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Investigations on the structure of 4-methyldihydro-1,3,4-benzotriazepin-5-ones. Tautomer reassignment

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The tautomerism of 4-methyldihydro-1,3,4-benzotriazepin-5-ones (**2**,**3**) is re-investigated by means of X-ray diffraction and quantum chemical calculations. The data revealed that the model compound (**2a**) exists in the amidrazone 1,4-dihydro tautomeric form (**A**), but not in the alternate 3,4-dihydro tautomer (**B**) as was previously reported.

Introduction

An unambiguous synthesis of some dihydro-1,3,4-benzotriazepin-5-ones (**2**,**3**) had been reported earlier by Sunder *et al.*,[1] and by Leiby and Heidel[2] (Scheme 1). Of the two possible tautomeric forms (**A**) and (**B**), all products (**2a–d**,**3a–d**) obtained from the condensation of the hydrazides (**1**) with orthoesters were assigned the 3,4-dihydro form (**B**) rather than the alternate 1,4-dihydro tautomer (**A**).

Evidence in support of the chosen tautomer (**B**) for compounds (**2**,**3**) rested solely on comparisons of their ^{1}H-NMR and UV spectral data with the model (**4**) and what seemed to be analogous systems (**1**,**5**; Scheme 1).[1,2] Such spectral comparisons might not, however, be taken as adequate enough from which to draw definitive conclusions with regard to the constitution of the prevailing tautomer.

Quite recently, we have established by X-ray diffraction measurements that the closely related 2-acetyl-4-aryldihydro-1,3,4-benzotriazepin-5-ones (**6**), exemplified by **6a**, exist in the solid state as 1,4-dihydro tautomers (**A**) rather than the 3,4-dihydro tautomers (**B**)[3] (Scheme 2). In light of this *ipso facto* result, we consider that our findings would call into question the validity of the earlier reported tautomer (**B**) for those benzotriazepine-5-ones (**2**,**3**),[1,2] and a re-study is thus justified.

Accordingly, we have prepared one of the earlier compounds namely, 4-methyldihydro-1,3,4-benzotriazepin-5-one (**2a**: R = X = H), following the reported procedure,[1] and report herein the X-ray crystal structure determination. The crystallographic data and *ab initio* quantum chemical calculations provide unequivocal evidence that in the solid state, compound (**2a**) exists as the 1,4-dihydro structure (tautomer **A**, Scheme 1) (*vide infra*).

Results and discussion

Spectral data

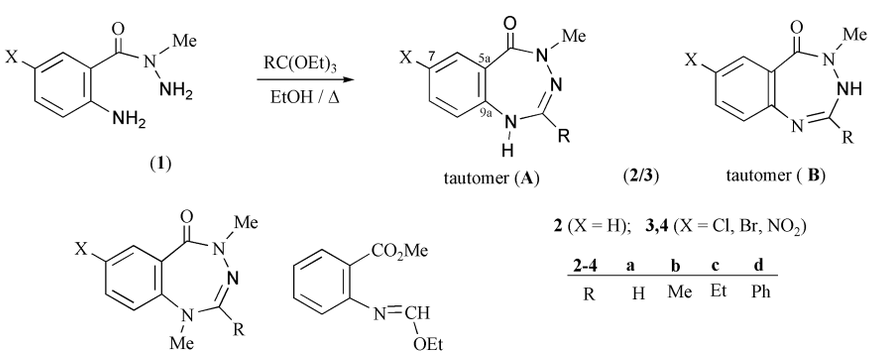
The IR, MS, and NMR spectral data and microanalysis of compound **2a** conform to the suggested structure, and are given in the Experimental section. The MS spectrum of compound **2a** displayed the correct molecular ion for which the measured high resolution datum (175.076980) is in good agreement with the calculated value (175.074562). ^{1}H and ^{13}C NMR signal assignments follow from DEPT and 2D (COSY, HMQC and HMBC) experiments.

Crystal structure determination of 2a

Crystal data.† $C_9H_9N_3O$, M = 175.19, monoclinic, a = 16.905(8), b = 14.087(7), c = 7.001(4) Å, β = 90.368(10) °, D_{calcd} = 1.396 g cm^{-3}, U = 1667.3(14) Å^3, T = 203(2) K, space group $P2_1/c$, Z = 8, μ(Mo–K$_\alpha$) = 0.096 mm^{-1}, 9461 reflections measured ($2\theta_{max}$ = 48°), 2925 unique [$R_{int}(F^2)$ = 0.0677] which were used in all calculations. The final R_1 was 0.0714 (F_o>4σ(F)), and wR_2 (F^2) = 0.2075 (all data).

