Structure Investigation of Bridgehead Aziridine: Synthesis, Theoretical, and Crystallographic Study of 2,4,6-Triphenyl-1,3-diazabicyclo[3.1.0]hex-3-ene

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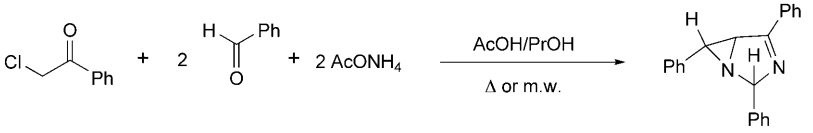
A one-pot three-component procedure to efficiently create the 1,3-diazabicyclo[3.1.0]hex-3-ene system is reported. The molecular structure of 2,4,6-triphenyl-1,3-diazabicyclo[3.1.0]hex-3-ene (**3**) was studied by X-ray diffraction and compared to *ab initio* and density-functional-theory (DFT) calculations restricted to the core moiety. Geometry optimizations for structural isomers and tautomeric forms of this aziridine fragment, taken as simplified models, were carried out at high calculation levels. Moreover, the same methods were utilized to evaluate the proton affinity of two crucial aziridine tautomers.

Introduction. – Functionalized bridgehead aziridines are an important class of compounds because of their occurrence in nature as well as their pharmacological activities [1–9]. Consequently, there is a rising interest in setting up effective synthetic methodologies and also in studying structural and electronic properties of these derivatives. In the present paper, we report a straightforward procedure for the diastereoselective synthesis of the 1,3-diazabicyclo[3.1.0]hex-3-ene system [10]. This is based on a one-pot multi-component mechanism [11] involving α-halogeno ketones such as **1** and aldehydes such as **2** in the presence of $AcOH/AcONH_4$ [12] (*Scheme*). We carried out a study of the structural characteristics of the new derivative 2,4,6-triphenyl-1,3-diazabicyclo[3.1.0]hex-3-ene (**3**) by using the X-ray diffraction technique. The structural data of **3** were compared with a series of molecular geometries of all diastereoisomers of **3** which were optimized by using *ab initio* and density-functional-theory (DFT) calculations carried out either with compound **3** or with its tautomer 2,4,6-triphenyl-1,3-diazabicyclo[3.1.0]hex-2-ene (**3T**). These calculations were with the intermediate level of basis set [6-311 + G(2d,p) and 6-31 + G(d,p)] and gave results in good agreement with the experimental geometry obtained by the diffraction data. The B3LYP hybrid method appears to be very suitable to the best-fitting of the geometrical parameters obtained by diffraction data.

We also performed several *ab initio* and DFT calculations in the gas phase of simplified models related to the core molecular skeleton of **3** and thoroughly discussed the relative stability of all 22 possible isomers and tautomers. We found a wide range (49

Scheme. *Synthesis of Compound* **3** *in its* 'exo' *form*



1 **2** **3**
'*exo*' form

kcal/mol) for their relative thermodynamic energies with respect to the isomer **R5** which was assessed to be the most stable one at any level of calculation.

One of the most important chemical processes is the protonation reaction. It does not only play an important role in general chemistry but is also of highest physiological relevance. Therefore, a secure computational prediction of proton affinities (*PA*) is of utmost importance. Since many of the pharmacologically active compounds are of such a large size that treatment on a reasonable *ab initio* level is still excluded, we limited these studies to simplified models. Thus, the proton affinity of both N-atoms *PA*(N(1)) and *PA*(N(4)) of the tautomers **R0** and **R0T** was determined by a wide variety of computational methods which allowed us to evaluate the relative importance of adding extra diffuse and polarization functions for the *PA* calculations; zero-point corrections was also applied at the HF/6-31 + G(d,p) level.

Experimental. – *Synthesis.* In a typical experiment, phenacyl chloride (1) and benzaldehyde (2) were treated with an excess of AcOH/$AcONH_4$ in EtOH for 1 h under reflux. After workup, 3 was isolated in 90% yield.

Only the formation of the '*exo*' form **3** was observed in contrast to previous synthetic procedures which led to diastereoisomer mixtures [13–15]. Thus, our reaction is practically simple, starting from inexpensive and easily available products, and diastereoselective (*Scheme*).

