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Notes

Heterocyclic Betaines. 20.[1] Unconventional Extended π-Systems Containing Imidazolium (Pyridinium) and Benzimidazolate Subunits. Synthesis and Structural Aspects

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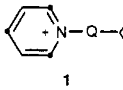
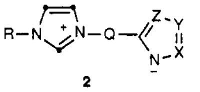
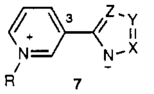
Heterocyclic betaines of pyridinium azolate (**1**) and imidazolium azolate (**2**) with several interannular spacers comprise a vast array of high dipolar entities with low molecular weight; examples of the *N*-ylides **3**[2] and **4**[2] (C–N bond) and their homologues **5**[3] and **6**[3] have been carefully studied. As for the inner salts of type **7** (C–C bond), Butler *et al.*[4] reported the case of the novel tetrazolate ylide **8**, and some examples of their vinylogues **9** [(*E*)-CH=CH bond] have been recently investigated, e.g., **10**[1,5] in Chart 1.



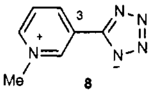
1
3 (Q:-)
5 (Q: CH$_2$)



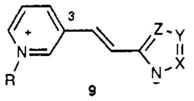
2
4 (Q: -)
6 (Q: CH$_2$)



7



8

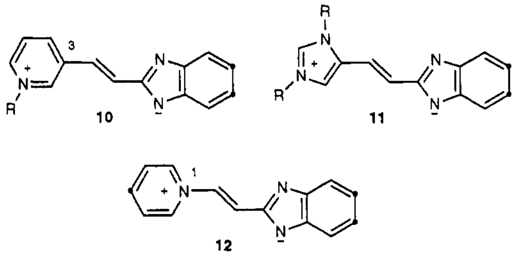


9

X, Y, Z: =CR—; =N—. •: =CR—

Pursuing our search for unconventional extended π-system[6] aza-analogues of (*E*)-stilbene,[1a,5,7] we now describe examples of (*E*)-2-[2-(1,3-dialkyl-4-imidazolio)vinyl]benzimidazolates **11**,[8] analogues of **10**, and the available results of the 2-[2-(1-pyridinio)vinyl]benzimidazolates **12**, vinylogues of the *N*-ylides **1** (Chart 1).

Chart 1



10 **11** **12**

Synthesis. The selected compound pairs **13**, **14** and **15**, **16** were prepared according to the procedure shown in Scheme 1. Firstly, urocanic acid **17**[9] reacted with an excess of alkyl iodide to give the (carboxyvinyl)imidazolium quaternary salts **18** and **19** together with their corresponding monoalkylated counterparts **20** and **21** (see Experimental Section). Secondly, the (*E*)-1,3-dialkyl-4-[2-(1*H*-benzimidazol-2-yl)vinyl]imidazolium salts **13** and **14** were obtained by condensation of compounds **18** and **19** with 4,5-dimethyl-1,2-phenylenediamine **22** using poly(phosphoric acid) as cyclodehydrating agent in Hein's benzimidazole synthesis.[10] Transformation of compounds **13** and **14** into the inner salts **15** and **16** was carried out using an anion-exchange resin (OH$^-$ form).[11] In addition, the (*E*)-2-[2-(1*H*-imidazol-4-yl)vinyl]-5,6-dimethylbenzimidazole (**23**), the neutral counterpart of the selected compound pairs **13**, **14** and **15**, **16** was prepared from urocanic acid **17**.

A route to (*E*)-2-[2-(1-pyridinio)vinyl]benzimidazolate inner salts **12** (i.e., **26**) was explored as shown in Scheme 2. Condensation of the *o*-arylenediamine **22** with (*E*)-1-[2-(methoxycarbonyl)vinyl]pyridinium tetrafluoroborate (**24**), prepared according to Yung and Buzek,[12] was achieved by application of either Hein's benzimidazole synthesis (method A) or the classical Phillips synthesis (method B), and several attempts were made.[13] Neither method A nor B gave the selected (benzimidazolylvinyl)pyridinium salt **25**,[14] and these were not further investigated.

Physical data of the betaines **15** and **16**, their immediate precursors **13** and **14**, and their neutral counterpart **23** are listed in Table 1 (see Experimental Section). All gave satisfactory elemental analysis.

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(1) (a) Part 19: Alcalde, E.; Dinarés, I.; Pons, J.-M.; Roca, T. *J. Org. Chem.*, previous paper in this issue. (b) Abstracted from Ph. D. Thesis of T.R., Facultad de Farmacia, Universidad de Barcelona, 1992 (microfilm no. 1796, 1993, Universidad de Barcelona).

(2) Alcalde, E.; Dinarés, I.; Frigola, J.; Jaime, C.; Fayet, J.-P.; Vertut, M.-C.; Miravitlles, C.; Rius, J. *J. Org. Chem.* **1991**, *56*, 4223 and references cited therein.

