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ORIGINAL PAPER

Synthesis, Spectral Characterization, Crystal Structure and Thermal Behavior of Tert-butyl 2,2-bis(2,4-dinitrophenyl)ethanoate

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Abstract Tert-butyl 2,2-bis(2,4-dinitrophenyl)ethanoate was prepared from the ethanolic solution of 1-chloro-2,4-dinitrobenzene, tert-butyl 3-oxobutanoate and triethylamine. Acetyl group in tert-butyl 3-oxobutanoate has cleaved off during the formation of the title molecule. UV–VIS, IR, 1H NMR, 13C NMR, Proton–Proton COSY data and single crystal XRD results support the proposed structure. Flammability test, impact sensitivity test and TG/DTA studies at different heating rates on the synthesized molecule imply that it is an insensitive high energy density material.

Keywords Tert-butyl 2,2-bis(2,4-dinitrophenyl) ethanoate · 1-Chloro-2,4-dinitrobenzene · Triethylamine · Tert-butyl 3-oxobutanoate · Insensitive high energy density material

Introduction

Mclvor and Miller have synthesized ethyl 2,2-bis(2,4-dinitrophenyl)ethanoate (EBDNE) in 32–71 % yield by mixing equimolar amounts of 1-chloro-2,4-dinitrobenzene (DNCB) and ethyl 2,4-dinitrophenylacetate in the presence of tripropylamine in dimethylformamide medium [1]. The same authors have also prepared methyl 2,2-bis(2,4-dinitrophenyl)ethanoate (MBDNE) only in 32 % yield by adopting the same procedure. Carbon-13 NMR study of EBDNE in liquid ammonia has been made already [2]. An article has appeared on the crystal structure of EBDNE [3]. This ethyl ester has also been used in colour indication paper for detecting chlorine containing organic solvents, alcohols and amines [4]. Ethyl ester has also been employed in the preparation of photodegradable aqueous inks [5] and tailor's chalk [6]. Though the applications of the ethyl ester (EBDNE) are well documented, only a few reports are noticed on the methyl ester (MBDNE) [1, 7–9]. No report has so far appeared on the preparation and applications of tert-butyl 2,2-bis(2,4-dinitrophenyl)ethanoate (TBDNE). In this article we report the synthesis and thermal behavior of tert-butyl 2,2-bis(2,4-dinitrophenyl)ethanoate.

Experimental

Materials and Methods

All reagents and solvents for synthesis and analysis were commercially available and used as received without further purification. The visible data were obtained on a Perkin-Elmer Lambda 15 UV/VIS spectrometer. The IR spectra were recorded using Perkin-Elmer RXI infrared spectrophotometer in KBr pellets. The NMR spectra were obtained from Bruker DRX-300 spectrometer with (DMSO) d6 as solvent and TMS as an internal reference. TGA/DTA data were collected employing Perkin-Elmer (Pyris Diamond model) at different heating rates under N2 (g) purge using alumina powder as reference.

Preparation of tert-butyl 2,2-bis(2,4-dinitrophenyl)ethnoate: 1-Chloro-2,4-dinitrobenzene (0.01 mol) in absolute ethanol was mixed with tert-butyl 3-oxobutanoate (0.01 mol)

