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# Structure of Furlone Yellow, $C_{30}H_{24}N_6O_3$

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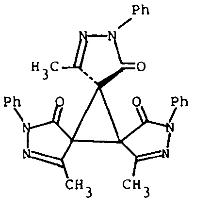
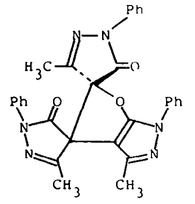
**Abstract.** Spiro([1,9]dimethyl[3,7]diphenyl[1,3]dioxepino[5,4-*d*:6,7-*d*′]dipyrazole-5,4′-[3]methyl[1]phenylpyrazol[5]one), $M_r = 516{\cdot}6$, monoclinic, $P2_1/c$ (No. 14), $a = 7{\cdot}106\,(2)$, $b = 17{\cdot}691\,(3)$, $c = 21{\cdot}691\,(4)$ Å, $\beta = 105{\cdot}64\,(2)°$, $V = 2625{\cdot}9$ Å$^3$, $Z = 4$, $D_x = 1{\cdot}307$ Mg m$^{-3}$, $\lambda(\text{Mo } K\alpha) = 0{\cdot}7107$ Å, $\mu = 0{\cdot}08$ mm$^{-1}$, $F(000) = 1080$, $T = 296$ K, final $R = 0{\cdot}031$ for 1094 unique observed reflections. In contrast to former assignments made in solution the compound was found to consist of a heterocyclic seven-membered ring system with 1,3-dioxepin (1,3-dioxacycloheptadiene) structure.

**Introduction.** 'Furlone yellow' (m.p. 428–429 K), a trimer of 3-methyl-1-phenyl-2-pyrazolin-5-one, was first prepared by Westöö (1953), who assigned the compound the structure *B* possessing a dihydrofuran ring.

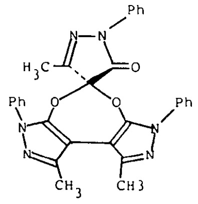
Investigations carried out in solution by $^1$H and $^{13}$C NMR spectroscopy (Mann, Hennig, Wilde, Hauptmann, Behrendt & Kretschmer, 1979) showed the compound to have $C_s$ symmetry, and DNMR measurements were in accordance with the structure *A*, possessing a three-membered ring. In solution, structure *A* was found to be in equilibrium with the non-symmetric isomer *B* proposed by Westöö (1953). However, the NMR data would also be in accordance with the structure *C*. To resolve this ambiguity, we undertook an X-ray diffraction study and in the present paper report the crystal and molecular structure of this quite unusual compound.



(*A*)



(*B*)



(*C*)

**Experimental.** Pale yellow crystals synthesized by addition of 4-bromo-3-methyl-1-phenyl-2-pyrazolin-5-one to the oxidized dimer of 3-methyl-1-phenyl-2-pyrazolin-5-one ('pyrazolone-blue') (Westöö, 1953), 0·20 × 0·20 × 0·15 mm, mounted on a glass fibre, Enraf–Nonius CAD-4 diffractometer, graphite-monochromatized Mo $K\alpha$, $\omega$–$2\theta$ method, lattice parameters from 25 reflections with $4 < \theta < 11°$, two standard reflections measured every hour, no loss of intensity, 2549 reflections ($h$: 0→6, $k$: −16→0, $l$: −20→20) with $\theta < 20°$, 2549 independent, 1094 with $I > 3\sigma(I)$, Lp correction, empirical absorption correction (Walker &

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Table 1. *Fractional coordinates and equivalent isotropic temperature factors for furlone yellow with e.s.d.'s in parentheses*

$$B_{eq} = \tfrac{4}{3}[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)].$$

