J. Chem. Research (S),
1997, 238–239
J. Chem. Research (M),
1997, 1615–1630

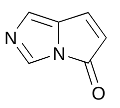
Crystal and Molecular Structures of Two Pyrrolo[1,2-*c*]imidazol-5-ones

Alexander J. Blake,*,† Hamish McNab* and (the late) Craig Thornley

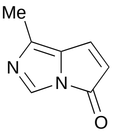
Department of Chemistry, The University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ, UK

The crystal structures of the pyrrolo[1,2-*c*]imidazol-5-ones **2** and **3** are reported; the results show that the system behaves structurally as a simple cyclic *N*-acylimidazole, with no special cyclic delocalisation.

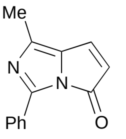
Some years ago, one of us (H. M.) reported the first synthesis of the parent compound of the pyrrolo[1,2-*c*]imidazol-5-one system **1**,[1] and more recently we have shown how this can be improved and extended to provide a versatile and convenient route to substituted members of this and related series.[2,3] Since these compounds are now readily available, we have embarked on a systematic study of their properties and report here the results of an X-ray crystallographic investigation of the pyrrolo[1,2-*c*]imidazol-5-ones **2** and **3**.[2] Previous structural studies of the fully unsaturated pyrrolizin-3-one system[4] are confined to our earlier results on the 6-bromo derivative **4**,[5] and no work on azapyrrolizinones has been reported. Pyrrolizinones possess an unusual conjugated system, in which 'normal' amide resonance creates a formally antiaromatic canonical form which is reflected in an unusually long C(3)–N(4) bond (Scheme 1). The effect, if any, of the replacement of a CH with an N on this delocalisation was a major focus for the present study.



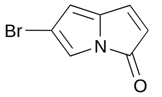
1



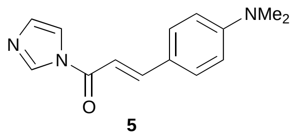
2



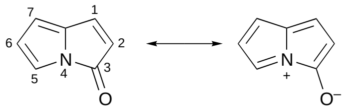
3



4



5



Scheme 1

The principal dimensions of **2** and **3** are summarised in Fig. 1, together with those of the model pyrrolizinone **4**. In addition, pyrrolo[1,2-*c*]imidazoles may be regarded as cyclic *N*-acylimidazoles, so the dimensions of the model *N*-cinnamoylimidazole **5**[6] are also included in Fig. 1. Views of **2** and **3** showing the crystallographic numbering schemes are shown in Fig. 2.

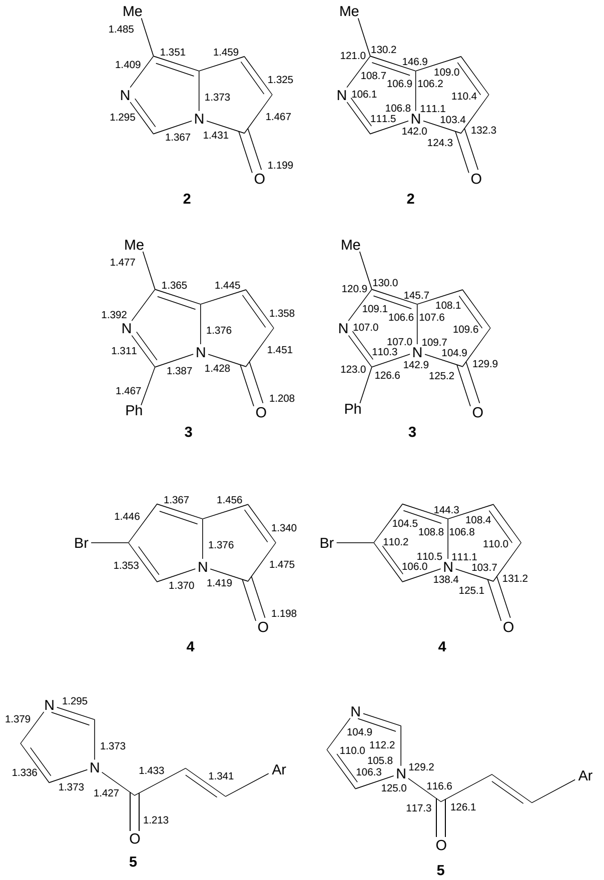


Fig. 1 Principal molecular dimensions of **2**, **3**, **4** and **5**. Typical ESDs of the bond lengths are 0.004, 0.005, 0.10 and 0.002 Å respectively and those of the bond angles are 0.3, 0.4, 0.7 and 0.2° respectively

