# Ultraviolet Spectral Correlation between the Cation of an Amino-*N*-heteroaromatic Compound and the Neutral Species of the Corresponding Oxo-analogue

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A new spectroscopic correlation is described, namely that the cation of a 2-amino-derivative of pyrimidine (or of a fused pyrimidine) has an u.v. spectrum similar to that of the neutral species of the 2-oxo-analogue. This correlation (which does not extend to the 4-derivatives) is attributed to a formal similarity between the guanidinium and the urea types of resonance. Correlation was found to be less tight in the corresponding pyridine series, where amidinium and amide resonances were concerned.

DURING investigation of the u.v. spectra of some amino-derivatives of nitrogenous heteroaromatics, it was observed that the cation of 2-aminopyrimidine had absorption maxima and extinction coefficients similar to those of the neutral species of 2-pyrimidone (see Table). Similarly the spectrum of the cation of 2-amino-4-pyrimidone resembled that of the neutral species of pyrimidine-2,4-dione; and the cation of 2,4-diaminopyrimidine and the neutral species of 4-amino-2-pyrimidone were similarly related.

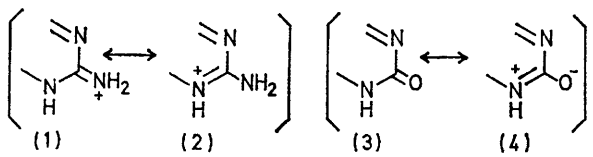
Thus the contribution of the guanidinium type of resonance to an u.v. spectrum seemed to be approximately equivalent to that of the urea-type of resonance. This correlation is what would be expected if the hybrids