| | $x$ | $y$ | $z$ | $B_{eq}$(Å$^2$) |
|---|---|---|---|---|
| O(11) | 0·3630 (5) | 0·1959 (2) | 0·3837 (2) | 2·97 (8) |
| O(21) | 0·1846 (5) | 0·3013 (2) | 0·3377 (2) | 3·23 (8) |
| O(31) | 0·6178 (5) | 0·3399 (2) | 0·3914 (2) | 3·94 (9) |
| N(11) | 0·6372 (6) | 0·1311 (2) | 0·3706 (2) | 3·0 (1) |
| N(12) | 0·7444 (6) | 0·1232 (2) | 0·3269 (2) | 3·3 (1) |
| N(21) | 0·1275 (6) | 0·3544 (3) | 0·2367 (2) | 3·7 (1) |
| N(22) | 0·1866 (7) | 0·3498 (3) | 0·1820 (2) | 5·0 (1) |
| N(31) | 0·4863 (6) | 0·3425 (3) | 0·4779 (2) | 3·5 (1) |
| N(32) | 0·3164 (6) | 0·3139 (3) | 0·4929 (2) | 3·8 (1) |
| C(11) | 0·5007 (7) | 0·2101 (3) | 0·2901 (2) | 2·6 (1) |
| C(12) | 0·4935 (7) | 0·1820 (3) | 0·3484 (2) | 2·7 (1) |
| C(13) | 0·6660 (7) | 0·1717 (3) | 0·2798 (2) | 3·2 (1) |
| C(14) | 0·6794 (7) | 0·0851 (3) | 0·4265 (2) | 2·9 (1) |
| C(15) | 0·7109 (7) | 0·0085 (3) | 0·4212 (3) | 3·7 (1) |
| C(16) | 0·7568 (8) | −0·0358 (4) | 0·4756 (3) | 4·6 (2) |
| C(17) | 0·7691 (8) | −0·0048 (4) | 0·5341 (3) | 5·1 (2) |
| C(18) | 0·7374 (8) | 0·0716 (4) | 0·5403 (3) | 4·6 (2) |
| C(19) | 0·6914 (7) | 0·1182 (3) | 0·4854 (2) | 3·9 (1) |
| C(21) | 0·3651 (8) | 0·2666 (3) | 0·2555 (2) | 3·3 (1) |
| C(22) | 0·2357 (7) | 0·3050 (3) | 0·2806 (2) | 2·8 (1) |
| C(23) | 0·3269 (9) | 0·2977 (3) | 0·1931 (3) | 4·6 (2) |
| C(24) | −0·0242 (7) | 0·4053 (3) | 0·2410 (2) | 3·0 (1) |
| C(25) | −0·1670 (7) | 0·3851 (3) | 0·2690 (3) | 3·8 (1) |
| C(26) | −0·3129 (8) | 0·4365 (3) | 0·2702 (3) | 4·5 (2) |
| C(27) | −0·3145 (8) | 0·5072 (3) | 0·2431 (3) | 4·5 (2) |
| C(28) | −0·1714 (8) | 0·5272 (4) | 0·2150 (3) | 4·7 (2) |
| C(29) | −0·0226 (8) | 0·4766 (3) | 0·2140 (3) | 3·8 (1) |
| C(31) | 0·3169 (7) | 0·2726 (3) | 0·3926 (2) | 2·7 (1) |
| C(32) | 0·4972 (7) | 0·3216 (3) | 0·4181 (2) | 2·8 (1) |
| C(33) | 0·2179 (7) | 0·2743 (3) | 0·4457 (2) | 2·9 (1) |
| C(34) | 0·6110 (8) | 0·3928 (3) | 0·5222 (3) | 4·0 (1) |
| C(35) | 0·5329 (9) | 0·4326 (3) | 0·5637 (3) | 4·3 (2) |
| C(36) | 0·654 (1) | 0·4823 (4) | 0·6061 (3) | 5·8 (2) |
| C(37) | 0·841 (1) | 0·4923 (4) | 0·6063 (3) | 7·3 (2) |
| C(38) | 0·915 (1) | 0·4542 (5) | 0·5647 (4) | 9·6 (3) |
| C(39) | 0·7986 (9) | 0·4044 (4) | 0·5208 (3) | 7·3 (2) |
| C(110) | 0·7624 (8) | 0·1760 (3) | 0·2257 (3) | 4·9 (2) |
| C(210) | 0·414 (1) | 0·2808 (4) | 0·1389 (3) | 7·8 (2) |
| C(310) | 0·0363 (7) | 0·2344 (3) | 0·4445 (3) | 4·3 (1) |

