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Structure of the Hydrazinium Complex of a Tetracarboxy-18-crown-6 Receptor Molecule

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Abstract. (2*R*,3*R*,11*R*,12*R*)-1,4,7,10,13,16-Hexaoxacyclooctadecane-2,3,11,12-tetracarboxylic acid monohydrazinium monotetramethylammonium salt monohydrate, $C_4H_{12}N^+.H_5N_2^+.C_{16}H_{22}O_{14}^{2-}.H_2O$, $M_r = 563{\cdot}6$, monoclinic, $P2_1$, $a = 12{\cdot}075\,(1)$, $b = 14{\cdot}436\,(4)$, $c = 8{\cdot}018\,(1)$ Å, $\beta = 95{\cdot}45\,(1)°$, $U = 1391$ Å^3, $Z = 2$, $D_x = 1{\cdot}35$ g cm^{-3}, $\lambda = 1{\cdot}5418$ Å, μ(Cu $K\alpha$) = 9·5 cm^{-1}, $F(000) = 604$, $T = 292$ K, $R = 0{\cdot}079$ and $wR = 0{\cdot}118$ for 2155 observed data. The macrocyclic dianionic ligand is in a relaxed conformation, with a rectangular array of ether O atoms in the mean plane of the ring, the two other O atoms being out of the plane in the direction towards the complexed cation. The hydrazinium monocation is anchored to the ligand by three N—H···O hydrogen bonds.

Introduction. The conjunction of a macrocyclic polyether core and anionic groups surrounding this molecular cavity makes the tetracarboxy-18-crown-6 ligand (Behr, Girodeau, Hayward, Lehn & Sauvage, 1980) a very powerful complexing agent for cations (Lehn, 1978; Behr, Lehn & Vierling, 1982). With the idea of taking advantage of this property to stabilize unusual cations (Behr, Dumas & Moras, 1982), we crystallized an adduct with hydrazine from water at pH = 4. We hoped that, although partly protonated, the ligand would still be a strong enough complexing agent to stabilize the $H_3\overset{+}{N}{-}\overset{+}{N}H_3$ dication which normally exists only in strong acid. Attempts to characterize this complex by indirect physical techniques (NMR, pH–metric titration) were unsuccessful since the sequential protonation of a tetracarboxylate ligand/hydrazine mixture leads to ambiguous interpretations of whether protonation occurs on a carboxylate or an amino group. We therefore undertook the X-ray analysis of a complex crystallized in medium acidic conditions.

Experimental. A single crystal with approximate dimensions 0·34 × 0·29 × 0·23 mm was sealed in a Lindemann-glass capillary and optically aligned on a Nonius CAD-4 diffractometer. Preliminary study and data collection were performed by using graphite-monochromated Cu $K\alpha$ radiation. Cell constants and an orientation matrix for data collection were obtained from least-squares refinement using the setting angles of 22 reflections centered automatically.

The diffraction data were collected at room temperature using the ω–2θ scan technique ($h > 0$, $k > 0$, $0 < l > 0$). During the intensity measurements, three reflections were used for checking the alignment and possible deterioration of the crystal every two hours; intensity variations of these standard reflections were all within counting statistics. Of the 2405 independent reflections measured out to $(\sin\theta)/\lambda = 0{\cdot}578$ Å^{-1}, all reflections having a net intensity smaller than $2\sigma(I)$ were taken to be unobserved. $h = 0$–13, $k = 0$–16, $l = 0$–9. 2155 independent data were coded as observed; this corresponds to a data:parameter ratio of 6·2 if H atoms are omitted. The intensity data were reduced to relative square amplitudes $(F_o)^2$ by application of the standard Lorentz and polarization factors. Absorption effects were neglected.

The structure was solved by direct methods. 20 of the 38 non-H atoms were localized on the best E map. The remaining non-H atoms were found on subsequent Fourier syntheses. In all structure-factor calculations the atomic scattering factors used were taken from the usual sources (Cromer & Waber, 1974). The structure was refined by full-matrix least-squares techniques. The quantity minimized was $w(|F_o| - |F_c|)^2$ where the weights w were taken as $1/\sigma^2(F_o)$. All non-H atoms were refined assuming anisotropic thermal motion. The H atoms of the macrocycle were then introduced at calculated positions (C—H: 0·95 Å). These H atoms were assumed to have isotropic thermal motion ($B_H = B_C + 2{\cdot}0$ Å^2) and added as fixed contributions in the refinement. Also added as fixed contributions were the methyl H atoms of the $N(CH_3)_4^+$ cation (calculated in staggered positions). A subsequent difference Fourier map clearly revealed H atoms of the water molecule, H(13*A*) and H(16*B*) of the carboxylic groups and H(1N1) of the $-NH_3^+$ fragment (Fig. 1). These and

