Heterocyclic tautomerism, part 12.[1] The structure of the product of reaction between 3-methyl-1-phenyl-2-pyrazolin-5-one and tetracyanoethylene

James A. M. Guard and Peter J. Steel*

Department of Chemistry, University of Canterbury, Christchurch, New Zealand
E-mail: p.steel@chem.canterbury.ac.nz

Dedicated to Prof. Don Cameron on the occasion of his retirement from the University of Melbourne

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Abstract

The title reaction produces 6-amino-3,3'-dimethyl-5'-oxo-1,1'-diphenylspiro[pyrano[2,3-c]pyrazole -4(1H),4'-[2]-pyrazoline]-5-carbonitrile 4, the structure of which has been determined by X-ray crystallography. It crystallizes in the orthorhombic space group *Pna*2_1, with two independent molecules in the asymmetric unit.

Keywords: Heterocyclic tautomerism, x-ray crystallography, 3-methyl-1-phenyl-2pyrazolin-5-one, tetracyanoethylene

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Introduction

Some years ago, Abdel Galil *et al.*[2] reported that tetracyanoethylene (TCNE) reacts with 3-methyl-1-phenyl-2-pyrazolin-5-one **1** in ethanol to produce a product to which they assigned the dipyrazolylmethane structure **2** (Scheme 1). To explain the non-equivalence of the two pyrazole rings in the NMR spectra, they proposed that one ring exists as the OH tautomer and the other as the NH tautomer. We considered this to be extremely improbable, as structurally related compounds have been shown[3] to display equivalence of the pyrazole signals in their NMR spectra. Although pyrazolones are known to exhibit desmotropy,[4] it would be unprecedented for a pyrazolone ring to exist as different tautomers within the same molecule. Furthermore, the authors listed two nitrile signals in the ^{13}C NMR spectrum, a feature that is incompatible with structure **2**. We now report the X-ray crystal structure of this compound.

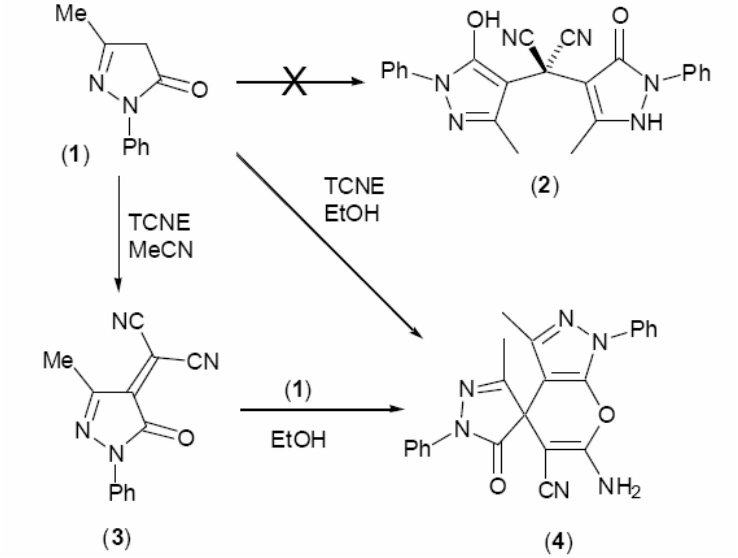
Results and Discussion

Whilst Abdel Galil *et al.*[2] were unable to isolate the proposed dicyanomethylene intermediate **3**, this compound can readily be prepared by reaction of **1** with TCNE in acetonitrile solution.[5] We have found that reaction of **1** with either TCNE or **3**, produces a product that on recrystallization from methanol affords needles suitable for X-ray crystal structure determination. This compound crystallizes in the orthorhombic space group *Pna*2_1, with two independent molecules in the asymmetric unit, which are related by a non-crystallographic pseudo-center of inversion.

Figure 1 shows a perspective view of the structure which is a spiro[pyrano[2,3-c]pyrazole-4,4'-pyrazoline, a well-known heterocyclic ring system,[6] although this is the first report of an X-ray crystal structure of such a compound. Structure **4** has independently been proposed by Metwally *et al.*[7] for the product of the reaction of **3** with **1**, although curiously they report a different melting point. This compound clearly results from reaction of **1** with the C4 carbon of **3**, rather than the exocyclic dicyanomethylene carbon that would lead to **2**. Both these modes of reaction have been reported for **3** and structurally related compounds.[6,8,9]

The pyranopyrazole ring system is approximately planar, and orthogonal to the other pyrazoline ring (angle between meanplanes = 88.6(5) and 91.1(5)° for the two independent molecules). The N1 phenyl rings are inclined to the planes of the pyranopyrazoles at angles of 41.4(5) and 41.1(5) °, for the two independent molecules. The N1' phenyl rings are twisted by 29.5(5) and 25.7(5)° from the planes of the attached pyrazoline rings. Intermolecular interactions are controlled by hydrogen bonds between symmetry related molecules. Specifically, each independent NH_2 hydrogen atom is hydrogen bonded to either N2 or O2 of an adjacent molecule, with distances ranging between 2.05 and 2.19 Å.

