Computational Assessment of the Electronic Structure of 1-Azacyclohexa-2,3,5-triene ($3\delta^2$-1*H*-Pyridine) and Its Benzo Derivative ($3\delta^2$-1*H*-Quinoline) as well as Generation and Interception of 1-Methyl-$3\delta^2$-1*H*-quinoline**

Jan C. Schöneboom, Stefan Groetsch, Manfred Christl,* and Bernd Engels*[a]

Dedicated to Professor Wolfgang Malisch on the occasion of his 60th birthday

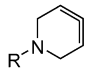
Abstract: Treatment of a solution of 3-bromo-1-methyl-1,2-dihydroquinoline (**9**) and [18]crown-6 in furan or styrene with KO*t*Bu followed by hydrolysis afforded a mixture of 1-methyl-1,2-dihydroquinoline (**10**) and 1-methyl-2-quinolone (**11**). If the reaction was performed in [D$_8$]THF and the mixture was immediately analysed by NMR spectroscopy, 2-*tert*-butoxy-1-methyl-1,2-dihydroquinoline (**17**) was shown to be the precursor of **10** and **11**. The structure of **17** is evidence for the title cycloallene **7**, which arises from **9** by β elimination of hydrogen bromide and is trapped by KO*t*Bu to give **17** so fast that cycloadditions of **7** with furan or styrene cannot compete. Since this reactivity is unusual compared to the large majority of the known six-membered cyclic allenes, we performed quantum-chemical calculations on **8**, which is the parent compound of **7**, and the corresponding isopyridine **6** to assess the electronic nature of these species. The ground state of **6** was no longer an allene (**6a**) but the zwitterion **6b**. In the case of **8**, the allene structure **8a** is more stable than the zwitterionic form **8b** by only $\approx$1 kcal mol^{-1}. These results suggest a high reactivity of **6** and **8** towards nucleophiles and explains the behaviour of **7**. In addition to the ground states, the low-lying excited states of **6** and **8** were considered, which are represented by the diradicals **6c** and **8c** and, as singlets, lie above **6b** and **8a** by 19.1 – 24.8 and 14.4 – 17.7 kcal mol^{-1}, respectively.

Keywords: allenes · eliminations · quantum-chemical calculations · strained molecules · zwitterions

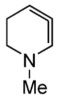
Introduction

Experimental studies of six-membered cyclic allenes[1, 2] that contain a nitrogen atom have been performed for the symmetrical isodihydropyridines **1**,[3] the unsymmetrical isodihydropyridine **2**, its borane complex **3**,[4] the isopyridines **5** and **6**[5] and the cephalosporine derivatives **4**.[6]

Akin to cyclohexa-1,2-diene,[1] the 1-azacyclohexa-3,4-dienes **1** can be trapped by activated olefins.[3] In contrast, attempts to generate 1-methyl-1-azacyclohexa-2,3-diene (**2**) did not furnish products that proved the existence of **2**. However, the intermediacy of its borane complex **3** has been secured by the isolation of cycloadducts of **3** with furan and styrene.[4] The liberation of the cephalosporins **4** proceeds under astoundingly mild conditions and their interception, even with nonactivated olefins and acetylenes, takes place with high efficiency.[6]



1 (R = aryl, alkyl)



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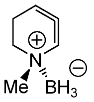

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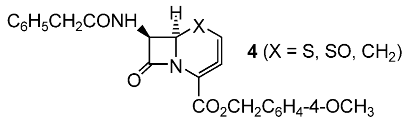

4 (X = S, SO, CH$_2$)

Isopyridines of types **5** and **6** have been postulated by Shevlin et al.[5] as intermediates in reaction sequences that start with the addition of carbon atoms onto the respective pyrroles. The structure of the products as well as preliminary quantum-chemical calculations support the dipolar nature of **5** and **6**, namely, the zwitterions **5b** and **6b** are more likely to be the ground state than the allenes **5a** and **6a**.[5] More recently, Yavari et al.[7] have theoretically studied the zwitterionic form **6b** and the triplet diradical ^{3}**6c**, but did not

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[a] Prof. Dr. M. Christl, Prof. Dr. B. Engels,
Dipl.-Chem. J. C. Schöneboom, Dr. S. Groetsch
Institut für Organische Chemie, Universität Würzburg
Am Hubland, 97074 Würzburg (Germany)
Fax: (+49) 931-8884606
E-mail: christl@chemie.uni-wuerzburg.de
bernd@chemie.uni-wuerzburg.de

[**] Cycloallenes; Part 18. For Part 17 see: ref. [9].

Supporting information for this article is available on the WWW under http://www.chemeurj.org or from the author: Cartesian coordinates for the structures **6a–c** and **8a–c**, obtained by various theoretical approaches, are provided.

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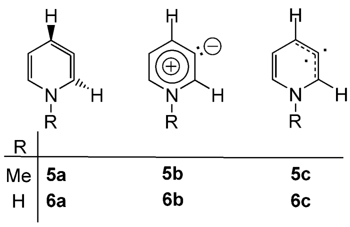
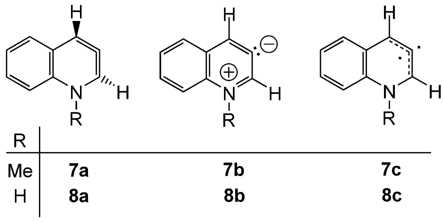




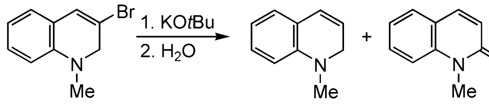
consider more closely the allene form **6a** and the singlet diradical ^{1}**6c**. The possible intervention of derivatives of $3\delta^2$-1*H*-quinoline (**8**) in the thermolysis of 1-(2-amino-5-chlorophenyl)propargyl carboxylates has recently been advanced by Frey et al.[8]

Herein, we report the generation of 1-methyl-$3\delta^2$-1*H*-quinoline (**7**). Since the consecutive products of **7** were surprising, we carried out a computational study of the parent heterocycle **8**. To assess the effect of the benzo group of **8**, we included the isopyridine **6** in our calculations, the principal goal of which was to answer the question as to the ground state of these species, whether they are allenes (**6a**, **8a**) or zwitterions (**6b**, **8b**). We have recently shown that, to understand the nature of systems with a strained allene moiety, the calculation of the respective global energy minimum alone is not sufficient and the electronic structures of the ground and the first excited state for the planar geometry have to be taken into account as well.[9] Thus, a second objective was the determination of the energetic distance of **6a** and **8a** as well **6b** and **8b** from the singlet diradical states **6c** and **8c**, respectively.

Regarding experiment and theory, the present work expands our previous one, in which we investigated the oxa and carba analogues of **5**–**8** (O or CH_2 instead of NR, see compounds **14** and **18** in Figure 4).[9] In this context, the present work also aims at a detailed understanding of the factors that govern the electronic and geometric structures in **6** and **8** as compared to **14** and **18**. Based on our model, we are able to present a complete picture of the differences that arise from benzannulation and heteroatom substitution.