(3) Alcalde, E.; Pérez-García, Ll.; Miravitlles, C.; Rius, J.; Valentí, E. *J. Org. Chem.* **1992**, *57*, 4829 and references cited therein.

(4) Butler, R. N.; Garvin, V. C. *J. Chem. Res., Synop.* **1982**, 122 and references cited therein.

(5) Alcalde, E.; Roca, T.; Fayet, J.-P.; Vertut, M.-C. *Chem. Lett.* **1991**, 2151.

(6) The fundamental and practical interest of extended π-systems has been the subject of extensive research,[1a] e.g., advanced materials.

(7) Alcalde, E.; Roca, T. *J. Org. Chem.* **1992**, *57*, 4834 and references cited therein.

(8) For an earlier report on examples of betaines **11**, see: Alcalde, E.; Pérez-García, Ll.; Pons, J.-M.; Roca, T. *Chem. Lett.* **1992**, 1779.

(9) (a) Urocanic acid (**17**) has been subject of intense photobiological interest.[9b] (b) Farrow, Sh. J.; Jones, C. R.; Severance, D. L.; Deibel, R. M.; Baird, W. M.; Morrison, H. A. *J. Org. Chem.* **1990**, *55*, 275 and references cited therein.

(10) Alcalde, E.; Dinarés, I.; Pérez-García, Ll.; Roca, T. *Synthesis* **1992**, 395.

(11) The method of choice for this transformation was the use of a strong anion-exchange Amberlite IRA-401 (OH$^-$ form), and this was also applied to other betaines or compounds with a betaine character.[1a,3,7]

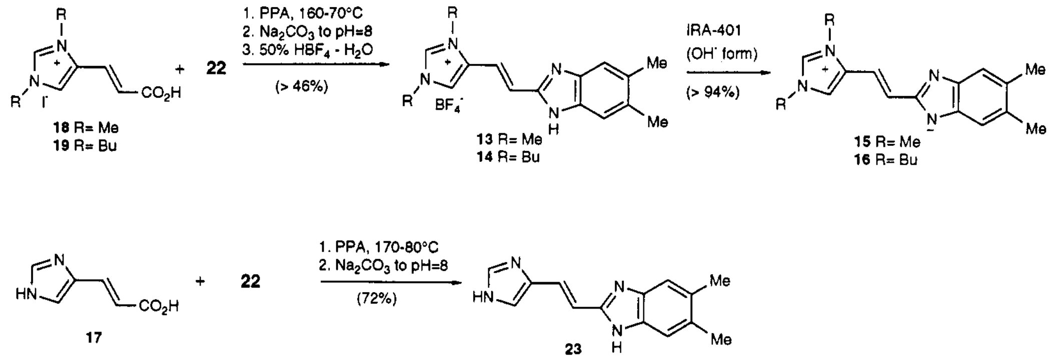
(12) Yung, M. E.; Buszek, H. L. *J. Am. Chem. Soc.* **1988**, *110*, 3965.

(13) (a) With similar reaction conditions previously applied to the synthesis of related compounds.[10,13b] (b) Alcalde, E.; Pérez-García, Ll.; Frigola, J. *Chem. Pharm. Bull.* **1993**, *41*, 614.

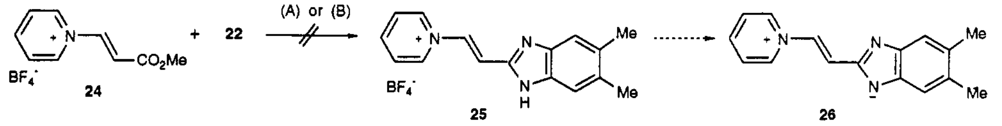
(14) The starting *o*-arylenediamine **22** was recovered unaltered from the reaction mixture.

0022-3263/94/1959-0644$04.50/0

Scheme 1



Scheme 2



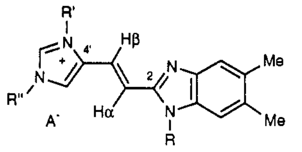
[a] Reagents and conditions: (A) method A; (1) 4,5-dimethyl-1,2-phenylenediamine (**22**) in poly(phosphoric acid), at 160–170 °C, 8 h; (2) ice–water; (3) Na_2CO_3 (2 N) to reach pH 7; (B) method B; (1) in 5 N HCl, at 135 °C, 43 h; (2) ice–water; (3) Na_2CO_3 (2 N) to reach pH 7.