Table 2. *Bond distances* (Å) *and angles* (°) *for furlone yellow with e.s.d.'s in parentheses*

| | | | |
|---|---|---|---|
| O(11)—C(12) | 1·375 (6) | C(15)—C(16) | 1·380 (8) |
| O(11)—C(31) | 1·420 (6) | C(16)—C(17) | 1·364 (9) |
| O(21) C(22) | 1·384 (6) | C(17)—C(18) | 1·382 (9) |
| O(21)—C(31) | 1·399 (5) | C(18)—C(19) | 1·411 (8) |
| O(31)—C(32) | 1·200 (7) | C(21)—C(22) | 1·368 (8) |
| N(11)—N(12) | 1·373 (6) | C(21)—C(23) | 1·417 (7) |
| N(11)—C(12) | 1·349 (6) | C(23)—C(210) | 1·498 (9) |
| N(11)—C(14) | 1·424 (6) | C(24)—C(25) | 1·363 (8) |
| N(12)—C(13) | 1·335 (6) | C(24)—C(29) | 1·393 (8) |
| N(21)—N(22) | 1·365 (7) | C(25)—C(26) | 1·384 (8) |
| N(21)—C(22) | 1·365 (6) | C(26)—C(27) | 1·382 (8) |
| N(21)—C(24) | 1·426 (7) | C(27)—C(28) | 1·365 (9) |
| N(22)—C(23) | 1·332 (8) | C(28)—C(29) | 1·391 (8) |
| N(31)—N(32) | 1·425 (6) | C(31)—C(32) | 1·522 (7) |
| N(31)—C(32) | 1·371 (7) | C(31)—C(33) | 1·504 (8) |
| N(31)—C(34) | 1·428 (6) | C(33)—C(310) | 1·465 (7) |
| N(32)—C(33) | 1·280 (6) | C(34)—C(35) | 1·374 (9) |
| C(11)—C(12) | 1·372 (7) | C(34)—C(39) | 1·358 (9) |
| C(11)—C(13) | 1·426 (7) | C(35)—C(36) | 1·389 (8) |
| C(11)—C(21) | 1·450 (7) | C(36)—C(37) | 1·345 (10) |
| C(13)—C(110) | 1·512 (8) | C(37)—C(38) | 1·342 (12) |
| C(14)—C(15) | 1·382 (7) | C(38)—C(39) | 1·395 (10) |
| C(14)—C(19) | 1·388 (8) | | |

