ions studied are found to be moderately or highly aromatic according to the bond-order definition of the ring-current concept. 1,3-Diphosphacyclopentadienyl anion is found to be more aromatic than the 1,2-diphospha isomer. Of the two triphospha analogues, the 1,2,4-triphospha isomer is predicted to be highly aromatic while the 1,2,3-triphospha isomer is moderately aromatic. The isomer predicted to be more aromatic is the one found to participate in complex formation.

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A MO Theoretical Study on the Rearrangement of 1-Hydroxy- and 1-(Acyloxy)-1,2,3-triazoles and Their Benzotriazole Analogues: Comparison of ab Initio and Semiempirical Calculations

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Energy differences between 1-hydroxy-1,2,3-triazole (**8a**) and its 2*H*- and 3*H*-tautomers **8b** and **8c** were calculated by semiempirical (AM1, PM3) and ab initio (from the 3-21G//3-21G up to the MP4SDTQ/MP2//6-31+G* level) methods and compared. With large basis set size and inclusion of electron correlation effects (ECE), these tautomers are found to be quite close in energy. The 2*H* tautomer **8b** is less stable by 2.57 kcal mol^{-1} and the 3*H* tautomer **8c** by 1.95 kcal mol^{-1} compared with the *N*1-hydroxy form **8a**. A satisfactory treatment of triazoles containing the $^{-}$O–N(1)$^{+}$ moiety by ab initio methods requires inclusion of ECE (at least second-order Møller–Plesset perturbation theory), while for 1*H*- and 2*H*-triazole (**9a**,**b**) inclusion of MP2 does not change the energy differences significantly. The differential solvent stabilization of **8c** compared with that of **8a** in the condensed phase was estimated using Tomasi's SCRF theory. The PM3- and AM1-calculated energy differences of isomers **1a**/**b**/**c**, **2a**/**b**/**c**, and **3a**/**b**/**c** (benzotriazole derivatives) and **5a**/**b**/**c**, **6a**/**b**/**c**, and **7a**/**b**/**c** (1,2,3-triazole derivatives) are mutually inconsistent. AM1 predicts the isomers **a**, but PM3 isomers **c** to be the most stable. The errors of both methods were estimated by comparison with ab initio calculations for the related model compounds **9a**, **9b** (1*H*- and 2*H*-1,2,3-triazole), **10a**, **10b** (1*H*- and 2*H*-benzotriazole), and (*Z*)/(*E*)-diazene (**12a**, **12b**). It is concluded that in almost all cases the PM3 method yields results which are more reliable than AM1. Our experimental finding that the rearrangement of **1a** proceeds intermolecularly to **1c**, with the isomer **1b** remaining undetectable, is understandable on the basis of these PM3-calculations. PM3- and AM1-calculated bond lengths are in acceptable agreement with those resulting from the 3-21G basis set but differ significantly from the respective MP2/6-31+G* values.

Introduction

One of our laboratories recently reported that 1-(aroyloxy)benzotriazoles such as **1a** in acetone solution in the presence of catalytic amounts of water and a base (potassium carbonate) rearrange intermolecularly to give exclusively *N*(3)-aroylbenzotriazole 1-oxides **1c**.[1] These, and previous investigations[2-6] on related compounds, reveal that such rearrangements are remarkably solvent-dependent. From our NMR studies[1] we concluded that the potential intermediate, the N(2) isomer **1b**, is unstable and does not have sufficient lifetime to exist in detectable concentration.

To what extent can these results be reproduced by "widely available" quantum mechanical methods? To the best of our knowledge, nothing has been published concerning theoretical investigations of the benzotriazole system **1a**/**b**/**c** or even the smaller systems **2a**/**b**/**c**, **3a**/**b**/**c**, and **4a**/**b**/**c**. The same is true for the related 1,2,3-triazole systems **5a**/**b**/**c**, **6a**/**b**/**c**, and **7a**/**b**/**c** (Chart I).

The most closely related theoretically investigated system is that of 1-hydroxy-1,2,3-triazole (**8a**) and its tautomers **8b** and **8c**. As concluded by Fabian[7] and by Giumon et al.,[8] semiempirical calculations, especially AM1,[9]

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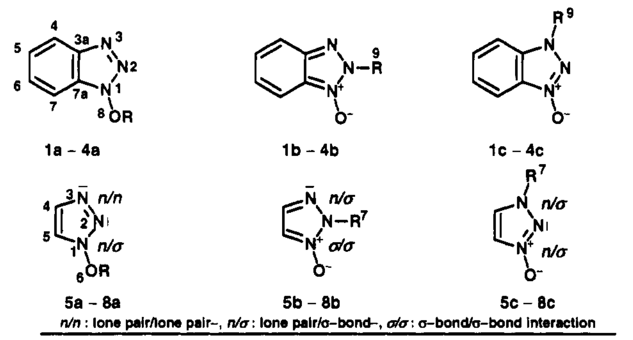
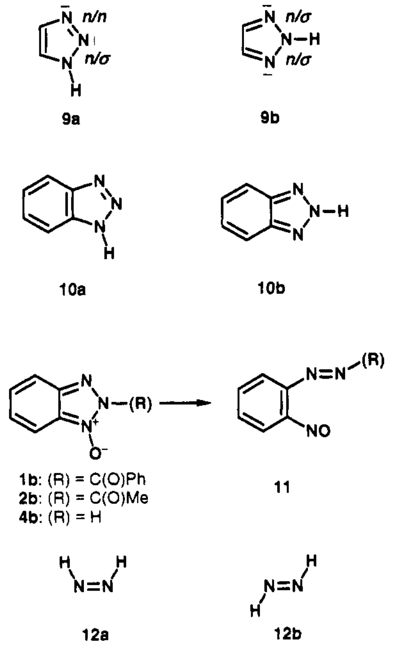
0022-3263/92/1957-3698$03.00/0

Chart I



1a, 1b, 1c and 5a, 5b, 5c: R = C(O)Ph
2a, 2b, 2c and 6a, 6b, 6c: R = C(O)Me
3a, 3b, 3c and 7a, 7b, 7c: R = C(O)H
4a, 4b, 4c and 8a, 8b, 8c: R = H

Scheme I



followed by MNDO,[10] seem to reproduce the relative thermodynamic stability of these tautomers quite well. PM3[11] results led Fabian to the statement[7] that this method "erroneously yields an equal stability" for the tautomers **8a** and **c**. Giumon et al. investigated this system by PE spectroscopy, demonstrating that **8a** exists under PES conditions from 20 °C up to its thermal decomposition temperature. Their MNDO calculations seem to confirm the experimental result, as they predict the hydroxy compound **8a** to be 22.8 kcal mol^{-1} more stable than the 3*H*-*N*(1)-oxide **8c**.

