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# THE CRYSTAL AND MOLECULAR STRUCTURE OF (8—10-$\eta$ : 12-TRICYCLO[5.3.2.$^{1,7}$.0$^{2,6}$]DODECA-2,4,6-TRIAZA-4-METHYL-3,5,11-TRIOXO-8,9-DIENYL)TRICARBONYLIRON

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## Summary

The reaction between tricarbonylcycloheptatrieneiron and *N*-methyltriazolinedione gives a prismatic yellow compound $C_{13}H_9FeN_3O_6$. Whereas this type of reaction usually involves 1,3-cycloaddition, in this case 1,5-cycloaddition occurs to give the title compound. This compound, which recrystallized from a methanol solution, has the cell dimensions: $a$ 8.726(2), $b$ 23.169(3), $c$ 6.719(1) Å; $\beta$ 91.2(1)°; $V$ 1358.8 Å$^3$; $Z = 4$; space group $P2_1/n$. The structure was solved by Patterson and Fourier methods and refined anisotropically down to $R = 0.039$. The iron atom shows an octahedral coordination, and bond distances and angles are in agreement with those observed in other compounds of comparable structure. In the organic ligand the dihedral angle between two parts of the seven-membered ring is 115.0°. The five-membered ring deviates slightly from planarity.

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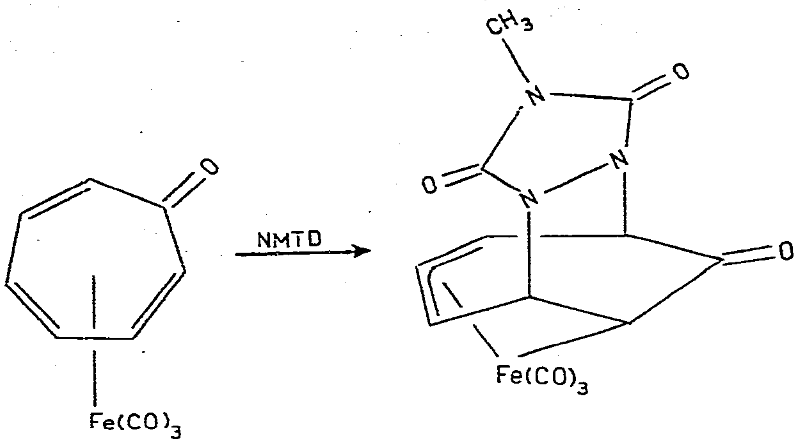
## Introduction

Recently a novel 1,5-cycloaddition of uni- and bi-particulate electrophiles to troponeiron tricarbonyl complexes was reported [1,2]. A subsequent study on a general oxidative rearrangement of $\sigma,\pi$-allyliron tricarbonyl cycloadducts showed that the reaction takes place through the free double bond, and whereas 1,3-cycloaddition usually occurs [3,4], with adduct I 1,5-cycloaddition is observed. This exceptional behaviour of I was further exemplified by reaction with the powerful electrophile *N*-methyltriazolinedione (NMTD) to give the cycloadduct II. While this study was in progress at the Pavia University [5], a paper appeared [6] describing an analogous reaction involving *N*-phenyltriazolinedione. To confirm the structure of II, proposed on the basis of elemental analysis and NMR spectroscopic data, an X-ray study was carried out.

SCHEME 1



(I) (II)

## Experimental

### *Collection and reduction of X-ray data*

A prismatic yellow crystal, recrystallized from methanol, with dimensions of 0.10 × 0.14 × 0.29 mm was used for data collection. Preliminary cell parameters obtained by rotation and Weissenberg photographs were subsequently refined by least-squares fit to 19 $(\theta, \chi, \phi)_{hkl}$ carefully measured on a Siemens AED single crystal diffractometer. Cell dimensions and crystal data are given in Table 1. A total of 3546 independent reflections were measured at room temperature, using the $\omega - 2\theta$ scanning technique and Zr-filtered Mo-$K_\alpha$ radiation. 1889 of these were not used in the structure analysis since their intensities were less than twice their standard deviations (from counting statistics). During the refinement 18 of the remaining reflections were seriously affected by large non systematic errors, and were omitted in the last cycles of refinement. No absorption correction was applied.

