A Novel Class of Aza-analogues of Sesquifulvalene with a Betaine Character: 1-Alkyl-4-(azolylidene)-1,4-dihydropyridines

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The first synthesis of 1-alkyl-4-(azolylidene)-1,4-dihydropyridines (**2A**) $\longleftrightarrow$ (**2B**) is described; their physicochemical properties clearly indicate a significant contribution of the dipolar structure (**2B**) to the ground state of (**2**) and this has been confirmed by the *X*-ray crystal structure of 1-methyl-4-(benzimidazolylidene)-1,4-dihydropyridine (**4a**).

In general, aza-analogues of sesquifulvalene are formally derived from sesquifulvalene (**1**) by replacement of the seven-membered carbocyclic ring by a quaternary heteroaromatic ring.[1,2]

Among the many types of aza-analogues of sesquifulvalene, the azolylidenedihydropyridines (**2**) and (**3**) were hitherto unknown. These compounds should show a spectrum of properties ranging between those of ethylenes and betaines.

In connection with our interest in the chemistry of heterocyclic betaines,[3,4] we now report the first synthesis and structural characterisation of examples of compounds of type (**2**), the 1-alkyl-4-(azolylidene)-1,4-dihydropyridines (**4**) and (**5**). Their physicochemical properties favour the betainic structures of (**4B**) and (**5B**); this has been confirmed by a single crystal *X*-ray diffraction study of compound (**4a**).

Compounds (**4**) and (**5**) were prepared by a three-step procedure (Scheme 1). First, 2-(4-pyridyl)-1*H*-benzimidazoles and 5-methyl-3-(4-pyridyl)-1*H*-pyrazole (**6**) were obtained by standard methods.[5] *N*-Alkylation of the 4-pyridylazoles (**6**) with alkyl halides under neutral conditions gave the 1-alkyl-4-azolylpyridinium salts (**7**), which were deprotonated using an anionic (OH^- form) ion-exchange resin. The new aza-analogues (**4**) and (**5**) of sesquifulvalene were obtained; they gave satisfactory elemental analyses and their electron-impact mass spectra showed the molecular peak: for compounds (**4a**) and (**4c**) these were base peaks and for the others these had a relative abundance in the range 45—95%.

The ^1H and ^{13}C n.m.r. spectra for compounds (**4**) and (**5**) were vital for structural proof and also for providing evidence of charge distribution, which clearly indicated the dipolar forms (**4B**) and (**5B**). Both the ^1H and ^{13}C n.m.r. chemical shifts, in $(CD_3)_2SO$ and $CDCl_3$, of these compounds accord perfectly with data reported for anionic species in the azole series, quaternary pyridinium compounds, and the valuable data obtained from the mesomeric betaines of the pyridinium azolate class.[3]

Compounds (**4a—d**) are not suitable for experimentally determining rotational barriers owing to their symmetry, and compounds (**5a,b**) are very insoluble in low-melting solvents. Nevertheless, the ^1H n.m.r. spectrum of a saturated solution of (**5a**) in $(CD_3)_2CO$ has been recorded at 100 MHz and 263 K; the aromatic protons of the pyridinium appeared as a well resolved AA′BB′ system ($\delta\, H^{-3} = \delta\, H^{-5}$), indicating that this temperature is well below the coalescence temperature.†

The experimental dipole moments (dioxane, 298 K, determined as in ref. 3) of the anhydrous 1-alkyl-4-(azolylidene)-1,4-dihydropyridines (**4a**), (**4b**), and (**5b**) were high, which implies a substantial charge separation, and the values extrapolated to infinite dilution were: (**4a**) 9.03, (**4b**) 9.71, and (**5b**) 9.42 Debye.

Spectroscopic data and experimental dipolar moment values were consistent with the dipole form (**B**) [(**4B**) and (**5B**)] but definite structural assignment of the title compounds was unambiguously determined for (**4a**) by *X*-ray crystallo-

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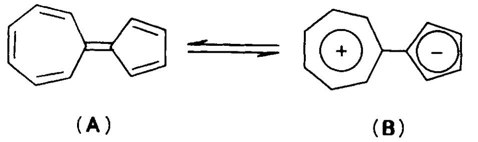
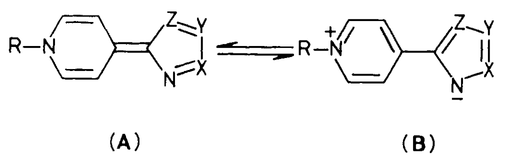
† Below about 263 K, compound (**5a**), 2 mg in 1 ml, crystallises. These results correspond to a rotational barrier lower than 53.1 kJ mol^{-1}. In general, reported rotational barriers in derivatives of biphenyl[6a] were found to be >50 kJ mol^{-1} and the predicted barrier to rotation in biphenyl itself[6b] is ~ 8 kJ mol^{-1} at 340 K.