In conclusion, we have unambiguously identified the structure of the product of the title reaction as 6-amino-3,3'-dimethyl-5'-oxo-1,1'-diphenylspiro[pyrano[2,3-c]pyrazole-4(1H),4'-[2]-pyrazoline]-5-carbonitrile.



Scheme 1. Formation of **4**.

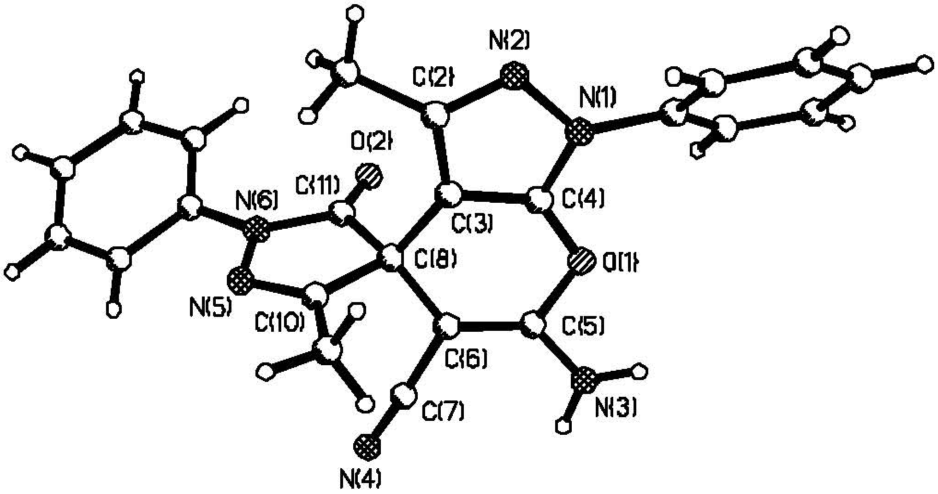


Figure 1. Perspective view of one of the two independent molecules of **4**.

Table 1. Selected bond lengths (Å) and angles (^{o}) for each of the two independent molecules of **4**.

Bond Length			Bond Angles		
O(1)-C(4)	1.356(6)	1.357(6)	C(4)-O(1)-C(5)	114.3(4)	114.0(4)
O(1)-C(5)	1.379(5)	1.379(5)	C(4)-N(1)-N(2)	108.6(4)	108.7(4)
O(2)-C(11)	1.210(5)	1.210(5)	C(2)-N(2)-N(1)	106.1(4)	106.1(4)
N(1)-C(4)	1.351(6)	1.351(6)	C(10)-N(5)-N(6)	107.5(4)	107.5(4)
N(1)-N(2)	1.375(5)	1.374(5)	C(11)-N(6)-N(5)	112.5(4)	112.5(4)
N(2)-C(2)	1.336(6)	1.336(6)	N(2)-C(2)-C(3)	110.3(5)	110.2(5)
N(3)-C(5)	1.336(6)	1.336(6)	C(4)-C(3)-C(2)	104.4(5)	104.4(5)
N(4)-C(7)	1.132(6)	1.132(6)	C(4)-C(3)-C(8)	121.6(5)	121.7(5)
N(5)-C(10)	1.271(6)	1.271(6)	C(2)-C(3)-C(8)	133.9(5)	133.9(5)
N(5)-N(6)	1.429(5)	1.429(5)	C(3)-C(4)-N(1)	110.5(5)	110.6(5)
N(6)-C(11)	1.374(6)	1.374(6)	C(3)-C(4)-O(1)	128.1(5)	128.3(5)
C(2)-C(3)	1.418(6)	1.419(6)	N(1)-C(4)-O(1)	121.2(5)	121.2(5)
C(3)-C(4)	1.337(6)	1.336(6)	N(3)-C(5)-C(6)	128.5(5)	128.4(5)
C(3)-C(8)	1.485(6)	1.485(6)	N(3)-C(5)-O(1)	108.5(4)	108.7(4)
C(5)-C(6)	1.344(6)	1.344(6)	C(6)-C(5)-O(1)	122.8(5)	122.9(5)
C(6)-C(7)	1.428(6)	1.428(6)	C(5)-C(6)-C(7)	119.3(5)	119.2(5)
C(6)-C(8)	1.513(6)	1.513(6)	C(5)-C(6)-C(8)	124.9(5)	125.0(5)
C(8)-C(11)	1.519(6)	1.519(6)	C(7)-C(6)-C(8)	115.8(4)	115.8(4)
C(8)-C(10)	1.526(6)	1.526(6)	N(4)-C(7)-C(6)	178.0(8)	176.8(11)
			C(3)-C(8)-C(6)	107.5(4)	107.6(4)
			C(3)-C(8)-C(11)	111.2(4)	111.2(4)
			C(6)-C(8)-C(11)	110.8(4)	110.8(4)
			C(3)-C(8)-C(10)	114.4(5)	114.3(4)
			C(6)-C(8)-C(10)	112.6(4)	112.6(4)
			C(11)-C(8)-C(10)	100.3(4)	100.3(4)
			N(5)-C(10)-C(8)	113.6(5)	113.6(5)

