The 1-Alkoxy-4,5-dichloro-1,2,3-benzotriazole System

W. A. Feld, P. G. Seybold and M. P. Servé

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

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The 1-alkoxy-4,5-dichloro-1,2,3-benzotriazole system has been synthesized and characterized *via* its physical and chemical properties. INDO/S MO calculations provide a good account of the ultraviolet absorption spectrum.

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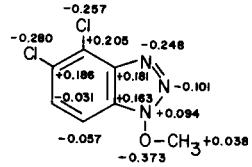
Derivatives of the 1,2,3-benzotriazole molecule (**1**) have been shown to possess varying degress of biological activity. In addition, halogens, especially chlorine atoms, are known to increase the pesticidal activity of molecules (1). Thus, it was not surprising that members of the 1-alkoxy-5-chloro-1,2,3-benzotriazole system possessed minor activity as anthelmintic and anti-tick agents (2). Because of the widespread damage inflicted by ticks on the human food supply, we decided to prepare the 1-alkoxy-4,5-dichloro-1,2,3-benzotriazole system in the hope that the added chlorine substituent would increase the pesticidal activity of the 1,2,3-benzotriazole molecule.

Here we wish to report the synthesis, physical and spectral properties of several 1-alkoxy-4,5-dichloro-1,2,3-benzotriazole derivatives (**3-9**). The compounds were prepared by reaction of the sodium salt of 1-hydroxy-4,5-dichloro-1,2,3-benzotriazole (**2**) with the appropriate alkyl halide. The compounds all gave satisfactory elemental analyses (Table I). The ultraviolet spectra of **3-9** possessed significant absorption at 209, 264, 272, and 294 nm, the absorption at 209 nm being especially strong. These absorptions can be ascribed to $\pi \rightarrow \pi^*$ transitions (3).

The infrared spectra showed absorptions at 1240, 1270 and 1390 cm^{-1} which are characteristic of a 5-membered ring fused to a benzene nucleus (4); a pair of bands in the vicinity of 1030 and 1100 cm^{-1}, which have been reported for a triazole 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 requisite alkoxy hydrogens. The aromatic hydrogens were represented by a singlet indicating the similarity of electronic and magnetic environments for H-6 and H-7.

We previously examined the electronic spectrum of 1-methoxy-1,2,3-benzotriazole (**10**) using CNDO/S MO calculations and standard bond distances for the atomic coordinates (7). Here we report spectroscopic molecular orbital calculations using the all-valence-electron INDO/S method recently developed by Ridley and Zerner (8). Atomic distances for the benzotriazole molecule were taken from the X-ray analysis of Escande *et al.* (9), and standard bond distances were employed for other atoms (10), with R (C-Cl) = 1.718 Å (11). The configuration interaction treatment included the 50 lowest configurations.

Figure 1



(All hydrogens carry charges of +0.09 to +0.10)

INDO/S Atomic Charge Densities for 1-Methoxy-4,5-dichloro-1,2,3-benzotriazole

INDO/S results for **3** and **10** are shown in Table II. These results are seen to be in excellent agreement with the experimental spectrum, especially for **3**. In contrast to the earlier CNDO/S results, the lowest excited singlet state is predicted to be of $^1(\pi,\pi^*)$ character. The lowest $n \rightarrow \pi^*$ transition is calculated to fall roughly 2000 cm^{-1} higher in energy than the lowest $\pi \rightarrow \pi^*$ transition, and to involve principally excitation of an electron from nitrogen 3 to a π^* orbital. The basic pattern of the three electronic transition bands falling near 283 nm, 263 nm and 220 nm found for the parent **10** appears not to be strongly altered by 4,5-dichloro substitution.

The INDO/S calculated atomic charge densities for **3** are shown in Figure 1.

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.

Materials.

1-Hydroxy-4,5-dichloro-1,2,3-benzotriazole (**2**) was prepared according to the procedure of Singh and Kapic (12). The melting point of **2**, recrystallized from aqueous ethanol was 223-225°.

Anal. Calcd. for $C_6H_3Cl_2N_3$: C, 35.22; H, 1.48; Cl, 34.76; N, 20.60. Found: C, 35.17; H, 1.44; Cl, 34.52; N, 20.86.

The procedure for the preparation of the 1-alkoxy-4,5-dichloro-1,2,3-benzotriazoles has been previously delineated (7).