For the tautomerism of the related systems 1*H*-1,2,3-triazole (**9**) and 1*H*-benzotriazole (**10**), ab initio calculations by Begtrup et al.,[12] Elguero et al.,[13] and our group[14] led us to the conclusion that PM3 predicts (gas-phase) heats of formation which are in better agreement with experimental values than those resulting from AM1 or MNDO. Again, this illustrates the uncertainty in selection of the most reliable semiempirical method.

Table I. Energies[a] of Substituted Benzotriazoles, 1,2,3-Triazoles, or Related Compounds and Their Relative Stabilities (AM1 and PM3 Results)

struct.	R	ΔH_f AM1	ΔH_f PM3	relative stabilities, $\Delta\Delta H_f$ AM1	relative stabilities, $\Delta\Delta H_f$ PM3
		Benzotriazoles			
1a	C(O)Ph	110.3	83.0	0.0	0.0
1b		–[b]	95.4	–	+12.4
1c		126.6	75.7	+16.3	–7.3
2a	C(O)Me	76.2	43.3	0.0	0.0
2b		–[b]	58.1	–	+14.8
2c		89.6	39.4	+13.4	–3.9
3a	C(O)H	80.9	51.4	0.0	0.0
3b		112.3	66.0	+31.4	+14.6
3c		98.8	48.6	+18.9	–2.8
4a	H	106.1	81.8	0.0	0.0
4b		–[b]	99.5	–	+17.7
4c		121.9	82.2	+15.8	+0.4
		1,2,3-Triazoles			
5a	C(O)Ph	98.6	64.4	0.0	0.0
5b		119.9	69.0	+21.3	+4.6
5c		109.1	60.5	+10.5	–3.9
6a	C(O)Me	61.3	28.9	0.0	0.0
6b		79.9	33.1	+18.6	+4.2
6c		72.4	24.0	+11.1	–4.9
7a	C(O)H	67.6	36.0	0.0	0.0
7b		85.0	41.3	+17.4	+5.3
7c		79.2	32.3	+11.6	–3.7
8a[c]	H	91.0	66.6	0.0	0.0
8b[c]		107.1	74.8	+16.1	+8.2
8c[c]		103.9	66.6	+12.9	0.0
9a[d]	1*H*-1,2,3-triazole	86.4	67.9	0.0	0.0
9b[d]	2*H*-1,2,3-triazole	92.3	70.7	+5.9	+2.8
10a[d]	1*H*-benzotriazole	104.2	85.4	0.0	0.0
10b[d]	2*H*-benzotriazole	117.0	93.2	+12.8	+7.8
12a	(*Z*)-diazene	32.4	42.9	0.0	0.0
12b	(*E*)-diazene	31.5	37.8	–0.9	–5.1

[a] Energies in kcal mol^{-1}. [b] Using the AM1 Hamiltonian for these structures no minimum was found. [c] See also ref 7. [d] See also ref 14.

To invesigate this question, we first calculated the heats of formation for compounds **1a/b/c** using both the AM1 and the PM3 Hamiltonians. As the results were mutually inconsistent, we reduced the molecular size and calculated the heats of formation for simplified acetyl and formyl models of the benzoyl-substituted compounds by semiempirical and ab initio methods. Results from these calculations and their impact in assessing the reliability of the semiempirical methods are the basis of this discussion.

Semiempirical and ab Initio Calculations of Benzotriazoles and 1,2,3-Triazoles 1–8. Procedure. Semiempirical Calculations. Starting geometries were generated by force-field calculations using PCMODEL and ALCHEMY II.[15] Where different conformations exist (molecules **1–3** and **5–7**) the most stable was selected. All structures were completely optimized without any sym-

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(15) PCMODEL force field calculations: They are based on MM2, and the included VESCF routines of MMP1 (Allinger, N. L.) were applied. The program is distributed by Serena Software, Box 3076, Bloomington, IN 47402-3076. ALCHEMY II force field calculations: The software is supplied by Tripos Associates, 1699 S. Hanley Rd. Suite 303, St. Louis, MN 63144.

metry restrictions. The structural and energetic refinement was performed using the PRECISE option of MOPAC 5.[16] Structures of Table I are characterized as true minima by force constant calculations.

Ab Initio Calculations. Calculations were performed using the GAUSSIAN[17a,b] 82 and 90 or CADPAC[17c] program series with a CRAY-2,[18] CRAY-YMP,[19] and a CONVEX-210[20] computer. In general, the semiempirical optimized geometries were used as starting points for ab initio optimizations, and geometries from prior calculations were used as starting points for calculations using the higher level basis set. The applied basis sets are specified in the text.[21] Geometry optimizations for the triazoles **8a**/**b**/**c** (up to the MP2/6-31+G* level) and **4a**/**b**/**c** (3-21G) were performed without symmetry restrictions. **8a**/**b**/**c** (MP2/6-31+G*) and the benzotriazoles **4b** and **c** are found to be planar. This includes the oxygen and the N2- or N3-hydrogen atoms. In **4a** the N1-oxygen is found to be out of the N3–N2–N2 plane by 8.60°, but the MP2/6-31+G* calculations for **8a** indicate that this nonplanarity is an artifact of the 3-21G basis. Planarity was assumed for the analogous benzotriazole derivatives **3b** and **c** under inclusion of the N^+–O^- oxygen and the carbon atoms C9 at N2 or N3 (Table VII). For **3a** the ring system was assumed to be planar. All parameters of the OC(O)H moiety were optimized. Solvent effects were estimated using Tomasi's SCRF procedure[22] which was installed in the CONVEX version of GAUSSIAN 82 by Clark.[23]

Results and Discussion

AM1 Results. The heats of formation for both the RCO-substituted benzotriazole and triazole isomers fall in the same order, with the N(1)-substituted compounds **a** significantly more stable than the N(2)- or N(3)-substituted *N*(1)-oxides **b** and **c**. The energy differences are noteworthy: relative to the **a** isomers, the **b** isomers are computed to be between 31 and 16 kcal mol^{-1} and the **c** isomers between 19 and 11 kcal mol^{-1} more energetic. For three examples of N(2)-substituted *N*(1)-oxides in the benzotriazole series (the **b** isomers of **1**, **2**, and **4**) the heat of formation of the desired structures could not be calculated because during the optimization they underwent ring opening to yield the structures **11** (Scheme I). Such ring opening has never been observed in our experimental investigation of system **1a**/**b**/**c**. For example, the heat of formation of compound **3b** which can be considered a polyaza analogue of *o*-benzoquinone is predicted to be 31.4 kcal mol^{-1} above the *O*-acyl derivative **3a**. This value and our ab initio calculations (see Table IV, compounds **3a**/**b**/**c**) lead to the conclusion that AM1 overestimates the instability of such systems.

