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THE DIPYRIDO[1,2-c:2',1'-e]IMIDAZOLIUM CATION, A NEW AROMATIC RING SYSTEM

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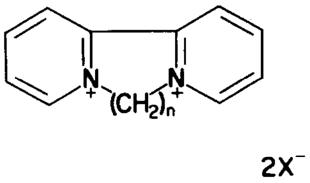
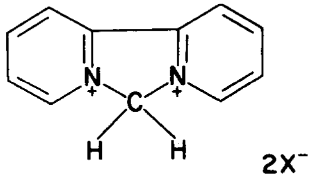
HOMER and Tomlinson have shown that 2,2'-bipyridyl reacts readily with polymethylene α,ω-dihalides to give bridged quaternary salts (I; n = 2, 3 or 4). These authors also tried to prepare 6H-dipyrido[1,2-c:2',1'-e]-imidazolium salts (II) but failed to isolate a pure product from reactions of 2,2'-bipyridyl with methylene dihalides.[1]

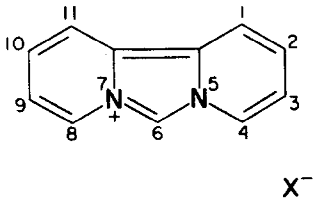


I

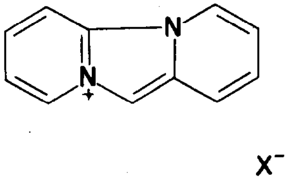


II

We now report that the main product formed in the reaction of 2,2'-bipyridyl with methylene iodide is dipyrido[1,2-c:2',1'-e]imidazolium iodide (III; X=I) rather than its 6H-derivative (II; X=I).



III

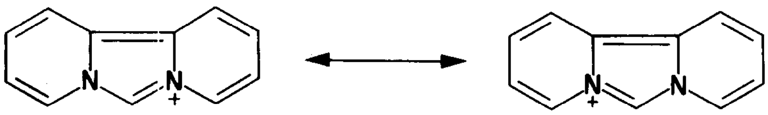


IV

[1] R.F. Homer and T.E. Tomlinson, J. Chem. Soc. 2489 (1960).

The cation of III was first detected as a highly fluorescent spot on paper chromatograms (R_f 0.55; solvent butanol-concentrated hydrochloric acid-water, 8:2:6; maxima of fluorescence at 415, 440, and 465 mμ). The iodide of III can be prepared in 24% yield by reacting two moles of 2,2'-bipyridyl with one mole of methylene diiodide in boiling acetonitrile for about five days while light and air are being excluded. After crystallisation from ethanol *dipyrido[1,2-c:2',1'-e]imidazolium iodide* forms dark green needles, m.p. 255.5-256.5° (uncorr.) (Found: C, 44.63; H, 3.08; N, 9.30; I, 42.6%; mol. weight (ebullioscopically in acetonitrile), 300. $C_{11}H_9N_2I$ requires C, 44.61; H, 3.06; N, 9.46; I, 42.9%; mol. weight, 296). The ultraviolet spectrum of this salt (λ_{max}^{EtOH} at 241, 285, 295, 338, 353, 390, and 412 mμ (ε 3417, 2320, 3130, 1539, 1492, 2800, 1300) and λ_{min}^{EtOH} at 275, 287.5, 300.5, 346, 383, 405.5 mμ (ε 1740, 2220, 2520, 1225, 2180, 880) resembles that of the dipyrido[1,2-a:1',2'-c]imidazolium cation (IV) first prepared by Brown and Humphreys.[2]

The dipyrido[1,2-c:2',1'-e]imidazolium cation represents a new aromatic ring system with two nitrogen atoms at bridge head positions common to one ring. Because of the equivalence of the classical structures V and VI the new cation is a mesomeric ion which possesses a plane of symmetry:



V VI

This view is in accord with the n.m.r. spectrum of this cation which shows only four groups of signals (measured at 60 mc/sec. in

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[2] B.R. Brown and J. Humphreys, *J. Chem. Soc.* 2040 (1959).

water and deuterium oxide; shifts are given in ppm relative to water as internal standard; τ approximately 5.2). A singlet at -4.91 ppm (one proton) is assigned to the 6-proton (numbering as in III). This signal showed no resolvable fine structure, and the coupling to other protons in the molecule must be 0.5 cps or less. In deuterium oxide the area of this signal decreased with time, and after 72 hours it could no longer be detected. Two sets of two overlapping quartets (two protons each) occurred at -3.72 ppm and -3.23 ppm. These groups are assigned to the protons at the 1- and 11-positions, and at the 4- and 8-positions respectively. The assignment of the group at -3.23 ppm is based on the observation that its fine structure can be resolved only after the 6-proton has been exchanged for deuterium. In the remaining group of signals which is centered at -2.53 ppm (four protons) thirteen lines were discerned. If it is assumed that this pattern represents an incompletely resolved set of four overlapping quartets, the n.m.r. spectra of the cation of III in water and deuterium oxide may be interpreted as an ABXYZ system[cf 3] in which the two six-membered rings are equivalent.