X-Ray Crystallographic Study of **3**. A summary of crystal and intensity data as well as refinement details is presented in *Table 1*. Crystallographic data were collected, at r.t., on a *Siemens-P4* diffractometer, by using the MoK_α radiation. Cell constants were determined by using 70 reflections. Intensity data were corrected for *Lorentz* and polarization effects. ψ-Scan absorption correction was applied [16]. The structure was solved by using the package SIR-97 [17] and subsequently refined on the F^2 values by the full-matrix least-squares programs SHELXL-97 [18]. Non-H-atoms were refined anisotropically. H-Atoms were located from *Fourier* difference maps and then fixed in idealized positions with an isotropic value determined by the 'riding-model' technique. Atom scattering factors and anomalous dispersion corrections for all the atoms were taken from the international crystallographic tables [19]. Geometrical calculations were performed by PARST97 software[20]. The molecular plots were produced by the ORTEP program [21]. The absolute configuration for structure **3** is unknown since the scarce anomalous scattering did not allow an exact *Flack* parameter [22] determination.

Ab initio *and DFT Calculations.* The experimental structure model of **3** (*Fig. 2*) was used as input for the GAUSSIAN 98 [23] program. The diastereoisomers of **3** as well as those of the tautomer **3T** were made up by GaussView, therefore they were optimized by the HF/6-31 + G(d,p), B3LYP/6-31 + G(d, p), and B3LYP/6-311 + G(2d,p) functionals. All the optimized geometries were confirmed to be stationary points by the absence of imaginary frequencies in the computed IR spectra. Frequency calculations were carried out at the HF/6-31 + G(d,p) level to characterize stationary points and to estimate the zero-point-energy corrections in computing the proton affinity (*PA*) of **R0** and **R0T** and the relative-energy order of the simplified isomers.

Table 1. *Crystal Data and Structure Refinement for* **3**

Empirical formula	$C_{22}H_{18}N_2$	θ range for data collection	2.23–26.00°
M_r	310.38	Index ranges	$-1 \le h \le 11$, $-6 \le k \le 1$, $-20 \le l \le 20$
Temperature	298(2) K		
Wavelength	0.71073 Å	Reflections collected/unique	2550/2161 ($R_{int} = 0.0183$)
Crystal system	Monoclinic		
Space group	$P2_1$	Completeness to $\theta = 26°$	98.6%
Unit cell dimensions	$a = 9.1360(10)$ Å	Absorption correction	ψ scan
	$b = 5.4923(6)$ Å	Max. and min. transmission	0.993 and 0.945
	$c = 16.7284(18)$ Å		
	$\alpha = 90°$	Refinement method	full-matrix least-squares on F^2
	$\beta = 94.004(7)°$	Data, restraints, parameters	2161, 1, 219
	$\gamma = 90°$		
Volume	837.34(16) Å^3	Goodness-of-fit on F^2	1.059
Z	2	Final R indices ($I > 2\sigma(I)$)	$R_1 = 0.0405$, $wR_2 = 0.0814$
Calc. density	1.231 Mg/m^3	R indices (all data)	$R_1 = 0.0669$, $wR_2 = 0.0928$
Absorption coefficient	0.072 mm^{-1}	Extinction coefficient	0.023(4)
$F(000)$	328	Largest diff. peak and hole	0.110 and -0.113 e·Å^{-3}
Crystal size	$0.44 \times 0.38 \times 0.10$ mm^3		

Ab initio calculations of all 22 potential isomers shown in *Fig. 1*, taken as models for the core moiety of **3**, were carried out with the GAUSSIAN 98 package. Geometry optimization was reached by using B3LYP/6-311++G(2df,2p), HF/6-311++G(2df,2p), MP2(FU)/6-31+G(d,p), and HF/6-31+G(d,p). These same calculation levels were employed for the *PA* evaluation of the N(1) and N(4) atoms of the two tautomers **R0** and **R0T**. *PA*s at the HF/6-311++G(2df,2p) and MP2(FU)/6-311++G(2df,2p) levels were obtained by the *SPE* (single-point-energy) difference between protonated and unprotonated forms. *SPE*s were computed on the structures obtained by B3LYP/6-311++G(2df,2p) optimization.

Results and Discussion. – *X-Ray Crystal Structure of* 'exo'-*2,4,6-Triphenyl-1,3-diazabicyclo[3.1.0]hex-3-ene* (**3**). As expected, the bridgehead aziridine moiety of **3** exhibits a 'Tuareg'-saddle conformation with three Ph residues attached to C(6), C(5), and C(3)[1]) (*Fig. 2*). The orientation of the Ph group at C(6), as demonstrated by the dihedral angles about N(1)–C(6) and C(6)–C(7), is in an *anti–anti* conformation with respect to the fused rings, which, on their turn are considerably bent to each other, the angle between the mean planes being 73.9(2)°. Significant bond distances and angles of the aziridine moiety are: N(1)–C(6) 1.472(3) Å, N(1)–C(2) 1.483(3) Å, N(1)–C(5) 1.490(3) Å, C(2)–N(1)–C(6) 61.3(1)°, and N(1)–C(2)–C(6) 59.0(1)°, N(1)–C(6)–C(2) 59.7(1)°. These distances and angles are all comparable with the corresponding data reported for 2-(4-bromophenyl)-1,3-diazabicyclo[3.1.0]hexane [24] and parent aziridine compounds reported in the CSD [25]. The entire molecular geometry of **3** was optimized by *ab initio* and DFT methods. Structural parameters, obtained at the B3LYP level, employing the two basis sets 6-311+G(2d,p) and 6-31+G(d,p), are

[1]) Arbitrary numbering, see *Fig. 2*.