In the asymmetric unit cell, there are two independent molecules, referred to as molecules 1 and 2, producing slightly different environments, and for which relevant crystallographic data are summarized in Table 1. The molecular structure of **2a**, based on crystallographic data, is displayed in Fig. 1. These data revealed that the protic hydrogen H(1) is σ-bonded to N(1), while the double bond is situated at the C(2)–N(3) locus (Fig. 1

† CCDC reference number 200677. See http://www.rsc.org/suppdata/ob/b3/b301047c/ for crystallographic data in .cif or other electronic format.



2 (X = H); **3,4** (X = Cl, Br, NO$_2$)

2-4	a	b	c	d
R	H	Me	Et	Ph

Scheme 1

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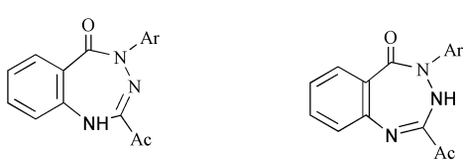
Table 1 Comparison of relevant X-ray crystallographic and calculated (*ab initio*, AM1, PM3)[a] parameters of **2a** (**A**)

	X-Ray molecule 1	X-Ray molecule 2	*Ab initio* 3-21G	AM1	PM3
Bond lengths/Å					
N(1)–C(9A)	1.407(3)	1.386(4)	1.389	1.402	1.438
N(1)–C(2)	1.366(4)	1.378(4)	1.377	1.402	1.429
N(3)–C(2)	1.274(4)	1.256(4)	1.254	1.301	1.295
N(3)–N(4)	1.416(3)	1.423(3)	1.408	1.377	1.396
N(4)–C(5)	1.365(4)	1.349(4)	1.363	1.422	1.464
C(5)–C(5A)	1.491(4)	1.486(4)	1.501	1.486	1.489
C(5A)–C(9A)	1.390(4)	1.399(4)	1.391	1.411	1.400
N(4)–C(10)	1.463(4)	1.458(4)	1.472	1.468	1.491
C(5)–O(1)	1.230(3)	1.235(4)	1.225	1.246	1.216
N(1)–H(1)	0.89	0.82	0.998	1.000	0.997
C(2)–H(2)	0.95	0.95	1.071	1.116	1.103
H(1). . .O(1)[b]	2.03	2.01	[c]	2.163	2.479
N(1). . .O(1)[b]	2.83	2.80	[c]	3.139	3.459
Bond angles/°					
C(2)–N(1)–C(9A)	122.7(2)	124.0(3)	129.9	122.4	121.0
N(3)–C(2)–N(1)	130.1(3)	130.9(3)	132.6	132.8	129.6
C(2)–N(3)–N(4)	118.0(2)	117.7 (3)	126.0	127.4	128.7
N(3)–N(4)–C(5)	126.1(2)	126.0(2)	131.6	127.2	120.7
N(4)–C(5)–C(5A)	121.0(2)	122.4(3)	123.9	121.7	117.0
C(5)–C(5A)–C(9A)	125.2(2)	123.7(3)	128.2	125.6	122.7
C(5A)–C(9A)–N(1)	123.5(2)	123.5(3)	125.1	123.0	121.3
N(3)–N(4)–C(10)	110.0(2)	109.6(2)	110.5	114.7	110.9
N(4)–C(5)–O(1)	119.3(3)	119.4(3)	117.8	117.9	119.2
C(2)–N(1)–H(1)	109	114	114.8	113.6	110.4
N(1)–C(2)–H(2)	115	115	112.4	114.0	116.4
N(1)–H(1). . .O(1)[b]	165	166	[c]	163.6	167.3
Dihedral angles/°					
C(9a)–N(1)–C(2)–N(3)	47.3(5)	43.3(5)	−13.2	35.8	40.7
N(1)–C(2)–N(3)–N(4)	6.1(5)	8.7(5)	−2.9	−4.9	−9.4
C(2)–N(3)–N(4)–C(5)	−57.3(4)	−56.6(4)	17.7	5.2	21.4
N(3)–N(4)–C(5)–C(5a)	35.6(4)	32.9(4)	−11.3	−34.9	−59.0
C(2)–N(3)–N(4)–C(10)	150.8(3)	150.0(3)	−172.8	161.2	161.8
N(3)–N(4)–C(5)–O(1)	−150.4(3)	−152.0(3)	169.6	152.3	127.7
C(10)–N(4)–C(5)–C(5a)	−174.5(3)	−176.0(3)	179.7	168.9	162.2
C(6)–C(5a)–C(5)–O(1)	12.6(4)	14.7(4)	−2.5	30.5	47.5
C(6)–C(5a)–C(5)–N(4)	−173.4(3)	−170.1(3)	178.5	−142.1	−125.4
C(2)–N(1)–C(9a)–C(9)	145.9(3)	147.9(3)	−169.9	144.2	133.9
C(9)–C(9a)–N(1)–H(1)	7	−3	3.6	0.7	1.6
H(2)–C(2)–N(1)–C(9a)	133	136	167.0	−148.7	−146.9
H(2)–C(2)–N(3)–N(4)	−174	−172	176.9	179.6	178.0