In agreement with the proposed structure the dipyrido[1,2-c:2',1'-e]imidazolium cation is a weak base (pK_a -0.7 ± 0.3, spectroscopic value), and we failed to methylate it with methyl iodide in boiling acetonitrile (one week). The n.m.r. spectrum of the protonated species (at 60 mc/sec., determined in trifluoroacetic acid with tetramethylsilane as internal standard) showed a singlet at 482 cps (two protons), a broad singlet with unresolved fine structure at 513 cps (two protons), a complex multiplet at 552 cps (four protons), and a doublet with unresolved fine structure at 584 cps (two protons). This spectrum suggests that protonation of the dipyrido-[1,2-c:2',1'-e]imidazolium cation occurs at the 6-position to give the

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[3] J.A. Pople and T. Schaeffer, Mol. Phys. **3**, 546 (1960).

cation of II, and in the absence of strong coupling we tentatively assign the singlet at 482 cps to the protons at the 6-position, the doublet at 584 cps to the 4- and 8-protons, and the multiplet at 551 cps to the 1-, 3-, 9- and 11-protons.

Comparison of the ultraviolet spectra of I(n=2; X=Br) [$\lambda_{max}^{70\%\ H_2SO_4}$ at 308-311 mμ (ε 18500)] and of II (X=Cl) [$\lambda_{max}^{70\%\ H_2SO_4}$ at 223, 249, 262, 272, 311, and 323 mμ (ε 14210, 5710, 3020, 1360, 15500, and 18000)] shows that the shortening of the bridge by one carbon atom results in splitting of the broad adsorption band of I (n=2) into two discrete bands, one of which occurs at longer wave lengths. This effect is reminiscent of the differences in the ultraviolet spectra of fluorene and 9,10-dihydrophenanthrene,[4] and by analogy with these hydrocarbons we suggest that the pyridine rings in I (n=2) are in an collinear configuration without being accurately coplanar, while the opposite should hold for II.[cf 5]

While salts of the dipyrido[1,2-c:2',1'-e]imidazolium cation are stable in the solid state, their solutions in water are decomposed by sun light. The only product so far identified in the photo-decomposition of III (X=Cl) is 2,2'-bipyridyl hydrochloride (70% after three weeks).

The dipyrido[1,2-c:2',1'-e]imidazolium cation reacts with nucleophiles and electrophiles at the 6-position, but the primary products formed in the reactions studied so far are not very stable. Thus III (X=Cl) reacted at room temperature slowly with an aqueous solution of either potassium hydroxide (10%) or potassium cyanide (5%) to give deep red coloured water soluble compounds which on exposure to air were rapidly converted to 2,2'-bipyridyl (yield after three weeks 38 and 49% respectively).

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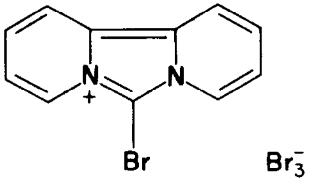
[4] R.N. Jones, J. Amer. Chem. Soc. 67, 2127 (1945).

[5] D.M. Burns and J. Iball, Proc. Roy. Soc. A, 227, 200 (1955).

Bromination in hot aqueous acetic acid also gave 2,2'-bipyridyl (43%), but bromination of III (X=Br) in glacial acetic acid at room temperature gave a quantitative yield of 6-bromodipyrido[1,2-c:2',1'-e]imidazolium tribromide (VII), m.p. 146-148° (uncorr.), with decomposition. This compound was rapidly destroyed by water, and it reacted only slightly less rapidly with methanol, ethanol, acetone and dimethyl sulphoxide. Rapid crystallisation from methanol gave a dark-green micro-crystalline powder (5% recovery), m.p. 146-148° (with decomposition) (Found: C, 27.05; H, 1.79; N, 5.60%. $C_{11}H_9N_2Br_4$ requires C, 27.07; H, 1.65; N, 5.7%).



VII

The structure of VII follows from its conversion to 2,2'-bipyridyl (58%) by means of aqueous sodium hydroxide, and from its ultraviolet spectrum λ_{max}^{MeOH} at 248, 286, 296, 345, 363, 381, 403, and 447 mμ (ε 31830, 4970, 6290, 10575, 15015, 14600, 5130, 4420, 2600) and λ_{min}^{MeOH} at 279, 290, 310, 357, 398, 417 mμ (ε 15230, 3440, 4810, 4810, 10260, 12900, 4810, 3170, 2060); this spectrum was determined within two minutes of dissolving the compound[6]).

In view of the herbicidal activity of I (n=2; X=Br) and related compounds,[7] the effect of III (X=Cl) on the elongation of wheat coleoptiles

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[6] We thank Dr. R.A. Jones for this spectrum.

[7] R.J. Fielder, R.F. Homer and R.L. Jones, Brit. Patent No. 785,732; Chem. Abstr. 52, 6707 (1958).

was compared with that of I (n=2; X=Br). After 24 hours (under red light) and at concentration of 10^{-3} mole/l I and III had the same activity. At 10^{-4} mole/l III had about 1/3 of the inhibiting effect of I.[8]

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[8] We thank Drs. M.R. Atkinson and N.G. Marinos of the Waite Agricultural Research Institute, Adelaide, for these tests.