

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

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The 1-alkoxy-1,2,3-benzotriazole system has been synthesized and defined on the basis of its physical and spectral properties. Bond orders and charge densities of the parent compound in the series 1-methoxy-1,2,3-benzotriazole have been calculated. All-valence-electron calculations with configuration interaction give a reasonable account of the observed absorption spectrum.

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In our laboratory, we recently have become interested in derivatives of 1-alkoxy-1,2,3-benzotriazole (**1**) as a potential new fungicide system. The reported physical data on this system, however, are quite sparse. The parent compound 1-methoxy-1,2,3-benzotriazole (**2**) was synthesized by Brady and Reynolds (1), who identified it solely on the basis of its elemental analysis. There appears to have been no attempt made to delineate the physical and spectral properties of this important system.

We would like to report several new examples of **1** along with the relevant physical and spectral data. All the compounds were prepared by treating the sodium salt of 1-hydroxy-1,2,3-benzotriazole (**3**) with the appropriate alkyl halide. The elemental analyses (Table I) lend support to the assigned structures. The ultraviolet spectra of **1** have two major absorptions near 263 nm and 283 nm, which can be ascribed to $\pi \rightarrow \pi^*$ transitions. The infrared spectra of **1** all possess bands at 1240, 1270 and 1380 cm^{-1} which are typical of molecules containing a 5-membered ring fused to a benzene nucleus (2). The pair of bands in the vicinity of 1100 and 1000 cm^{-1} have been previously reported for the triazole ring (3), while the band at 940 cm^{-1} has been ascribed to the N-O stretching mode in alkyl nitrites (4). The nmr spectra of **1** all possess peaks in the areas where alkyl groups attached to an ether oxygen normally appear. In addition the nmr spectra of **1** showed two complex multiplets centered at 7.4 ppm and 7.9 ppm in the intensity ratio of 3:1, which correlate well with the aromatic hydrogen positioning in the nmr spectra of other 1,2,3-benzotriazole derivatives previously reported (5).

The mass spectrum of **2** revealed a weak molecular ion peak at 149.0597 ($\text{C}_7\text{H}_7\text{N}_3\text{O} = 149.0588$). There were also prominent peaks at 121.0541 ($\text{C}_7\text{H}_7\text{NO} = 121.0528$),

106.0339 ($\text{C}_6\text{H}_4\text{NO} = 106.0293$) and 90.0349 ($\text{C}_6\text{H}_4\text{N} = 90.0343$) which may be ascribed to M-N_2 , $\text{M-N}_2\text{CH}_3$ and $\text{M-N}_2\text{OCH}_3$, respectively.

To obtain a clearer understanding of the electronic properties involved in the **1** system, calculations using HMO theory (6) were made on the bond orders and charge densities of **1**. For simplification purposes, **2** was selected as the model compound: The charge densities indicate that the ground state electrophilic attack is most likely to occur at positions 5 and 7 of the phenyl ring.

Spectral molecular orbital calculations on **2** were carried out using the all-valence-electron CNDO/S method of Del Bene and Jaffe (7). Two-center electron repulsion integrals were calculated using the Nishimoto-Magata formula (8), and the lowest 80 singly excited configurations were included in the configuration interaction treatment. Two geometries were treated: A) a geometry having the N-O-C link in the plane of the molecule, and B) a geometry with the methyl group sticking out of the molecular plane ($\text{N-O-C} = 120^\circ$). In each case standard bond lengths and bond angles were assumed. The results are given in Table II.