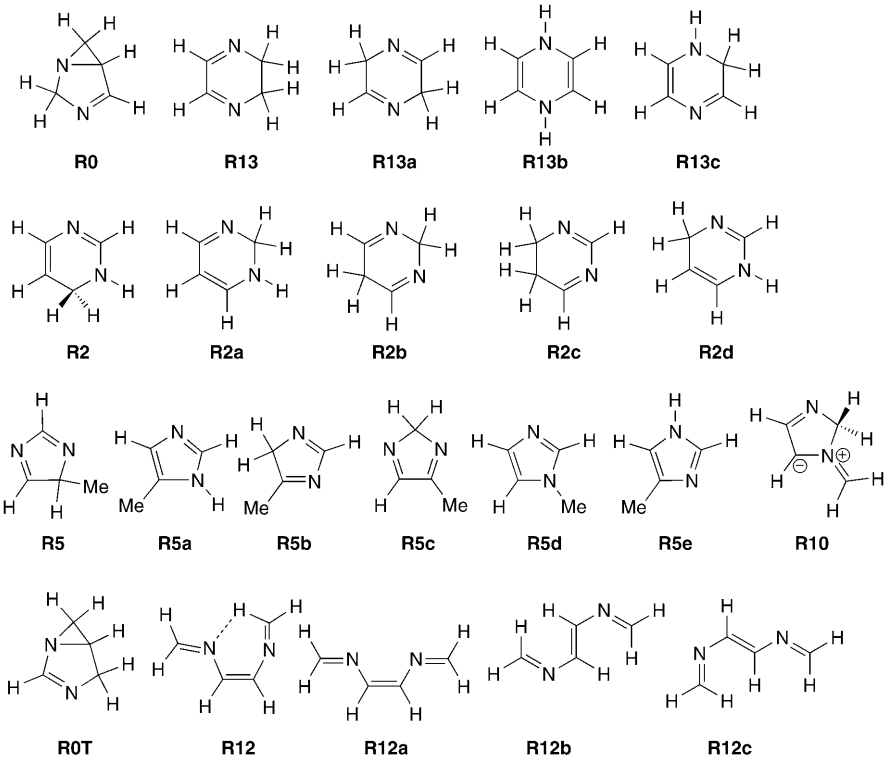


Fig. 1. *Structures of the studied 22 isomers of the core aziridine skeleton of* **3**

in good agreement with those obtained from diffraction data (*Table 2*). Both these levels reproduced exactly the X-ray data, whereas the HF/6-31 + G(d,p) optimization gave definitely different parameters. Therefore, once again the good agreement of B3LYP calculations with data obtained by X-ray diffraction is evidenced . The expected differences concern just the dihedral angles defining the orientation of the Ph rings with respect to the aziridine core. These are due to the particular solid-state interactions responsible of the molecular packing, while in the gas phase, the low rotational barriers drive molecules to the lower individual conformational energy. The interesting intramolecular H-bond involving a Ph C–H H-atom and N(1) (C(12)···N(1) 2.913(4) Å, C(12)–H(12)···N(1) 102.3°) has to be mentioned. The molecular packing of **3** (*Fig. 3*) is mainly determined by *Van der Waals* interactions and few weak H-bonds involving both the N(1) and N(4) atoms.

Ab initio *Calculations.* We optimized the geometry of compound **3** and also of its three diastereoisomers and all four diastereoisomers of the tautomer **3T** by *ab initio* and DFT methods employing the basis set 6-31 + G(d,p). The geometry of these eight diastereoisomers with their stereodescriptors for C(2), C(5), and C(6)[1]), their absolute and relative stability energies within each group of diastereoisomers and

