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The 1-alkoxy-4-nitro-1,2,3-benzotriazole system was prepared using a phase transfer catalysis procedure. The physical and spectral properties of the system are reported. Molecular orbital calculations on the 1-methoxy derivative are used to explain the spectroscopic and electronic properties of the system.

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The biological activity of the 1,2,3-benzotriazole molecule **1** and its derivatives is well known. Organic molecules containing nitro groups have found uses as herbicides because of their ability to inhibit root and shoot growth in plants that absorb them [1]. Thus, due to the critical role that herbicides play in grain production, we decided to prepare derivatives of the 1-alkoxy-4-nitro-1,2,3-benzotriazole system in the hope that a more effective and potentially less toxic herbicide system could be defined.

We wish to report the synthesis, physical and spectral properties of several 1-alkoxy-4-nitro-1,2,3-benzotriazoles **3-8**. The compounds were prepared by reacting the sodium salt of 1-hydroxy-4-nitro-1,2,3-benzotriazole **2** with the appropriate alkyl halide using a phase transfer catalytic procedure for all the compounds except **3**. Each compound gave a satisfactory elemental analysis (Table I). The ultraviolet spectra of **3-8** possessed significant absorptions near 215 and 278 nm. These absorptions can be ascribed to $\pi \rightarrow \pi^*$ transitions [2].

The infrared spectra all possessed absorptions at 1240, 1260 and 1380 cm^{-1} which are characteristic of a 5-membered ring fused to a benzene nucleus [3]; a pair of bands in the vicinity of 1000 and 1100 cm^{-1} , which have been reported for a thiazole ring [4]; two strong absorption bands in the region of 1300 and 1500 cm^{-1} , which are characteristic of a nitro group conjugated to an aromatic nucleus [5];

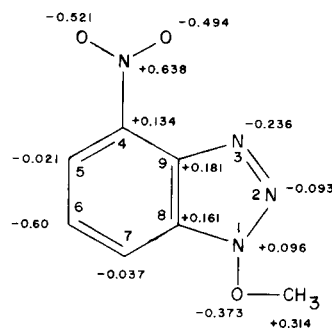


Figure 1. INDO Charge Densities for **3**

Table I
Physical and Spectral Properties

Compound No.	Elemental Analysis NMR Spectrum (δ) R	Mp ($^{\circ}\text{C}$)	Calcd.	Found	in Ethanol (nm)	Ultraviolet Spectrum Deuteriochloroform
3	methoxy	149-151	C, 43.41 H, 3.12 N, 28.86	43.19 3.24 28.64	278 (log ϵ = 3.86) 215 (log ϵ = 3.72)	4.5 ppm (s, 1H) 7.5-8.3 ppm (m, 3H)
4	ethoxy	96-97	C, 46.16 H, 3.87 N, 26.91	45.92 3.89 26.76	278 (log ϵ = 4.40) 215 (log ϵ = 4.80)	1.5 ppm (t, 3H, J = 7 Hz) 4.7 ppm (q, 2H, J = 7 Hz) 7.5-8.3 ppm (m, 3H)
5	<i>n</i> -propoxy	67-68	C, 48.65 H, 4.54 N, 25.21	48.77 4.55 25.13	278 (log ϵ = 4.24) 215 (log ϵ = 3.56)	1.2 ppm (t, 3H, J = 7 Hz) 1.9 ppm (m, 2H) 4.7 ppm (t, 2H, J = 6 Hz) 7.5-8.3 (m, 3H)
6	<i>n</i> -butoxy	59-60	C, 50.84 H, 5.12 N, 23.72	51.02 5.14 24.02	278 (log ϵ = 3.94) 215 (log ϵ = 3.66)	1.0 ppm (t, 3H, J = 7 Hz) 1.3-2.0 ppm (m, 4H) 4.7 ppm (t, 2H, J = 6 Hz) 7.5-8.3 ppm (m, 3H)
7	cyclopentoxy	93-84	C, 53.22 H, 4.87 N, 22.84	52.93 5.12 22.34	278 (log ϵ = 3.99) 215 (log ϵ = 3.56)	2.0 ppm (m, 8H) 5.4 ppm (m, 1H) 7.5-8.3 ppm (m, 3H)
8	cyclopentoxy	74-76	C, 56.51 H, 5.84 N, 20.29	56.47 6.05 20.03	278 (log ϵ = 4.02) 215 (log ϵ = 3.74)	1.6-2.0 ppm (m, 12H) 4.9 ppm (m, 1H) 7.5 ppm (m, 3H)