Results and Discussion

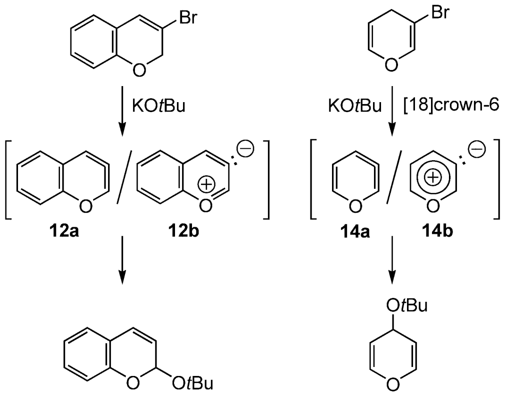
Generation and interception of 1-methyl-$3\delta^2$-1*H*-quinoline (7): On treatment of 3-bromo-2*H*-chromene with potassium *tert*-butoxide (KO*t*Bu) in the presence of activated olefins, we recently obtained cycloadducts of $3\delta^2$-chromene (2,3-didehydro-2*H*-1-benzopyran, **12**),[10] the oxa analogue of **7** and **8**. This encouraged us to test whether **7** can be generated by the same procedure, particularly because 3-bromo-1-methyl-1,2-dihydroquinoline (**9**), the starting material, is a known compound.[11, 12] However, the reaction of **9**, dissolved in furan or styrene, with KO*t*Bu in the presence of [18]crown-6 did not furnish any product that arose by participation of furan or styrene. After the usual workup, the result was a mixture of 1-methyl-1,2-dihydroquinoline (**10**) and 1-methyl-2-quinolone (**11**) as the major components in a 1:2 ratio (Scheme 1). A similar mixture was formed when the reaction was carried out in THF as the solvent in the absence of furan and styrene. In this case, **9** was consumed at an appreciable rate, even in the absence of [18]crown-6. To characterise **10** and **11**, we prepared these compounds by known routes[13, 14] and completely assigned their ^{1}H and ^{13}C NMR spectra.



9 **10** **11**

Scheme 1.

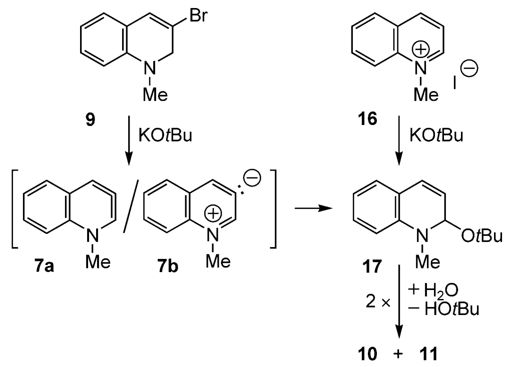
When **12** was generated in the absence of activated olefins, the acetal **13** resulted with high efficiency. Obviously, *tert*-butoxide added to the allene terminus of **12** that carries the oxygen atom (Scheme 2).[10] The liberation of $3\delta^2$-pyran (**14**), the monocycle related to **12**, from 3-bromo-4*H*-pyran by KO*t*Bu yielded 4-*tert*-butoxy-4*H*-pyran (**15**) as the only identified product, regardless of whether activated olefins were present or not (Scheme 2).[9] Again, the nucleophile attacked an allene terminus.



13 **15**

Scheme 2.

These findings made us assume that the desired cyclic allene **7** had formed from **9** by β elimination of hydrogen bromide and was rapidly trapped by KO*t*Bu to give the *N*,*O*-acetal **17** eventually (Scheme 3). In that case, furan and styrene would have been inferior compared to the nucleophile in competition for **7**. Grignon-Dubois and Meola[14] have mentioned **17**, but did not characterise it. They gave a plausible postulation of the formation of **17** on treatment of *N*-methylquinolinium iodide (**16**) with KO*t*Bu and took advantage of its sensitivity towards molecular oxygen to prepare the quinolone **11**. We repeated this experiment with THF as the solvent, filtered the complete mixture through



Scheme 3.

basic Al_2O_3 (activity IV) and obtained **10** and **11** in a 1.0:1.3 ratio. When we performed the reaction in $[D_6]$DMSO and immediately thereafter recorded the ^{1}H and ^{13}C NMR spectra of the mixture, they each exhibited one set of signals, which match perfectly with the structure of **17**. Moreover, the ^{1}H NMR spectrum of the mixture measured immediately after combining **9** and KO*t*Bu in $[D_8]$THF exhibited only one set of signals, which we also ascribe to **17**. In view of the different solvents in which the ^{1}H NMR spectra have been determined, the chemical shifts of the products formed from **9** ($[D_8]$THF) and **16** ($[D_6]$DMSO) are in excellent agreement, and hence the products are the same, namely **17**.

The transformation of **17** to **10** and **11** apparently occurs when a hydrolytic workup is performed. Under these conditions, the *tert*-butoxy group is probably replaced by a hydroxy group and the resulting pseudo-base undergoes the redox process to afford **10** and **11**. Disproportionations of that kind are well-known.[15] The fact that the above product mixtures contained invariably more **11** than **10** is readily explained by the susceptibility of the latter to autoxidation, which is the key of the efficient preparation of 2-quinolones and related compounds from quinolinium salts and KO*t*Bu and exposure of the resulting *N*,*O*-acetals to air.[14]

Thus, the formation of **10** and **11** on treatment of **9** with KO*t*Bu clearly supports the intermediacy of the cyclic allene **7**. However, cycloadditions of **7** onto activated olefins do not proceed under these conditions since KO*t*Bu traps **7** much more efficiently. The high sensitivity toward this nucleophile as well as the site of attack are evidence for a ground state of **7** that is strongly polar if not entirely zwitterionic (**7b**) in nature. Six-membered cyclic allenes that definitely or presumably have a chiral ground state are attacked by nucleophiles at the central carbon atom of the allene moiety: cyclohexa-1,2-diene, 1,1-dimethyl-$3\delta^2$-1*H*-naphthalene[1] (**1**, $R = C_6H_5$),[3a] 1-oxacyclohexa-3,4-diene[16] and $3\delta^2$-1*H*-naphthalene.[17] However, if the ground state is zwitterionic, as calculations demonstrate for **14** in solution, that is **14b**,[9] or if the zwitterionic state is only a few kcal mol^{-1} less stable than the chiral state, as in the case of **12** (energy difference of 3.2 kcal mol^{-1} in solution),[9] KO*t*Bu interacts with an allene terminus exclusively (Scheme 2). This is readily explained since these steps can be considered as an addition to a quasi-carbonyl group (**12b**) and as conjugated addition to an α,β-unsaturated quasi-carbonyl compound (**14b**). Such a situation is already approximated in 1-oxacyclohexa-2,3-diene, the dihydro derivative of **14**, which clearly should have a chiral ground state, but is attacked by KO*t*Bu[18] and enolates[19] either at the central or a terminal allene atom. By analogy, these findings support the ground state of **7** to be rather polar, and this is indeed corroborated by the calculations presented below.

We recently reported that cycloadducts of **2** with activated olefins could not be obtained. However, if the lone pair of the nitrogen atom of **2** was withdrawn from service, as in the borane complex **3**, cycloadditions became feasible.[4] This recipe could not be applied to **7**, since it is too weak a base to bind borane.