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Table 1. *Atomic coordinates in the asymmetric unit cell*

Numbers in parentheses here and in succeeding tables are e.s.d.'s for the last significant figure. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as

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

	x	y	z	B_{eq}(Å^2)
C(1)	0·2360 (4)	0	0·8403 (7)	4·2 (1)
C(2)	0·2207 (4)	−0·0132 (4)	0·6551 (7)	4·0 (1)
O(1)	0·1832 (3)	0·0731 (3)	0·5854 (4)	4·23 (8)
C(3)	0·1321 (6)	0·0680 (6)	0·4175 (7)	5·7 (2)
C(4)	0·0944 (6)	0·1605 (7)	0·364 (1)	7·1 (2)
O(2)	0·1833 (5)	0·2233 (5)	0·3528 (6)	7·1 (1)
C(5)	0·1532 (9)	0·3136 (8)	0·299 (1)	8·3 (2)
C(6)	0·1162 (6)	0·3792 (6)	0·422 (1)	6·3 (2)
O(3)	0·2004 (3)	0·3818 (4)	0·5585 (5)	4·97 (9)
C(7)	0·1894 (4)	0·4510 (5)	0·6804 (8)	4·5 (1)
C(8)	0·3039 (4)	0·4622 (4)	0·7730 (7)	4·3 (1)
O(4)	0·3299 (3)	0·3772 (3)	0·8556 (5)	4·51 (8)
C(9)	0·4062 (7)	0·3830 (7)	0·9981 (9)	6·3 (2)
C(10)	0·4151 (9)	0·2860 (8)	1·076 (1)	9·3 (2)
O(5)	0·4566 (5)	0·2250 (5)	0·9825 (7)	7·5 (1)
C(11)	0·4617 (7)	0·1367 (7)	1·057 (1)	7·3 (2)
C(12)	0·3600 (6)	0·0795 (6)	1·0476 (8)	5·2 (1)
O(6)	0·3212 (3)	0·0677 (3)	0·8764 (4)	4·23 (8)
C(13)	0·1277 (5)	0·0259 (5)	0·9143 (7)	4·4 (1)
O(13*A*)	0·0582 (4)	−0·0410 (4)	0·9037 (7)	6·8 (1)
O(13*B*)	0·1130 (4)	0·1016 (4)	0·9681 (7)	6·9 (1)
C(14)	0·3280 (5)	−0·0488 (5)	0·5902 (7)	4·5 (1)
O(14*A*)	0·3596 (4)	−0·1269 (4)	0·6264 (7)	6·4 (1)
O(14*B*)	0·3781 (4)	0·0090 (4)	0·5027 (6)	5·9 (1)
C(15)	0·1009 (5)	0·4291 (5)	0·799 (1)	5·1 (1)
O(15*A*)	0·1009 (4)	0·4829 (4)	0·9222 (6)	6·8 (1)
O(15*B*)	0·0354 (5)	0·3678 (5)	0·7644 (9)	10·2 (2)
C(16)	0·3888 (4)	0·4922 (5)	0·6502 (7)	4·2 (1)
O(16*A*)	0·3733 (4)	0·5656 (4)	0·5795 (6)	6·0 (1)
O(16*B*)	0·4670 (3)	0·4363 (4)	0·6367 (5)	5·6 (1)
N(1)	0·3547 (6)	0·2195 (5)	0·6304 (9)	6·7 (1)
N(2)	0·4592 (9)	0·2224 (9)	0·563 (2)	11·9 (3)
N(3)	0·1864 (4)	0·7111 (4)	0·1868 (7)	5·2 (1)
C(31)	0·1160 (9)	0·7253 (9)	0·023 (1)	8·4 (2)
C(32)	0·243 (1)	0·8010 (9)	0·235 (2)	10·1 (3)
C(33)	0·2677 (9)	0·6359 (9)	0·173 (2)	9·8 (3)
C(34)	0·113 (1)	0·687 (1)	0·314 (1)	10·3 (3)
O(H2O)	0·2634 (7)	−0·2892 (7)	0·716 (1)	11·8 (2)

Table 2. *Bond lengths* (Å), *bond angles* (°) *and torsion angles* (°)

E.s.d.'s for torsion angles are < 1·0°.