Table 1. Continued

O(2)-C(11)-N(6)	126.1(5)	126.0(5)
O(2)-C(11)-C(8)	127.8(5)	127.9(5)
N(6)-C(11)-C(8)	106.0(5)	106.0(4)

Experimental Section

Preparation of (4). Tetracyanoethylene (1.95 g, 0.0152 mol) and 3-methyl-1-phenylpyrazol-5-one (5.3 g, 0.0304 mol) were refluxed in ethanol (75 mL) for two hours. The resulting solid was filtered off and recrystallized from methanol. Yield 2.8 g (45%), mp 192 °C, lit.[2] 195 °C.

X-Ray Crystallography. Intensity data were collected with a Nicolet P4s four-circle diffractometer using graphite-monochromatized Mo Kα radiation (λ 0.7107Å). Cell parameters were determined by least-squares refinement using the setting angles of 25 accurately centred reflections ($2\theta > 15°$). Throughout data collection (ω scans) the intensities of three standard reflections were monitored and this showed no significant crystal decomposition. The intensities were corrected for Lorentz, polarisation and absorption effects. The structure was solved by direct methods using SHELXS[10] and refined on F^2 by full-matrix least squares procedures using SHELXL.[11] All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogens were included in calculated positions, with the conformational orientation of the methyl hydrogens chosen to optimise agreement with the electron density of a difference Fourier map. All data were used in the refinement; the function minimised was $\Sigma w(F_o^2 - F_c^2)$, with $w = [\sigma^2(F_o^2) + 0.032P^2]^{-1}$where $P = [\max(F_o^2 + 2F_c^2]/3$. Final Fourier syntheses showed no significant residual electron density in chemically sensible locations. Selected bond lengths and angles are listed in Table 1.

Crystal Data for 4 at 130 K. $C_{23}H_{18}N_6O_2$, *M* 410.43, orthorhombic, space group $Pna2_1$, *a* 15.947(2), *b* 10.128(2), *c* 24.958(6) Å, *V* 4031.0(14) Å^3, *F*(000) 1712, *D*c(Z=8) 1.353 g cm^{-1}, μ(Mo Kα) 0.91 cm^{-1}, crystal dimensions 0.45 x 0.25 x 0.07 mm, 2θmax 50°, wR (all 3619 data) 0.087, conventional R (922 data with $I > 2\sigma(I)$) 0.038.

References and Notes

1. For part 11, see: Steel, P. J. *J. Chem. Crystallogr.* **1996**, *26*, 399.
2. Abdel-Galil, F. M.; Barsoum, B. N.; Said, M.M.; Saleh, S.S. *Bull. Chim. Soc. Fr.* **1988**, 658.
3. Stefan, S. L.; El-Behary, M.; Ramadan, A. A.; Mahmoud, S. H. *J. Chem. Res.(S)*, **1992**, 246.
4. (a) O'Connell, M. J.; Ramsay, C. G.; Steel, P. J. *Aust. J. Chem.* **1985**, *38*, 401. (b) Guard, J. A. M.; Steel, P. J. *Aust. J. Chem.*, **1994**, *47*, 1453.
5. Junek, H.; Klade, M.; Sterk, H.; Fabian, W. *Monatsh. Chem.* **1988**, *119*, 993.

6. Younes, M. I.; Atta, A. H.; Metwally, S. A. M.; Elnagdi, M. H. *Gazz. Chim. Ital.* **1991**, *121*, 185.
7. Metwally, S. A. M.; El-Naggar, G. M.; El-Emary, T. I. *Liebigs Ann. Chem.* **1991**, 961.
8. Dworczak, R.; Fabian, W. M. F.; Sterk, H.; Kratky, C.; Junek, H. *Liebigs Ann. Chem.* **1992**, 7.
9. El-Ahl, A. A. S.; Afeefy, H.; Metwally, M. A. *J. Chem. Res. (S)* **1994**, 14.
10. Sheldrick, G. M. *Acta Crystallogr., Sect. A* **1990**, *46*, 467.
11. Sheldrick, G. M. SHELXL-97, University of Göttingen, 1997.