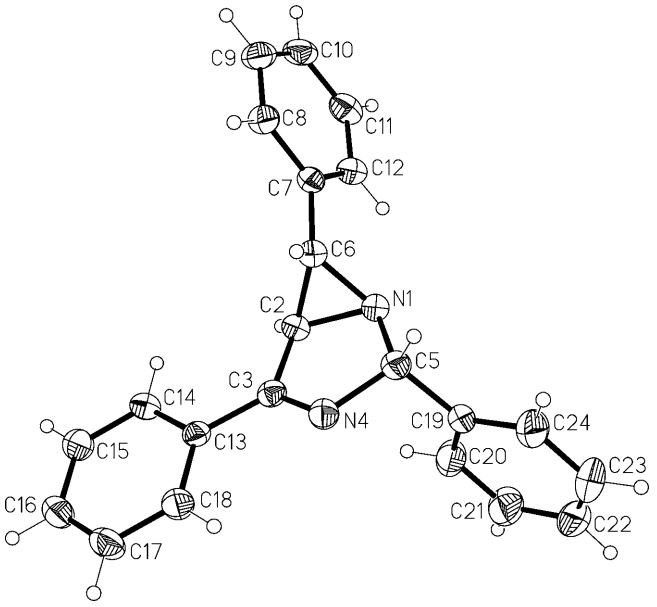


Fig. 2. *Crystal structure of* **3***, with 30% of anisotropic ellipsoid probability.* Arbitrary atom numbering

the relative stability energies between equivalent tautomers are reported in *Fig. 4*. In agreement with the stereoselectivity of the reaction [12], compound **3** (denoted by **3** (2*R*,5*S*,6*R*) in *Fig. 4*) appears to be the most stable of the diastereoisomers. The energy difference between the two most stable diastereoisomers of **3** is only 0.51 kcal/mol, the most stable is that obtained under thermodynamic control. The four diastereoisomeric tautomers **3T** are systematically *ca.* 2.5 kcal/mol more stable than the corresponding **3**, as evidenced in *Fig. 4*.

Among all cyclic and open isomers and tautomers of the aziridine core moiety of compound **3**, 22 structures were taken as models (*Fig. 1*) and their relative energies computed at various levels of calculation (*Table 3*). At every level of calculation, isomer **R5e** is the most stable and **R12** the least stable one. Between these two isomers, we calculated at the B3LYP/6-311++G(2df,2p) level an energy gap of 49.40 kcal/mol. At this same level, the energy gap between the isomers **R0** and **R0T** is just 2.20 kcal/mol. *Table 3* shows that the ranking of the relative isomer stability at different calculation levels is roughly the same. However, when electronic corrections are not considered (HF methods), isomer **R10**, characterized by charge separation, evidences anomalies becoming the least stable isomer.

Although the absolute energies in considering the zero-point corrections are obviously less than the corresponding energies computed at the HF/6-31+G(d,p) level, the relative ranking order remains unchanged.

The proton affinities of the N(1) and N(4) atoms[1]), *i.e.*, *PA*(N(1)) and *PA*(N4)) of the tautomers **R0** and **R0T** were calculated at several levels. The structure parameters