In the full text version of this paper, we present a detailed analysis of the data presented in Fig. 1, and the major conclusions are as follows: (i) The bond lengths in the amide region [N(4)—C(5)—O(5)] are not significantly different in **2**, **3** or the model compounds **4** and (especially) **5**, confirming that the pyrrolo[1,2-*c*]imidazoles may be regarded structurally as *N*-acylazoles, with no special contribution due to cyclic delocalisation of electrons. However, it should be emphasised that the N(4)—C(5) bonds in particular are almost 0.1 Å longer than is typical for a cyclic tertiary γ-lactam[7] [1.335(9) Å], presumably owing to competitive delocalisation of the nitrogen atom lone pair into the imidazole ring as well as into the carbonyl group. (ii) The formal double and single bonds are consistently longer and shorter respectively in **3** than in **2** for the conjugating pathway C(3)—N(2)—C(1)—C(8)—C(7)—C(6)—C(5) linking the 3-phenyl substituent with the carbonyl group. This confirms earlier spectroscopic studies[2] which suggest that the phenyl group in **3** behaves as a net electron donating group. (iii) The individual 5-membered rings of the two pyrrolo[1,2-*c*]imidazoles are both essentially flat, but the systems as a whole are not perfectly planar, with the angles between the two 5-membered rings in **2** and **3** being 2.5 and 4.2° respectively. (iv) Both compounds **2** and **3** display very large exocyclic bond angles (142.0–146.9°) at the ring junctions which is a characteristic feature of the geometry of such fused 5-membered rings.[5] (iv) Crystal packing

---

*To receive any correspondence.
†*Present address:* Department of Chemistry, University of Nottingham, University Park, Nottingham NG7 2RD, UK.

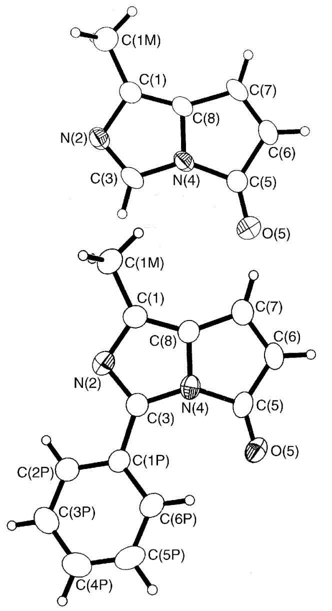


Fig. 2 Views of **2** and **3** showing the crystallographic numbering schemes. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radius

in **2** involves N(2)···H—C(3) contacts which lead to helices of molecules in the *a* crystallographic direction.

Crystal Data for **2**.—$C_7H_6N_2O$, $M = 134.14$, orthorhombic, $a = 4.3013(4)$, $b = 11.3334(7)$, $c = 13.4102(7)$ Å, $V = 653.73(8)$ Å^3 [from 2θ values of 26 reflections measured at $\pm\omega$ ($28 \le 2\theta \le 30°$, $\lambda = 0.71073$ Å, $T = 280$ K)], space group $P2_12_12_1$ (No. 19), $Z = 4$, $D_x = 1.363$ g cm^{-3}, yellow equant crystal, $0.46 \times 0.39 \times 0.39$ mm, μ(Mo-Kα) = 0.095 mm^{-1}.

Data collection and processing. Stoe Stadi-4 four-circle diffractometer, $\omega/2\theta$ scans, graphite-monochromated Mo-Kα X-radiation; 940 reflections measured ($5 \le 2\theta \le 45°$, $\pm h, k, l$), 857 unique [merging $R = 0.038$], giving 704 with $F \ge 4\sigma(F)$ and 857 which were retained in all calculations. No crystal decay was observed and no corrections were applied for absorption.