### *Solution and refinement of the structure*

The iron atom was located by a three-dimensional Patterson synthesis, and an electron density calculation, phased with the coordinates of this atom, revealed

TABLE 1

CRYSTAL DATA FOR $Fe(CO)_3C_{10}H_9N_3O_3$

| | |
|---|---|
| $a$ 8.726(2) Å | Monoclinic |
| $b$ 23.169(3) | Space group $P2_1/n$ |
| $c$ 6.719(1) | Mo-$K_\alpha$ radiation |
| $\beta$ 91.2(1)° | $\mu$ 11.77 cm$^{-1}$ |
| $V$ 1358.3 Å$^3$ | $Z = 4$ |
| | $D_{calc.}$ 1.75 g cm$^{-3}$ |

TABLE 2

ATOMIC COORDINATES ($\times 10^4$ for Fe, O, N and C, $\times 10^3$ for H atoms)

| | $x/a$ ($\sigma$) | $y/b$ ($\sigma$) | $z/c$ ($\sigma$) |
|---|---|---|---|
| Fe | 4688(1) | 6754(1) | 3641(1) |
| O(1) | 5511(6) | 7289(2) | 7493(7) |
| O(2) | 3944(6) | 7864(2) | 1791(9) |
| O(3) | 7812(5) | 6730(3) | 2275(10) |
| O(4) | 2143(5) | 6851(2) | −667(6) |
| O(5) | 3591(5) | 4432(2) | 1712(7) |
| O(6) | −894(5) | 5382(2) | 2862(7) |
| N(1) | 1128(5) | 4760(2) | 2211(8) |
| N(2) | 1518(5) | 5681(2) | 2038(8) |
| N(3) | 2872(5) | 5396(2) | 1515(8) |
| C(1) | 5182(7) | 7078(3) | 6024(9) |
| C(2) | 4233(6) | 7437(3) | 2535(9) |
| C(3) | 6619(6) | 6734(3) | 2858(10) |
| C(4) | 4145(6) | 6317(2) | 996(9) |
| C(5) | 2601(6) | 6522(2) | 636(8) |
| C(6) | 1595(6) | 6304(2) | 2273(9) |
| C(7) | 2360(6) | 6486(3) | 4227(9) |
| C(8) | 3474(7) | 6146(3) | 5201(10) |
| C(9) | 4554(6) | 5838(3) | 4143(9) |
| C(10) | 4275(6) | 5725(2) | 1957(9) |
| C(11) | 2641(7) | 4814(2) | 1830(8) |
| C(12) | 415(7) | 5288(2) | 2450(9) |
| C(13) | 409(10) | 4201(3) | 2482(13) |
| H(1) | 481(6) | 633(2) | −29(9) |
| H(2) | 61(7) | 642(3) | 219(10) |
| H(3) | 173(7) | 675(3) | 493(9) |
| H(4) | 365(7) | 620(3) | 663(11) |
| H(5) | 531(7) | 566(3) | 500(9) |
| H(6) | 507(6) | 553(2) | 149(8) |
| H(7) | 97(8) | 396(3) | 222(12) |
| H(8) | −28(7) | 409(3) | 173(10) |
| H(9) | −74(9) | 429(3) | 358(11) |

all the remaining non-hydrogen atoms of the structure. The refinement was carried out by least-squares full-matrix cycles using the SHELX system of programs [7] with, initially isotropic and then anisotropic thermal parameters. A subsequent difference Fourier map based on the above refinement showed the position of all the hydrogen atoms. Continuation of least-squares refinement, now with positional and isotropic thermal parameters for the hydrogen atoms, converged at a final agreement factor $R = 0.039$. The scattering factors used throughout the analysis were those reported in the International Tables [8]. A list of observed and calculated structure factor amplitudes is available from the authors on request. The atomic coordinates and their standard deviations are given in Table 2, and thermal parameters in Table 3.