Computational details: For a reliable description of systems which possess diradical character, a multireference treatment is essential in most cases. Since the planar diradical species appeared to be important for the understanding of the chemistry of cyclic allenes,[9] MR-CI and CASPT2 single-point energy calculations were employed in the present work. The geometric parameters of the stationary points were optimised with analytical gradients of the complete active space SCF (CASSCF) method and of the density functional theory (DFT). To obtain the minima of a given multiplicity, we performed optimisations without symmetry constraints. The geometric parameters of the planar singlet species were optimised with C_s symmetry constraints.

For the geometry optimisations that employed DFT methods, we used the B88 or B3 exchange expressions[20, 21, 22] in combination with the correlation functionals by Lee, Yang and Parr (LYP).[23] The unrestricted ansatz was used for all DFT computations. The singlet diradical species were calculated and their structures optimised with broken-spin symmetry determinants. Although the DFT methodology employed in the present work is a single reference method, it has proven to be capable of describing the geometries of diradical systems similar to **6** and **8** in our previous work.[9] Nevertheless, a careful validation of the used functional and basis set against reliable multireference treatments is required from case to case. In this work, MR-CI and CASPT2 results from **6** were used to check the validity of the present DFT approach. The nature of the various stationary points was analysed by calculation of the DFT harmonic frequencies. The vibrational analysis at the DFT level was also utilised to determine the thermal corrections necessary for obtaining the enthalpy values. All DFT calculations were performed with the Gaussian 98 program package.[24]

A comparison of different choices for the active space in the CAS treatment showed that an adequate description in C_s symmetry (compounds **6b** and **6c**) includes the three occupied a'' (π) orbitals with the corresponding number of virtual orbitals and the nonbonding a' (σ) orbital mainly located at the central allene carbon, thus defining an [8,7]-CASSCF method. The active space for the C_1-symmetrical species **6a** was chosen as the three highest occupied and three lowest unoccupied molecular orbitals (MOs) of the a irreducible representation, leading to a [6,6] active space. The CASPT2 single-point energy calculations utilised [6,6]-CASSCF wave functions as a reference. The CASSCF as well as the CASPT2 calculations were performed with the MOLCAS program package.[25]

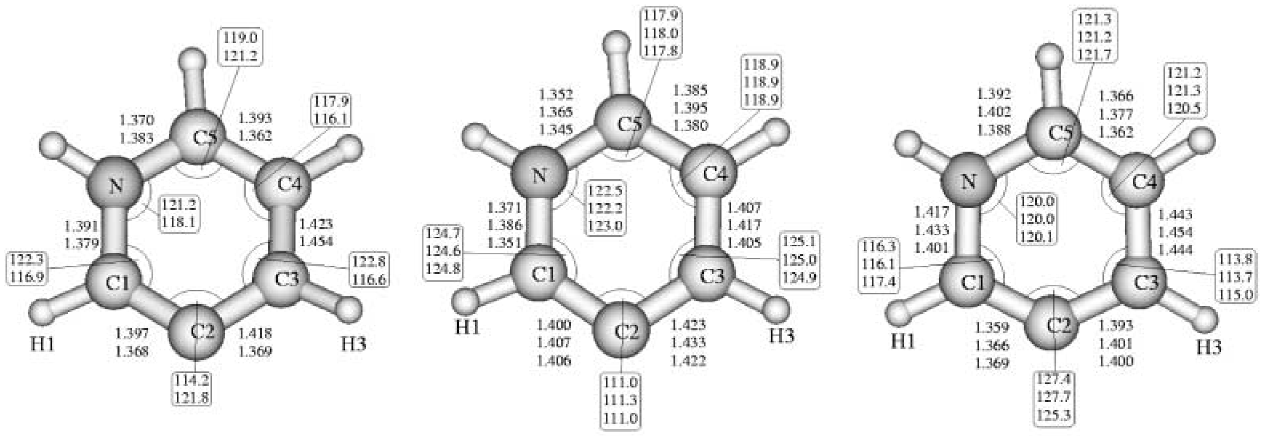
The MR-CI approach used in this study is based on an individually selecting multireference CISD algorithm[26] to reduce the dimension of the CI eigenvalue problem. The contribution of the configurational state functions neglected in the CI procedure was taken into account by the Buenker–Peyerimhoff extrapolation scheme.[27, 28] The influence of higher excitations was estimated by the normalised form of the usual Davidson correction.[29] In the following, these calculations are abbreviated as MR-CI + Q. They were performed with the DIESEL-CI program package[30] and utilised the orbitals obtained from a [6,6]-CASSCF calculation. Thermal corrections were obtained from DFT (UB3LYP/cc-pVDZ) frequency calculations.

For the CASPT2 and the MR-CI calculations, we employed the cc-pVDZ basis set of Dunning.[31] Geometry optimisations were performed with the cc-pVDZ or 6-31G(d) basis sets.

While a multireference approach is necessary for an accurate computation of the energetics, a qualitative description of the electronic situation can already be obtained on the basis of less sophisticated treatments. This can be seen from the orbitals resulting from the CASSCF and the DFT calculations, which do not differ significantly. This shows that the electron densities provided by the various treatments are qualitatively equal. Consequently, the natural resonance theory (NRT)[32] analysis based on the DFT result was employed to obtain qualitative insights into electron-density distributions.

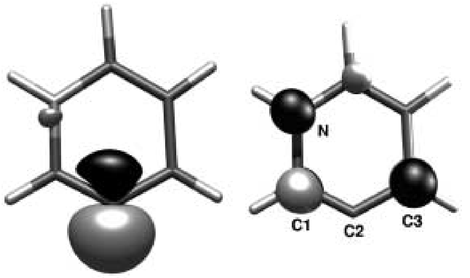
Calculations of 3δ^2-1*H*-pyridine (6): The optimised geometries of allene **6a**, the zwitterion **6b**, and the singlet diradical **^{1}6c** are depicted in Figure 1. The [6,6]-CASSCF calculation predicts an unsymmetrical species **6a** as global minimum. The average of its dihedral angles C1-C2-C3-H3 and C3-C2-C1-H1 (see Figure 1 for the numbering of atoms) is 159° and the angle at the central allene carbon atom is 122°, indicating a highly strained allenic structure. In contrast, DFT calculations result in a geometry much closer to the planar arrangement, which possesses no allene character. The deviations from planarity are very small in the case of BLYP computations (average of the above dihedral angles = 171°) and even negligible according to the B3LYP result. We assume that the deviation from planarity obtained with the BLYP functional is a symmetry-breaking effect, which is why this geometry was not considered any further. At the CASPT2 level, single-point calculations favour the planar structure over the allenic one by 1–2 kcal mol^{-1}. Since CASPT2 calculations represent a more sophisticated approach than the CASSCF method, the allenic structure can be ruled out as energy minimum of **6** in the ground state. On the basis of this finding, structure **6a** seems to be an artefact and only represents a minimum if dynamic correlation effects are neglected. Obviously, in the case of the ground state of **6**, which has a closed-shell single-determinant nature, the DFT methods perform better than CASSCF calculations, since they offer a more balanced description of dynamic and non-dynamic correlation effects. The results of the CASSCF and DFT calculations are in much better agreement for the species **6b** and **6c**, where the larger [8,7] active space could be used. In general, the geometries optimised with DFT methods gave lower absolute single-point energies at the CASPT2 level, and we will focus on these structures in the following.

