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Electronic Structure and Stability of Benzotriazoles

Igor Novak* and Tareq Abu-Izneid
Charles Sturt University, P.O. Box 883, Orange NSW 2800, Australia

Branka Kovač* and Leo Klasinc
"R. Bošković" Institute, Bijenička cesta 54, HR-10000 Zagreb, Croatia

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The electronic structures and relative stabilities of N-substituted benzotriazoles (BtR) have been studied by UV photoelectron spectroscopy (UPS) and high-level ab initio methods. We show that the UPS spectrum of 1H-benzotriazole corresponds to a mixture of tautomers. The N-substituent effects in benzotriazoles were shown to depend on the mode of attachment of the substituent to the Bt residue. We have estimated the conjugation effects between benzene and triazole rings in N-substituted benzotriazoles by using isodesmic reactions and high-level composite ab initio methods. The 2H-benzotriazoles (Bt2R) appear to be stabilized upon ring conjugation while on the other hand the 1H-benzotriazoles (Bt1R) are destabilized. The electronic structure of benzotriazoles can be related to photocycloaddition reactions and to regioselectivity exhibited during nitration.

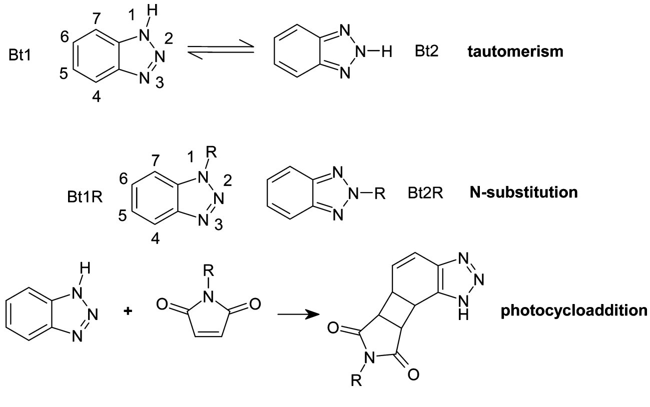
Introduction

1H-benzotriazole (Bt1 in Scheme 1) and its derivatives are interesting compounds because of their diverse molecular structures (tautomerism) and practical applications. Bt1 is a synthetic reagent that is used in reactions and synthetic procedures by which carbon insertion, amidoalkylation, and aminoalkylation can be performed.[1] Bt1 can also serve as a ligand in large polymetallic clusters that may contain up to 26 metal atoms.[2] These clusters exhibit unusual magnetic properties with high spin ground states and single-molecule magnetism. Bt1 is used as a corrosion inhibitor for copper and its alloys. Bt1 undergoes unusual photocycloaddition reaction with maleimide (Scheme 1) and this reaction can be used as an entry into the synthesis of strained molecules comprising several fused rings including cyclobutane.[3]

Unsubstituted benzotriazoles can exist in two tautomeric forms, Bt1 and Bt2 (Scheme 1) and whose relative stability has been studied extensively. The experimental data have shown that while the Bt1 tautomer is the only stable one in the solid state, in gas phase the Bt2 tautomer also appears.[4] Spectroscopic measurements revealed that Bt1 is more stable than Bt2 by 5 kJ/mol[4]. This energy difference determines relative amounts of each tautomer present in the gas phase. For example at 413 K (the temperature at which our Bt1 spectrum was measured), Bt1 can be expected to comprise 81% of the mixture. Finally, there is an interest in thermal stability of Bt1 versus 1,2,3-triazole. The recent work by Katritzky et al.[5] has shown that Bt1 is more stable than 1,2,3-triazole toward thermal decomposition.

Bt represents an interesting compound and we can expect that its diverse chemical behavior is due to its molecular electronic structure. The electronic structures of Bt and some of its substituted derivatives have been studied previously by UV photoelectron spectroscopy (UPS).[6,7] However, these studies focused exclusively on the assignment of photoelectron spectra and did not explicitly compare the spectra of N-substituted Bt1R and Bt2R derivatives. We decided to reinvestigate some of the reported spectra of N-substituted benzotriazoles using HeI and HeII radiation and also to study new derivatives. The aim is to investigate the electronic structure in the context of chemical reactivity and stability.

