Structure of 2-Chloro-4-nitro-*N*-(2-nitrovinyl)aniline

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Abstract. $C_8H_6ClN_3O_4$, $M_r = 243 \cdot 608$, monoclinic, $P2_1/c$ (systematic absences $h0l$: $l = 2n + 1$, $0k0$: $k = 2n + 1$), $a = 8 \cdot 7368$ (8), $b = 9 \cdot 2068$ (6), $c = 13 \cdot 655$ (2) Å, $\beta = 116 \cdot 705$ (7)°, $V = 981 \cdot 2$ (5) Å^3, $F(000) = 496$, $Z = 4$, $D_m = 1 \cdot 65$, $D_x = 1 \cdot 648$ Mg m^{-3}. Among the 2128 unique reflections, 1389 were considered observed. The final R value $= 0 \cdot 055$. The molecules of the crystal structure are nearly planar with delocalization of π electrons in the nitrovinyl moiety. An intramolecular hydrogen bond stabilizes the planar configuration. A comparison between observed and calculated endocyclic angles gave some information about the charge distribution in the nitrovinyl moiety.

Introduction. This structure determination is part of a study of aliphatic nitro compounds, nitronate salts and tautomeric forms of these compounds. Meister (1907) has described some Schiff bases with the general formula $R-(C_6H_4)-N=CH-CH_2-NO_2$. The title compound [alias $RR'-(C_6H_3)-N=CH-CH_2-NO_2$, 2-chloro-4-nitro-*N*-(2-nitroethylidene)aniline] has been investigated as a representative of this type of compound, especially to elucidate the structure of the nitro-Schiff-base moiety. It was prepared according to Meister (1907). Suitable crystals separated from a hot 2/1 solution of nitrobenzene/chloroform.

Unit-cell dimensions were determined by least-squares refinement of data from a Guinier powder photograph taken with Cu $K\alpha_1$ radiation ($\lambda = 1 \cdot 54056$ Å) and calibrated with silicon as an internal standard.

A single crystal with dimensions $0 \cdot 3 \times 0 \cdot 4 \times 0 \cdot 7$ mm was chosen for data collection on an Enraf–Nonius CAD-3 diffractometer using graphite-monochromatized Mo $K\alpha$ radiation. All reflections $+h$, $+k$, $\pm l$ in the range $2 \cdot 8° < \theta < 27°$ were measured with the ω-scan technique. A reflection was designated unobserved if $I < 2 \cdot 2\sigma(I)$. With this criterion, 1389 out of 2128 measured reflections were regarded as observed. One of the three reflections $\overline{3}08$, $60\overline{2}$ and 040 was monitored every fifteen reflections. Lorentz and polarization corrections were applied, but no extinction or absorption corrections were made.

The structure was solved by direct methods using XRAY 76 (Stewart, 1976) and all subsequent calculations were performed with this program system. Atomic scattering factors for the neutral atoms were taken from *International Tables for X-ray Crystallography* (1974). In the full-matrix minimization of $\sum w(|F_o| - |F_c|)^2$ the weighting function was $w = 1 \cdot 0/\{1 + [(F_o - b)/a]^2\}$ with $a = 40 \cdot 0$ and $b = 35 \cdot 0$, as this choice gave an acceptable weight analysis. Contributions from unobserved reflections were included if $F_c > F_o$. From a difference Fourier map all the H atoms were located, and they were given the same isotropic temperature factors as the atoms to which they are bonded. The refinement was performed with fixed H temperature parameters; anisotropic thermal parameters were used for all other atoms. The final residual

Table 1. *Fractional coordinates* ($\times 10^4$, *for* H $\times 10^3$) *and isotropic thermal parameters* (Å^2)

B_{eq} is equivalent to the anisotropic parameters actually refined for non-H atoms (Hamilton, 1959).

	x	y	z	B_{eq}/B
Cl	2362·3 (5)	6599·4 (4)	4455·0 (4)	4·74 (3)
O(41)	4450 (2)	1360 (2)	5771 (1)	6·8 (1)
O(42)	2386 (2)	−112 (1)	4883 (1)	8·5 (2)
O(81)	−1753 (2)	8754 (1)	2998 (1)	5·3 (1)
O(82)	−4297 (2)	9584 (2)	1964 (1)	6·9 (1)
N(1)	−1244 (2)	5921 (1)	3147 (1)	3·9 (1)
N(4)	2970 (2)	1108 (2)	5120 (1)	5·5 (1)
N(8)	−3297 (2)	8547 (2)	2358 (1)	4·9 (1)
C(1)	−253 (2)	4680 (2)	3598 (1)	3·6 (1)
C(2)	1520 (2)	4863 (2)	4272 (1)	3·7 (1)
C(3)	2571 (2)	3709 (2)	4778 (1)	3·9 (1)
C(4)	1857 (2)	2347 (2)	4583 (1)	4·4 (1)
C(5)	128 (2)	2098 (2)	3916 (1)	4·9 (1)
C(6)	−919 (2)	3272 (2)	3424 (1)	4·6 (1)
C(7)	−2929 (2)	5946 (2)	2458 (1)	4·2 (1)
C(8)	−3910 (2)	7144 (2)	2066 (1)	4·7 (1)
H(1)	−58 (5)	696 (4)	338 (3)	4·5
H(3)	397 (5)	399 (4)	541 (3)	4·2
H(5)	−32 (5)	96 (5)	379 (3)	5·3
H(6)	−215 (5)	317 (5)	283 (3)	5·1
H(7)	−342 (5)	497 (4)	207 (3)	4·8
H(8)	−528 (5)	705 (5)	131 (3)	5·5

