achieved by column chromatography on silica gel with benzene as eluent.

Indoline-2-thione (12). This compound was synthesized by following the literature procedure.[18] Oxindole (1.33 g, 0.01 mol) and phosphorus pentasulfide (0.45 g, 0.002 mol) were heated to reflux in 50 mL of benzene for 2 h. Filtration of the hot solution followed by the addition of hexane to the filtrate yielded 0.5 g of yellow solid. An additional 0.75 g of solid was obtained by concentrating the filtrate under reduced pressure. Multiple recrystallization of the first 0.5 g of solid gave 300 mg of yellow needles: mp 142-43.5 °C (lit.[24] mp 147-9 °C); NMR δ 4.02 (s, 2 H), 6.7-7.3 (m, 4 H), 10.5-10.8 (broad, 1 H).

***N*-Methylindoline-2-thione (13).** 1-Methylindolin-2-one (1.0 g, 0.0068 mol) and phosphorus pentasulfide (0.3 g, 0.0013 mol) were heated over a steam bath for 4 h in 50 mL) of toluene. Upon cooling, the reaction mixture was decanted and concentrated under reduced pressure to give a gummy yellow solid (1.0 g). Multiple recrystallization from hexane gave yellow needles: mp 106.5-8.0 °C (lit.[24] mp 109-10 °C); NMR δ 3.60 (s, 3 H), 4.08 (s, 2 H), 7.24 (s, 4 H).

***N,N*-Dimethylphenylthioacetamide (15).** Phosphorus pentasulfide (0.35 g, 0.0015 mol) was added to *N,N*-dimethylphenylacetamide (1.2 g, 0.0074 mol) in 20 mL of toluene. This solution was heated on a steam bath for 3 h, decanted, and concentrated in vacuo, leaving 1.0 g (75%) of a yellow solid. Repeated recrystallization from benzene/hexane solution followed by sublimation (40 °C, 0.5-1.0 mm) afforded the pure white product: mp 74.0-5.5 °C (lit.[25] mp 79 °C); NMR δ 3.20 (s, 3 H), 3.50 (s, 3 H), 4.31 (s, 2 H), 7.31 (s, 5 H).

***N,N*-Dimethylthioacetamide (16).** Phosphorus pentasulfide (6.6 g, 0.30 mol) was added to a solution of *N,N*-dimethylacetamide (12.9 g, 0.148 mol) in 10 mL of toluene whereupon a highly exothermic reaction ensued causing the solution to reflux. This solution was maintained at reflux for 4 h and then concentrated under reduced pressure leaving a yellow solid (8.6 g, 56%). Multiple recrystallization from hexane gave long spiny white needles melting at 72-3 °C (lit.[26] mp 74.5 °C): NMR δ 2.61 (s, 3 H), δ 3.30 (s, 3 H), δ 3.48 (s, 3 H).

γ-Crotonolactone (25). This compound was prepared according to the Organic Synthesis procedure.[27] γ-Butyrolactone was brominated by reaction with bromine and phosphorus. The α-bromo lactone was then dehydrohalogenated using trimethylamine to afford the desired product: bp 61-3 °C (1.8 mm); NMR δ 4.99 (m, 2 H), 6.16 (m, 1 H), 7.77 (m, 1 H).

$\Delta^{\beta,\gamma}$-5-Methylbutenolide (26). A p*K* pure sample was graciously provided by Dr. G. Kraus.

Acknowledgment. This research was supported by the National Science Foundation.

(24) Brown, J. P.; Thompson, M. *J. Chem. Soc., Perkin Trans 1* **1974**, 863-866.

(25) Sherry, A. D.; Purcell, K. F. *J. Am. Chem. Soc.* **1972**, *94*, 1848-1853.

(26) Price, C. E.; Judge, J. M. *Organic Syntheses*; Wiley: New York, 1973, Collect. Vol. V, p 255.

(27) Brewster, J. H.; Fusco, A. M.; Carosino, L. E.; Corman, B. G. *J. Org. Chem.* **1963**, *28*, 498-501.

Heterocyclic Betaines. Aza Analogues of Sesquifulvalene. 1. Structural Studies of 1-Alkyl-4-azolylidene-1,4-dihydropyridines and Azolium Azolate Inner Salts

Ermitas Alcalde,*[,1a] Immaculada Dinarès,[1a] Jordi Frigola,[1b] Carlos Jaime,[1c] Jean-Pierre Fayet,[1d] Marie-Claire Vertut,[1d] Carlos Miravitlles,[1e] and Jordi Rius[1e]

Laboratorio de Química Orgánica, Facultad de Farmacia, Universidad de Barcelona, E-08028-Barcelona, Spain, Laboratorios Dr. Esteve S.A., E-08026-Barcelona, Spain, Universidad Autónoma de Barcelona, 08193-Bellaterra, Spain, Laboratoire de Chimie Organique Structurale, URA 1311, Université Paul Sabatier, F-31077-Toulouse Cédex, France, and Instituto de Ciencia de Materiales, C.S.I.C., E-08028-Barcelona, Spain

Received July 20, 1990

The aza analogs of sesquifulvalene may adopt various structures, and of these several 1-alkyl-4-azolylidene-1,4-dihydropyridines **8A** ↔ **8B** have been prepared by deprotonation of their corresponding 1-alkyl-4-azolylpyridinium salts. These novel structures **8** could show a spectrum of properties ranging from those of ethylenes to betaines. Semiempirical (MNDO//MNDO), experimental dipole moment values (ca. 9.05 D), ^{1}H and ^{13}C NMR data, and single-crystal X-ray diffraction analysis of compound **16** are consistent with the betaine character of these compounds. The electronic and molecular structure of azolium azolate inner salts **10** has been investigated. Theoretical calculations (MNDO//MNDO), experimental dipole moments (9.18 to 11.33 D), ^{1}H and ^{13}C NMR spectra, EIMS, and single-crystal X-ray diffraction analysis of compound **35** are consistent with the highly dipolar structure of this type of mesomeric betaines.

A general principle of heterocyclic chemistry is to relate heterocyclic compounds to aromatic ones. This is obvious when the aromatic compound is a classical one, but when the reference compound is an unusual structure, such as sesquifulvalene (**1**),[2] the possibilities are richer. Sesquifulvalene (**1**) can be described in a first approximation by covalent resonance structure **1A** and a dipolar one, **1B**.

At least three reasonable possibilities exist (i → iii) and Figure 1 shows structures **2-5** represented in their dipolar resonance form B. The first possibility has been carefully explored, and the term hetero analogues of sesquifulvalene is usually used for compounds that are formally derived from **1** by replacement of the seven-membered carbocyclic ring by a quaternary heteroaromatic ring.[3] To the best

(1) (a) Universidad de Barcelona. (b) Laboratorios Dr. Esteve S.A. (C) Universidad Autónoma de Barcelona. (d) Univesité Paul Sabatier, Toulouse. (e) Instituto de Ciencia de Materiales, Barcelona.

(2) Prinzbach, H.; Knöfel, H.; Woischnik, E. In *Aromaticity, Pseudo-Aromaticity, Anti-Aromaticity*, The Jerusalem Symposia on Quantum Chemistry and Biochemistry, The Israel Academy of Sciences; 1971; Vol. III, p 269.

(3) (a) Seitz, G. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 478. (b) Rodig, O. R. *Chem. Heterocycl. Compd.* **1974**, *14* (part 1), 349-350. (c) Micetich, R. G. *Chem. Heterocycl. Compd.* **1974**, *14*(part 2), 378-381.

(4) Ollis, W. D.; Stanforth, S. P.; Ramsden, C. A. *Tetrahedron* **1985**, *41*, 2239.

0022-3263/91/1956-4223$02.50/0

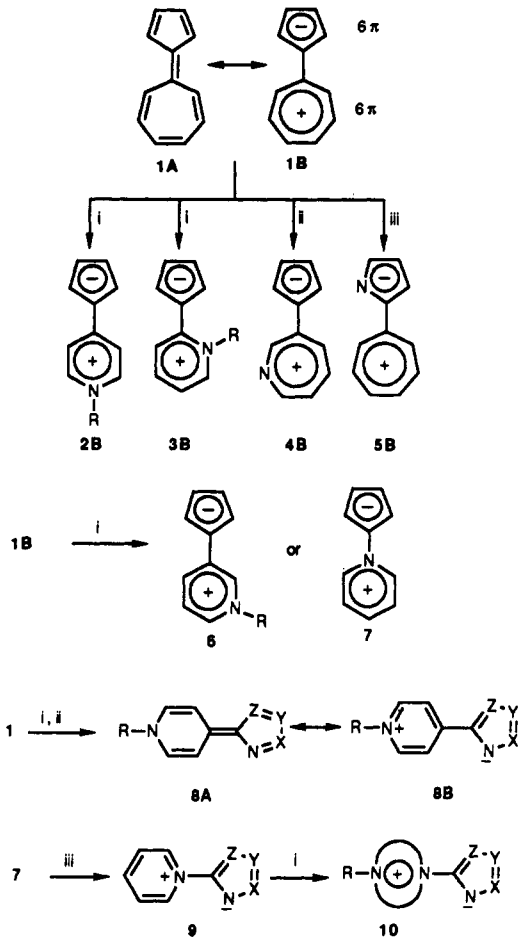


Figure 1. Aza analogues of sesquifulvalene (1): (i) >C=C< → -NR-; (ii, iii) >C=C< → >C=N-.

of our knowledge, the second and the third possibilities are unknown. Within the first possibility, it is of interest to consider structures 6 and the *N*-ylide 7[4] in which a covalent (nondipolar) resonance structure is forbidden. They may only exist as betaines, being aza analogues of the dipolar form of sesquifulvalene (1B).

In connection with our interest in the chemistry of heterocyclic betaines,[5-7] we have now investigated the case of 1-alkyl-4-azolylidene-1,4-dihydropyridines 8 in which possibilities i and iii are combined.[8] These compounds should show a spectrum of properties ranging between those of ethylenes and betaines.