C(1)–C(2)	1·491 (6)	C(10)–O(5)	1·286 (9)
C(1)–O(6)	1·429 (6)	O(5)–C(11)	1·408 (8)
C(1)–C(13)	1·533 (6)	C(11)–C(12)	1·476 (9)
C(2)–O(1)	1·422 (6)	C(12)–O(6)	1·418 (6)
C(2)–C(14)	1·531 (6)	C(13)–O(13*A*)	1·277 (7)
O(1)–C(3)	1·429 (6)	C(13)–O(13*B*)	1·194 (7)
C(3)–C(4)	1·46 (1)	C(14)–O(14*A*)	1·216 (7)
C(4)–O(2)	1·414 (9)	C(14)–O(14*B*)	1·279 (6)
O(2)–C(5)	1·41 (1)	C(15)–O(15*A*)	1·254 (7)
C(5)–C(6)	1·46 (1)	C(15)–O(15*B*)	1·202 (8)
C(6)–O(3)	1·424 (7)	C(16)–O(16*A*)	1·207 (7)
O(3)–C(7)	1·412 (7)	C(16)–O(16*B*)	1·255 (6)
C(7)–C(8)	1·514 (6)	N(1)–N(2)	1·42 (1)
C(7)–C(15)	1·532 (6)	N(3)–C(31)	1·512 (8)
C(8)–O(4)	1·415 (6)	N(3)–C(32)	1·50 (1)
C(8)–C(16)	1·549 (5)	N(3)–C(33)	1·475 (9)
O(4)–C(9)	1·400 (7)	N(3)–C(34)	1·449 (9)
C(9)–C(10)	1·53 (1)		

C(2)–C(1)–O(6)	107·9 (3)	C(10)–O(5)–C(11)	112·2 (6)
C(2)–C(1)–C(13)	112·8 (4)	O(5)–C(11)–C(12)	118·9 (5)
O(6)–C(1)–C(13)	112·2 (4)	C(11)–C(12)–O(6)	108·3 (4)
C(1)–C(2)–O(1)	106·5 (4)	C(1)–O(6)–C(12)	116·3 (4)
C(1)–C(2)–C(14)	110·6 (4)	C(1)–C(13)–O(13*A*)	111·6 (5)
O(1)–C(2)–C(14)	114·1 (3)	C(1)–C(13)–O(13*B*)	121·6 (5)
C(2)–O(1)–C(3)	114·7 (4)	O(13*A*)–C(13)–O(13*B*)	126·7 (4)
O(1)–C(3)–C(4)	109·0 (5)	C(2)–C(14)–O(14*A*)	119·1 (4)
C(3)–C(4)–O(2)	112·8 (5)	C(2)–C(14)–O(14*B*)	115·3 (4)
C(4)–O(2)–C(5)	115·9 (6)	O(14*A*)–C(14)–O(14*B*)	125·6 (5)
O(2)–C(5)–C(6)	118·8 (6)	C(7)–C(15)–O(15*A*)	114·4 (4)
C(5)–C(6)–O(3)	107·0 (5)	C(7)–C(15)–O(15*B*)	119·2 (6)
C(6)–O(3)–C(7)	116·4 (4)	O(15*A*)–C(15)–O(15*B*)	126·2 (5)
O(3)–C(7)–C(8)	105·8 (3)	C(8)–C(16)–O(16*A*)	117·5 (4)
O(3)–C(7)–C(15)	113·7 (4)	C(8)–C(16)–O(16*B*)	115·1 (4)
C(8)–C(7)–C(15)	112·0 (4)	O(16*A*)–C(16)–O(16*B*)	127·5 (4)
C(7)–C(8)–O(4)	106·8 (4)	C(31)–N(3)–C(32)	108·2 (6)
C(7)–C(8)–C(16)	110·3 (4)	C(31)–N(3)–C(33)	110·8 (6)
O(4)–C(8)–C(16)	114·2 (4)	C(31)–N(3)–C(34)	108·3 (7)
C(8)–O(4)–C(9)	115·5 (4)	C(32)–N(3)–C(33)	111·6 (6)
O(4)–C(9)–C(10)	107·0 (6)	C(32)–N(3)–C(34)	108·3 (7)
C(9)–C(10)–O(5)	114·0 (6)	C(33)–N(3)–C(34)	109·4 (7)