[a] Full geometry optimization was performed with no geometry constraints. [b] Calculated for an intermolecularly hydrogen bonded dimer of **2a** (tautomer **A**). [c] Due to size restrictions, no *ab initio* calculations were done on the intermolecularly hydrogen-bonded dimer of **2a**.



6 (**A**) **6a** (Ar: *p*-MeC$_6$H$_4$) **6** (**B**)

Scheme 2

and Table 1). As can be seen from Table 1 (for molecule 1), the N(1)–C(2) bond length is 1.366 Å (an acceptable value for a C–N sp^2–sp^3 σ-bond), whereas that of C(2)–N(3) is 1.274 Å, in agreement with an azomethine π-bond character. The amide C(5)–N(4) bond length is 1.365 Å, being intermediate between the single bond length of 1.47 Å and the double bond length of 1.24 Å.[4] Collectively, the data noted above are in conformity with tautomer **2a** (**A**) as the stable form in the crystal. The 3,4-dihydro tautomer **2a** (**B**) suffers from inherently dominant repulsive interactions involving the lone pairs of vicinal sp^3-nitrogens. Since the structure of the compound in the solid state usually represents the more stable tautomer, it is expected to be retained in solution.[5] In this context, it is worth mentioning that a number of related aza-heterocycles are known to display

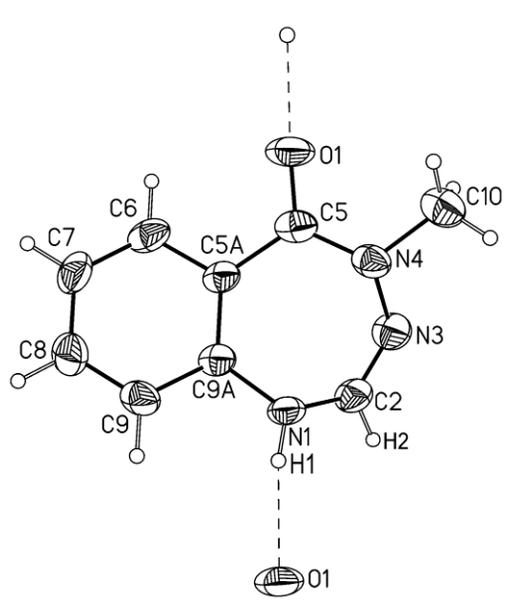
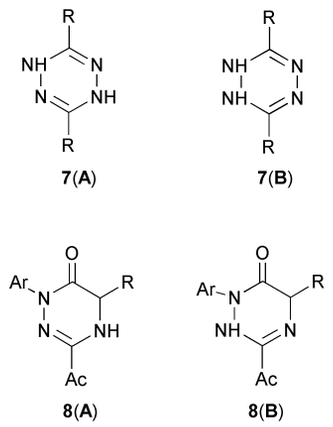


Fig. 1 ORTEP plot of the molecular structure of **2a** (only one molecule is shown)

comparable tautomeric trends. Amongst these, are the dihydro-3,6-disubstituted-*s*-tetrazines (**7**) and tetrahydro-1,2,4-triazin-6-ones (**8**), which adopt the amidrazone (1,4-dihydro) tautomeric forms (**7A**)[6] and (**8A**),[7] respectively, rather than the alternate hydrazino (1,2-dihydro) tautomers (**7B** and **8B**) (Scheme 3).