Thus, in accordance with previous studies,[5, 7] we find the zwitterion **6b** to be the equilibrium structure of 3δ^2-1*H*-pyridine (**6**) in the ground state. The striking structural feature of **6b** is the small magnitude of the angle C1-C2-C3 (≈111°), which originates from the electronic repulsion of the lone pair in a σ orbital at C2 and the neighbouring C–C bonds. This "chemically" intuitive representation of the electronic structure is corroborated by the analysis of the frontier orbitals (Figure 2) and the strongly dominating configuration of the CI expansion (coefficient 0.967) (Table 1): the electronic state is of $^1A'$ symmetry, with the non-bonding σ orbital 18*a'* being the HOMO and three occupied *a''* orbitals constituting a positively charged aromatic π system. This shows that the p orbital of the nitrogen atom arranged perpendicularly to the molecular plane is integrated into the ring π system.



6a (C_1, ^1A)[a,b] **6b** (C_s, $^1A'$)[c] **^{1}6c** (C_s, $^1A''$)[c]

Figure 1. Optimised C–C and C–N bond lengths [Å] and bond angles [°] computed for the isopyridine **6**. From bottom to top, the values given were obtained by CASSCF/cc-pVDZ, BLYP/cc-pVDZ and B3LYP/cc-pVDZ . [a] No stationary point on the ^1A surface was located with B3LYP/cc-pVDZ; [b] [6,6]-CASSCF; [c] [8,7]-CASSCF.



6b/6c: σ FO (18a') **6b/6c**: π* FO (4a'')

Figure 2. Frontier orbitals (FO) of different states of the isopyridine **6**.

Table 1. Dominating configurations of the CI expansion for three stationary points of the isopyridine **6**.

Stationary point	Symmetry, State	Configuration	Coefficient
6b	C_s, $^1A'$	$\vert(1a')^2 \ldots (18a')^2; (1a'')^2 (2a'')^2 (3a'')^2>$	0.9673
		$\vert(1a')^2 \ldots (18a')^2; (1a'')^2 (2a'')^2 (4a'')^2>$	–0.1629
		$\vert(1a')^2 \ldots (18a')^2; (1a'')^2 (3a'')^2 (5a'')^2>$	–0.1235
		$\vert(1a')^2 \ldots (18a')^2; (1a'')^2 \mathbf{(2a'')^1 (3a'')^1 (4a'')^1 (5a'')^1}>$	0.1139
6c	C_s, $^1A''$	$\vert(1a')^2 \ldots (17')^2 \mathbf{(18a')^1;} (1a'')^2 (2a'')^2 (3a'')^2 \mathbf{(4a'')^1}>$	0.9732
		$\vert(1a')^2 \ldots (17')^2 \mathbf{(18a')^1}; (1a'')^2 (2a'')^2 \mathbf{(4a'')^1} (5a'')^2>$	–0.1293
		$\vert(1a')^2 \ldots (17')^2 \mathbf{(18a')^1;} (1a'')^2 (2a'')^2 \mathbf{(3a'')^1 (4a'')^1 (5a'')^1}>$	0.1255
		$\vert(1a')^2 \ldots (17')^2 \mathbf{(18a')^1}; (1a'')^2 \mathbf{(2a'')^1} (3a'')^2 \mathbf{(4a'')^1 (6a'')^1}>$	0.1067
6c	C_s, $^3A''$	$\vert(1a')^2 \ldots (17')^2 \mathbf{(18a')^{1;}} (1a'')^2 (2a'')^2 (3a'')^2 \mathbf{(4a'')^1}>$	0.9918
		$\vert(1a')^2 \ldots (17')^2 \mathbf{(18a')^1}; (1a'')^2 (2a'')^2 \mathbf{(4a'')^1} (5a'')^2>$	–0.1277

The partial atomic charges obtained from a Natural Population Analysis (C1: –0.029; C2: –0.317; C3: –0.205) indicate that the "central allene" carbon atom C2 is, in fact, a nucleophilic centre. This is in contrast with the prototypical allene moiety with an electrophilic central allene carbon atom—a situation that is also found in strained carbocyclic allenes, such as 1,2-cyclohexadiene or 1,2,4-cyclohexatriene (isobenzene **18**, see Figure 4).[9]

The first excited singlet state of **6** in the planar arrangement is of $^1A''$ symmetry and corresponds to the σ,π diradical ^{1}**6c**. The strongly dominating configuration in the CI expansion shows that it results from the excitation of an electron from the non-bonding σ orbital (18a') into an antibonding MO (4a'') of the cyclic π-electron system (Figure 2), which now hosts seven electrons. As expected for this unfavourable electronic situation, all theoretical approaches predict this species to lie significantly higher in energy than **6b** (Table 2).

Table 2. Relative energies [kcal mol^{-1}] for various states of isopyridine **6**, as calculated by different methods.

Method	**6a**	**6b**	^{1}**6c**	^{3}**6c**
B3LYP/cc-pVDZ	–	0	+23.0	+23.7
BLYP/cc-pVDZ	–0.4	0	+24.8	+25.0
MR-CI+Q/cc-pVDZ//DFT[a]	–	0	+23.9	+27.3
CASPT2/cc-pVDZ//DFT[a]	–	0	+19.1	+21.3
CASPT2/cc-pVDZ//CASSCF[b]	+1.3	0	+20.2	+21.8
Thermochemistry:				
B3LYP/cc-pVDZ: $\Delta\Delta H_{298}$	–	0	+21.4	+22.1
B3LYP/cc-pVDZ: $\Delta\Delta G_{298}$	–	0	+22.0	+21.3

[a] B3LYP/cc-pVDZ. [b] See text.

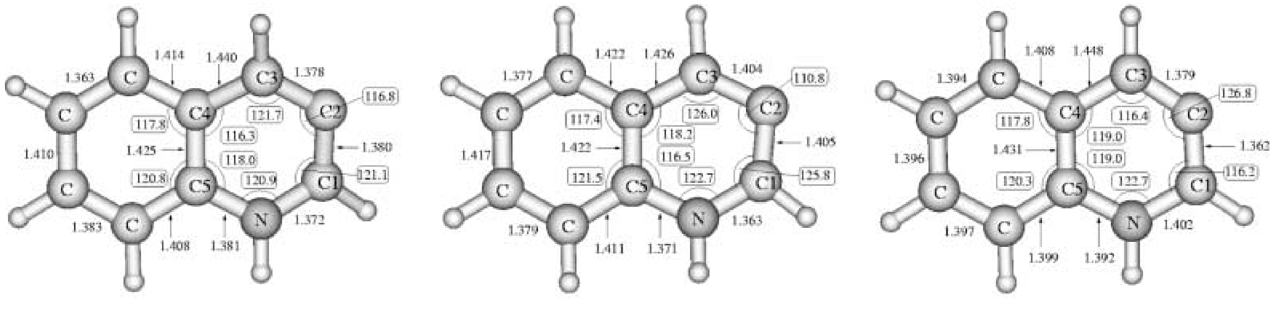
At the MR-CI+Q level, ^{1}**6c** is calculated to lie 23.9 kcal mol^{-1} (1.04 eV) above **6b**, while the CASPT2 calculation yields a relative energy of +19.1 kcal mol^{-1} (0.83 eV). The corresponding triplet diradical ^{3}**6c** is computed to be 27.3 (MR-CI+Q) and 21.3 (CASPT2) kcal mol^{-1} higher in energy than **6b**. Yavari et al.[7] have reported a relative energy for ^{3}**6c** of +37.9 kcal mol^{-1} at the QCISD/6-31G(d)//HF/6-31G(d) level. The optimised singlet and triplet diradical structures **6c** are virtually identical. Most notably, the angle C1-C2-C3 is calculated to be ≈127° and is thus significantly larger than in the zwitterionic structure **6b** (Figure 1). This larger value is in agreement with the much smaller electronic repulsion in **6c** as compared to **6b**, since the σ orbital is only singly occupied.