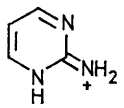
| | Ionisation in water (20—25°) | | U.v. data (water) [b] | | | | |
|---|---|---|---|---|---|---|---|
| | | | $\lambda_{max.}$/nm | | log ε | | |
| Compound | Species [a] | p$K_a$ | | | | | pH [c] |
| 2-Aminopyrimidine | 0 | | 224 | 292 [d] | 4·13 | 3·50 | 7·0 |
| | + | 3·54 [e] | 221 | 302 [d] | 4·17 | 3·60 | 1 |
| 2-Pyrimidone | 0 | | <215 | 298 [f] | >4·0 | 3·67 [g] | 6·21 |
| 4-Aminopyrimidine | 0 | | 234 | 268 [h] | 4·08 | 3·55 | 7·73 |
| | + | 5·71 [e] | 246 [h] | | 4·27 | | 0·00 |
| 4-Pyrimidone | 0 | | 223 | *260* [d] | 3·87 | *3·57* | 6·2 |
| 2-Amino-4-pyrimidone | 0 | | 280 [i] | | 3·64 | | 7·0 |
| | + | 4·0 [i] | 257 [j] | | 3·82 | | 1 |
| Pyrimidine-2,4-dione | 0 | | 258 [k] | | 3·91 [g] | | 7 |
| 2,4-Diaminopyrimidine | 0 | | 227 | 282 [l] | 3·96 | 3·84 | 10·0 |
| | + | 7·26 [e] | *232* | 266 [l] | *4·09* | 3·81 | 7·26 |
| 4-Amino-2-pyrimidone | 0 | | 267 | | 3·79 | | 7·0 |
| 2-Amino-4-pteridone | 0 | | 270 | 340 [m] | 4·05 | 3·76 | 5·25 |
| | + | 2·31 [m] | <220 | 315 [m] | >4·1 | 3·88 | 0 |
| Pteridine-2,4-dione | 0 | | 230 | 324 [n] | 4·00 | 3·84 | 5·9 |
| 2,4-Diaminopteridine | 0 | | 324 | 255 | 4·07 | 4·32 | 8·0 |
| | | | 364 [o] | | 3·86 | | |
| | + | 5·32 [m] | 240 | 284 | 4·10 | 3·73 | 3·0 |
| | | | *318* | 332 | *3·91* | 3·98 | |
| | | | *345* [o] | | *3·90* | | |
| 4-Amino-2-pteridone | 0 | | 240 | *286* | 4·08 | *3·63* | 7·0 |
| | | | 337 | *350* [o] | 3·94 | *3·87* | |
| 2-Aminopurine | 0 | | *236* | 305 [p] | *3·70* | 3·78 | 7·0 |
| | + | 3·80 [p] | *237* | 314 [p] | *3·62* | 3·60 | 1·84 |
| Purin-2-one | 0 | | 238 | 315 [p] | 3·46 | 3·69 | 6·05 |
| 6-Aminopurine | 0 | | 260 [p] | | 4·13 | | 7·03 |
| | + | 4·22 [p] | 262 [p] | | 4·12 | | 2·10 |
| Purin-6-one | 0 | | 249 [p] | | 4·02 | | 5·18 |
| 2-Aminopurin-6-one | 0 | | 246 | 275 [p] | 4·01 | 3·89 | 6·20 |
| | + | 3·3 [p] | 248 | 271 [p] | 4·03 | 3·85 | 1·00 |
| Purine-2,6-dione | 0 | | 267 [p] | | 3·90 | | 5·05 |
| 2,6-Diaminopurine | 0 | | 246 | 279 [p] | 3·85 | 3·95 | 7·48 |
| | + | 5·09 [p] | 241 | 282 [p] | 3·96 | 4·02 | 3·0 |
| 6-Aminopurin-2-one | 0 | | 240 | 286 [p] | 3·89 | 3·90 | 6·98 |
| 2-Amino-7-methyl-8-azapurin-6-one | 0 | | 239 | 297 [q] | 3·85 | 3·70 | 5 |
| | + | 1·58 [q] | 270 [q] | | 3·78 | | −2 |
| 7-Methyl-8-azapurine-2,6-dione | 0 | | 274 [r] | | 3·78 | | 5 |
| 2-Amino-8-methyl-8-azapurin-6-one | 0 | | 243 | 293 [q] | 3·82 | 3·80 | 6 |
| | + | 1·86 [q] | 268 [q] | | 4·00 | | −1 |
| 8-Methyl-8-azapurine-2,6-dione | 0 | | 272 [r] | | 3·94 | | 4 |
| 2,6-Diamino-7-methyl-8-azapurine | 0 | | <230 | *249* | >3·5 | *3·78* | 7 |
| | | | 309 [q] | | 3·79 | | |
| | + | 4·27 [q] | 218 | 258 | 4·13 | 4·07 | 1 |
| | | | 282 [q] | | 3·90 | | |
| 6-Amino-7-methyl-8-azapurin-2-one | 0 | | 255 | 287 [q] | 3·93 | 3·83 | 6 |
| 2,6-Diamino-8-methyl-8-azapurine | 0 | | 257 | 307 [q] | 3·77 | 3·91 | 8 |
| | + | 5·17 [q] | 259 | 284 [q] | 4·11 | 4·08 | 2 |
| 6-Amino-8-methyl-8-azapurin-2-one | 0 | | 256 | 285 [q] | 4·03 | 4·03 | 7 |
| 2-Aminopyridine | 0 | | 229 | 287 [s] | 3·97 | 3·58 [g] | 9·5 |
| | + | 6·86 [e] | 229 | 300 [s] | 3·95 | 3·76 [g] | 1 |

| Compound | Ionisation in water (20—25°) Species [a] | $pK_a$ | U.v. data (water) [b] $\lambda_{max.}$/nm | | log ε | | pH [c] |
|---|---|---|---|---|---|---|---|
| 2-Pyridone | 0 | | 224 | 293 [t] | 3·86 | 3·77 [g] | 6 |
| 2-Aminoquinoline | 0 | | 210 [u] | 310 [u,v] | 4·5 | 3·7 | A |
| | + | 7·34 [e] | 210 [u] | 230 [u] | 4·3 | 4·2 | B |
| | | | 260 [u] | 308 [u] | 3·8 | 3·9 | |
| | | | *320* [u,v] | | *3·8* | | |
| 2-Quinolone | 0 | | 224 | 245 | 4·43 | 3·93 | 4·7 |
| | | | 270 | 323 [w] | 3·82 | 3·80 | |
| 3-Aminoisoquinoline | 0 | | 231 | 269 | 4·74 | 3·67 | 9·21 |
| | | | 278 | *288* | 3·73 | *3·58* | |
| | | | 353 [x] | | 3·42 | | |
| | + | 5·05 [x] | 237 | 277 | 4·76 | 3·53 | 2·54 |
| | | | 285 | 296 | 3·52 | 3·21 | |
| | | | 390 [x] | | 3·62 | | |
| 3-Isoquinolone | 0 | | 274 [u] | 285 [u] | 3·5 | 3·5 | C |
| | | | *297* [u] | 395 [y] | *3·2* | 3·60 [g] | |
| 2-Aminopyrazine | 0 | | 230 | *285* | 4·02 | *3·33* | 7·0 |
| | | | 316 [w] | | 3·70 | | |
| | + | 3·14 [e] | 229 | 325 [w] | 4·03 | 3·77 | 1·0 |
| Pyrazin-2-one | 0 | | 221 | 316 [z] | 3·96 | 3·74 | 5·1 |
| 2-Aminoquinoxaline | 0 | | 240 | *290—310* | 4·33 | *3·39* | 7·2 |
| | | | 353 [aa] | | 3·80 | | |
| | + | 3·96 [e] | 231 | 252 | 4·25 | 4·05 | 1·0 |
| | | | 257 | *310—326* | 4·07 | *3·76* | |
| | | | 348—352 [aa] | | 3·84 | | |
| 2-Quinoxalone | 0 | | 228 | 250 | 4·32 | 3·79 | 4·0 |
| | | | 254 | 287 | 3·78 | 3·70 | |
| | | | 343 [aa] | | 3·74 | | |