Scheme 3

Calculations, based on X-ray data, relating to the plane of the 1,4-dihydro-1,3,4-triazepine ring, show that atoms N(1)–C(9A)–C(5A)–C(5)–C(4) are lying quite well in the same plane and are coplanar with the benzo-fused ring, while the doubly-bonded atoms C(2)–N(3) are folded away, out of the plane, in a "*boat*"-like manner (Fig. 1). The solid state structure of **2a** (**A**) is stabilized by intermolecular hydrogen bonds involving N(1)–H(1). . .O(1): D = 2.826, d = 2.03 Å, Θ = 165.3°, and N(11)–H(11). . .O(11): D = 2.803, d = 2.01 Å, Θ = 160.6°#[8] for molecules 1 and 2, respectively (Fig. 2(a)). A boat-shaped conformation was likewise established, by computational and X-ray diffraction techniques,[9–12] for the nonplanar heteroring in related 1,2,3,4-tetrahydro-1,3,4-benzotriazepin-5-ones,[9] 2,3-dihydro-1*H*-1,4-benzodiazepines,[10,12] and 4,5-dihydro-1*H*-2,4-benzodiazepines.[11,12]

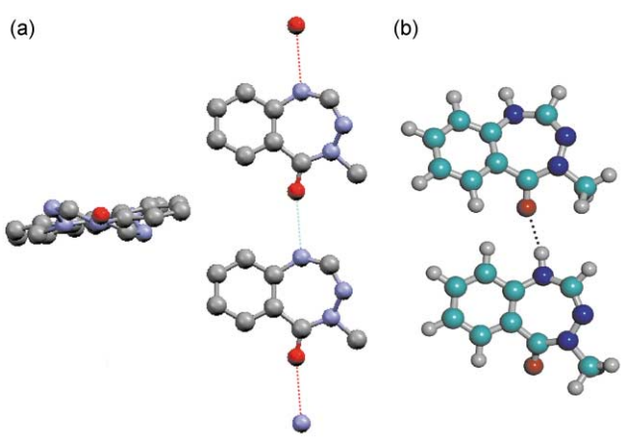


Fig. 2 Intermolecular hydrogen bonding of **2a**: (a) in the crystal viewing along [010] (b) in AM1-calculated boat conformer.

Quantum chemical calculations

We also sought to compare stabilities of tautomers **2a** (**A** and **B**) by calculation of their relative energies obtainable by a variety of computational methods. To our knowledge, computational studies on the dihydro-1,3,4-benzotriazepin-5-ones are hitherto not reported. Herein, the structural and energetic aspects of the tautomerism in 4-methyldihydro-1,3,4-benzotriazepin-5-one (**2a**) are studied using *ab initio* and semi-empirical SCF-LCAO-MO methods. In all cases, full geometry optimization was performed with no geometrical constraints. At the *ab initio* level, the size of the molecule dictated the use of the medium sized HF/3-21G basis set for geometry optimization, but the energies were computed at a higher level using extended HF/6-31G** basis sets with diffuse functions. The calculated geometrical parameters from both the *ab initio* and semi-empirical (AM1 and PM3) methods are given alongside the X-ray crystallographic data in Table 1. The calculated values are in satisfactory agreement with the observed X-ray results. The *ab initio* calculations were found to be more accurate than AM1 and PM, with AM1 being slightly better than PM3. At the HF/3-21G level, the bond lengths are reproduced to within ±0.01 Å, while the AM1 method gave bond lengths accurate to within ±0.03 Å, in agreement with the average reported errors.[13–15] On the other hand, the AM1 gave more accurate bond angles and dihedral angles than both of the HF/3-21G and the PM3 methods. The calculated dihedral angles, however, are usually subject to larger errors at both the *ab initio* and semi-empirical levels of theory.[16,17]

The energy difference between the two conformers of **2a** was calculated at the HF/6-31G** level which is known[16] to reproduce conformational energy differences satisfactorily to within 2.5 kJ mol^{-1}. The present HF/6-31G** calculations predicted that the 1,4-dihydro structure (tautomer **A**) is more stable than the 3,4-dihydro structure (tautomer **B**) by 23.7 kJ mol^{-1}. The AM1/PM3 semi-empirical calculations also predicted tautomer (**A**) to be more stable than (**B**), with calculated energy differences of 52.3 and 25.9 kJ mol^{-1} by AM1 and PM3, respectively. Tautomer (**A**) is also predicted by the present HF/6-31G** calculations to be more polar, with a dipole moment (μ) of 4.70 D compared to 3.34 D for tautomer (**B**). This is in accord with the enhanced liability of **2a** to form intermolecular hydrogen bonding in the solid state. The structure, shown in Fig. 2(b), was calculated by the AM1 method, under full geometry optimization, and was found to reproduce the crystal structure in Fig. 2(a). The AM1-calculated geometrical parameters of the intermolecular hydrogen bond (Table 1) are in satisfactory agreement with the observed X-ray results.