No systematic dependence of the relative stabilities of isomers on the moiety R (Table I) was found for the benzotriazoles **1**–**4** or the triazoles **5**–**8**.

For the model compounds **8** and the *H*-benzotriazoles **10**, significant stabilization of about 13 kcal mol^{-1} is predicted for the isomers **a**.

PM3 Results. The computed energy differences between the three isomers for compounds **1**–**8** are much smaller than those from AM1. For almost all cases the N(3)-substituted *N*(1)-oxides **c** are predicted to be more stable than the N(1) isomers **a** (Table I, last column). For all systems **1**–**8**, the isomers **b** were characterized as true minima, which are predicted to lie above that of the isomers **a** by 12–18 kcal mol^{-1} (benzotriazoles) or 5–8 kcal mol^{-1} (triazoles). A general trend was identified relating to the influence of the R substituent: compared with their protonated analogues (**4** and **8**), acyl substituents in compounds **1**–**3** and **5**–**7** seem to increase the stability of the isomers **c**. Initially this seems to be in agreement with experimental observations[1] especially for our benzoyl-substituted system **1a**/**b**/**c**. Of course, this encouraging theoretical result should be treated with caution, since it refers to gas-phase calculations while our experimental results reflect equilibria in solution. The relatively polar solvent (acetone) should stabilize polar moieties (especially the N^+–O^- group) of the isomer **1c**. This is supported by ab initio calculations including solvation described below. In agreement with the results reported by Fabian, **8a** is equal in energy with **8c**, but **8b** is destabilized by 8.2 kcal mol^{-1}. As previously reported for the 1- and 2*H*-benzotriazoles **10a** and **b**, PM3 (+7.8 kcal mol^{-1}) as well as AM1 (+12.8 kcal mol^{-1}) predict the **b** isomer to be significantly less stable.[14]

1*H*-1,2,3-Triazole (**9a**) and its 2*H*-tautomer **9b** together with (*Z*)- and (*E*)-diazene (**12a**,**b**)[21] are included in this investigation as examples where interaction involving cis-coplanar lone pairs on adjacent nitrogen atoms occurs (**9a**, **12a**) or not (**9b**, **12b**). Both semiempirical methods encounter difficulties in describing these molecules, but to a different extent: AM1, and to a much lesser extent PM3, predict **9a** to be significantly more stable than **9b** (AM1, 5.9; PM3, 2.8 kcal mol^{-1}). The experimental difference is −4.5 kcal mol^{-1}.[12] Therefore, the "error" of AM1 for that energy difference is 10.4, that of PM3 7.3 kcal mol^{-1}. This again indicates a slight superiority of PM3. Furthermore, this improvement in accuracy for structures with two adjacent cis-coplanar nitrogen lone pairs (n/n interaction, see Scheme I) appears in the results for the diazenes **12a** and **b**. AM1 barely distiguishes between the

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(16) (a) MOPAC: Stewart, J. J. P. *QCPE* **1985**, *5*, 455. (b) AMPAC: Stewart, J. J. P., *QCPE* **1986**, *6*, 509. (c) VAMP: Vectorized version of AMPAC: Clark, T. (Erlangen), unpublished material.

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(18) CRAY-2: Minnesota Supercomputer Center, Minneapolis, MN.

(19) CRAY-YMP: Landesrechenzentrum der Technischen Universität München, Germany.

(20) CONVEX 210: Institut für Organische Chemie der Universität Erlangen-Nürnberg, Germany.

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(23) For a brief introduction to Tomasi's SCRF theory and a description of the parameters used see: Steinke, T.; Hänsele, E.; Clark, T. *J. Am. Chem. Soc.* **1989**, *111*, 9107 and references cited therein. For the solvent calculations at 298.15 K of **8a** and **8b** the same principles were applied, especially for the sphere radii of atoms to construct the cavity (to be 20% larger than their van der Waals radii). Geometries were optimized using the 6-31+G* basis set. Further specific parameters of the solvents were as follows [σ, solvent diameter (A); V, volume (cm^3/mol); α, thermal expansion coefficient; ϵ, dielectric constant]: water $\sigma = 2.77$, $V = 18.07$, $\alpha = 0.000\,257$, $\epsilon = 78.39$; ethanol $\sigma = 4.36$, $V = 58.7$, $\alpha = 0.001\,103$, $\epsilon = 24.55$; acetone $\sigma = 4.47$, $V = 74.04$, $\alpha = 0.001\,430$, $\epsilon = 20.56$; CH_2Cl_2 $\sigma = 4.76$, $V = 64.50$, $\alpha = 0.001\,391$, $\epsilon = 8.93$.

Table II. Ab Initio Results for the 1,2,3-Triazole System 8a/8b/8c and 1- and 2*H*-1,2,3-Triazoles 9a,b

	methods			
struct.	3-21G// 3-21G	6-31+G*// 6-31+G*	MP2/ 6-31+G*// MP2/ 6-31+G*	MP4SDTQ/ 6-31+G*// MP2/ 6-31+G*
		Energies[a]		
8a	−313.761 59	−315.569 75	−316.536 07	−316.569 85
8b	−313.741 72	−315.553 71	−316.532 18	−316.565 68
8c	−313.739 87	−315.555 00	−316.532 84	−316.566 67
		Relative Energies[b]		
8a	0.0	0.0	0.0	0.0
8b	+12.47	+10.06	+2.44	+2.57
8c	+13.47	+9.26	+2.02	+1.95
		Energies[a]		
9a[c]	−339.392 66[c]	−240.776 96	−241.555 81	-
9b[c]	−339.399 01[c]	−240.784 75	−241.563 79	-
		Relative Energies[b]		
9a	0.0[c]	0.0	0.0	-
9b	−4.0[c]	−4.89	−5.00	-

SCRF Calculations,[d] Total Energies in Solvent[a]

	solvent: water	ethanol	acetone	CH_2Cl_2
8a	−315.626 99	−315.616 16	−315.611 68	−315.596 83
8c	−315.673 03	−315.659 21	−315.653 45	−315.632 51
		Relative Energies[b]		
8a	0.0	0.0	0.0	0.0
8c	−28.89	−27.01	−26.21	−22.39

[a] Energies in au (= 627.472 37 kcal mol^{-1}).[11c] [b] Relative energies in kcal mol^{-1}. [c] Further data: see ref 13. [d] Based on the 6-31+G* optimized structures.