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in absolute ethanol. Triethylamine (0.05 mol) was then added and the mixture was shaken well for 5–6 h. On standing, pale yellow crystals come out from the solution after 15 days. The crystals were filtered and washed well with distilled water and dried. The dried crystals were powdered and washed with 30 ml of ether to remove the unreacted reactants and then with little absolute alcohol. The crystals obtained after washing were recrystallized from ethylacetate. Good quality single crystals of the title compound were obtained from ethanol at room temperature by slow evaporation (m.p. 427 K, yield 75 %). Micro analysis, calcd.: C, 48.2; H, 3.6; N, 12.5; found: C, 48.3; H, 3.3; N, 12.2. Solubility: freely soluble in dimethylsulphoxide and sparingly soluble in water, ethanol, chloroform, ethylacetate and ether. UV ($CHCl_3$, λ_{Max}): 257 nm. ^{1}HNMR 300 MHz, (DMSO)d6: δ 1.4s, 9H, $C(CH_3)_3$, δ 6.3 (s, 1H, CH), δ 8.9 (s, 2H, two rings-Ar–H), δ 8.6 (d, $J = 14.7$ Hz, 2H, two rings-Ar–H), δ 7.6 (d, $J = 8.7$ Hz, 2H, two rings-Ar–H). ^{13}C NMR: δ 27, 51, 84, 121, 128, 133, 137, 147, 148, 167. IR (KBr, v_{max}): 1531, 1351, 1723, 2988, 2940, 3114, 1607, 1149, 1063, 837 cm^{-1}. Qualitative tests [10] on the synthesized tert-butyl 2,2-bis (2,4-dinitrophenyl)ethanoate reveal the presence of nitrogen atom, nitro groups and the absence of chlorine atom.

Crystal Structure Determination

A single crystal of the dimension 0.43 × 0.36 × 0.29 was selected for X-ray diffraction study. Crystallographic measurements were made employing a Bruker Smart Apex CCD diffractometer with graphite monochromated MoKα radiations ($\lambda = 0.71073$ Å). The data were collected at 293(2) K using ω scan modes. All hydrogen atoms were geometrically fixed and allowed to ride with the respective non hydrogen atoms to which they were covalently bonded.

Table 1 Crystal data

$C_{18}H_{16}N_4O_{10}$	$V = 2037.9(10)$
Mr = 448.35	$Z = 4$
Monoclinic, P21/*n*	MoKα = radiation
$a = 12.770$ (4) Å	$\mu = 0.122$ mm^{-1}
$b = 11.676$ (3) Å	T = 293 K
$c = 14.310$ (4) Å	0.43 × 036 × 0.29
$\beta = 107.277$ (6)°	
Data collection	
Bruker SMART APEX CCD diffractometer	17,527 measured reflections
	4,831 independent reflection
Absorption correction : multi-scan (SADABS; Bruker, 2006)	$T_{min} = 0.9492$, $T_{max} = 0.9659$
	$R_{int} = 0.0479$
2,641 reflection with $I > 2\sigma(I)$	
Refinement	
$R\ [F^2 > 2\sigma\ (F^2)] = 0.0618$	292 parameters
WR $(F^2) = 0.2681$	H-atom parameters constrained
4,831 reflections	Goodness of fit (S) = 1.01

Table 2 Selected bond distances

Bond distance	Å
C1–C2	1.535(6)
C2–C3	1.522(3)
C3–C4	1.394(5)
C4–C5	1.384(1)
C5–C6	1.365(4)
C6–C7	1.370(1)
C7–C8	1.375(6)
C1–O1	1.196(7)
C15–C16	1.513(4)
C15–C17	1.501(2)
C15–C18	1.514(5)
C4–N1	1.471(2)
N1–O3	1.196(7)
N1–O4	1.204(5)
C6–N2	1.468(9)
N2–O5	1.197(8)
N2–O6	1.188(9)
C17–H17A	0.96
C18–H18A	0.96
C2–H2	0.98

Table 3 Selected bond angles

Bond angles	°
C1–C2–C9	109.6(7)
C2–C3–C4	123.3(4)
C3–C4–C5	122.7(8)
C4–C5–C6	118.1(2)
C5–C6–C7	121.8(9)
C6–C7–C8	118.5(6)
C7–C8–C3	122.5(6)
C5–C6–N2	118.1(2)
C6–N2–O6	117.8(9)
C6–N2–O5	119.4(5)
O5–N2–O6	122.5(6)
C4–N1–O3	119.6(7)
C4–N1–O4	122.0(1)
C2–C1–O2	109.3(4)
C2–C1–O1	123.4(5)
O1–C1–O2	127.0(1)
C17–C15–C18	111.2(3)
C16–C15–C18	110.7(8)