[a] Neutral species (0), cation (+). [b] Inflections are in italics. [c] Negative values are acidity function ($\delta H_0$), of appropriate dilutions of sulphuric acid;[3] A: in 0·01N-NaOH; B: in 0·01N-HCl; C: in water. [d] D. J. Brown and L. N. Short, *J. Chem. Soc.*, 1953, 331. [e] A. Albert, R. Goldacre, and J. Phillips, *J. Chem. Soc.*, 1948, 2240. [f] D. J. Brown, E. Hoerger, and S. F. Mason, *J. Chem. Soc.*, 1955, 211. [g] These values were converted into log ε. [h] M. P. V. Boarland and J. F. W. McOmie, *J. Chem. Soc.*, 1952, 3716. [i] D. J. Brown and T. Teitei, *Austral. J. Chem.*, 1965, **18**, 559. [j] D. Isbecque, R. Promel, R. C. Quinaux, and R. H. Martin, *Helv. Chim. Acta*, 1959, **42**, 1317. [k] A. R. Katritzky and A. J. Waring, *J. Chem. Soc.*, 1962, 1540. [l] D. J. Brown and J. M. Lyall, *Austral. J. Chem.*, 1962, **15**, 851. [m] A. Albert, D. J. Brown, and G. Cheeseman, *J. Chem. Soc.*, 1952, 4219. [n] A. Albert, D. J. Brown, and G. Cheeseman, *J. Chem. Soc.*, 1951, 474. [o] D. J. Brown and N. W. Jacobsen, *J. Chem. Soc.*, 1961, 4413. [p] S. F. Mason, *J. Chem. Soc.*, 1954, 2071. [q] A. Albert and H. Taguchi, *J.C.S. Perkin I*, 1972, 449. [r] G. Nübel and W. Pfleiderer, *Chem. Ber.*, 1965, **98**, 1060. [s] S. F. Mason, *J. Chem. Soc.*, 1960, 219. [t] S. F. Mason, *J. Chem. Soc.*, 1957, 5010. [u] Approximate values estimated from the spectral curves in the literature. [v] E. A. Steck and G. W. Ewing, *J. Amer. Chem. Soc.*, 1948, **70**, 3397. [w] D. J. Brown and S. F. Mason, *J. Chem. Soc.*, 1956, 3443. [x] A. R. Osborn, K. Schofield, and L. N. Short, *J. Chem. Soc.*, 1956, 4191. [y] D. A. Evans, G. F. Smith, and M. A. Wahid, *J. Chem. Soc.* (*B*), 1967, 590. [z] G. W. H. Cheeseman, *J. Chem. Soc.*, 1960, 242. [aa] G. W. H. Cheeseman, *J. Chem. Soc.*, 1958, 108.

of each canonical form of (1) ⟷ (2) and of (3) ⟷ (4) make similar electronic contributions to the ground and the excited states. Hence the correlation in the u.v. spectrum is consistent with existence of the cation of 2-aminopyrimidine principally as the imino-form (5)




as has been concluded (for the solid state) from i.r. evidence.[1]

This correlation was extended to the cations of 2-amino-derivatives of *fused* pyrimidines, which were found to have u.v. spectra similar to those of the neutral species of the 2-oxo-analogues. For example, the u.v. absorption maxima of the cation of 2,4-diaminopteridine closely resemble those of 4-aminopteridin-2-one (neutral species) (see Table); the cation of 2-amino-4-pteridone and the neutral species of pteridine-2,4-dione are related likewise. In the purine and the 8-azapurine series, a similar spectral correlation exists between the cations of 2-amino-derivatives and the neutral species of the corresponding 2-oxo-analogues. However, no cation of a 4-aminopyrimidine (or fused pyrimidine) was related to the neutral species of the corresponding oxo-analogue. This lack of correlation may be explained by the fact that the neutral species of 4-pyrimidone exists mainly in the form (6) [2] whereas 4-aminopyrimidine is commonly held to be protonated in the 1-position [3] to give the hybrid (7).