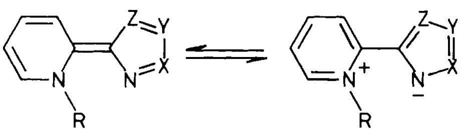
(A) **(B)**

(1)



(A) **(B)**

(2)



(A) **(B)**

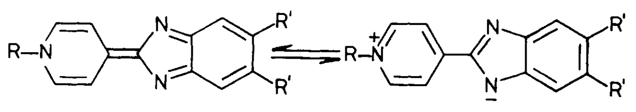
(3)

X,Y,Z: =CR–; =N–

graphy (Figure 1). To the best of our knowledge, this is the first *X*-ray determination of an aza-analogue of sesquifulvalene.

Recrystallisation of (**4a**) from 70% ethanol provided crystals, m.p. 255 °C, suitable for *X*-ray diffraction.‡ Careful inspection of the diffraction pattern indicates that the true Laue class of the crystal is $\bar{1}$. However, intensity differences between pseudo-symmetrical reflections according to Laue class $4/mmm$ are, in almost all cases, very small. Moreover, the presence of very weak superstructure reflections fulfilling the condition $h + k + 1 = 2n + 1$ confirm the absence of the *I* centring. Owing to the difficulty of determination of this kind of superstructure, and owing to the chemical interest of the compound, the superposition structure in $I4_1/amd$ has been determined.

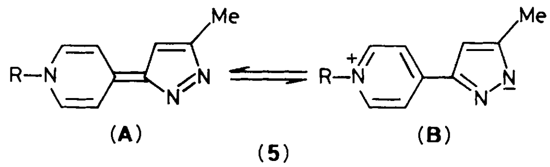
Probable causes for the appearance of the superstructure are the existence of a small twist angle between the benzimidazolate and the pyridinium rings, and a slight asymmetry in both rings. As shown in Figure 1, the molecule is effectively



(A) **(B)**

(4)

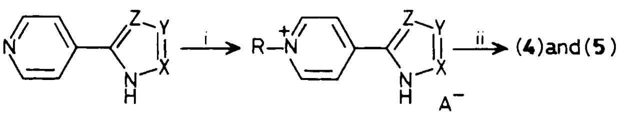
	R	R'
a;	Me	H
b;	Me	Me
c;	Bu^t	Me
d;	n–C$_{10}$H$_{12}$	H



(A) **(B)**

(5)

a; R = Me
b; R = Bu^t



(6) **(7)**

Scheme 1. *Reagents and conditions:* i, MeI or Bu^{t}I in anhydrous acetone, reflux; Bu^{t}Br and n-C$_{10}$H$_{21}$Br in dimethylformamide (DMF) at 85 °C; ii, anion-exchange Amberlite resin IRA-401 (OH$^-$ form).[3] Overall yields: (**4**) >65% and (**5**) >43%.

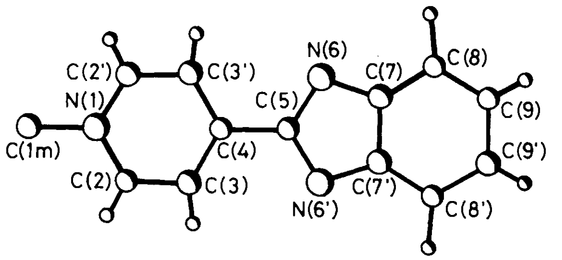


Figure 1. Computer-generated perspective drawing[9] of (**4a**).

planar, the torsion angle between the rings being ≤2.5°; otherwise, the superstructure character of compound (**4a**) would disappear. The interannular C(4)–C(5) bond length is 1.448 Å, consistent with a C(sp^2)–C(sp^2) single bond. Neither the benzimidazolate ring nor the pyridinium ring is symmetrical and the molecular bond lengths and angles correspond to the mean values, which are similar to those previously described[3] for 2-(1-pyridinio)benzimidazolate. The fact that the molecules are stacked§ in the head-to-tail orientation is