SCHEME 1: Structures and Reactivity of the Molecules Studied



Experimental and Theoretical Methods

The compounds studied in this work (Bt1R; R = CH_3, CH_2Cl, $CH_2CH{=}CH_2$, CH_2CCH, $CO(CH_2)_2Cl$, $COC(CH_3)_3$, $CH_2Si(CH_3)_3$, $COCH_3$, CH_2NHCOH) were purchased from Sigma-Aldrich (except Bt1Me and Bt2Me which were prepared according to the ref 8) and used without further purification after confirming their identity and purity by NMR spectroscopy.

The HeI and HeII photoelectron spectra were recorded on the Vacuum Generators UV-G3 spectrometer and calibrated with small amounts of Xe or Ar gas which was added to the sample flow. The spectral resolution in HeI and HeII spectra was 25 and 70 meV, respectively when measured as fwhm of the $3p^{-1}\ ^2P_{3/2}\ Ar^+ \leftarrow Ar\ (^1S_0)$ line. The samples were recorded with the inlet probe which was heated to temperatures in the range

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* To whom correspondence should be addressed. E-mail: (I.N.) inovak@csu.edu.au; (B.K.) bkovac@irb.hr.

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25−140 °C. The spectra obtained were reproducible and showed no signs of decomposition (except in $Bt1COCH_2CH_2Cl$ where traces of HCl were detected). The lack of decomposition was established by the measurement of NMR spectrum of the sample residue (i.e., the sample left in the probe after the completion of the spectral measurement).

The quantum chemical calculations were performed with the Gaussian 03 program.[9a] The total electronic energy for each molecule (when investigating thermodynamic stability) was computed using the G3MP2/B3LYP method,[9b] which has root-mean-square deviation of approximately 4 kJ/mol. The method includes full geometry optimization at the B3LYP/6-31G* level followed by single point QCISD type calculations. All the optimized structures corresponded to the minima on their potential energy surfaces as was inferred from the absence of imaginary vibrational frequencies. The B3LYP/6-31G* geometries (bond lengths, angles) were in good agreement with the molecular structures of Bt1R derivatives determined by X-ray diffraction.[10] The agreement between calculated and measured bond lengths and angles was within 0.01 Å and 1°, respectively. The X-ray data showed that the whole ring system is planar, that is, that nitrogen atoms are sp^2 hybridized.

For the assignment of photoelectron spectra, full geometry optimization was performed first using the density functional theory (DFT) method at B3LYP/6-31G* level (no imaginary frequencies were detected). Subsequently, a single point Green's functions (GF) type calculation[11] (starting with DFT formalism and 6-311G** basis) was performed in order to obtain vertical ionization energies. The use of this method obviates the need to rely on Koopmans' approximation. Nucleus independent chemical shifts NICS(0) were calculated at GIAO/6-311+G(d,p)//B3LYP/6-31G(d) level.

