Ab initio and semiempirical calculations on the tautomeric equilibria of N-unsubstituted and N-substituted benzotriazoles

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Ab Initio and Semiempirical Calculations on the Tautomeric Equilibria of N-Unsubstituted and N-Substituted Benzotriazoles

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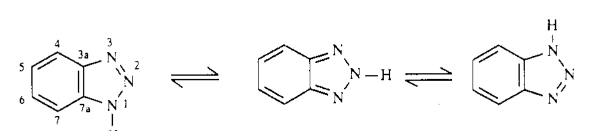
The geometries, relative stabilities, ionization potentials, and dipole moments for benzotriazole tautomers and their (dimethylamino)methyl derivatives were calculated by PM3, AM1, and MNDO semiempirical methods with full geometry optimization and with an ab initio 3-21G basis set. The geometries optimized by semiempirical methods are comparable with those obtained with partial optimization ab initio (6-31G and 3-21G levels) and available crystallographic data. Ab initio and semiempirical calculations failed to reproduce the N2–N3 bond length in 1*H*-benzotriazole. The X-ray dimensions of compound **4**, which due to its structural and electronic properties can be considered as a model compound for the 1-[(dimethylamino)methyl]benzotriazole **2a**, indicate that the "small" 3-21G basis set predicts bond lengths for this 1-substituted derivative, which are close to experimental data. The PM3 method gives ΔH_f in agreement with ab initio calculations, but both the AM1 and the MNDO methods do not. For benzotriazole, both semiempirical and ab initio calculations predict a large energy preference of the 1*H* over the 2*H* form. For the *N*-[(dimethylamino)methyl] derivatives, the ab initio results correctly predict an almost equal stability of the two forms (**2a** and **2b**) but the semiempirical methods fail. The influence of the fused benzo ring, together with the electronic properties of the N substituents, determines the relative stabilities of 1- and 2-substituted benzotriazoles.

Introduction

The tautomeric equilibrium of unsubstituted benzotriazole has been studied extensively and has been summarized in several reviews.[1,2] All indications are that the 1*H* form **1a** (**1c**) predominates strongly under all conditions studied. Thus, in the crystalline state the sole existence of form **1a** is demonstrated by X-ray studies[3] and also by ^{13}C NMR.[4] In solution, comparisons of the ultraviolet spectra of benzotriazole with those of the 1- and 2-methyl derivatives demonstrate that **1a** dominates,[5] and infrared studies agree.[6] Proton NMR comparisons with the *N*-methyl derivatives[7] and a variable-temperature

Scheme I



1a 1b 1c = 1a

(1) Katritzky, A. R.; Lagowski, J. M. *Adv. Heterocycl. Chem.* **1963**, *2*, 27.

(2) Elguero, J.; Marzin, C.; Katritzky, A. R.; Linda, P. The Tautomerism of Heterocycles. *Adv. Heterocycl. Chem.* **1976**, Supplement 1.

(3) (a) Escande, A.; Lapasset, J.; Faure, R.; Vincent, E. J.; Elguero, J. *Tetrahedron* **1974**, *30*, 2903; Erratum. **1975**, *31*, 2. (b) Escande, A.; Galigne, J. L.; Lapasset, J. *Acta Crystallogr.* **1974**, *B30*, 1490.

(4) Faure, R.; Vincent, E. J.; Elguero, J. *Heterocycles* **1983**, *20*, 1713.

(5) (a) Dal Monte, D.; Mangini, A.; Passerini, R.; Zauli, C. *Gazz. Chim. Ital.* **1958**, *58*, 977. (b) Potts, K. T. *Chem. Rev.* **1961**, *61*, 87. (c) Specker, H.; Gawrosch, H. *Chem. Ber.* **1942**, *75*, 1338. (d) Derkosch, J.; Polansky, O. E.; Rieger, E.; Derflinger, G. *Monatsh. Chem.* **1961**, *92*, 1131. (e) Roberts, N. K. *J. Chem. Soc.* **1963**, 5556.

(6) O'Sullivan, D. G. *J. Chem. Soc.* **1960**, 3653.