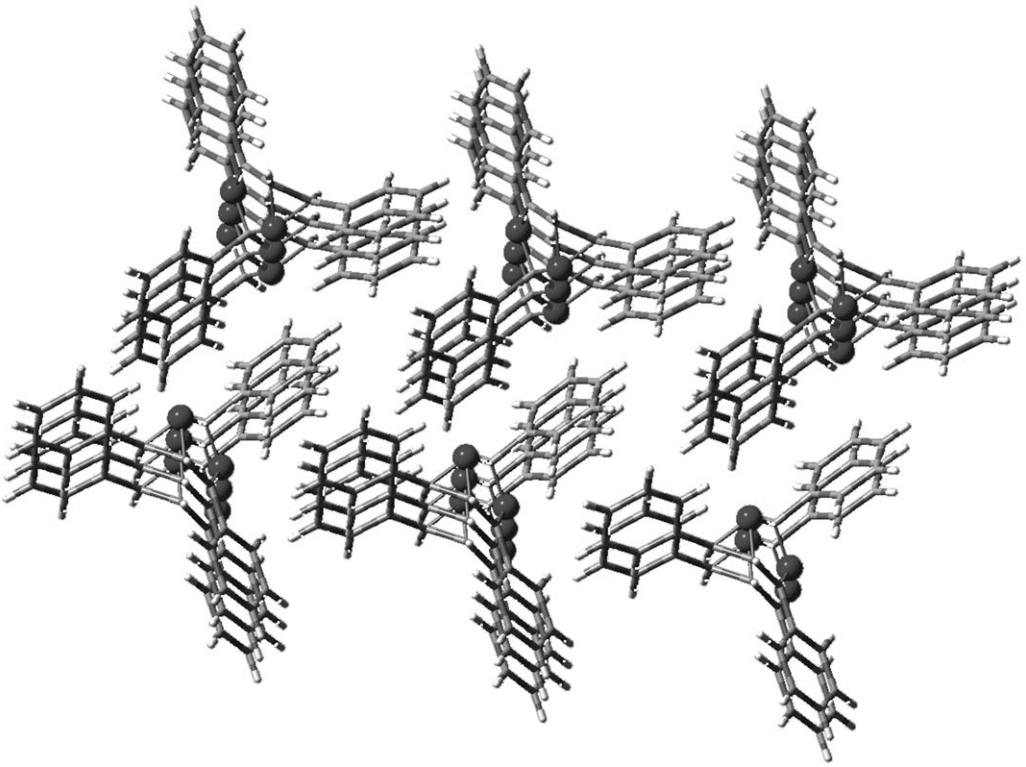


Fig. 3. *Crystal packing of* **3** *along the* b *crystallographic axis*

of **R0** and **R0T** together with those of the corresponding mono- and diprotonated forms were optimized and reported in *Table 4*. We assume that exploitation of the large basis set 6-311++G(2df,2p) combined with the hybrid density-functional theory B3LYP would be the more appropriate for both geometric and *PA*s evaluation. As already stated for the protonation of saturated alkylamines [26], whatever kind of N-protonation triggers a significant stretching of the close N–C bond distances and a shortening of the next C–C (or C–N) ones.

When N(4) of **R0T** is protonated, a major change affects the N(1)–C(5) bond distance, *i.e.*, N(1)–C(5) shrinks from 1.4288 to 1.3566 Å ($\Delta = 0.072$ Å). Other changes to be mentioned involve the bond angles N(4)–C(5)–N(1) of all protonated species. Thus the bond angle of 109.27° in **R0** and 119.17° in **R0T**, typical for sp^3 and sp^2 of C(5), respectively, decreases by 7.87 and 7.56°, respectively, on protonation at N(1) and N(4). The only structural parameters not really affected by protonation are the C(2)–C(3) and C(2)–C(6) bond lengths. Bond distances and angles of the tautomer **R0** computed at every B3LYP level are in good agreement with the corresponding values recorded at the B3LYP/6-31G(d) level for the similar l-azabicyclo[3.1.0]hexane [27]. In *Table 5*, the *PA*(N(1)) and *PA*(N(4)) of **R0** and **R0T** are reported. To get a bet-

Table 2. *Selected Structure Parameters* (bond lengths [Å] and angles [°]) *Obtained from the X-Ray Crystal Structure and from* ab initio *and DFT Gas-Phase Calculations of* **3**. Arbitrary atom numbering[1]).

	X-Ray	B3LYP/6-311 + G(2d,p)	B3LYP/6-31 + G(d,p)	HF/6-31 + G(d,p)
Bond lengths:				
N(1)–C(6)	1.472(3)	1.4642	1.4653	1.4413
N(1)–C(2)	1.483(3)	1.4676	1.4698	1.4436
N(1)–C(5)	1.490(3)	1.4875	1.4904	1.4686
N(4)–C(3)	1.282(3)	1.2793	1.2869	1.2594
N(4)–C(5)	1.481(3)	1.4971	1.4707	1.4585
C(13)–C(3)	1.479(3)	1.4717	1.4742	1.4802
C(6)–C(7)	1.486(3)	1.4883	1.4924	1.4958
C(6)–C(2)	1.506(3)	1.5053	1.5094	1.4880
C(3)–C(2)	1.490(3)	1.4971	1.5011	1.4994
C(5)–C(19)	1.510(3)	1.5231	1.5260	1.5226
Angles:				
C(6)–N(1)–C(2)	61.3(1)	61.79	61.90	62.10
C(6)–N(1)–C(5)	112.8(2)	113.80	113.93	114.84
C(2)–N(1)–C(5)	103.9(2)	104.54	104.63	105.66
C(3)–N(4)–C(5)	107.6(2)	108.96	108.75	109.41
N(1)–C(6)–C(7)	117.4(2)	118.50	118.40	118.42
N(1)–C(6)–C(2)	59.7(1)	59.22	59.20	59.03
C(7)–C(6)–C(2)	120.8(2)	122.39	122.46	122.50
N(4)–C(3)–C(13)	123.1(2)	123.55	123.54	123.81
N(4)–C(3)–C(2)	114.0(2)	112.78	112.80	112.58
C(13)–C(3)–C(2)	122.9(2)	123.67	123.65	123.61
N(1)–C(2)–C(3)	105.2(2)	105.41	105.37	104.71
N(1)–C(2)–C(6)	59.0(1)	59.00	58.91	58.87
C(3)–C(2)–C(6)	112.6(2)	113.93	113.94	113.54
N(4)–C(5)–N(1)	108.8(2)	108.21	108.34	107.54
N(4)–C(5)–C(19)	109.7(2)	111.28	111.21	111.42
N(1)–C(5)–C(19)	111.1(2)	112.11	112.02	112.21
C(18)–C(13)–C(3)–N(4)	– 6.6(4)	– 10.48	– 10.34	– 12.95

ter insight into the protonation effect, we used the *ab initio Hartree-Fock* (HF), second-order *Möller-Plesset* (MP2), and density-functional theory (DFT) methods with medium and large basis sets. Zero-point-energy corrections at the HF/6-31 + G(d,p) level exhibits an overestimated value of *ca.* 3.8% in *PA* with respect to the corresponding uncorrected one.