Table 1. Physical Data of Compounds 13–16, 18–21, and 23

compd	yield[a]	mp (°C) (solvent)[b]	molecular formula[c]
13	46	280–1 (A)	$C_{16}H_{19}N_4BF_4$
14	49	198–9 (B)	$C_{22}H_{31}N_4BF_4\cdot1H_2O$
15	99	180–2	$C_{16}H_{18}N_4\cdot2.5H_2O$
16	94	153–5	$C_{22}H_{30}N_4\cdot3H_2O$
18	71	269–70 (C)	$C_8H_{11}N_2O_2I$
19	8	148–50	$C_{14}H_{23}N_2O_2I$
20	12	223–5 (C)	$C_7H_9N_2O_2I$
21	37	197–9 (D)	$C_{10}H_{15}N_2O_2I$
23	72	292–3 (E)	$C_{14}H_{14}N_4\cdot1H_2O$

[a] Yields were not optimized. [b] Crystallization solvent: A, methanol; B, water/acetone (2:1); C, water; D, acetonitrile; E, ethanol. [c] Satisfactory analytical data (±0.4% for C, H, N) were obtained for all new compounds.

Table 2. Selected ^{1}H and ^{13}C NMR Data of Compounds 13–16 and 23



	R	R'	A⁻
13	H	Me	BF_4^-
14	H	Bu	BF_4^-
15	--	Me	--
16	--	Bu	--

compd	H-5′	H-α	H-β	H-4,7	C-α	C-β	C-2
15[a,b]	7.66	7.15	7.23	7.35	129.6	113.5	157.1
13[a,b]	8.10	7.28	7.50	7.43	123.9	117.3	149.9[c]
Δδ[d]	−0.44	−0.13	−0.27	−0.08	+5.7	−3.8	+7.2
16[a]	7.98	7.26	7.38	7.39	129.2	113.2	156.0
14[a]	8.20	7.31	7.48	7.41	124.0	117.2	149.9
Δδ[d]	−0.22	−0.05	−0.10	−0.02	+5.2	−4.0	+6.1
23[e]	7.35	6.98	7.45	7.24	125.7	115.1	151.3

[a] In CD_3OD. $J_{H\alpha,H\beta} = 15.5$ Hz. [b] Assignation of signals by HMQC and HMBC (ref 15d). [c] HETNOE $^{13}C\{^{1}H\}$ on weak irradiation at δ H 7.28 ppm [$n = 0.26$] (26%). [d] Δδ: observed chemical shift difference between betaines **15** and **16** and their corresponding benzimidazolylimidazolium salts **13** and **14**. [e] In DMSO-d_6.

Structural Aspects. The IR spectra of compounds **13** and **14** showed absorptions in the ranges of 3500–3400 cm^{-1} (ν NH) and 1100–1000 cm^{-1} (ν BF_4^-), while these bands were absent for betaines **15** and **16**.

Table 2 shows the more relevant ^{1}H and ^{13}C NMR chemical shifts of compounds **13–16** and **23** (see Tables 3 and 4 in the supplementary material); individual assignments were made using the appropriate NMR techniques[15] as for the push–pull aza analogues of (*E*)-stilbene described in the companion paper.[1a] Both the ^{1}H and ^{13}C NMR parameters for betaines **15** and **16** have proven to be decisive for structural proof of their dipolar structure in solution,[15e,f] as they have for other heterocyclic betaine systems **3–9**.[1–5] For proton spectra, in which electron density has an important role, all the NMR peaks were found upfield for betaines **15** and **16** with respect to their precursors **13** and **14**. Curiously, the δ H-5′ are shifted further upfield (Δδ H-5′ in Table 2) in agreement with data for examples of the *N*-ylides **4**.[2] As for carbon-13 spectra, the observed deshielding effect at C-2 (*ca.* +6.6 ppm) in the π-excessive nucleus[16] are in agreement with data for a variety of pyridinium(imidazolium) inner salts of types **3–6**.[2,3]

One of the interesting aspects of this ensemble of unconventional extended π-systems is the unambiguous assignment of the olefinic proton and carbon atoms to the interannular spacer.[1a] In this connection, a small amount of information is available concerning NMR studies on (*E*)-stilbene aza analogues and their charged derivatives.[18–20] We can briefly summarize the ^{1}H and ^{13}C NMR results for compound pairs **13** and **15** (see Δδ, Tables 2–4 (Tables 3 and 4 in the supplementary material)). Determination of long-range ^{1}H–^{13}C connectivity by HMBC

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(15) (a) Unambiguous assignments have been made by DEPT,[15b] HETNOE,[15c] heteronuclear multiple-quantum coherence (HMQC),[15d] and heteronuclear multiple-bond correlation (HMBC).[15d] (b) Breitmeier, E.; Voelter, W. In *Carbon-13 NMR Spectroscopy*; VHC: Weinheim, 1987; p 80. (c) Sánchez-Ferrando, F. *Magn. Reson. Chem.* **1985**, *23*, 185. (d) Summers, M. F.; Marzilli, L. G.; Bax, A. *J. Am. Chem. Soc.* **1986**, *108*, 4285. (e) Methanol-d_4 was previously dried with activated molecular sieves 3A to reduce the presence of water in the solvent. (f) The instability of betaines **15** and **16** in DMSO-d_6 precludes recording of their ^{1}H or ^{13}C NMR spectra.