The results of the DFT methods (B3LYP/BLYP) for the relative energies of the diradical states are in remarkably good agreement with the ab initio approaches: ^{1}**6c**: +23.0/24.8, ^{3}**6c**: +23.7/25.0 kcal mol^{-1}. Table 2 also contains values for $\Delta\Delta H_{298}$ and $\Delta\Delta G_{298}$ calculated at the B3LYP level of theory. These results indicate that thermal and entropic effects cause only a slight stabilisation of the diradical states by 1–2 kcal mol^{-1}.

Relative free energies $\Delta\Delta G_{298}$ may also be estimated by adding the free energy corrections obtained from DFT calculations to the electronic energies resulting from the MR-CI+Q approach. On this scale, the diradical minima are predicted to lie 22.8 (^{1}**6c**) and 24.9 (^{3}**6c**) kcal mol^{-1} above the zwitterion **6b**.

Calculations of 3δ²-1*H*-quinoline (8) and explanation of the reactivity of its *N*-methyl derivative (7): Since the DFT approaches gave results in fair agreement with the more sophisticated ab initio methods and we were mainly interested in the qualitative changes of the electronic structure that arise from benzannulation, only the DFT methods were utilised for the investigation of the quinoline **8**.

The optimised geometries of the allenic form **8a**, the zwitterion **8b** and the diradical ^{1}**8c** were calculated by the B3LYP method and are presented in Figure 3. In contrast to the situation of the isopyridine **6**, the ground state equilibrium structure of **8** possesses some allene character (**8a**), as is apparent from the average of the dihedral angles C1-C2-C3-H3 and C3-C2-C1-H1 of 166°, the rather short bonds C1–C2 (1.380 Å) and C2–C3 (1.378 Å) and the relatively large angle C1-C2-C3 of 117° (see Figure 3 for the numbering of atoms). The length of the bond C4–C5 (1.425 Å) is increased with respect to the corresponding bond in **6** (1.385 Å), which is a consequence of the aromatic delocalisation of the π bond in **8**. For the planar arrangement (C_s symmetry), we have considered the zwitterionic and diradical states as for the isopyridine **6**. The calculation of the harmonic frequencies characterised the zwitterion **8b** as a saddle point of first order, which serves as transition state for the racemisation of the allene species. The geometrical parameters of the diradical **8c** show trends



8a (C_1, ^1A) **8b** (C_s, $^1A'$) ^{1}**8c** (C_s, $^1A''$)

Figure 3. Optimised C–C and C–N bond lengths [Å] and bond angles [°] computed [B3LYP/6–31G(d)] for various stationary points of $3\delta^2$-1*H*-quinoline (**8**).

analogous to those of the isopyridine state **6c** and will not be discussed further.

The calculated relative energies of the different stationary points of **8** are summarised in Table 3. According to these data, the allene **8a** is the most stable species, which will, however, undergo a quick racemisation through the zwitterion **8b** with a barrier of about 1–3 kcal mol^{-1}. Thus, compared with the isopyridine **6**, benzannulation in **8** stabilises the allene form relative to the zwitterion. This can probably be attributed to the increased length of the C4–C5 bond, which effectively increases the length of the tether across the allene termini and thereby reduces the ring strain in **8a**. Interestingly, the diradical ^{1}**8c** is calculated to lie only 14–18 kcal mol^{-1} above the zwitterion **8b**. The comparison with the parent diradical **6c** shows that the gap between the ground and the first excited singlet state is reduced by 7–9 kcal mol^{-1}. The same effect is calculated for the triplet diradical. Since the change of the geometric parameters on going from **8b** to **8c** is similar to that on going from **6b** to **6c**, electronic factors are likely to cause this difference in the energy gaps between zwitterionic and diradical structures. The possible nature of these factors will be discussed below.

Table 3. Relative energies [kcal mol^{-1}] for various states of quinoline **8**, as calculated by DFT methods.

Method	**8a**	**8b**[a]	^{1}**8c**	^{3}**8c**
B3LYP/6–31G(d)	0	+1.3	+14.4	+15.4
BLYP/6–31G(d)	0	+2.7	+17.7	+18.0
thermochemistry:				
B3LYP/6–31G(d): $\Delta\Delta H_{298}$	0	+0.8	+14.9	+14.2
B3LYP/6–31G(d): $\Delta\Delta G_{298}$	0	+1.4	+14.8	+13.2

[a] Transition state.

A resemblance of the energies of the allene **8a** and the zwitterion **8b**, which should also hold for the *N*-methyl derivative **7**, has already been calculated for the pyran **14** and was taken there as the reason for the rapid reaction with KO*t*Bu and the attack of the latter at an allene terminus.[9] The arguments advanced there should also apply to the formation of **17** from **7**, even in the presence of furan or styrene. As in the case of **6** (Figure 2), the LUMO of **7** should have large coefficients in positions 2 and 4 of the quinoline system (C1 and C3 in Figure 3). Therefore, the attack of KO*t*Bu at the allene terminus next to the nitrogen atom is not astounding, giving rise to **17** eventually. In other words, the reactivity of **7** towards nucleophiles is obviously similar to that of quinolinium salts, such as **16**. In this respect, **7** and the chromene **12** show the same behaviour. However, in the case of **12**, furan and styrene react faster than KO*t*Bu and furnish cycloadducts.[10] On the basis of the calculations, the different sensitivity of these intermediates towards nucleophiles may be caused by different relative energies of the allene structures and the zwitterions, which represent the transition states for the racemisation of the allene enantiomers. The smaller this difference is, the greater should be the zwitterionic character of the allene ground state. Whereas the free energy difference of **12a** and **12b** in solution amounts to ≈3 kcal mol^{-1},[9] that of **8a** and **8b** in the gas phase is only ≈1 kcal mol^{-1} (Table 3) and most probably the zwitterion **8b** will become the global minimum in a polar solution.

Comparison of the isopyridine 6 with the pyran 14 and the isobenzene 18: The free energies of the different states of the isopyridine **6** are compared with those of two isoelectronic species, namely the pyran **14** and the isobenzene **18**, which have recently been investigated by means of MR-CI, CASPT2 and DFT methods,[9] in Figure 4. The variations in the electronic structures of these species can be best understood, when the nature of the electronic ground state S_0 and the first excited singlet state S_1 for the planar arrangement (C_s symmetry) are analysed.