Results and Discussion

Photoelectron Spectra. The UPS spectra are depicted in Figures 1−9 of Supporting Information. The spectra have been placed in Supporting Information because our primary aim is not to report spectral assignments but to use the spectral data for analysis of relationships between electronic structure, thermodynamic stability, and chemical reactivity. The assignments of the spectra are summarized in Table 1. The assignments were based on the comparison with the previously reported spectra of substituted benzotriazoles,[6,7] GF calculations, relative HeII/HeI band intensities, and comparison with the spectra of related small molecules like *N*-methylformamide, hydroxylamine, propene, methylacetylene, and acetone.[12] The HeII/HeI band intensity changes related to the photoionization cross sections below can be used as an assignment aid, especially for bands corresponding to halogen lone pair ionizations. The HeII/HeI photoionization cross-section ratios for C, N, O, Si, and Cl np atomic orbitals are 0.31, 0.44, 0.64, 0.99, and 0.05, respectively.[13] We expect that bands corresponding to ionizations from oxygen lone pairs and Si−C bonding MOs will show relative intensity increases on going from HeI to HeII radiation. On the other hand, chlorine lone pairs will show pronounced relative intensity decrease under the same conditions. For example, in the spectra of $BtCH_2Cl$ (Figure 2, Supporting Information) the overlapping bands at 11.54 and 11.8 eV show a pronounced decrease in intensity on going from HeI to HeII, which is consistent with their assignment to chlorine lone pair ionizations. In the spectrum of $BtCH_2SiMe_3$ the band at 11.3 eV exhibits intensity increase and can be associated with ionization from σ MO of the trimethylsilyl group.

The spectrum of Bt1 had been reported previously[7a] but some of its features were not analyzed in detail. For example, the Bt1 spectrum (Figure 1, Supporting Information) displays the first sharp, intense peak at 8.67 eV that was attributed to vibrational transition within the X band of Bt1. We found the intensity and width of this peak to be unusual even assuming that the contour of the X band at 8.67 eV comprises several superimposed vibronic progressions whose Franck−Condon envelopes have 0-0 as the most intense transition. In view of the fact that both Bt1 and Bt2 tautomers exist in the gas phase,[4] we have investigated the spectra of their N-methyl derivatives. This is because Bt1 and Bt2 are in tautomeric equilibrium and therefore cannot be obtained in pure form at the temperatures of UPS measurements. N-methyl derivatives of Bt1 and Bt2 of course do not have tautomers. The calculated GF ionization energies (Table 1) of the two tautomers suggest that the measured spectrum of Bt1 corresponds to the mixture of Bt1 and Bt2 tautomers. The calculated HOMO ionization energy of Bt2 is 0.3 eV smaller than for Bt1 (Table 1). These theoretical values are consistent with the spectra shown in Figure 1 and indicate that the previously reported spectrum of Bt1 does correspond to the mixture of Bt1 and Bt2 tautomers with Bt1 tautomer predominating. The first adiabatic ionization energy of the Bt2 tautomer has been determined independently by mass analyzed threshold ionization spectroscopy (MATI) and was found to be 8.73 eV.[14] This value is in very good agreement with the peak recorded at 8.67 eV in our spectra (Figure 1, Supporting Information). MATI data thus support our conclusion that the measured spectrum of Bt1 corresponds in fact to the superimposed spectra of tautomers. The relative intensity of the 8.67 eV peak (assigned to Bt2) appears to be larger than its stated abundance of 19%. This apparent discrepancy may be explained as follows. The photoionization cross sections of 0-0 transitions in the two tautomers may be different. Furthermore, the relative intensities of 8.97 and 8.67 eV peaks cannot be used to assess relative abundance of the two tautomers, because the former peak contains ionization contributions from both tautomers, as the GF results demonstrate (Table 1). Ionization energy shifts, induced by methylation of Bt1 and Bt2, exhibited by the first peaks in the photoelectron spectra of Bt1 (from 8.97 to 8.73 eV) and Bt2 (from 8.67 to 8.50 eV) amount to approximately 0.24 and 0.17 eV, respectively. The value of 0.24 eV is an approximate one because the peak at 8.97 eV contains two unresolved ionizations. However, the two shifts are of similar magnitude which indicates that they are due to inductive rather than to resonance destabilization by the methyl group. If resonance effect was important the two shifts would differ greatly in magnitude; the methylation effect on Bt2 would be much smaller than on Bt1 because of different localization properties of the π_5 MO in the two tautomers (Scheme 2). The GF ionization energies of uppermost occupied MOs in unsubstituted and N-methyl-substituted molecules (Table 1) also exhibit energy shifts of comparable magnitude toward lower ionization energies.