Table I. Geometries of Benzotriazoles

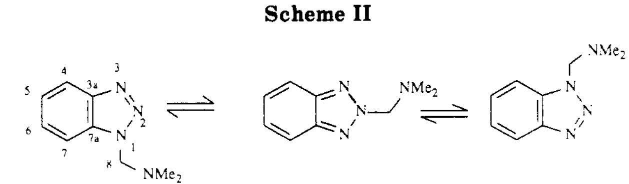
	1*H*-benzotriazole						2*H*-benzotriazole					benzotriazole anion				
	exptl[a]	6-31G[b]	3-21G	PM_3	AM1	MNDO	6-31G	3-21G	PM_3	AM1	MNDO	6-31G	3-21G	PM_3	AM1	MNDO
							Bond Lengths (Å)									
N1-N2	1.346	1.359	1.395	1.384	1.351	1.347	1.321	1.344	1.327	1.331	1.326	1.327		1.309	1.305	1.299
N2-N3	1.310	1.269	1.277	1.259	1.263	1.261	1.321	1.344	1.327	1.331	1.326	1.327		1.309	1.305	1.299
N3-C3a	1.377	1.389	1.390	1.428	1.428	1.415	1.334	1.328	1.390	1.377	1.364	1.362		1.402	1.399	1.389
C3a-C4	1.408	1.395	1.391	1.398	1.397	1.414	1.420	1.420	1.413	1.419	1.439	1.404		1.402	1.402	1.419
C4-C5	1.368	1.374	1.369	1.384	1.387	1.395	1.356	1.348	1.371	1.369	1.375	1.372		1.379	1.382	1.389
C5-C6	1.405	1.413	1.409	1.408	1.408	1.429	1.439	1.441	1.423	1.428	1.450	1.418		1.413	1.412	1.432
C6-C7	1.367	1.375	1.370	1.383	1.388	1.394	1.356	1.348	1.371	1.369	1.376	1.372		1.379	1.382	1.390
C7-C7a	1.404	1.397	1.394	1.398	1.398	1.415	1.420	1.420	1.413	1.420	1.439	1.404		1.403	1.403	1.419
C7a-C3a	1.389	1.389	1.389	1.413	1.451	1.436	1.415	1.418	1.427	1.479	1.462	1.406		1.425	1.473	1.453
C7a-N1	1.366	1.362	1.358	1.417	1.403	1.396	1.334	1.328	1.390	1.376	1.363	1.362		1.402	1.399	1.387
C4-H		1.071	1.070	1.094	1.100	1.089	1.070	1.070	1.094	1.099	1.089	1.074		1.093	1.098	1.090
C5-H		1.072	1.071	1.095	1.101	1.091	1.072	1.072	1.095	1.101	1.091	1.075		1.093	1.098	1.091
C6-H		1.073	1.072	1.096	1.101	1.091	1.072	1.071	1.095	1.101	1.091	1.075		1.094	1.099	1.092
C7-H		1.071	1.070	1.094	1.097	1.088	1.070	1.070	1.094	1.099	1.089	1.074		1.092	1.098	1.089
N1-H		0.987	0.994	0.990	0.990	1.002										
N2-H							0.984	0.994	0.987	1.004	1.1015					
							Bond Angles (deg)									
N1-N2-N3	108.8	109.1	108.3	110.8	112.1	111.2	116.4	115.6	114.7	118.0	117.3	112.7		113.2	115.8	114.9
N2-N3-C3a	108.2	109.0	109.3	109.8	108.9	109.2	103.6	103.3	105.8	104.1	104.2	106.5		107.7	106.9	107.1
C3a-C4-C5	116.2	117.4	117.8	116.7	117.7	117.8	116.9	117.6	116.7	118.2	117.2	118.1		117.2	118.4	117.6
C4-C5-C6	122.2	121.1	120.8	121.9	121.9	121.8	122.1	121.8	122.2	122.2	122.2	121.2		121.7	121.8	121.8
C5-C6-C7	126.6	121.9	121.9	122.0	122.1	122.1	122.1	121.8	122.2	122.2	122.2	121.2		122.1	121.8	122.0
C6-C7-C7a	115.3	116.6	117.0	116.5	116.8	116.5	116.9	117.6	116.7	118.0	117.2	118.1		116.7	118.4	117.3
C7-C7a-C3a	122.7	121.8	121.3	121.6	121.4	121.7	121.0	120.6	120.8	119.7	120.4	120.7		121.4	119.8	120.8
C3a-C7a-N1	104.2	103.8	104.6	104.4	103.2	102.8	108.1	108.8	106.9	106.9	107.1	107.2		105.8	105.3	105.4
C7a-N1-N2	110.3	110.8	109.6	108.0	109.5	110.1	103.6	103.3	105.8	104.1	104.2	106.5		107.6	106.9	107.1
C7a-C3a-C4	120.9	121.2	121.2	120.1	120.0	120.9	121.0	120.6	120.8	119.7	120.4	120.7		120.8	119.8	120.6
C7a-C3a-N3	108.4	107.9	108.2	106.7	106.2	106.7	108.1	108.8	106.9	106.9	107.1	107.2		105.7	105.3	103.3
H-N1-N2		119.5	119.4	122.5	122.3	122.0										
H2-N2-N3							121.8	122.2	122.6	121.0	121.3					
H-C4-C5		121.8	122.0	122.1	121.9	121.7	122.5	121.3	122.6	122.1	122.5	121.1		121.7	121.1	121.2
H-C5-C6		119.9	119.1	118.6	118.6	118.4	118.2	118.2	118.0	117.8	117.5	118.9		118.1	118.5	118.2
H-C6-C5		119.0	118.8	119.0	118.8	118.4	118.2	118.2	118.0	117.8	117.5	118.9		118.2	118.5	118.1
H-C7-C6		121.7	121.3	121.9	121.6	121.7	122.5	122.3	122.6	122.1	122.5	121.1		122.0	121.1	121.3