Calculated HMO Bond Orders for 1-Methoxy-1,2,3-benzotriazole

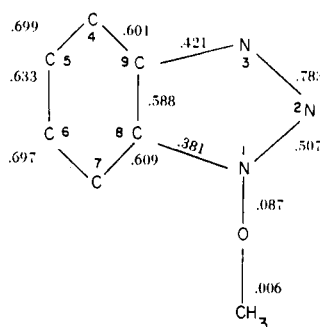


Table I
Physical and Spectral Properties of 1

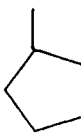
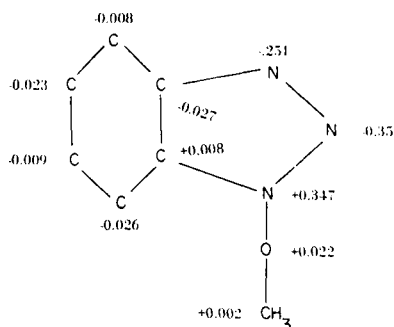
R	Boiling Point	Elemental Calcd.	Analysis Found	Ultraviolet (nm) in Ethanol	Infrared cm^{-1}	Nmr
-CH ₃		C, 56.37% H, 4.73% N, 28.17%	56.20% 4.52% 28.16%	175 (log $\epsilon = 3.74$) 263 (log $\epsilon = 3.73$) 283 (log $\epsilon = 3.60$)	745 (s), 770 (s), 785 (s), 920 (s), 960 (s), 1095 (s), 1105 (m), 1160 (m), 1240 (s), 1270 (s), 1380 (s), 1470 (s)	4.3 ppm (3H, s)
-CH ₂ CH ₃	82-84° C (0.7 mm)	C, 58.88% H, 5.56% N, 25.75%	58.61% 5.67% 25.90%	262 (log $\epsilon = 3.82$) 283 (log $\epsilon = 3.76$)	745 (s), 770 (s), 785 (s), 960 (s), 1015 (s), 1000 (m), 1095 (s), 1110 (m), 1155 (m), 1240 (s), 1270 (s), 1380 (s),	1.45 ppm (3H, t) 4.6 ppm (2H, q)
-CH ₂ CH ₂ CH ₃	94-96° C (0.7 mm)	C, 61.00% H, 6.26% N, 23.71%	61.12% 6.31% 23.42%	264 (log $\epsilon = 3.84$) 283 (log $\epsilon = 3.76$)	740 (s), 770 (m), 782 (m), 930 (m), 962 (m), 1095 (s), 1110 (m), 1155 (m), 1240 (s), 1270 (s), 1370 (s)	1.85 ppm (5H, m) 4.5 ppm (2H, t)
-CH ₂ CH ₂ CH ₂ CH ₃	118-120° C (0.7 mm)	C, 68.20% H, 6.85% N, 21.97%	68.53% 6.54% 22.23%	264 (log $\epsilon = 3.88$) 283 (log $\epsilon = 3.81$)	748 (s), 770 (m), 785 (m), 845 (m), 915 (m), 940 (s), 960 (m), 1000 (m), 1020 (m), 1060 (m), 1095 (s), 1110 (s), 1160 (s), 1240 (s), 1270 (s), 1370 (s)	1.75 ppm (7H, m) 4.55 ppm (2H, t)
-CH ₂ CH ₂ CH ₂ CH ₂ CH ₃	138-140° C (0.7 mm)	C, 64.36% H, 7.37% N, 20.47%	63.11% 7.56% 20.73%	264 (log $\epsilon = 3.74$) 283 (log $\epsilon = 3.65$)	745 (s), 770 (s), 780 (s), 960 (s), 1000 (w), 1040 (w), 1095 (s), 1110 (m), 1155 (m), 1240 (s), 1270 (s), 1370 (s)	1.6 ppm (9H, m) 4.5 ppm (sH, t)
-CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₃	154-156° C (0.8 mm)	C, 65.72% H, 7.82% N, 19.16%	65.55% 7.99% 18.83%	264 (log $\epsilon = 3.69$) 283 (log $\epsilon = 3.65$)	745 (s), 770 (s), 785 (s), 910 (m), 915 (m), 925 (m), 945 (m), 985 (m), 1000 (m), 1040 (m), 1095 (s), 1110 (m), 1155 (s), 1240 (s), 1270 (s), 1370 (s)	1.6 ppm (11H, m) 4.5 ppm (2H, t)
	142-144° C (0.8 mm)	C, 65.00% H, 6.45% N, 20.67%	65.23% 6.51% 20.22%	264 (log $\epsilon = 3.78$) 283 (log $\epsilon = 3.71$)	745 (s), 770 (s), 782 (s), 952 (w), 1000 (w), 1035 (w), 1095 (w), 1110 (m), 1155 (m), 1170 (m), 1240 (s), 1270 (s), 1340 (s)	1.7 ppm (8H, m) 5.15 ppm (1H, m)