Some of the spectra in Figures 1−9 in Supporting Informationhave been reported previously[7] but only at HeI photon energy. Our spectra are in very good agreement with the earlier data as can be seen from Table 1. We have measured HeI and HeII spectra to validate previously reported spectral assignments which were obtained with semiempirical PM3 molecular orbital (MO) method. The spectra contain several bands in the region of 8−13 eV. The bands correspond to ionizations of six MOs of the Bt skeleton (Scheme 2) with additional bands originating from the substituent localized MOs.

TABLE 1: Vertical Ionization Energies and Band Assignments for N-Substituted 1H-benzotriazoles[a–c] (Bt1R) and Methyl-2H-benzotriazole (Bt2Me)

substituent (R)	band	E_i/eV	GF/eV	MO	substituent (R)	band	E_i/eV	GF/eV	MO
Bt1[a] (Bt2)	X	8.97 (9.05)	8.65 (8.30)	π_5	$COCH_2CH_2Cl$	X-A	9.45	8.99, 9.30	π_5, π_4
	A	9.45 (9.49)	8.88 (8.92)	π_4		B	10.2	10.63	n^-
	B	10.03 (10.09)	10.46 (10.97)	n^-		C	10.6	11.07	n_O
	C	11.28 (11.35)	11.34 (11.59)	π_3		D-F	11.25	11.14, 11.60, 11.66	π_3 n_{Cl} n_{Cl}
	D	11.92 (11.97)	12.20 (11.61)	n^+		G	12.1	12.60	n^+
	E	12.68 (12.68)	12.32 (12.20)	π_2	$COCMe_3$[a]	X	9.05 (9.15)	8.70	π_5
	F	12.9 (12.9)	13.19 (13.19)	σ		A-B	9.5, *9.7* (9.45)	8.98	π_4, n^-
	G	13.37 (13.35)	13.28 (13.44)	σ		C	10.3 (10.25)	10.34	n_O
Bt2Me[b]	X	8.50 (8.54)	8.12	π_5		D-E	11.1 (11.15)	10.91, 11.12	π_3 σ_{alkyl}
	A	9.14 (9.16)	8.65	π_4		F-G	12.0	11.88, 12.03	n^+ σ_{alkyl}
	B-C	10.75 (10.7)	10.77	$n^-\pi_3$		H	12.80 (12.75)	12.40	π_2
	D	11.52	11.35	n^+	CH_2SiMe_3	X	8.45	8.00	π_5
	E	12.59	11.41	π_2		A	9.0	8.57	π_4
	F	13.11	11.85	σ		B	9.55	9.52	n^-
Me[a]	X	8.73 (8.78)	8.37	π_5		C-D	10.5	10.17, 10.42	π_3 σ_{Si}
	A	9.27 (9.29)	8.72	π_4		E-F	11.3	11.34, 11.61	n^+ σ_{Si}
	B	9.82 (9.84)	10.29	n^-		G	12.4	12.20	π_2
	C	10.77 (10.73)	10.86	π_3	$COCH_3$[a]	X	9.2 (9.21)	8.80	π_5
	D	11.71 (11.67)	12.04	n^+		A	9.5 (9.56)	9.13	π_4
	E	12.54 (12.48)	12.13	π_2		B	10.05 (10.11)	9.79	n^-
	F	13.17 (13.18)	12.93	σ		C	10.55 (10.58)	10.68	n_O
CH_2Cl[a]	X	8.95 (9.05)	8.71	π_5		D	11.2 (11.2)	11.01	π_3
	A	9.45 (9.52)	9.02	π_4		E	12.1 (12.04)	12.01	n^+
	B	10.05 (10.10)	10.12	n^-		F	12.9 (12.85)	12.87	π_2
	C	11.0 (11.05)	10.76	π_3	CH_2NHCOH	X-A	8.9	8.41, 8.98	π_5 π_4
	D	11.54 (11.55)	11.24	n_{Cl}		B	9.4	9.80	n^-
	E-F	11.80 (11.8)	11.56, 12.35	n_{Cl}, n^+		C-D	10.4	9.90, 10.39	n_N n_O
	G	12.7 (12.71)	12.57	π_2		E	11.3	11.0	π_3
Allyl[a]	X	8.55 (8.66)	8.31	π_5		F	11.75	11.85	n^+
	A	9.2 (9.21)	8.69	π_4		G	12.7	12.0	π_2
	B	9.7 (9.75)	10.08	n^-	OH[c]	X	8.95		π_5
	C	10.35 (10.35)	10.32	π_{CC}		A	9.50		π_4
	D	10.75 (10.85)	10.76	π_3		B	10.2		n^-
	E	11.6 (11.63)	11.98	n^+		C	11.0		π_3
	F	12.5 (12.43)	12.93	π_2		D-E	11.95		n^+ n_O
CH_2CCH	X	8.75	8.43	π_5		F	12.5		π_2
	A	9.38	8.76	π_4	OCH_3[c]	X	8.80		π_5
	B	9.9	10.25	n^-		A	9.35		π_4
	C	10.7	10.35	π_{CC}		B	9.90		n^-
	D	10.95	10.43	π_{CC}		C	10.85		π_3
	E	11.2	11.08	π_3		D-E	11.80		n^+ n_O
	F	11.7	12.10	n^+					
	G	12.6	12.30	π_2					