[a] Data from ref 4. Average from four independent molecules in one cell.

NMR study in THF[8] again clearly show that **1a** strongly predominates. ^{15}NMR indicates only the 1*H* form in solution.[9] Dipole moment comparisons with the *N*-methyl derivatives indicate close to 100% of **1a** in benzene solution.[10] In the vapor phase, mass spectrometry showed only the 1*H* form[11] (Scheme I).

In contrast to this clear-cut preference for the 1*H* form of benzotriazole itself, the corresponding equilibria for N-substituted derivatives have been shown to be much less one-sided. Lindsay-Smith and Sadd[12] first demonstrated the existence of equilibria of type **2a** = **2b** = **2c**. Subsequent publications from one of our laboratories[13,14] have shown conclusively that the N1 and N2 isomers are of nearly equal stability in nonpolar solvents and in the gas phase (2:1 ratio on statistical grounds). Polar solvents favor the 1- and 3-substituted forms (**2a**, **2c**) over the 2-substituted (**2b**), and conversely substituents at positions 4 and 7 favor the 2-substituted form (Scheme II).

Scheme II



2a 2b 2c = 2a

This dichotomy of behavior presents a test for the predictive capabilities of MO methods. The present paper reports the application of both semiempirical and ab initio methods to this problem and in particular to the tautomerism of compounds **1** and **2**. Previous theoretical work has been limited to unsubstituted benzotriazole: LCAO[15] and ppp[16] calculations indicated a predominance of the 1*H* form by 17 kcal/mol. INDO calculations[17] concluded that "form is twice as stable as form **1b**". Recently, Elguero and co-workers[18] have demonstrated that according to 6-31G calculations 1*H*-benzotriazole is more stable than 2*H*-benzotriazole by 4.8 kcal/mol.

Method of Calculation

All the present semiempirical calculations were carried out with complete geometry optimization. The MNDO-