Regarding their zwitterionic states **6b** and **14b**, respectively, **6** and **14** exhibit closely related structural and electronic features. In the planar arrangement, the zwitterionic $^1A'$ state represents the electronic ground state of both species. However, **14b** serves as the transition state for the racemisation of the allene state and is calculated to lie 1.0 kcal mol^{-1} above the latter. The question arises as to why in the case of **6**, **6b** is more stable than the allene structure **6a**. A qualitative explanation to this question is offered by an analysis of the electron densities, calculated by the DFT method, by means of the Natural Resonance Theory (Table 4). Accordingly, the two Kekulé forms, which localise the formal positive charge at the heteroatom, are the dominating resonance structures of **6b**, summing up to 35% weight. In **14b**, however, these structures contribute only 22% to the resonance hybrid.[9]

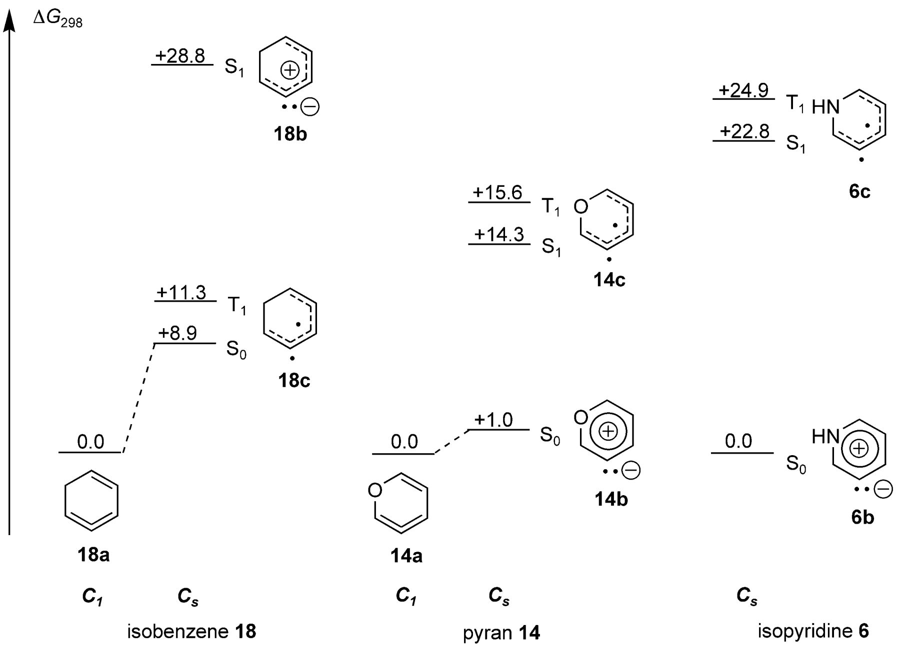
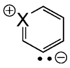
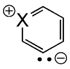
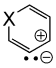
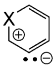
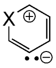


Figure 4. Comparison of the relative state energies of the isopyridine **6** (this work) with those of the isobenzene **18** and pyran **14** (taken from ref. [9]). Relative ΔG_{298} values were obtained by adding the thermal corrections from a DFT vibrational analysis to the MR-CI + Q calculated electronic energies.

Table 4. Natural resonance theory (NRT) analysis of the minimum structures **6b** and **14b** (C_s, $^1A'$) of the isopyridine **6** and the pyran **14**, respectively.

					
X = NH (**6b**)[a]	18 %	17 %	14 %	7 %	5 %
X = O (**14b**)[b]	11 %	11 %	21 %	8 %	6 %

[a] This work. [b] Taken from reference [9].

These findings mirror the chemical experience that nitrogen, being less electronegative than oxygen, is the better π donor and thus provides greater stabilisation of the zwitterion.

As can be seen from the CI wavefunctions discussed above (Table 1), the most important configurations in the CI expansions arise from the differential occupation of two MOs, the non-bonding σ orbital (18*a*′ in **6b/6c**) and the first antibonding π* orbital (4*a*″ in **6b/6c**, Figure 2). A clear picture of the electronic structure is provided by the simplest CI approximation to the electronic structure of this system, in which only the three lowest-lying singlet configurations and the lowest-lying triplet configuration are taken into account. They can be constructed from the different occupations of the above-mentioned non-bonding σ orbital and first antibonding π* orbital with two electrons. These four configurations have been previously analysed for the general case of a planarised and bent allene.[1, 33] The situation here, where the two critical MOs do not interact as a result of the symmetry but differ in their energy, is usually discussed in the general formalism of heterosymmetric diradicaloids.[34] Which electronic state is lowest in energy depends on the electronegativity difference between the two orbitals σ and π*, a measure of which is the energy difference between the configurations σ^2 and π^{*2}. Owing to its higher s character, the σ orbital has the lower orbital energy, favouring the zwitterionic configuration σ^2. On the other hand, electron repulsion and the avoidance of charge separation favours the diradical configuration $\sigma^1\pi^{*1}$. According to the relative state energies calculated for the isopyridine **6**, the zwitterionic state is the ground state and the diradical corresponds to the first excited singlet state. Such systems are classified as strongly heterosymmetric diradicaloids.[34] The underlying reason for this electronic situation stems from the shape of the frontier orbitals as the π* orbital has a strong antibonding and hence destabilising contribution from the nitrogen atom. The weaker the destabilisation of the π* orbital, the smaller will be the energy gap between the zwitterionic and the diradical state, and vice versa.

From this, the differences in the energy gaps between **6b/6c** and **8b/8c** can be understood. As to the planar structure of the quinoline **8**, the π* orbital should be stabilised with respect to the σ orbital, as compared to the situation in **6b/6c**, since it is delocalised into the benzo subunit, whereas such an effect should not be possible for the σ orbital. This is corroborated by the calculated energy difference between the π* and the σ orbital of 3.42 and 3.26 eV for **^{3}6c** and **^{3}8c**, respectively, at the B3LYP/6-31G(d) level. As a consequence, the calculated energy gap between the zwitterionic and the diradical state is significantly reduced by almost 10 kcal mol^{-1} in **8** (Table 3) as compared to **6** (Table 2).

The correlation of the relative state energies with the relative energies of the π* orbital and the σ orbital is becoming even clearer, when the isoelectronic systems **14** and **18** are considered (Figure 4).[9] Similar to **6**, the pyran **14** is a strongly heterosymmetric diradicaloid, characterised by a closed-shell, zwitterionic electronic ground state for the planar geometry. However, the destabilising contribution of the oxygen atom to the π* orbital is less pronounced as it is obvious from the energy difference between the π* and the σ orbital at the B3LYP/6-31G(d) level in the triplet diradicals, which is only 2.99 eV in **^{3}14c** but 3.42 eV in **^{3}6c**. This agrees with the qualitative notion that oxygen is a poorer π donor than nitrogen, and thus its contributions to the bonding and antibonding π-frontier orbitals are smaller. In agreement with these arguments, the energy gap between the zwitterionic and the S_1 diradical state is smaller by ≈10 kcal mol^{-1} in **14** as compared to **6**. The most intriguing species, however, is the isobenzene **18**. Owing to the membership of the methylene group within the ring, the antibonding character of the π* orbital is further reduced, as shown by the energy difference of the π* and the σ orbital of 1.60 eV in the triplet diradical. In this case, commonly referred to as a weakly heterosymmetric diradicaloid,[34] the state ordering is reversed and, at the planar geometry, the diradical state (**18c**) represents the ground state S_0, whereas the zwitterion with the σ^2 configuration (**18b**) now dominates the S_1 state.

