The Synthesis and Crystal Structure of N-*tert*-Butyl-3-(*tert*-butylimino)-2-nitropropen-1-amine

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The unit cell of N-*tert*-butyl-3-(*tert*-butylimino)-2-nitropropen-1-amine (**4**) is monoclinic, space group $P2_1/C$, with $a = 9.669(4)$, $b = 16.415(6)$, $c = 17.341(7)$ Å, and $Z = 4$. Hydrolysis of **4** leads to (E)-3-(N-*tert*-butylamino)-2-nitro-2-propenal (**5**), whose unit cell is monoclinic, space group $P2_1/n$, with $a = 6.821(1)$, $b = 20.707(6)$, $c = 6.303(1)$ Å, and $Z = 4$. Compounds **4** and **5** both possess C_2 symmetry in the solid state, their “U-shaped” conjugated cores being essentially planar. In each case this planarity is enforced by an intramolecular hydrogen bond.

Introduction

Although considerable effort has been devoted to the study of the chemical [2, 3] and spectral properties [4–6] of vinamidinium salts **1**, relatively few reports have appeared regarding the neutral vinamidines [7–10]. An early suggestion [11] that appropriate “U-shaped” open chain vinamidines **2** (–NH...N-intramolecular hydrogen bonding) possess a non-classical closed aromatic system **3** of six pi electrons involving the N–H bonds was later ruled out [12].

Title compound **4** combines the nitroenamine and vinamidine systems within its cross conjugated core. It was originally isolated by one of us as an unexpected minor product during the synthesis of the nitroenamine 1-(N-*tert*-butylamino)-2-nitroethene [13]. We have now prepared **4** directly from nitromalonaldehyde [14] and established its “U-shaped” structure and C_2 symmetry in the solid state *via* a single crystal X-ray diffraction study [15].

Experimental

The ^{13}C NMR spectrum was recorded at 22.639 MHz, and the ^1H NMR spectra were obtained at 90 MHz. Mass spectra were obtained on a Kratos MS 902 mass spectrometer equipped with a Finnigan Incos data system. IR spectra were recorded on a Beckmann Acculab I spectrophotometer. Melting points were determined using open capillaries and are uncorrected.

N-*tert*-Butyl-3-(*tert*-butylimino)-2-nitropropen-1-amine (**4**)

Method A [13]: A mixture of 1-(N,N-dimethylamino)-2-nitroethene (2.00 g, 17.2 mmol) and *tert*-butylamine (30 ml, 286 mmol) was refluxed under a dinitrogen atmosphere for 1 h, by which time a clear solution had formed. After an additional 20 h at room temperature followed by 1 h of reflux, the solution was concentrated under reduced pressure to yield an amorphous reddish-brown solid. Column chromatography (alumina with diethyl ether elution) of the crude sample gave 1-(N-*tert*-butylamino)-2-nitroethene as the major product (1.09 g, 44%) [13], together with a small quantity of **4**, which was recrystallized from diethyl ether. Yield 0.13 g (7%), pale yellow rhombuses, m.p. 144–146 °C. IR (Nujol) 3080, 1641, 1585, 1490, 1310, 1290, 1235, 1200 cm^{-1} ; ^1H NMR

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(CDCl₃) 10.5 (1H, broad s, NH), 8.72 (2H, s, CH=N), 1.36 (18H, s, CMe₃); ¹³C NMR (CDCl₃) 150.8 (CH=N), 121.1 (CNO₂), 55.7 (CMe₃), 29.9 (Me); MS, *m/e* (rel intensity): 227 (P⁺, 11), 212 (13), 156 (17), 154 (36), 98 (51), 57 (100), 41 (33).

C₁₁H₂₁N₃O₂ (227.3)

Calcd C 58.1 H 9.3 N 18.5%,

Found C 58.1 H 9.4 N 18.8%.