(*Z*)- and (*E*)-isomer (−0.9 kcal mol^{-1}) ignoring the n/n interaction in **12a** almost completely. PM3 calculations yield a significant stabilization for the (*E*)-isomer (−5.1 kcal mol^{-1}, Table I).

The results in Table I demonstrate that for the acyl-substituted benzotriazoles **1–3** and their 1,2,3-triazole analogues **5–7** the AM1 and PM3 relative computed stabilities are mutually inconsistent. To a lesser extent this is true also for the model compounds.

Ab Initio Results and Comparison with AM1 and PM3 Calculations. The benzotriazoles **3** and **4** were optimized using the 3-21G basis set. These 3-21G geometries were used in single-point calculations to examine the changes in relative energies resulting from inclusion of polarization and diffuse functions (6-31G* for molecules **3a/b/c** and 6-31+G* for molecules **4a/b/c**). Previous calculations using these basis sets have been applied to the tautomeric equilibria of **9a/b** and **10a/b**.[12–14] To a certain degree these results appear to support the AM1 rather than the PM3 results, as shown in Table IV. But for structures specifically containing the an *N*-oxide moiety, the ab initio results are highly dependent on the basis sets.[21] This is confirmed by an ab initio study for the model compounds **8**, **9** and **12**, respectively (Tables II and III).

The energy difference between **9a** and **b** (the 1,2,3-triazoles) is almost independent (± 1 kcal mol^{-1}) of the basis set and the inclusion of electron correlation effects (Table II). The relative energy of the isomer **b** at the MP2/6-31+G*[17d] level (−5.00 kcal mol^{-1}) compared to isomer **a** agrees quite well with the experimentally observed value of −4.5 kcal mol^{-1},[12] quoted above, and will be used for further discussion. This energy difference can be interpreted somewhat roughly as the result of an exchange of a lone pair/lone pair (n/n) by a lone pair/σ-bond (n/σ) interaction (Scheme I).[24]

Table III. Ab Initio Results for (*Z*)- and (*E*)-Diazene (12a,b)[a]

method	(*Z*)-diazene (**12a**)	(*E*)-diazene (**12b**)	relative energies[b] (**12a–12b**)
3-21G	−109.342 40	−109.354 77	−7.76
6-31+G*	−109.987 38	−110.000 08	−7.97
MP2/6-31G**	−110.330 30	−110.340 33	−6.29
MP2/6-31+G*	−110.319 25	−110.331 54	−7.71
MP4/6-31+G*[c]	−110.341 49	−110.353 16	−7.32
MP4/6-311+G**[d]	−110.403 42	−110.414 40	−6.89

[a] For further investigations see ref 21. [b] In kcal mol^{-1}. [c] Single-point calculation with MP2/6-31+G* geometry. [d] Single-point calculation with MP2/6-31G** geometry.

Table IV. Ab Initio Results for the Benzotriazole Systems 3a/b/c, 4a/b/c, and 10a/b

		methods		
struct		3-21G// 3-21G[a]	6-31G*// 3-21G	6-31+G*// 3-21G
3a	energies[b]	−577.663 34	−580.939 77	-
3b		−577.628 81	−580.899 33	-
3c		−577.650 21	−580.925 93	-
3a	relative energies[c]	0.0	0.0	-
3b		+21.66	+25.36	-
3c		+8.24	+8.68	-
4a	energies	−465.566 83	−468.203 16	−468.216 61
4b		−465.534 30	−468.171 17	−468.188 27
4c		−465.547 84	−468.183 91	−468.200 20
4a	relative energies	0.0	0.0	0.0
4b		+20.41	+20.07	+17.78
4c		+11.92	+12.08	+10.30
10a	energies	−391.197 77[d]	−393.241 73[e]	
10b		−391.188 98[d]	−393.234 01[e]	
10a	relative energies	0.0	0.0	
10b		+5.51	+4.80	

[a] Assuming the ring system to be planar. For further details, e.g., for compounds **3a/b/c**, see text and Table VII. [b] Energies in au. [c] Relative energies in kcal mol^{-1}. [d] Data taken from ref 14. [e] 6-31G//6-31G optimizations. Data taken from ref 13.

The same essential independence of basis set sizes and electron correlation effects is seen for the energy difference between (*Z*)- and (*E*)-diazene (**12a**, **b**; Table III); it varies between 7.76 (3-21G) and 6.89 kcal mol^{-1} (MP4SDTQ/6-311+G**).[21] Again n/n in **12a** is replaced by n/σ in **12b**, while the σ/σ in **12a** turns to a n/σ-interaction in **12b**. Assuming that −5.00 kcal mol^{-1} results from the n/n to n/σ exchanges as above, the σ/σ to n/σ exchange yields another −1.89 kcal mol^{-1} (MP4) of stabilization for **12b**. For these molecules, the AM1 error for the total stabilization energy is +6.0, with that of PM3 just +1.8 kcal mol^{-1}.

For compounds **8a/b/c**, *N*-oxide structures are involved and we investigated the influence of the basis set sizes and the inclusion of electron correlation effects in these systems. As summarized in Table II, such structures require at least the MP2/6-31+G* basis set to calculate reliable energy differences. Again, these differences remain almost constant when proceeding from MP2 to the MP4SDTQ Møller–Plesset perturbation theory. The 6-31+G* basis set is inadequate. Based on the MP4 results, the errors of AM1 and PM3 treatments can be estimated from the energy difference **8a–8b**, +13.5 (AM1), +5.6 kcal mol^{-1}

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[24] This model does not include changes in energy explicitly caused by further structural changes in the triazole ring systems of involved tautomers, e.g., the different double bond characters of the C(4)–C(5) bond in **9a** and **b**.