Other hetero analogues of sesquifulvalene have been described, i.e., 11,[9] 12,[10] 13,[11] 14, and 15.[12] The hetero analogues of sesquifulvalene are relatively stable compounds and the dipolar resonance form makes a contribution to the ground state in contrast with sesquifulvalene

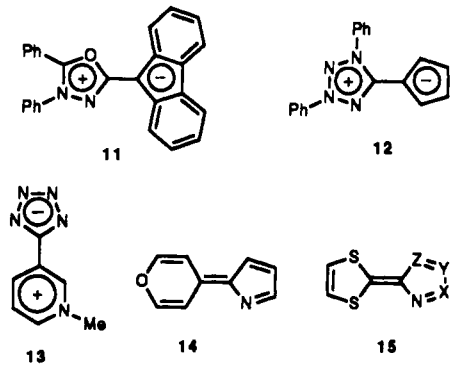
(5) Dinarès, I. Ph.D. Thesis, Facultad de Farmacia, Universidad de Barcelona, 1988 (microfilm no. 520, 1989, University of Barcelona).
(6) (a) Alcalde, E.; Dinarès, I.; Elguero, J.; Fayet, J.-P.; Vertut, M.-C.; Miravitlles, C.; Molins, E. *J. Org. Chem.* **1987**, *52*, 5009. (b) Alcalde, E.; Dinarès, I.; Elguero, J.; Frigola, J.; Osuna, A.; Castanys, S. *Eur. J. Med. Chem.* **1990**, *25*, 309.
(7) (a) Alcalde, E.; Dinarès, I.; Frigola, J. *Tetrahedron Lett.* **1988**, *29*, 491. (b) Alcalde, E.; Dinarès, I. *J. Org. Chem.*, following paper in this issue.
(8) For an earlier report, see: Alcalde, E.; Dinarès, I.; Frigola, J.; Rius, J.; Miravitlles, C. *J. Chem. Soc., Chem. Commun.* **1989**, 1086.
(9) Boyd, G. V.; Harms, M. D. *J. Chem. Soc.* **1970**, 807.
(10) Araki, S.; Butsugan, Y. *J. Chem. Soc., Perkin Trans. I* **1984**, 2545 and references cited therein.
(11) Butler, R. N.; Garvin, V. C. *J. Chem. Res., Synop.* **1982**, 122.
(12) (a) Gompper, R.; Guggenberger, R. *Tetrahedron* **1986**, *42*, 839; (b) **1986**, *42*, 849 and references cited therein.

Table I. Semiempirical Calculations (MNDO//MNDO) of Sesquifulvalene and Its Aza Derivatives

compd	torsion angle τ^a	ΔH_f^b	$\delta\Delta H_f^b$	μ^c	interannular distance[d]
1	0.0	400.56	0	1.29	1.368
	90.0	549.16	194.38	0.88	1.376
2	1.5	360.57	0	5.22	1.375
(R = Me)	90.0	466.17	105.61	7.55	1.407
3	10.2	379.23	0	3.02	1.378
(R = Me)	90.0	447.85	68.61	7.23	1.419
16	0.3	453.34	0	7.69	1.396
	30.0	463.38	10.04	8.37	1.401
	90.0	524.21	70.86	18.07	1.458
17	0.0	407.35	0	8.08	1.398
	90.0	475.59	68.24	18.67	1.459
20	0.1	355.23	0	8.87	1.381
	90.0	443.59	88.36	12.74	1.444
21	0.1	304.12	0	9.34	1.381
	90.0	391.02	86.90	13.45	1.420

[a] In degrees. [b] In kJ/mol. [c] In Debye; 1 D = 3.34 × 10^{-30} C m. [d] In angstroms.

(1) itself. The latter is a highly unstable compound with the properties of a reactive polyolefin rather than an aromatic compound.[13]



According to Ollis, Stanforth, and Ramsden,[4] *N*-pyridinium cyclopentadienide (7) is a typical example of conjugated heterocyclic *N*-ylides isoconjugated with odd nonalternant hydrocarbon anions. The azinium azolate 9 and azolium azolate 10 inner salts,[5-7] aza analogues of the *N*-ylide 7, belong to this class of mesomeric betaines (see, Figure 1).

The synthesis and reactivity of mesomeric betaines of azolium azolate (10) have been described.[7] In view of their interest from a physical organic viewpoint, we now report the results for theoretical MNDO//MNDO calculations, the physicochemical properties (spectroscopic data and experimental dipole moments), and one X-ray structure determination of this type of mesomeric betaines 10.

Results and Discussion

1-Alkyl-4-azolylidene-1,4-dihydropyridines 8. Theoretical Study. The calculations were carried out by using the MNDO SCF-MO[14] procedure employing a standard s/p valence basis and with full optimization of all geometric variables.

The semiempirical calculations (MNDO//MNDO) have been performed for sesquifulvalene (1), its aza analogues 2 (R = Me) and 3 (R = Me), and the 1-alkyl-4-azolylid-

(13) (a) Neuenschwander, M.; Schenk, W. K. *Chimia* **1972**, *26*, 194. (b) Hollenstein, R.; Moser, A.; Neuenschwander, M.; Philipsborn, W. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 551. (c) Neuenschwander, M. *Pure Appl. Chem.* **1986**, *58*, 55.
(14) (a) Steward, J. P. P. MOPAC Program, *QCPE Bull.* **1985**, *5*, 133. (b) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899.

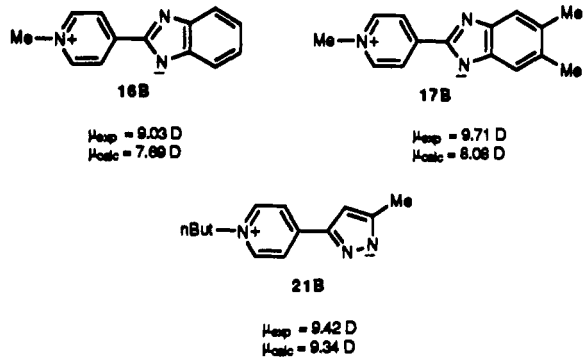
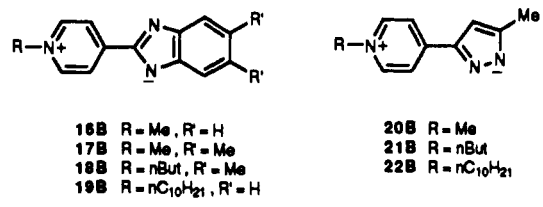


Figure 2. Experimental and calculated (τ_{min}) dipolar moment values for compounds **16**, **17**, and **21**.

ene-1,4-dihydropyridines **16**, **17**, **20**, and **21**. Heats of formation for some selected torsional angles, dipole moments, and interannular distances are given in Table I.



In all cases the most stable conformation is the planar one ($\delta\Delta H_f \approx 0$). The calculated barrier of rotation around the interannular bond decreases in the order **1** ≫ **2** > **20** ≈ **21** > **16** ≈ **17** ≈ **3**. Considering the canonical dipolar structures, B, the aforementioned results correspond to the facts that a positive charge is better stabilized in a pyridinium ring that in a tropylium one (compare **1B** and **2B**) and that a negative charge is better stabilized in an azolate anion that in a cyclopentadienyl one. Taking into consideration the acidic pK_as of cyclopentadiene (≈15),[15] benzimidazole (12.86),[16] 5,6-dimethylbenzimidazole (12.36),[16] and 3(5)-methylpyrazole (14.21),[16] a linear relationship can be established for the four 1-methyl-(4-substituted)pyridinium derivatives **2**, **16**, **17**, and **20**: $\delta\Delta H_f$ (kcal·mol^{-1}) = −26.0 + 3.38pk_a, R^2 = 0.97. This relationship reflects the fact that the stability of the anion influences similarly the pK_a and the rotational barrier.

Concerning aza analogues of sesquifulvalene, the only reported data refer to compound **3** (R = Me) and its experimental rotational barrier of 47.42 kJ mol^{-1} at 223 K.[17] For compound **3** (R = Me) the calculated barrier is 68.52 kJ mol^{-1} (see Table I), which is too high, but still reflects the destabilization of the ground state by the *N*-methyl ortho effect (compare **2** and **3**). Thus, in the present study, the calculated rotational barriers in MNDO (Table I) are overestimated. Nonetheless, the overall magnitude of the rotational barrier is not important for our purposes; the relative ordering of the series thus far investigated is **1** ≫ **2** > **20** ≈ **21** > **16** ≈ **17** ≈ **3**).

The 1-alkyl-4-benzimidazolylidene-1,4-dihydropyridines **16–19** are not suitable for experimental determination of rotational barriers owing to their symmetry. The 1-alkyl-4-pyrazolylidene-1,4-dihydropyridines **20** and **21** are very insoluble in low-melting solvents. Nevertheless, the ^{1}H NMR spectra of a saturated solution of **20** and **21** have

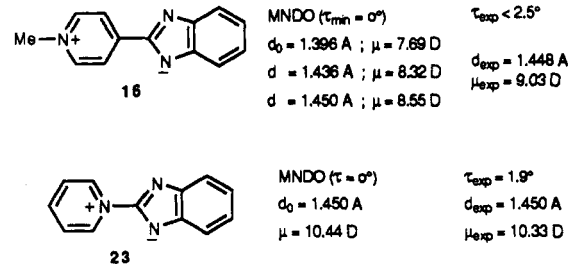


Figure 3. For **16** different μ's were obtained upon variation the interannular C–C bond distance. A MNDO SCF-MO was done for **23** on a geometry equal to that obtained by X-ray analysis.[6]

shown that their experimental rotational barrier is well below 53 kJ mol^{-1} (see below: Spectroscopic Methods).

Concerning the dipole moments, Figure 2 shows the experimental and the calculated values for compounds **16**, **17**, and **21** (see below: Dipole Moments).