Conclusion

The structure of the 4-methyldihydro-1,3,4-benzotriazepin-5-ones remained uncertain, being regarded as the 3,4-dihydro derivatives in most reports,[1,2,18] but rarely referred to as the 1,4-dihydro forms.[19] Based on the clear 1,4-dihydro structure for the model compound (**2a**) as presented herein, it can be inferred that compounds (**2b**–**d**)[1] and (**3a**–**d**)[2] as well as all of the dihydro-1,3,4-benzotriazepin-5-ones, recently synthesized and reported as the 3, 4-dihydro tautomers,[18] should be correctly reassigned as the respective 1,4-dihydro-1*H*-1,3,4-benzotriazepin-5-ones. This 1,4-dihydro tautomer also prevails in the related 4-aryl-2-substituted analogs (*e.g.* **6**)[3] and, most probably, is retained for derivatives substituted at the benzo-fused ring.

Experimental

Isatoic anhydride, methylhydrazine and triethyl orthoformate were purchased from Acros. ^{1}H- and ^{13}C-NMR spectra were measured on a Bruker DPX-400 instrument with Me_4Si as internal reference. J values are given in Hz. MS spectral data were obtained using a Finnigan MAT TSQ-70 spectrometer at 70 eV; ion source temperature = 200 °C. The IR spectrum was recorded as a KBr disc on a Nicolet Impact-400 FTIR spectrophotometer. All *ab initio* quantum chemical calculations were carried out with the Hyperchem-5 program.[20]

1-(2-Aminobenzoyl)-1-methylhydrazine 1 (X = H)

This compound was prepared *via* interaction of isatoic anhydride with methylhydrazine according to a literature method.[1]

4-Methyl-1,4-dihydro-1*H*-1,3,4-benzotriazepin-5-one 2a

This compound was prepared by adopting the following reported[1] procedure: A solution of 1-(2-aminobenzoyl)-1-methylhydrazine (**1**) (0.83 g, 5 mmol) and triethyl orthoformate (0.74 g, 5 mmol) in ethanol (10 cm^3) was heated at reflux for 16 h. The resulting yellow solution was concentrated *in vacuo* and the residual yellow oil solidified upon cooling and triturating with ethanol. The solid product was recrystallized from ethanol in the form of yellow plates. Yield 0.28 g (32%), mp 161–162 °C (Lit.[1] 159–161 °C) (Found: C, 61.5; H, 5.1; N, 23.85. $C_9H_9N_3O$ requires C, 61.7; H, 5.2; N, 24.0%); (ν_{max}(KBr)/cm^{-1} 3479, 3415, 3280, 3131, 3037, 2930, 1681, 1615, 1581, 1485, 1366, 1325, 1256, 1203, 1129 and 1030; δ_H (400 MHz; $CDCl_3$; Me_4Si) 3.37 (3H, s, N(4)–Me), 6.52 (1H, br d, *J* 4.9, N(1)–H), 6.61 (1H, dd, *J* 8.0 and 0.9, C(9)–H), 6.92 (1H, d, *J* 4.9, C(2)–H), 6.98 (1H, ddd, *J* 8.0, 8.3 and 1.6, C(8)–H), 7.29 (1H, ddd, *J* 7.9, 8.3 and 0.9, C(7)–H) and 7.92 (1H, dd, *J* 7.9 and 1.6, C(6)–H); δ_C(100 MHz; $CDCl_3$; Me_4Si) 39.7 (N–CH_3), 117.5 (C-9), 122.4 (C-9a), 122.7 (C-8), 133.2 (C-6), 133.6 (C-7), 143.6 (C-2), 145.0 (C-5a) and 166.2 (C(5)=O); *m*/*z* (EI) 175.076980 ($C_9H_9N_3O$ requires 175.074562), 175 (M^+, 59), 160 (14), 146 (61), 132 (100), 120 (35), 104 (21) and 92 (23).

Collection of X-ray diffraction data and structure analysis of 2a

Yellow plate crystals were grown by allowing a clear solution of **2a** in hot ethanol to evaporate slowly at room temperature such that its volume was reduced by about 20% over 2–3 days. Crystal data collection was made using a Siemens SMART CCD diffractometer [graphite monochromator] operating in the omega scan mode (0.3°). The data were reduced with the Siemens-Bruker program suite XSCANS,[21] and the structure was solved by direct methods using SHELXTL PLUS programs.[22] All non-hydrogen atoms were refined anisotropically by a full-matrix, least-squares procedure based on F^2 using all unique data. The hydrogen atoms were located from the difference Fourier electron density synthesis and were then refined isotropically using a 'riding model'.

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