(16) The deshielding effect at C-2 in the benzimidazole series **3–6**[2,3] and higher homologues[17] is the most characteristic feature in ^{13}C NMR spectra of these dipolar molecules and reveals a fairly constant Δδ C-2 irrespective of the nature of the interannular spacer.

(17) Alcalde, E.; Gisbert, M.; Pérez-García, Ll. *Chem. Lett.* **1992**, 2357.

(18) A search in *Chem. Abstr.* (1972–1991) of NMR for 2-, 3-, and 4-vinylpyridinium salts showed that very few proton[19] and carbon-13[20] NMR studies were reported. Most of the available data come from papers dealing mainly with aromatic systems: styrenes, stilbenes, and related extended π-systems.

(19) (a) Coletta, F.; Gambaro, A.; Paimeni, L. *Gazz. Chim. Ital.* **1973**, *103*, 265. (b) Rowbotham, J. B.; Schaefer, T. *Can. J. Chem.* **1974**, *52*, 136. (c) Vansant, J.; Smets, G.; Declercq, J. P.; Germain, G.; Van Meerssche, M. *J. Org. Chem.* **1980**, *45*, 1557.

spectroscopy has been crucial for providing complete proton and carbon assignments. The most relevant multiple-bond ^{1}H–^{13}C connectivities observed for the olefinic proton atoms of **13** and **15** are mapped out in Figures 1 and 2 in the supplementary material. Furthermore, two-bond heteronuclear selective ^{13}C{^{1}H} NOE difference showed well-resolved correlation on irradiation to the olefinic proton signal at 7.28 ppm for **13** (see Tables 2–4 (Tables 3 and 4 in the supplementary material)), and this experiment also confirmed the resonance assignments obtained on the basis of the HMBC spectra.[21] On the other hand, in the case of betaine **15** it was not possible to perform an HETNOE experiment due to the minimum difference between the δ values of Hα and Hβ atoms.

The differences in chemical shift values for the (*E*)-vinylene spacer shows the dipolar nature in solution of betaines **15** and **16** (see $\Delta\delta$, Table 2–4 (Tables 3 and 4 in the supplementary material)). The shielding effect observed at C-β is consistent with the β-substituent effects in the ^{13}C NMR data of a series of β-heteroaryl styrenes[20c,d] and related unconventional extended π-systems with a betaine character.[7]

As for dipole moments, the experimental values of various examples of heterocyclic mesomeric betaines **3**[2] and **4**,[2] their homologues **5**[3] and **6**,[3] and the inner salts of type **9**[1a,5] are in the range of 9.2–15.3 D, which has provided us with a greater understanding of the electronic structure in the ground state within these series. However, the perturbing effect of self-association involves additional experimetal difficulty in the measurement of these dipolar molecules,[22] which brings about a reduction in the value of the μ_{exp} and lowers the electrostatic energy. The same effect occurred in the present study, and it was not possible to measure a coherent experimental dipole moment value for betaine **15**.[23ab] Unfortunately, betaines **15** and **16** were not suitable for further experimental structural studies.[23b,c] It was, however, possible to record a fairly coherent dipole moment of 2-[2-(1-butyl-3-pyridinio)vinyl]benzimidazolate (**28**), which was found to be 13.0 D, but the perturbing influence of self-association was not completely eliminated.[1a,22]

The semiempirical MNDO SCF-MO[24a] and AM1 SCF-MO[24b] models have proven to be suitable tools for reproducing experimental data for heterocyclic betaines of types **3–6**, such as dipole moments and molecular geometries.[2,3] Moreover, the AM1 SCF-MO is better suited to predict experimentally observed trends of betaines **5** and **6** than MNDO SCF-MO[3] and, from these results, any heterocyclic betaine emerging from the general type structures **1** and **2**. Running the molecular orbital calculations in the same way as for betaines **5** and **6**, six simple molecules from the ensemble constituted by the inner salts **10–12** (Chart 1) were studied, providing information on most ground-state properties of these novel extended π-systems.

The geometries of the (*E*)-vinylpyridinium and (*E*)-vinylimidazolium benzimidazolate betaines **15**, **16**, and **27–30** were constructed by using the molecular modeling program CHEMX[24c] and fully optimized at the RHF, closed-shell, ground-state level using both the MNDO SCF-MO[24a] and the AM1 SCF-MO[24b] programs implemented in the MOPAC package (version 6.0).[24d]

For compounds **15**, **16**, **27**, and **28**, eight conformations are possible (ϕ_1 = 0, 90° and ϕ_2 = 0, 90, 180, and −90°). However, we consider only six conformations, since those with (ϕ_1, ϕ_2) of (0, 90°) and (90, 90°) are chiral, and therefore their enantiomers (0, −90°) and (90, −90°) would have the same heats of formation and dipolar moments. In the case of compounds **29** and **30** only four conformations are possible (ϕ_1 and ϕ_2 = 0, 90°) due to the symmetry of the heterocycles connected by the vinylic spacer. For the lateral alkyl chains of compounds **16** and **28**, the alternated conformations were taken from the starting geometries. All the stationary states obtained for each compound were shown to be real minima by force calculations.[25] The more relevant results obtained are gathered in Table 5 (see Table 6, Figures 4–6, and detailed information in supplementary material).

