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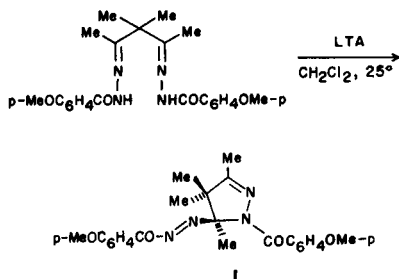
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The crystal and molecular structure of the title compound, derived by lead tetraacetate oxidation of the bis-*p*-methoxybenzoylhydrazone of 3,3-dimethylpentane-2,4-dione, is studied by an X-ray crystallographic analysis.

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Due to an ambiguity [1,2] in the structure of the lead tetraacetate oxidation products of bis-aryldiazones of β -dicarbonyl compounds, the present X-ray crystallographic analysis was undertaken for a definite solution of the problem. The results of this study completely confirm the pyrazoline structure previously proposed [3] for the oxidation products in question.



Bond lengths and angles as well as an ORTEP drawing for 3,4,4,5-tetramethyl-1-(*p*-methoxybenzoyl)-5-(*p*-methoxybenzoylazo)-2-pyrazoline (**1**) are given in Figures 1 and 2 respectively, whereas crystal and other related experimental data as well as positional parameters are given in Tables I and II, respectively.

The main characteristic of the structure is that the 1-*p*-methoxybenzoyl group exists in two different orientations (A) and (B) (Figure 1) forming an angle of 3.7° in respect to C₁₆-C₁₇ bond, whereas the dihedral angle between the phenyl planes in (A) and (B) orientations is equal to 8.2°. A similar disorder has been reported for other heterocyclic systems [4] and although this effect reduces the accuracy in the determination of the bond lengths and angles of 1-*p*-methoxybenzoyl group it does not have any effect on the structure and stereochemistry of the other part of the molecule.

Bond lengths and angles have values similar to those previously reported. In respect to the stereochemistry of the system it is mentioned that the pyrazoline ring is not planar the C₃ atom being out of the plane determined by