Table 4 Hydrogen bond geometry of tert-butyl 2,2bis(2,4-dinitrophenyl)ethanoate

D–H···A (°)	d D–H (Å)	d H···A (Å)	d D–A (Å)	<DHA (°)
C2–H2···O5(#1)	0.98	2.52	3.370 (4)	144
C5–H5···O2(#2)	0.93	2.93	3.712 (4)	142
C7–H7···O10(#3)	0.93	2.81	3.670 (5)	154
C14–H14···O1(#4)	0.93	2.56	3.342 (5)	141
C17–H17B···O10(#5)	0.96	2.79	3.708 (6)	158
C18–H18B···O4(#6)	0.96	2.93	3.557 (6)	124

(#1) x − ½, −y + ½, +z − ½; (#2) x + ½, −y + ½, +z + ½; (#3) x + ½, −y − ½, +z + ½; (#4) −x, −y, −z + 2; (#5) −x − ½, +y + ½, −z + ½ + 1; (#6) −x, −y + 1, −z + 2

The programs used for the crystal structure determination are—data collection: APEX2 [11]; cell refinement: SAINT [11]; data reduction: SAINT [11]; program used to solve structure: SHELXS97 [12]; program used to refine structure: SHELXL97 [12]; molecular graphics: ORTEP-III [13]. Important information concerning crystallographic data are summarized in Table 1. Selected bond distances and angles are listed in Tables 2 and 3 respectively. A number of weak C–H···O hydrogen bonds is observed (Table 4). The ORTEP diagram of title molecule is presented in Fig. 1.

Results and Discussion

Ketones, beta diketones and beta ketoesters, in the presence of tertiary amine usually form carbanionic sigma adducts or bicyclic complexes with electron-deficient nitro aromatics [14–20]. In the present investigation, a new ester containing two dinitrophenyl moieties is formed on adding excess triethylamine to the ethanolic solution containing 1-chloro-2,4-dinitrobenzene (an electron-deficient nitro aromatic compound) and tert-butyl 3-oxobutanoate (a betaketo ester). The same product has been obtained in