(7) Müller, E.; Meier, H. *Liebigs. Ann. Chem.* **1968**, *716*, 11.
(8) Nesmeyanov, A. N.; Babin, V. N.; Fedorov, L. A.; Rybinskaya, M. I.; Fedin, E. I. *Tetrahedron* **1969**, *25*, 4667.
(9) Wofford, D. S.; Forkey, D. M.; Russell, J. G. *J. Org. Chem.* **1982**, *47*, 5132.
(10) Mauret, P.; Fayet, J.-P.; Fabre, M.; Elguero, J.; de Mendoza, J. *J. Chim. Phys.* **1974**, *71*, 115.
(11) Maquestiau, A.; Van Haverbeke, Y.; Flammang, R.; Pardo, M. C.; Elguero, J. *Org. Mass Spectrom.* **1973**, *7*, 1267.
(12) Lindsay-Smith, J. R.; Sadd, J. S. *J. Chem. Soc., Perkin Trans. 1* **1975**, 1181.
(13) Katritzky, A. R.; Yannakopoulou, K.; Kuzmierkiewicz, W.; Aurrecoechea, J. M.; Palenik, G. J.; Koziol, A. E.; Szczesniak, M. *J. Chem. Soc., Perkin Trans. 1* **1987**, 2673.
(14) Katritzky, A. R.; Jóźwiak, A.; Lue, P.; Yannakopoulou, K.; Palenik, G. J.; Zhang, Z. Y. *Tetrahedron* **1990**, *46*, 633.
(15) Polansky, O. E.; Derflinger, G. *Monatsh. Chem.* **1961**, *92*, 1114.
(16) Kamiya, M. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 3344.
(17) Abu-Eittah, R. H.; Hamed, M. M.; Nigm, A.; El-Azhary, A. *Int. J. Quantum Chem.* **1985**, *28*, 731.
(18) Tomás, F.; Abboud, J.-L. M.; Laynez, J.; Notario, R.; Santos, L.; Nilsson, S. O.; Catalan, J.; Claramunt, R. Ma.; Elguero, J. *J. Am. Chem. Soc.* **1989**, *111*, 7348.

Table II. Calculated Geometries of 1- and 2-[(Dimethylamino)methyl]benzotriazoles

	1-$(Me)_2NCH_2$-Bt (2a)				2-$(Me)_2NCH_2$-Bt (2b)			
	3-21G	PM3	AM1	MNDO	3-21G	PM3	AM1	MNDO
				Bond Lengths (Å)				
N1-N2	1.392	1.389	1.361	1.353	1.335	1.337	1.339	1.330
N2-N3	1.280	1.259	1.261	1.257	1.347	1.337	1.339	1.330
N3-C3a	1.387	1.424	1.428	1.415	1.333	1.384	1.373	1.362
C3a-C4	1.392	1.400	1.397	1.413	1.424	1.416	1.421	1.441
C4-C5	1.368	1.382	1.388	1.396	1.345	1.370	1.368	1.375
C5-C6	1.410	1.410	1.405	1.427	1.423	1.424	1.428	1.450
C6-C7	1.369	1.382	1.390	1.398	1.345	1.370	1.367	1.376
C7-C7a	1.396	1.400	1.398	1.416	1.424	1.414	1.421	1.442
C7a-C3a	1.390	1.413	1.451	1.434	1.443	1.427	1.476	1.461
C7a-N1	1.359	1.414	1.409	1.410	1.333	1.386	1.373	1.361
C4-H	1.070	1.095	1.099	1.089	1.070	1.094	1.099	1.088
C5-H	1.071	1.095	1.101	1.091	1.072	1.096	1.101	1.092
C6-H	1.072	1.096	1.101	1.091	1.072	1.095	1.101	1.091
C7-H	1.070	1.095	1.092	1.087	1.070	1.095	1.099	1.088
N1-C8	1.474	1.484	1.467	1.488				
N2-C8					1.495	1.498	1.510	1.507
C8-N9	1.437	1.478	1.447	1.451	1.463	1.487	1.436	1.445
N9-C10	1.470	1.478	1.444	1.464	1.467	1.479	1.444	1.462
N9-C11	1.465	1.479	1.445	1.467	1.467	1.479	1.445	1.463
C8-H	1.077	1.109	1.133	1.121	1.077	1.112	1.131	1.201
C8-H	1.080	1.109	1.132	1.121	1.077	1.113	1.130	1.200
C10-H	1.083	1.098	1.122	1.114	1.086	1.098	1.124	1.112
C10-H	1.088	1.098	1.122	1.114	1.086	1.101	1.121	1.112
C10-H	1.082	1.100	1.124	1.116	1.086	1.096	1.122	1.113
C11-H	1.081	1.098	1.122	1.114	1.086	1.098	1.124	1.112
C11-H	1.083	1.098	1.121	1.113	1.086	1.097	1.122	1.113
C11-H	1.087	1.100	1.124	1.116	1.086	1.101	1.122	1.112
				Bond Angles (deg)				
N1-N2-N3	109.0	110.2	112.5	112.1	114.9	114.0	116.5	116.1
N2-N3-C3a	108.9	110.2	109.2	109.1	104.5	105.7	104.8	104.9
C3a-C4-C5	117.8	116.8	117.4	116.9	117.7	116.8	118.0	117.2
C4-C5-C6	120.7	121.7	122.2	121.6	122.4	122.2	122.3	122.7
C5-C6-C7	121.9	122.1	122.3	122.1	122.4	122.2	122.1	121.8
C6-C7-C7a	117.2	116.6	116.8	116.6	117.7	116.8	118.1	117.6
C7-C7a-C3a	121.0	121.4	121.2	121.3	119.9	121.5	119.7	120.4
C3a-C7a-N1	105.2	104.1	103.8	103.5	107.8	107.1	107.0	107.0
C7a-N1-N2	108.8	108.6	108.6	108.6	104.9	106.0	104.8	104.9
C7a-C3a-C4	121.4	121.4	120.4	121.4	119.9	121.0	116.7	120.3
C7a-C3a-N3	108.1	106.9	106.0	106.6	108.5	107.1	106.9	107.0
C8-N1-C7a	132.3	127.3	126.3	130.3				
C8-N2-N1					122.6	122.9	121.7	122.0
N9-C8-N1	115.8	116.1	118.4	114.0				
N9-C8-N2					111.7	108.1	116.9	109.2
C10-N9-C8	115.5	115.4	115.2	119.1	113.3	115.8	115.5	119.4
C11-N9-C8	116.4	115.4	114.9	118.8	113.2	115.8	115.5	119.2

