

Synthesis, structure, and isomerism of *N*-2,4-dinitrophenylbenzotriazoles

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Received 5 December 2006; revised 13 February 2007; accepted 20 February 2007

Available online 23 February 2007

Dedicated to Professor Guy Ourisson in memoriam

Abstract—Both isomers of *N*-(2',4'-dinitrophenyl)benzotriazole, the 1(3)- and 2-substituted, have been characterized and their reciprocal isomerism was studied. Cross-experiments in the presence of 5(6)-nitro-1*H*-benzotriazole proved that the isomerization of 2-(2',4'-dinitrophenyl)-2*H*-benzotriazole into the 1-isomer occurs by an intermolecular mechanism. The reported reaction of 5(6)-nitro-1*H*-benzotriazole with 1-chloro-2,4-dinitrobenzene has been reexamined discovering that there is an error in the proportions of *N*-substituted isomers. A possible explanation for the observed isomerizations was proposed. Identification of all compounds by multinuclear magnetic resonance, including solid-state studies, has been achieved.

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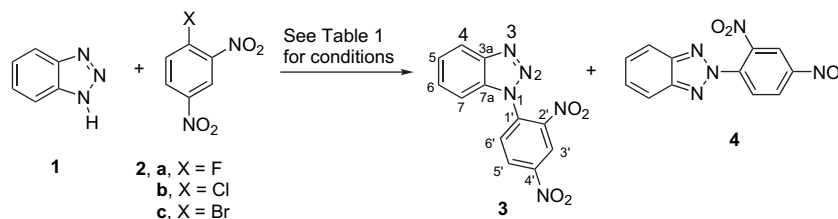
1. Introduction

In 1966–1967 three groups studied simultaneously the reaction between 1*H*-benzotriazole (**1**) and 1-halo-2,4-dinitrobenzenes (**2**) (Scheme 1).^{1–3} Some of us carried out the reaction of **2a** and **1** in xylene at reflux and obtained exclusively the 1-isomer **3**.² On the other hand, Kamel et al. carried out the reaction of **2b** and **1** in ethanol in the presence of sodium acetate obtaining both isomers **3** and **4** in a 70:30 ratio.³ Wilshire¹ also did the reaction of **2a** and **1** in a variety of solvents and reported that the ratio of **3/4** is 98:2 in benzene and 74:26 in ethanol, the highest proportion of **4** being obtained in DMF (62:38 ratio). The 1-isomer **3** has long been known since Borsche and Rantschegg prepared it (mp 186–187 °C)

by cyclization of the mono-(2',4'-dinitrophenyl)-*o*-phenylenediamine with nitrous acid.^{4,5} Afterward, compounds **3** and **4** have been published several times,^{6–12} but only Davydov et al.⁸ have described again the formation of both isomers, 1-(2',4'-dinitrophenyl)-1*H*-benzotriazole (**3**) and 2-(2',4'-dinitrophenyl)-2*H*-benzotriazole (**4**).

We have summarized in Table 1 all the results reported so far on these two compounds.

In view of the inconsistency in the melting points reported in Ref. 8 and, especially, the result that a reaction of *N*-arylation is so dependent of the experimental conditions varying from pure **3** to pure **4** (even assuming that minute quantities



Scheme 1. Formation of dinitrophenylbenzotriazoles (**3** is represented in the *Z* conformation with the nitro group pointing toward the N2 of the benzotriazole). We have extended the *E/Z* nomenclature to the conjugate N1-aryl single bond.

Keywords: Benzotriazoles; 2,4-Dinitrophenyl group migration; Kinetics; NMR; GIAO/B3LYP/6-31G* absolute shieldings; B3LYP/6-31G** stabilization energies.

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Table 1. Literature results on benzotriazole derivatives **3** and **4**

Entry	2, X	Conditions	Isomer 1-R 3	Isomer 2-R 4	Ref.	3/4 ratio	NMR
1	a, F	Diff. solv., rt	185–187 °C	167–168 °C	1	98:2 ^a 74:26 ^b	¹ H
2	a, F	Xylene, reflux	182–183 °C	—	2	>99	¹ H
3	b, Cl	EtOH, reflux	186 °C	165 °C	3,12	70:30	None
4	b, Cl	Toluene, reflux	182–184 °C	—	6,12	>99	¹ H
5	c, Br	DMSO/NaH/rt	—	166–167 °C ^c	7	<0.01	¹ H, ¹³ C
6	b, Cl	PTC	232 °C	192 °C	8	76:19 ^d	¹ H
7	a, F	Cs ₂ CO ₃ , DMF, rt	185 °C	—	9	>99	None
8	b, Cl	PTC; MW	181–182 °C	—	10	>99	¹ H
9	b, Cl	Ionic liquid	Not reported	—	11	>99	None
10	This work		185.7 °C (DSC)	167.9 °C (DSC)	—	62:38 ^e	¹ H, ¹³ C, ¹⁵ N

^a In benzene.^b In ethanol.^c The authors do not assign the structure but from the melting point and the ¹H and ¹³C NMR data they report that the compound is undoubtedly the 2-isomer **4**.^d For 12 h with K₃PO₄.^e In DMF.

of the other isomer were lost in the purification), we decided to repeat the synthesis (Table 1, entry 10) and to carry out a complete NMR study as well as to examine the relative stabilities of compounds **3** and **4**.

2. Results and discussion

2.1. Synthesis and DSC melting points

We have used the Wilshire's procedure to obtain both isomers of *N*-(2',4'-dinitrophenyl)benzotriazole, the 1(3)- and the 2-substituted, using DMF as solvent.¹ The melting points were determined by DSC as being very close to those reported by all authors save those of Beletskaya et al.,⁸ which should be considered erroneous. We have also noted, during the DSC experiments, the absence of any phase transition.