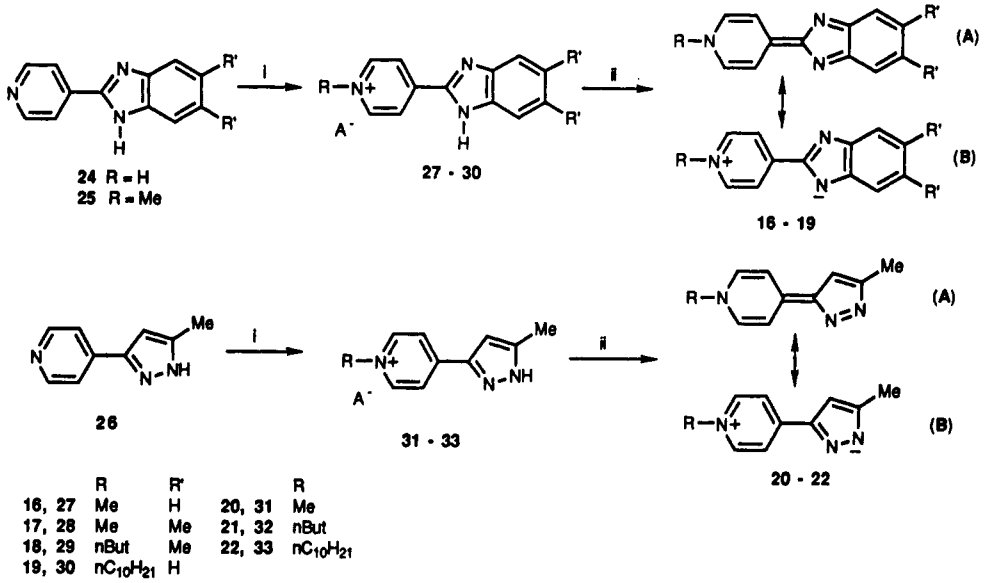
For compound **21**, there is an excellent agreement between the experimental and calculated (for τ_{min} = 0°) values of μ. For compounds **16** and **17** (benzimidazole derivatives) their dipolar moments are moderately well predicted and underestimated in MNDO, but this does not point to a nonplanar structure. First, in compounds **16** and **17** the coplanar conformations possess two attractive "aromatic C–H/lone pair" interactions,[18] which stabilize the ground state. On the contrary, for compound **21** in the coplanar conformation one attractive and one repulsive "aromatic C–H/aromatic C–H" interaction is seen.[18] Second, a twist of 30° of τ only increases the calculated dipole moment of **16** to 8.37 D. The experimental dipole moment should of course reflect a dynamic situation in which all conformations will be populated according to their energies. If the energy differences are overestimated, the contribution from conformers with high dipole moments could be significant. Third, MNDO-calculated μs are usually smaller than the experimental ones,[14b] the difference being larger in organic molecules containing sp^2 or sp N atoms. This tendency of the MNDO approach is also observed in the calculated dipole moments of hydrocarbons. Indeed, the calculated μ for **1** is 1.29 D, while it has been estimated to be 2.2 D.[2]

The interannular distances collected in Table I show that $d_{90} > d_0$ and both d_0 and d_{90} invariably increase when $\delta\Delta H_f$ diminishes, d_{90} showing the more rapid increase. The fact that no X-ray determination of an aza analogue of sesquifulvalene was known when these MNDO calculations were carried out is noteworthy. Based only on the results in Table I, the C–C interannular bond length could be too short in this class of molecules, and everything seems to indicate that this distance is of crucial importance in these structures for predicting the dipolar moment values. Thus, for compound **16** at τ = 0° and the fixed C–C interannular bond length d = 1.450 Å, the calculated dipolar moment value is 8.55 D, in agreement with the experimental value (see Figure 3 and Table VI). Furthermore, when one MNDO SCF-MO was done for 2-(1-pyridino)benzimidazolate (**23**) on a geometry equal to the X-ray data,[6] the calculated and experimental dipole moment values agree perfectly (10.44 and 10.33 D, respectively).

In the light of the available theoretical (MNDO SCF-MO method[14]) and experimental data for the aza analogues of sesquifulvalene of type **8** (C–C bond) in which resonance forms (**8A** ↔ **8B**) are possible, the C–C interannular bond length may be partially responsible for the low dipole

(15) Buncel, E. In *Carbanions: Mechanistic and Isotopic Aspects*; Elsevier: Amsterdam, 1975.
(16) Catalán, J.; Abboud, J. L. M.; Elguero, J. *Adv. Heterocycl. Chem.* **1987**, *41*, 187.
(17) Crabtree, J. H.; Bertelli, D. J. *J. Am. Chem. Soc.* **1967**, *89*, 5384.
(18) Castellanos, M. L.; Olivella, S.; Roca, N.; De Mendoza, J.; Elguero, J. *Can. J. Chem.* **1984**, *62*, 687.

Scheme I[a]



[a] Reagents and conditions: (i) MeI in anhydrous acetone, reflux; Bu^{t}Br, Bu^{t}I, and $nC_{10}H_{21}Br$ in dimethylformamide at 85 °C; (ii) anion-exchange Amberlite resin IRA-401 (OH^- form).[6] Overall yields: 16–19 > 65% and 20–22 > 43%.

Table II. Physical Data of 1-Alkyl-4-azolylidene-1,4-dihydropyridines 16–22 and Their Corresponding 1-Alkyl-4-azolylpyridinium Salts 27–33

compd[a]	azolyl or azolylidene	alkyl	method	reactn time (h)	yield[b] (%)	mp (°C)[c] (solvent)
27	1*H*-benzimidazol-2-yl	Me	A	3	88	266–8 (*d*)
28	5,6-dimethyl-1*H*-benzimidazol-2-yl	Me	A	4	80	269–70 (*d*)
29	5,6-dimethyl-1*H*-benzimidazol-2-yl	nC_4H_9	B	12	88	208–9 (*e*)
30	1*H*-benzimidazol-2-yl	$nC_{10}H_{21}$	B	4	98	80 (*f*)
31	5-methyl-1*H*-pyrazol-3-yl	Me	A	4	93	248 (*f*)
32	5-methyl-1*H*-pyrazol-3-yl	nC_4H_9	C	5.5	80	106.7 (*g*)
33	5-methyl-1*H*-pyrazol-3-yl	$nC_{10}H_{21}$	B	4	60	*h*
16	benzimidazolyl-2-idene	Me	D		99	255 (*i*)
17	5,6-dimethylbenzimidazolyl-2-idene	Me	D		99	283–4 (*i*)
18	5,6-dimethylbenzimidazolyl-2-idene	nC_4H_9	D		98	237–8 (*i*)
19	benzimidazolyl-2-idene	$nC_{10}H_{21}$	D		99	222–3 (*j*)
20	5-methylpyrazolyl-3-idene	Me	D		99	205 (*i*)
21	5-methylpyrazolyl-3-idene	nC_4He	D		98	160–1 (*j*)
22	5-methylpyrazolyl-3-indene	$nC_{10}H_{22}$	D		95	*k*

[a] Satisfactory analytical data (±0.4% for C, H, N) were obtained for all new compounds. [b] Yields were not optimized. [c] Some pyridinium salts have been described: 27, mp 270–1 °C (ref 19); 28, mp 303–4 °C (ref 19); 31, mp 252–3 °C (ref 35); 32, mp 211–2 °C (Br^-), mp 195–6 °C (Cl^-) (ref 35). [d] Ethanol. [e] Methylene chloride/ethyl acetate (1:1). [f] Ethyl ether. [g] 2-Propanol/tetrafluoroboric acid. [h] Oily compound. [i] 70% ethanol. [j] Acetonitrile. [k] Inestable oily compound, air- and thermal-sensitive.

moments (see Table I and Figure 3) and for the aforementioned high rotational barriers calculated for these molecules.

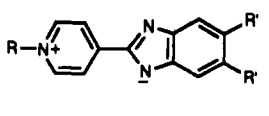
The present theoretical evaluation of 1-alkyl-4-azolylidene-1,4-dihydropyridines 16–22 has revealed that these compounds show an intermediate behavior between an olefin (8A) and a betaine (8B). More interestingly, this behavior is linked to the torsion interannular angle. The olefinic character appears in the $\tau = 0°$ conformation with its relatively short interannular distance and relatively low dipole moment. The betaine character explains the low rotational barriers and the very high dipole moment of the $\tau = 90°$ conformation. Two possibilities are feasible for increasing the betaine character of 4-azolylidene-1,4-dihydropyridines: the use of ortho steric effects to increase the angle of torsion to obtain more betaine character (higher dipole moments and chemical reactivity) or use of dipolar aprotic solvents to stabilize the betaine with a concomitant increase of the torsion angle.

Finally, it had been possible to obtain suitable single crystals of 1-methyl-4-benzimidazolylidene-1,4-dihydropyridine (16) and the X-ray diffraction study[8] has shown that the torsion angle between the rings is ≤2.5° and the interannular bond length is 1.448 Å. It is now possible to check the MNDO data obtained with this novel class of aza analogues of sesquifulvalene with a betaine character (8). The MNDO data for 16 are shown in Figure 3. For an interannular distance of 1.450 Å the μ_{calcd} is 8.55 D, with μ_{exp} = 9.03 D (d = 1.448 Å).

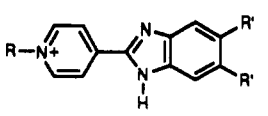
Synthesis. The 1-alkyl-4-benzimidazolyl-2-idene-1,4-dihydropyridines 16–19 and 1-alkyl-4-(5-methylpyrazolyl-3-idene)-1,4-dihydropyridines 20–22 were prepared by a three-step procedure (Scheme I). First, 2-(4-pyridyl)-1*H*-benzimidazoles 24 and 25 and 5-methyl-3-(4-pyridyl)-1*H*-pyrazole (26) were obtained by standard methods[5] (see Experimental Section). N-Alkylation under neutral conditions gave the 1-alkyl-4-(1*H*-benzimidazol-2-yl)pyridinium salts 27–30 and 1-alkyl-4-(5-methyl-1*H*-pyrazol-3-yl)pyridinium salts 31–33, which were deprotonated by using an anionic (OH^- form) ion-exchange resin. The new aza analogues of sesquifulvalene 16–22 were obtained. The physical data of compounds 16–22 and their corresponding 1-alkyl-4-azolylpyridinium salts 27–33 are listed in Table II.