O(6)–C(1)–C(2)–O(1)	−63·2	C(6)–O(3)–C(7)–C(8)	−160·2
O(6)–C(1)–C(2)–C(14)	61·4	C(6)–O(3)–C(7)–C(15)	76·4
C(13)–C(1)–C(2)–O(1)	61·4	O(3)–C(7)–C(8)–O(4)	−64·3
C(13)–C(1)–C(2)–C(14)	−174·0	O(3)–C(7)–C(8)–C(16)	60·3
C(2)–C(1)–O(6)–C(12)	−170·5	C(15)–C(7)–C(8)–O(4)	60·1
C(13)–C(1)–O(6)–C(12)	64·6	C(15)–C(7)–C(8)–C(16)	−175·3
C(2)–C(1)–C(13)–O(13*A*)	67·8	O(3)–C(7)–C(15)–O(15*A*)	170·3
C(2)–C(1)–C(13)–O(13*B*)	−109·7	O(3)–C(7)–C(15)–O(15*B*)	−13·8
O(6)–C(1)–C(13)–O(13*A*)	−170·1	C(8)–C(7)–C(15)–O(15*A*)	50·4
O(6)–C(1)–C(13)–O(13*B*)	12·5	C(8)–C(7)–C(15)–O(15*B*)	−133·7
C(1)–C(2)–O(1)–C(3)	−161·9	C(7)–C(8)–O(4)–C(9)	−154·6
C(14)–C(2)–O(1)–C(3)	75·7	C(16)–C(8)–O(4)–C(9)	83·2
C(1)–C(2)–C(14)–O(14*A*)	68·7	C(7)–C(8)–C(16)–O(16*A*)	62·1
C(1)–C(2)–C(14)–O(14*B*)	−110·2	C(7)–C(8)–C(16)–O(16*B*)	−118·3
O(1)–C(2)–C(14)–O(14*A*)	−171·2	O(4)–C(8)–C(16)–O(16*A*)	−177·7
O(1)–C(2)–C(14)–O(14*B*)	9·9	O(4)–C(8)–C(16)–O(16*B*)	2·0
C(2)–O(1)–C(3)–C(4)	178·2	C(8)–O(4)–C(9)–C(10)	175·4
O(1)–C(3)–C(4)–O(2)	65·3	O(4)–C(9)–C(10)–O(5)	64·9
C(3)–C(4)–O(2)–C(5)	179·2	C(9)–C(10)–O(5)–C(11)	−179·0
C(4)–O(2)–C(5)–C(6)	81·4	C(10)–O(5)–C(11)–C(12)	80·2
O(2)–C(5)–C(6)–O(3)	53·7	O(5)–C(11)–C(12)–O(6)	57·1
C(5)–C(6)–O(3)–C(7)	171·1	C(11)–C(12)–O(6)–C(1)	168·4

H(2N1), H(3N1), assuming a tetrahedral geometry for N(1), were added as fixed contributions in the last cycles of refinement. The two H atoms on the strongly agitated N(2) atom were not localized.

The final agreement factors R and wR reached respectively 0·079 and 0·118. The standard deviation of an observation of unit weight was $S = 2{\cdot}03$. The $(\Delta/\sigma)_{max}$ of 1·29 affected the anisotropic thermal parameters of the C(10) atom. A final difference Fourier map revealed a peak of 0·8 e Å^{-3} located close to the C(5) atom. The high values of the R and wR discrepancy indexes and Δ/σ probably arise in part from the relatively large thermal motion of some atoms. All calculations were performed on a PDP-11/44 computer using the *SDP* programs (Frenz, 1978). The atomic positional parameters are listed in Table 1.* The illustrations were prepared with *ORTEP* (Johnson, 1971) using *MOPS* (Chevrier & Ripp, 1986) in order to select a desired orientation.

Discussion. Bond lengths and angles, torsion angles, and hydrogen bonds are given in Tables 2 and 3. Fig. 1 shows the stereochemistry together with the atomic labeling scheme used. The geometry of the complex is illustrated in Fig. 2 by a stereoscopic view.

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* Lists of anisotropic thermal parameters of non-H atoms, fractional coordinates of H atoms, least-squares planes and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44080 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Hydrogen bonds*

Atoms not in the crystal chemical unit (*i.e.* not listed in Table 1) are specified by the subscript *N*/*uvw* which denotes the manner in which the atomic parameters can be derived from the corresponding atom in the crystal unit. *N* refers to one of the following symmetry operations: (1) *x*, *y*, *z*; (2) $-x, y + \frac{1}{2}, -z$. The *u*, *v*, *w* digits code a lattice translation as $u\mathbf{a} + v\mathbf{b} + w\mathbf{c}$.