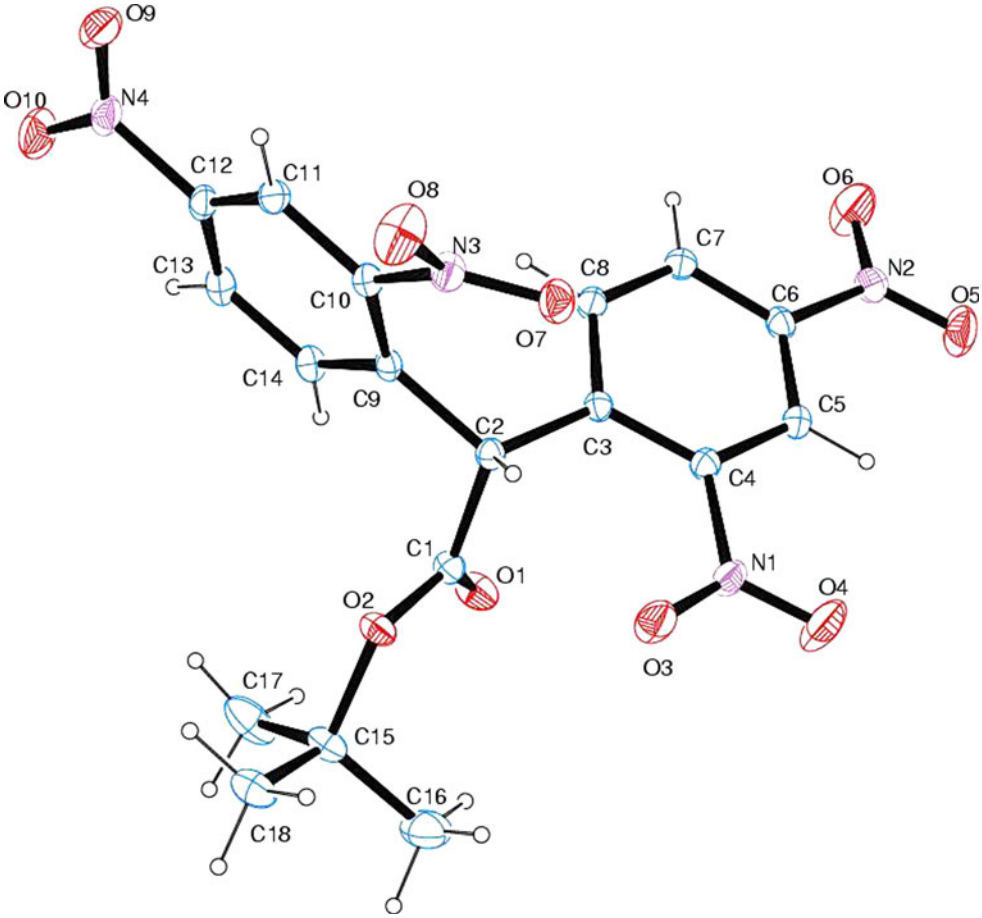

Fig. 1 ORTEP view of tert-butyl 2,2-bis(2,4-dinitrophenyl)ethanoate

solvents like methanol or 1-propanol and when the bases such as trimethylamine, tri-*n*-butylamine, *N*,*N*-diethylethanolamine or triethanolamine are used instead of triethylamine. The yield of the product is <60 % with these bases. The title molecule probably may have formed through the carbanionic sigma complex 1 [21] as indicated in the schematic representation (Fig. 2). Acetyl group of tert-butyl 3-oxobutanoate has cleaved off during the formation of the title molecule. Similar type of cleavage is reported by us from ethyl benzoyl acetoacetate in related system [15]. Spectral and single crystal XRD results are in consistent with the structure of the product (title molecule).

FT-IR Spectra

In the reactant, [1-chloro-2,4-dinitrobenzene (DNCB)], a strong sharp absorption band characteristic of C–Cl stretching mode has been observed at 732 cm^{-1} which is absent in the isolated product, shows that during the formation of the product chlorine is remove from DNCB. The asymmetric and symmetric stretching modes of nitro groups of the title molecule exhibit bands at 1,532 and 1,352 cm^{-1} respectively. The carbonyl stretching frequency band appears at 1,723 cm^{-1}. The C–O stretching frequency of ester group appears at 1,150 as a strong sharp band and the band at 1,063 cm^{-1} is assigned to C–N stretching mode. As the methine carbon atom of the title molecule is attached to two electron—with drawing dinitrophenyl moieties, the methine C–H stretching bond of the isolated molecule appears in the high frequency region (3,115 cm^{-1}).