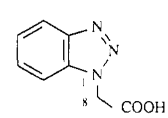
PM3[19] and AM1[20] calculations were performed with AMPAC[21] and MOPAC[22] programs, respectively, on a micro VAXII. The ab initio calculations were performed with the GAUSSIAN 86 program,[23] using the default settings, on a Cray XMP-4.

The ab initio calculations at the 3-21G basis set level used full geometry optimization except that the torsional angles for rings were not optimized for **2a** and **2b**. Planarity of the benzotriazole ring was assumed, but the conformations of substituents were optimized.

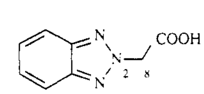
Results and Discussion

Optimized Geometry. The optimized bond lengths and bond angles for the five molecules (**1a**, **1b**, **2a**, **2b**, and the benzotriazole anion) studied are given in Tables I and II. To check our calculated geometries by comparison with experimental results, we use the following group of compounds of known crystal structure: 1*H*-benzotriazole (**1a**),[3a] benzotriazole-1-acetic acid (**3a**),[24] benzotriazole-2-acetic acid (**3b**),[25] and 1-[2-(naphthyloxy)methyl]benzo-

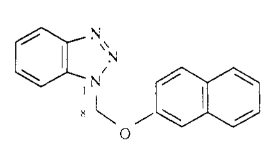
Chart I



3a



3b



4

(19) Stewart, J. J. P. *J. Comput. Chem.* **1989**, *10*, 209, 221.
(20) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902.
(21) Dewar, M. J. S.; Stewart, J. J. P. QMPAC (Version 1.1). *QCPE 506*.
(22) Stewart, J. J. P. MOPAC (Version 4.0). *QCPE 455*.
(23) Frisch, M. J.; Binkley, J. S.; Schlegel, H. B.; Raghavachari, K.; Melius, C. F.; Martin, R. L.; Stewart, J. J. P.; Bobrowicz, F. W.; Rohlfing, C. M.; Kahn, L. R.; DeFrees, D. J.; Seeger, R.; Whiteside, R. A.; Fox, D. J.; Fluder, E. M.; Pople, J. A. Carnegie-Mellon Quantum Chemistry Publishing Unit, Pittsburgh, PA, 1984.
(24) Giordano, F.; Zagari, A. *Acta Crystallogr.* **1977**, *B33*, 1288.
(25) Giordano, F.; Zagari, A. *J. Chem. Soc., Perkin Trans. 2*, **1978**, 312.