Table II
Calculated Electronic States of 1-Methoxy-1,2,3-benzotriazole

Planar Geometry			
E (eV)	f	Type of Electronic Transition	μ (D)
0.0	-----	-----	2.60
4.03	0.016	$\eta \rightarrow \pi^*$	2.28
4.08	0.112	$\eta \rightarrow \pi^*$	6.73
4.47	0.0	$\eta \rightarrow \pi^*$	3.99
4.57	0.308	$\eta \rightarrow \pi^*$	8.40
5.26	0.243	$\eta \rightarrow \pi^*$	4.11
5.83	0.281	$\eta \rightarrow \pi^*$	3.04
6.00	0.149	$\eta \rightarrow \pi^*$	5.35
Out-of-Plane Geometry			
E (eV)	f	Type of Electronic Transition	μ (D)
0.0	-----	-----	4.04
4.00	0.015	$\eta \rightarrow \pi^*$	6.02
4.10	0.108	$\eta \rightarrow \pi^*$	8.04
4.56	0.001	$\eta \rightarrow \pi^*$	6.29
4.60	0.309	$\eta \rightarrow \pi^*$	10.10
5.28	0.228	$\eta \rightarrow \pi^*$	6.35
5.85	0.289	$\eta \rightarrow \pi^*$	3.89

Calculated Net π Electron Densities for 1-Methoxy-1,2,3-benzotriazole



The calculated results are in reasonable agreement with the observed transitions near 283 nm (4.38 eV) and 263 nm (4.71 eV). Both transitions involve significant intramolecular charge-transfer character as indicated by their dipole moments.

It is apparent that the calculated transition energies and intensities are quite insensitive to the change in geometry between A and B. However, the dipole moments calculated for the ground and excited states of the non-planar form tend to be 20-50% higher than those found for the same states of the planar form. The in-plane configuration is calculated to be 0.6 eV more stable than the out-of-plane configuration. Both calculations predict the lowest excited singlet state to be $^1(\eta, \pi^*)$, but with a $^1(\pi, \pi^*)$ state lying very close in energy. Presumably solvent-solute

interactions could determine which of these two states is actually lowest in any particular solvent, thereby influencing the lowest singlet lifetime, fluorescence intensity, and inter system crossing (ISC) rate to the triplet state. A lowest $^1(\eta, \pi^*)$ state should favor ISC to the triplet manifold, with a resulting high triplet yield for reactivity at that level. In the absorption spectrum the weak $^1(\eta, \pi^*)$ state is presumably masked by the more intense $^1(\pi, \pi^*)$ state, but the presence of the $^1(\eta, \pi^*)$ state might be detectable from emission or polarization measurements. The lowest triplet state ($E_{\text{calc}} = 2.15$ eV) is a $^3(\pi, \pi^*)$ state.

These results should help explain and predict the chemistry of 1.

EXPERIMENTAL

The infrared spectra were obtained on a Beckman IR-4 spectrophotometer. The ultraviolet spectra were obtained on a Cary 14 spectrophotometer. High-resolution mass spectra were obtained on a CEC-21-110 instrument.

Materials.

1-Hydroxy-1,2,3-benzotriazole was prepared according to the procedure of Macbeth and Price (9).

Preparation of 1-Alkoxy-1,2,3-benzotriazole.

A solution of 1-hydroxy-1,2,3-benzotriazole (5 g., 0.037 mole) in ethanol was added to an ethanolic solution of sodium ethoxide (prepared from 0.65 g. of sodium). The appropriate alkyl iodide (0.05 mole) was then added with stirring. The solution was then refluxed for 3 hours. The alcohol was then removed under reduced

pressure. Steam distillation yielded the 1-alkoxy-1,2,3-benzotriazole, which was then vacuum distilled. The relevant data concerning each of the products is listed in Table I.

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