



Synthesis and Crystal Structure of *trans*-2-(2,4,6-Trimethylphenyl)-1-Nitroethylene

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A nitroalkene compound, *trans*-2-(2,4,6-trimethylphenyl)-1-nitroethylene [C₁₁H₁₃NO₂ (**I**)] has been synthesized and structurally characterized by elemental analysis, ¹H (¹³C) NMR spectra and single-crystal X-ray diffraction. Compound (**I**) crystallizes in the triclinic, space group P-1 with a = 9.700(5), b = 13.784(7), c = 15.306(8) Å, α = 80.976(15), β = 84.85(2), γ = 86.523(19)°, V = 2010.8(18) Å³, Z = 4, C₂₂H₂₆N₂O₄, M_r = 382.45, D_c = 1.263 g/cm³, F₍₀₀₀₎ = 816, μ (MoKα) = 0.087 mm⁻¹, the final R₁ = 0.0714 and wR₂ = 0.1685 for 4737 observed reflections [I > 2σ(I)]. In addition, X-ray analysis reveals that both the C-H...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, Intermolecular interaction.

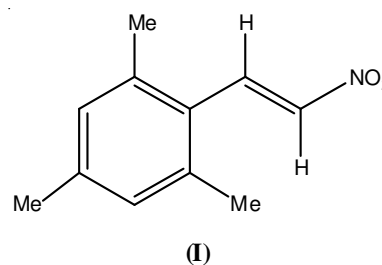
INTRODUCTION

The nitroalkene compounds are commonly synthesized by the dehydration of β-nitroalcohols that are *in situ* prepared by Henry reaction of various aldehydes with a nitroalkane in a basic condition, in which the dehydration of β-nitroalcohols are achieved by a transformation of the hydroxyl group into a good leaving group or simply by heating in an acidic condition^{1,2}. Particularly, the aromatic nitroalkene compounds have been proved to be a significant class of the nitroalkenes, which possess diverse biological activities such as molluscicidal activities^{3,4}, insecticidal activities⁴, antimicrobial activities^{5,6}, anticancer activities⁷ and anti HVI-1 activities⁸ *etc.* Detailed study on the synthesis and structures of such compounds seems very important to better understand the relationship between molecular structures and biological activities.

In view of the above information and as a continuation of our studies on such compounds, we herein report the synthesis and crystal structure of an aromatic nitroalkene compound, *trans*-2-(2,4,6-trimethylphenyl)-1-nitroethylene (**I**) (Scheme-I).

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. ¹H (¹³C) NMR spectra were obtained



(**I**)
Scheme-I

on a Bruker AV-400 instrument (400 MHz) using TMS as an internal standard and CDCl₃ as solvent.

Synthetic procedure: 2,4,6-Trimethylbenzaldehyde (1.48 g, 10.0 mmol), nitromethane (1.36 mL, 25.0 mmol) and methanol (4.20 mL) are added to a 3-neck round bottomed flask and cooled to 0 °C. While maintaining the internal reaction temperature between 0-15 °C, 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 °C for 0.5 h. The reaction mixture is slowly added to aqueous 8M 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**) (0.82 g, 43 %) was obtained as a brightly-yellow solid. m.p. 106-108 °C. Anal. calcd. (%) for C₁₁H₁₃NO₂: C, 69.09, H, 6.85, N, 7.32; Found (%): C, 69.29, H, 6.66, N, 7.19. ¹H NMR (400 MHz,

CDCl₃, TMS) δ /ppm: 8.28 (d, $J = 14.0$ Hz, 1H, =CH), 7.31 (d, $J = 14.0$ Hz, 1H, =CH), 6.95 (s, 2H, PhH), 2.40, 2.31 (2s, 9H, CH₃). ¹³C NMR (100.6 MHz, CDCl₃, TMS) δ /ppm: 140.9, 139.7, 138.5, 136.6, 129.9, 125.8, 21.5, 21.2.

