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Synthesis and Crystal Structure of *trans*-2-(2-Chlorophenyl)-1-nitroethylene

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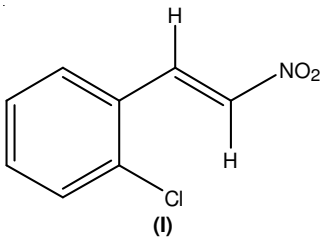
A nitroalkene compound [*trans*-2-(2-chlorophenyl)-1-nitroethylene (**I**)], derived from the condensation of *o*-chlorobenzaladehyde with nitromethane, has been synthesized and structurally characterized by elemental analysis, ^{1}H NMR spectrum and single-crystal X-ray diffraction analysis. Compound (**I**) crystallizes in the monoclinic, space group P2(1)/n with a = 4.7364(9), b = 11.908(2), c = 14.914(3) Å, α = 90, β = 91.21(3), γ = 90º, V = 841.0(3) Å^3, Z = 4, $C_8H_6ClNO_2$, M_r = 183.59, D_c = 1.450 g/cm^3, $F_{(000)}$ = 376, μ(MoK$_\alpha$) = 0.408 mm^{-1}, the final R_1 = 0.0550 and wR_2 = 0.1430 for 1306 observed reflections [I > 2σ(I)]. In addition, X-ray analysis reveals that both the C-Cl···O short contacts and the π-π stacking interactions are observed in the crystal structure. The two kinds of intermolecular interactions extend the molecules into an infinite three-dimensional network.

Key Words: Nitroalkene, Synthesis, Crystal structure.

INTRODUCTION

The nitroalkene compounds are generally prepared by an aldol type C-C bond formation process, in specific Henry condensation of carbonyl compounds with a nitroalkane to β-nitroalcohol followed by dehydration[1-3]. Most particularly, the reactions of nitroalkenes and their derivatives have attracted much attention because from a synthetic point of view these compounds are recognized as one of the most valuable building blocks in the organic synthesis. On the one hand, the nitro functionality with the multiple reactivity undergoes a variety of useful synthetic transformations, *e.g.*, conversion to 1,3-dipoles, oxidation to carboxylic acids and reduction to hydroxylamines[4-6]. On the other hand, the C=C double bond activated by the nitro group is an excellent electrophile and therefore Michel addition reactions of various nucleophiles with nitroalkenes are widely documented in the literatures[7-11].

In continuation of the studies on such important compounds, we herein report the synthesis and crystal structure of an aromatic nitroalkene compound, *trans*-2-(2-chlorophenyl)-1-nitroethylene (**I**) (Fig. 1).



(I)

Fig. 1

EXPERIMENTAL

All the chemicals were of reagent grade and used without further purification. Melting points were determined on a YRT-3 apparatus and are uncorrected. Elemental analyses for carbon, hydrogen and nitrogen were performed on a Perkin-Elmer 240C analyzer. ^{1}H NMR spectrum was obtained on a Bruker AV-400 instrument (400 MHz) using TMS as an internal standard and $CDCl_3$ as solvent.

Synthetic procedure: *o*-Chlorobenzaladehyde (1.41 g, 10.0 mmol), nitromethane (1.36 mL, 25.0 mmol) and methanol (4.20 mL) are added to a three-neck round bottomed flask and cooled to 0 ºC. While maintaining the internal reaction temperature between 0-15 ºC, aqueous 1 M NaOH (25.00 mL, 25.0 mmol) is added by an addition funnel and the mixture is stirred for 15 min. Ice water mixture (17.50 mL) is added and the reaction is stirred at 0 ºC for 0.5 h. The reaction mixture is slowly added to aqueous 8 M HCl (16.80 mL, 134.0 mmol) and allowed to stir until the reaction is confirmed complete by TLC. After the reaction mixture is filtered and recrystallized from ethanol, the title compound (**I**) was afforded as the light-yellow solid (1.83 g, yield of 53 %). m.p. 45-46 ºC. Anal.

calcd. (%) for $C_8H_6ClNO_2$: C, 53.34, H, 3.29, N, 7.63. Found (%): C, 52.51, H, 3.53, N, 7.43. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ/ppm: 8.28 (d, *J* = 13.6 Hz, 1H, =C*H*), 7.83 (d, *J* = 13.6 Hz, 1H, =CH), 7.56 (m, 2H, PhH), 7.32 (m, 2H, PhH).

