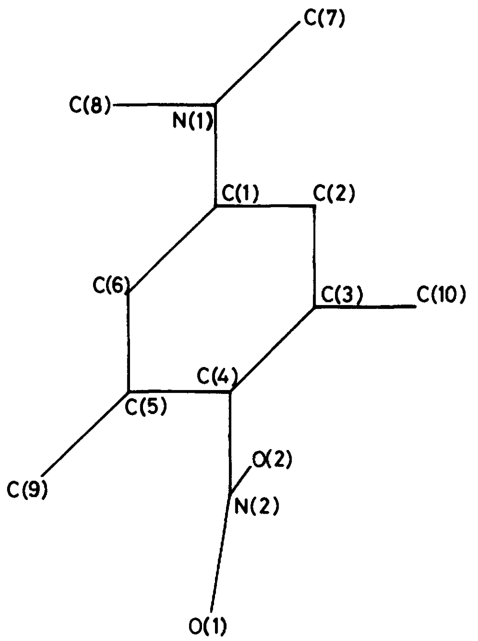


Figure 1. Atom numbering and projection of the molecule along the c axis of the elementary cell.

because of their greater electron-donating power over NH_2, in addition to the better defined geometry of the $N(Alk)_2$ plane, as compared with NH_2, in X-ray diffraction measurements.

Experimental

Crystal Data.—Crystals of *N,N*-dimethyl-4-nitro-3,5-xylidine, $C_{10}H_{14}N_2O_2$, were grown from ethanol solutions; an orange prismatic crystal with dimensions *ca.* 0.3 × 0.3 × 0.25 mm was mounted on a CAD-4 single crystal diffractometer. Monoclinic, $a = 8.338(2)$, $b = 12.308(4)$, $c = 10.221(1)$ Å, $\beta = 104.02(1)°$, $V = 1\,107.7$ Å^3, $Z = 4$. $M_r = 194.234$, $D_m = 1.254(5)$, $D_x = 1.268(10)$ g cm^{-3}; λ(Cu-K_α) = 1.541 84 Å; μ(Cu-K_α) = 6.952 cm^{-1}, $F(000) = 416$; $T = 297 \pm 1$ K; final R = 0.047 for 1 404 observed intensities. Cell constants were determined by a least-squares treatment of 25 reflections of θ range 6.5–36.0°. Systematic absences: $h0l$, $h + l$ odd, and $0k0$, k odd lead to $P2_1/n$ space group. Intensities were collected at 297 ± 1 K using Cu-K_α radiation monochromatized by graphite up to 2θ angle 120.0° ($-9 \leqslant h \leqslant 0$; $-13 \leqslant k \leqslant 0$; $-11 \leqslant l \leqslant 11$), $\omega - 2\theta$ scan mode was performed. No significant variation for three standard reflections was observed. 1 709 Unique reflections were measured, of which 1 404 were classified as applying the criterion $I_0 \geqslant 3\sigma(I)$. Corrections for Lorentz-polarization effects but not for absorption or extinction were performed. The structure was solved by use of routine application of MULTAN-80.[16] An E-map gave positions of all 14 non-hydrogen atoms. Isotropic refinement in two cycles led to $R = 0.147$. Full-matrix anisotropic refinement with location of all H-atoms and use of weightings [$w_i = \sigma^{-2}(F_i)$] reduced R to 0.047 and wR to 0.051. The number of reflections per refined parameter was 8.3; $(\Delta/\sigma)_{max.}$ in the final cycle was 0.31 with average value 0.025. The peaks in the final difference Fourier map ranged from −0.198 to 0.221 e Å^{-3}.

Results and Discussion

Table 1 contains final atom parameters and Figure 1 presents the atom numbering of 3,5-DNXy and a spatial view along the c axis of the elementary cell. In order to facilitate the analysis described in the introduction, mean values of structural parameters (CN and endocyclic bond lengths and angles) of DPNA,[14] 2,6-DNXy,[15] and 3,5-DNXy (this work) are presented in Table 2. The next step is a detailed analysis of the differences between the respective structural parameters of the molecules in question.