Table V. Energy Difference between Tautomeric Pairs 8a/b/c, 9a/b, 10a/b, and 12a/b from Best Available ab Initio Results (ΔH) and Deviations from These Energy Differences at Lower Levels of Theory ($\Delta\Delta H$)

	energy (kcal mol^{-1})				
		deviations from best available method ($\Delta\Delta H$)			
tautomeric pair	difference (ΔH) best available method	6-31+G*	3-21G	PM3	AM1
8a–8b	+2.57[a]	+7.49	+9.90	+5.63	+13.53
8a–8c	+1.95[a]	+7.31	+11.52	−1.95	+10.95
9a–9b	−5.00[b]	+0.11	+1.00	+7.80	+10.90
10a–10b	+4.80[c]	–[e]	+0.71	+3.00	+8.00
12a–12b	−6.89[d]	−1.08	−1.07	+1.79	+5.99

[a] MP4SDTQ/6-31+G*//MP2/6-31+G*, Table II. [b] MP2/6-31+G*//MP2/6-31+G*, Table II. [c] 6-31G*//3-21G, Table IV. [d] MP4SDTQ/6-311+G**//MP2/6-31G**, Table III. [e] Not available.

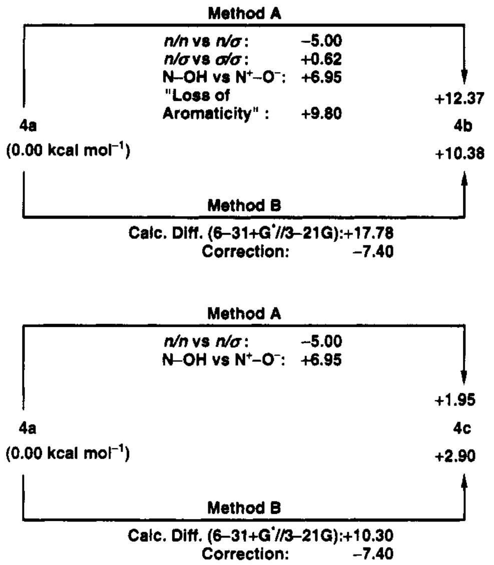
(PM3), for **8a–8c**, +11.0 (AM1), −2.0 kcal mol^{-1} (PM3). AM1 significantly overestimates the instability of the *N*(1)-oxides **b** and **c**, PM3 slightly overestimates the stability of the tautomer **c**, and, to a lesser extent than AM1, the instability of the tautomer **b**.

What explains the energetic similarity of the three tautomers **8a/b/c** as found by the MP2 and MP4 calculations? We first discuss the difference between **8a** and **8c**. For brevity we call the following procedure to estimate relative energies of isomers "method A". Two effects are responsible for the overall energy difference. As the change from the n/n to n/σ interaction increases the stability by −5.0 kcal mol^{-1} and the n/σ interaction of the N(2) lone pair with the N–O σ-bond is present in both molecules, the calculated difference (+1.95 kcal mol^{-1}) reflects the *dominant* destabilizing influence of the $^{-}$O–N^{+} moiety of the isomer **c**, which can be estimated to be about +6.95 kcal mol^{-1}. The difference between **8a** and the isomer **8b** is slightly more complex as the n/n (**8a**) changes to the n/σ interaction simultaneously with the change of n/σ (**8a**) to σ/σ (**8b**) at the atoms N(1) and N(2). Compared with the diazene, **12a/b**, again the exchange of n/σ by σ/σ increases the energy, in this case by +0.62 (diazenes: +1.98) kcal mol^{-1}. This is an approximate picture of the mutual influence of electronically different subunits, but it helps to understand the resulting relative energies.

For reasons discussed above, for the structures **10a/b**, the 3-21G basis set, at least (or better: the 6-31G basis set[13]), is needed for an adequate description of this pair of benzotriazole tautomers. Higher level calculations rapidly become prohibitively expensive at present, but extension of method A allows estimation of the energetic changes for more complex structures (see also Scheme II). In the fused benzene ring system **10a** the n/n is replaced by n/σ interaction in **10b** giving −5.0 kcal mol^{-1} of stabilization. As **10b** is calculated to be 4.8 kcal mol^{-1} less stable (Table IV), the overall change costs 9.8 kcal mol^{-1}. As pointed out previously,[14] rather than reflecting the "loss of aromaticity" this value characterizes the change of a 1-amino-2-azobenzene (tautomer **10a**) to a polyaza analogue of the *o*-benzoquinonoid system. Again the error for the relative energies of PM3 (+3.0) is smaller than that of AM1 (+8.0 kcal mol^{-1}).

We now discuss *N*(1)-hydroxybenzotriazole (**4a**) and its tautomers as well as *N*(1)-(formyloxy)benzotriazole (**3a**) and its isomer **b** and **c**. Both systems were optimized with the inadequate 3-21G basis and subsequently refined energetically by a 6-31+G* single-point calculation (Table IV). We now invoke the fact that with 6-31+G* calculations for the $^{-}$O–N^{+}(1)–N(2)H–N(3) or the $^{-}$O–N^{+}(1)–N(2)–N(3)H moieties, the error is almost constant (see Table V, molecules **8b** and **8c**). This leads to a second procedure (method B, Scheme II) for more accurate estimation of relative energies in larger molecules. To exemplify the procedure, substracting the averaged difference of 7.4 kcal mol^{-1} from the 6-31+G* differences between **4b** and **4a** gives +10.38 kcal mol^{-1} and +2.90 kcal mol^{-1} for of **4c–4a**. Following the "incremental" procedure (method A) described above, exchanges of n/n by n/σ interactions, the "loss of aromaticity" effect, and the exchange of the HO–N(1) by the $^{-}$O–N(1)$^{+}$– moiety give an energy difference of +12.37 kcal mol^{-1} for **4b–4a** and +1.95 kcal mol^{-1} for **4c–4a**. This agrees quite well with the energy difference estimated by method B. Again, these corrected values are in better agreement with PM3 than with the AM1 results (Table I: PM3 **4b–4a**, +17.4, **4c–4a**, +0.4; AM1 **4b–4a**, not calculable, **4c–4a**, +15.8 kcal mol^{-1}).

Scheme II



Finally, as a check of the reliability of the extension of method B, the procedure was applied to the model system **3a/b/c**, selected to simulate the isomerism of O-acylated *N*(1)-hydroxybenzotriazoles (Table IV, 6-31G*/3-21G results). As diffuse functions were not included, the uncertainty for the corrected energy differences (**3b–3a**, +17.96; **3c–3a**, +1.28 kcal mol^{-1}) is larger than for the system **4a/b/c**. Furthermore, now we are confronted with the replacement of the HC(O)O–N(1)–N(2)–N(3) of **4a** by the $^{-}$O–N(1)$^{+}$–N(2)C(O)H–N(3) of **4b** or $^{-}$O–N(1)$^{+}$–N(2)–N(3)C(O)H moiety of **4c**, respectively, which differ from the analogous structural elements of **8** by the electron-withdrawing formyl group. Nevertheless, some interesting trends can be derived. The 6-31G* and the 3-21G basis set results, together with the corrected energy differences, indicate that the formyl group C(O)H decreases the value for the **4c–4a** differences about 3.5 kcal mol^{-1}, compared with that of the hydrogen atom in **3c**. The difference **4b–4c** increases. These trends are not apparent from AM1 calculations but appear at significant level in the PM3 results (Table I).