For all the compounds studied, coplanar structures (ϕ_1 = 0°, ϕ_2 = 0, 180°) were found to be energetically more stable, except for compound **30** at the MNDO level of calculation, in which the (ϕ_1, ϕ_2) (0, 90°) conformer was 0.4 kcal·mol^{-1} more stable than the coplanar structure.[26] In all the coplanar conformations the vinylene linkage allows an extended conjugated π-system, which explains the stability of these structures when compared with the nonplanar ones.

There is a good parallelism between the results obtained by these two methods. Thus, for all the compounds and for both semiempirical methods, coplanar conformers showed smaller dipolar moments with differences of about

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(20) (a) Coletta, F.; Gambaro, A.; Rigatti, G. *Spectrosc. Lett.* **1976**, *9*, 469. (b) Clavreul, R.; Bloch, B. *Makromol. Chem.* **1987**, *188*, 67. (c) Happer, D. A. R.; Steenson, B. E. *J. Chem. Soc., Perkin Trans. 2* **1988**, 19. (d) Aun, C. E.; Clarkson, T. J.; Happer, D. A. R. *J. Chem. Soc., Perkin Trans. 2* **1990**, 635.

(21) Both HMBC[15d] and HETNOE[15c] techniques had provided unambiguous assignments of the (*E*)-vinylene interannular linkage for several examples of (*E*)-1-alkyl-2(3 or 4)-[2-(imidazol-2-ylidene)ethylidene]-dihydropyridines and their corresponding (*E*)-(imidazolylvinyl)pyridinium salts.[1b,7]

(22) (a) The dipolar structural pattern that characterizes heterocyclic betaines **1** implies strong intramolecular forces.[22b] Both the solute–solvent and solute–solute interaction forces should be taken into account for reliable interpretation of their physicochemical parameters measured in solution. (b) To reduce the perturbing influence of these effects as far as possible *high dilution* of the *anhydrous* sample **1** should be used and the water in the solvent should be reduced (i.e., ref 15e).

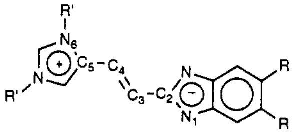
(23) (a) Fayet, J.-P. Personal comunication. (b) Different dipole moment measurements were assayed for betaine **15** in dioxane at 298 K as described.[2] The best recorded value for **15** was found to be 10.41 D. Limit of measurement: $\omega < 0.0002$ for **15**. (c) It was not possible to obtain suitable single crystals of **15** or **16** for an X-ray structure analysis under standard recrystallization techniques. Moreover, compounds **15** and **16** are air and light sensitive as well as rather unstable in solution, although less so than compounds of type **10** (i.e., **28**).[1a]

(24) (a) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899. (b) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902. (c) CHEMX, developed and distributed by Chemical Design Ltd., Oxford, England (1991). (d) MOPAC (Version 6.0), QCPE no. 455, Department of Chemistry, Indiana University, Bloomington, IN, 1991.

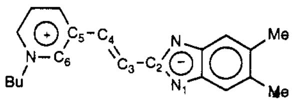
(25) (a) For the planar conformers of compounds **29** and **30** the initial geometry needed to be defined carefully by first optimizing the vinylpyridinium moiety in the planar configuration and then adding the bezimidazolate ring in order to optimize the planar structures, since, when starting from the planar structures, nonplanar nonstationary structures were found to be similar in energy to the real planar minima.[25b] (b) In a conformational search, low energy minima and *bumps* can be found close together in the conformational space.[25c] (c) Däppen, R.; Karfunkel, H. R.; Leusen, F. J. J. *J. Comput. Chem.* **1990**, *11*, 181 and references cited therein.

(26) The energy difference calculated by AM1 is 13.0 to 5.6 kcal·mol^{-1} for compound **15**, 12.0 to 3.9 kcal·mol^{-1} for **16**, 13.3 to 5.5 kcal·mol^{-1} for **27**, 18.9 to 12.2 kcal·mol^{-1} for **28**, 17.1 to 8.0 kcal·mol^{-1} for **29**, and 11.2 to 3.2 kcal·mol^{-1} for **30**. By using the MNDO method these energy differences decrease were 13.6 to 2.0 kcal·mol^{-1} for compound **15**, 12.4 to 0.2 kcal·mol^{-1} for **16**, 12.6 to 1.4 kcal·mol^{-1} for **27**, 14.1 to 9.5 kcal·mol^{-1} **28**, and 14.2 to 4.2 kcal·mol^{-1} for **29**.