$(R = \sum ||F_o| - |F_c||/\sum |F_o|)$ was 0·055. The atomic parameters are given in Table 1.*

Discussion. To analyze the planarity of the title compound, it has been divided into three molecular fragments: (I) the Schiff-base function [N(1),C(7),C(8),N(8),O(81),O(82)]; (II) the benzene ring [C(1)—C(6)]; and (III) the aromatic nitro group [N(4),O(41),O(42)] (Fig. 1). The least-squares planes defined by (I) and (II) show no significant deviation from planarity, as the maximum deviations are 0·008 (6) Å in (I) and 0·0011 (7) Å in (II). The planar configuration of (I) is stabilized by an intramolecular hydrogen bond, N(1)—H(1)···O(81) [N(1)—O(81) 2·638 (3) Å]. The aromatic nitro group (III) and the Schiff-base moiety (I) are slightly out of plane with the benzene ring (II). The dihedral angles are (II)/(III) 6·2 (7)° and (I)/(II) 7·6 (9)°. The (I)/(II) dihedral angle is very small compared to the corresponding value of 50·2° quoted for the related compound *N*-(*p*-methylbenzylidene)-*p*-nitroaniline (Bürgi & Dunitz, 1970).

The bond angles around each of the atoms C(7) and C(8) indicate a rather trigonal symmetry. The bond
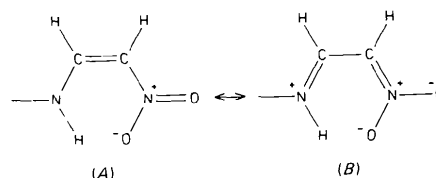
* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36738 (22 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
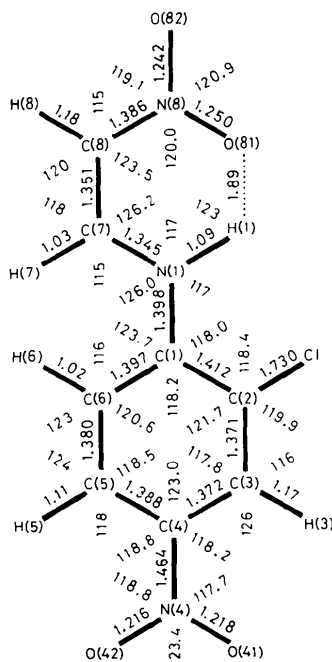

Fig. 1. Bond distances (Å), bond angles (°) and the atom numbering scheme for the title compound. The estimated standard deviations are 0·003 Å and 0·2° when no H atoms are involved, otherwise 0·04 Å and 2°.

Fig. 2. Mesomeric structures showing delocalization of π electrons in the Schiff-base moiety.

Table 2. *Endocyclic angles* (°) *in benzene ring* (II) *compared with angles calculated from deformation parameters given by Norrestam & Schepper* (1981, Table 4)

	Observed values, benzene ring (II)	Calculated values; substituents: $-NH_2,-Cl,-NO_2$	Calculated values; substituents: $-NH_3^+,-Cl,-NO_2$
C(1)	118·2 (2)	118·2 (2)	121·6 (3)
C(2)	121·7 (2)	121·6 (2)	120·0 (2)
C(3)	117·8 (2)	118·0 (2)	117·4 (2)
C(4)	123·0 (2)	122·6 (2)	123·5 (3)
C(5)	118·5 (2)	118·6 (2)	118·0 (2)
C(6)	120·6 (2)	121·0 (2)	119·4 (2)

distance C(7)—C(8) is 1·351 (3) Å, near to the expected value of 1·337 (6) Å for a C—C double bond (*International Tables for X-ray Crystallography*, 1962); thus the atoms C(7) and C(8) can be considered as sp^2 hybridized.