Crystal structure determination: Single crystal of the *trans*-2-(2,4,6-trimethylphenyl)-1-nitroethylene (**I**) suitable for X-ray diffraction analysis was grown by slow evaporation of the CH₂Cl₂/hexane solution at 5 °C. The crystal of (**I**) with dimensions of 0.40 mm × 0.12 mm × 0.10 mm was mounted on a Rigaku Saturn CCD area-detector diffractometer with a graphite-monochromated MoK α radiation ($\lambda = 0.71073$ Å) by using a phi and scan modes at 113(2) K in the range of $1.35^\circ \leq \theta \leq 25.02^\circ$. The crystal belongs to triclinic system with space group P-1 and crystal parameters of $a = 9.700(5)$ Å, $b = 13.784(7)$ Å, $c = 15.306(8)$ Å, $\alpha = 80.976(15)^\circ$, $\beta = 84.85(2)^\circ$, $\gamma = 86.523(19)^\circ$, $V = 2010.8(18)$ Å³, $D_c = 1.263$ g/cm³. The absorption coefficient $\mu = 0.087$ mm⁻¹ and $Z = 4$. The structure was solved by direct methods using the SHELXS-97 program⁹ and refined by full-matrix least-squares techniques on F^2 data using SHELXL-97¹⁰. The empirical absorption corrections were applied to all intensity data. All the H atoms were positioned geometrically and refined using a riding model, with $d(\text{C-H}) = 0.95\text{--}0.98$ Å and $U_{\text{iso}}(\text{H}) = 1.2$ Ueq(C) or 1.5 Ueq(C_{methyl}). The final full-matrix least squares refinement gave $R = 0.0714$, $wR = 0.1685$ ($w = 1/[\sigma^2(F_o)^2 + (0.0800P)^2 + 0.0000P]$, where $P = (F_o^2 + 2F_c^2)/3$), $S = 1.017$, $(\Delta/\sigma)_{\text{max}} = 0.001$, $(\Delta\rho)_{\text{max}} = 0.653$ and $(\Delta\rho)_{\text{min}} = -0.246$ e/Å³.

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 spectra 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. 1. The crystal packing diagram of (**I**) is shown in Fig. 2.