A duplicate experiment involving a total of 10 h of reflux and 7 days at room temperature gave 0.10 g (4%) of 1-(*N-tert*-butylamino)-2-nitroethene and 0.47 g (24%) of **4**, the products being isolated by column chromatography (Florisil with 2:1 v:v cyclohexane:diethyl ether elution). TLC examination of mother liquors from the crystallizations of 1-(*N-tert*-butylamino)-2-nitroethene (lowest *R_f*) and **4** (highest *R_f*) revealed a new compound **5**, whose isolation and characterization is given later in this section.

Method B: When a solution of *tert*-butylamine (2.92 ml, 27.8 mmol) in 95% ethyl alcohol (10 ml) was added dropwise at room temperature to a stirred solution of sodium nitromalonate monohydrate (1.40 g, 8.9 mmol) in 5% aq sodium hydrogen carbonate (30 ml), solid **4** formed immediately. The precipitate was collected after 30 min, washed with cold 95% ethyl alcohol, and recrystallized from methyl alcohol. Yield 1.70 g (84%), m.p. 144–145 °C.

(*E*)-3-(*N-tert*-Butylamino)-2-nitro-2-propenal (**5**)

The mother liquor referred to in Method A above was evaporated, and the resulting brown solid was then dissolved in 30 ml of diethyl ether. Extraction of the ethereal solution with 2 × 5 ml of 2% aq hydrochloric acid to remove residual **4** was followed by a water wash, drying over disodium sulfate, and concentration, with the final solution depositing white platelets of **5** as it stood in the refrigerator. Yield 0.06 g (4%), m.p. 108–109 °C. IR (Nujol) 3060, 1662, 1652, 1597, 1499, 1410, 1360, 1335, 1325, 1311, 1258 cm⁻¹; ¹H NMR (Me₂SO-*d*₆/HOAc-*d*₄) 10.6 (1H, broad s, NH), 9.96 (1H, d, *J* = 2.6 Hz, CH=O), 8.43 (1H, broad s, CH=N), 1.33 (9H, s, Me₃C); MS, *m/e* (rel intensity): 173 (PH⁺, 4), 172 (P⁺, 3), 127 (6), 116 (21), 110 (6), 95 (3), 83 (4), 71 (10), 57 (100), 55 (17), 42 (5), 41 (58).

X-ray crystal structure determination of **4**

Crystal data of C₁₁H₂₁N₃O₂. *M* = 227.3, monoclinic, *a* = 9.669(4), *b* = 16.415(6), *c* = 17.341(7) Å, β = 150.69(2)°, *Z* = 4, *V* = 1347.4 Å³, *D*_{calc} = 1.120 g cm⁻³, *F*(000) = 496; λ(MoKα) =

0.71069 Å, μ(MoKα) = 1.54 cm⁻¹, space group P2₁/C from systematic absences.

Structure Analysis. A crystal of **4** suitable for X-ray diffraction studies was mounted on a Syntex P2₁ automated diffractometer and data (1 ≤ 2θ ≤ 50°) were collected using a θ/2θ scan. Of the 2458 unique reflections collected, 1415 were considered observed [*I* > 2σ(*I*)]. The structure was solved using the direct methods package MITHRIL and the model refined using full-matrix least squares techniques. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined with isotropic thermal parameters. The function w(|*F_o*| - |*F_c*|)² was minimized with *w*^{1/2} = 1 for |*F_o*| ≤ 15 and 15/|*F_o*| for |*F_o*| > 15; *R* = 0.058; *wR* = 0.061. No short intermolecular contacts were observed.

X-ray crystal structure determination of **5**

Crystal data of C₇H₁₂N₂O₃, *M* = 172.2, monoclinic, *a* = 6.821(1), *b* = 20.707(6), *c* = 6.303(1) Å, β = 91.34(1)°, *Z* = 4, *V* = 890.0 Å³, *D*_{calc} = 1.284 g cm⁻³, *F*(000) = 368; λ(MoKα) = 0.71069 Å, μ(MoKα) = 1.09 cm⁻¹, space group P2₁/*n* from systematic absences.