Spectroscopic Methods. 2-(4-Pyridinyl)-1*H*-benzimidazoles 24 and 25 were previously studied by ^1H and

Table III. ^1H and ^{13}C NMR Spectra Data of 1-Alkyl-4-benzimidazolyl-2-idene-1,4-dihydropyridines 16–19 and Their Corresponding 1-Alkyl-4-benzimidazol-2-ylpyridinium Salts 27–30[a]

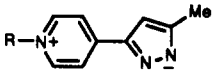


16B - 19B

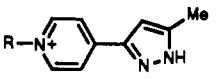


27 - 30

	R	R'
16, 27	Me	H
17, 28	Me	Me
18, 29	nBut	Me
19, 30	$nC_{10}H_{21}$	H



20B - 22B



30 - 32

	R
20, 30	Me
21, 31	nBut
22, 32	$nC_{10}H_{21}$

	16	27[b]	Δδ[c]	17	28[b]	Δδ[c]	18	29	Δδ[c]	19	30	Δδ[c]
H-4′,7′	7.61	7.66	−0.05	7.23	7.44	−0.21	7.28	7.44	−0.16	7.67	7.75	−0.08
R-5′, R-6′	7.10	7.30	−0.20	2.25	2.33	−0.08	2.28	2.30	−0.02	7.06	7.29	−0.23
NH		d			d			d			d	
H-2,6	8.81[e]	9.03[f]	−0.22	8.55[g]	9.01[h]	−0.46	8.58[i]	9.21[j]	−0.63	8.21[k]	8.69	−0.48
H-3,5	8.61[e]	8.52[f]	+0.09	8.42[g]	8.53[h]	−0.11	8.47[i]	8.65[j]	−0.18	7.42[k]	8.69	−1.27
R	4.27	4.34	−0.07	4.14	4.33	−0.19	4.31	4.60	−0.29	4.25 (2 H)	4.87 (2 H)	−0.62
							1.85	1.91	−0.06	1.84 (2 H)	1.97 (2 H)	−0.13
							1.29	1.30	−0.01	1.22 (14 H)	1.21 (14 H)	−0.01
							0.91	0.89	+0.02	0.89 (3 H)	0.85 (3 H)	+0.04
C-2′	151.0	143.5	+7.5	d	143.8		151.7	144.6	+7.1	153.6	139.5	+14.1
C-4′,7′	117.7	116.3	+1.4	118.3	115.9	+2.4	118.2	116.1[l]	+2.1	118.4	116.3	+2.1
C-5′,6′	122.6	124.3	−1.7	128.4	133.5	−5.1	128.5	133.9	−5.4	121.2	124.6	−3.4
C-3′a,7′a	145.4	139.6	+5.8	d	138.6		142.6	138.6[l]	+0.4	148.2	144.2[n]	+4.0
Me-C-5′,6′				20.6	20.1	+0.5	20.3	20.2	+0.1			
C-2,6	145.0	145.9	−0.9	143.7	145.7	−2.0	142.6	145.2	−2.6	140.9	144.4	−4.4
C-3,5	121.8	123.1	−1.3	121.3	122.7	−1.4	121.4	123.3	−1.9	122.6	124.1	−1.8
C-4	148.6	145.4	+3.2	d	144.6		148.4	144.0[m]	+4.4	150.7	143.9[n]	+6.8
R	47.0	47.8	−0.8	46.1	47.5	−1.4	58.5	60.1	−1.6	59.4[o]	61.3[p]	−1.9
							32.2	32.7				
							18.7	19.0				
							13.1	13.6				

[a] In DMSO-d_6, except for compounds 19 and 30 ($CDCl_3$). For the AA′BB′ system, δH corresponds to the center of the multiple signal. [b] Reported in ref 19. [c] Δδ, observed chemical shift difference between the benzimidazolylidene-1,4-dihydropyridines 16–19 and their benzimidazolylpyridinium salts 27–30. [d] Signal not observed. [e] J_{AB} = 6.5 Hz. [f] J_{AB} = 6.6 Hz. [g] J_{AB} = 6.8 Hz. [h] J_{AB} = 6.6 Hz. [i] J_{AB} = 7.0 Hz. [j] J_{AB} = 5.8 Hz. [k] J_{AB} = 6.0 Hz. [l] Broad signal due to prototropic annular tautomerism. [m] HETNOE $^{13}C\{^1H\}$ on irradiation at δH 8.66 ppm [n = 0.937 (93.7%)]. [n] Signals can be interchanged. [o] 59.4; 31.6; 29.9; 21.1; 28.5; 25.7; 22.4; 13.8. [p] 61.3; 34.7; 31.5; 29.1; 29.0; 28.7; 25.8; 22.2; 13.7.

^{13}C NMR spectroscopy,[19] and the asymmetric pyrazole nucleus of 5-methyl-3-(4-pyridyl)-1*H*-pyrazole (**26**) has been assigned as the 5-methyl tautomer via two-bond heteronuclear selective NOE difference[20] and by the chemical shift of C–Me at 10.8 ppm characteristic of 5-methylpyrazoles[21] (see Figure 4, supplementary material).

The ^1H and ^{13}C NMR spectra for 1-alkyl-4-benzimidazolyl-2-idene-1,4-dihydropyridines **16–19** and 1-alkyl-4-(5-methylpyrazolyl-3-idene)-1,4-dihydropyridines **20–22** were vital for structural proof and also for providing evidence of charge distribution, which clearly indicated the dipolar resonance forms **16B–22B**.

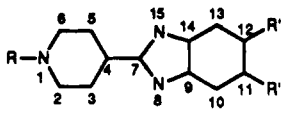
The ^1H and ^{13}C NMR parameters of benzimidazole derivatives **16–19** and **27–30**, as well as of pyrazole derivatives **20–22** and **31–33**, are given in Tables III and IV, respectively; additional ^{13}C NMR experiments allowed assignment of all carbon resonances (Table V, supplementary material). For compound **20**, a NOE experiment revealed that the molecule is coplanar, in good agreement with the calculated minimized torsion angle between the two rings (see Tables I and V). Comparison of the ^1H and ^{13}C chemical shifts, in $(CD_3)_2SO$ and $CDCl_3$, of 1-alkyl-4-azolylidene-1,4-dihydropyridines **16–22** with data reported for quaternary pyridinium compounds,[22] anionic species in the azole series, and the valuable data obtained for mesomeric betaines of the azinium azolate class[6] **8** left no doubt that these compounds had a betaine character and that the NMR signals correspond to their dipolar resonance forms **16B–22B**.

Comparison of ^1H and ^{13}C chemical shifts in DMSO-d_6 of two 2-(1-pyridinio)benzimidazolate mesomeric betaines **9** (C–N interannular bond, only a dipolar form is possible)[6a] and their corresponding analogues 1-alkyl-4-benzimidazolylidene-1,4-dihydropyridines **16B** and **18B** clearly show the large charge separation in both series (see Figure 5, supplementary material). Thus, the benzimidazolate ring showed similar proton and carbon-13 chemical shifts in both series (**9** and **8A** ↔ **8B**), which provides evidence of the anionic species in solution for compounds **16B–19B**.

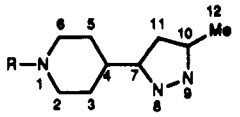
As mentioned before, 1-alkyl-4-azolylidene-1,4-dihydropyridines **8A** ↔ **8B** should be considered as a novel class of push–pull ethylenes for which barriers of rotation about the interannular C=C bond in **8A** should be considerably lower due to the presence of a 1,4-dihydropyridine moiety (a potentially heteroaromatic ring) attached to one end of the olefinic bond. Thus, the dipolar

(19) Marzin, C.; Peek, M. E.; Elguero, J.; Figeys, H. P.; Defay, N. *Heterocycles* **1977**, *6*, 911.
(20) Sanchez-Ferrando, F. *Magn. Reson. Chem.* **1985**, *23*, 185.
(21) Elguero, J. In *Comprehensive Heterocyclic Chemistry*; Katritzky, A. R., Rees, C. W.; Eds.; Pergamon Press: Oxford, 1984; Vol. 5, p 167.
(22) (a) Boyd, G. V.; Ellis, A. W.; Harms, M. D. *J. Chem. Soc. C* **1970**, 800 and references therein. (b) Batterham, T. J. In *NMR Spectra of Simple Heterocycles*; Wiley: New York, 1973; p 57.

Table IV. ^1H and ^{13}C NMR Spectral Data of 1-Alkyl-4-(5-methylpyrazolyl-3-indene)-1,4-dihydropyridines 20–22 and Their Corresponding 1-Alkyl-4-(5-methyl-1*H*-pyrazol-3-yl)pyridinium Salts 31–33[a]



16B - 18B



20B - 21B

	20	31	$\Delta\delta^b$	21	32	$\Delta\delta^b$	22	33	$\Delta\delta^b$
H-4′	6.56	6.92	−0.36	6.44[c]	6.93	−0.38	6.23	6.36	−0.13
Me	2.23	2.29	−0.06	2.22	2.30	−0.08	2.34	2.35	−0.01
NH		13.30			13.45			9.46	
H-2,6	8.38[d]	8.90[e]	−0.52	8.47[f]	8.91[j]	−0.44	7.91[h]	8.95[i]	−1.04
H-3,5	7.98[d]	8.31	−0.33	7.97[f,j]	8.34[g]	−0.37	7.66[h]	8.03	−0.37
R	4.07	4.31	−0.24	4.25	4.51	−0.26	4.00 (2 H)	4.60 (2 H)	−0.60
				1.73	1.84	−0.09	1.65 (2 H)	1.88 (2 H)	−0.23
				1.20	1.25	−0.05	1.23 (14 H)	1.21 (14 H)	−0.03
				0.87	0.89	−0.02	0.84 (3 H)	0.81 (3 H)	+0.02
C-3′	144.9	145.0	−0.1	145.1	145.8	−0.7			
C-4′	104.5	104.8	−0.4	104.7	105.0	−0.3			
C-5′	147.1	141.7	+6.6	148.5	141.9	+6.6			
C-Me	12.9	10.6	+2.3	13.7	10.6	+3.1			
C-2,6	143.9	145.2	−1.3	142.8	144.8	−2.0			
C-3,5	119.1	121.7	−2.6	118.7	122.4	−3.7			
C-4	149.3[h]	147.7[l]	+1.6	149.9	148.8	+1.1			
R	45.7	47.3	−1.5	58.1	59.9	−1.8			
				32.6	32.8				
				19.0	19.1				
				13.6	13.5				

[a] In DMSO-d_6, except for compounds 22 and 33 ($CDCl_3$). For the AA′BB′ system, δH corresponds to the center of the multiple signal. [b] Δδ, observed chemical shift difference between the pyrazolylidene-1,4-dihydropyridines 20–22 and their pyrazolylpyridinium salts 31–33. [c] Proton enhanced, NOE 29.3% on irradiation at 7.97 ppm. [d] J_{AB} = 6.9 Hz. [e] J_{AB} = 6.4 Hz. [f] J_{AB} = 6.9 Hz. [g] J_{AB} = 6.7 Hz. [h] J_{AB} = 5.0 Hz. [i] J_{AB} = 6.0 Hz. [j] Proton enhanced, NOE 16.1% on irradiation at 6.55 ppm. [k] By analogy with compound 21. [l] Assignation of signals by heteronuclear NOE $^{13}C\{^1H\}$.

canonical form 8B can make an important contribution to the ground state due to the stability of the aromatic electronic structure: the pyridinium ion and the azolate ions (see Theoretical Study). In general, reported rotational barriers of potentially aromatic systems[23a,c] and the derivatives of biphenyl[23b] barriers are rather low ones (ca. 50 kJ·mol^{-1}).