The **R0** model shows a similar *PA* for both N atoms at every calculation level: at the highest calculation level *PA*(N(1)) is 225.65 and *PA*(N(4)) 225.47 kcal/mol. On the other hand, a relevant *PA* difference between the N(1) and N(4) positions is recorded for the **R0T** tautomer: at the same highest calculation level this difference is 8.97 kcal/mol, the *PA*(N(4)) (229.10 kcal/mol) always being the highest one. In these tautomers, the *PA*(N(1)) are mutually comparable and anyway higher than those calculated for 2-ethenylaziridine and 1-ethenylaziridine [28] (216.56 and 215.96 kcal/mol, resp.). For the

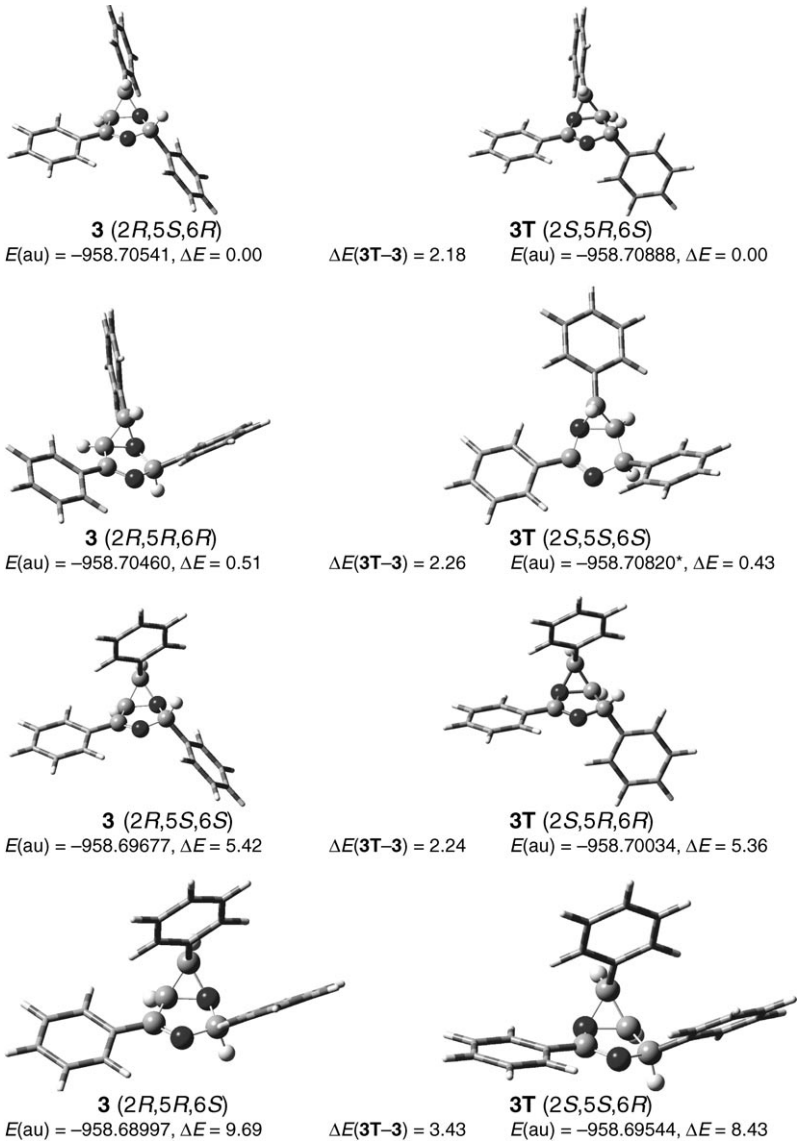


Fig. 4. *Optimized geometries of the diastereoisomers of* **3** *and* **3T**, *and absolute and relative stability energies computed at the B3LYP/6-31+G(d,p) level.* au = arbitrary unit. ΔE in kcal/mol. Arbitrary atom numbering[1]).

isomer **R0T**, structural changes undergone by protonation are consistent with an increased availability of electron density around N(4), which explains why *PA*(N(4)) is always higher than *PA*(N(1)). In **R0**, the sp^3-hybridized C(5) atom hampers the par-

Table 3. *Absolute and Relative Energy of Several Isomers Reported in* Fig. 1. a.u. = arbitrary unit. ΔE in kcal/mol.