Structure analysis

Crystal mounting of **5** and data collection were as for **4**. Of the 1629 unique reflections collected 539 were considered observed [*I* > 2σ(*I*)]. The structure was solved as above. Non-hydrogen atoms were refined anisotropically and hydrogen atoms, with the exception of H(N) were assigned isotropic thermal parameters. Atom H(N) was refined isotropically. The function w(|*F_o*| - |*F_c*|)² was minimized with *w*^{1/2} = 1 for |*F_o*| ≤ 28 and 28/|*F_o*| for |*F_o*| > 28; *R* = 0.067; *wR* = 0.076. No short intermolecular contacts were observed.

Results and Discussion

The molecular structures of **4** and **5** are depicted in Figures 1 and 2, respectively, and the atom numbering is keyed to the composite list of bond distances and angles found in Table I.

Compound **4** is seen to exist as a highly polarized molecule in the solid state, its cross conjugated core being very nearly planar. This planarity is enforced by an intramolecular hydrogen bond linking the two amino nitrogen atoms, the C–N...N–C virtual angle being 0.6(3)°. The N...N separation is only 2.684(4) Å and the

Fig. 1. X-ray crystal structure of **4**. Fig. 2. X-ray crystal structure of **5**.

NH $\cdots$ N distance is 1.75(5) Å. The largest deviation from planarity shown by the molecule, excluding the methyl groups of the *tert*-butyl substituents, is evidenced by a C–C–N–O dihedral angle of 4.0(3)°. This demonstrates that even the nitro group is not twisted from the plane of the molecule.

The N(1)–C(2) and C(4)–N(12) bond distances in **4** are 1.296(4) Å and 1.293(4) Å, respectively, indicating each is essentially a double bond; e.g., an average C=N length of 1.28 Å has been reported for imines and oximes [16]. Pi electron delocaliza-

Table I. Bond lengths (Å) and angles (deg) for **4** and **5**, with estimated standard deviations in parentheses*.

	4	5
	X = N	X = O
a) Bond lengths		
N(1)–C(2)	1.296(4)	1.279(10)
N(1)–C(8)	1.478(4)	1.499(10)
C(2)–C(3)	1.400(4)	1.409(11)
C(3)–C(4)	1.426(4)	1.405(12)
C(3)–N(5)	1.418(4)	1.436(11)
C(4)–X(12)	1.293(4)	1.214(10)
N(5)–O(6)	1.221(4)	1.235(8)
N(5)–O(7)	1.229(4)	1.222(9)
C(8)–C(9)	1.522(6)	1.516(15)
C(8)–C(10)	1.516(6)	1.514(12)
C(8)–C(11)	1.522(5)	1.514(15)
X(12)–C(13)	1.481(4)	
C(13)–C(14)	1.513(5)	
C(13)–C(15)	1.528(6)	
C(13)–C(16)	1.523(6)	
b) Valency angles		
	X = N	X = O
C(2)–N(1)–C(8)	124.7(3)	128.4(7)
C(2)–N(1)–H(N)	110(3)	125(6)
C(8)–N(1)–H(N)	125(3)	107(6)
N(1)–C(2)–C(3)	122.4(3)	120.3(7)
C(2)–C(3)–C(4)	124.4(3)	123.9(7)
C(2)–C(3)–N(5)	118.2(3)	117.3(7)
C(4)–C(3)–N(5)	117.4(3)	118.8(7)
C(3)–C(4)–X(12)	121.2(3)	123.0(7)
C(3)–N(5)–O(6)	119.1(3)	119.3(7)
C(3)–N(5)–O(7)	119.4(3)	118.5(6)
O(6)–N(5)–O(7)	121.5(3)	122.2(7)
N(1)–C(8)–C(9)	105.5(3)	106.7(7)
N(1)–C(8)–C(10)	108.4(3)	112.0(6)
N(1)–C(8)–C(11)	111.8(3)	105.2(7)
C(9)–C(8)–C(10)	111.2(3)	110.1(8)
C(9)–C(8)–C(11)	109.2(3)	112.5(8)
C(10)–C(8)–C(11)	110.6(3)	110.3(8)
C(4)–X(12)–C(13)	122.4(3)	
C(4)–X(12) $\cdots$ H(N)	101(2)	102(3)
C(13)–X(12) $\cdots$ H(N)	136(2)	
X(12)–C(13)–C(14)	105.1(3)	
X(12)–C(13)–C(15)	106.9(3)	
X(12)–C(13)–C(16)	112.6(3)	
C(14)–C(13)–C(15)	110.8(3)	
C(14)–C(13)–C(16)	112.2(3)	
C(15)–C(13)–C(16)	109.2(3)	
N(1)–H(N) $\cdots$ X(12)	140(4)	126(8)