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Table I

Physical and Spectral Properties

Compound No.	R	Melting Point (°C)	Elemental. Calcd.	Analysis Found	Ultraviolet (nm) In Ethanol	Nmr in Deuterochloroform
3	O-CH_3	115-116	C, 38.56	38.58	294 (log ε = 3.82)	4.40 ppm (s, 3H)
			H, 2.31	2.44	272 (log ε = 4.00)	7.50 ppm (s, 2H)
			N, 19.27	19.55	264 (log ε = 3.98)	
			Cl, 32.52	32.36	209 (log ε = 4.52)	
4	O-C_2H_5	95-96	C, 41.40	41.39	294 (log ε = 3.81)	1.40 ppm (t, 3H, J = 4 Hz)
			H, 3.04	3.28	272 (log ε = 3.95)	4.65 ppm (q, 2H, J = 4 Hz)
			N, 18.11	18.55	264 (log ε = 3.94)	7.50 ppm (s, 2H)
			Cl, 30.56	30.36	209 (log ε = 4.51)	
5	O-$CH_2CH_2CH_3$	74-76	C, 43.92	43.81	294 (log ε = 3.84)	1.15 ppm (t, 3H, J = 4 Hz)
			H, 3.69	3.84	272 (log ε = 3.92)	1.80 ppm (m, 2H)
			N, 17.08	17.17	265 (log ε = 3.91)	4.60 ppm (t, 2H, J = 4 Hz)
			Cl, 28.81	29.07	209 (log ε = 4.52)	7.55 ppm (s, 2H)
6	O-$CH_2CH_2CH_2CH_3$	42-43	C, 46.16	46.28	294 (log ε = 3.87)	1.05 ppm (t, 3H, J = 4 Hz)
			H, 4.26	4.24	272 (log ε = 3.98)	1.75 ppm (m, 4H)
			N, 16.15	16.48	265 (log ε = 3.95)	4.60 ppm (t, 2H, J = 4 Hz)
			Cl, 27.26	27.00	209 (log ε = 4.51)	7.55 ppm (d, 2H, J = 1 Hz)
7		78-80	C, 48.55	48.62	294 (log ε = 3.80)	1.90 ppm (m, 8H)
			H, 4.08	4.08	272 (log ε = 3.91)	5.25 ppm (m, 1H)
			N, 15.44	15.49	265 (log ε = 3.90)	7.45 ppm (d, 2H, J = 1 Hz)
			Cl, 26.06	25.89	209 (log ε = 4.49)	
8		82-83	C, 50.37	50.51	294 (log ε = 3.83)	1.80 ppm (m, 10H)
			H, 4.58	4.42	272 (log ε = 3.97)	4.65 ppm (m, 2H)
			N, 14.68	14.57	265 (log ε = 3.96)	7.50 ppm (s, 2H)
			Cl, 24.78	24.83	209 (log ε = 4.48)	
9		73-74	C, 52.01	51.71	294 (log ε = 3.75)	1.55 ppm (m, 12H)
			H, 5.04	5.22	272 (log ε = 3.91)	4.90 ppm (m, 1H)
			N, 14.00	14.13	265 (log ε = 3.90)	7.45 ppm (d, 2H, J = 1 Hz)
			Cl, 23.62	23.49	209 (log ε = 4.42)	7.45 ppm (d, 2H, J = 1 Hz)

Table II

Comparison of INDO/S Calculated Electronic Transitions and Experimental Spectra

Compound	Calculated (osc. str.)	Experimental (log ε)
1-Methoxy-1,2,3-benzotriazole	296 nm (f = 0.106)	283 nm (log ε = 3.74)
	280 nm (f = 0.024)	
	267 nm (f = 0.288)	263 nm (log ε = 3.73)
	228 nm (f = 0.349)	
	212 nm (f = 0.305)	
	204 nm (f = 0.248)	
	195 nm (f = 0.560)	
1-Methoxy-4,5-dichloro-1,2,3-benzotriazole	295 nm (f = 0.088)	294 nm (log ε = 3.82)
	275 nm (f = 0.023)	
	267 nm (f = 0.254)	272 nm (log ε = 4.00)
		264 nm (log ε = 3.98)
	226 nm (f = 0.433)	209 nm (log ε = 4.52)
	216 nm (f = 0.436)	

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