As to experimentally determining rotational barriers, the pyrazole derivatives 20–22 can serve as models for evaluation of these barriers. A serious additional problem is, however, present: the elevated lack of solubility of compounds 20 and 21 in low-melting solvents as well as the lack of stability of the product 22. The ^1H NMR spectrum of a saturated solution of 20 in $(CD_3)_2CO$ has been recorded at 263 K; the aromatic protons of the pyridinium ring appeared as a well resolved AA′BB′ system (δH-3 = δH-5), indicating that this temperature is well above the decoalescence temperature. Unfortunately, below about 263 K it was not possible to record the proton NMR spectrum of compound 20, because 2 mg in 1 mL crystallizes. This result corresponds to a rotational barrier of below 53.1 kJ·mol^{-1}.[24]

The 1-butyl-4-(5-methylpyrazolyl-3-idene)-1,4-dihydropyridine (21) invariably crystallized before reaching decoalescence temperature. In spite of this, it has been possible to record the proton NMR spectrum (80 MHz) of a saturated solution of 21 in deuterated acetone at 243 K (the lowest temperature that could be achieved), and the AA′BB′ (δH-3 = δH-5) system, corresponding to the dipolar form of the pyridinium ring 21B, could be clearly seen, indicating that at 243 K the decoalescence was still distant. The rotation barrier may thus be situated at below 49.1 kJ/mol.[24] (See Figure 6, supplementary material.)

The majority of the 1-alkyl-4-azolylidene-1,4-dihydropyridines showed intense molecular ions in their electron-impact mass spectra: for compounds 16 and 18 they were base peaks and were relatively abundant in the range 45–95% for the others (17, 19–22).

Table VI. Dipole Moments and Polarization Data in Dioxane at 298 K for 1-Alkyl-4-azolylidene-1,4-dihydropyridines 16, 17, and 21 and for Imidazolium Benzimidazolate Inner Salts 35, 45, and 46

compd	α	β	R_{MD}	$P_{2\infty}$	μ (D)
16	a	a	a	a	9.03
17	49.93	0	72.33	2020.82	9.71
21	51.18	0	64.23	1877.87	9.42
35	80.26	≈0	54.27	2677.82	11.33
45	46.78	≈0	68.21	1921.51	9.52
46	39.00	≈0	77.51	1801.39	9.18

[a] Data not available.

Dipole Moments. The experimental dipolar moment values extrapolated to infinite dilution in dioxane at 298 K of the anhydrous 1-alkyl-4-azolylidene-1,4-dihydropyridines 16, 17, and 21 were high in the range of 9.0–9.7 D (see Theoretical Study, Figures 2 and 3), which implies a substantial charge separation, and the values extrapolated to infinite dilution are given in Table VI.

Azolium Azolate Inner Salts (10). Theoretical Study. MNDO//MNDO calculations[14] have been performed with full optimization of all geometric variables for

(23) (a) Oki, M. In *Applications of Dinamic NMR Spectroscopy to Organic Chemistry*; VCH Publishers: FL, 1985; Chapter 3, pp 125–139. (b) Reference 23a, Chapter 4. (c) Gallo, R.; Roussel, Ch.; Berg, U. *Adv. Heterocycl. Chem.* **1988**, *43*, 253.

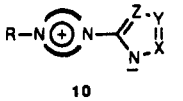
(24) Values of rotational barriers ($\Delta G_{T_c}^{\ddagger}$) for compounds 20 and 21 were calculated according to the method of ref 25, considering a rotamer population 1:1. Frequency separation at slow rotation of the two coalescing lines H-3′ and H-5′ (pyrazole ring protons) has been estimated to be of 0.7 ppm on the basis of the value established in the case of *N*-arylazoles.[26]

Table X. τ_{min}, Dipolar Moments, Interannular Distance, and Bond Order of Azolium Azolate Inner Salts 34–44

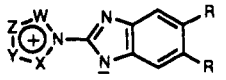
compd	τ_{min}	μ^a	interannul distance[b]	bond order[b]
34	52.5	10.09	1.422	0.905
35	0.0	12.30	1.413	0.938
36	1.7	12.82	1.415	0.934
37	31.4	12.21	1.419	0.921
38	45.8	8.52	1.418	0.910
39	0.1	12.52	1.412	0.954
40 anti	42.8	12.15	1.406	0.957
40 syn	−37.7	11.96	1.405	0.956
41	1.3	9.12	1.404	0.973
42 anti	11.0	11.93	1.405	0.957
42 syn	−5.3	11.64	1.404	0.962
43	14.5	14.76	1.403	0.950
44 anti	2.0	11.86	1.404	0.960
44 syn	19.2	11.80	1.404	0.957

[a] In Debye; 1 D = 3.34 ~ 10^{-30} C m. [b] In angstroms.

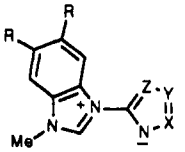
11, azolium azolate betaines **34–44** and the results are given in Tables X and XI (supplementary material).



10



34 - 39



40 - 44

Type A

	X	Y	Z	W	R
34	NMe	CH	CH	CH	H
35	CH	NMe	CH	CH	H
36	CH	NMe	CH	CH	Me
37	CH	NMe	(CH=CH)$_2$		H
38	CH	N	CH	NMe	H
39	CH	NMe	CH	N	H

Type B

	X	Y	Z	R
40	N	CH	CH	H
41	CH	CH	N	H
42	N	CH	N	H
43	N	N	N	H
44	N	CH	N	Me

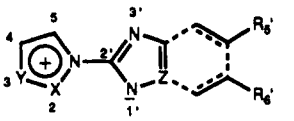
The mesomeric betaine character of the studied compounds is well reflected by the bond order of the interannular C–N bond (around 1.0) and this bond does not change with the system planarity. The results in Table I can be qualitatively discussed as follows. Compounds are divided into two main types depending on the charge carrying the benzimidazole moiety: type A (compounds **34–39**) and type B (compounds **40–44**).

The presence of two methyl groups in the benzene ring does not appreciably modify the calculated dipole moment, either in type A (compare **35** with **36**) or in type B (compare **42** with **44**). When the positive moiety of type A compounds has an *N*-Me group in the ortho position, the dipole moment is significantly smaller. It is worth noting here that the N atom is not responsible for this (note the μ_{calcd} for **39**). In contrast, the position of the N atoms in the negative moiety of type B is important for the magnitude of μ. The calculated dipole moment is larger when the system is a pyrazolate than when it is an imidazolate (compare **40** to **41**). Moreover, the number of N atoms also affects the dipolar moment value. Compound **43**, having four N atoms in its negative moiety, presents the largest calculated μ, but there is almost no difference between **40** and **42** (or **44**).

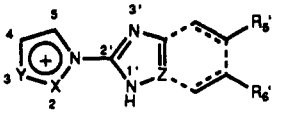
Concerning the interannular linkage between the azolium and azolate moieties, the minimized torsion angle (τ_{min}) is in the range of 0° to 52°, which shows that the preferred conformation around the central C–N bond depends on the nature of the ortho interactions of the azolium and/or azolate rings.[6a,18] Their energy barriers for free rotation around the interannular bond are 6.33–7.00 kJ/mol. The central C–N bond is of crucial importance for predicting the dipolar moments and the calculated values of the interannular bond lengths (1.403 to 1.422 Å) and bond order (0.905 to 0.973) are underestimated by MNDO.[14] A calculated dipolar moment value of 13.26 D is obtained using the X-ray determined bond lengths of **35** (see below).

Finally, the electronic structure of azolium azolate inner salts **10** is well reflected in their calculated dipolar moments, which are in the range of 8.52 to 14.76 D (see Dipole Moments).

Table XII. Selected ^{1}H NMR Spectroscopic Data of Compounds 34–36 and 45–57[a]



34-36 , 45-49



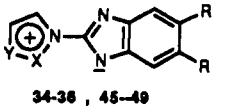
50 - 57

X, Y, Z: = CR-; -NR-; = N-

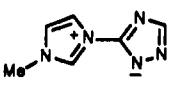
compd	H-2	H-3	H-4	H-5	H-4′,7′	H-5′,6′
34		8.81[b]	7.03	9.06	7.61	7.12
35	9.86		7.77[c]	8.34	7.47	6.99
36	9.73		7.72	8.23	7.17	
45	10.04		7.82	8.39	7.48	6.98
46	9.83		7.75	8.25	7.19	
47[d]	10.00		7.80	8.27	7.20	
48	9.86		7.79	8.26	7.19	
48[d]	9.10		6.46	7.81	7.15	
50		9.16[e]	7.27	9.31	7.74	7.33
51	10.28		8.06	8.73	7.61	7.28
52	10.17		7.99	8.65	7.39	
53	10.46		8.20	8.79	7.64	7.29
54	10.46		8.16	8.76	7.35	
55[d]	10.16		7.83	8.43	7.13	
56[d]	10.66		7.36	8.21	7.08	
					H-4′	
49	9.70		7.81	8.09	7.81	
57	10.12		8.17	8.30	8.88	

[a] DMSO-d_6. [b] On radiation at 4.47 ppm, N-Me showed NOE (17.4%). [c] On radiation at 3.92 ppm, N-Me showed NOE (8.7%). [d] $CDCl_3$. [e] On radiation at 4.43 ppm, N-Me showed NOE (17%).

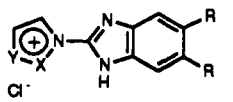
Spectroscopic Methods. Eight mesomeric betaines of the azolium azolate type **34–36, 45–49**, and their corresponding 1-alkyl-1*H*-benzimidazol-2-ylazolium salts **50–56** and 1-methyl-3-[1*H*-1,2,4-triazol-3(5)-yl]imidazolium salt **57** were prepared[7b] and in this article we described their spectroscopic data.



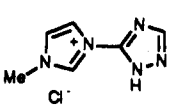
34-36 , 45-49



49



50-56



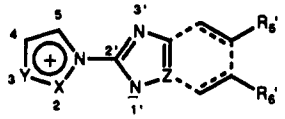
57

	X	Y	R
34 , 50	NMe	CH	H
35 , 51	CH	NMe	H
36 , 52	CH	NMe	Me
45 , 53	CH	NnBut	H

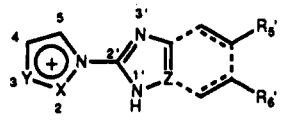
	X	Y	R
46 , 54	CH	NnBut	Me
47 , 55	CH	NCH$_2$Ph	Me
48 , 56	CH	NnC$_{10}$H$_{21}$	Me

^{1}H and ^{13}C NMR data for betaines **34–36** and **45–49** were very important for structural proof of their highly dipolar structure. Selected ^{1}H and ^{13}C chemical shifts of betaines **34–36, 45–49**, and their corresponding *N*-azolylazolium salts **50–57** are shown in Tables XII and XIII (see Tables XIV and XV in supplementary material).