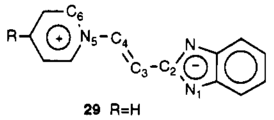
Table 5. AM1 and MNDO Semiempirical Calculations of 2-[2-(1,3-Dialkyl-4-imidazolio)vinyl]benzimidazolates 15, 16, and 27, 2-[2-(1-Butyl-3-pyridinio)vinyl]benzimidazolate (28), and 2-[2-(1-Pyridinio)vinyl]benzimidazolates 29 and 30



15 R=R'=Me
16 R=Me; R'=Bu
27 R=H; R'=Me



28



29 R=H
30 R=NMe$_2$

	AM1				MNDO			
compd	ϕ_1 (min)[a,b]	ϕ_2 (min)[a,b]	ΔH_f[c]	μ_{calcd}[d]	ϕ_1 (min)[a,b]	ϕ_2 (min)[a,b]	ΔH_f[c]	μ_{calcd}[d]
15	1.0	178.4	175.5	17.7	0.3	−179.6	123.8	18.5
	1.3	0.1	175.7	17.6	−0.6	2.1	127.3	18.6
16	1.4	173.7	134.9	18.5	1.5	177.6	94.9	19.5
	5.6	−3.4	136.1	18.4	−0.7	7.8	97.9	19.5
27	1.2	178.7	188.1	18.0	1.1	177.7	136.7	17.8
	0.3	1.3	188.6	17.9	0.0	1.7	139.6	17.6
28	0.7	−178.8	137.7	14.6[e]	1.3	−178.1	115.8	14.7[e]
	0.8	0.8	137.9	13.9[e]	1.3	1.5	115.2	14.2[e]
29	−0.1	−0.2	171.3	9.4	−0.1	−0.5	143.7	9.2
30	−0.1	0.3	177.2	17.6	−0.2	0.3	152.8	16.7

[a] In degrees. [b] $\phi_1(N_1C_2C_3C_4)$ and ϕ_2 $[C_3C_4C_5N_6(C_6)]$. [c] In kcal/mol. [d] In D; 1 D = 3.34×10^{-30} cm. [e] μ_{exp} for compound **28** was found to be 13.0 D (see text and ref 5).

12–8 D for AM1 and about 13–8 D for MNDO.[27] The dipole moments calculated for the coplanar conformations of betaine **28** were found to range between 13.9 and 14.7 D, and the agreement with the best experimentally measured value of 13.0 D is satisfactory (see above and Table 5).

Both AM1 and MNDO methods predicted well-correlated dipole moments for compounds **15**, **16**, and **28** together with the unknown betaines **27**, **29**, and **30**. Their electronic structure is reflected in their μ_{calcd} and sheds light on their high dipolar character. The values shown in Table 5 can be taken as a good approximation to the dipole moments for betaines **15**, **16**, and **28**.

As mentioned, the structural characteristics of the compounds reported made them attractive from the advanced materials point of view. Some of these structures have an elongated geometry similar to ionic liquid crystals recently reported in the literature.[6,28a–c] Likewise, the push–pull conjugated systems of the betaines and their immediate precursors are closely related with structures successfuly studied in nonlinear optics which show high second order parameters (β and/or $X^{(2)}$). As examples, we can mention the crystals of (dimethylamino)stilbazolium salts (DMSM)[28d] or the Blodgett–Langmuir films based on hemicyanines[28e] with important second-harmonic generation activity.

Among several examples of extended π-system aza analogues of (*E*)-stilbene, neither the betaine **28** nor related push–pull conjugated π-systems[1a] showed thermotropic (phase state changes with temperature) or lyotropic (phase state changes with concentration) mesophases.[28f,29] Due to the instability of betaines **15** and **16**,[23c] the π-conjugated intramolecular donor–acceptor substrate **14** together with the previously reported (*E*)-imidazolylvinylpyridinium salts **31**–**33**[7,30] were selected for a study of the mesogenic behavior. Surprisingly, none of them showed a clear liquid–crystal behavior.[29,31] Other unconventional push–pull extended π-systems may be suitable as model compounds in which to study the capacity for specific physical behavior in the field of advanced materials.