Conclusion

The reactivity of the six-membered cyclic allenes towards nucleophiles seems to be closely connected to the structure associated with the global energy minimum. In the case of the isobenzene **18** and its benzo derivative $3\delta^2$-1*H*-naphthalene, the allene forms are by far the most stable structures.[9] Both species can be trapped by activated olefins with formation of cycloadducts,[35] even in the presence of KO*t*Bu.[17, 36] Although the zwitterionic state (**12b**) of the chromene **12** approaches the allene form (**12a**) to within a few kcal mol^{-1},[9] the formation of cycloadducts is still the major process, in spite of the presence of KO*t*Bu.[10] However, the pyran **14**[9] and the quinoline **7** do not furnish any cycloadducts but only products resulting from the interception by KO*t*Bu. If the energetics of **8** can be applied to the *N*-methyl derivative **7**, the free energy difference between allene form **7a** and the zwitterion **7b** amounts only to ≈1 kcal mol^{-1} in the gas phase. Such a small preference of the allene form (**14a**) over the zwitterion (**14b**) was also calculated for the pyran **14**.[9] On consideration of the solvent effect, the zwitterion **14b** is even the more stable form in solution,[9] which may be valid for **7b** as well. Thus, the high polarity of the ground state seems to be in agreement with a particular sensitivity towards the KO*t*Bu. Whether this property is accompanied by a low reactivity towards activated olefins is an open question, which could be answered by the generation of **7** and **14** in the absence of KO*t*Bu. However, there is no promising method to reach that goal. This is also true for the *N*-methylisopyridine **5**, the intermediacy of which was supported by experimental evidence,[5b] but under conditions that are unsuitable for a test to prove whether or not **5** can be intercepted by an activated olefin or not.

Experimental Section

NMR measurements: Bruker AC200 and DMX600 instruments were used. Solvent signals were taken as internal standards.

3-Bromo-1-methylquinolinium iodide: This salt was prepared according to Kreevoy et al.[11] Since virtually no NMR spectroscopic data are published, we report them here: ^{1}H NMR [600 MHz, $(CD_3)_2SO$]: $\delta = 4.63$ (br s, 3H; CH_3), 8.09 (ddd, $J_{5,6} = 8.1$, $J_{6,7} = 7.0$, $J_{6,8} = 0.8$ Hz, 1H; H6), 8.30 (ddd, $J_{7,8} = 8.9$, $J_{6,7} = 7.0$, $J_{5,7} = 1.4$ Hz, 1H; H7), 8.40 (dm, $J_{5,6} = 8.1$ Hz, 1H; H5), 8.51 (dm, $J_{7,8} = 8.9$ Hz, 1H; H8), 9.65 (br dd, $J_{2,4} = 1.9$ Hz, 1H; H4), 9.91 ppm (br dd, $J_{2,4} = 1.9$ Hz, 1H; H2); the assignment is based on H,H COSY and NOESY experiments [NOEs inter alia between following signal pairs: 4.63 (CH_3)–8.51 (H8), 4.63 (CH_3)–9.91 (H2), 8.40 (H5)–9.65 (H4)]; ^{13}C NMR [151 MHz, $(CD_3)_2SO$]: $\delta = 45.3$ (CH_3), 114.4 (C3), 119.2 (C8), 129.48 (C5), 129.52 (C4a), 130.7 (C6), 135.6 (C7), 137.1 (C8a), 148.0 (C4), 151.3 ppm (C2); the assignment is based on a C,H COSY experiment.

3-Bromo-1-methyl-1,2-dihydroquinoline (9): The published procedure[12] was scaled up and modified. Lithium aluminium hydride (1.10 g, 29.0 mmol) was added in small portions to a stirred suspension of 3-bromo-1-methylquinolinium iodide (10.0 g, 28.6 mmol) in anhydrous diethyl ether (200 mL), kept at room temperature under nitrogen, within 1 h. Afterwards, cold water (0 °C, 270 mL) was cautiously added with continued stirring. The layers were separated, the aqueous layer was extracted with ether (3 × 50 mL) and the combined organic layers were dried with $MgSO_4$ and concentrated in vacuo. The residual yellow oil was filtered through basic Al_2O_3 (activity IV) with diethyl ether, and the solvent was evaporated in vacuo to give **9** as an orange oil (5.76 g, 90 %), which could be stored under nitrogen at −30 °C over several weeks. ^{1}H NMR (600 MHz, $CDCl_3$): $\delta = 2.79$ (s, 3H; CH_3), 4.26 (d, $J_{2,4} = 1.6$ Hz, 2H; H2), 6.53 (br d, $J_{7,8} = 8.2$ Hz, 1H; H8), 6.70 (td, $J_{5,6} = J_{6,7} = 7.4$, $J_{6,8} = 0.9$ Hz, 1H; H6), 6.72 (br t, $J_{2,4} = 1.6$ Hz, 1H; H4), 6.87 (dd, $J_{5,6} = 7.4$, $J_{5,7} = 1.6$ Hz, 1H; H5), 7.16 ppm (≈td, average of $J_{6,7}$ and $J_{7,8} = 7.8$ Hz, $J_{5,7} = 1.6$ Hz, 1H; H7); the assignment is based on H,H COSY and NOESY experiments [NOEs inter alia between following signal pairs: 2.79 (CH_3)–6.53 (H8), 6.72 (H4)–6.87 (H5)]. These data are in accord with the scant information published.[11, 12] ^{13}C NMR (151 MHz, $CDCl_3$): $\delta = 36.9$ (CH_3), 58.5 (C2), 110.0 (C8), 114.9 (C3), 117.4 (C6), 121.7 (C4a), 126.3 (C5), 128.4 (C4), 129.3 (C7), 143.8 ppm (C8a); the assignment is based on C,H COSY experiment.

Treatment of 9 with KO*t*Bu

Furan, styrene or THF as the solvent: KO*t*Bu (700 mg, 6.24 mmol) was added in small portions, under nitrogen, to a stirred solution of **9** (673 mg, 3.00 mmol) and [18]crown-6 (794 mg, 3.00 mmol) in furan (10 mL) at room temperature within 5 min, whereby the mixture warmed and turned brown. Stirring was continued for 2 h and then water (5 mL) was added to the mixture. The layers were separated, the aqueous layer was extracted with ether (3 × 20 mL), then the combined organic layers were dried with $MgSO_4$ and concentrated in vacuo. As shown by a ^{1}H NMR spectrum, the residual dark oil contained 1-methyl-1,2-dihydroquinoline (**10**) and 1-methyl-2-quinolone (**11**) as major components in a ratio of 1:2. If styrene or anhydrous THF was used as the solvent instead of furan, the result was virtually the same. In the case of THF, 18-crown-6 was not added and the yield was determined to be 16 % by means of an internal standard.