Table XIII. Selected ^{13}C NMR Spectroscopic Data of Compounds 34–36 and 45–57[a]



34-36 , 45-49



50 - 57

X, Y, Z: = CR -; - NR -; = N -

compd	C-2	C-3[b]	C-4[c]	C-5[d]	C-2′	C-3′a,7′a
34		139.7	107.7	136.6	147.9	143.3
35	134.1		123.8	119.1	148.9	144.2
36	133.5		123.6	118.95	150.0	144.3
45	133.3		122.5	119.4	150.8	145.8
46	132.7		122.1	119.0	150.2	144.5
47[e]	132.8		122.2	119.4	150.1	144.6
48	132.7		122.1	119.0	150.1	144.5
50		142.1	108.8	138.9	138.4	137.1
51	136.1		124.8	119.8	140.9	137.1
52	135.9		124.6	119.8	140.1	135.6
53	135.7		123.7	120.2	141.2	137.1
54	135.3		123.4	119.9	141.0	135.6
55	135.4		123.4	120.5	140.3	135.8
56	135.25		123.4	119.9	140.0	135.5
					C-2′	C-4′
49	136.1		124.1	119.2	153.1	150.3
57	135.7		125.1	119.4	153.0	145.6

[a] DMSO-d_6. SFORD experiments at a moderate (DP = 40H) decoupler power setting showed the following C–H decoupled carbons upon irradiation at the frequencies indicated in brackets. [b] C-3 (δH_3 = 8.74) (34) and (δH_3 = 9.04) (50) [c] C-4 (δH_4 = 7.77) (35). [d] C-5 (δH_3 = 8.28) (35). [e] $CDCl_3$.

The chemical shifts of the azolate ring protons were shifted to lower frequencies compared with the protons of the corresponding *N*-azolylazolium salts,[27] and the δC values of the carbon atoms were in excellent agreement with data reported for anionic species in the azole series and the useful comparative data for pyridinium azolate inner salts.[6a] Both the ^1H and ^{13}C NMR chemical shifts of the quaternary azolium ring accord very well with data reported for pyrazolium derivatives[29] and the not less frequently reported imidazolium salts.[30] These spectral properties indicate the high electron density on the azolate ring of **34–36** and **45–49**.

The hydrogen atoms H_4 and H_5 of the imidazolium derivatives and H_3 and H_5 of the pyrazolium derivatives were unambiguously assigned by NOE experiments (see Table XIV); the results are consistent with the ^1H chemical shifts previously reported.[28,29] As to the ^{13}C NMR signals of betaines **34–36, 45–49**, and their salts **50–57** (Table XV), it is particularly noteworthy among the data that in imidazolium derivatives the chemical shifts of C_4 and C_5 were assigned by intermediate power selective decoupling of the corresponding protons (SFORD technique) previously assigned by NOE experiments. To the best of our knowledge, this is the first unambiguous assignment of C_4 and C_5 atoms in an imidazolium quaternary nucleus.

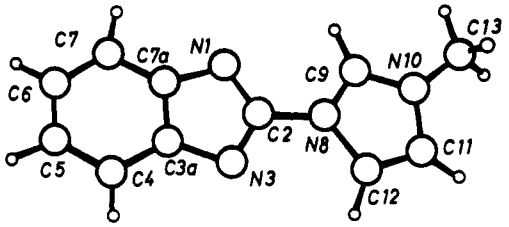


Figure 7. Computer-generated perspective drawing of **35**.

The majority of the mesomeric betaines **34–36** and **45–49** showed an intense molecular peak in their electron-impact mass spectra. For betaines **35, 36, 45–47**, and **49** they were the base peaks and for **34** and **48** the relative abundance was ca. 64%.

Dipole Moments. In our previous work[6a] on heterocyclic mesomeric betaines of pyridinium azolate, it was pointed out that coplanar inner salts (i.e., compound **23**) were strongly associated when the weight fraction was greater than 0.0002, and their dipole moment values tend to move to zero when concentration increases, indicating a head-to-tail orientation to form nonpolar dimers. This orientation of **23** was further confirmed in its unit cell by X-ray analysis.

In the present study, different dipole moment measurements were measured in three examples of azolium azolate mesomeric betaines **10**. Owing to the perturbing influence of self-association[31] (nonpolar dimers), extreme dilution was required for experimental determination of the dipole moments in anhydrous dioxane at 293 K of the anhydrous betaines **35, 45**, and **46** (See Experimental Section), and their values were in the range of 9.18 to 11.33 D.

Although the dipole moments were extrapolated to infinite dilution, the effect of self-association was not completely eliminated, with consequent decrease of the measured values. The quasicoplanar structures **35, 45**, and **46** were strongly associated when $\omega \geq 0.0003$ and their dipole moment values decrease with increasing concentration (see below and Figure 8).

For betaine **35**, the dipole moment was calculated to be 12.30 D and the experimental value was 11.35 D (See Table VI and X). Thus, the μ_{calcd} showed that the betaine structure of **35** and with regard to the μ_{exp} is overestimated.[32] The implication of this result—μ_{calcd} versus μ_{exp}—should take into account the possible dominance of self-association even when this was substantially reduced (see Experimental Section). Solution of this contraversy[33] is beyond the scope of the present work. Nonetheless, both the calculated and the experimental dipole moment data of **35** showed a large charge separation, in keeping with a high dipolar structure for organic molecules excluding polymers (natural or synthetic).

X-ray Data. A single-crystal X-ray diffraction analysis of 2-(3-methyl-1-imidazolium)benzimidazolate inner salt

(25) Martin, M. L.; Delpuech, J.-J.; Martin, G. J. In *Practical NMR Spectroscopy*; Heiden, Ed., Londres: 1980; p 297.

(26) Elguero, J.; Jacquier, R.; Mondon, S. *Bull. Chem. Soc. Fr.* **1970**, 1346.

(27) The azolium azolate inner salts re-formed the *N*-azolylazolium salts with acids: ^1H NMR spectra of the mesomeric betaines were measured in $(CD_3)_2SO$ with 10% TFAA and the chemical shifts were similar to those observed for their corresponding *N*-azolylazolium salt. The *N*-azolylazolium trifluoroacetates reversibly regenerated the betaine on treatment with 25% ammonium hydroxide.

(28) The numbering system for NMR assignments of the azolium azolate mesomeric betaines in this paper is not the same as the IUPAC numbering system to facilitate comparison of spectroscopic data.

(29) Hoz, A. de la; Pardo, C.; Elguero, J.; Fruchier, A. *Magn. Reson. Chem.* **1989**, *27*, 603 and references therein.

(30) (a) Claramunt, R. M., Elguero, J.; Meco, P. *J. Heterocycl. Chem.* **1983**, *20*, 1245. (b) Claramunt, R. M.; Elguero, J. *Anal. Quim.* **1986**, *82*, 162.

(31) (a) Fayet, J.-P.; Vertut, M.-C.; Cativiela, C.; Melendez, E.; Elguero, *J. Bull. Soc. Chem. Fr.* **1984**, 233. (b) Beak, P.; Covington, J. B.; White, J. M. *J. Org. Chem.* **1980**, *45*, 1347. (c) Beak, P.; Covington, J. B.; Smith, S. G.; White, J. M.; Zeigler, J. M. *J. Org. Chem.* **1980**, *45*, 1354.

(32) (a) Betaine **35**: μ_{exp} = 11.33 D; μ_{calcd} 12.30 D; μ_{calcd} = 13.26 D using the X-ray determined bond lengths. Compared with data for 2-(1-pyridinio)benzimidazolate inner salt (**23**) (Figure 3). (b) MNDO calculated dipole moments[14b] are usually smaller than those obtained experimentally.

(33) Evaluation of the effect of self-association for reliable interpretation of solution data and to carry out an extensive theoretical study by semiempirical methods (i.e., MNDO and AM1).

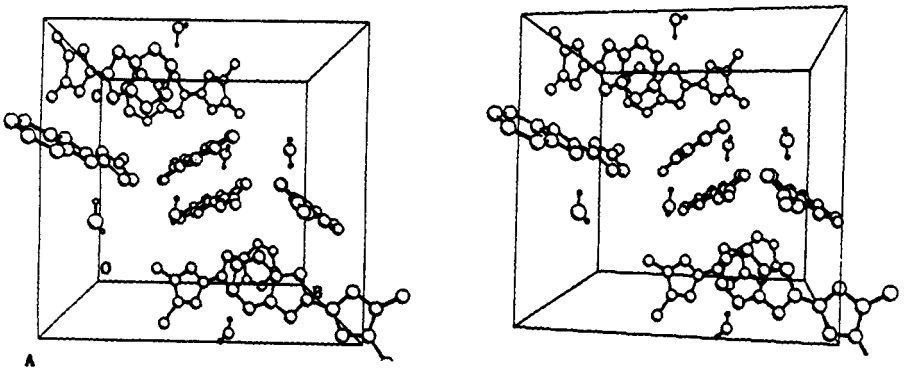


Figure 8. Unit cell packing diagram (stereo pair) for compound **35**.

(**35**) shows that the unit cell contains two symmetry-independent molecules. The first molecule, hereafter called (A), is completely ordered; the second one (B) is indistinctly found in the two different orientations. Figure 7 shows molecule A with the corresponding atom numbering. The atoms of molecule B are named by adding a'. The disorder becomes evident during refinement from the excessively high temperature coefficient of C(13') and the apparition of C(14') bound to C(11'). The introduction of an occupation factor of $^2/_3$ for C(13') and $^1/_3$ for C(14') yields reasonable refined temperature coefficients. Hence, N(10') is occupied by $^2/_3$N + $^1/_3$C and C(11') by $^1/_3$N + $^2/_3$C.

The molecule **35** is quasicoplanar, the angle between the mean plane of the benzimidazole ring (rms distance 0.02 Å) and the mean plane imidazole ring (rms distance 0.003 Å) 10.6° for molecule A. The C(2)–N(8) interannular bond length is 1.431 (4) Å. The benzimidazole ring may be considered as symmetrical within experimental error, and the mean values are close to those described for related heterocycles.[6a,8] In the case of molecule B, the angle between the mean plane of the benzimidazole ring (rms distance 0.03 Å) and the mean plane of the imidazole ring (rms distance 0.005 Å) is 3.8°. The C(2')–N(8') bond length is 1.432 (4) Å. Selected bond lengths (Å) for molecule A and molecule B are given in Table XVI, and further details are provided in the supplementary material. Due to the disorder, the difference between the two bond lengths N(8)–C(9) = 1.33 and N(8)–C(12) = 1.39 Å of the asymmetrical ring is larger than between the N(8')–N(9') = 1.34 and N(8')–C(12') = 1.35 Å.