## Results

The structure of the molecule is consistent with that predicted from NMR spectroscopy. Figure 1 shows a drawing of the structure with the arbitrary numbering scheme used in the analysis. Bond distances and angles are given in Table

*(continued on p. 90)*

TABLE 3

THERMAL PARAMETERS[a] ($\times 10^4$ for Fe, O, N and C, $\times 10^3$ for H atoms)

| | $U_{iso}$ or $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
|---|---|---|---|---|---|---|
| Fe | 267(4) | 278(4) | 331(4) | —7(4) | 3(3) | —29(4) |
| O(1) | 674(31) | 649(32) | 401(29) | —82(25) | —18(24) | —240(26) |
| O(2) | 727(35) | 325(26) | 969(46) | 98(27) | —221(31) | —42(23) |
| O(3) | 306(23) | 857(40) | 1248(48) | —176(39) | 175(28) | —2(27) |
| O(4) | 478(23) | 409(24) | 389(24) | 92(20) | —82(20) | 51(19) |
| O(5) | 660(28) | 322(23) | 465(28) | —25(20) | 41(23) | 78(21) |
| O(6) | 339(21) | 462(26) | 672(32) | —53(24) | 79(21) | —86(19) |
| N(1) | 461(28) | 302(26) | 381(30) | —1(22) | —2(24) | —150(21) |
| N(2) | 280(23) | 269(24) | 617(35) | —37(24) | 58(24) | —19(19) |
| N(3) | 320(23) | 230(22) | 535(33) | —23(22) | 13(22) | 10(19) |
| C(1) | 412(33) | 438(36) | 357(43) | —3(29) | 13(31) | —133(28) |
| C(2) | 313(28) | 341(32) | 456(39) | —25(30) | —14(26) | —60(25) |
| C(3) | 325(29) | 426(35) | 624(43) | 4(35) | —9(29) | 3(29) |
| C(4) | 287(26) | 315(28) | 255(31) | —17(23) | 52(24) | 30(22) |
| C(5) | 323(26) | 262(26) | 300(32) | —55(24) | —27(25) | —4(23) |
| C(6) | 249(27) | 285(28) | 447(39) | —64(26) | 27(26) | 10(23) |
| C(7) | 325(27) | 296(29) | 364(34) | —76(26) | 95(27) | —34(24) |
| C(8) | 460(34) | 393(33) | 276(36) | 17(27) | —11(28) | —142(28) |
| C(9) | 346(30) | 331(30) | 409(42) | 79(25) | —13(30) | —33(25) |
| C(10) | 261(27) | 271(28) | 463(38) | 4(26) | 42(26) | 17(23) |
| C(11) | 578(37) | 231(27) | 266(32) | —44(24) | —2(27) | —9(27) |
| C(12) | 410(32) | 349(32) | 244(32) | 0(25) | 6(25) | —88(25) |
| C(13) | 681(56) | 341(34) | 611(53) | 89(36) | 41(48) | —200(37) |
| H(1) | 23(14) | | | | | |
| H(2) | 32(18) | | | | | |
| H(3) | 43(18) | | | | | |
| H(4) | 52(19) | | | | | |
| H(5) | 54(18) | | | | | |
| H(6) | 28(14) | | | | | |
| H(7) | 81(20) | | | | | |
| H(8) | 87(19) | | | | | |
| H(9) | 98(20) | | | | | |

[a] Anisotropic temperature factors are of the form:
$T = \exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hk\;{}^{*}b^{*} + 2U_{13}hla^{*}c^{*} + U_{23}klb^{*}c^{*})]$.

TABLE 4

BOND DISTANCES (Å)

| | | | |
|---|---|---|---|
| Fe—C(1) | 1.812(5) | N(3)—C(10) | 1.466(5) |
| Fe—C(2) | 1.791(5) | N(3)—C(11) | 1.380(6) |
| Fe—C(3) | 1.776(5) | C(4)—C(5) | 1.444(6) |
| Fe—C(4) | 2.091(4) | C(4)—C(10) | 1.520(6) |
| Fe—C(7) | 2.167(4) | C(5)—C(6) | 1.509(6) |
| Fe—C(8) | 2.060(5) | C(6)—C(7) | 1.520(7) |
| Fe—C(9) | 2.150(5) | C(7)—C(8) | 1.403(7) |
| O(1)—C(1) | 1.133(5) | C(8)—C(9) | 1.389(6) |
| O(2)—C(2) | 1.133(6) | C(9)—C(10) | 1.507(7) |
| O(3)—C(3) | 1.120(5) | C(4)—H(1) | 1.05(5) |
| O(4)—C(5) | 1.221(5) | C(6)—H(2) | 0.90(5) |
| O(5)—C(11) | 1.217(5) | C(7)—H(3) | 0.95(5) |
| O(6)—C(12) | 1.201(5) | C(8)—H(4) | 0.98(6) |
| N(1)—C(11) | 1.355(6) | C(9)—H(5) | 0.96(5) |
| N(1)—C(12) | 1.383(6) | C(10)—H(6) | 0.90(4) |
| N(1)—C(13) | 1.452(6) | C(13)—H(7) | 1.14(6) |
| N(2)—N(3) | 1.404(5) | C(13)—H(8) | 1.04(6) |
| N(2)—C(6) | 1.453(6) | C(13)—H(9) | 0.98(6) |
| N(2)—C(12) | 1.358(5) | | |