Analysis of Bond Lengths and Bond Angles.—From the study of Hiberty and Ohanessian[4] it follows that the C(1)–N(amine) bond lengths should be much more sensitive to substitution by methyl groups at the *ortho* position than at the C(4)–N(nitro) bond. This is due to the higher weighting given to structures with a double-bond character in the case of the C(1)–N(amine) bond; the ratio[4] [%C=N(amine)] : [%C=N(nitro)] depends on the basis set applied but is always >14:1. Table 3 gathers together the differences between respective bond lengths (averaged structures, assumed C_{2v} symmetry) in DPNA, 2,6- and 3,5-DNXy expressed both in pm and in units of estimated standard deviation, σ. If the difference is greater than 3σ then the difference is statistically significant. It is immediately clear that the differences between 3,5-DNXy and DPNA are low and statistically insignificant (the greatest difference for C–C bond lengths is 2.8σ). In contrast, the difference in bond lengths between 2,6-DNXy and DPNA is significant, the lowest [for C(2)–C(3)] being 3.0σ. Thus we may conclude: dimethyl substition in both the 2,6- and 3,5-positions of DPNA results in a considerable dihedral angle between the planes of the amino and nitro groups and that of the ring, equal[15] to 60.4 and 50.6(2)°, respectively. Only in the case of 2,6-substitution *i.e.* when the $NAlk_2$ group is out of the ring plane are the consequences in geometry (bond lengths) significant.

Thus the resonance effect from the $N(Alk)_2$ group to the ring is of great importance whereas the electron-withdrawing property of NO_2 is of less importance as far as the π-electron charge gransfer to this group is concerned, *i.e.*. the dominant role of structure (7) is assumed. This conclusion is in line with earlier finding by Exner[17,18] that the assumed conjugation of opposite substituents through the benzene ring is merely conjugation of the donating substituent with the benzene π-systems, while the accepting substituent acts chiefly by its inductive effect.

Application of substituent angular parameters[19–21] permits a study of the non-additivity of substituent effects on angles in the ring.[3,22–26] Table 2 presents both determined and calculated (in parentheses) valance angles. The non-additivity parameter calculated for DPNA, 2,6-, and 3,5-DNXy reads 0.83, 0.45, and 1.98°, respectively. It is immediately clear that in the first two

Table 2. Summary of bond angles and bond lengths determined by *X*-ray analysis; bond angles calculated from substituent angular parameters[19–21] and bond angles corrected for libration[a] are given in parentheses. Averaged values given; C_{2v} symmetry assumed.

	DNPA[14] (mean geometry of two independent molecules)	2,6-DNXy[15]	3,5-DNXy (present paper)
Bond length/pm			
C(1)–N(NAlk$_2$)	135.4 (4) (135.9)	139.6(2) (140.2)	136.1(3) (136.7)
C(1)–C(2)	142.0(5) (142.9)	140.6(3) (141.1)	140.7(3) (141.3)
C(2)–C(3)	136.6(5) (137.1)	138.5(4) (138.8)	137.9(3) (138.5)
C(3)–C(4)	138.6(5) (139.6)	137.1(3) (137.7)	139.4(3) (140.1)
C(4)–N(NO$_2$)	143.3(4) (143.8)	146.6(3) (147.3)	145.3(3) (145.9)
Bond angles/°			
C(2)–C(1)–C(6)	116.8(3) (118.0)	120.7(2) (121.2)	117.5(2) (120.0)
C(1)–C(2)–C(3)	121.4(3) (120.9)	118.9(2) (118.8)	122.7(2) (120.8)
C(2)–C(3)–C(4)	120.3(3) (119.5)	119.5(2) (118.5)	118.0(2) (119.7)
C(3)–C(4)–C(5)	120.3 (121.2)	122.6(2) (123.7)	122.5(2) (124.7)

[a] Using the THMB-6 program.[30] [b] Norrestam and Schepper angular parameter[20] used for non-coplanar NO$_2$-groups; others taken from ref. 21.

Table 3. Analysis of differences in bond lengths between DPNA, 2,6-, and 3,5-DNXy. (Data corrected for thermal motion applied).

	Differences[a] between bond lengths/pm and in units of e.s.d.[b] = σ (in parenthesis)				
Molecules compared	C(1)–N (am)	C(1)–C(2)	C(2)–C(3)	C(3)–3(4)	C(4)–N (nitro)
2.6-DNXy	4.3	−1.9	+1.9	−1.9	3.5
and DNPA	(9.6)	(−3.1)	(3.0)	(−3.3)	(7.0)
3,5-DNXy	0.8	−1.6	1.4	0.5	2.1
and DPNA	(1.6)	(−2.8)	(2.4)	(0.7)	(4.2)

[a] Differences obtained by subtraction of the bond lengths in 2,6- and 3,5-DNXy from those in DPNA. [b] For the difference, $\sigma = (\sigma_1^2 + \sigma_1^2)^{\frac{1}{2}}$.