* Further details of the structure determinations have been deposited as Supplementary Publication CSD-56658. Copies may be obtained through Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-W-7154 Eggenstein-Leopoldshafen 2.

tion effects are evident as well in a C(2)–C(3) bond length of 1.400(4) Å and a C(3)–C(4) bond length of 1.426(4) Å.

The C–N(nitro) bond distance of 1.418(4) Å is considerably longer than either a calculated [17a] value of 1.295 Å or an experimental [17b] value of 1.293 Å for C=N within a nitronate anion, C=NO₂[−], but it is significantly shorter than the C–N(nitro) bond distance of 1.453 Å in N,N-dimethyl-4-nitro-3,5-xylidine [18a]. The observed C–N(nitro) length in **4** is slightly longer than analogous ones found for related nitroenamines: 1-(N-methylamino)-2-nitroethene [19a], 1.378(6) Å; 1-(N,N-dimethylamino)-2-nitroethene [19b], 1.394(4) Å; 1-(N-morpholino)-2-nitroethene [19c], 1.385(2) Å.

The length of the C–N(nitro) bond in **4** suggests the importance of accumulated negative charge on C(3), the enhanced electron density of this central carbon being characteristic of the vinamidine system [2]. Electrostatic stabilization of the negative charge on C(3) by the nitro substituent is consistent with a number of studies [18] which attribute a dominant inductive-field effect to this group.

The bond equalization apparent within the vinamidine framework of **4** is less important in crystalline N-phenyl-4-phenylimino-2-penten-2-amine (**6**) [20]. Proceeding counterclockwise along the vinamidine core of **6**, the observed bond distances are: 1.376(8) Å (=CH–N), 1.352(8) Å (C=C), 1.447(8) Å (C–C), and 1.314(8) Å (CH=N).

Chromatographic separation of **4** from 1-(N-*tert*-butylamino)-2-nitroethene on Florisil is accompanied by partial hydrolysis of **4** to aldehyde **5**. The structure of **5** (see Fig. 2) has been confirmed by X-ray crystallography. The molecule is quite similar to **4**, with a planar structure that in-

corporates an intramolecular hydrogen bond between the protonated amino nitrogen and the aldehydic oxygen. The N...O separation is quite short [21] at 2.641(8) Å; the NH...O separation is 2.02(10) Å. Dihedral angles, except those involving the methyl groups on the *tert*-butyl substituent, are all within 3.8(9)° of planarity, with the C–N...O–C virtual torsion angle being −1.0(7)°.

Bond lengths in **5** follow the same trends as do those in **4**. The significant differences are that the C–N(amino) distance of 1.279(10) Å indicates more localized double bond character, and the C–N(nitro) distance of 1.436(11) Å indicates more single bond character than is apparent in the analogous bonds in **4**.

The ¹H NMR spectra of **4** and **5** are revealing. Rapid intramolecular proton exchange within molecule **4** in solution effectively creates a mirror plane of symmetry, leading to the two proton singlet at δ 8.72 for –CH=N. The corresponding pair of hydrogen nuclei in molecule **5** are no longer equivalent, the aldehydic proton resonating at δ 9.96, and the aldiminic proton resonating at δ 8.43. A planar W-configuration for these heterotopic protons, enforced by the intramolecular hydrogen bond, is confirmed by a four bond coupling constant of 2.6 Hz [22].

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