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‡ *Crystal data* for (**4a**): $C_{13}H_{11}N_3{\cdot}2H_2O$, $M = 245.3$, tetragonal, space group $I4_1/amd$, $a = 7.193(1)$, $c = 46.63(1)$ Å, $U = 2415$ Å^3 (by least-squares refinement on diffractometer angles for 25 automatically centred reflections, $\lambda = 0.71069$ Å), $Z = 8$, $D_c = 1.35$ g cm^{-3}. Colourless prisms, 0.30 × 0.25 × 0.45 mm, μ(Mo-K_α) = 0.876 cm^{-1}, $F(000) = 1040$. All crystallographic measurements were made on a CAD4 diffractometer, ω–2θ mode with ω scan width = 2.40 + 1.05tan θ, ω scan speed 1.5—6.7 deg min^{-1}, graphite-monochromated Mo-K_α radiation; 8590 reflections measured [$1.0 \leq \theta \leq 25°$, $-8 \leq h \leq 8$, $-8 \leq k \leq 8$, $0 \leq l \leq 55$; 630 unique substructure reflections giving 538 with $I > 2.5\sigma(I)$]. Stability of intensity control, *ca.* 1%. The substructure was solved by Patterson search methods[7] using as search fragment the known skeleton of a related compound.[3] Full-matrix least-squares refinement with all non-hydrogen atoms anistropic. All the non-methyl H-atoms were determined experimentally with one, overall refined U_{iso} [= 0.067(8) Å^2]. The weighting scheme $w = 1/[\sigma^2(F_o) + 0.00012F_o^2]$ with $\sigma(F_o)$ from counting statistics gave satisfactory agreement between analyses. Final R and R_w values were 0.074 and 0.075. Highest and lowest peaks in final ΔF map (e Å^{-3}) 0.35 and 0.42. Programs used and sources of scattering factor data are given in refs. 7, 9, 10, and 8, respectively. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

§ The *X*-ray analysis shows that all the molecules in the unit cell are parallel to the long faces of the unit cell, forming layers normal to the *c*-axis, *i.e.* $c = 4 \times 11.66 = 46.63$ Å (Figure 2). Each layer is built by alternating rows of (**4a**) molecules and water molecules. The molecules are stacked in a head-to-tail manner, *i.e.* the N(1) atom of one molecule is located between the centres of the imidazole rings of the two neighbouring molecules in the row (stacking distance 3.60 Å).

The peaks of the O-atoms follow the $I4_1/amd$ symmetry. The two shortest contacts in each layer involving water molecules are: O · · · N(6)[1/2 + x,y,1/2 − z] = 2.97 Å, O · · · N(6)[1/2 − x,y,1/2 − z] = 2.97 Å and O · · · C(2) = 3.10 Å. There is an additional close distance to a symmetry-related water molecule, *i.e.* O · · · O' 3.36 Å.

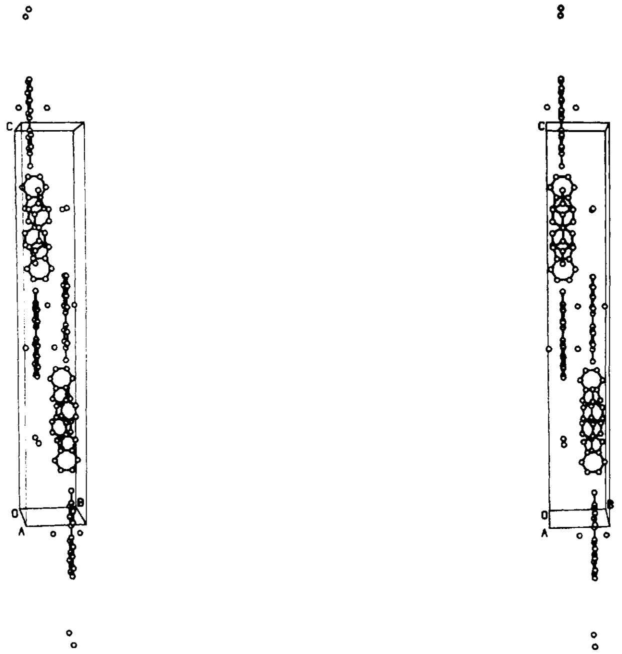

Figure 2. Unit cell packing diagram (stereo-pair) for compound (**4a**).

noteworthy, as this has been found for the inner salts of pyridinium benzimidazolate with an unsubstituted pyridinium ring.[3] In summary, all these experimental results are fully consistent with the betainic character of compounds (**4**) and (**5**).

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