Table III. Specific Bond Lengths of Some Substituted Benzotriazoles (X-ray Data)

bond length, Å	1-(HOO-CH_2)Bt[a,b]	2-(HOO-CH_2)Bt[c]	1-(β-$C_{10}H_7$-OCH_2)Bt[d,e]
N1-N2	1.352	1.326	1.364
N2-N3	1.312	1.326	1.284
N3-C3a	1.381	1.354	1.385
C3a-C4	1.403	1.410	1.356
C4-C5	1.367	1.365	1.396
C5-C6	1.424	1.413	1.395
C6-C7	1.377	1.365	1.373
C7-C7a	1.402	1.410	1.385
C7a-C3a	1.395	1.404	1.381
C7a-N1	1.366	1.354	1.356
N1-C8	1.452		1.434
N2-C8		1.469	

[a] Bt = benzotriazole. [b] Reference 24. [c] Reference 25. [d] Reference 26. [e] β-$C_{10}H_7$ = β-naphthyl.

triazole (4)[26] (Table III; Chart I). Since 4 independent molecules are found in the unit cell[3a] of 1*H*-benzotriazole, the data listed in Table I are averages. The experimental and theoretical results are summarized as follows:

(i) For 1-[(dimethylamino)methyl]benzotriazole (**2a**) the calculated N2-N3 bond length (using the 3-21G basis set) is almost identical with the X-ray value of the model compound **4** (Tables II and III). Neither the ab initio nor the semiempirical calculations reproduced the N2-N3 bond length in **1a**. The calculated values are smaller by 0.03-0.05 Å in comparison with the experimental data. For the 2*H* compounds **1b** and **2b**, all the methods predict correctly both N1-N2 and N2-N3 bond lengths. This indicates the well-known tendency of all single-determinant MO methods to underestimate the repulsion of lone pairs at adjacent atoms.[27] Similar effects have previously been observed in five- and six-membered heterocycles.[28]

All the semiempirical calculations for **1a** and **2a** predict for the C3a-N3 and C7a-N1 bonds lengths that are too long (by 0.03-0.056 Å). However, these bond lengths are correctly predicted by both the 6-31G and 3-21G basis sets.

The various semiempirical methods generally reproduce the bond lengths with comparable accuracy. An exception is the AM1 method, which predicts a longer C7a-C3a bond than do the PM3 and MNDO methods. The ab initio results are in satisfactory agreement with available experimental data.

The benzotriazole ring bond angles obtained by the PM3, AM1, and MNDO methods are close to those found by the ab initio treatments (3-21G and 6-31G levels), and all reproduce the experimental data to within about ±1°. Larger differences between bond angles obtained from semiempirical methods and those from the ab initio treatments are found for H1-N1-N2 in **1a** (up to 3°). Bond angle C8-N1-7a is sensitive to the method of calculation and varies from 126.3 to 132.2°. The following discussion is based on the 3-21G calculations.

(ii) The exocyclic N-C8 bond lengths increase from the "1" to the "2" isomers. The X-ray results of **3a,b** (1.452 and 1.469 Å) and the calculated results of **2a,b** (1.474 and 1.494 Å) reveal the significance of this. The calculated N1-C8 bond length of **2a** represents—compared with the respective X-ray data of **3a** and **4**—the maximum in this series of **2a**, **3a**, and **4** (decreasing bond lengths).

(iii) Substitution of the N1 hydrogen atom by the CH_2NMe_2 group does not influence the ring system bond lengths (for **1a** and **2a**). However, for the 2*H* compounds, change of NH to NCH_2NMe_2 enlarges the bicyclic system of **2b** more than that of **1b**.

Table IV. Calculated Energies and Relative Stability (au,[a] kcal/mol) of 1*H*- (1a) and 2*H*-Benzotriazoles (1b)

method	energy, kcal/mol 1a	1b	anion	stability of 1a over 1b, kcal/mol
MNDO//MNDO	64.89	76.00	17.15	11.11
AM1//AM1	104.21	116.96	64.48	12.75
PM3//PM3	85.449	93.198	42.84	7.75
3-21G//3-21G	-391.19777[a]	-391.18898[a]		5.51
6-31G*//3-21G	-393.41770[a]	-393.41338[a]		2.71
6-31G//6-31G[b]	-393.24173[a]	-393.23401[a]	-392.66995[a]	4.84

[a] 1 au = 627.51 kcal/mol. [b] Reference 18.