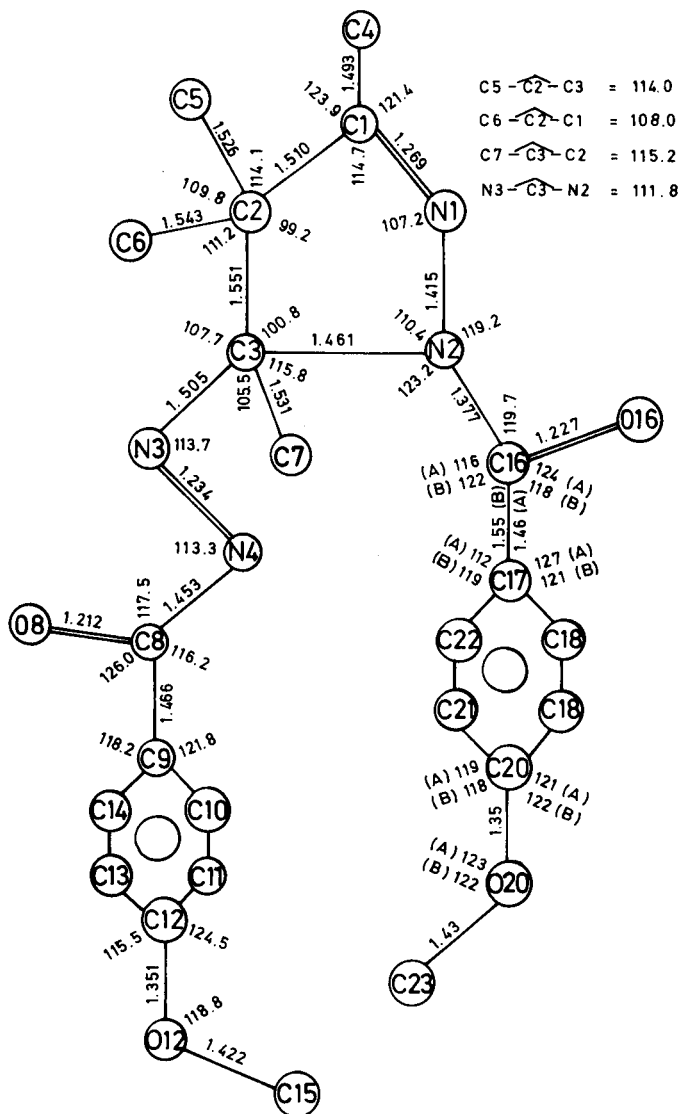


Figure 1. Bond lengths and angles for **1**. (A) and (B) refer to two disordered positions. Standard deviations are 2-4 in the last significant figure. For phenyl rings see Experimental.

Table I

Summary of Crystal and Intensity Collection Data for Compound 1

formula	C ₂₃ H ₂₆ N ₄ O ₄
f _w	422.53
a, b, c, Å	32.392(5), 8.927(1), 16.424(3)
β	108.30(1)
V, Å ³	4509(1)
Z	8
D _{calcds} g/cm ³	1.244
D _{measds} g/cm ³	1.23
space group	C ₂ /c
cryst. dimers, mm	0.2 × 0.3 × 0.5
radiation	MoKα (0.71069) Zr-filtered
μ, cm ⁻¹	0.52
scan speed	Variable between 1 and 8 deg. in 2θ/min
scan range	0.8 below Kα ₁ to 0.8 above Kα ₂
bkgd counting, s	0.4 of scan time
2θ limit, deg.	40.0
data collected/unique	3728/3344
data used	2590 with F _o ≥ 6.1σ(F _o)
R	0.0443, 0.0610 (All data)
Rw	0.0670, 0.0790 (All data)

the atoms N₂-N₁-C₁-C₂ (plane 1) by 0.434 Å.

The plane defined by the atoms C₃-N₃-N₄-C₈ (plane 2) is almost perpendicular to plane 1 forming a dihedral angle of 81.6° and almost perpendicular to plane 3 defined by the phenyl attached to the azo group, the corresponding dihedral angle being equal to 85.1°, whereas the azo group is found in E-configuration. On the other hand the carbonyl and methoxy group of the aroylazo function are found in almost coplanar position with the phenyl, the corresponding dihedral angles being equal to 8.0° and 1.85°, respectively.

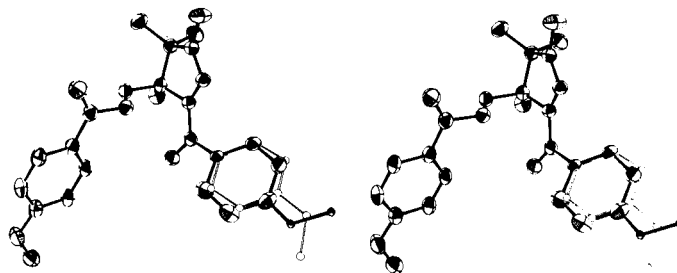


Figure 2. ORTEP drawing at 40% probability ellipsoid. Open circles refer to disordered position (B).

EXPERIMENTAL

Crystallographic Analysis.

Compound 1 was prepared as described previously [3], mp 139-141°. Yellow orange single crystals of 1 suitable for X-ray work were obtained by slow evaporation of a methylene chloride solution. Photographic investigations and intensity statistics indicated the space group (Table I). All data were collected on a Syntex P2₁ diffractometer. Lattice parameters (Table I) were refined by a least-squares procedure using 15 automatically centered reflections. Periodically monitored reference reflections showed no significant changes in intensity. Lorenz and polarization but no absorption corrections were made. The direct methods program of SHELX was used to solve the structure. After all nonhydrogen atoms were located it became apparent that the one methoxyphenyl group existed in two different orientations (disordered). Attempts to refine our model in the noncentrosymmetric space group Cc, gave slightly higher R values. Refinement was continued in C₂/c with the occupation factors of all atoms in the disordered methoxyphenyl group tied to one free variable which was refined. Our model included as well the second position of the disordered group with the occupation factors of all its atoms tied to a free variable. The values of the two free variables were constrained to add up to 1 during the refinement. Their final values were 0.6 for (A) and 0.4 for (B) (Figure 1). The final full-matrix least-squares cycle used