All the ab initio calculations indicate for the gas phase the energy of the three isomers is **a** < **c** < **b**. The situation in solution was simulated for **8a** and **8c**, using Tomasi's approach (Table II). The resulting relative energies in solvent are in agreement with our expectation that tautomer **8c** should be stabilized significantly in polar solvents. Furthermore, the increasing stabilization of that isomer parallels the increasing polarity of the solvent. Thus, our experimental results for the quantum mechan-

Table VI. Selected Bond Lengths[a] and Semiempirical and ab Initio Results

	1-(benzoyloxy)-Bt[b] (**1a**)		2-benzoyl-Bt 1-oxide (**1b**)		3-benzoyl-Bt 1-oxide (**1c**)	
	AM1	PM3	AM1[c]	PM3	AM1	PM3
N1–N2	1.428	1.415	–	1.446	1.318	1.303
N2–N3	1.238	1.247	–	1.401	1.376	1.472
N3–C3a	1.450	1.440	–	1.345	1.417	1.419
C3a–C4	1.386	1.392	–	1.432	1.398	1.398
C4–C5	1.401	1.389	–	1.359	1.393	1.386
C5–C6	1.395	1.402	–	1.437	1.404	1.404
C6–C7	1.402	1.389	–	1.359	1.393	1.385
C7–C7a	1.384	1.392	–	1.427	1.391	1.396
N1–O	1.324	1.429	–	1.223	1.206	1.217
N2–C9	–	–	–	1.509	–	–
N3–C9	–	–	–	–	1.421	1.442

	1-(formyloxy)-Bt (**3a**)			2-formyl-Bt 1-oxide (**3b**)			3-formyl-Bt 1-oxide (**3c**)		
	AM1	PM3	3-21G[d]	AM1	PM3	3-21G[d]	AM1	PM3	3-21G[d]
N1–N2	1.392	1.426	1.393	1.451	1.461	1.361	1.282	1.282	1.282
N2–N3	1.244	1.243	1.277	1.336	1.414	1.361	1.396	1.452	1.408
N3–C3a	1.448	1.445	1.393	1.370	1.342	1.381	1.412	1.413	1.374
C3a–C4	1.387	1.389	1.391	1.427	1.433	1.426	1.397	1.397	1.387
C4–C5	1.400	1.392	1.369	1.367	1.358	1.344	1.394	1.387	1.376
C5–C6	1.397	1.340	1.410	1.429	1.436	1.448	1.404	1.404	1.407
C6–C7	1.401	1.392	1.370	1.369	1.358	1.344	1.395	1.386	1.373
C7–C7a	1.384	1.389	1.390	1.418	1.428	1.416	1.389	1.395	1.379
N1–O	1.327	1.452	1.389	1.203	1.216	1.376	1.212	1.222	1.327
N2–C9	–	–	–	1.456	1.468	1.416	–	–	–
N3–C9	–	–	–	–	–	–	1.411	1.434	1.383

	1-hydroxy-Bt (**4a**)			2*H*-Bt 1-oxide (**4b**)			3*H*-Bt 1-oxide (**4c**)		
	AM1	PM3	3-21G	AM1[c]	PM3	3-21G	AM1	PM3	3-21G
N1–N3	1.427	1.439	1.388	–	1.438	1.341	1.318	1.306	1.286
N2–N3	1.239	1.240	1.212	–	1.384	1.350	1.366	1.412	1.388
N3–C3a	1.449	1.446	1.392	–	1.351	1.329	1.416	1.415	1.360
C3a–C4	1.387	1.389	1.292	–	1.430	1.422	1.397	1.398	1.359
C4–C5	1.400	1.392	1.386	–	1.360	1.348	1.392	1.385	1.371
C5–C6	1.396	1.399	1.412	–	1.435	1.442	1.404	1.406	1.412
C6–C7	1.401	1.393	1.369	–	1.360	1.348	1.393	1.384	1.368
N1–O	1.330	1.421	1.401	–	1.226	1.372	1.206	1.219	1.354
N2–H	–	–	–	–	0.997	0.999	–	–	–
N3–H	–	–	–	–	–	–	1.100	0.990	0.994

	1-(benzoyloxy)-Tr[e] (**5a**)		2-benzoyl-Tr 1-oxide (**5b**)		3-benzoyl-Tr 1-oxide (**5c**)	
	AM1	PM3	AM1	PM3	AM1	PM3
N1–N2	1.376	1.377	1.420	1.524	1.325	1.318
N2–N3	1.260	1.269	1.359	1.405	1.364	1.406
N3–C4	1.421	1.412	1.344	1.324	1.411	1.398
C4–C5	1.395	1.378	1.450	1.440	1.386	1.376
N1–O	1.321	1.429	1.204	1.216	1.280	1.221
N2–C7	–	–	1.454	1.486	–	–
N3–C7	–	–	–	–	1.431	1.456

	1-(formyloxy)-Tr (**7a**)		2-formyl-Tr 1-oxide (**7b**)		3-formyl-Tr 1-oxide (**7c**)	
	AM1	PM3	AM1	PM3	AM1	PM3
N1–N2	1.379	1.380	1.421	1.475	1.324	1.318
N2–N3	1.259	1.268	1.354	1.401	1.386	1.408
N3–C4	1.423	1.411	1.345	1.325	1.411	1.398
C4–C5	1.395	1.397	1.454	1.443	1.385	1.375
N1–O	1.326	1.435	1.208	1.226	1.207	1.219
N2–C7	–	–	1.442	1.465	–	–
N3–C7	–	–	–	–	1.419	1.447