2.2. NMR characterization

Although there are some previous reports on the NMR spectra of 1-(2',4'-dinitrophenyl)-1*H*-benzotriazole (**3**) and 2-(2',4'-dinitrophenyl)-2*H*-benzotriazole (**4**) (see Table 1), we have recorded the ¹H (Table 2), ¹³C (Table 3), and ¹⁵N NMR spectra (Table 4) in DMSO-*d*₆ solution and for the two last nuclei also in the solid state (CPMAS).

A NOESY experiment in DMSO-*d*₆ solution of compound **3** shows a correlation between H6' and H7 (Fig. 1), which is consistent with a *Z* conformation in such polar solvent, contrary to the theoretical predictions in the gas phase (see Section 2.3).

The assignments were based on the usual 2D methodologies and are consistent with literature results on benzotriazoles

Table 2. ¹H NMR (δ in ppm and *J* in Hz) of **3** and **4** in DMSO-*d*₆

Compound	H-4	H-5	H-6	H-7	Others
3	8.27 (ddd), ³ <i>J</i> _{H5} =8.6, ⁴ <i>J</i> _{H6} = ⁵ <i>J</i> _{H7} =0.9	7.60 (ddd), ³ <i>J</i> _{H6} =7.7, ⁴ <i>J</i> _{H7} =0.9	7.75 (ddd), ³ <i>J</i> _{H7} =8.3	7.85 (ddd)	9.07 (d, 1H, H-3', ⁴ <i>J</i> _{H-5'} =2.5); 8.80 (dd, 1H, H-5', ³ <i>J</i> _{H-6'} =8.8); 8.39 (d, 1H, H-6')
4	8.04 (m), ³ <i>J</i> _{H5} =8.8, ⁵ <i>J</i> _{H7} =0.8	7.58 (m), ³ <i>J</i> _{H6} =6.6, ⁴ <i>J</i> _{H7} =0.9	7.58 (m)	8.04 (m)	9.02 (d, 1H, H-3', ⁴ <i>J</i> _{H-5'} =2.5); 8.72 (dd, 1H, H-5', ³ <i>J</i> _{H-6'} =8.9); 8.51 (d, 1H, H-6')

Table 3. ¹³C NMR (δ in ppm and *J* in Hz) of **3** and **4** in DMSO-*d*₆ and in the solid state

Compound	C-4	C-5	C-6	C-7	C-3a	C-7a
3 (DMSO- <i>d</i> ₆)	120.1, ¹ <i>J</i> =166.9, ³ <i>J</i> ₇ =7.6	125.6, ¹ <i>J</i> =163.9, ³ <i>J</i> ₇ =7.5	129.8, ¹ <i>J</i> =164.3, ³ <i>J</i> ₇ =7.9	110.3, ¹ <i>J</i> =170.0, ³ <i>J</i> ₇ =8.3	145.3, ² <i>J</i> =10.0, ³ <i>J</i> ₄ =4.9	132.4, ³ <i>J</i> =10.6, ³ <i>J</i> ₆ =6.5
3 (CPMAS) ^a	119	127	130	111	146	134
4 (DMSO- <i>d</i> ₆)	118.4, ¹ <i>J</i> =168.1	129.2, ¹ <i>J</i> =163.2, ³ <i>J</i> ₇ =8.2, ² <i>J</i> ₆ =1.6	129.2	118.4	145.2, ³ <i>J</i> ₄ =9.4, ³ <i>J</i> ₅ =5.4	145.2
4 (CPMAS)	121.4 ^b	122.9 ^b	124.6 ^b	115.1 ^b	145.4 ^b	140.7 ^b
Other signals						
3 (DMSO- <i>d</i> ₆)	147.4 (C-4', ³ <i>J</i> ₄ =10.6, ² <i>J</i> ₅ =5.1); 121.8 (C-3', ¹ <i>J</i> ₃ =177.2, ³ <i>J</i> ₄ =5.1)	144.1 (C-2', ³ <i>J</i> ₂ =8.2, ² <i>J</i> ₃ =4.9);	132.6 (C-1', ³ <i>J</i> ₁ =9.8, ³ <i>J</i> ₂ =6.9);	129.2 (C-5'); 128.9 (C-6', ¹ <i>J</i> ₆ =174.5);		
3 (CPMAS) ^a	146 (C-4'); 146 (C-2'); 134 (C-1'); 130 (C-5', C-6'); 124 (C-3')					
4 (DMSO- <i>d</i> ₆)	147.3 (C-4', ³ <i>J</i> ₄ =10.6, ² <i>J</i> ₅ =4.9, ² <i>J</i> ₃ =3.3); 128.3 (C-5', ¹ <i>J</i> ₅ =176.2); 127.5 (C-6', ¹ <i>J</i> ₆ =176.3); 121.2 (C-3', ¹ <i>J</i> ₃ =177.1, ³ <i>J</i> ₄ =5.7, ⁴ <i>J</i> ₅ =1.6)	143.0 (C-2', ³ <i>J</i> ₂ =7.9, ² <i>J</i> ₃ =4.3, ⁴ <i>J</i> ₅ =1.6); 135.0 (C-1', ³ <i>J</i> ₁ =9.8, ³ <i>J</i> ₂ =6.9, ² <i>J</i> ₃ =2.0);				
4 (CPMAS)	146.2 (C-4'); 144.2 (C-2'); 131.5 (C-1'); 130.2 (C-5'); 129.1 (C-6'); 122.9 (C-3')					

^a Very broad signals, between 1.1 and 1.8 ppm of width.^b The assignment of these signals can be exchanged.

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