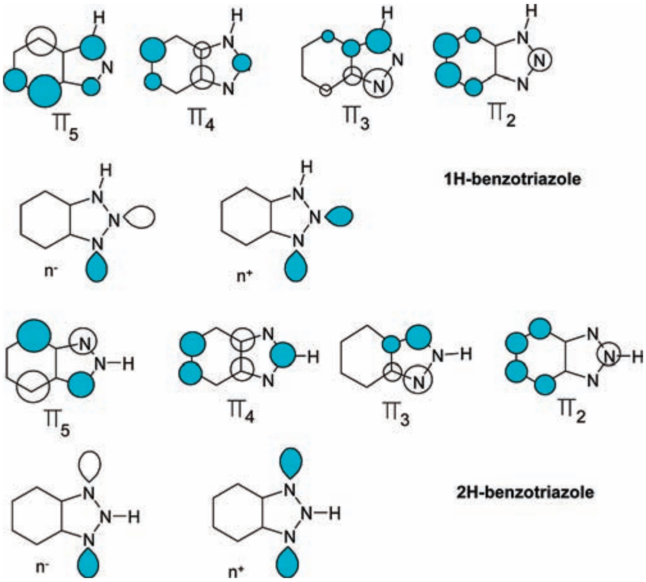
[a] The E_i values in brackets are from ref 7a; the GF values in brackets are for 2H-benzotriazole. [b] The values in brackets are from ref 6. [c] The values and assignments are from ref 7b. [d] The ionization energies in italic font correspond to shoulders of the main band.

The interaction between substituent R and Bt skeleton depends on whether the substituent is attached to the ring nitrogen via the CH_2 group or not. If the CH_2 ("spacer") group is present, the ionizations from MOs localized on the substituent will have ionization energies close to their values in the corresponding molecular fragment and can be readily identified. If not, the resonance interaction can be detected between the π-system of Bt skeleton and the MOs originating from the substituent. We shall briefly mention some interesting features of the spectra which have not been discussed previously.[7a] Rademacher et al.[7a] stated that the influence of substituents on the parent Bt molecule is weak and mainly inductive in nature.[7a] The only exception was found to be π_3 MO. This conclusion was based on the correlation analysis that compared Taft substituent parameters and ionization energies of MOs depicted in Scheme 2. The π_3 MO exception is not surprising in view of its localization properties. π_3 MO is (unlike π_5) more localized on the triazole than on the benzene ring. We would like to comment on this correlation further by stating that one needs to consider two points, mode of attachment of the substituent to the Bt skeleton and the fact that Taft σ parameters are deduced from kinetic rather than spectroscopic measurements. σ parameter values are therefore related to reaction activation energies (transition states) and not to the ionic electronic states. This may be one of the reasons why the aforementioned correlation analysis did not detect significant substituent effects.