	1-hydroxy-Tr (**8a**)				2*H*-Tr 1-oxide (**8b**)				3*H*-Tr 1-oxide (**8c**)			
	AM1	PM3	3-21G	MP2/ 6-31+G*	AM1	PM3	3-21G	MP2/ 6-31+G*	AM1	PM3	3-21G	MP2/ 6-31+G*
N1–N2	1.380	1.365	1.367	1.334	1.423	1.470	1.384	1.364	1.333	1.335	1.302	1.365
N2–Ne	1.259	1.281	1.304	1.344	1.345	1.388	1.355	1.337	1.345	1.376	1.373	1.353
N3–C4	1.423	1.397	1.373	1.357	1.351	1.330	1.316	1.351	1.390	1.373	1.351	1.356
C4–C5	1.394	1.389	1.362	1.389	1.450	1.438	1.409	1.391	1.399	1.392	1.352	1.370
N1–O	1.318	1.416	1.404	1.376	1.204	1.255	1.373	1.264	1.211	1.223	1.356	1.261
N2–H	–	–	–	–	1.010	0.997	0.996	1.017	–	–	–	–
N3–H	–	–	–	–	–	–	–	–	0.993	0.987	0.994	1.013

	1*H*-Tr (**9a**)				2*H*-Tr (**9b**)			
	AM1	PM3	6-31+G*	MP2/6-31+G*	AM1	PM3	6-31+G*	MP2/6-31+G*
N1–N2	1.345	1.356	1.318	1.355	1.338	1.339	1.302	1.333
N2–N3	1.273	1.281	1.267	1.330	1.338	1.339	1.302	1.333
N3–C4	1.411	1.398	1.356	1.362	1.358	1.364	1.306	1.353
C4–C5	1.406	1.386	1.358	1.382	1.459	1.414	1.404	1.396
N1–H	0.992	0.988	0.994	1.014	–	–	–	–
N2–H	–	–	–		1.000	0.987	0.994	1.015
N1–N2	1.197	1.211	1.260[f]	1.212	1.219	1.266[f]		
N–H	1.020	0.997	1.036	1.018	0.998	1.031		

[a] In angstroms (Å). [b] Bt: Benzotriazole. [c] Using the AM1 Hamiltonian; for 2-benzoyl-Bt 1-oxide and 2*H*-Bt 1-oxide no local minimum was found. [d] 3-21G//3-21G-optimization, assuming the ring systems to be planar. [e] Tr: 1,2,3-Triazole. [f] Experimental bond length: 1.252 Å, see ref 21.

Table VII. Selected Dihedral Angles (deg) of Compounds 3a/b/c and 8a/b/c

method	dihedral angles[a]			
		3a		
	N3–N2–N1–O8	N2–N1–O8–C9	N1–O8–C9–O[b]	N1–N2–N3–C3a
3-21G	−176.19	−82.79	−4.49	0.00[c]
PM3	142.05	107.66	4.94	−6.22
AM1	147.22	−56.58	−3.77	−7.06
		3b		
	N3–N2–N1–O8	N1–N2–N3–C9	N1–N2–C9–O[b]	N1–N2–N3–C3a
3-21G	180.00[c]	180.00[c]	180.00	0.00[c]
PM3	−179.93	−163.00	−1.92[d]	3.08
AM1	170.57	156.13	−170.40	−10.98
		3c		
	N3–N2–N1–O8	N1–N2–N3–C9	N2–N3–C9–O[b]	N1–N2–N3–C3a
3-21G	180.00[c]	180.00[c]	180.00	0.00[c]
PM3	179.79	179.22	−179.35	0.39
AM1	−179.93	179.96	179.93	−0.09
		8a		
	N3–N2–N1–O6	N2–N1–O6–H7	N1–N2–N3–C4	
MP2/6-31+G*	179.94	−0.33	0.00	
6-31+G*	−176.95	−68.94	0.48	
3-21G	−175.50	−55.83	1.13	
PM3	−179.94	−0.28	0.02	
AM1	−157.73	78.61	−4.84	
		8b		
	N3–N2–N1–O5	N1–N2–N3–H7	N1–N2–N3–C4	
MP2/6-31+G*	180.00	180.00	0.00	
6-31+G*	180.00	180.00	0.00	
3-21G	−179.98	−179.97	0.00	
PM3	−175.20	−138.44	8.31	
AM1	−179.27	−137.22	10.14	
		8c		
	N3–N2–N1–O6	N1–N2–N3–H7	N1–N2–N3–C4	
MP1/6-31+G*	180.00	180.00	0.00	
6-31+G*	179.98	180.00	0.03	
3-21G	180.00	180.00	0.05	
PM3	180.00	180.00	0.00	
AM1	180.00	180.00	0.00	

[a] For the numbering of atoms see Chart I. 3-21G calculations of molecules **3a**/**b**/**c**: optimized by assuming the ring system to be planar, for **3b** and **c** the N^+–O^- oxygen was assumed to be coplanar with the ring system. Molecules **8a**/**b**/**c** were optimized without any symmetry restrictions. [b] The carbonyl oxygen. [c] Fixed parameter. [d] For **3b** PM3 predicts a conformer which is near to a "syn-coplanar" arrangement of the N^+–O^- and the C═O oxygen atoms. The corresponding "anti-coplanar" conformer is less stable by 0.9 kcal mol^{-1}.

ically "large" system **1a**/**b**/**c** become understandable. The intermolecular rearrangement corresponding to a formal 1,4-sigmatropic hydrogen shift is evidently feasible due to the similar energy of the isomers **1a** and **1c**. Such a rearrangement is promoted by the better stabilization of the isomer **c** in the polar solvent (acetone). Computations at an appropriate level for Horiki's system **2a**/**c**[3] (acetyl derivatives of the benzotriazole series) exceeds our present computer budget, but his findings, indicating that the fused benzene ring system decreases the solvation energy, are reproduced at least in part. Therefore, only in the most polar solvent mixture (water:acetone = 80:20) **2c** does become the predominant isomer. In future research we plan to compare more precisely the energies of molecules in the gas and the condensed phase.

Ab Initio and Semiempirically Calculated Bond Lengths and Dihedral Angles.[25] Based on the MP2/6-31+G* optimizations for **8a**/**b**/**c** and **9a**/**b** the accuracy of bond lengths resulting from the basis sets 3-21G or 6-31+G* and from AM1 or PM3 calculations are compared in Table VI. For the O–N(1)–N(2)–N(3) system, the MP2 calculations indicate the following general trends: taking the bonds of **8a** as a standard, the N(1)–N(2) bond of **8a** (1.334 Å) is shorter than its equivalent in **8b** or **c**. For the N(2)–N(3) bonds the values for **8b** and **8c** show only small differences from that of isomer **8a**. As expected the N(2)–N(3) length in **8a** is longer than that of the N═N (isolated) double bonds of the diazenes **12a**, **b** (1.260 and 1.266 Å, respectively). More significant changes are found for the O–N(1) bonds which are shorter in **8b** (1.264) and **8c** (1.261 Å) than in **8a** (1.376 Å), this shortening can be attributed to an increased coulombic attraction from oppositely charged moieties (the negatively charged oxygen and the positively charged heterocyclic ring system).[26] The N(3)–C(4) bond length remains almost constant in all tautomers **8** (1.351–1.357 Å).