[D$_8$]THF as solvent, immediate analysis by ^{1}H NMR spectroscopy: KO*t*Bu (55 mg, 0.49 mmol) was added to a solution of **9** (30.0 mg, 0.134 mmol) in [D$_8$]THF (0.7 mL) in an NMR tube. The ^{1}H NMR spectrum recorded immediately afterwards showed that **9** had been completely consumed and that only one product had been formed, the signals of which are in perfect agreement with the structure of 2-*tert*-butoxy-1-methyl-1,2-dihydroquinoline (**17**). ^{1}H NMR (200 MHz, [D$_8$]THF): $\delta = 1.23$ [s, 9H; $OC(CH_3)_3$], 3.05 (s, 3H; NCH_3), 5.38 (d, $J_{2,3} = 5.1$ Hz, 1H; H2), 5.83 (dd, $J_{3,4} = 9.4$, $J_{2,3} = 5.1$ Hz, 1H; H3), 6.56–6.74 (m, 3H; H4, H6, H8), 7.03 (d, $J_{5,6} = 7.4$, 1H; H5), 7.11 ppm (t, average of $J_{6,7}$ and $J_{7,8} = 7.5$ Hz, 1H; H7); since the reaction mixture was analysed, the line width was not small enough for the resolution of coupling constants over four bonds. The assignment is in agreement with that of the signals of **10**. After having been kept at room temperature for two weeks, the sample gave a ^{1}H NMR spectrum that showed, as judged on the basis of N-CH_3 signals ($\delta = 3.00$, 3.05, 3.09, 3.62 ppm), four major components, among them the quinolone **11** and still **17**.

Treatment of 1-methylquinolinium iodide with KO*t*Bu

*THF as solvent, formation of **10** and **11** and conversion of the mixture into pure **11***: A suspension of 1-methylquinolinium iodide (5.00 g, 18.4 mmol) and KO*t*Bu (2.07 g, 18.4 mmol) in anhydrous THF (100 mL) was stirred under nitrogen for 30 min at room temperature. Then the mixture was filtered through basic Al_2O_3 (activity IV) with diethyl ether as the washing solvent. The filtrate was concentrated in vacuo to give a brown oil (2.03 g), which contained **10** and **11** as the major components in a ratio of 1.0:1.3. For the oxidation of **10** to **11**, a procedure of Grignon-Dubois and Meola,[14] described for the conversion of *N*,*O*-acetals, such as **17**, was utilised. Thus, silica gel (5 g) was added to a solution of the brown oil in dichloromethane and the surplus solvent was removed in a rotary evaporator. The silica gel was exposed to air for 4 h and then extracted with acetone (100 mL). Evaporation of the acetone in vacuo yielded 1-methyl-2-quinolone (**11**, 1.69 g, 58 %) as a reddish brown solid. ^{1}H NMR (600 MHz, $CDCl_3$): $\delta = 3.73$ (s, 3H; CH_3), 6.71 (d, $J_{3,4} = 9.5$ Hz, 1H; H3), 7.24 (ddd, $J_{5,6} = 7.7$, $J_{6,7} = 7.3$, $J_{6,8} = 1.0$ Hz, 1H; H6), 7.37 (br d, $J_{7,8} = 8.4$ Hz, 1H; H8), 7.56 (br dd,

$J_{5,6}=7.7$, $J_{5,7}=1.4$ Hz, 1H; H5), 7.57 (ddd, $J_{7,8}=8.4$, $J_{6,7}=7.3$, $J_{5,7}=1.4$ Hz, 1H; H7), 7.67 ppm (d, $J_{3,4}=9.5$ Hz, 1H; H4); the assignment is based on a NOESY experiment [NOE inter alia between the following signal pair: 3.73 (CH_3)–7.37 (H8)]; ^{13}C NMR (151 MHz, $CDCl_3$): $\delta=29.4$ (CH_3), 114.1 (C8), 120.7 (C4a), 121.8 (C3), 122.1 (C6), 128.7 (C5), 130.6 (C7), 138.9 (C4), 140.1 (C8a), 162.3 ppm (C2); the assignment is based on C,H COSY spectrum.

These ^{1}H and ^{13}C NMR data are in agreement with those in reference [14], where the assignment is less specific, however. In addition, the ^{1}H NMR chemical shifts of reference [14] are systematically smaller by ≈0.3 ppm.

$(CD_3)_2SO$ as the solvent, immediate analysis by NMR spectroscopy: KO*t*Bu (10 mg, 0.089 mmol) was added to a solution of 1-methylquinolinium iodide (17.0 mg, 0.0627 mmol) in $(CD_3)_2SO$ (0.7 mL) in an NMR tube. The NMR spectra recorded immediately afterwards showed that the quinolinium salt had been completely consumed and that only one product had been formed. The ^{1}H NMR spectrum is in agreement with that obtained from product **17**, prepared from **9**. ^{1}H NMR [200 MHz, $(CD_3)_2SO$]: $\delta=1.15$ [s, 9H; $OC(CH_3)_3$], 2.92 (s, 3H; NCH_3), 5.44 (d, $J_{2,3}=4.4$ Hz, 1H; H2), 5.73 (dd, $J_{3,4}=9.6$, $J_{2,3}=4.4$ Hz, 1H; H3), 6.27 (d, $J_{3,4}=9.6$, 1H; H4), 6.43–6.53 (m, 2H; H6, H8), 6.91 (dd, $J_{5,6}=7.5$, $J_{5,7}=1.5$ Hz, 1H; H5), 7.01 ppm (≈td, average of $J_{6,7}$ and $J_{7,8}=7.7$ Hz, $J_{5,7}=1.5$, 1H; H7); ^{13}C NMR [50 MHz, $(CD_3)_2SO$]: $\delta=31.3$ ($OC(\mathit{C}H_3)_3$, 35.4 (NCH_3), 66.9 (C2), 78.8 [$O\mathit{C}(CH_3)_3$], 110.6 (C8), 116.0 (C6), 120.1 (C4a), 123.1 (C3), 125.0 (C4), 126.6 (C5), 128.5 (C7), 142.3 ppm (C8a). The assignments of the signals in these spectra are just guesses based on the data of **10**.

1-Methyl-1,2-dihydroquinoline (10): The original procedure[13] was modified to resemble the preparation of **9**. Thus from 1-methylquinolinium iodide (3.00 g, 11.1 mmol), the product **10** (1.22g, 76%) was obtained as a yellow oil, which was sensitive to air, but could be stored without decomposing at −30 °C under nitrogen. ^{1}H NMR (600 MHz, $CDCl_3$): $\delta=2.74$ (s, 3H; CH_3), 4.00 (dd, $J_{2,3}=3.9$, $J_{2,4}=1.9$ Hz, 2H; H2), 5.79 (dt, $J_{3,4}=9.8$, $J_{2,3}=3.9$ Hz, 1H; H3), 6.32 (dt, $J_{3,4}=9.8$, $J_{2,4}=1.9$ Hz, 1H; H4), 6.47 (br d, $J_{7,8}=7.8$ Hz, 1H; H8), 6.60 (td, $J_{5,6}=J_{6,7}=7.4$, $J_{6,8}=1.1$ Hz, 1H; H6), 6.84 (dd, $J_{5,6}=7.4$, $J_{5,7}=1.6$ Hz, 1H; H5), 7.05 ppm (≈td, average of $J_{6,7}$ and $J_{7,8}=7.6$, $J_{5,7}=1.6$ Hz; H7); the assignment is based on H,H COSY and NOESY experiments [NOEs inter alia between the following signal pairs: 2.74 (CH_3)–6.47 (H8), 6.32 (H4)–6.84 (H5)]. The data published previously[37] contain less information. ^{13}C NMR (151 MHz, $CDCl_3$): $\delta=37.1$ (CH_3), 51.7 (C2), 109.7 (C8), 117.0 (C6), 122.2 (C3), 122.3 (C4a), 126.5 (C5), 126.6 (C4), 128.9 (C7), 146.0 ppm (C8a); the assignment is based on a C,H COSY spectrum.

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