Structure solution and refinement. Automatic methods[8] (all non-H atoms). Full-matrix least-squares refinement[9] with all non-H atoms anisotropic. Methyl hydrogen atoms were located from a ΔF synthesis and others were introduced at geometrically calculated positions: subsequent refinement allowed rotation of the rigid methyl group hydrogens while a riding model was adopted for the others [$U_{iso}(H) = xU_{eq}(C)$; $x = 1.5$ for methyl hydrogens and 1.2 for others]. The weighting scheme $w^{-1} = [\sigma^2(F_o^2) + (0.0964P)^2]$, $P = \frac{1}{3}[\mathrm{MAX}(F_o^2,0) + 2F_c^2]$, gave satisfactory agreement analyses. Final R_1 [$F \ge 4\sigma(F)$] = 0.0529, wR_2 [all data] = 0.1330, $S[F^2] = 1.09$ for 93 refined parameters. An extinction correction[9] refined to 0.015(10) and the final ΔF synthesis showed no peaks out of the range 0.25 to -0.18 eÅ^{-3}.

Crystal Data for **3**.—$C_{13}H_{10}N_2O$, $M = 210.23$, monoclinic, $a = 7.227(3)$, $b = 20.063(9)$, $c = 7.107(4)$ Å, $\beta = 97.18(6)°$, $V = 1022.4(8)$ Å^3 [from 2θ values of 25 reflections measured at $\pm\omega$ ($28 \le 2\theta \le 30°$, $\lambda = 0.71073$ Å, $T = 150$ K)], space group Cc (No. 9), $Z = 4$, $D_x = 1.366$ g cm^{-3}, red columnar crystal, $0.74 \times 0.16 \times 0.08$ mm, μ(Mo-Kα) = 0.089 mm^{-1}.

Data collection and processing. Data collection as for **2** above; 1051 reflections measured ($5 \le 2\theta \le 45°$, $\pm h$, $\pm k$, l), 679 unique [merging $R = 0.099$], giving 610 with $F \ge 4\sigma(F)$ and 679 which were retained in all calculations. No crystal decay was observed and no corrections were applied for absorption.

Structure solution and refinement. The structure was solved and refined as for **2** above. The weighting scheme $w^{-1} = [\sigma^2(F_o^2) + (0.076P)^2 + 0.21P]$, $P = \frac{1}{3}[\mathrm{MAX}(F_o^2,0) + 2F_c^2]$, gave satisfactory agreement analyses. Final $R_1[F \ge 4\sigma(F)] = 0.0343$, wR_2 [all data] = 0.1032, $S[F^2] = 1.12$ for 145 refined parameters. An extinction correction[9] refined to 0.009(4) and the final ΔF synthesis showed no peaks out of the range 0.16 to -0.19 eÅ^{-3}.

Technique used: X-ray diffraction

References: 9

Fig. 3: Packing diagram for **2**

Fig. 4: Packing diagram for **3**

Tables 1–8: Lists of refined parameters and molecular geometry descriptors for both structures

We are grateful to The University of Edinburgh for a Research Studentship (to C. T.) and to the EPSRC (formerly the SERC) for the provision of a four-circle diffractometer.

Received, 12th March 1997; Accepted, 3rd April 1997
Paper E/7/01729D

References cited in this synopsis

1 H. McNab, *J. Chem. Soc., Perkin Trans. 1*, 1987, 653.
2 H. McNab and C. Thornley, *J. Chem. Soc., Perkin Trans. 1*, in the press.
3 S. E. Campbell, M. C. Comer, P. A. Derbyshire, X. L. M. Despinoy, H. McNab, R. Morrison, C. C. Sommerville and C. Thornley, *J. Chem. Soc., Perkin Trans. 1*, in the press.
4 H. McNab and C. Thornley, *Heterocycles*, 1994, **37**, 1977.
5 A. J. Blake, H. McNab and R. Morrison, *J. Chem. Soc., Perkin Trans. 1*, 1988, 2145.
6 C. P. Huber, *Acta Crystallogr., Sect. C*, 1985, **41**, 1076.
7 P. Chakrabarti and J. D. Dunitz, *Helv. Chim. Acta*, 1982, **65**, 1555.
8 SHELXS86, G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 1990, **46**, 467.
9 SHELXL96, G. M. Sheldrick, University of Göttingen, Germany, 1996.