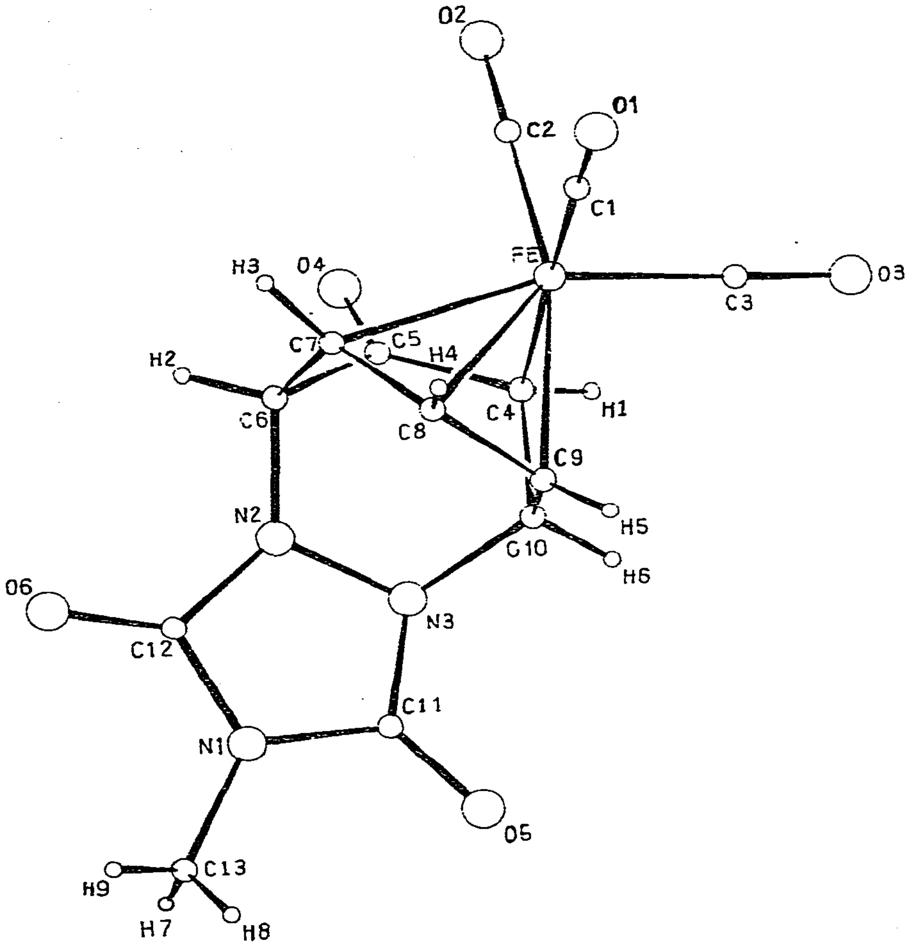


Fig. 1. Projection of the molecule.

TABLE 5

BOND ANGLES (deg.)