		Distances (Å)			Angles (°)
a *b* *c*	*N*/*uvw*	*a–b*	*b–c*	*a–c*	*a–b–c*
O(13*A*)–H(13*A*)···O(15*A*)	2/0$\bar{1}$2	0·59	1·94	2·503 (8)	159·4 (8)
O(14*A*)···H(2H2O)–O(H2O)	1/000	1·78	1·00	2·740 (5)	160·2 (5)
O(14*B*)···H(16*B*)–O(16*B*)	2/1$\bar{1}$1	1·56	0·95	2·498 (8)	169·5 (1·3)
O(15*A*)···H(13*A*)–O(13*A*)	2/002	1·94	0·59	2·503 (8)	159·4 (8)
O(16*A*)···H(1H2O)–O(H2O)	1/010	1·70	1·16	2·760 (11)	148·6 (8)
O(16*B*)–H(16*B*)···O(14*B*)	2/101	0·95	1·56	2·498 (8)	169·5 (1·3)
N(1)–H(1N1)···O(2)	1/000	0·91	2·02	2·893 (7)	161·3 (1·0)
N(1)–H(2N1)···O(4)	1/000	0·95	2·01	2·939 (7)	162·9 (6)
N(1)–H(3N1)···O(6)	1/000	0·99	2·02	3·002 (7)	173·3 (1·0)

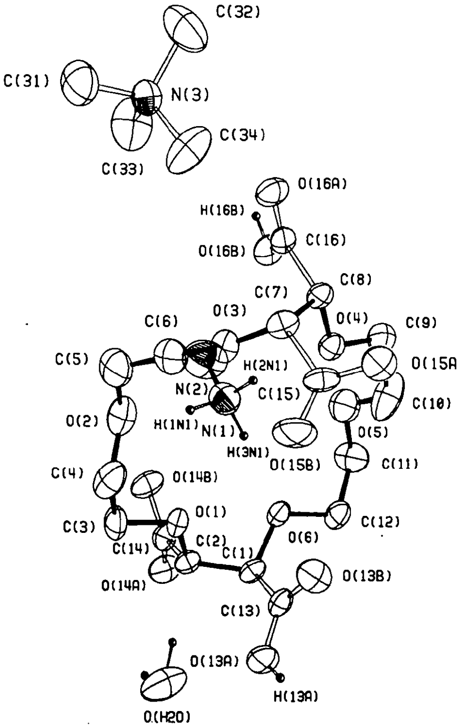

Fig. 1. Stereochemistry of the complex including some interesting H atoms.

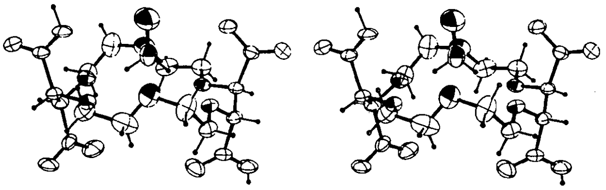

Fig. 2. Stereoscopic view showing the hydrazinium monocation on top of a face of the macrocyclic ring.

The macrocyclic ligand has its tartaric acid residues in a diaxial relationship and each O—C—CO_2 fragment is almost planar (see Table 2), as found for tartaric acid itself (Okaya, Stemple & Kay, 1966). With respect to the macrocyclic ring, the face on which the cation is bound is much more 'open' [O(14*B*)···O(16*B*) = 6·34 Å] than the opposite one [O(13*B*)···O(15*B*) = 4·25 Å], a situation which seems to be a general occurrence when the cation sits on top of a face (Daly, Schonholzer, Behr & Lehn, 1981), but not if the cation fits into the macrocyclic cavity without forming hydrogen bonds (Behr, Lehn, Dock & Moras, 1982; Dock, Moras, Behr & Lehn, 1983). This structural finding provides an explanation for the unusually high pK_4 (> 6) of the ligand in the former complexes, which may be attributed to the difficulty in generating two carboxylates at close distances and perhaps to the formation of a (weak) trans-annular hydrogen bond —COOH···OOC— [the trans-annular intercarboxyl distance is even shorter than the corresponding separation in a tartaric residue (4·6 Å), leading to the following sequence of pK_4's for the ligand: 4·7 (K^+) < 5·0 (free ligand) < 6·0–6·2 (*R*—NH_3^+, Cs^+); unpublished results].