Crystal structure determination: Single crystals of the title compound (**I**) suitable for X-ray diffraction analysis were grown by slow evaporation of the CH_2Cl_2/hexane solution at 5 ºC. The single crystal with dimensions of 0.25 mm × 0.21 mm × 0.16 mm for (**I**) was mounted on a Rigaku Saturn CCD area deterctor. Data were collected at 293(2) K for (**I**) by using a graphite monochromator with MoK_α radiation (λ = 0.71073 Å). A total of 8378 reflections were collected in the range of $2.19^o \leq \theta \leq 27.88^o$ by using an the ω-φ scanning mode, of which 1998 were unique with R_{int} = 0.041 and 1306 were observed with $I > 2\sigma(I)$. The structures were solved by direct methods using the SHELXS-97 program[12] and refined by full-matrix least-squares techniques (SHELXL-97)[13] on F^2. Hydrogen atoms were located by using the geometric method. The final R = 0.0550, wR = 0.1603 ($w = 1/[\sigma^2(F_o)^2 + (0.0947P)^2 + 0.0000P]$, where $P = (F_o^2 + 2F_c^2)/3$), S = 0.990, $(\Delta/\sigma)_{max}$ = 0.000, $(\Delta\rho)_{max}$ = 0.218 and $(\Delta\rho)_{min}$ = -0.253 e/Å^3.

RESULTS AND DISCUSSION

The single crystal of the title compound (**I**) was obtained by slow diffusion of *n*-hexane to the dichloromethane solution of the compound, which was crystallized as air-stable brightly-yellow crystals. The elemental analyses and NMR spectrum are in good agreement with the formulae proposed by the X-ray crystallography.

Structure of the title compound (I): Crystallographic and refinement parameters are listed in Table-1. The selected bond lengths and angles are given in Tables 2 and 3. The structure was solved by direct methods. Anisotropic displacement parameters were applied to all nonhydrogen atoms in full-matrix least-square refinements based on F^2. The hydrogen atoms were set in calculated positions with a common fixed isotropic thermal parameter.

The molecular structure of (**I**) is depicted in Fig. 2. The crystal packing diagram of (**I**) is shown in Fig. 3.

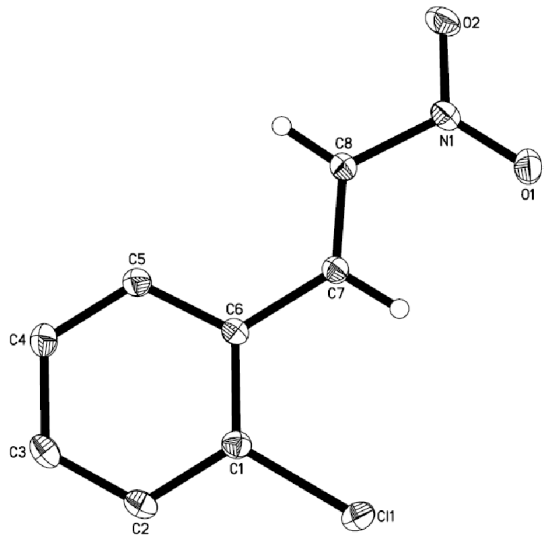


Fig. 2. Molecular structure of (**I**) with 30 % probability thermal ellipsoids

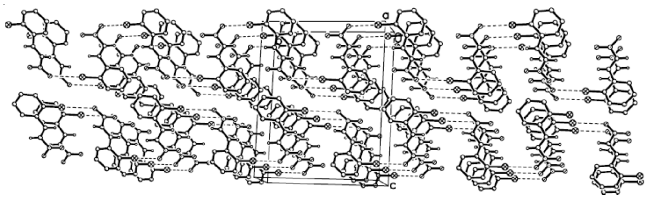


Fig. 3. Crystal packing diagram of (**I**) along the a-axis

TABLE-1
CRYSTAL DATA AND STRUCTURAL REFINEMENT FOR (**I**)

Parameters	Values
Empirical formula	$C_8H_6NO_2Cl$
Formula weight	183.59
Crystal system	Monoclinic
Unit cell dimensions	
a (Å, º)	4.7364(9)
b (Å, º)	b = 11.908(2)
c (Å, º)	c = 14.914(3)
Unit cell angles (º)	
α	90
β	91.21(3)
γ	90
Volume (Å^3)	841.0(3)
Z	4
Temperature (K)	293(2)
Space group	P2(1)/n
Wavelength (Å)	0.71073
Calculated density (g cm^{-3})	1.450
Absorption coefficient μ (mm^{-1})	0.408
$F_{(000)}$	376
Crystal size (mm^3)	0.25 x 0.21 x 0.16
θ range for data collection (º)	2.19 - 27.88
Limiting indices	-6 ⇐ h ⇐ 6, -15 ⇐ k ⇐ 15, -19 ⇐ l ⇐ 19
Reflection collected	8378
Independent reflection	1998 (R_{int} = 0.0408)
Completeness to λ_{max} (%)	99.6
Data/restraints/parameters	1998/0/110
Goodness-of-fit on F^2	0.990
Final R indices [$I > 2\sigma I$)]	R_1 = 0.0550, wR_2 = 0.1430
R indices (all data)	R_1 = 0.0780, wR_2 = 0.1603
Largest diff. peak and hole (e A^{-3})	0.218 and -0.253

