The 1-Alkoxy-6-nitro-1,2,3-benzotriazole System

P. Jung, P. G. Seybold and M. P. Servé*

Department of Chemistry and Biochemistry, Wright State University,
Dayton, Ohio 45435

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The 1-alkoxy-6-nitro-1,2,3-benzotriazole system has been synthesized and characterized *via* its physical and chemical properties. INDO/molecular orbital calculations provide a good account of the major bands in its ultraviolet absorption spectrum.

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The 1,2,3-benzotriazole molecule (**1**) and its derivatives are known to be biologically active. In addition, the nitro group has been shown to possess herbicidal properties in inhibiting root and shoot growth when taken up by plants (1). Thus, because of the importance that herbicides have on our food supply, we decided to prepare the 1-alkoxy-6-nitro-1,2,3-benzotriazole system in the hope that a new and safer herbicidal system could be defined.

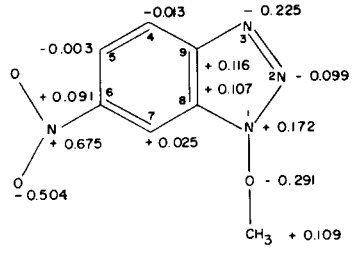
We wish to report the synthesis, physical and spectral properties of several 1-alkoxy-6-nitro-1,2,3-benzotriazoles (**3-8**). The compounds were prepared by treating the sodium salt of 1-alkoxy-6-nitro-1,2,3-benzotriazole (**2**) with the appropriate alkyl halide. All of the compounds gave satisfactory elemental analyses (Table I). The ultraviolet spectra of **3-8** possessed significant absorptions at 216, 247 and 280 nm. These absorptions can be ascribed to strong $\pi \rightarrow \pi^*$ transitions (2).

The infrared spectra all possessed absorptions at 1240, 1270 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 triazole 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); and a band at 940 cm^{-1} which has been assigned to the N-O stretching mode of alkyl nitrites (6). The nmr spectra all showed the alkoxy hydrogens. The aromatic hydrogens were represented by a pair of multiplets centered at 8.2 and 8.6 ppm in a ratio of 2:1. This indicates that the magnetic environments of two aromatic hydrogens (H_4 and H_5) are very similar while the magnetic environment of H_7 is more deshielded.

Molecular orbital calculations were performed on 1-methoxy-6-nitro-1,2,3-benzotriazole (**3**) using the spectroscopic all-valence electron INDO/S method of Ridley and Zerner (7). Coordinates for the benzotriazole portion were taken from the X-ray study of Escande *et al.* (8), and standard bond distances were used for the methoxy group (9). For the nitro group values of R (C-N) = 1.47 Å, R (N-O) = 1.22 Å and the angle of (O-N-O) = 124° were taken as representative from literature studies (10-13), and the nitro group was assumed to lie in the gross molecular plane (10).

The electronic spectral results are shown in Table II. Addition of the nitro substituent clearly causes a major alteration in the electronic spectrum (15) and introduces several weak transitions in the near ultraviolet region. When the transitions are assigned according to wavelength, the INDO/S calculations provide an excellent account of the positions of the four most intense bands. In this assignment the intensity of the 315 nm band is overestimated, and the three weak transitions predicted at longer wavelengths are apparently obscured under a broad absorption tail extending to the blue edge of the visible region. The lowest energy transition, predicted to lie near 400 nm, is predicted by the calculations to be an n $\rightarrow \pi^*$ transition.

The INDO/S calculated atomic charge densities for **3** are shown in Figure 1. The atomic charge densities indicate that position 7 is electropositive and would be susceptible to nucleophilic attack. For the 5-chloro- and 4,5-dichloro-1-methoxy-1,2,3-benzotriazoles, position 7 is electronegative (14,15). Another interesting observation from Figure 1 is that position 5 is almost neutral. This is unusual since positions *ortho* to aromatic nitro groups are normally very electropositive.