If substituent is attached to Bt skeleton via CH_2 (spacer) group, the substituent's influence can be expected to be mainly inductive. If there is no intervening CH_2 group considerable modification of the electronic structure of Bt may take place. The latter case is exemplified by molecules where carbonyl group is in α-position to N1 nitrogen (Figures 5, 6, 8, Supporting Information). Even if the substituent's influence is mainly inductive as in, for example, $BtCH_2SiMe_3$ (Figure 7, Supporting Information), considerable broadening of bands belonging to Bt skeleton takes place.

In the previous correlation analysis,[7a] all substituents were analyzed together (irrespective of their mode of attachment). This may have "smeared out" discernible trends. It is not easy to distinguish between inductive and resonance effects on the

SCHEME 2: Important MOs in Bt1 and Bt2 Obtained at B3LYP/6-31G* Level



SCHEME 3: Isodesmic Reactions Used to Estimate Conjugation Effects of Benzene and Triazole Rings

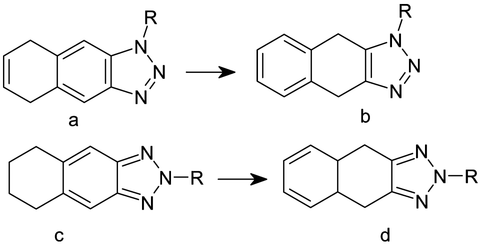


TABLE 2: Relative Stability of N-Substituted Bt1R and Bt2R versus Their 1,2,3-Triazole Analogues Calculated from Total Energies of the Reactions in Scheme 3[a]

R	Bt1R	Bt1R	Bt2R	Bt2R
	a-b /kJmol^{-1} a /au b/au	NICS(0)−6 NICS(0)−5	c-d /kJmol^{-1} c /au d/au	NICS(0)−6 NICS(0)−5
H	44 −549.825295 −549.842052	−9.76 ppm −12.92 ppm	−71.4 −551.031299 −551.004091	−8.06 ppm −15.3 ppm
CH_3	43.8 −589.059753 −589.076463	−9.80 ppm −12.7 ppm	−75.6 −590.267472 −590.238669	−8.96 ppm −14.6 ppm
Cl	46.2 −1008.939638 −1008.957239	−10.01 ppm −13.65 ppm	−73.8 −1010.144676 −1010.116556	−8.4 ppm −15.6 ppm
OH	50.7 −624.912185 −624.931494	−9.81 ppm −14.15 ppm	−78.4 −626.123096 −626.093225	−8.53 ppm −15.6 ppm
NH_2	46.3 −605.074699 −605.092332	−9.05 ppm −13.73 ppm	−77.0 −606.280578 −606.251255	−8.76 ppm −14.20 ppm
$COCH_3$	39.8 −702.271410 −702.286562	−6.62 ppm −14.36 ppm	−65.7 −703.468407 −703.443393	−9.71 ppm −9.93 ppm
OCH_3	47.9 −664.136311 −664.154558	−9.79 ppm −14.68 ppm	−77.2 −665.346338 −665.316937	−9.19 ppm −14.45 ppm
CCH	41.8 −625.838220 −625.854147	−9.78 ppm −12.30 ppm	−68.0 −627.038735 −627.012831	−7.05 ppm −15.4 ppm

[a] The enthalpies are calculated from total energies of species a−d in au at G3MP2B3 level. NICS values are shown for six-member and five-member rings as NICS(0)-6 and NICS(0)-5.