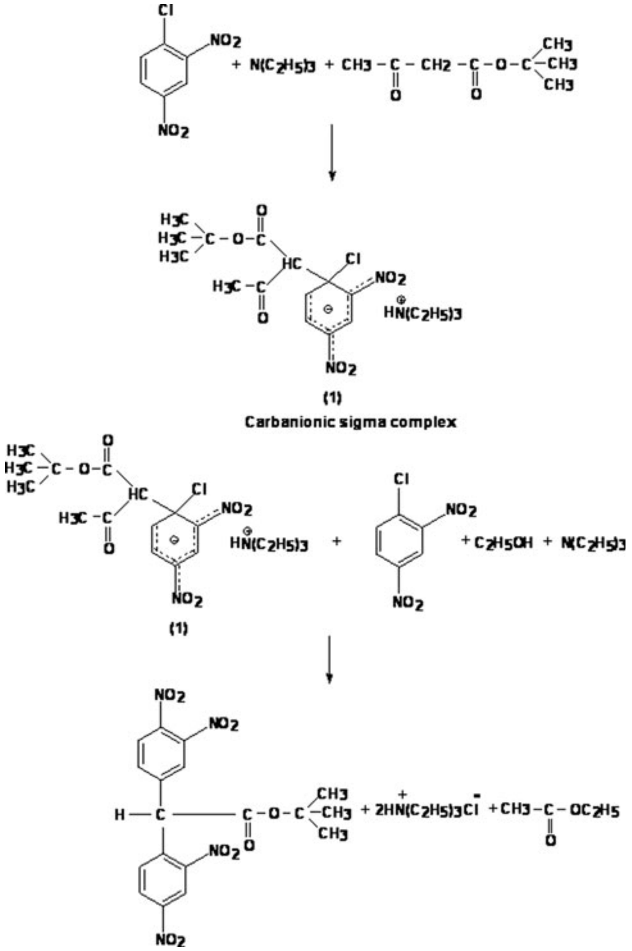

Fig. 2 Schematic representation of the formation of tert-butyl 2,2-bis(2,4-dinitrophenyl)ethanoate

^{1}H–^{1}H COSY and ^{13}C NMR Spectra

Methyl protons of tert-butyl group appears as a singlet at δ 1.4. The proton flanked by nitro groups of the aromatic nitro moiety appears as a singlet at δ 8.9. Adjacent ring protons of nitro moiety resonate at δ 8.6 and 7.6 as doublets due to ortho coupling. Small para coupling is also noticed between the ring protons. As the methine proton of the molecule is highly deshielded due to the attachment of two electron-withdrawing nitro aromatic moieties, it displays a signal at the low field region δ 6.3. Proton–Proton COSY of the title molecule exhibits off-diagonal peaks between δ 7.4 and 9.0 (Fig. 3). COSY spectrum substantiates that besides ortho coupling, para coupling has also occurred between the protons of nitro ring moiety of the title molecule. As expected, ten signals corresponding to ten different carbon environments are noticed in the ^{13}C NMR spectrum of the isolated molecule (Fig. 4).

Description of the Crystal Structure

The nearly similar bond lengths of various C–C bonds of dinitroaromatic rings imply that there is charge

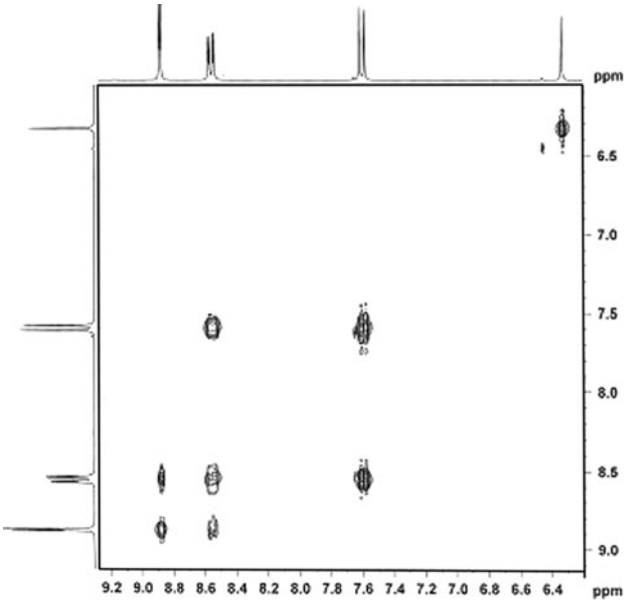

Fig. 3 Proton–proton COSY of tert-butyl 2,2-bis(2,4-dinitrophenyl) ethanoate (δ 6.4–9.2)