(All hydrogens carry charge densities of +0.04 to +0.08)
Net charges on the nitro group = −0.328
Net charges on the methoxy group = −0.040
Net charges on the benzotriazole molecule (including hydrogens) = +0.370

Figure 1. INDO/S atomic charge densities for 1-methoxy-6-nitro-1,2,3-benzotriazole.

Table I

Physical and Spectral Properties

Compound No.	R	Melting Point (°C)	Elemental Analysis Calcd.	Found	Ultraviolet Spectrum λ max, nm in Ethanol	NMR Spectum (δ) Deuteriochloroform
3	methoxy	130-131	C, 43.31	43.22	280 (log ε = 3.70)	4.5 ppm (s, 1H)
			H, 3.12	3.17	247 (log ε = 3.93)	8.2-8.6 ppm (m, 3H)
			N, 28.86	28.70	216 (log ε = 4.16)	
4	ethoxy	81-82	C, 46.16	46.18	280 (log ε = 3.76)	1.5 ppm (t, 3H, J = 7 Hz)
			H, 3.87	3.65	247 (log ε = 3.98)	4.7 ppm (q, 2H, J = 7 Hz)
			N, 26.91	26.94	216 (log ε = 422)	8.2-8.6 ppm (m, 3H)
5	*n*-propoxy	62-63	C, 48.65	48.94	280 (log ε = 3.80)	1.0 ppm (t, 3H, J = 7 Hz)
			H, 4.54	4.92	247 (log ε = 3.97)	1.8 ppm (m, 2H)
			N, 25.21	24.80	216 (log ε = 4.24)	4.7 ppm (t, 2H, J = 6 Hz)
						8.2-8.6 ppm (m, 3H)
6	*n*-butoxy	60-61	C, 50.84	50.50	280 (log ε = 3.86)	1.1 ppm (t, 3H, J = 7 Hz)
			H, 5.12	5.10	247 (log ε = 4.09)	1.7 ppm (m, 4H)
			N, 23.72	23.82	216 (log ε = 4.20)	4.7 ppm (t, 2H, J = 6 Hz)
						8.2-8.6 ppm (m, 3H)
7	cyclopentyloxy	93-94	C, 53.22	53,61	280 (log ε = 3.82)	2.0 ppm (m, 8H)
			H, 4.87	4.85	247 (log ε = 4.09)	5.4 ppm (m, 1H)
			N, 22.57	22.68	216 (log ε = 4.26)	8.2-8.6 ppm (m, 3H)
8	cycloheptyloxy	59-61	C, 56.51	56.18		1.6-2.0 ppm (m, 12H)
			H, 5.84	5.63	280 (log ε = 3.83)	4.9 ppm (m, 1H)
			N, 20.29	19.94	247 (log ε = 4.22)	8.2-8.6 ppm (m, 3H)

Table II

Comparison of INDO/S Calculated Electronic Transition and Experimental Spectra for 1-Methoxy-6-nitro-1,2,3-benzotriazole

Wavenumber (cm^{-1})	Calculated Wavelength, λ (nm)	Oscillator Strength (log *f*) (a)	Experimental Wavelength, (log ε) λ (nm)
24,630	406	0.0 (−) (a)	
27,600	362	0.054 (−1.268)	
28,570	350	0.0 (−)	
31,200	321	0.47 (−0.328)	315 sh (3.64)
25,890	279	0.018 (−1.745)	
36,500	274	0.11 (−0.959)	280 (3.70)
40,140	249	0.15 (−0.824)	247 (3.93)
44,560	224	0.11 (−0.959)	216 (4.16)
46,480	215	0.034 (−1.469)	

(a) $\log f + 4 = \log \epsilon$.

EXPERIMENTAL

The infrared spectra were obtained on a Perkin-Elmer 735-B spectrophotometer. The ultraviolet spectra were obtained on a Cary 14 spectrophotometer. The nmr spectra were obtained on a Varian EM-360 spectrometer.

Materials.

1-Hydroxy-6-nitro-1,2,3-benzotriazole was prepared according to the precedure of Boyle and Jones (16). The procedure for the preparation of the 1-alkoxy-6-nitro-1,2,3-benzotriazoles has been previously delineated (15,16).

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