Experimental Section

General Methods. Melting point: CTP-MP 300 hot-plate apparatus with ASTM 2C thermometer. IR (KBr disks): Perkin-Elmer 1430 spectrophotometer. ^{1}H NMR: Varian Unity 300 and Varian Gemini 200 spectrometer (300 and 200 MHz). ^{13}C NMR: Varian Unity 300 andVarian Gemini 200 spectrometer (75.4 and 50.2 MHz). HETNOE:[15d] Varian Unity 300 spectrometer. HMQC and HMBC:[15e] Varian VXR-500 spectrometer. NMR spectra were determined in methanol-d_4[15f] and dimethyl-d_6 sulfoxide, and chemical shifts are expresed in parts per milion (δ) relative to the central peak of methanol-d_4 or dimethyl-d_6 sulfoxide. TLC: Merck precoated silica gel 60 F_{254} plates; detection by UV light. Ion-exchange resin: Amberlite 401 OH^- form.[7] When a rotary evaporator was used, the bath temperature was 25 °C. In general, the compounds were dried overnight at 25 °C in a vacuum oven. Microanalyses were performed on a Carlo Erba 1106 analyzer.

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[27] If one considers that for almost the same distance between charges, in the case of planar structures, this result is quite obvious; because of the π conjugation, the positive and negative character of the hetero-rings decreases. However, the μ_{calcd} for the planar conformation of betaine **29** is underestimated.[25]

[28] (a) Marcos, M.; Ros, M. B.; Serrano, J. L.; Esteruelas, M. A.; Sola, E.; Oro, L. A.; Barberá, J. *Materials* **1990**, *2*, 748. (b) Navarro-Rodriguez, D.; Frere, Y.; Gramain, P.; Guillon, D.; Skoulios, A. *Liq. Cryst.* **1991**, *9*, 321. (c) Nusselder, J. J. H.; Engberts, J. B. F.; Van Doren, H. A. *Liq. Cryst.* **1993**, *13*, 213. (d) Williams, D. J. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 690. (e) Fuchs, H.; Ohst, H.; Prass, W. *Adv. Mater.* **1991**, *3*, 10. (f) Collings, P. J. *Liquid Crystals: Nature's Delicate Phase of Matter*; Princenton University Press: Princeton, NJ, 1990.

[29] The mesogenic behavior was studied by using optical microscopy at variable temperature (Nikon polarizing microscope equipped with a Mettler FP82 hot stage and FP80 central precessor) and differential scanning calorimetry operating at a scanning rate of 10 k min^{-1} (Perkin-Elmer DSC-7). In order to study the lyotropic properties of the compounds, water and dichloromethane were used as solvents.

[30] (*E*)-1-Butyl-4-[2-(1*H*-imidazol-2-yl)vinyl]pyridinium tetrafluoroborate (**31**), (*E*)-2-[2-(1*H*-imidazol-2-yl)vinyl]-1-isopropylpyridinium tetrafluoroborate (**32**), and (*E*)-1-butyl-2-[2-(1*H*-imidazol-2-yl)vinyl]-pyridinium tetrafluoroborate (**33**).

[31] Furthermore, the second-order hyperpolarizability (β) of compounds **14** and **31**–**33** was first studied by the EFISH method (electric field induced second harmonic generation). However, due to the effect of self-association and the ionic nature of the products, no second-order parameter could be evaluated, thus necessitating other experimental methods which are not available to us at present.

Preparation of (*E*)-1,3-Dialkyl-4-[2-(5,6-dimethyl-1*H*-benzimidazol-2-yl)vinyl]imidazolium Tetrafluoroborates 13 and 14 (Table 1). A suspension of 4,5-dimethyl-*o*-phenylenediamine (**22**) (8.50 mM) and (*E*)-4-(2-carboxyvinyl)-1,3-dialkyl iodides **18** or **19** (8.50 mM) in polyphosphoric acid (20 g) was stirred and maintained in a bath at 160–70 °C for 2.5 h and left to cool. The mixture was then poured into ice–water (60 mL) and was treated with 2 N Na_2CO_3 to reach pH 8. Then 50% aqueous fluoboric acid was added to pH 6, and a solid precipitated. The crude products were filtered and recrystallized (Table 1).

Preparation of (*E*)-2-[2-(1,3-Dialkyl-4-imidazolio)vinyl]-5,6-dimethylbenzimidazolates 15 and 16 (Table 1). A column packed with Amberlite IRA-401 anion-exchange resin was used, and the chloride form was converted to the hydroxide form.[7] A solution of 1,3-dialkyl-4-(benzimidazolylvinyl)imidazolium tetrafluoroborates **13** or **14** in ethanol was passed through the column. The neutral eluates were evaporated to dryness, and the residue was washed in diethyl ether (20 mL) to afford a yellow solid of **15** and **16** (Table 1).

Preparation of (*E*)-4-(2-Carboxyvinyl)-1,3-dimethylimidazolium Iodide (18) (Table 1). Methyl iodide (290 mM) was added dropwise at 0–5 °C to a suspension of urocanic acid (**17**) (29 mM) in dry DMF (45 mL) under an atmosphere of nitrogen, and stirring was continued at 80–5 °C for 50 h. The precipitate was filtered, washed in diethyl ether (30 mL), and then recrystallized from water to afford **18**: ^{1}H NMR (DMSO-d_6) δ 3.84 (3H, MeN), 3.90 (3H, MeN$^+$), 6.56 (1H, $=CHCO_2H$), 7.40 (1H, $=CH$-Iz), 8.30 (1H, H-5), 9.17 (1H, H-2).