$$\mathrm{NAP} = \sum_{i=1}^{6} \left|\varphi_{\mathrm{calc}.i} - \varphi_{\mathrm{obs}.i}\right| \frac{1}{6}$$

cases deformations are similar and not too large, at the limit of significance, whereas for 3,5-DNXy the non-additivity effect is significantly greater. In DPNA both angles at *ipso* carbon atoms are significantly distorted from the value predicted by the additivity rule; both values are decreased to lower values by 1.2°. This finding is in agreement with our earlier[26] study on the substituent effects on angular distortion in the ring in *p*-(*N*,*N*-dimethyl)aminobenzoic acid, for which Δ values ar 1.3 and 1.2°. It is quite common that an increased weighting of partial quinoid structures (**5**) and (**6**) causes this kind of effect, but a simple rationalization is difficult.

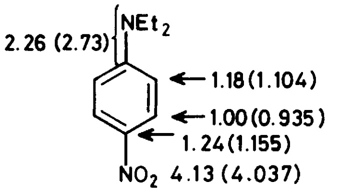


Figure 2. Net π-electron population, from a Mulliken population analysis, of the MOs for *p*-nitroaniline[4] (in parentheses) and estimated by use of the HOSE-model,[27] for *N*,*N*-diethyl-*p*-nitroaniline (geometry taken from ref. 14).

Table 4 Weighting (in %) of the canonical structures (**1**)–(**7**) calculated by means of the HOSE-model[24] for DPNA, and 2,6-, and 3,5-DHXy.

Canonical structures	3,5-DNXy		2,6-DNXy		DPNA[a]	
(**1**) and (**2**)	31.5		41.1		25.2 28.0	
(**3**) and (**4**) (symmetrized)	36.4	57.2	33.1	49.6	36.7 36.7	60.7
(**5**) and (**6**)	20.8		16.5		25.4 22.7	
(**7**)	11.4		9.3		12.7 12.6	

[a] Two independent molecules in asymetric unit.

Analysis of Resonance Structure Weightings.—When the precise geometry of the π-electron system is known it is possible to estimate the canonical structure distribution by using the HOSE-model.[27] It has recently been applied in many cases[24–29] as a reliable tool to translate the geometry of these systems into the language of resonance structure contributions. Application of the HOSE-model to structures (**1**)–(**7**), taking into account the geometries of DPNA, 2,6- and 3,5-DNXy, led to the results summarized in Table 4. Again it is clear that there is a substantial similarity between 3,5-DNXy and DPNA and a great disparity with 2,6-DNXy. A consideration of the mono-ionic quinoid structure distribution for (**3**),(**4**) and (**5**),(**6**) reveals that the sum of their weightings is 57.2 and 60.7% for 3.5-DNXy and DPNA and only 49.6% for 2,6-DNXy. Evidently non-coplanarity of the NO$_2$ group with the ring, caused by the 3,5-methyl groups, does not disturb π-electron delocalization in such a way as to eliminate the similarity between 3,5-DNXy and DPNA. In contrast, the methyl groups in the 2,6-position, and consequent noncoplanarity of the NAlk$_2$ group with the ring, causes a dramatic effect in π-electron delocalization; a significant decrease of the weighting of mono-ionic structures (**3**) and (**6**) is observed. The results presented in Table 4 confirm quantitatively the results of Ohanessian and Hiberty.[4]* Nevertheless, our results give full support to the theory that significant contributions are made by structures (**3**)–(**6**), with partial charge transfer from the NAlk$_2$-group to the *ortho*- and *para*-positions in the ring, and a relatively small contribution of the structure with full charge transfer from the NAlk$_2$ group to NO$_2$ [structure (**7**)]. Finally, a direct comparison of the net π-electron populations calculated by Hiberty and Ohanessian[4] with those calculated from the weightings for structures (**1**)–(**7**) (Scheme 1) is shown in Figure 2. The calculations were carried out assuming unit charges (positive and negative) localized in the positions shown in structures (**3**)–(**7**); (**1**) and (**2**) have all atoms in the structure fully neutral. Taking into account the very rough approximation within the HOSE-model, as well as the assumptions made in the calculation of charges (too few structures taken into account), it seems that the agreement between theoretical[4] and empirical π-electron population in DPNA is encouraging.

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* We obtained a difference in the ratio (**3**)/[(**7**)/(**7**)] for DPNA of *ca.* 5; *cf. ca.* 15 obtained by Hiberty and Ohanessian.[4]

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