| | | | |
|---|---|---|---|
| C(1)—Fe—C(2) | 92.7(2) | N(2)—C(6)—C(7) | 112.8(4) |
| C(1)—Fe—C(3) | 93.6(2) | C(5)—C(6)—C(7) | 106.5(3) |
| C(1)—Fe—C(4) | 175.5(2) | C(6)—C(7)—C(8) | 122.3(4) |
| C(1)—Fe—C(7) | 99.5(2) | C(7)—C(8)—C(9) | 121.4(5) |
| C(1)—Fe—C(8) | 87.1(2) | Fe—C(9)—C(8) | 67.3(3) |
| C(1)—Fe—C(9) | 106.4(2) | Fe—C(9)—C(10) | 91.6(3) |
| C(2)—Fe—C(3) | 95.9(2) | C(8)—C(9)—C(10) | 119.4(4) |
| C(2)—Fe—C(4) | 91.8(2) | N(3)—C(10)—C(4) | 109.1(4) |
| C(2)—Fe—C(7) | 97.3(2) | N(3)—C(10)—C(9) | 113.9(4) |
| C(2)—Fe—C(8) | 134.7(2) | C(4)—C(10)—C(9) | 105.4(4) |
| C(2)—Fe—C(9) | 157.7(2) | N(3)—N(2)—C(6) | 117.2(3) |
| C(3)—Fe—C(4) | 86.3(2) | N(3)—N(2)—C(12) | 109.9(4) |
| C(3)—Fe—C(7) | 160.9(2) | C(6)—N(2)—C(12) | 132.5(4) |
| C(3)—Fe—C(8) | 129.3(2) | N(2)—N(3)—C(10) | 114.1(3) |
| C(3)—Fe—C(9) | 94.3(2) | N(2)—N(3)—C(11) | 107.1(4) |
| C(4)—Fe—C(7) | 79.6(2) | C(10)—N(3)—C(11) | 126.9(4) |
| C(4)—Fe—C(8) | 89.6(2) | O(5)—C(11)—N(3) | 126.8(5) |
| C(4)—Fe—C(9) | 69.2(2) | O(5)—C(11)—N(1) | 127.8(4) |
| Fe—C(4)—C(5) | 100.2(3) | N(1)—C(11)—N(3) | 105.4(4) |
| Fe—C(4)—C(10) | 93.5(3) | O(6)—C(12)—N(1) | 128.3(4) |
| C(5)—C(4)—C(10) | 115.4(4) | O(6)—C(12)—N(2) | 127.4(4) |
| O(4)—C(5)—C(4) | 128.0(4) | N(1)—C(12)—N(2) | 104.3(4) |
| O(4)—C(5)—C(6) | 123.0(4) | C(11)—N(1)—C(12) | 112.5(4) |
| C(4)—C(5)—C(6) | 108.8(4) | C(11)—N(1)—C(13) | 122.1(5) |
| N(2)—C(6)—C(5) | 106.3(4) | C(12)—N(1)—C(13) | 125.2(4) |

TABLE 6a

DISTANCES (Å) OF RELEVANT ATOMS FROM MEAN PLANES THROUGH THE MOLECULE

| | |
|---|---|
| Plane I: | C(6), C(5), C(4), C(10)<br>C(6) −0.09, C(5) 0.16, C(4) −0.18, C(10) 0.10, O(4) 0.50 |
| Plane II: | C(6), C(7), C(8), C(9), C(10)<br>C(6) −0.08, C(7) 0.21, C(8) −0.14, C(9) −0.04, C(10) 0.05 |
| Plane III: | C(6), N(2), N(3), C(10)<br>C(6) 0.06, N(2) −0.09, N(3) 0.09, C(10) −0.06 |
| Plane IV: | N(1), C(11), N(3), N(2), C(12)<br>N(1) 0.04, C(11) −0.05, N(3) 0.05, N(2) −0.02, C(12) −0.01, O(5) −0.15, O(6) 0.00, C(13) 0.08 |
| Plane V: | Fe, C(7), C(9) |
| Plane VI: | C(7), C(8), C(9) |

TABLE 6b

NORMAL EQUATIONS OF PLANES IN THE FORM $lX + mY + nZ = p$ ($X$, $Y$ and $Z$ are in Å, referred to orthogonal axes $x$, $y$ and $z^*$)

| Plane | $l$ | $m$ | $n$ | $p$ |
|---|---|---|---|---|
| I | 0.3192 | 0.5787 | 0.7505 | 9.9459 |
| II | 0.4991 | 0.8196 | −0.2812 | 12.3022 |
| III | −0.0169 | 0.2130 | −0.9769 | 1.5365 |
| IV | 0.2512 | 0.0409 | 0.9671 | 2.1656 |
| V | 0.1441 | 0.1471 | 0.9786 | 5.2769 |
| VI | 0.6171 | 0.7858 | 0.0422 | 13.1620 |

TABLE 6c

DIHEDRAL ANGLES (deg.) BETWEEN PLANES

| | | | |
|---|---|---|---|
| I—II | 115.0 | III—IV | 19.9 |
| I—III | 52.0 | V—VI | 75.8 |
| II—III | 63.8 | | |

4 and in Table 5, respectively. Table 6 presents some mean planes and the dihedral angles between them.