Table V. Calculated Energies (au,[a] kcal/mol) and Relative Stability (kcal/mol) of 1- and 2-[(Dimethylamino)methyl]benzotriazoles (2a and 2b)

method	energy 2a	2b	stability of 2a over 2b, kcal/mol
MNDO//MNDO	70.10	79.93	9.83
AM1//AM1	115.79	128.92	13.13
PM3//PM3	83.59	92.82	9.23
3-21G//3-21G	-562.34414[a]	-562.34369[a]	0.28
6-31G*//3-21G	-565.53398[a]	-565.53323[a]	0.47
experiment			≈0.3[b]

[a] 1 au = 627.51 kcal/mol. [b] See refs 2 and 3.

Relative Stabilities. The experimental heat of formation, ΔH_f, for 1*H*-benzotriazole is 83 kcal/mol.[29] This is predicted well by the PM3 method whereas the MNDO and the AM1 methods give results lower and higher by ca. 20 kcal/mol, respectively (Table IV). Calculated relative stabilities of benzotriazoles **1a**, **1b**, **2a**, and **2b** are summarized in Tables IV and V. All the methods favor 1*H*- over the 2*H*-benzotriazoles, AM1 and MNDO particularly strongly. The results for **1a** > **1b** agree qualitatively with experiment. Compared with the ab initio results, the semiempirical methods more strongly emphasize the stability of the 1*H* structure.

2*H*-1,2,3-Triazole has been found to be 4.7 kcal/mol more stable than its 1*H* isomer.[30] This was attributed to the loss of lone pair/lone pair repulsion in this molecule; the calculated value is in acceptable agreement with the experimental results (6.5 kcal/mol).[30] Though this repulsion should be active in 1*H*-benzotriazole and its derivatives, these bicyclic compounds reveal inverse stabilities compared with the triazoles. This is explained by the different electronic structures of the benzo ring moieties in **1a** and **1b**. In **1a**, this moiety is close to an 1-amino-2-azobenzene system. Due to the steric constraint of the fused five-membered heterocycle, interaction of the N1 lone pair and the N2-N3 double bond is allowed with the π system of the benzene ring. Overall, this results in a modified but quite "normal" aromatic benzene ring system

(26) Katritzky, A. R.; Palenik, G. J.; Anders, E.; Tropsch, J. G.; Vanden Eynde, J.-J.; Zhang, Z. *Chem. Ber.* **1990**, *123*, 1185.

(27) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986. E.g., for hydrazine and hydrogen peroxide the inclusion of electron correlation leads to improved agreement with experimental data. Comparable semiempirical data are summarized in refs 19 and 20. If configuration interaction is included in the semiempirical calculations (keyword C.I.=2 in AMPAC), no significant changes in the geometrical data or relative energies are found for all five molecules.

(28) Katritzky, A. R.; Szafran, M.; Malhotra, N.; Chaudry, S. U.; Anders, E. Unpublished work.

(29) Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* **1988**, *17*, Supplement No. 1.

(30) Catalán, J. C.; Sanches-Cabezudo, M.; de Paz, J. L. G.; Elguero, J.; Taft, R. W.; Anvia, F. *J. Comput. Chem.* **1989**, *10*, 426.

Table VI. Comparison of Experimental and Calculated Dipole Moments and Ionization Potentials

compound	dipole moment exptl[a]	dipole moment PM3	dipole moment AM1	dipole moment MNDO	ionization potential exptl[b]	ionization potential PM3	ionization potential AM1	ionization potential MNDO
1*H*-benzotriazole	4.15 ± 0.02	3.84	3.66	3.55	9.20	9.31	9.13	9.33
1-methylbenzotriazole	3.95 ± 0.02	3.96	3.83	3.61		9.15	9.23	9.24
2*H*-benzotriazole		0.33	0.12	0.18		9.20	9.12	9.09
2-methylbenzotriazole	0.49 ± 0.10	1.05	0.78	0.50		9.09	9.00	9.01
1-[(dimethylamino)methyl]benzotriazole		3.35	3.34	3.35		9.24	9.24	9.21
2-[(dimethylamino)methyl]benzotriazole		2.39	0.94	1.50		8.95	8.93	8.86

[a] Reference 10. [b] Zimmerman, H.; Geisenfelder, H. *Z. Elektrochem.* **1961**, *65*, 368.