The filtrate was evaporated to dryness, and the residue was washed in diethyl ether (3 × 100 mL) and then in acetone (100 mL). The resulting solid recrystallized from water to afford (*E*)-4-(2-carboxyvinyl)-3-methylimidazolium iodide (**20**): ^{1}H NMR (DMSO-d_6) δ 3.86 (3H, MeN), 6.50 ($=CHCO_2H$), 7.44 (1H, $=CH$-Iz), 8.04 (1H, H-5), 9.22 (1H, H-2).

Preparation of (*E*)-1,3-Dibutyl-4-(2-carboxyvinyl)imidazolium Iodide (19) (Table 1). Butyl iodide (145 mM) was added to a suspension of urocanic acid (**17**) (29 mM) in dry DMF (45 mL) and triethylamine (3 mL) under an atmosphere of nitrogen, and stirring was continued at 90–5 °C for 24 h. The reaction mixture was evaporated to dryness, dichloromethane (20 mL) was added to the residue, and the resulting solid recrystallized from acetonitrile to afford (*E*)-3-butyl-4-(2-carboxyvinyl)imidazolium iodide (**21**): ^{1}H NMR (DMSO-d_6) δ 4.18 (2H, $-CH_2N$), 6.53 (1H, $=CHCO_2H$), 7.43 (1H, $=CH$-Iz), 8.16 (1H, H-5), 9.29 (1H, H-2).

The filtrate was washed in water (2 × 30 mL), the organic layer was dried and concentrated to dryness, and the residue was washed, first, in diethyl ether (3 × 100 mL) and then in dichloromethane/diethyl ether (1:1) (50 mL) to afford the iodide **19** in a high state of purity: ^{1}H NMR (DMSO-d_6) δ 4.17 (2H, $-CH_2N$), 4.31 (2H, $-CH_2N^+$), 6.62 (1H, $=CHCO_2H$), 7.46 (1H, $=CH$-Iz), 8.47 (1H, H-5), 9.36 (1H, H-2).

Preparation of (*E*)-2-[2-(1*H*-Imidazol-4-yl)vinyl]-5,6-dimethylbenzimidazole (23) (Table 1). A suspension of 4,5-dimethyl-*o*-phenylenediamine (**22**) (21 mM) and urocanic acid **17** (21 mM) in polyphosphoric acid (20 g) was stirred and heated at 170–80 °C for 1.5 h. The cooled mixture was poured into ice–water (100 mL), and the resulting solution was treated with 2 N Na_2CO_3 to reach pH 8. The precipitated product was filtered, washed in water, and recrystallized from ethanol to provide **23**.

Attempted Preparation of (*E*)-1-[2-(5,6-Dimethyl-1*H*-benzimidazol-2-yl)vinyl]pyridinium Salt (25). Method A. A suspension of 4,5-dimethyl-*o*-phenylenediamine (**22**) (4 mM) and (*E*)-1-[2-(methoxycarbonyl)vinyl]pyridinium tetrafluoroborate (**24**)[12] (4 mM) in polyphosphoric acid (15 g) was stirred and maintained in a bath at 160–5 °C for 8 h. The cooled mixture was poured into ice–water (30 mL), the resulting solution was treated with 2 N Na_2CO_3, and only 4,5-dimethyl-*o*-phenylenediamine (**22**) precipitated. On the other hand, pyridine was detected in the filtrate by TLC.

Method B. A solution of 4,5-dimethyl-*o*-phenylenediamine (**22**) (1 mM) and (*E*)-1-[2-(methoxycarbonyl)vinyl]pyridinium tetrafluoroborate (**24**)[12] (1 mM) in 5 N HCl (3 mL) was stirred and heated at 130–5 °C for 43 h. The cooled mixture was treated with 2 N Na_2CO_3 and extracted with dichloromethane. The organic layer was dried and concentrated to dryness, and the diamine **22** was recovered.

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Supplementary Material Available: HMBC correlations of compounds **13** and **15** (Figures 1 and 2), computer-generated perspective drawing obtained by using a PLUTO program for **15**, **16**, and **27–30** (Figures 3–5), ^{1}H NMR data for compounds **13–16** and **23** (Table 3), ^{13}C NMR data of compounds **13–16** and **23** (Table 4), AM1 and MNDO semiempirical calculations of **15**, **16**, and **27–30** (Table 6), elemental analysis of new compounds (Table 7), and AM1 and MNDO data of **15**, **16**, and **27–30** (160 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from ACS; see any current masthead page for ordering information.