## Discussion

### *The diene tricarbonyliron moiety*

The structure is of the type in which the complete conventional 18-electron configuration of the metal in tricarbonyliron derivatives is completed by one $\eta^3$-allyl group (donating three electrons) and a $\sigma$-bonded carbon atom (donating one electron). If we assume that the $\pi$-allyl system can occupy two coordination sites (the $M_1$ and $M_2$ midpoints between the atoms C(7) — C(8) and C(8) — C(9) respectively) the coordination around the iron atom is approximately octahedral and the vertices of the octahedron are directed towards $M_1$, $M_2$, C(4), and the three carbonyl carbon atoms. In the molecule it is possible to identify three types of iron—carbon bonds: the $\sigma$-bond between Fe and C(4), the $\pi$-bonds between the iron and the carbons of the $\eta$-allyl group [C(7), C(8), C(9)], and the bonds between iron and the C(1), C(2), C(3) atoms of the carbonyl group.

As previously observed in similar compounds [9—11], the value of the $\sigma$-bond Fe—C(4) (2.091(4) Å) is of the same order of the $\pi$-bonds between the iron and the $\pi$-allyl group (Fe—C(7) 2.167(4), Fe—C(8) 2.060(5), Fe—C(9) 2.150(5) Å). If we subtract from the $\sigma$-bond distance the value of the covalent radius of a tetrahedral carbon atom (0.77 Å) we obtain a value for the covalent single bond iron radius of 1.32 Å, very close to the value observed by Rodrique et al. (1.34 Å) [12].

As previously observed for similar compounds [9—11,13,14] and for several $\pi$-allyl-palladium and -nickel complexes [15], the distance between the iron to the "inner" carbon of the $\pi$-allyl group (Fe—C(8) 2.060(6) Å) is significantly shorter than the values of the two Fe—C distances of the "outer" atoms (Fe—C(7) 2.167(4), Fe—C(9) 2.150(5) Å). Furthermore the allyl—iron bonding is not precisely symmetrical, the Fe—C(7) bond being slightly longer than the Fe—C(9) bond. Similar behaviour was observed by Cotton et al. [14,16].

The tilt of the plane formed by the diene group [C(7), C(8), C(9)] with respect to the plane formed by Fe, C(7), C(9) is 104.2°. The three carbonyl groups are approximately orthogonal to one another and the Fe—C and C—O bond lengths are similar to those observed in other iron—carbonyl compounds of comparable structure [9—11,13,17,18]. The slight deviations from collinearity of the Fe—C—O linkage (average angle 177.8°) may be the result of the molecular packing.

### *The seven-membered ring of the ligand*

The conformation of the seven-membered ring is remarkable similar to that found in the similar compounds previously mentioned [10,11]. It is of a "V" shape hinged along the C(6), C(10) direction, and with a dihedral angle of 115.0° between the two parts formed by C(10), C(4), C(5), C(6) and by C(6), C(7), C(8), C(9), C(10), respectively. The values of allyl C—C bond lengths in this type of complex have been found to vary in the range 1.37—1.49 Å [9—12] which spans the two observed values of 1.389(6) and 1.403(7) Å. All the other C—C bond distances of the ring show a satisfactory agreement with those expected. The marginally significant shortening of the C(4)—C(5) bond distance (1.444(6) Å) is probably a result of a partial delocalisation of the O(4)—C(5) $\pi$-electrons (1.221(5) Å).

The C—C—C allyl bond angle is close to the value of 120° required by an $sp^2$-hybridised carbon atom. The other angles of the ring are substantially larger than the tetrahedral value, except for those at C(6) and C(10) where the strain of the ring is greatest. The value of the angle at C(5) (108.8(4)°), similar to that observed in the barbalone derivative [11] (109.4(2)°), is unusually small for a ketone carbon atom.

### *The five-membered ring.*

The triazole ring slightly deviates from planarity and forms a dihedral angle of 19.9° with the mean plane N(2), N(3), C(6), C(10). All the distances in the ring are in agreement with the values observed by Senko and Templeton [19]. The distances C(11)—O(5) (1.217(5) Å), C(12)—O(6) (1.201(5) Å) and N(1)—C(13) (1.452(6) Å) are in the range expected for this type of bond.

The packing is consistent with Van der Waals interactions.

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