| | | | |
|---|---|---|---|
| C(12)—O(11)—C(31) | 117·5 (4) | O(21)—C(22)—N(21) | 114·8 (4) |
| C(22)—O(21)—C(31) | 120·1 (4) | O(21)—C(22)—C(21) | 134·4 (4) |
| N(12)—N(11)—C(12) | 109·2 (4) | N(21)—C(22)—C(21) | 110·7 (4) |
| N(12)—N(11)—C(14) | 120·1 (4) | N(22)—C(23)—C(21) | 112·5 (5) |
| C(12)—N(11)—C(14) | 130·6 (5) | N(22)—C(23)—C(210) | 116·2 (5) |
| N(11)—N(12)—C(13) | 105·6 (4) | C(21)—C(23)—C(210) | 131·2 (5) |
| N(22)—N(21)—C(22) | 108·7 (4) | N(21)—C(24)—C(25) | 122·0 (5) |
| N(22)—N(21)—C(24) | 120·6 (4) | N(21)—C(24)—C(29) | 116·9 (5) |
| C(22)—N(21)—C(24) | 130·7 (5) | C(25)—C(24)—C(29) | 121·1 (5) |
| N(21)—N(22)—C(23) | 105·9 (4) | C(24)—C(25)—C(26) | 119·2 (5) |
| N(32)—N(31)—C(32) | 112·8 (4) | C(25)—C(26)—C(27) | 120·5 (6) |
| N(32)—N(31)—C(34) | 118·6 (4) | C(26)—C(27)—C(28) | 120·2 (6) |
| C(32)—N(31)—C(34) | 128·4 (5) | C(27)—C(28)—C(29) | 120·1 (6) |
| N(31)—N(32)—C(33) | 109·1 (4) | C(24)—C(29)—C(28) | 119·0 (6) |
| C(12)—C(11)—C(13) | 102·0 (4) | O(11)—C(31)—O(21) | 111·0 (4) |
| C(12)—C(11)—C(21) | 122·9 (5) | O(11)—C(31)—C(32) | 113·0 (4) |
| C(13)—C(11)—C(21) | 135·1 (5) | O(11)—C(31)—C(33) | 107·3 (4) |
| O(11)—C(12)—N(11) | 118·7 (4) | O(21)—C(31)—C(32) | 114·1 (4) |
| O(11)—C(12)—C(11) | 130·2 (4) | O(21)—C(31)—C(33) | 107·4 (4) |
| N(11)—C(12)—C(11) | 111·0 (5) | C(32)—C(31)—C(33) | 103·4 (4) |
| N(12)—C(13)—C(11) | 112·2 (5) | O(31)—C(32)—N(31) | 127·8 (4) |
| N(12)—C(13)—C(110) | 116·3 (5) | O(31)—C(32)—C(31) | 128·3 (4) |
| C(11)—C(13)—C(110) | 131·5 (4) | N(31)—C(32)—C(31) | 103·9 (4) |
| N(11)—C(14)—C(15) | 119·4 (5) | N(32)—C(33)—C(31) | 110·8 (4) |
| N(11)—C(14)—C(19) | 119·3 (5) | N(32)—C(33)—C(310) | 124·6 (5) |
| C(15)—C(14)—C(19) | 121·2 (5) | C(31)—C(33)—C(310) | 124·6 (4) |
| C(14)—C(15)—C(16) | 119·5 (5) | N(31)—C(34)—C(35) | 118·3 (5) |
| C(15)—C(16)—C(17) | 120·5 (6) | N(31)—C(34)—C(39) | 120·9 (6) |
| C(16)—C(17)—C(18) | 120·8 (6) | C(35)—C(34)—C(39) | 120·7 (5) |
| C(17)—C(18)—C(19) | 119·8 (5) | C(34)—C(35)—C(36) | 118·2 (6) |
| C(14)—C(19)—C(18) | 118·2 (5) | C(35)—C(36)—C(37) | 121·4 (7) |
| C(11)—C(21)—C(22) | 124·1 (5) | C(36)—C(37)—C(38) | 120·0 (6) |
| C(11)—C(21)—C(23) | 133·7 (5) | C(37)—C(38)—C(39) | 120·6 (7) |
| C(22)—C(21)—C(23) | 102·2 (5) | C(34)—C(39)—C(58) | 119·1 (7) |

Stuart, 1983); correction factors: max. = 1·231 and min. = 0·864, direct methods, refinement by full-matrix least-squares method using unit weights and $F$'s, all non-H atoms anisotropic, H atoms calculated (1·03 Å) and used as riding atoms with fixed isotropic temperature factor ($B_{eq}$ = 5·0 Å$^2$), 352 parameters, max. shift/$\sigma$ = 0·01 on final cycle, $R$ = 0·031, $wR$ = 0·031, $S$ = 1·43, final difference map with no features greater than 0·11 (2) e Å$^{-3}$, scattering factors from *International Tables for X-ray Crystallography* (1974), computer programs *MULTAN*11/82 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982), *SDP* (Frenz, 1978), *PLUTO* (Motherwell, 1978).

**Discussion.** The atomic coordinates and isotropic temperature factors are listed in Table 1, and the bond distances and angles are given in Table 2.* A view of the molecule and the numbering scheme are shown in Fig. 1. A stereoscopic view of the packing is presented in Fig. 2.