	E(a.u.)[a])	ΔE	E(a.u.)[b])	ΔE	E(a.u.)[c])	ΔE	E(a.u.)[d])	ΔE	E(a.u.)[e])	ΔE
R5e	−265.63095	0.00	−263.94333	0.00	−264.78736	0.00	−263.87667	0.00	−263.77063	0.00
R5a	−265.63010	0.53	−263.94256	0.48	−264.78645	0.57	−263.87599	0.43	−263.76981	0.51
R5d	−265.61933	7.29	−263.93176	7.26	−264.77645	6.85	−263.86495	7.35	−263.75864	7.52
R5c	−265.60566	15.87	−263.92353	12.42	−264.76293	15.33	−263.85754	12.00	−263.75223	11.55
R5b	−265.60527	16.11	−263.92533	11.29	−264.76093	16.58	−263.85880	11.21	−263.75410	10.37
R2d	−265.59862	20.29	−263.91499	17.78	−264.74913	23.99	−263.84722	18.48	−263.74005	19.19
R2	−265.59802	20.66	−263.91553	17.44	−264.74690	25.39	−263.84789	18.06	−263.74074	18.76
R5	−265.59783	20.78	−263.91900	15.27	−264.75672	19.23	−263.85247	15.19	−263.74677	14.97
R2a	−265.59348	23.51	−263.90658	23.10	−264.74492	26.63	−263.84042	22.75	−263.73328	23.44
R2c	−265.59036	25.47	−263.91078	20.42	−264.74512	26.51	−263.84444	20.22	−263.73752	20.78
R2b	−265.58939	26.08	−263.91081	20.41	−264.74255	28.12	−263.84348	20.83	−263.73680	21.23
R13a	−265.58563	28.44	−263.90728	22.62	−264.73632	32.03	−263.83952	23.31	−263.73303	23.59
R13c	−265.58305	30.06	−263.89703	29.05	−264.72854	36.97	−263.82954	29.57	−263.72401	29.25
R13	−265.57842	32.96	−263.89665	29.29	−264.72964	36.22	−263.83033	29.08	−263.72354	29.55
R13b	−265.57130	37.43	−263.88456	36.88	−264.70998	48.55	−263.81395	39.36	−263.70978	38.18
R12b	−265.56346	42.35	−263.87806	40.96	−264.70486	51.77	−263.81020	41.71	−263.70777	39.44
R0T	−265.56008	44.47	−263.87836	40.77	−264.72131	41.45	−263.81226	40.42	−263.70491	41.24
R12a	−265.55735	46.18	−263.87255	44.41	−264.69850	55.76	−263.80367	45.81	−263.70121	43.56
R0	−265.55658	46.67	−263.87484	42.98	−264.71796	43.55	−263.80891	42.52	−263.70150	43.38
R12c	−265.55244	49.26	−263.86704	47.87	−264.69418	58.47	−263.79868	48.94	−263.69653	46.50
R10	−265.55243	49.27	−263.84396	62.35	−264.70062	54.43	−263.77655	62.83	−263.67202	61.88
R12	−265.55223	49.40	−263.86698	47.91	−264.69454	58.24	−263.79957	48.38	−263.69691	46.26

[a]) B3LYP/6-311++G(2df,2p). [b]) HF/6-311++G(2df,2p). [c]) MP2(FU)/6-31+G(d,p). [d]) HF/6-31+G(d,p). [e]) HF/6-31+G(d,p), zero-point-energy corrected.

tial delocalization of the N(1) nonbonding (n) orbital, thus resulting in a high s-character over the N(1)–C(5)–N(4) moiety.

Conclusions. – We reported the structure characterization of 2,4,6-triphenyl-1,3-diazabicyclo[3.1.0]hex-3-ene (**3**), which we chose as a model for the generation of focused chemical libraries. Compound **3** is part of a class scarcely represented in the crystallographic database (CSD). Therefore, the stabilities of related isomers and the *PA*s of the aziridine models **R0** and **R0T** were evaluated with the hybrid B3LYP calculation method which seems always the best performing one, especially with extended basis sets. Beyond the confirmation of the structure considerations already drawn for the protonation of alkylamines, we established in this paper the *PA* differences due to allowed or hampered conjugation between two N-atoms in similar tautomeric systems like **R0** and **R0T**.