basis of MO ionization energies alone. One possible method tthat can help in making the distinction is the measurement of HeI and HeII spectra. Resonance effect changes MO character and this is reflected in the corresponding changes of MO photoionization cross sections, band profiles, and band intensities. No HeII spectra of benzotriazoles were reported previously. Our HeI and HeII spectra of Bt1CO(CH$_2$)$_2$Cl, Bt1COCMe$_3$, and Bt1COMe (Figures 5, 6, 8, Supporting Information) show distinct changes in the profile of band manifolds at 9−11 eV. The π_5 and π_3 MOs (Scheme 2) in these manifolds have symmetry properties suitable for interaction with the carbonyl group and can be expected to acquire some oxygen character which will enhance their relative HeII intensity. This was observed in the spectrum of Bt1COCMe$_3$ (Figure 6, Supporting Information) where the band at 11.1 eV (corresponding to π_3 ionization) increases its intensity significantly on going from HeI to HeII radiation. On the other hand, π_4 and n$^-$ MOs have low electron densities at N1 nitrogen where the substituent is attached, they cannot have resonance interactions with the carbonyl group, and consequently have no oxygen 2p character. One can then expect to observe nonuniform intensity changes in the ionization manifold profile on going from HeI to HeII radiation which is indeed the case. We conclude that substituent effects in Bt1R are not solely inductive in nature.

Thermodynamic Properties. We performed G3MP2B3 type calculations for tautomers Bt1 and Bt2 and established that in the gas phase Bt2 is less stable than Bt1 by 1.1 kJ/mol. This calculated value is small and falls within the range of uncertainty of the computational method employed (4 kJ/mol), but it is consistent with the order of stability observed experimentally: Bt2 is less stable than Bt1 by 5 kJ/mol.[4a] The results of previous theoretical studies[4b] were inconclusive and suggested that the predicted relative stability of Bt1 or Bt2 depends on the calculation method employed.

The relative thermal stability (i.e., stability toward decomposition at high temperatures) of 1H-benzotriazole versus the parent 1,2,3-triazole was discussed recently by Katritzky et al.[5] The authors used thermogravimetric and differential thermal analysis and concluded that Bt1 is significantly more stable than 1,2,3-triazole toward thermal decomposition. This thermal stability is a kinetic stability and depends on the height of activation energy barrier separating reactants and products of thermal decomposition.

We wished to determine a different thermodynamic effect, that is, the effect of conjugation of benzene and triazole rings. This was determined by comparing Bt1R and Bt2R where the benzene and triazole rings are conjugated with reference compounds where the two rings are unconjugated and separated by spacer −CH$_2$− groups (Scheme 3). Bt1 and Bt2 are subject to tautomeric conversion; they are difficult to obtain in pure form so it is necessary to perform a computational analysis of this problem.

We used isodesmic reactions (Scheme 3) in calculating these conjugation effects. Species b and d simulate separated triazole and benzene rings while a and c correspond to fused rings extant in Bt1R and Bt2R, respectively. The enthalpies of these hypothetical reactions give estimates of conjugation effects.

The isodesmic reaction data are summarized in Table 2. We note that in 1H-benzotriazoles the conjugation between benzene and triazole ring is destabilizing by approximately 44 kJ/mol, while in 2H-triazoles the conjugation is stabilizing by 71 kJ/mol. The substitution does not influence this stability trend.

These results are interesting because they show that the higher thermal stability of benzotriazole vs triazole determined previously[5] is not influenced by benzene-triazole ring conjugation.