The crystal structure is built by alternating layers of the type A and type B molecules. The layers are parallel to (001) and the arrangement of the two types of molecules within each layer is completely different. As shown in Figure 8, only the type A molecules are placed pairwise in a head-to-tail orientation (shortest contacts between the molecules forming one pair: C(11)···N(1) = 3.41 Å; C(12)···N(1) = 3.43 Å; C(7a)···C(11) = 3.46 Å). This could be an explanation of why only one type of molecules is disordered.

The X-ray study indicates that this compound forms a dihydrate. The water molecules are predominantly placed between the layers. The shortest contacts and H-bonds involving water molecules are O(1)–H···N(1) = 2.87 (1) Å; O(1)–H···N(1') = 2.85 (1) Å; O(1)···C(12) = 3.41 (1) Å; O(2)–H···N(3) = 2.88 (1) Å, O(2)–H···O(1) = 2.79 (1) Å; O(2)···C(12') = 3.23 (1) Å.

Conclusions

To sum up, all the theoretical and experimental results on 1-alkyl-4-azolylidene-1,4-dihydropyridines **8A** ↔ **8B** are consistent with a betaine character for this class of aza analogues of sesquifulvalene. Thus, their spectroscopic data and large dipole moments favor the betainic canonical form **16B–22B**, which had been unambigously confirmed by the X-ray crystal structure[8] of 1-methyl-4-benzimidazolylidene-1,4-dihydropyridine (**16B**).

The theoretical and experimental study of azolium azolate mesomeric betaines **10** shows their highly dipolar structure, in agreement with data reported on closely related betaines of pyridinium azolate.[6a]

Table XVI. Selected Bond Lengths (Å) with Esds in Parentheses for Compound 35 (Molecules A and B)

molecule A		molecule B	
C2–N1	1.316 (4)	C2'–N1	1.303 (5)
C7A–N1	1.390 (4)	C7A'–N1	1.386 (5)
N3–C2	1.331 (4)	N3'–C2'	1.312 (5)
N8–C2	1.431 (4)	N8'–C2'	1.432 (5)
C3A–N3	1.396 (4)	C3A'–N3'	1.393 (5)
C4–C3A	1.396 (5)	C4'–C3A'	1.396 (6)
C7A–C3A	1.405 (5)	C7A'–C3A'	1.378 (5)
C5–C4	1.389 (6)	C5'–C4'	1.388 (7)
C6–C5	1.390 (6)	C6'–C5'	1.372 (7)
C7–C6	1.392 (7)	C7'–C6'	1.375 (6)
C7A–C7	1.388 (5)	C7A'–C7'	1.380 (5)
C9–N8	1.329 (4)	C9'–N8'	1.337 (5)
C12–N8	1.389 (4)	C12'–N8'	1.353 (5)
N10–C9	1.323 (5)	N10'–C9'	1.330 (5)
C11–N10	1.373 (5)	C11'–N10'	1.373 (5)
C13–N10	1.460 (5)	C13'–N10'	1.493 (7)
C12–C11	1.329 (5)	C12'–C11'	1.326 (5)
		C14'–C11'	1.365 (15)

Experimental Section

General Methods. Melting point (uncorrected): CTP-MP 300 hot-plate apparatus. IR (KBr disks): Perkin-Elmer 1430 spectrophotometer. ^{1}H NMR: Bruker AM-100 or Perkin-Elmer R-24B spectrometers (100 and 60 MHz, respectively). ^{13}C NMR: Bruker AM-100 Fourier transform spectrometer (25.1 MHz). NMR spectra were determined in dimethyl sulfoxide-d_6, and chemical shifts are expressed in parts per million (δ) relative to TMS as internal standard or the central peak of dimethyl sulfoxide-d_6. EIMS: Finnigan TSQ-70 and Hewlett-Packard 5988A spectrometers. TLC: Merck precoated silica gel 60 F_{254} plates. Solvent systems: A, diethyl ether–methanol (8:2); B, chloroform–methanol (8:2); C, diethyl ether–methanol (9.5:0.5); detection by UV light. Ion-exchange chromatography: Amberlite IRA-401 (OH^- form).[6a] If necessary the compounds were dried by overnight heating at 110 °C in a vacuum oven. Where microanalyses are indicated by symbols of the elements, the analytical results were within ±0.4‰ of the theoretical values; they were performed on a Carlo Erba 1106 analyzer by the Instituto de Química Bioorgánica, Barcelona, Spain.

Materials. 2-(4-Pyridyl)-1*H*-benzimidazole (**24**),[19] 5,6-dimethyl-2-(4-pyridyl)-1*H*-benzimidazole (**25**),[19] and 5-methyl-3-(4-pyridyl)-1*H*-pyrazole (**26**)[34] were prepared according to literature procedures. Mesomeric betaines of the azolium azolate type

(34) Fabrini, L. *Il Farmaco, Ed. Sc.* **1954**, *9*, 603.

34–36, 45–49, and their corresponding 1-alkyl-(1*H*-benzimidazol-2-yl)azolium salts **50–56** and 1-methyl-3-[1*H*-1,2,4-triazol-3(5)-yl]imidazolium salt **57** were prepared according to the companion paper.[7b]

Preparation of 1-Alkyl-4-(1*H*-benzimidazol-2-yl)-pyridinium Salts 27–30 and 1-Alkyl-4-(5-methyl-1*H*-pyrazol-3-yl)pyridinium Salts 30–33 (Table II). Method A. A solution of methyl iodide (1.24 mL, 20 mmol) in dry acetone (10 mL) was added dropwise at 0–5 °C to a stirred solution of 4-pyridylazoles **24**, **25**, or **26** (5 mmol) in dry acetone (150 mL) under an atmosphere of nitrogen. The reaction mixture was refluxed for the time specified in Table II. After cooling, the precipitate was filtered, washed with diethyl ether, and then recrystallized for compounds **27** and **28** while compound **31** was obtained pure (see Table II).

Method B. *n*-Butyl bromide (2.69 mL; 25 mmol) or *n*-decyl bromide (5.18 mL, 25 mmol) was added to a stirred solution of 4-pyridylazoles **24**, **25**, or **26** (5 mmol) in dimethylformamide (10 mL) under an atmosphere of nitrogen and then heated at 85–95 °C (bath temperature) for the time specified in Table II. Diethyl ether (150 mL) was added to the dimethylformamide solution and the precipitated **29** or **30** was filtered, washed with diethyl ether, and recrystallized (Table II).

The reaction mixture of **33** was washed with 3 × 15 mL portions of diethyl ether; the solutions were decanted from the oily and hygroscopic product, which was identified as pure **33** (see Table II).

Method C. *n*-Butyl iodide (5.35 mL, 47 mmol) was added to a stirred solution of 5-methyl-3-(4-pyridyl)-1*H*-pyrazole (**26**) in dry dimethylformamide (10 mL) under an atmosphere of nitrogen and was then heated at 85–95 °C (bath temperature) for 5.5 h. Diethyl ether (20 mL) was added to the reaction mixture; the solution was decanted from the oily product, which was washed with 3 × 10 mL portions of diethyl ether and then triturated with diethyl ether. The solid, rather hygroscopic residue was dissolved in 70% ethanol and passed through a column packed with Amberlite resin IRA-401 (OH^- form). The neutral eluates were concentrated to dryness in a rotary evaporator at 25 °C and the residue was recrystallized (Table II).

In the alkylation of the pyridylazoles **24–26** described above, the progress of the reaction was monitored by TLC (chloroform–methanol, 8:2 or 9.5:0.5) and by ^1H NMR of aliquots.

Preparation of 1-Alkyl-4-azolylidene-1,4-dihydropyridines 16–22 (Table II). Method D. A column packed with anion-exchange Amberlite IRA-401 resin was used and the chloride form was converted to the hydroxide form.[6] A solution of 1-alkyl-4-azolylpyridinium salt (1 mmol) in 70% ethanol (50 mL) was passed through the column. The neutral eluates were concentrated on a rotary evaporator at 25 °C (**20–22**) or 45 °C (**16–19**) to give the corresponding 1-alkyl-4-azolylidene-1,4-dihydropyridine (Table II). The 1-alkyl-4-(5-methylpyrazolyl-3-idene)-1,4-dihydropyridines **20–21** are heat-sensitive, and compound **22** is air- and heat-sensitive.

Experimental Procedure for Determination of Dipole Moments. The method used for determination of experimental dipole moments is based on the Debye equation as well as the Halverstadt and Kumler extrapolation method[36] for calculation of the total polarization ($P_{2\infty}$) of a infinite dilution of the anhydrous mesomeric betaines **35**, **45**, and **46** in dioxane at 298 K.

This procedure is based on the calculation of $P_{2\infty}$ from the equation

$$P_{2\infty} = M_2\left[\frac{\epsilon_1 - 1}{\epsilon_1 + 2}(V_1 + \beta) + \frac{3V_1}{(\epsilon_1 + 2)^2}\alpha\right]$$

in which ϵ_1 is the dielectric constant and V_1 the specific volume of the solvent, M_2 is the molar mass and ω_2 is the weight fraction of the solute.

α is determined from the slope of the line obtained by plotting the dielectric constant against the weight fraction of the solute to infinite dilution ($\omega_2 \to 0$). Similarly, β is determined by plotting the specific volume against the weight fraction.

$$\alpha = \left(\frac{d\epsilon}{d\omega_2}\right)_{\omega_2 \to 0}$$

$$\beta = \left(\frac{dV}{d\omega_2}\right)_{\omega_2 \to 0}$$

After obtaining the P_∞ for a molecule, the Debye equation is used to determine the dipolar moment value in Debye units from the equation $\mu = 0.01281[(P_\infty - R_{MD})_T]^{0.5}$.

The fact that extreme dilution of the sample is necessary for measurement of the electric dipolar moments is noteworthy. First, the problem of low solubility of the mesomeric betaines **35**, **45**, and **46** in dioxane was resolved by using an ultrasound bath for 10 min. Second, the self-association of the quasicoplanar betaines was much easier than that for the pyridinium azolate inner salts previously reported.[6a] The weight fractions were in the range of 0.0003 and 0.0008 and Table VI lists the slopes of the graph of electric polarizability (α) and specific volume (β), together with the polarization data and dipole moments (μ).

When the plot of electric polarizability (α) against weight fraction (ω) was not linear, the points were fitted to an equation of the form $\epsilon = \epsilon + \alpha\omega_2 + \alpha'\omega_2^2$ and the limiting gradient at infinite dilution (α) was employed to calculate the experimental dipole moment value in order to readjust α the value for $\omega_2 \to 0$ as described for 2-pyridone.[31a] The dipole moments computed from a linear plot, $\epsilon = f(\omega)$, may be the more reliable results.