Comparison of the 1*H*-1,2,3-triazole (**9a**) bond lengths with that of **8a** indicate that the triazole ring system of **8a** is almost unaffected by the *N*(1)-hydroxy group. By contrast, the value for the N(1)–N(2) distance of the polar structure **8b**, which is elongated (from 1.333 to 1.364 Å), could be the result of a 1,3 lone pair/lone pair repulsion between an oxygen (O^-) and the N(3) lone pair.

The 6-31+G* and MP2/6-31+G* results for **9a** and **b** allow estimation of the influence of the electron correlation of the bond lengths. As previously reported for a variety of other structures,[21] we observe that MP2 yields for almost

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(25) For a related discussion see ref 14.

(26) A further explanation for this bond shortening may arise from the influence of the anomeric effect, which is the interaction of an oxygen lone pair with a σ^* bond orbital of the N(1)–ring bonds. Compared with **8a**, this effect should be more expressed in the presence of a negatively charged oxygen atom (structures **8b** and **8c**).

all bonds in both molecules a significant elongation. These MP2 calculated lengths should be in better agreement with "real" values.[21]

Most of these general trends are reproduced in bond lengths calculated by the semiempirical methods. Unfortunately, the values summarized in Table VI do not allow a decision as to which semiempirical method is better suited to calculate bond lengths closer to ab initio results. For the N(2)–N(3) bond of **8a** and **9a**, the semiempirical methods and to a lesser extent the smaller ab initio basis sets produce distances which are too short. To select typical examples, the N(1)–N(2) bonds of the tautomers **8** are in better agreement with PM3 results, while AM1 is superior for the N(2)–N(3) bonds of **8b** and **c**. Significant errors in both methods are found for the O–N(1) bond of **8a** and **8c**; however, for **8b** that bond is in acceptable agreement with the PM3 value. For **9a** and **9b** almost all bond lengths agree better with the PM3 results.

Using 0.02 Å to define a significant increment in bond lengths changes for 3-21G calculations, the results of Table VI reveal the influence of the benzo-condensed ring on the 1,2,3-triazole system. Comparing the results for **8a**/**b**/**c** with those of **4a**/**b**/**c**, respectively, annelation leads to shorter N(2)–N(3) (**4a**) and N(1)–N(2) (**4c**) bonds, indicating greater double bond character. In the benzotriazole systems **3** and **4**, the bond lengths of analogues compounds are quite similar; thus, the influence of the formyl group on the ring and N–O distances is small. Exceptions are the N(1)–N(2) bond of **3b** and the N(2)–N(3) bond of **3c**, which are elongated by about 0.02 Å. The PM3 and AM1 calculated bond lengths of the molecules **1**, **5**, and **7** are included in Table VI for completeness, but for reasons given above we avoid a further detailed discussion.[27]

Dihedral Angles. As mentioned above, the MP2/6-31+G* structures of the model compounds **8a**/**b**/**c** turn out to be planar. Lower level ab initio theories and the semiempirical methods reveal their difficulties in describing the dihedral angles of the N1, N2, or N3 substitutents correctly (Table VII). Especially for **8a** the AM1 calculated angle N3–N2–N1–O6 (−157.73°) indicates a significant pyramidalization of the N1 center. A more significant deviation from planarity or increasing pyramidalization results on the semiempirical level for the N2 center of **8b** (N1–N2–N3–H7).[28] While all ab initio methods agree in predicting a (almost) planar ring system for the compounds **8** (dihedral angle N1–N2–N3–C3a), especially AM1 and PM3 indicate a certain nonplanarity of the five-membered ring of **8b**. Similar trends were found for the sterically more congested compounds **3a**/**b**/**c**.

Conclusion

From these investigations we conclude that the reported results for the system **8a**/**b**/**c**[7] based on the PES results[8] mentioned above, need a reinterpretation. The observation of tautomer **8a** only in the gas phase of course does not exclude the possibility that it can be almost equal in energy to **8c**. Gas-phase rearrangements normally proceed intramolecularly and depend on the heights of activation barriers. Since intramolecular 1,4-sigmatropic hydrogen shifts are thermally forbidden, it is not surprising that **8a** does not rearrange up to its thermal decomposition temperature.

The energy differences between the tautomers **8**–**10** and the diazenes **12** presented in this study show that the PM3 method better compares with quite large basis set ab initio calculations than the AM1 method, and we believe that Fabians's statement about the deficiencies of PM3 compared with AM1 is not justified. The increased stabilization predicted by the PM3 method for the acylated compounds **c** compared with that of their isomers appears to be reliable, although preference of **1c** by −7.3 kcal mol^{-1} might be over emphasized.

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Registry No. **1a**, 54769-36-7; **1b**, 141090-52-0; **1c**, 137379-04-5; **2a**, 18355-05-0; **2b**, 141090-53-1; **2c**, 64656-28-6; **3a**, 42039-28-1; **3b**, 141090-54-2; **3c**, 141090-55-3; **4a**, 2592-95-2; **4b**, 141090-56-4; **4c**, 2273-05-4; **5a**, 141090-57-5; **5b**, 141090-58-6; **5c**, 141090-59-7; **6a**, 141090-60-0; **6b**, 141090-61-1; **6c**, 141117-96-6; **7a**, 141090-62-2; **7b**, 141090-63-3; **7c**, 141090-64-4; **8a**, 116932-70-8; **8b**, 107716-48-3; **8c**, 133560-87-9; **9a**, 288-36-8; **9b**, 288-35-7; **10a**, 95-14-7; **10b**, 273-02-9; **12a**, 15626-42-3; **12b**, 15626-43-4.

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(27) Additional structural data (e.g., the preferred conformations of compounds 1–8) are available on request. For a related discussion of bond lengths alternation and the errors of the semiempirical methods, see: Katritzky, A. R.; Szafran, M.; Malhotra, N.; Chaundry, S. U.; Anders, E. *Tetrahedron Comput. Meth.* **1990**, *3*, 247.

(28) For a related discussion concerning 1,2,4-triazoles, see: Ritchie, J. P. *J. Org. Chem.* **1989**, *54*, 3553.