We also investigated the aromaticity of benzotriazoles. While there is presently no unambiguous criterion of aromaticity, the magnetic criteria seem to be most generally applicable.[15] The idea behind magnetic criteria is that delocalized π-electrons produce diamagnetic ring current under the influence of external magnetic field. The existence of induced diamagnetic ring current is therefore an indication of aromaticity. One such approach which uses magnetic criterion of aromaticity is nucleus independent chemical shift (NICS). Here, a ghost atom (no nucleus, no basis functions) is placed at the desired point in space. The chemical shift of this atom is then calculated by the procedures used to compute NMR chemical shifts thus indicating the chemical (via magnetic) environment of this ghost atom. NICS(0) values for benzene and triazole rings (Table 2) were calculated in order to estimate aromaticities of these rings in benzotriazoles. NICS values suggest that the benzene ring is less aromatic in Bt2R than in Bt1R isomer. The opposite is however true for the triazole ring; this ring is more aromatic in Bt2R than in the Bt1R isomer. In general, the presence of substituents affects the stability and aromaticity of Bt2R derivatives to a greater extent than Bt1R derivatives. Our conclusions about the pronounced aromaticity of the five member ring are consistent with the study by Mandado et al.[16] who used electron density calculated by DFT method and electron delocalization indices to deduce ring aromaticity of heterocycles. The authors[16] claimed that the aromaticity of five-member ring rises with the number of nitrogen atoms in the ring.

Chemical Reactivity. The interesting examples of chemical reactivity pertaining to 1H-benzotriazoles include the unusual photocycloaddition reaction[3] and regioselectivity in nitration reactions.[17] The photocycloaddition reaction involving Bt1 was explained by the authors[3] as follows. The tautomeric conversion from Bt1 to Bt2 facilitates the cycloaddition reaction because in Bt2 the C4−C5 bond is more localized and has more double bond character than in Bt1. This enhanced C═C character makes the photochemical reaction possible. Our results based on NICS(0) values and UPS data can also be connected to the observed chemical reactivity. NICS values show that in Bt2 the benzene ring is less aromatic than in Bt1 and that it has more bond localization which facilitates the photocycloaddition as proposed in ref.3 The connection between UPS data and reactivity can be outlined as follows. In pericyclic reactions, the properties of frontier MOs highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are important. HOMO ionization energies in Bt2 and Bt1 are 8.67 and 8.97 eV, respectively (Figure 1, Supporting Information). The HOMO in Bt2 is therefore destabilized by approximately 29 kJ/mol, which can be expected to facilitate photocycloaddition. In nitration reactions, the electrophilic substitution takes place at positions C4 or C7. This regioselectivity was explained[17] by the localization properties of HOMO π_5 (Scheme 2). Properties of HOMO are important in electrophilic substitution reactions, for example, nitration. HOMOs in Bt1 and Bt2 have higher electron densities at C4 and C7 centers than at C5 or C6 (Scheme 2). This makes C4 and C7 preferred sites for electrophilic attack and regioselectivity subsequently ensues. We propose (on the basis of UPS data) that the mechanism of nitration of Bt1 also involves prior tautomeric conversion from Bt1 to Bt2 as in the photocycloaddition discussed above. Tautomeric conversion makes HOMO more localized on C4 or C7 centers (Scheme 2).

Summary

We have investigated the electronic structures of substituted isomeric benzotriazoles and related these structures to thermodynamic properties and chemical reactivity. We suggest that the previously reported UPS of Bt1 corresponds to the mixture of Bt1 and Bt2 tautomers with the former tautomer predominating. The N-substituted Bt1R derivatives are less stable than their reference compounds which contain isolated (unconjugated) benzene and triazole rings. For N-substituted Bt2R derivatives the opposite is the case, that is, the benzotriazole is more stable than its unconjugated analogue. The extent to which substituents influence the electronic structure of the Bt1 skeleton depends on their mode of attachment to the skeleton. When the substituent is attached via the spacer group ($-CH_2-$), the substituent effect is mainly inductive. We found that N-substitution by an electron donating group (e.g., CMe_3 or even more $SiMe_3$) destabilizes HOMO which should enhance reactivity of Bt1R derivatives in photocycloaddition or nitration reactions. N-substitution by the same groups also changes HOMO localization properties by reducing somewhat (compared with Bt1) the electron density along C4−C5 bond.

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Supporting Information Available: Pictures of photoelectron spectra, B3LYP energies, and calculated geometries for benzotriazoles. This material is available free of charge via the Internet at http://pubs.acs.org.

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