The bond distances and angles are normal. The compound can be formulated as a ketal derived from pyrazoline-4,5-dione. The mechanistic details concerning the formation of the compound are discussed elsewhere (Mann, Hennig, Herzschuh & Rissanen, 1988). The heterocyclic 1,3-dioxepin ring has a slightly distorted envelope conformation with the spiro carbon as the off-plane atom. The pyrazoline rings are planar, but the substituents attached to these rings have small deviations from the calculated least-squares planes {max. deviation is 0·086 (6) Å [C(34)]}. The angle of 9·7 (10)° between pyrazoline rings 1 and 2 [C(11)—N(12) and C(22)—N(22), respectively] causes a slight

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* Lists of structure factors, anisotropic thermal parameters, least-squares-planes data and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44658 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

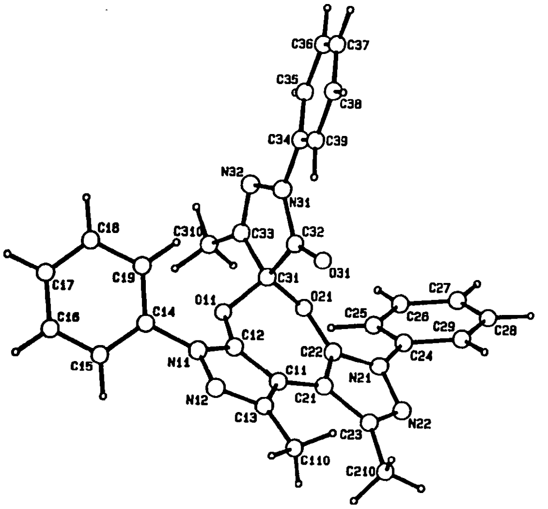

Fig. 1. *PLUTO* plot (Motherwell, 1978) and numbering scheme for furlone yellow.

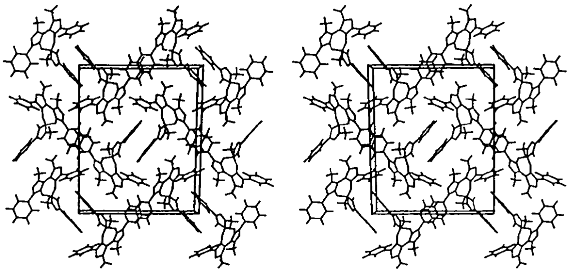

Fig. 2. A stereoscopic view of the packing. The *b* axis is horizontal and the *c* axis vertical.

distortion in the dioxepin ring. The spiro pyrazoline ring lies in nearly perpendicular arrangement with the other pyrazoline rings, at an angle of 101·4 (2)° with ring 1 and 100·1 (2)° with ring 2. The perpendicularity is due to the steric repulsion between the methyl and keto groups attached to the spiro pyrazoline ring and the phenyl rings attached to the other pyrazoline rings. The twist angles between the phenyl and the pyrazoline rings, 47·5 (2), 41·2 (3) and 24·5 (4)° for pyrazoline rings 1, 2 and spiro, respectively, are mainly caused by the packing forces. The packing is maintained by the $\pi$-electron overlap between the phenyl rings in adjacent molecules, in such a way that the phenyl rings attached to the adjacent spiro pyrazoline rings overlap each other (spiro↔spiro) and the phenyl rings attached to the pyrazoline rings 1 and 2 overlap in a head-to-tail fashion with those in adjacent molecules (1↔2↔1↔2). There are no intermolecular contacts shorter than the sum of van der Waals radii.

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*Acta Cryst.* (1988). C**44**, 847–850

# Conformation of Methylated Amino Acids: Structure of 3,4-Dimethoxy-α-methyl-DL-phenylalanine Sesquihydrate

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**Abstract.** $C_{12}H_{17}NO_4.1{\cdot}5H_2O$, $M_r = 266{\cdot}3$, triclinic, $P\bar{1}$, $a = 5{\cdot}872\,(1)$, $b = 11{\cdot}437\,(2)$, $c = 20{\cdot}434\,(1)$ Å, $\alpha = 95{\cdot}74\,(1)$, $\beta = 96{\cdot}91\,(1)$, $\gamma = 89{\cdot}18\,(1)°$, $V = 1355{\cdot}5$ Å$^3$, $Z = 4$, $D_m = 1{\cdot}29$, $D_x = 1{\cdot}305$ g cm$^{-3}$, $\lambda(\text{Cu}\ K\alpha) = 1{\cdot}5418$ Å, $\mu = 8{\cdot}3$ cm$^{-1}$, $F(000) = 572$, $T = 294$ K, $R = 0{\cdot}038$ for 4006 reflections, $I \geq 3\sigma(I)$.

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