C(8)—N(8) 1·386 (3), N(8)—O(81) 1·250 (3) and N(8)—O(82) 1·242 (3) Å are comparable to the corresponding bond distances [1·397 (4), 1·249 (4), 1·244 (3) Å] in nitromalonamide (Simonsen & Thorup, 1979). The C—N bond distances in *N*-benzylideneaniline have the values 1·460 (3) and 1·237 (3) Å (Bürgi & Dunitz, 1970); N(1)—C(7) 1·345 (3) Å is between these values, indicating partial double-bond character for N(1)—C(7). Thus the structure of (I) can be represented as a resonance hybrid of the mesomeric forms (*A*) and (*B*) (Fig. 2) by analogy with the structure of *trans-N,N*-dimethyl-2-nitroethenamine (Hazell & Mukhopadhyay, 1980). Norrestam & Schepper (1981) have described how to predict the geometries of aromatic six-membered rings using some substituent parameters. The endocyclic bond angles in benzene ring (II) have been calculated by this method and compared with the observed values (Table 2). This supports the view that the mesomeric form (*A*) (Fig. 2) must predominate. The molecules in the crystal structure stack nearly parallel to the planes (204) (Fig. 3) in agreement with the observation that 204 is the strongest reflection. The, distance Cl(*x,y,z*)—O(42)(*x*, *y* + 1, *z*) of 3·082 (3) Å is slightly shorter than the sum of the van der Waals radii given by Pauling (1970) (Cl 1·80, O 1·40 Å).
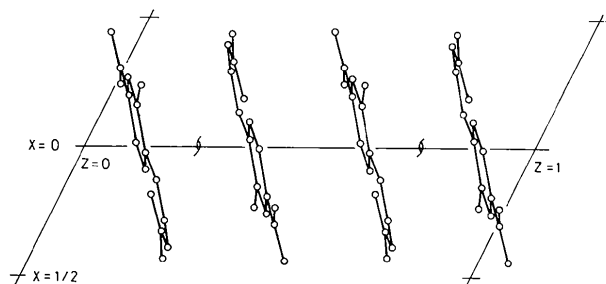
Fig. 3. Projection of the crystal structure down the b axis.

References

BÜRGI, H. B. & DUNITZ, J. D. (1970). Helv. Chim. Acta, 53, 1747–1764.

HAMILTON, W. C. (1959). Acta Cryst. 12, 609–610.

HAZELL, A. & MUKHOPADHYAY, A. (1980). Acta Cryst. B36, 747–748.

International Tables for X-ray Crystallography (1962). Vol. III, p. 276. Birmingham: Kynoch Press.

International Tables for X-ray Crystallography (1974). Vol. IV, pp. 99, 149. Birmingham: Kynoch Press.

MEISTER, W. (1907). Ber. Dtsch. Chem. Ges. 40, 3435–3449.

NORRESTAM, R. & SCHEPPER, L. (1981). Acta Chem. Scand. Ser. A, 35, 91–103.

PAULING, L. (1970). General Chemistry, p. 197. San Francisco: W. H. Freeman.

SIMONSEN, O. & THORUP, N. (1979). Acta Cryst. B35, 432–435.

STEWART, J. M. (1976). The XRAY system. Tech. Rep. TR-446. Computer Science Center, Univ. of Maryland, College Park, Maryland.

(4-Chlorophenoxy)acetic Acid

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Abstract. $C_8H_7ClO_3$, triclinic, $P\bar{1}$, $Z = 2$, $a = 7\cdot108$ (1), $b = 7\cdot407$ (1), $c = 8\cdot1217$ (6) Å, $\alpha = 88\cdot11$ (1), $\beta = 108\cdot24$ (1), $\gamma = 94\cdot05$ (1)°, $V = 405\cdot1$ Å³, $\rho_c = 1\cdot531$, $\rho_m = 1\cdot525$ g cm⁻³, $M_r = 186\cdot6$, m.p. $= 433 \pm 1$ K. The structure was solved by the heavy-atom method and refined by full-matrix least squares to an R value of $0\cdot059$ for 819 observed reflections. The molecules dimerize about a centre of symmetry, as is usual with simple carboxylic acids, and are linked by a pair of hydrogen bonds with O···O $2\cdot610$ (7) Å. A short intermolecular Cl···Cl distance $3\cdot349$ (3) Å was observed.

Introduction. (4-Chlorophenoxy)acetic acid, a potent auxin, was crystallized from methanol by slow evaporation. A crystal of dimensions $0\cdot15 \times 0\cdot45 \times 0\cdot48$ mm was mounted on a Nonius CAD-4 diffractometer and the cell parameters were refined by a least-squares method from the measured angular settings of 24 well centred reflections lying in the θ range 16–44°. Data were collected at room temperature in the ω–2θ scan mode with graphite-monochromatized Cu $K\alpha$ radiation. Three standard reflections, well distributed in reciprocal space, were monitored for every 50 min of data collection and their intensities did not show any systematic change. 1186 independent reflections in the θ range 2–60° were measured and 819 reflections were considered above threshold at the $2\cdot75\sigma(I)$ level of significance. The intensities were corrected for Lorentz and polarization effects, but not for absorption [μ(Cu $K\alpha$) $= 3\cdot95$ mm⁻¹].

The scale factor to place the data on the absolute scale and the overall temperature factor ($B = 2\cdot5$ Å²) were determined from a Wilson plot. The $N(z)$ statistical test indicated a centre of symmetry in the unit cell. The Patterson map was completely interpreted for intramolecular vectors and the Fourier map taken with the Cl position alone ($R = 0\cdot54$) revealed a major fragment of the molecule. One more Fourier synthesis gave the complete molecule ($R = 0\cdot25$). The positions of all H atoms, including the one participating in the dimer formation, were obtained from a difference Fourier map (at $R = 0\cdot09$). Further refinement by