Table II

Positional Parameters (× 10⁴) for the Nonhydrogen Atoms

Atom	x	y	z	Atom	x	y	z
O(8)	1264(1)	-2287(2)	-1008(8)	C(12)	99(1)	-2861(1)	-3849(1)
O(12)	-188(1)	-3437(2)	-4566(1)	C(13)	367(1)	-3892(1)	-3305(1)
O(16)	841(1)	2696(2)	-2664(1)	C(14)	677(1)	-3413(1)	-2561(1)
O(20)A	2479(3)	3595(16)	-3764(7)	C(15)	-465(1)	-2441(3)	-5170(2)
O(20)B	2567(3)	4141(16)	-3578(8)	C(16)	1211(1)	2917(2)	-2185(1)
N(1)	1721(1)	2771(2)	-759(1)	C(17)A	1586(3)	3084(12)	-2479(5)
N(2)	1290(1)	2951(2)	-1312(1)	C(18)A	1925(3)	4088(12)	-2176(5)
N(3)	890(1)	759(2)	-1052(1)	C(19)A	2222(3)	4291(12)	-2616(5)
N(4)	1120(1)	146(2)	-1427(1)	C(20)A	2180(3)	3489(12)	-3358(5)
C(1)	1700(1)	2532(2)	-12(1)	C(21)A	1841(3)	2486(12)	-3661(5)
C(2)	1247(1)	2614(2)	60(1)	C(22)A	1544(3)	2283(12)	-3221(5)
C(3)	980(1)	2406(2)	-898(1)	C(23)A	2866(3)	4450(10)	-3446(6)
C(4)	2099(1)	2241(4)	729(2)	C(17)B	1567(3)	3365(14)	-2598(6)
C(5)	1154(1)	1439(3)	654(2)	C(18)B	1866(3)	4481(14)	-2243(7)
C(6)	1183(1)	4197(3)	378(2)	C(19)B	2208(3)	4741(14)	-2557(7)
C(7)	534(1)	3164(3)	-1179(2)	C(20)B	2253(3)	3886(14)	-3227(7)
C(8)	1041(1)	-1452(3)	-1551(1)	C(21)B	1954(3)	2770(14)	-3582(7)
C(9)	719(1)	-1904(1)	-2362(1)	C(22)B	1612(3)	2510(14)	-3268(7)
C(10)	451(1)	-873(1)	-2906(1)	C(23)B	2567(4)	3467(16)	-4361(7)
C(11)	141(1)	-1352(1)	-3650(1)				

weights calculated by the formula $1/\omega = \sigma^2(F_o) + 0.0012F_o^2$, and refined the positional parameters of all atoms, isotropic thermal parameters for the hydrogen atoms and anisotropic for the rest. All phenyl groups were refined as rigid bodies with the bonds C-C = 1.385 Å, C-H = 1.00 Å and all angles 120°. A difference map calculated at this point showed no unusual parameters for all atoms and structure factor amplitudes may be obtained from the author (A. T.).

REFERENCES AND NOTES

[1] J. Stephanidou-Stephanatou and N. E. Alexandrou, Eighth

International Congress of Heterocyclic Chemistry, Graz, 1981.

[2] R. N. Butler and J. P. James, *J. Chem. Soc., Perkin Trans. I*, 553 (1982).

[3] J. Stephanidou-Stephanatou, *J. Heterocyclic Chem.*, **20**, 845 (1983).

[4] J. F. Barnes, M. J. Barrow, M. M. Harding, R. M. Paton, A. Sillitoe, P. L. Ashcroft, R. Bradburg, J. Crosby, C. J. Joyce, D. R. Holmes and J. Milner, *J. Chem. Soc., Perkin Trans. I*, 293 (1983); A. K. Sillitoe and M. M. Harding, *Acta Crystallogr.*, **B34**, 2021 (1978); M. J. Barrow, *ibid.*, **38**, 308 (1982).