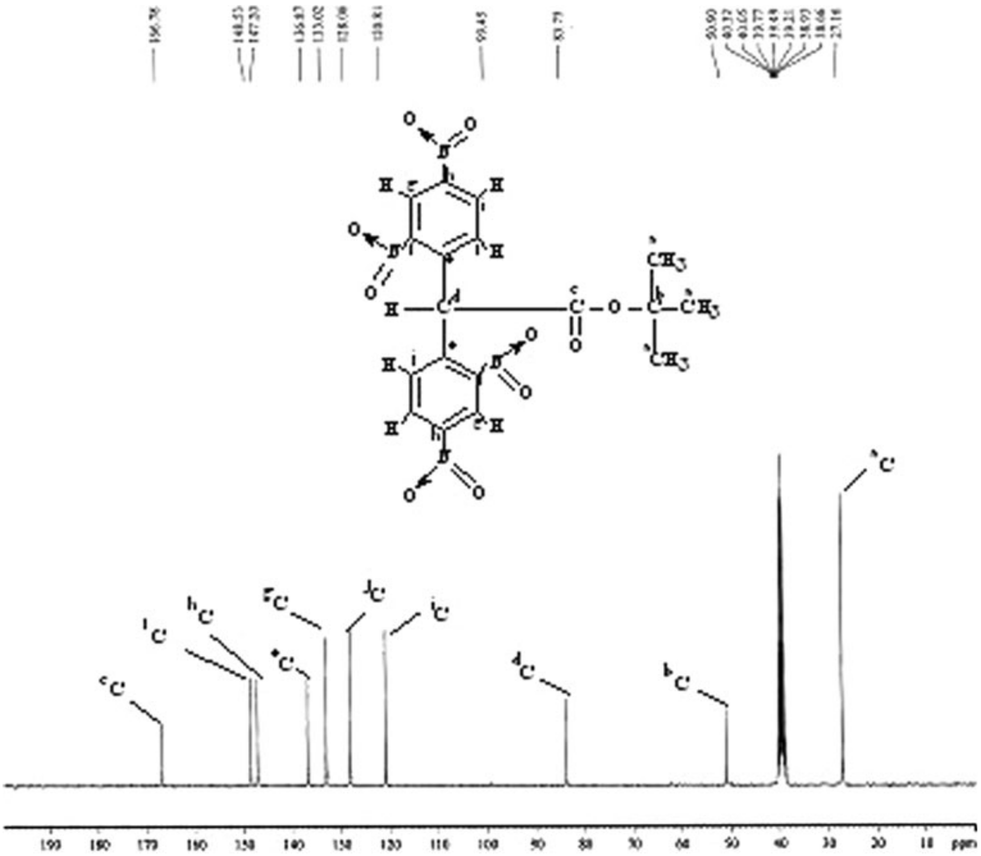

Fig. 4 ^{13}C NMR spectrum of tert-butyl 2,2-bis(2,4-dinitrophenyl)ethanoate

delocalization of cyclic π-electron cloud inside the phenyl ring. As the methine carbon atom is attached to two electron-withdrawing aromatic moieties, the C(sp^3)–H bond length of it is reduced from the normal value (1.1 Å). The C(sp^3)–H bonds of the methyl group are also shortened and this can be accounted in terms of the delocalization of the lone pair on the oxygen atom of the ester group over the adjacent carbonyl group. Thus the hydrogen atoms of methine and methyl groups are made slightly acidic and are involved in the formation of a number of weak C–H···O hydrogen bonds which stabilize the structure.

Thermal Behaviour

Many nitro aromatic molecules are high energy materials to be used as explosives [22]. Primary explosives such as lead azide, lead styphnate etc., are highly susceptible to initiation and secondary explosives which include nitro aromatics and nitramines are more prevalent at military sites than primary explosives [23]. The interest in developing better insensitive high energy density materials (IHEDMS) to be used in explosives, propellants and pyrotechnics is growing steadily [24–31]. At present there is a strong requirement for explosives having good thermal stability, impact insensitivity and explosive performance. Good thermal stability provides safety in manufacturing, storage and handling of energetic materials. Emphasis has also been on cost-effectiveness and eco-friendlyness during the synthesis of explosives [32–34]. As the title molecule has four nitro groups, its thermal properties are also examined. About 5 mg of the title sample was taken in a nickel spatula and heated over a flame. The substance melts and moves away from the flame with a hissing sound producing a dense cloud of black particles characteristics of secondary explosives. The synthesized molecule was found to be insensitive towards impact of 2 kg mass hammer up to the height limit (160 cm) of the instrument. Many other explosives have also been reported as insensitive towards impact [35, 36]. Activation energies for the decomposition of the synthesized compound was determined from the TG/DTA curves (Fig. 5) obtained at three different heating rates (5, 10, and 20 K/min) applying Ozawa [37] and Kissinger [38] methods. The decompositions of tert-butyl 2,2-bis(2,4-dinitrophenyl)-ethanoate has occurred in four different stages. The temperature ranges of decomposition processes are summarized in Table 5. The activation energies of different stages are slightly higher than the reported insensitive explosives [23, 39–42].