TABLE-2
SELECTED BOND LENGTHS (Å) FOR (**I**)

Bonds	Dist.	Bonds	Dist.
O(1)-N(1)	1.214(3)	C(6)-C(7)	1.472(3)
O(2)-N(1)	1.230(2)	C(7)-C(8)	1.296(3)
N(1)-C(8)	1.448(3)	Cl(1)-C(1)	1.733(2)

TABLE-3
SELECTED BOND ANGLES (°) FOR (**I**)

Angles	(º)	Angles	(º)
O(2)-N(1)-O(1)	123.54(19)	C(1)-C(6)-C(7)	120.51(19)
O(1)-N(1)-C(8)	120.29(18)	C(8)-C(7)-C(6)	125.9(2)
O(2)-N(1)-C(8)	116.2(2)	C(7)-C(8)-N(1)	121.3(2)
C(5)-C(6)-C(1)	117.60(18)	C(6)-C(1)-Cl(1)	120.97(16)
C(5)-C(6)-C(7)	121.88(18)	–	–

As depicted in Fig. 2, the title compound (**I**) displays a *trans* configuration about the C=C double bond. The average bond lengths and angles are within normal ranges[14-18]. The C(7)=C(8) bond length is 1.296(3) Å which is a typical double bond, but it is shorter than those observed in the crysta structures

of the reported nitroalkene compounds (1.313-1.328 Å)[16,18]. The C(8)-N(1) bond length (1.448(3) Å) is shorter than the normal C-N single bond (1.47 Å)[19] whereas the C(6)-C(7) bond length (1.472(3) Å) is longer than the normal C-C single bond (1.46 Å)[20].These results indicate that C(7)=C(8) double bond are simultaneously conjugated with the benzene ring and the nitro group[19]. Furthermore, the dihedral angle between the C(7)/C(8)/N(1)/O(1)/O(2) plane (r.m.s deviation 0.0209 Å) and the C(1)-C(6) plane (r.m.s. deviation 0.0026 Å) is 1.8º, which suggests that the nitroethylene moiety is almost planar with the 2-chlorophenyl moiety. In addition, the C(7)-C(8)-N(1) bond angle (121.3(2)°) is different from the C(8)-C(7)-C(6) bond angle (125.9(2)°), probably due to the certain steric repulsion between the chloride atom and the ethylene hydrogen atoms. The N(1)-O(1) bond length (1.214(3) Å) is unequal to the N(1)-O(2) bond length, possibly owing to the weak interaction between O atom of the nitro group and the Cl atom of the 2-chlorophenyl group[14].

As shown in Fig. 3, the ethylene molecules are linked by the C-Cl···O short contacts involving the Cl atom of the 2-chlorophenyl group and the O atom of the nitro group[15], where the distance between the O atom of the nitro group and the Cl atom attached to the 2-chlorophenyl group is 3.100 Å. Furthermore, there are π-π stacking interactions between the benzene rings of two adjacent molecules, in which the two rings are parallel to each other with the centroid-to-centroid separation of 4.736 Å. As a result, the two kinds of intermolecular interactions extend the molecules into an infinite three-dimensional network (Fig. 3).

Conclusion

In summary, the nitroalkene compound [*trans*-2-(2-chlorophenyl)-1-nitroethylene (**I**)] has been synthesized and structurally characterized elemental analysis and ^{1}H NMR spectrum. Particularly, the molecular structure of (**I**) was unequivocally determined by single-crystal X-ray diffraction analysis, in which the C=C double bond is in a *trans* configuration in the solid state. In addition, not only the C-Cl···O short contacts but also the π-π stacking interactions exist in the crystal structure of (**I**). The two kinds of intermolecular interactions link the molecules into an infinite three-dimensional network.

Supplementary data

CCDC-892538 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge *via* http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; or E-mail: deposit@ccdc.cam.ac.uk).

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