The macrocyclic ring has the C—C and C—O bonds respectively *gauche* and *trans* (Table 2), except for O(2)–C(5) and O(5)–C(11) which are *gauche*. This leads to a rectangular array of binding sites in the mean plane [O(1), O(3), O(4), O(6)] of the ring, the two other O atoms being raised towards the complexed cation.

The hydrazinium ion is anchored to the macrocycle by three N(1)—H···O hydrogen bonds (Table 3), the question remaining being whether it is a mono- or a dication. The N(1)–N(2) bond length of 1·421 (10) Å is equal to that of hydrazinium dihydrochloride and dihydrofluoride: $H_3\overset{+}{H}—\overset{+}{N}H_3$ = 1·420 (4) Å (Donohue & Lipscomb, 1947; Giguere & Schomaker, 1943) and shorter than in the 18-crown-6 complex with $H_2N—\overset{+}{N}H_3$: 1·449 (4) Å (Trueblood, Knobler, Lawrence & Stevens, 1982). The presence of the dicationic form together with a tetramethylammonium ion would require the tetracarboxy ligand to be in a trianionic state; although the C(1) carboxy group bond length and angles are clearly that of a COOH group [Table 2; for comparison with literature data, see Daly, Schonholzer, Behr & Lehn, (1981)], the ionization state of the remaining groups cannot be unambiguously deduced from their geometries. A definitive answer to this question comes from examination of the intermolecular hydrogen-bonding network involved in the crystal packing which agrees with the residual electron density found on two carboxyl residues and interpreted as COOH H atoms.

Indeed, the crystal is stabilized by –CO···HOH···OC– and –COOH···OOC– hydrogen bonds (Table 3) running respectively parallel and perpendicular to the macrocycles. Thus C(1) and C(8) bear carboxylic acid groups and, in order to keep the electronic balance, hydrazine must be in the monocationic form. Nevertheless, the importance of packing forces in crystallizing this particular complex as well as the existence of an $H_3\overset{+}{N}-\overset{+}{N}H_3$ complex at a slightly more acidic pH remain to be answered.

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CI Pigment Yellow 74, α-(2-Methoxy-4-nitrophenylhydrazono)-α-aceto-2′-methoxyacetanilide

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Abstract. 2-[(2-Methoxy-4-nitrophenyl)hydrazono]-*N*-(2-methoxyphenyl)-3-oxobutanamide, $C_{18}H_{18}N_4O_6$, $M_r = 386{\cdot}4$, triclinic, $P\bar{1}$, $a = 10{\cdot}729$ (2), $b = 11{\cdot}976$ (2), $c = 7{\cdot}628$ (1) Å, $\alpha = 103{\cdot}43$ (1), $\beta = 110{\cdot}28$ (1), $\gamma = 88{\cdot}06$ (1)°, $V = 892{\cdot}6$ (3) Å^3, $Z = 2$, $D_m = 1{\cdot}433$ (5), $D_x = 1{\cdot}4376$ (5) Mg m^{-3}, Cu $K\alpha$, $\lambda = 1{\cdot}54184$ Å, $\mu = 0{\cdot}83$ mm^{-1}, $F(000) = 404$, room temperature, $R = 7{\cdot}2$% for 3385 independent non-zero intensities. The molecule exists as the hydrazone tautomer and four intramolecular hydrogen bonds keep it approximately planar. There is one intermolecular hydrogen bond per molecule and this causes the compound to pack as dimers. The planar dimers are linked by van der Waals forces into columns.

Introduction. This article is one of a series (Whitaker, 1983*a*,*b*, 1984*a*,*b*, 1985*a*; Whitaker & Walker, 1985; Whitaker, 1985*b*, 1986) concerned with the structure of some acetoacetanilide azo-pigments, with a long-term aim of relating colour and crystal structure in pigments.

CI Pigment Yellow 74 (CI No. 11741) (I) is available commercially and is used in the manufacture of paint and printing inks. It was investigated to see what effect the two methoxy groups in the molecule have on the intramolecular hydrogen bonding. One of these groups is in the *ortho* position of the phenyl adjacent to the azo bond; this is unusual, as most commercial pigments of this type have a nitro group in this position. After the intensity data had been collected, the crystal structure

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