X-Ray measurements were performed at CISDRX (Centro Interdipartimentale di Servizi per la Diffrattometria a Raggi-X), University of Messina, which is kindly acknowledged. CCDC-258949 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the *Cambridge Crystallographic Data Centre via* http://www.ccdc.cam.ac.uk/data_request/cif.

Table 4. *Results of the B3LYP/6-311++G(2df,2p) Geometry Optimization of Free and Protonated Tautomers* **R0** *and* **RT**. Arbitrary atom numbering[1]).

	R0	Protonated **R0**			**R0T**	Protonated **ROT**		
		H–N(1)$^+$	H–N(4)$^+$	H–N(1)$^+$/ H–N(4)$^+$		H–N(1)$^+$	H–N(4)$^+$	H–N(1)$^+$/ H–N(4)$^+$
Bond Lengths [A]:								
N(1)–C(2)	1.4784	1.4989	1.4888	1.5141	1.4868	1.5095	1.4996	1.5501
N(1)–C(6)	1.4612	1.4891	1.4430	1.4963	1.4892	1.5059	1.5157	1.5616
N(1)–C(5)	1.4801	1.5281	1.4543	1.4898	1.4288	1.4877	1.3566	1.4125
N(1)–H	–	1.0146	–	1.0215	–	1.0164	–	1.0231
C(2)–C(6)	1.4897	1.4837	1.5139	1.4930	1.4770	1.4743	1.4739	1.4644
C(2)–C(3)	1.4905	1.5038	1.4516	1.4785	1.5257	1.5293	1.5245	1.5255
C(3)–N(4)	1.2698	1.2649	1.2873	1.2798	1.4761	1.4648	1.4851	1.4886
N(4)–C(5)	1.4687	1.4325	1.5000	1.4775	1.2670	1.2466	1.2964	1.2734
N(4)–H	–	–	1.0149	1.0233	–	–	1.0131	1.0236
Bond angles [°]:								
C(2)–N(1)–C(6)	60.89	59.55	62.15	59.46	59.51	58.54	58.52	56.15
C(2)–C(6)–N(1)	60.12	60.55	60.41	60.86	60.16	60.85	60.20	61.53
C(5)–N(1)–C(6)	113.67	118.82	115.46	120.18	110.59	115.85	114.25	116.89
C(3)–C(2)–N(1)	104.54	101.70	105.84	102.65	106.19	103.65	107.05	104.01
C(6)–C(2)–C(3)	113.31	115.61	112.00	115.79	118.43	118.43	121.09	119.02
C(2)–C(3)–N(4)	114.51	114.75	110.94	111.46	104.96	106.16	100.49	102.27
C(3)–N(4)–C(5)	107.54	111.57	111.80	115.16	107.31	111.44	111.95	114.95
N(4)–C(5)–N(1)	109.27	105.62	104.09	101.40	119.17	114.04	115.06	111.61

Table 5. *Absolute Energy* [a.u.] *and Proton Affinity* [kcal/mol] *of the N Atoms of the Tautomers* **R0** *and* **R0T**

	E [a.u.]	H–N(1)$^+$	H–N(4)$^+$	*PA*(N(1))	*PA*(N(4))
R0					
B3LYP/6-311++G(2df,2p)	−265.55658	−265.91618	−265.91589	225.65	225.47
//MP2/6-311++G(2df,2p)	−265.04237	−265.39288	−265.39446	219.95	220.94
//HF/6-311++G(2df,2p)	−263.87484	−264.24160	−264.24226	230.14	230.56
B3LYP/6-31+G(d,p)	−265.48741	−265.84447	−265.85544	224.06	230.94
MP2(FU)/6-31+G(d,p)	−264.71796	−265.07308	−265.07189	222.84	222.09
HF/6-31+G(d,p)	−263.80891	−264.17544	−264.17583	230.00	230.24
HF/6-31+G(d,p)ZPEc	−263.70150	−264.05328	−264.05413	220.74	221.28
R0T					
B3LYP/6-311++G(2df,2p)	−265.56008	−265.91088	−265.92518	220.13	229.10
//MP2/6-311++G(2df,2p)	−265.04573	−265.39043	−265.40244	216.30	223.84
//HF/6-311++G(2df,2p)	−263.87836	−264.23829	−264.25299	225.86	235.08
B3LYP/6-31+G(d,p)	−265.49102	−265.84208	−265.85544	220.29	228.68
MP2(FU)/6-31+G(d,p)	−264.72130	−265.07038	−265.08029	219.68	225.27
HF/6-31+G(d,p)	−263.81226	−264.17210	−264.18610	225.80	234.59
HF/6-31+G(d,p)ZPEc	−263.70491	−264.05055	−264.06443	216.89	225.60

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