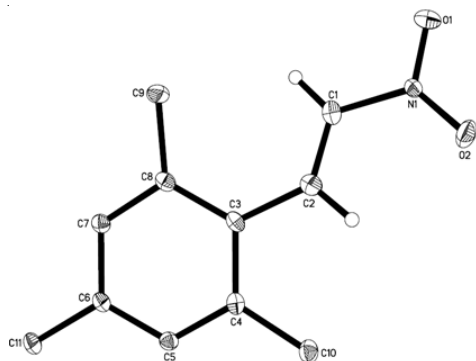


Fig. 1. Molecular structure of (**I**) with 30 % probability thermal ellipsoids

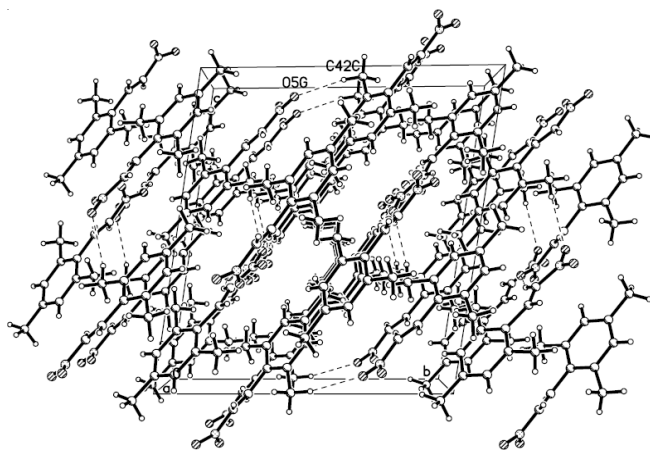


Fig. 2. Crystal packing diagram of (**I**) along the a-axis

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

Items	Values
Empirical formula	C ₂₂ H ₂₆ N ₂ O ₄
Formula weight	382.45
Crystal system	Triclinic
Unit cell dimensions	
a (Å, °)	9.700(5)
b (Å, °)	13.784(7)
c (Å, °)	15.306(8)
Unit cell angles (°)	
α	80.976(15)
β	84.85(2)
γ	86.523(19)
Volume (Å ³)	2010.8(18)
Z	4
Temperature (K)	113(2)
Space group	P-1
Wavelength (Å)	0.71073
Calculated density (g cm ⁻³)	1.263
Absorption coefficient μ (mm ⁻¹)	0.087
$F_{(000)}$	816
Crystal size (mm ³)	0.40 × 0.12 × 0.10
θ range for data collection (°)	1.35 - 25.02
Limiting indices	$-10 \leq h \leq 11$, $-16 \leq k \leq 16$, $-18 \leq l \leq 18$
Reflection collected	17260
Independent reflection	7066 ($R_{\text{int}} = 0.0630$)
Completeness to θ_{max} (%)	99.3
Data/restraints/parameters	7066/0/517
Goodness-of-fit on F^2	1.017
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0714$, $wR_2 = 0.1685$
R indices (all data)	$R_1 = 0.1028$, $wR_2 = 0.1911$
Largest diff. e peak and hole (e Å ⁻³)	0.653 and -0.246

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

Bond lengths	X-Ray crystal	Bond lengths	X-Ray crystal
O(1)-N(1)	1.239(3)	C(2)-C(3)	1.477(3)
O(2)-N(1)	1.216(3)	C(4)-C(10)	1.516(3)
N(1)-C(1)	1.459(3)	C(6)-C(11)	1.514(3)
C(1)-C(2)	1.303(4)	C(8)-C(9)	1.512(3)

As depicted in Fig. 1, the title compound (**I**) displays a *trans* configuration about the C=C double bond. The average bond lengths and angles are within normal ranges¹¹⁻¹⁹. The C1=C2 bond length is 1.303(4) Å which is a typical double bond, but it is shorter than those observed in the crystal structures

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

Bond angles	X-Ray crystal	Bond angles	X-Ray crystal
O(2)-N(1)-O(1)	122.5(2)	C(4)-C(3)-C(2)	115.8(2)
O(2)-N(1)-C(1)	121.9(2)	C(8)-C(3)-C(2)	125.4(2)
O(1)-N(1)-C(1)	115.6(2)	C(2)-C(1)-N(1)	119.4(2)
C(4)-C(3)-C(8)	118.8(2)	C(1)-C(2)-C(3)	129.2(3)

of the reported nitroalkene compounds (1.313–1.328 Å)^{13–17}. The C1–N1 bond length (1.459(3) Å) and the C2–C3 bond length (1.477(3) Å) are shorter than the normal C–N single bond (1.47 Å)²⁰ and the normal C–C single bond (1.46 Å)²¹, respectively, which indicates that the C1–N1 bond and the C2–C3 bond are simultaneously conjugated with the C1=C2 double bond²⁰. Furthermore, the dihedral angle between the C3–C8 plane (r.m.s. deviation 0.0030 Å) and the N1/O2/O3/C1/C2 plane (r.m.s. deviation 0.0032 Å) is 19.7°, suggesting that the nitroethylene moiety is less planar with the 2,4,6-trimethylphenyl moiety. This is probably due to the steric repulsion between the methyl substituents and the ethylene hydrogen atoms, which further results in the C(2)–C(1)–N(1) bond angle (119.4(2)°) being different from the C(1)–C(2)–C(3) bond angle (129.2(3)°). In addition, the N1–O1 bond length is *ca.* 0.023 Å longer than the N1–O2 bond length, possibly owing to the weak interaction between O atom of the nitro group and the H atom of the methyl group¹¹.

As shown in Fig. 2, the ethylene molecules are linked by the C–H...O short contacts involving the H atoms of the methyl group and the O atoms of the nitro group^{12,15}. For example, the distance between the O5G atom of the nitro group and the H atom attached to the methyl C42C atom is 2.686 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 3.985 Å. As a result, the two kinds of intermolecular interactions extend the molecules into an infinite three-dimensional network (Fig. 2).

Conclusion

In summary, the nitroalkene compound [*trans*-2-(2,4,6-trimethylphenyl)-1-nitroethylene (I)] has been synthesized and structurally characterized elemental analysis and ¹H (¹³C) NMR spectra. 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–H...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-892536 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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