Single-Crystal X-ray Structure Determination of Compound 35. Crystal data for **35**: $C_{11}H_{10}N_4 \cdot H_2O$, M = 216.3, monoclinic, space group $P2_1/a$, a = 12.225 (8), b = 14.090 (3), and c = 12.890 (8) Å, β = 99.54 (4)°, U = 2190 Å^3 (by least-squares refinement on diffractometer angles for 25 automatically centered reflections, λ = 0.71069 Å), Z = 8, D_c = 1.31 g/cm^3; colorless, 0.20 × 0.19 × 0.80 mm^3, μ(Mo K_α) = 0.824 cm^{-1}, F(000) = 912. All crystallographic measurements were made on a CAD4 diffractometer, ω–2θ mode with ω scan width = 2.40 + 1.05 tan θ, ω scan width 1.5–6.7 deg/min, graphite-monochromated Mo K_α radiation; 3234 unique reflections [$1.0 \le \theta \le 23.5°$, $-13 \le h \le 13$, $0 \le k \le 15$, $0 \le l \le 14$; 990 observed reflections with $I > 2.5\sigma(I)$]. Stability of intensity control, ca. 1%. The structure was solvent by multisolution direct methods using the Ω tangent formula;[37] full-matrix least-squares refinement with all non-H atoms anisotropic. All the non-methyl H-atoms of the disordered molecule were determined experimentally. Final R and R_w values are 0.055 and 0.067; the weighting scheme is $w = 1/[\sigma^2(F_o) + 0.0042\,F_o^2]$ with $\sigma(F_o)$ from counting statistics. Highest and lowest peaks in final ΔF map (e Å^{-3}) were 0.41 and 0.37. Programs used and sources of scattering factor data are given in refs 37–40 respectively. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Center.

Acknowledgment. We extend our special thanks to Professor J. Elguero, Instituto de Química Médica, Madrid, for his continuous encouragement and stimulating discussions. The low-temperature ^1H NMR spectra (80 MHz) of compound **21** were kindly determined by Professor F. Sanchez-Ferrando, Universitat Autônoma de Barcelona. This work was supported by the Fondo de Investigaciones Sanitarias de la Seguridad Social (projects No. 87/1570, 88/0832, 89/0012). We gratefully acknowledge the postgraduate scholarship (I.D.) awarded by the Ministerio de Educación y Ciencia.

Supplementary Material Available: Percentages of heteronuclear NOE enhancements on orders of some protons in

(35) Bauer, V. J.; Dalalian, H. P.; Fanshawe, W. J.; Safir, S. R.; Tocus, E. C.; Boshart, C. R. *J. Med. Chem.* **1968**, *11*, 981.
(36) Halverstadt, I. F.; Kumler, W. D. *J. Am. Chem. Soc.* **1942**, *64*, 2988.
(37) Rius, J.; Miravitlles, C. *Acta Crystallogr.* **1989**, *A45*, 490.
(38) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, 1974; Vol. IV, pp 99, 149.
(39) Scheldrick, G. M. SHELX 76: Program for Crystal Structure Determination, University of Cambridge, England, 1976.
(40) Mothelwell, W. D. S.; Clegg, W. PLUTO 78: Program for Plotting Molecular and Crystal Structures, University of Cambridge, England, 1978.

DMSO-d_6 for compounds 21, 31 and 32 (Table V), ^1H and ^{13}C chemical shifts of compound 26 in DMSO-d_6 (Figure 4), comparison of ^1H and ^{13}C chemical shifts (in DMSO-d_6) of two 2-(1-pyridinio)benzimidazolate mesomeric betaines 10 and their analogues 1-alkyl-4-benzimidazolylidene-1,4-dihydropyridines 8 (Figure 5), 80-MHz ^1H NMR spectrum of compound 21 at 243 K (Figure 6), total charges at τ_{min} for compounds 16B–18B and 20B–21B (Table VII), comparison of experimental and calculated geometry of compound 16 (Table VIII), elemental analyses of new compounds (Table IX), heats of formation, total enegy, energy barriers, dipolar moments, and bond orders of azolium azolate inner salts 34–44 (Table XI); ^1H NMR spectroscopic data of compounds 34–36 and 45–57 (Table XIV), ^{13}C NMR spectroscopic data of compounds 34–36 and 45–57 (Table XV), total charges at τ_{min} for compounds 34–44 (Table XVII), comparison of experimental and calculated geometry of 2-(3-methyl-1-imidazolium)benzimidazolate inner salt (35) (Table XVIII), list of final positional parameters for non-hydrogen atoms and equivalent temperature coefficients (Table XIX), thermal coefficients for non-H atoms (Table XX), bond lengths and bond angles (Table XXI), and found positional parameters for H atoms (Table XXII) for compound 35 (18 pages). Ordering information is given on any current masthead page. Structure factors tables are available from the authors.

Heterocyclic Betaines. Aza Analogues of Sesquifulvalene. 2. Azolium Azolate Inner Salts: Synthesis, Reactivity, and Structure of a 1:1 Adduct with Dimethyl Acetylenedicarboxylate

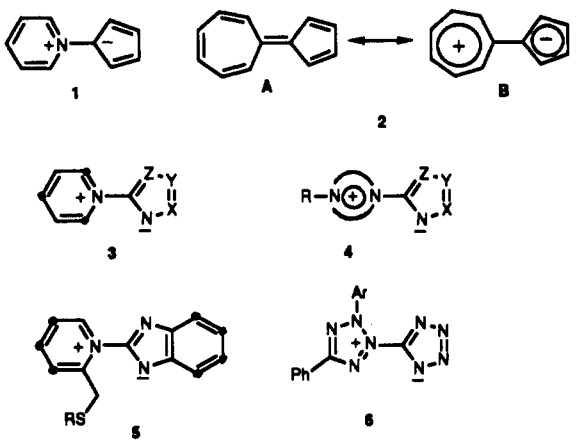
Ermitas Alcalde* and Immaculada Dinarès

Laboratorio de Química Orgánica, Facultad de Farmacia, Universidad de Barcelona, E-08028-Barcelona, Spain

Received July 20, 1990

Reaction of an activated 2-chloroazole with several *N*-alkylazoles afforded the *N*-azolylazolium salts, deprotonation of which results in a series of the title mesomeric betaines 7 and 8. Their reactivity toward electrophiles and dipolarophiles under mild conditions reflects the highly dipolar structures of 7 and 8. The thermal stability and dequaternization reactions of some of their corresponding *N*-azolylimidazolium and -pyrazolium salts have also been studied.

Of the vast variety of structures that conjugated heterocyclic mesomeric betaines adopt,[1] few reports have appeared of aza analogues of the *N*-ylide 1 and the dipolar resonance form of sesquifulvalene (2B). Several representative mesomeric betaines of azinium azolate 3 and azolium azolate 4 have been previously reported as part of our research work on aza analogues of 1.[2-5] Other pyridinium benzimidazolate 5 and tetrazolium tetrazolate 6 inner salts have been prepared.[6,7]



The highly dipolar character of mesomeric betaines 3 and 4 has a dominant influence upon their chemistry, which merits study. These systems are suited to a study of their behavior as *dipoles*, where the dipolar moiety contains more than four π electrons, and their reactions with dipolarophiles should be a potentially attractive route for the synthesis of a variety of heterocyclic structures, as well as novel polycyclic ring systems.

As to quaternary salts of nitrogen heteroaromatic compounds, these are usually stable and their dealkylation reactions are of interest. In this context, pyridinium salts, and to a lesser extent, condensed systems derived from six-membered nitrogen heterocycles, are by far the most commonly investigated. This is presumably due to the fact that such studies were directed toward seeking insight into fundamental topics of heteroaromatic chemistry[8a] such as aliphatic nucleophilic substitution reactions, forward and reverse Menschutkin reactions,[9] and the use of pyridine as a leaving group.[8b,10] Furthermore, synthetic methods have been developed during the last two decades using polar aprotic solvents and soft nucleophiles.[8a,11]

Dequaternization of azolium quaternary salts initially involved pyrazolium compounds,[12] which could be pyro-

(1) Ollis, W. D.; Stanforth, S. P.; Ramsden, C. A. *Tetrahedron* **1985**, *41*, 2239.
(2) Dinarès, I. Ph.D. Thesis, Facultad de Farmacia, Universidad de Barcelona, 1988 (microfilm no. 520, 1989, University of Barcelona).
(3) Alcalde, E.; Dinarès, I.; Elguero, J.; Fayet, J.-P.; Vertut, M.-C.; Miravitlles, C.; Molins, E. *J. Org. Chem.* **1987**, *52*, 5009 and references cited therein.
(4) Alcalde, E.; Dinarès, I.; Frigola, J. *Tetrahedron Lett.* **1988**, *29*, 491.
(5) Alcalde, E.; Dinarès, I.; Elguero, J.; Frigola, J.; Osuna, A.; Castanys, S. *Eur. J. Med. Chem.* **1990**, *25*, 309.
(6) (a) Ankner, K. F.; Brändström, A. E.; Lindberg, P. L.; Nordberg, M. P.; Wallmark, B. E. E. Patent 181.846 (1986). (b) Sturm, E.; Krüger, V.; Senn-Bilfinger, J.; Figala, V.; Klemm, K.; Kohl, B.; Rainer, G.; Schaefer, H.; Blake, T. J.; Darkin, D. W.; Ife, R. J.; Leach, C. A.; Mitchell, R. C.; Pepper, E. S.; Salter, C. J.; Viney, N. J.; Huttner, G.; Zsolnai, L. *J. Org. Chem.* **1987**, *52*, 4573; **1987**, *52*, 4582.
(7) Schichipanov, V. P.; Krashina, K. I.; Skachilova, A. A. *Khim. Geterotsikl. Soedin.* **1973**, 1570; **1974**, 268.
(8) (a) Gallo, G.; Roussel, Ch.; Berg, U. *Adv. Heterocycl. Chem.* **1988**, *43*, 201; (b) 278.
(9) (a) Deady, L. W.; Finlayson, W. L.; Korytsky, O. L. *Aust. J. Chem.* **1979**, *32*, 1735. (b) Deady, L. W. *Aust. J. Chem.* **1981**, *34*, 163.
(10) Katritzky, A. R.; Musumarra, G. *Chem. Soc. Rev.* **1984**, *13*, 47.
(11) Deady, L. W.; Finalayson, W. L. *Synth. Commun.* **1980**, *10*, 947 and references therein.

0022-3263/91/1956-4233$02.50/0