An interesting practical aspect of the rule is illustrated by the lack of correlation between the cation of 2-amino-9-methylpurin-6-one [$\lambda_{max.}$ 251 and 276 nm (log ε 4·08 and 3·88)] [4] and 9-methylpurine-2,6-dione (neutral species) [$\lambda_{max.}$ 234 and 265 nm (log ε 3·92 and

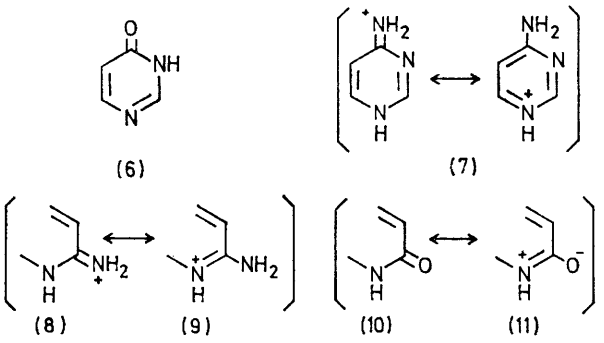
[1] E. Spinner, *J. Chem. Soc.*, 1962, 3119.

[2] (*a*) D. J. Brown and L. N. Short, *J. Chem. Soc.*, 1953, 331; (*b*) D. J. Brown, E. Hoerger, and S. F. Mason, *ibid.*, 1955, 211; (*c*) S. F. Mason, *ibid.*, 1957, 5010; (*d*) A. Albert and E. Spinner, *ibid.*, 1960, 1221.

[3] A. Albert, R. Goldacre, and J. Phillips, *J. Chem. Soc.*, 1948, 2240.

[4] W. Pfleiderer, *Annalen*, 1961, **647**, 167.

4·1)],[5] whereas 2-aminopurin-6-one cation was closely related to purine-2,6-dione (neutral species) (see (Table). This exceptional behaviour of the 9-methyl derivative suggests that it does not undergo protonation on the pyrimidine ring. In fact, the protonation has been shown to take place at the 7-position by the similarity of the u.v. spectrum of the 2-amino-9-methylpurin-6-one cation to that of the 2-amino-7,9-dimethyl-6-oxopurinium cation.[4]




Possible extension of this rule to the relation between the amidinium- and amide-type resonances, (8) ⟷ (9) and (10) ⟷ (11) respectively, was investigated (see Table for examples), but a less tight relationship was found. Thus a difference of 9 nm exists (in the absorption maximum of longer wavelength) between the 2-aminopyrazine cation and pyrazin-2-one (neutral species), although the cation of 3-aminoisoquinoline relates closely to the neutral species of 3-isoquinolone. One possible explanation why the amidinium and amide type of resonances are less closely related than in the guanidinium and urea resonance pair, is that the proportion of the exocyclic double bond form (8) in the amidinium ion might be expected to be somewhat different from that of the oxo-form (10) of the amide, principally because they are less symmetrical structures than the forms (1) and (2) respectively.

The new rule is distinct from that of Jones, who discovered the spectral correlation [6] between a phenolic anion and the corresponding aniline molecule, a rule which has been successfully extended to nitrogenous heteroaromatic chemistry.[7] The spectral correspondence between the cation of an amino-derivative and the corresponding oxo-analogue has remained undetected up to now, most likely because all aminoheteroaromatic cations have been thought to be overwhelmingly in the primary amino-form (2).

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[5] W. Pfleiderer and G. Nübel, *Annalen*, 1961, **647**, 155.
[6] R. N. Jones, *J. Amer. Chem. Soc.*, 1945, **67**, 2127.
[7] (*a*) A. Albert, *Quart. Rev.*, 1952, **6**, 197; (*b*) D. J. Brown and T. Teitei, *J. Chem. Soc.*, 1963, 4333.
[8] K. N. Bascombe and R. P. Bell, *J. Chem. Soc.*, 1959, 1096.