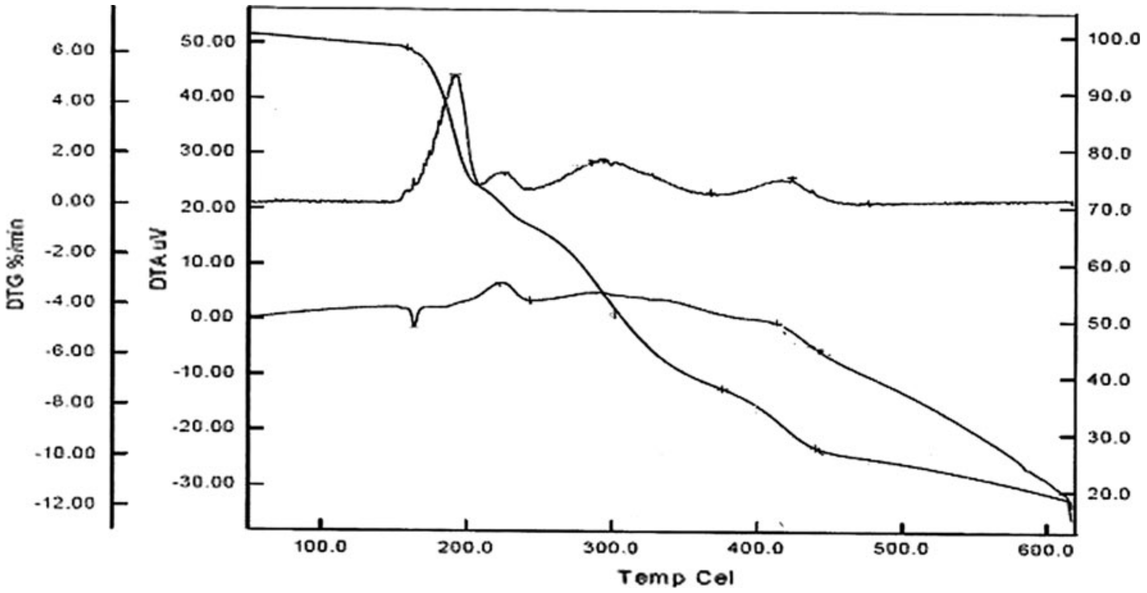

Fig. 5 TG/DTA curve of tert-butyl 2,2-bis(2,4-dinitrophenyl)ethanoate at the heating rate of 5 K/min

Table 5 Thermal decomposition of tert-butyl 2,2-bis(2,4-dinitrophenyl)ethanoate (TBDNE)

Compound	Temp. range (°C)	Stage	TG wt loss (%) found	DTG temp. peak (°C)	Activation energy kJ/mol (kcal/mol)	
					Using Ozawa method	Using Kissinger's method
TBDNE	150–200.5	1	22.4	191.8(*exo*)	254(60)	253(60)
	200.5–230	2	10.0	225.8(*exo*)	316(75)	308(73)
	230–350	3	27.0	300.0(*exo*)	93(22)	89(21)
	350–457	4	13.0	413.0(*exo*)	320(76)	321(76)

Conclusions

The method presented in this article involves ethanol as solvent which poses less environmental pollution than other organic solvents. The title molecule is obtained in good yield with high purity through one-pot synthesis from low cost materials. Structures of the explosives have profound effect on activation energy and thermal stability [23, 31, 43]. The slightly higher activation energy of the title molecule compared to the reported secondary explosives may be attributed to the presence of two phenyl rings.

Supplementary Data

CCDC No. 750313 contains the supplementary crystallographic data for tert-butyl 2,2-bis(2,4-dinitrophenyl)ethanoate. These data can be obtained free of charge from Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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