(see Table I, bond lengths C3a–C4, C4–C5, C5–C6, C6–C7, and C7–C7a).

The calculated values of the analogous bond lengths of the 2*H* isomer **1b** reflect the expected structure element of a polyaza analogue of the *o*-benzoquinonoid system. In this system, only the remote N2 lone pair (and not the N1/N3 lone pairs) interacts by overlap with the π system through the CN double bonds.

Compared with the properties of **1a**, the partial loss of aromaticity in the quinonoid system of **1b** increases energy, overcompensating the stabilizing effect due to the loss of N2/N3 lone pair/lone pair repulsion (−4.7 kcal/mol). To explain the relative stability of **1a** (6-31G, −4.8 kcal/mol; 3-21G, −5.5 kcal/mol), this destabilization can be estimated as about +9.5 kcal/mol (6-31G) or +10.2 kcal/mol (3-21G). This latter value agrees quite well with the result from 6-31G calculations found by Elguero et al.[18] For further research on this series of heterocycles (especially for larger molecules), it is both significant and encouraging that the smaller basis set 3-21G gives results in fine agreement with those obtained with the 6-31G set.

Table V summarizes data for the 1- to 2-[(dimethylamino)methyl]benzotriazole equilibrium. All the semiempirical methods predict the 1-substituted tautomer (**2a**) to be far more stable than the 2-substituted (**2b**), which does not agree with the experimental results. By contrast, the ab initio results do correctly predict the relative stabilities with only a small ΔG in favor of **2a** or **2b**. We believe that the explanation of this is connected with the well-known electronic influence of the NMe_2 substituent to facilitate N–C8 bond heterolysis. In structure **2b** the longer N2–C8 bond helps to stabilize this isomer (see the discussion above on bond lengths). Overall, this results in a stabilization of **2b** and, finally, in similar energies for **2a** and **2b**. From our 3-21G calculations this stabilizing effect of the CH_2NMe_2 substituent can be estimated to be about 5.8 kcal/mol (3-21G basis set).

Our general conclusion, from the present and related work,[19,31] is that, for mono- and bicyclic six-membered heterocycles, both AM1 and PM3 predict similar values of ΔH_f, which are within about 5 kcal/mol of experimental results unless there are three or more heteroatoms. For five-membered heterocycles and benzo-fused five-membered heterocycles, the AM1 results can differ by up to 20 kcal/mol from experiment, particularly if there are directly linked heteroatoms. In these cases, PM3 usually gives better predictions. Although the lone pair/lone pair repulsion in 1*H*-1,2,3-benzotriazoles is underestimated by the semiempirical methods, these methods also overestimate the instability of the *o*-benzoquinonoid moiety.

Dipole Moment. Experimental and calculated dipole moments are presented in Table VI. For 1*H*-benzotriazole and its N-substituted derivatives, the AM1 and PM3 methods are satisfactory and the latter gives the smallest difference from the experimental data. However, for 2-substituted benzotriazoles, the PM3 method seriously overestimates the dipole moments. The differences between experimental and calculated dipole moments for 1- and 2-substituted benzotriazoles are similar to those found by Stewart[19] for small molecules.

Ionization Potential. All semiempirical methods give very similar values for the first ionization potentials (Table VI). The calculated and the experimental data can be compared only in one case, and here the agreement is good.

Summary. For benzotriazole **1**, both semiempirical and ab initio calculations predict a large energy preference for the 1*H* over the 2*H* form. However, for the (dimethylamino)methyl derivative **2**, the ab initio results correctly predict the almost equal stability of the two forms **2a** and **2b**, whereas the semiempirical methods significantly overestimate the relative stability of **2a**.

Registry No. **1a**, 95-14-7; **1b**, 273-02-9; **2a**, 57684-30-7; **2b**, 99482-30-1; benzotriazole anion, 45665-96-1.

(31) (a) Nogaj, B.; Dulewicz, E.; Brycki, B.; Hrynio, A.; Barczynski, P.; Dega-Szafran, Z.; Szafran, M.; Koziol, P.; Katritzky, A. R. *J. Phys. Chem.* **1990**, *94*, 1279. (b) Katritzky, A. R.; Barczynski, P.; Szafran, M.; Feygelman, V.; Musmumarra, G. Unpublished work.