Table II

Calculated Spectral Results for 1-Methoxy-4-nitro-1,2,3-benzotriazole
Using INDO/S

Planar NO ₂		Twisted NO ₂ , 45°	
Energy (cm ⁻¹)	Osc Str	Energy (cm ⁻¹)	Osc Str
23,625	0.000	22,730	0.041
25,060	0.000	25,135	0.002
29,150	0.378	30,165	0.069
40,150	0.137	30,890	0.168
46,000	0.213	38,735	0.161
48,600	0.705	44,030	0.219
51,880	0.763	46,990	0.434
53,950	0.388	48,740	0.159
		49,200	0.135
		50,250	0.134
		51,050	0.736
		52,792	0.382

and a band at 940 cm⁻¹ which has been assigned to the N-O stretching mode of alkyl nitrites [6]. The nmr spectra showed all the alkoxy hydrogens. The aromatic protons appeared as a sharp multiplet from 7.8-8.4 ppm. Since the aromatic protons in benzotriazole are not abnormally deshielded beyond 7.6 ppm, it was evident that the nitro group was strongly interacting in a deshielding manner with the aromatic protons.

To determine electronic and spectral properties all-valence-electron molecular orbital calculations were performed using the INDO/S technique of Ridley and Zerner [7]. The benzotriazole geometry was taken from the X-ray study of Escande *et al.* [8], and standard bond lengths were used for the methoxy group [9]. A nitro group geometry with R(C-N) = 1.47 Å, R(N-O) = 1.22 Å, and an O-N-O angle of 124° was employed, based on averages from literature studies [10-13]. Two orientations of the nitro group were examined: in the first the nitro group was placed in the molecular plane and in the second the nitro group was twisted about the C-N axis by 45°. Configuration interaction was taken over the lowest 100 excited singlet configurations.

The calculated spectral results are shown in Table II. According to the calculations, placement of the 4-nitro group onto the 1-methoxy-1,2,3-benzotriazole framework causes the introduction of very weak $n \rightarrow \pi^*$ transitions, largely localized on the nitro group, at low energies. These were not detected experimentally. The stronger $\pi \rightarrow \pi^*$ transitions are also expected to be lowered in energy. The experimental uv spectrum of **3** in cyclohexane shows two broad peaks, centered near 292 nm (34,250 cm⁻¹) and 214 nm (46,730 cm⁻¹); in ethanol the longer wavelength peak shows a splitting, presumably due to the differences in solvent-solute interactions for the excited states composing the absorption band. The twisted -NO₂ geometry results

conform more closely to the experimental results than do those for the planar geometry. (The two forms are nearly identical in energy, with the twisted geometry lying *ca.* 0.07 eV lower.) The longer wavelength band would thus appear to be composite of two transitions of comparable intensity, and the band near 46,000 cm⁻¹ also includes two or more electronic transitions.

Alteration of the NO₂ orientation had only a very minor influence on the calculated molecular charge distribution, shown in Figure 1 for the planar form.

EXPERIMENTAL

The infrared spectra were obtained on a Perkin-Elmer 457 spectrophotometer. The ultraviolet spectra were obtained on a Cary 14 spectrophotometer. The nmr spectra were obtained on a Varian EM-360 spectrophotometer. Elemental analyses were performed by Midwest Micro Labs, Indianapolis, Indiana.

Materials.

1-Hydroxy-4-nitro-1,2,3-benzotriazole and **3** were prepared according to the procedures of Boyle and Jones [14].

General procedure for the preparation of the 1-alkoxy-4-nitro-1,2,3-benzotriazoles. To a solution of the sodium salt of 1-hydroxy-4-nitro-1,2,3-benzotriazole prepared from sodium hydroxide (0.02 mole) and 1-hydroxy-4-nitro-1,2,3-benzotriazole (3.60 g, 0.02 mole) in 75 ml of water was added to a solution of the alkyl halide (0.06 mole) in 75 ml of methylene chloride. After addition of the phase transfer catalyst tetrabutylammonium bromide (0.65 g), the mixture was stirred vigorously for three days. The organic layer after separation was washed twice with 50 ml portions of water. Upon evaporation of the methylene chloride, the residue was taken up in 100 ml of ethyl ether and chromatographed on neutral alumina. Evaporation of the ether yielded a solid which yielded orange crystals from 10% aqueous ethanol.

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